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Nanometer-size metal complexes: magnetic materials and DNA probes

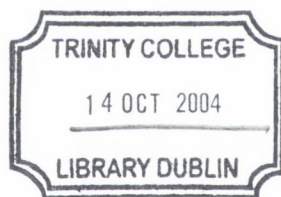
Volume I

Antonella Di Trapani

Doctor in Chemistry

Chemistry Department
University of Dublin
Trinity College
Dublin 2
Ireland

A thesis submitted to the University of Dublin, in partial fulfilment of the requirements for the degree of Ph.D.



7402.1

*'I write because I am a chemist. My trade provided my
raw material, the nucleus to which things join'*

Primo Levi

Declaration

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Antonella Di Trapani

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Summary

The work described in this thesis was carried out as part of the European TMR Network "Nanometer-size metal complexes" (Contract N ERBMRXCT980226).

The synthesis of Cr(III) homoleptic and heteroleptic polypyridyl complexes is presented ($[\text{Cr}(\text{LL}')_2(\text{LL}'')]^{3+}$ where $\text{LL}'=\text{LL}''=\text{bipy, phen, phendione, dpq, dppz}$ and tpphz or $\text{LL}'\neq\text{LL}''$, $\text{LL}'=\text{bipy, phen}$ and $\text{LL}''=\text{phendione, dpq, dppz}$ and tpphz). A study of the absorption properties of these complexes is presented.

Crystal structures of $[\text{Cr}(\text{LL})_2\text{X}_2]^+$ where $\text{LL}=\text{bipy}$ or phen and $\text{X}=\text{Cl}^-$ and $[\text{Cr}(\text{LL})_3]^{3+}$ where $\text{LL}=\text{phen}$ and Me_2phen are presented and analysed.

Fe(II) homoleptic complexes are investigated ($[\text{Fe}(\text{LL})_3]^{2+}$ where $\text{LL}=\text{phen, dpq, dppz}$ and tpphz). $[\text{M}(\text{phendione})_3]^{n+}$ (where $\text{M}=\text{Fe(II), Co(II/III)}$ and Cu(II)) have been synthesized and characterized and their crystal structures are presented.

The magnetic moments of these paramagnetic and diamagnetic complexes are studied. DNA binding of some Cr(III) homoleptic complexes ($[\text{Cr}(\text{LL})_3]^{3+}$ where $\text{LL}=\text{bipy, Me}_2\text{bipy, phen, Me}_2\text{phen}$) is investigated by UV/Vis, circular dichroism (CD) spectroscopy, emission spectroscopy and melting studies. The binding constants of these complexes are $\sim 8 \times 10^{-3} \text{ M}^{-1}$. Temperature dependence induced circular dichroism (ICD) allowed calculation of the thermodynamic parameters of $[\text{Cr}(\text{phen})_3]^{3+}$. Preliminary studies were also carried out on two heteroleptic Cr(III) complexes ($[\text{Cr}(\text{phen})_2(\text{LL})]^{3+}$ where $\text{LL}=\text{phendione}$ or dppz).

The synthesis of binuclear and tetranuclear complexes made of Cr(III) and Ru(II) metal centres and tpphz bridging ligand is presented. The tetranuclear complexes were also synthesized with Fe(II), Co(II), Cu(II) and Co(III) metal cores and Ru(II) terminal metal centres. The preliminary synthesis of some Cr(III) complexes with a tetrapodal ligand, TPA, is described.

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Abbreviations

Ligands

bipy: 2,2'-bipyridine

phen: 1,10-phenanthroline

2,9-phen: 2,9-dimethyl-1,10-phenanthroline

Me₂bipy: 4,4'-dimethyl-2,2'-bipyridine

Me₂phen: 4,7-dimethyl-1,10'-phenanthroline

TMP: 3,4,7,8-tetramethyl-1,10-phenanthroline

Ph₂phen or DIP: 4,7-diphenyl-1,10-phenanthroline

TPA: Tris[(2-pyridyl)methyl]amine

dpq: dipyrdo (3,2-d: 2', 3'-f)quinoxaline

dppz: dipyrdo (3,2-a:2',3' -c) phenazine

tpphz: tetrapyrdo[3,2-a: 2',3'-c: 3'', 2''-h: 2'''-3'''-j]phenazine

phendione or pd or dione: 1,10-phenanthroline-5,6-dione

HAT: 1,5,8,9,12-hexaazatriphenylene

biq: 2,2' -biquinoline

Terpy: 2,2',2''-terpyridine

TAP: 1,4,5,8-tetraazaphenanthrene

2,3-dpp: 2,3-bis(2-pyridyl)pyrazine

2,5-dpp: 2,5-bis(2-pyridyl)pyrazine

2,3-dpq: 2,3-bis(2-pyridyl)quinoxaline

Materials

CT-DNA: Calf Thymus- Deoxyribose nucleic acid

TBAPF₆: tetrabutyl ammonium hexafluorophosphate.

DAPI: 4',6'-diamino-2-phenylindole

Solvents

MeOH: methanol

EtOH: ethanol

MeCN: acetonitrile

en: ethylenediamine

DMSO: dimethylsulfoxide

DMF: N,N-dimethylformamide

THF: tetrahydrofuran

TFMS: trifluoromethane sulfonic acid

Spectroscopy

^1H NMR: proton nuclear magnetic resonance

IR: infrared

UV/vis: ultraviolet/visible

ESMS: electrospray mass spectrometry

ppm: parts per million

s: singlet

d: doublet

dd: doublet of doublets

t: triplet

q: quartet

m: multiplet

CD: circular dichroism spectroscopy

ICD: induced CD

General:

CT: charge transfer

MLCT: metal to ligand charge transfer

NHE: normal hydrogen electrode

RT: room temperature

Chapter 1

Nanometer size metal complexes: An Overview

Ma sopra tutte le invenzioni stupende qual eminenza di mente fu quella di colui che s'immagino' di trovar modo di comunicare i suoi piu' reconditi pensieri a qualsiasi voglia altra persona, benché' distante per il lunghissimo intervallo di luogo e di tempo?

Galileo Galilei- *Dialogo Sopra i due Massimi sistemi del mondo Tolemaico e Copernicano*, Firenze 1632/I giornata VII, 126-131

1.1. Introduction

The design and characterization of supramolecular species of nanoscopic dimension (Figure 1.1), starting from suitable molecular building blocks, is one of the most important challenges now facing chemistry.

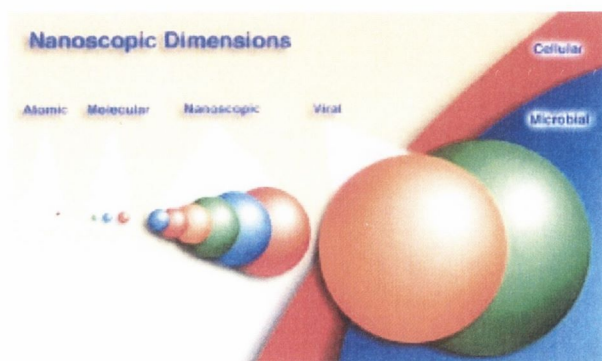


Figure 1.1: *Relative sizes shown to scale¹*

This type of *modular chemistry* is expected to lead to the development of *artificial nanostructures*, that is mesomolecular systems capable of performing specific useful functions, operating at the molecular level.²

Life makes great use of nanostructures: enzymes, antenna systems and reaction centres in photosynthetic organisms, are examples of supramolecular systems in which information is processed at the molecular level. Novel technological developments take advantage of nanostructures: miniaturization of electronic components is a clear example, although electronic components operate more as a bulk material than at the molecular level. Further miniaturization of electronic components, as well as development of a variety of molecular machines, would be of extreme importance for scientific and technological progress, however the *large-downward* approach (used for example in lithographic techniques) seems to be close to its scale limits. Chemists can construct nanometer-sized species by a *small-upward* approach starting with molecular components. This approach is very appealing since it allows the assembly of functionally integrated building blocks into structurally organized materials to obtain molecular-level devices ^{2,3} (Figure 1.2). This area of work will bridge the world of molecules and organized materials and looks very promising in view of the possible development of nanometer-sized species capable of performing useful photoinduced functions⁴. These multicomponent systems capable of performing useful light- and/or redox-induced functions are often called supramolecular species.

1.1.1. Supermolecules and supramolecular chemistry

Supermolecules are systems made of a small number of discrete molecular components held together by covalent bonds, electrostatic interaction, hydrogen bonds or other intermolecular forces, so that each chemical unit introduces into the supramolecular structure its own 'piece of information' (absorption spectra, redox properties, magnetic properties)

Supramolecular chemistry is the chemistry of systems (supermolecules) made up of molecular components in the same way as molecules are made up of atoms: adduct, catenanes, rotaxane, cage-type compounds, molecular devices, polynuclear metal complexes and helicates are all examples of supermolecules⁵. Besides their theoretical interest, it is clear that such multinuclear species become more and more interesting as they are able to perform 'useful functions'.

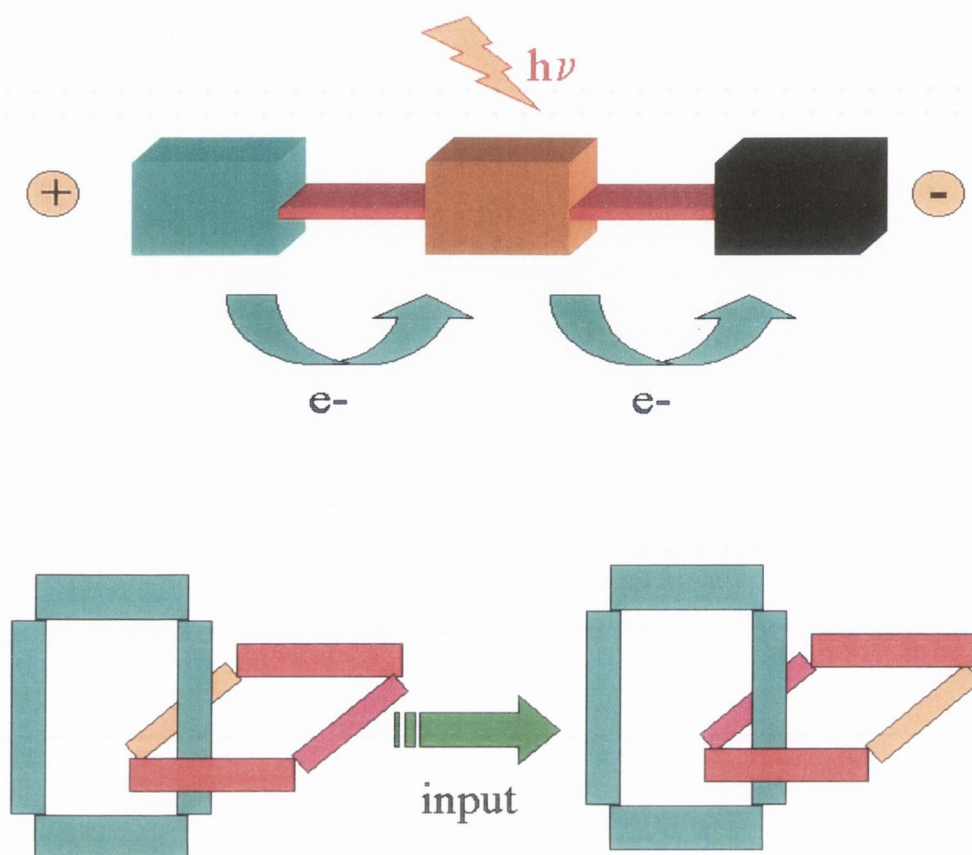


Figure 1.2: Schematic representation of a molecular device

To perform functions by operating at the molecular level, nanometer-sized systems have to contain specific information in their own structure and have to be activated by some form of *energy*. A very convenient energy to activate molecular components of supramolecular systems is *light* (Figure 1.2).

Nature relies on light to effect some of its most essential chemistry. Photochemical processes are of great importance to life on earth. Photosynthesis harvests the sun's energy and creates carbohydrates from atmospheric CO_2 , as well as liberating O_2 to the atmosphere. Man also tries to exploit light, with applications ranging from the synthesis of new and complex organic species to the gathering and storage of solar energy⁶. Particularly interesting nanometer-sized species are therefore supramolecular systems containing chromophores and/or luminophores. The information content embedded in the overall structures includes the properties of each individual molecular component and the structural

arrangements among the components. The preparation of nanometer-sized species containing light-active molecular components with well-defined, predetermined configurations can lead to systems in which properties such as the migration of electrons and the excitation energy within the supramolecular arrays can be highly controlled and multiple, properly arranged chromophores can cooperate for specific interaction and photoreactions with suitable substrates. This would be of outstanding interest for a large variety of purposes, such as solar energy conversion, treatment of information based on light and electronic signals, and the probing or marking of biological structures such as nucleic acids⁴.

1.1.2. Supramolecular systems based on polypyridyl metal complexes

Transition metal complexes of polypyridine-type ligands are ideal components in building up species of this type, because most of them exhibit strong luminescence and redox-active properties.

Various research groups have recently devoted much effort in the development of nanometer-sized systems based on building-blocks made of luminescent and redox-active bidentate polypyridine metal complexes.⁷ Many interesting compounds have been studied so far and very promising results have been obtained, for example in the field of light energy conversion.⁸ A number of useful synthetic strategies have been developed and suitable synthons have been selected so that topologically controlled supermolecules can be obtained. As a result, research on nanometer-sized luminescent oligometallic complexes has advanced considerably in the last few years.⁹

However, in spite of the large efforts made, progress is at present slowed down by a number of problems which are difficult to overcome, mainly the characterization of nanometer size species and the preparation of geometrically and enantiomerically pure species. Nevertheless, these species still attract the interest of chemists in the building-up of novel polynuclear transition metal complexes which contain both luminescent and redox-active as well as paramagnetic centres with the possibility of using these species to study:

- Photoinduced energy migration and charge separation within chirally resolved polynuclear systems;

- Interactions and photoreactions with DNA;
- Magneto-optical materials.

1.2. Polypyridyl complexes

Polypyridyl complexes of transition metals have a long history. Over a century ago, Blau¹⁰ noted the formation of intensely coloured substances when iron (II) salts were mixed with 2,2'-bipyridine (bipy). The latter and 1,10-phenanthroline (phen) are parent ligands of a broad family of polypyridine/polyimine ligands that have been shown capable of complexing a large number of metal ions.

Coordination complexes containing polypyridyl ligands have been characterized for a large number of transition metals. Photophysical and photochemical studies, however, have concentrated on complexes of a few metal ions mainly Ru(II) polypyridyl complexes, as demonstrated by the large number of reviews.^{7,8}

1.2.1. Polypyridyl Ligands

A remarkable aspect of the complexes with bipyridine-type ligands is the wide range of formal oxidation states that are available. Even for a single metal it is possible to find complexes with bipy ligands associated with formal oxidation states ranging from -2 to +7.

Depending on the ligand used polypyridyl complexes can be classified in three categories:

- Homo and heteroleptic chelates of type $[M(LL)_3]^{n+}$, $[M(LL)_2(LL')]^{n+}$, $[M(LL)(LL')(LL'')]^{n+}$, $[M(LL)_n(LL')_{3-n}]^{n+}$, where LL, LL' and LL'' are bidentate ligands such as bipy, phen, their peripherally substituted derivatives or polypyridine in general, and LLL is a tridentate ligand such as terpyridine;
- mixed ligand complexes of the type $[M(LL)_nX_{3-n}]^{n+}$ containing a single chromophoric polypyridine ligand (LL or LLL) and many non-chromophoric ligands ($X = Cl^-$, oxalate, CN^- ...);
- polynuclear polypyridyl complexes involving multidentate bridging ligands (BL) such as 2,2'-bipyrimidine (bpym) (doubly bidentate) or

4,4'-bipyridine (4,4'-bpy) (doubly monodentate) for example $[(LL)_2M_1(BL)M_2(LL')]^{m+}$.

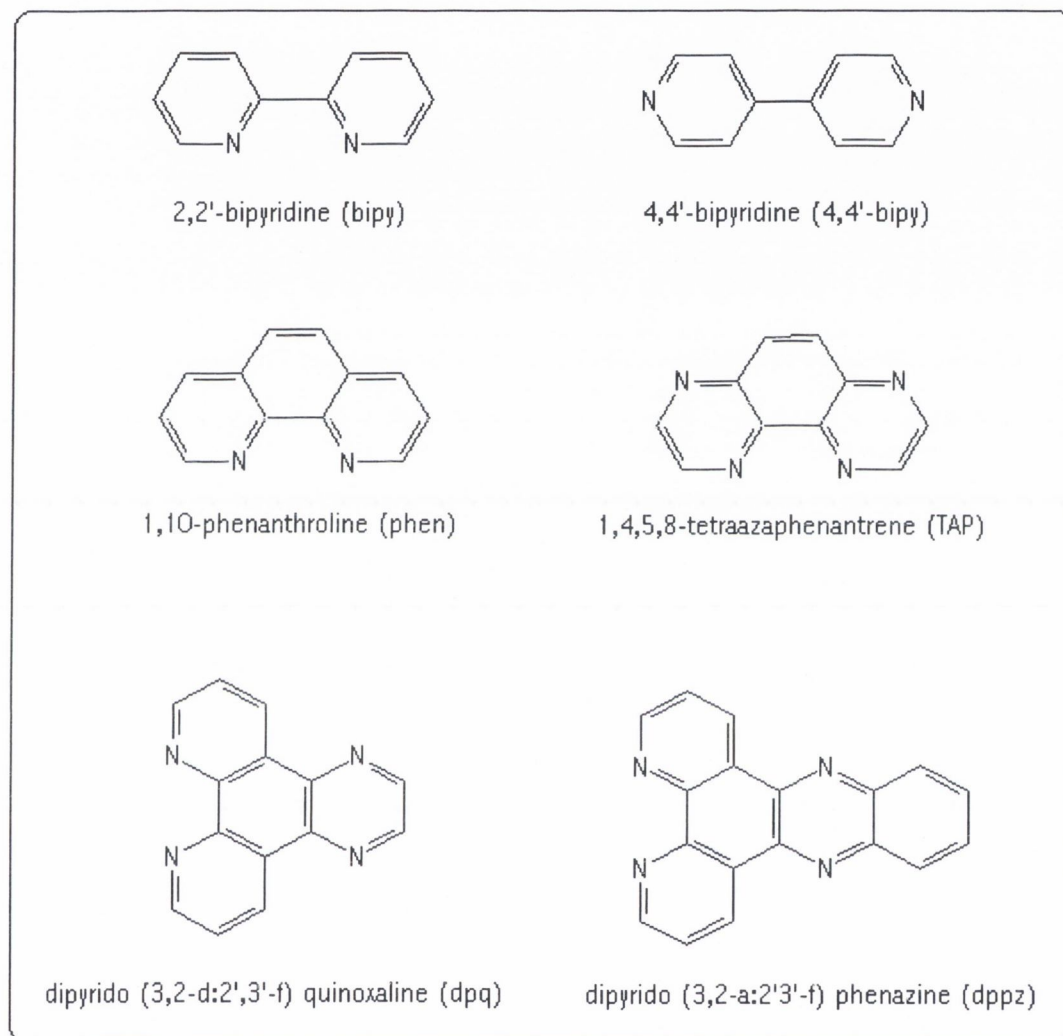


Figure 1.3: Structures of some of the polypyridyl ligands used in this thesis, with their abbreviations.

A common feature of these ligands is the presence of a vacant π orbital that can accept electron density from the metal centre to form a type of π bonding that supplements the σ bonding arising from the donation of a lone pair of electrons. A consequence is the stabilization of the resulting metal complexes, including those of metal ions in low oxidation states. High electron densities on the metal can thus be delocalised onto the ligand. The ability of the ligands to accept electron density into low-lying π^* orbital is often referred to as “ π acidity”, the word acidity being

used in the Lewis sense. On the other end these bipy-type ligands can also act as π donors in high-oxidation state complexes, the precise energies of the π and π^* orbitals depending on the metal ions.

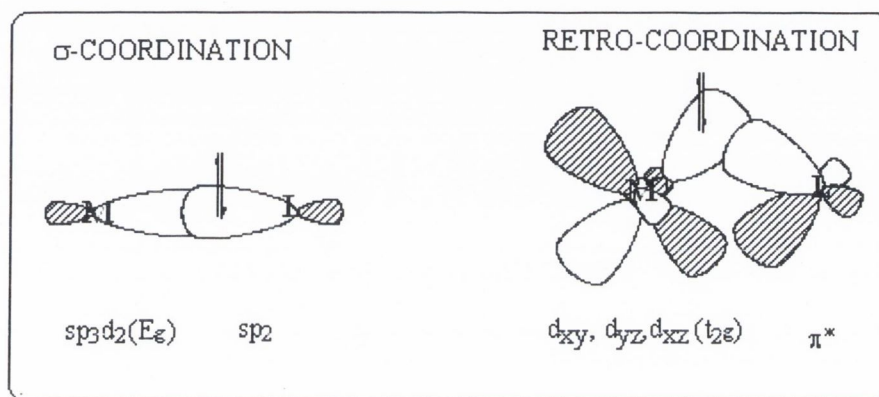


Figure 1.4: Schematic representation of bonding between metal and ligand.

Excited states of the polypyridyl ligands

Electronic transitions of heterocyclic ligands such as 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) are ($n-\pi^*$) and ($\pi-\pi^*$) type, both singlet and triplet. The ground state absorption spectra consist of two bands in the ultraviolet region. The lowest singlet ($n-\pi^*$) and ($\pi-\pi^*$) states lie relatively close to each other and can be coupled vibronically leading to mixed photophysical properties.

Like other azaaromatics, bipy and phen show weak fluorescence in inert solvents. The fluorescence properties depend strongly on the conditions: purity of the solvent, pH and even concentration of the polypyridine ligand. It has been claimed that the neutral ligand does not fluoresce while its protonated adduct luminesces.⁵¹

The ligands dppz (dipyrido (3,2-a:2',3'-c) phenazine) and tpphz (tetrapyrido[3,2-a: 2',3'-c: 3'', 2''-h: 2'''-3'''-j]phenazine)

The heterocyclic π system of dppz combines the chelating function of α -diimines (polypyridines such as 2,2'-bipyridine, or 1,10-phenanthroline)^{11,12} with the electron transfer/proton transfer capacity of 1,4-diazine (pyrazines, quinoxalines, phenazines etc).¹³

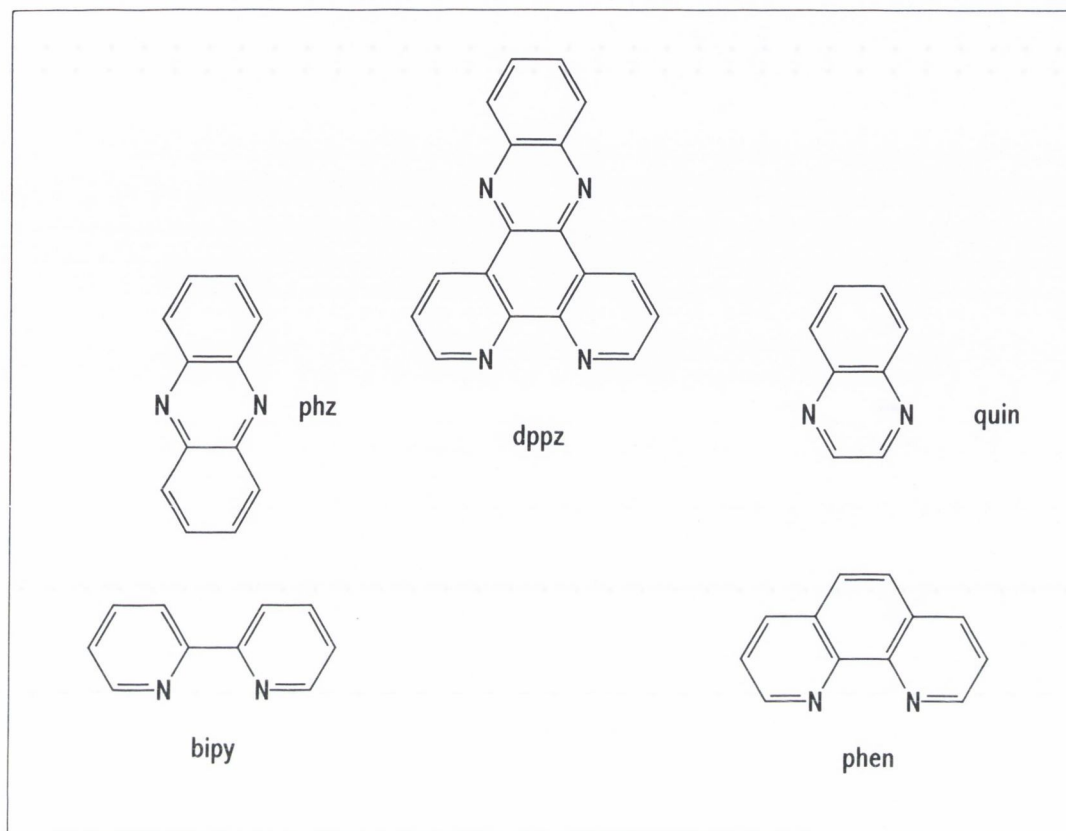


Figure 1.5: The *bipy/phen* and *phenazine/quinoline* components of the *dppz* ligand.

Molecular orbital calculations have shown that the particular connection between both functions in dppz leads to the controlled access of H^+ to the N sites which are also the centres of one- or two-electron reduction (1,4-diazine).^{14,15} The α -diimine π acceptor orbitals b_1 (ψ) and a_2 (χ) were shown to lie above the phenazine-based π^* M, b_1 (phz), and the latter seemed to have very little contribution from the α -diimine π centres.

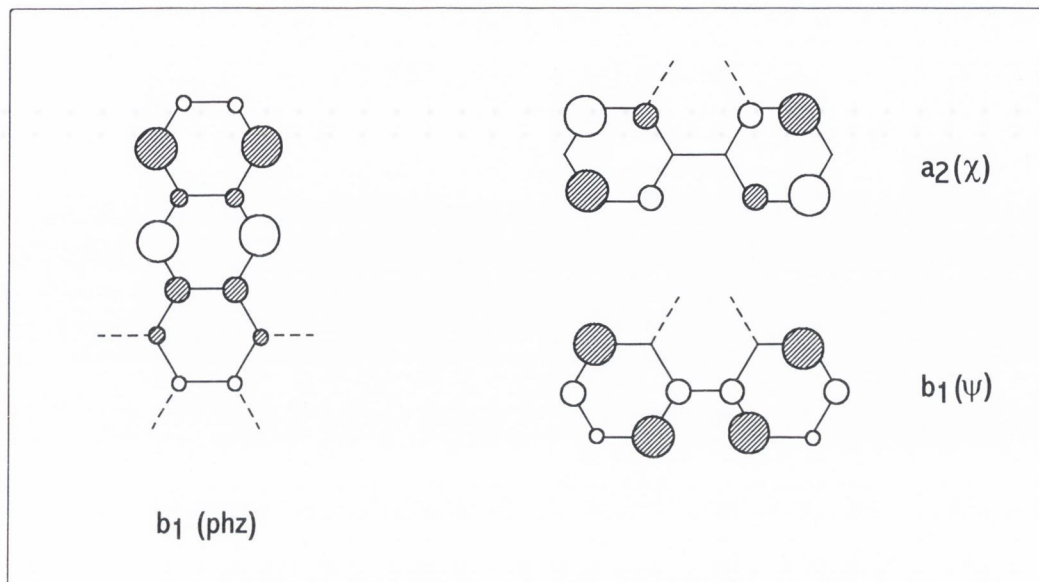
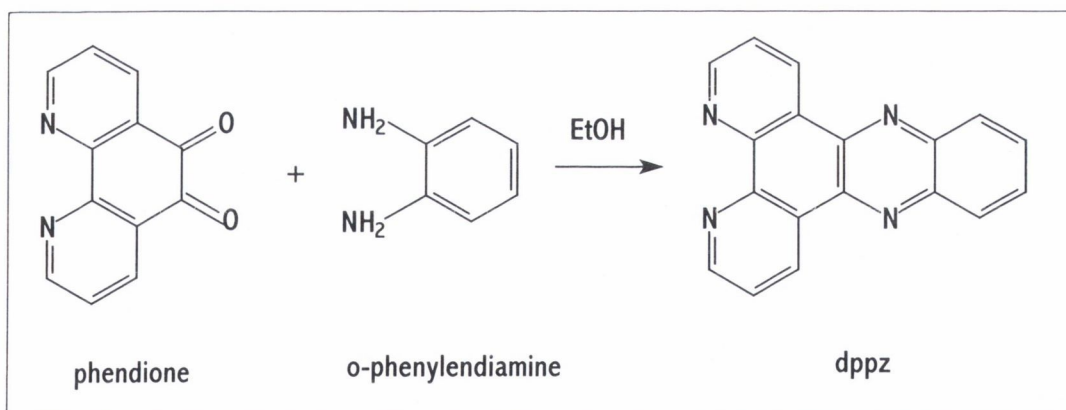


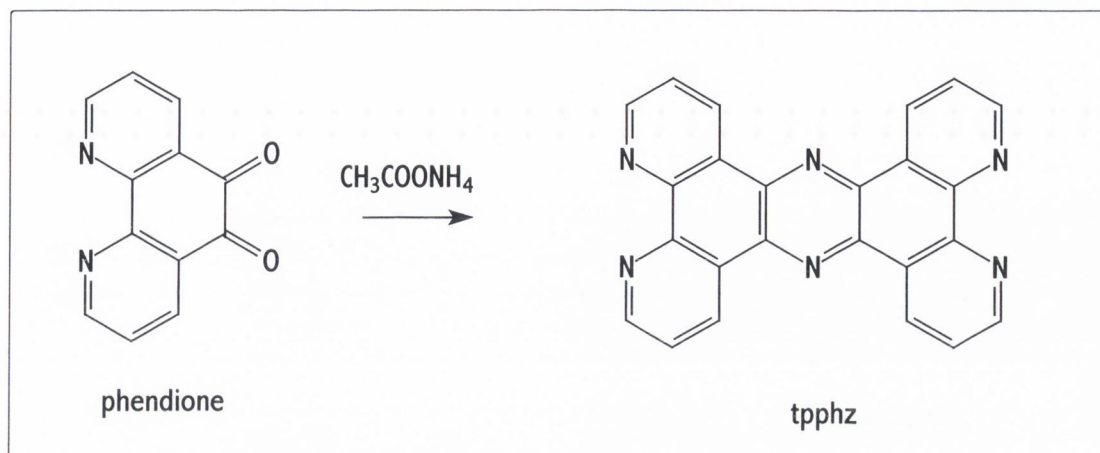
Figure 1.6: Molecular orbital representation of the dppz ligand according to Kaim *et al.*¹⁶

The ligand dppz can be prepared quite easily by condensation of phendione with *o*-phenyldiamine, as represented in Scheme 1.1.



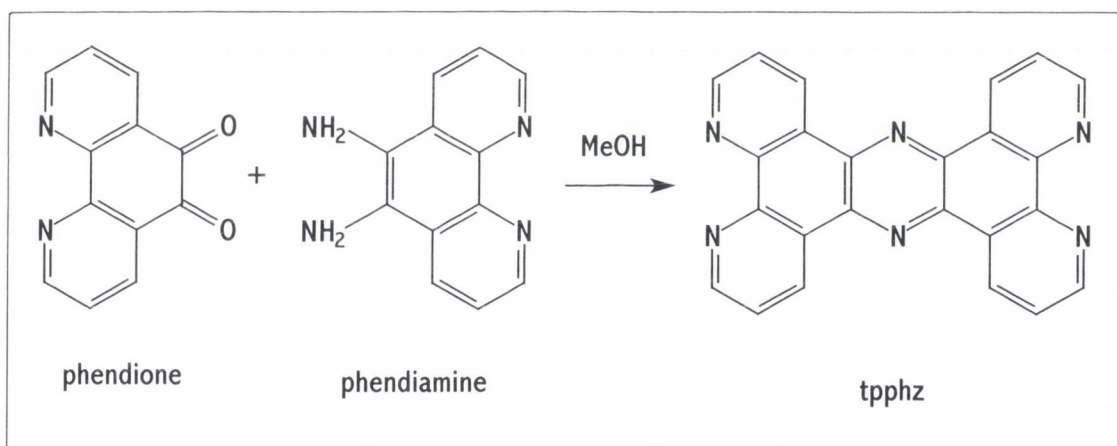
Scheme 1.1. Preparation of the dppz ligand.

The ligand tpphz can be obtained in 2 different ways represented in Scheme 1.2 and 1.3. It can be obtained in a single step by reaction of 1,10-phenanthroline-5,6-dione (phendione) with ammonium acetate as represented in Scheme 1.2



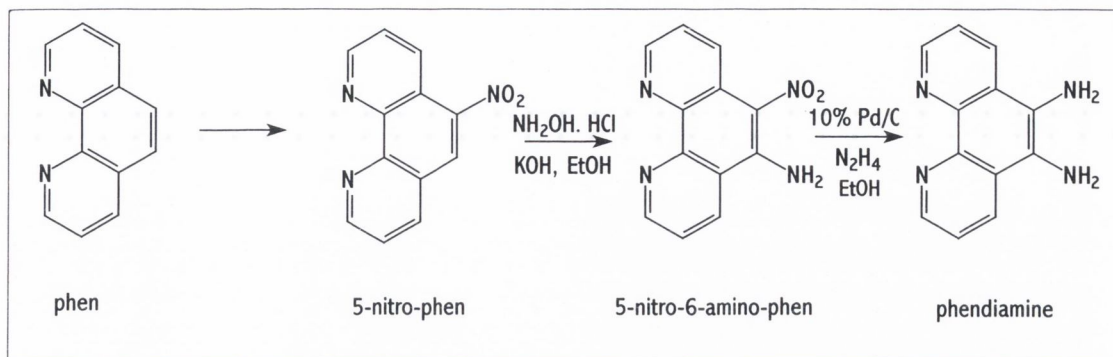
Scheme 1.2: Preparation of tpphz (method A).

It can also be prepared also by condensation of phendione with 5,6-diamino-1,10-phenanthroline (phendiamine).



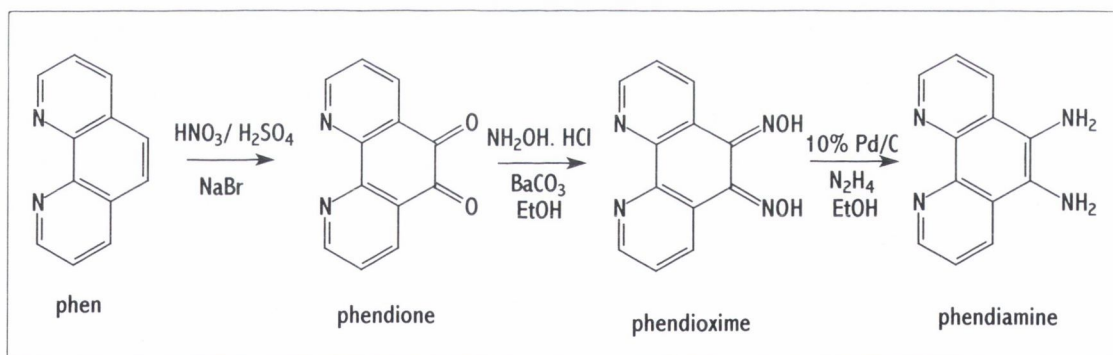
Scheme 1.3: Preparation of tpphz (method B)

The latter can be prepared by amination of 5-nitro-1,10-phenanthroline with hydroxylamine in a strongly basic medium,¹⁷ or with liquid ammonia in the presence of strongly oxidizing agent KMnO_4 ,¹⁸ and the subsequent reduction of 5-nitro-6-amino-1,10-phenanthroline.²¹



Scheme 1.4: Preparation of phendiamine, via 5-nitro-phenanthroline.

Recently a new synthesis for the preparation of phendiamine has been reported by MacDonnell *et al.*¹⁹ in which phendione is converted first to phendioxime by a modification reported by Inglett and Smith.²⁰ This method was followed because it gave higher yields, usually of the order of 80% against the 25 % of the previous method.



Scheme 1.5: Synthesis of phendiamine, with phendioxime as intermediate product.

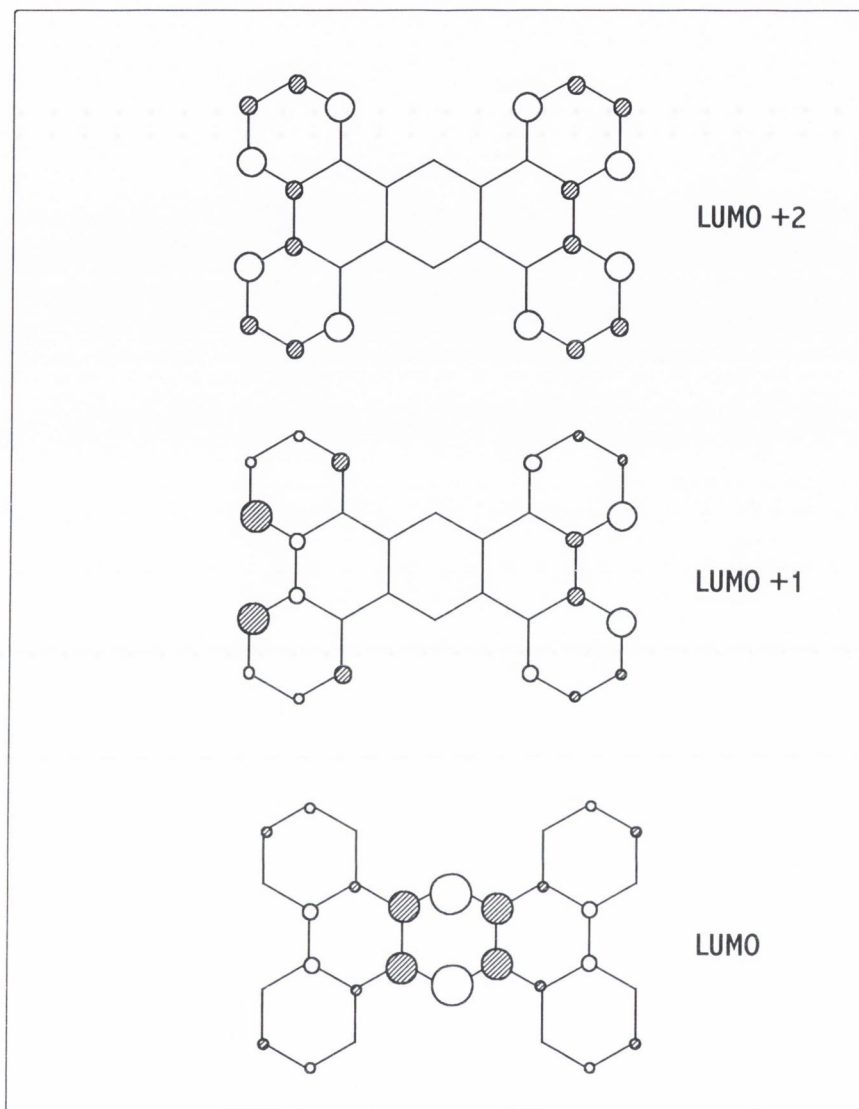


Figure 1.7: MOs of tpphz ligand according to Bolger *et al.*²¹

Extended Huckel calculations have been carried out by Bolger *et al.*²¹ in order to obtain the composition and energy of the tpphz ligand orbitals

Figure 1.7 shows a graphical representation of the squared MO coefficient for the three lowest lying unoccupied orbitals of tpphz. It can be seen the LUMO is mainly localized on the central phenazine part of the ligand, with little overlap with the bipyridine ends and small coefficients at the bipyridine nitrogen atoms. This orbital is at a significantly lower energy than the LUMO in isolated bipy, which reflects a more pronounced π -accepting character of tpphz vs bipy. The next two MOs, LUMO+1 and LUMO+2, are only localized on the bipyridine ends

of tpphz with no contribution from the phenazine central part and with large coefficients on the nitrogen atoms bonded to the metallic centre. In the case of metallic complexes, these LUMO+n ($n>1$) also contain metal and terminal ligand contributions. The HOMO is instead localized on the metal centre.

1.2.2. Excited States of polypyridyl complexes

A schematic diagram MO for an octahedral transition metal complex is shown in Figure 1.8.

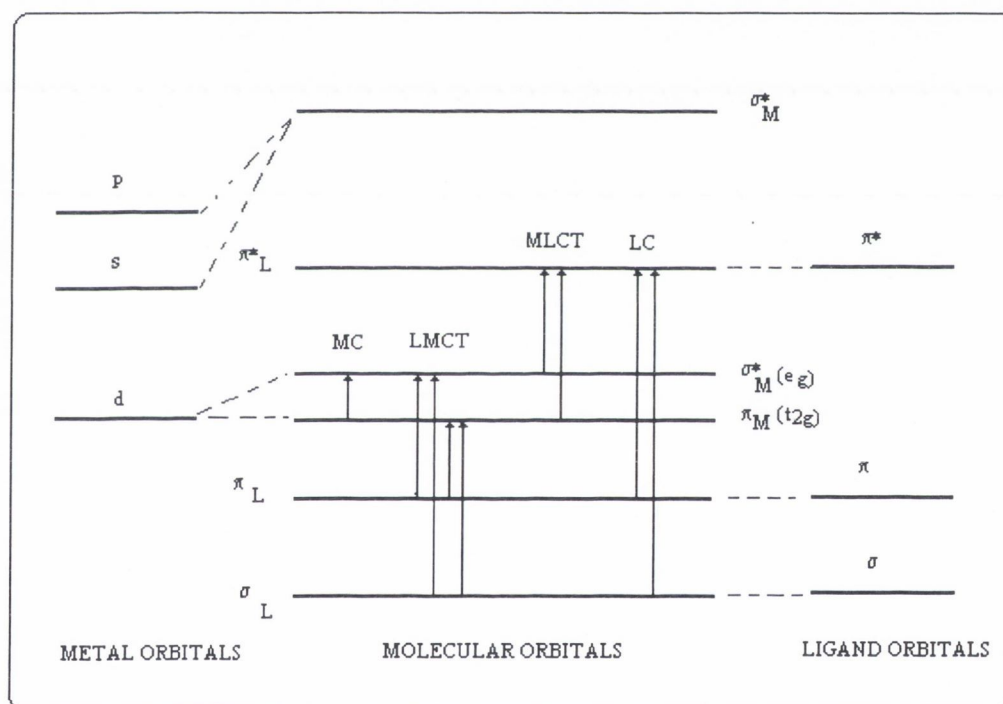


Figure 1.8: Simplified molecular orbital diagram of a typical octahedral polypyridine complex. The various kinds of electronic transitions are also indicated.

The various MOs can be conveniently classified according to their predominant atomic orbital contribution as:

- (i) strongly bonding, ligand-centred σ_L orbitals;
- (ii) bonding, ligand-centred π_L orbitals;

- (iii) essential non-bonding $\pi_M (t_{2g})$ metal-centred, predominantly d-orbitals;
- (iv) antibonding $\sigma^*_M(e_g)$ metal centred, predominantly d orbitals;
- (v) ligand centred, antibonding π^*_L orbitals;
- (vi) strongly antibonding, metal centred σ^*_M orbitals.

In the ground electronic configurations of an octahedral complex of a d^n metal ion, orbitals of types (i) and (ii) are completely filled, while n electrons occupy the orbitals of types (iii) and (iv).

As usual, excited configurations can be obtained from the ground configurations by promoting one electron from occupied to vacant MOs.

At relatively low energy, one expects to find electronic transitions of the following types:

MC (*metal centred*) also indicated as LF (ligand field) or d-d transitions from orbitals of type (iii) to orbitals of type (iv);

LC (*ligand centred*) often indicated as π - π^* transitions of type (ii) to (iv)

MLCT (*metal to ligand charge transfer*) often indicated as d- π^* transition of type (iii) to (iv) or (iv) to (v).

LMCT (*ligand to metal charge transfer*)

These two last transitions belong to the general group of CT (*charge transfer*).

Less frequently encountered types of transitions (not shown in Figure 1.8) are those from a metal- centered orbital to a solvent orbital, **CTTS** (*charge transfer to solvent*), or between two orbitals predominantly localized on different ligands of the same metal center, **LLCT** (*ligand to ligand charge transfer*).

The relative energy ordering of these types of configurations in any particular complex depends on the nature of metal and ligands in a more or less predictable way.

The excited states of polypyridyl complexes fall in general into three categories: MC for $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Fe}(\text{bipy})_3]^{2+}$, MLCT excited states for $[\text{Ru}(\text{bipy})_3]^{2+}$ and $[\text{Os}(\text{bipy})_3]^{2+}$ and intraligand excited states (LC or π - π^*) for $[\text{Rh}(\text{phen})_3]^{3+}$ and $[\text{Ir}(\text{bipy})_3]^{2+}$.

1.2.3. Electrochemical properties of metal complexes

Photoredox reactions are the most widely studied photoreactions of polypyridyl complexes. For a quantitative understanding of the process and development of potential applications, information on the ground state oxidation/reduction potentials and on the stability of various oxidized and reduced forms is required. This information is readily obtained from simple electrochemical measurements of redox potentials and reversibility of oxidation and reduction waves. Such studies, in addition to allowing assignment of donor or acceptor orbitals in electron transfer reactions with a high degree of certainty, allow estimation of the redox properties of the excited states.

Redox properties in the ground state

Oxidation and reduction processes are viewed as metal or ligand centered. The highest energy occupied molecular orbital (HOMO) is most usually metal centered whereas the lowest unoccupied molecular orbital (LUMO) is either metal or ligand centered, depending on the relative energy ordering.

Oxidation usually involves a MC orbital (parent π_M (t_{2g}) orbital in octahedral symmetry). Reduction of the complex may involve a metal-centred or a ligand centred orbital, depending on the relative energy ordering. When the ligand field is sufficiently strong and/or the ligands can be easily reduced, reduction takes place on a ligand π^* orbital. When the ligand field is weak and/or the ligand cannot be easily reduced, the lowest empty orbital in the reduction process can be metal centred (parent π_M^* (e_g) orbitals). Typical examples are the Ru(II) polypyridine complexes. Their oxidation is metal centred and leads to Ru(III) (low-spin t_{2g}^5) compounds which are inert to ligand substitution. Reduction of the Ru(II) –polypyridine complexes takes place on a π^* orbital of the ligands. Therefore the reduced form, keeping its low-spin t_{2g}^6 configuration, is usually quite inert and the reduction process is reversible. It is important to note that if Koopman's theorem is valid for the starting complex and for its one-electron reduced form, the π_L^* or σ_M^* orbitals that are involved in the reduction process (redox orbitals) are the same orbitals which are involved in the MLCT and MC transitions respectively (spectroscopic orbitals). Thus, reversibility of the first

reduction step, indicating a ligand centred LUMO, also implies (to a first approximation) that the lowest excited state is MLCT.

Redox properties in the excited state

All molecular excited states are potential redox agents since the absorption of light leads to excitation of an electron to a higher level where it is more weakly bound and at the same time to an electron hole in the lower level. Excited state species can thus be better oxidants as well as better reductants than corresponding ground state species. The ground and excited state redox potentials are related to each other via the relations:

$$E(M^+/M^*) \approx E(M^+/M) - E_{0-0}(M^*) \quad (1.1)$$

$$E(M^*/M^-) \approx E(M/M^-) + E_{0-0}(M^*) \quad (1.2)$$

The inter-relationship is best illustrated in the form of a Latimer-type diagram (Figure 1.9). The correlations between spectroscopy and electrochemical quantities are based on the assumption that the spatially isolated π^* acceptor orbital is the same for both the reduction process and the charge transfer transition. It turns out that for most transition metal polypyridyl complexes, the redox and spectroscopic orbitals are the same.

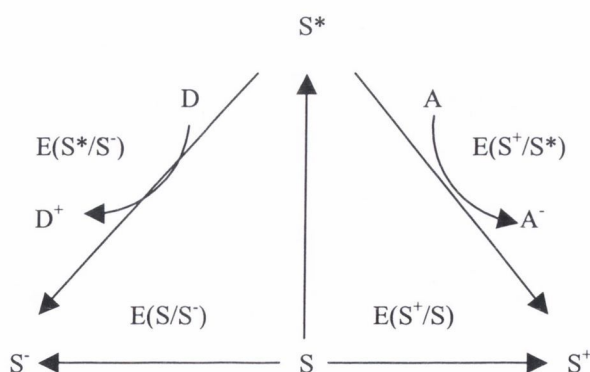


Figure 1.9: Latimer-type diagram illustrating the inter-relationship of ground state redox potentials with those of the excited state (where S is a generic species, D is a donor and A is an acceptor).

1.2.4. Polynuclear polypyridyl complexes

Polyimine ligands such as 2,3-bis(2-pyridyl)pyrazine (2,3-dpp) serve as templates for building polynuclear complexes. In these systems, by an appropriate synthetic design, it is possible to bring all reaction partners into a single supramolecular unit. When interaction between the metal-based components is weak, polynuclear transition metal complexes belong to the field of supramolecular chemistry. The metal-ligand interaction is in fact (i) weak enough to allow the manifestation of intrinsic properties of metal and ligand (ligand-centred and metal-centred absorption bands and redox waves), (ii) strong enough to cause appearance of new properties, characteristic of the whole compound (metal to ligand or ligand to metal charge transfer bands).

There is considerable interest in the study of the photophysics and photochemistry of these species for several reasons, some of which are:

- (i) study of interchromophore and chromophore-quencher interactions;
- (ii) design of photosensitizers (namely antenna systems);
- (iii) potential multi-electron transfer agents;
- (iv) study of mixed valence species.

Polypyridyl Bridging Ligands

In polynuclear complexes the metal-based components are linked together by bridging ligands. In several cases the coordinating moieties of the bridging ligands are linked together (and separated) by spacers. (see Figure 1.10.)

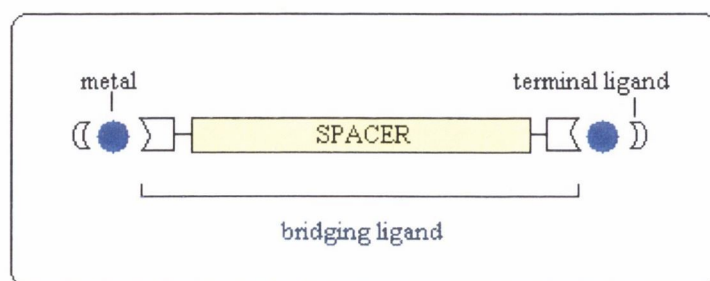


Figure 1.10: *Schematic representation of a dinuclear complex*

In the last few years the increasing interest in photoinduced energy and electron transfer processes in supramolecular systems has led to important progress in the design and preparation of new bridging ligands and in the development of versatile and selective synthetic strategies for the assembly of mononuclear complexes in supramolecular structures. The role of the bridging ligand is extremely important for the following reasons:

- (i) with their coordinating sites they contribute to the determination of the spectroscopic and redox properties of the active metal based units;
- (ii) their spacers and the connections between spacers and coordinating sites determine the structure of the supramolecular system;
- (iii) the chemical nature of the bridging ligand controls the electronic communication between the metal based units.

Therefore the choice of suitable bridging ligand is crucial in obtaining polynuclear complexes capable of showing luminescence, exhibiting interesting electrochemical properties and giving rise to photoinduced energy- and electron-transfer.

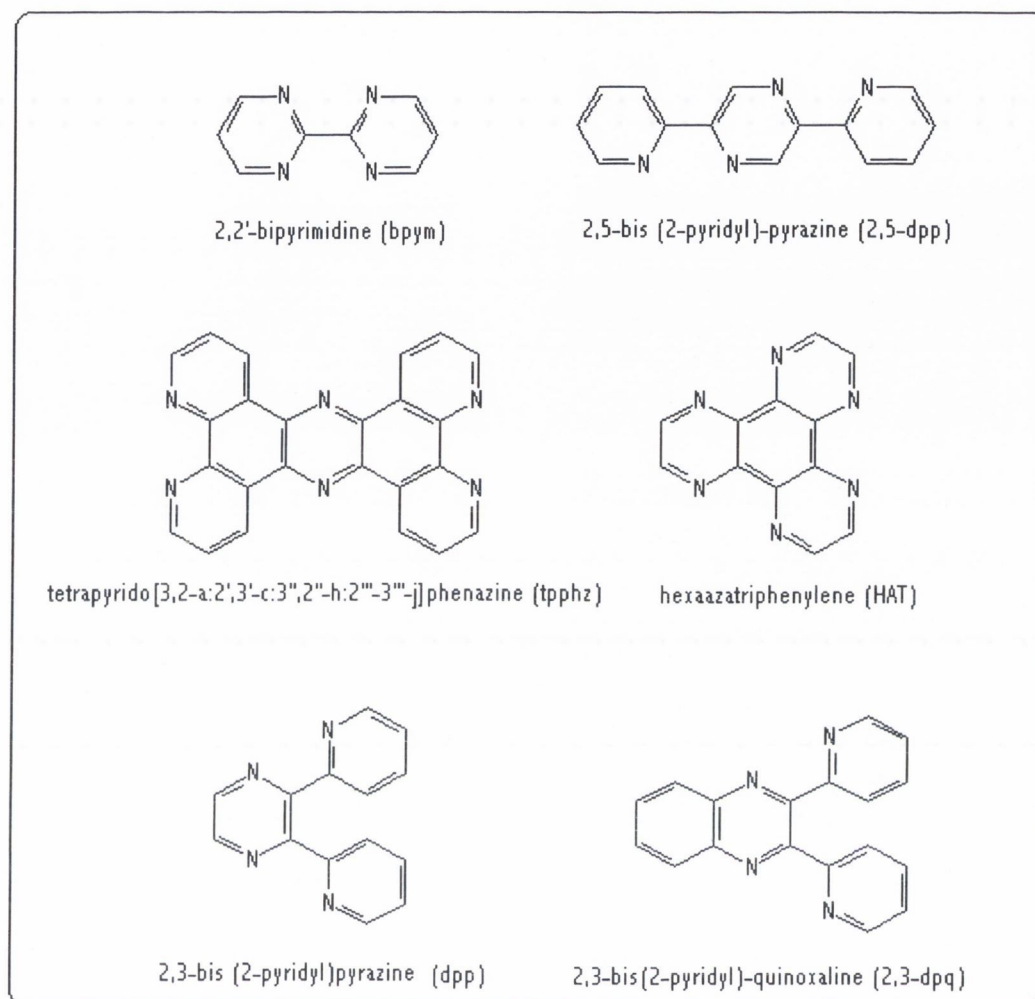


Figure 1.11: Structure of some multidentate polypyridyl ligands used in the synthesis of polynuclear polypyridyl complexes together with their abbreviations.

Energy- and electron transfer processes

On passing from a mononuclear to a polynuclear species we find, besides properties related to the individual component, properties related to the structure and composition of the whole array. A suitable choice of the mononuclear building-blocks and bridging ligands and an appropriate design of the supramolecular structure can in fact allow the occurrence of very interesting and useful processes. Important and distinctive photochemical processes of supramolecular species are those taking place between components. Particularly important are two processes that can follow light excitation of a component

(photoinduced electron and energy transfer) and an electron transfer process that takes place directly upon light excitation (optical electron transfer). We refer to a generic supramolecular system $A\sim B$, where A and B represent the donor and acceptor moieties linked covalently via a spacer bridge ($\sim$).

Photoinduced electron transfer It is well known that light excitation increases both the oxidising and the reducing power of a molecule. In a multicomponent supramolecular system therefore, light excitation can often be followed by an electron transfer process, e.g.



The electron transfer is therefore a radiationless process.

The relevant thermodynamic parameters are the reduction potentials of the $A^+/*A$, B/B^- and $*A/A^-$, B^+/B^- couples. To a first approximation, the reduction potentials for the excited state couples may be calculated from the reduction potentials of the ground state couples and the one-electron potential corresponding to the zero-zero excitation energy:

$$E(A^+/*A) \approx E(A^+/A) - E^{0-0};$$

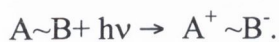
$$E(*A/A^-) \approx E(A/A^-) + E^{0-0}.$$

Energy transfer Electronic energy transfer $A^*\sim B \rightarrow A\sim B^*$ can occur by two mechanisms: the Forster type mechanism based on Coulombic interactions and the Dexter-type mechanism, based on exchange interactions.

The Forster type mechanism is a long-range mechanism that is efficient when the radiative transitions corresponding to the deactivation and the excitation of the two partners have high oscillator strength.

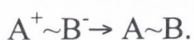
The Dexter-type mechanism is a short-range mechanism that requires orbital overlap between donor and acceptor.

Optical-electron transfer The absorption spectrum of a supramolecular system can differ substantially from the sum of the spectra of the molecular components. Some totally new bands can be present in the spectrum of the supermolecule. These bands correspond to the optical electron transfer process



Such a process should be distinguished from photoinduced electron transfer which corresponds to radiationless electron transfer following electronic excitation of a single component.

Both optical electron transfer and photoinduced electron transfer may be followed by a *thermal back-electron transfer-process*:



The relationship between optical, photoinduced and thermal-back-electron transfer processes in supramolecular species are illustrated in Figure 1.12.

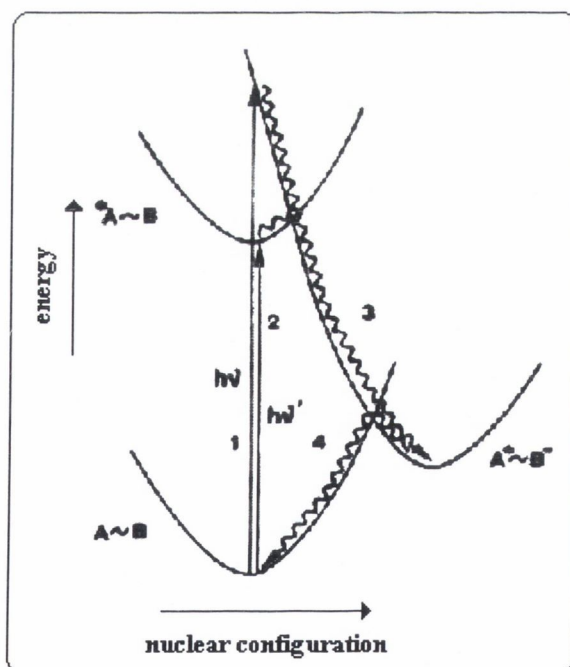


Figure 1.12: Relationship between optical (1), photoinduced (2) and (3) and thermal back (4) electron transfer processes in supramolecular species. Vibrational levels are omitted.

1.2.5. Stereochemistry of polypyridyl complexes

Chirality is expected to play important roles in long-distance and bridge-mediated energy-transfer when the dominant mechanism is Coulombic or electron-exchange operating in a non-adiabatic regime. Chiral control of energy and electron transfer within polynuclear complexes is expected to be a step forward with respect to simple topological control as it would ultimately lead to more efficient artificial systems for solar energy conversion and light information processing and storage.

The control of chirality will be of use in studying the interactions between polypyridyl complexes with DNA as it has been noted that these species bind to the DNA molecule enantioselectively.

Octahedral coordination of transition metal ions with polypyridyl ligands is one of the most common structural motifs observed in supramolecular chemistry.

Octahedral complexes of the type $[M(LL)_3]^{n+}$, where LL is a bidentate ligand such as bipy or phen, often have an overall symmetry D_3 . The reduction from O_h to D_3 has a number of important consequences, one of which is chirality. A $[M(LL)_3]^{n+}$ ion is not superimposable on its mirror image, so it is, in principle, possible to isolate the two enantiomers of the compound, namely the Λ and Δ forms (Figure 1.13).

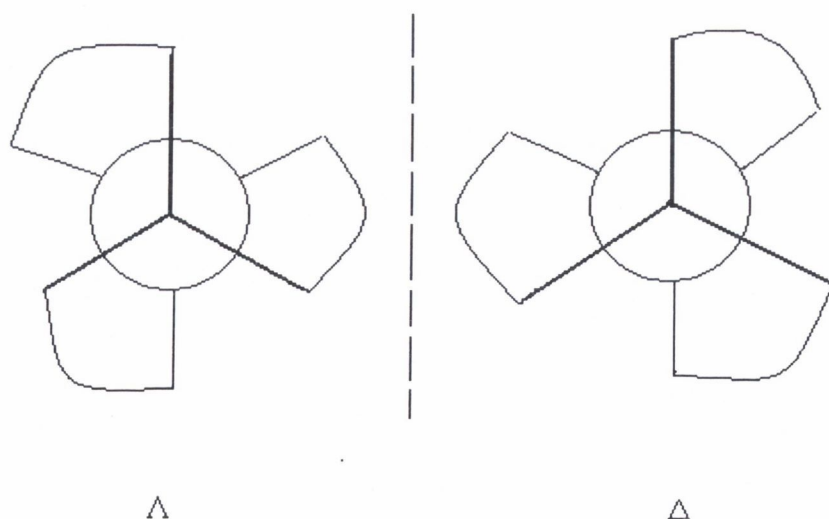
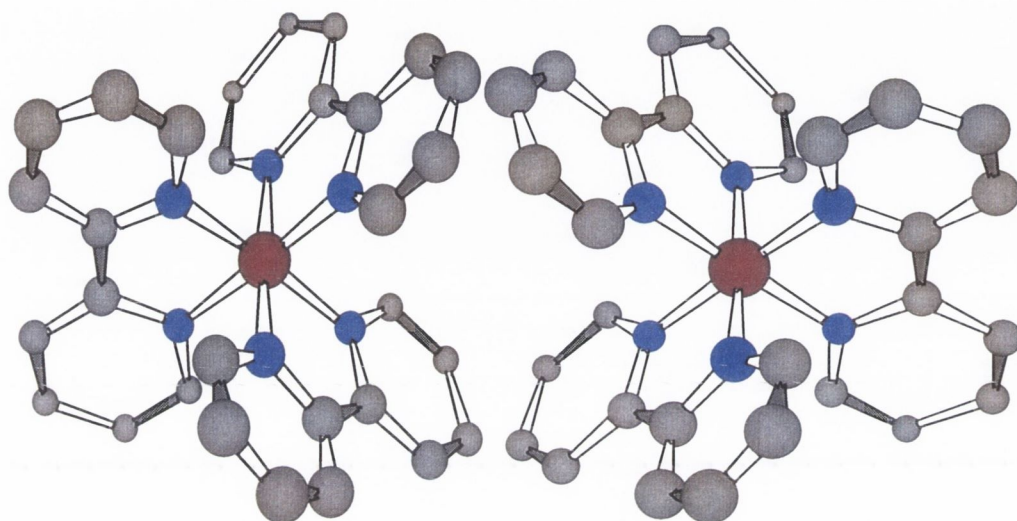


Figure 1.13: Fisher projections of the enantiomers of D_3 symmetric $[M(LL)_3]^{n+}$ cation.

Enantiomers of several non-labile tris-chelate complexes have been isolated. In Figure 1.14 the two enantiomers of $[\text{Ru}(\text{bipy})_3]^{2+}$ are represented.



Λ - $[\text{Ru}(\text{bipy})_3]^{2+}$

Δ - $[\text{Ru}(\text{bipy})_3]^{2+}$

Figure 1.14: Λ and Δ enantiomers of $[\text{Ru}(\text{bipy})_3]^{2+}$.

If the bipy or phen are asymmetrically substituted (i.e. no longer C_2 symmetric) even more isomers are obtained due to the formation of *mer* and *fac* isomers (Figure 1.15).

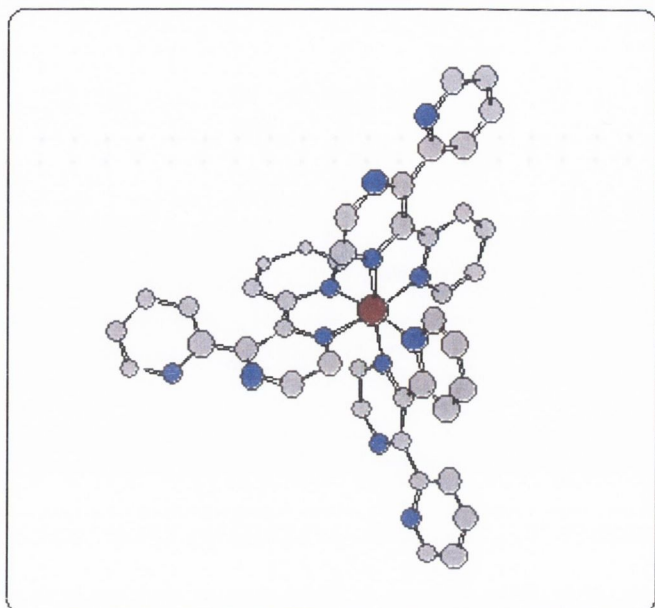


Figure 1.15: The *mer*- isomer of $[\text{Ru}(2,3\text{-dpp})_3]^{2+}$

As these units are connected into supramolecular species the number of possible isomers increases exponentially.

For instance, on going from mononuclear to binuclear complexes, two chiral centres are linked together and diastereoisomers are formed (Figure 1.16).

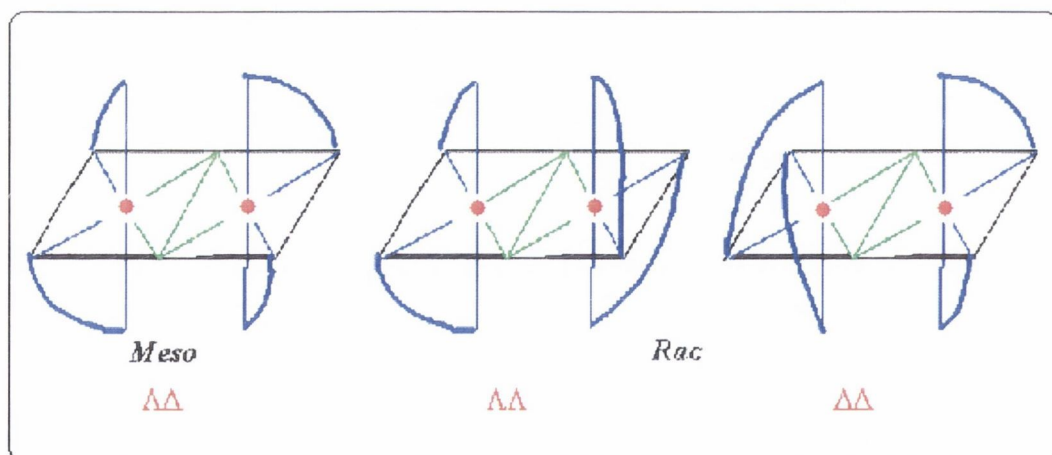


Figure 1.16: The isomeric possibilities of dinuclear species.

The use of stereochemically pure building blocks has proven to be applicable in several instances.

The complex $\Delta/\Lambda\text{-}[\text{Ru}(\text{bipy})_2(\text{py})_2]^{2+}$ has been found by von Zelewsky²² to selectively co-crystallize with chiral anions in remarkably high purity. These are

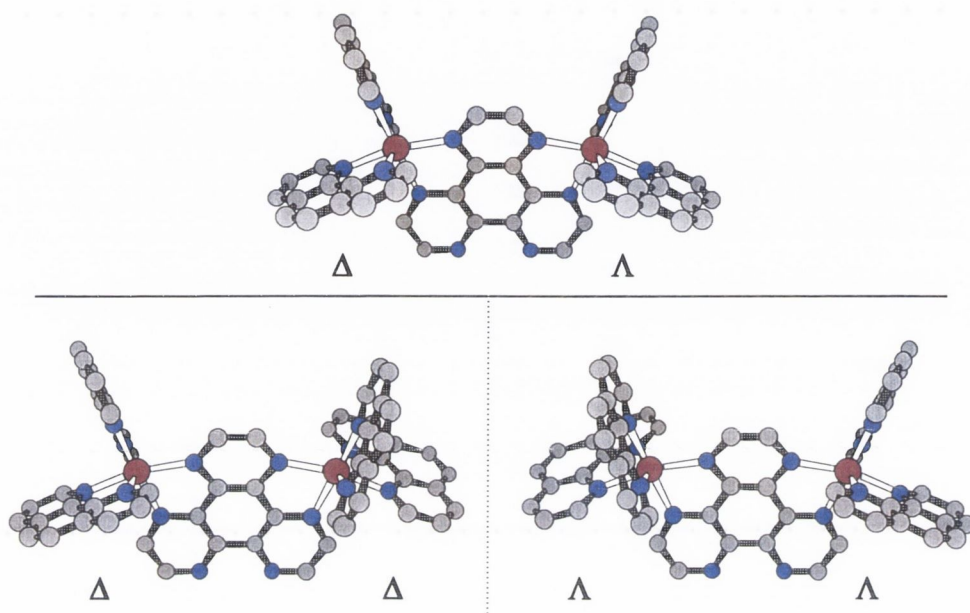


Figure 1.18: Diastereoisomers of $[(\text{phen})_2\text{Ru}(\text{HAT})\text{Ru}(\text{phen})_2]^{4+}$

Enantiomerically pure polynuclear complexes with up to 10 metal centres have been prepared by MacDonnell *et al.*²⁴ Only one of the possible enantiomers of a Ru(II) tetranuclear species is shown below in Figure 1.19.

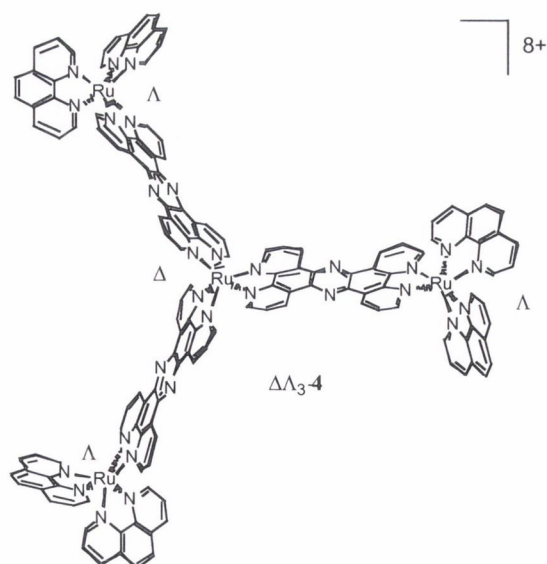


Figure 1.19: $\Delta\Lambda_3\text{-}\{[\text{Ru}(\text{phen})_2(\text{tpphz})]_3\text{Ru}\}(\text{PF}_6)_8$.

1.3. Polypyridyl Complexes and DNA

DNA is a marvellous molecule. It is a polyanion with a very complex structure and a rich selection of coordinating sites, which range from the hard phosphate oxygen atoms to the soft heterocyclic base nitrogen positions. The DNA molecule contains all the genetic information necessary for cellular function. The control and regulation of genetic information at the chemical level depend upon binding proteins or small molecules to specific sites along a DNA helix. Understanding the binding of small molecules to DNA is therefore potentially useful in developing design principles to guide the synthesis of new improved drugs which can recognize a specific site or conformation of DNA and to provide a good tool for biotechnology.

The design of molecules that target specific sites along a DNA helix is therefore a subject of considerable interest. The most important aims of these studies are:

- (i) The development of selective DNA –cleaving agents for mapping or footprinting experiments;²⁵
- (ii) The recognition of local structures along the DNA strand;^{26,27}
- (iii) The rational design of drugs.²⁸

In studying the interaction of small molecules with DNA, metal complexes are flexible reagents which offer the opportunity of exploring the effect of the central metal atom, the ligands and the coordination geometry on the binding event. The metal complexes bound to DNA through non-covalent interaction generally form an important subgroup, of which the members are cations and typically contain ligands bearing extended hydrophobic areas or surfaces. The examples of this category of DNA-binding agents are metal complexes with polypyridines or 1,10-phenanthroline and their derivatives such as 4,7-diphenyl-1,10-phenanthroline (DIP) and dipyrido[3,2-a;2',3'-c]phenazine (dppz). The structure, size and relative disposition of the ligands in the coordination sphere of the central metal atom directly affect the binding to DNA. Furthermore, since DNA is an optically active molecule, the specific binding sites may prefer one of the enantiomeric forms of the metal complexes. For that reason, metal complexes with phen and related ligands, in particular ruthenium(II) complexes, have been studied extensively either as structural probes or as mediators of DNA cleavage reactions.

1.3.1. Primary and Secondary Structure of DNA

The backbone of DNA is an alternate polymer of the sugar deoxyribose and phosphoric acid, the latter esterified to the primary 5'-hydroxyl group of one deoxyribose sugar and to the secondary 3'-hydroxyl group of the other. This phosphoric acid diester moiety still contains an acid proton and DNA is thus a polyanion at physiological pH. The sugars in turn form a glycosidic bond to a ring nitrogen of one of the four nucleobases: adenine (A), thymine (T), guanine (G) or cytosine (C) (shown in Figure 1.20).

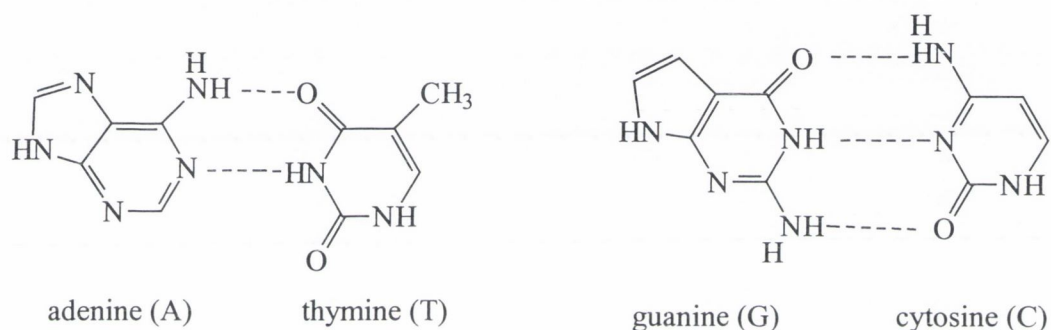


Figure 1.20. *The four bases of DNA*

The secondary structure of DNA is described by the Watson and Crick²⁹ model in which two complementary anti-parallel polymer strands are held together by hydrogen bonds between the heterocyclic bases, which are in turn stacked on top of each other. In this overall structure, the most stable hydrogen bonded basepairs are A-T and G-C, thus the sequence of bases in one strand completely determines the sequences of bases in the other, complementary, strand.³⁰ (Figure 1.21)

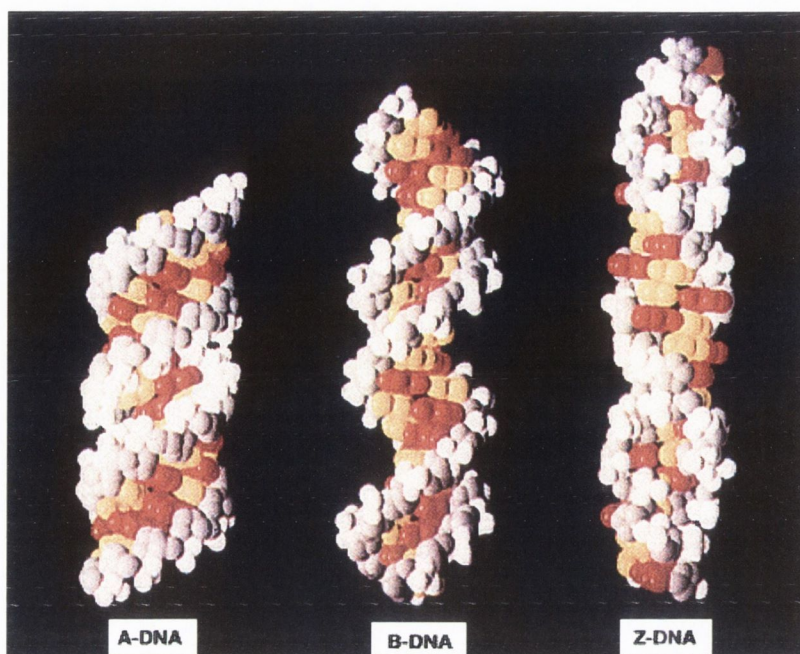


Figure 1.22: *Three polymorphic forms of DNA: right-handed A and B, left-handed Z-DNA.*

1.3.2. Interactions of small molecules with DNA

Among all the natural or synthetic molecules known, metallic ions and proteins are well known for adopting a non-covalent binding mode to DNA.³¹

The study of these interactions has a preponderant role in this area of research which has as its aim improving the action of the agent interacting with DNA.

Types of interactions

Upon binding to DNA, the small molecules are stabilized through a series of weak interactions such as π -stacking interactions of aromatic heterocyclic groups between the base pair (intercalation), hydrogen bonding and Van der Waals interactions of functional groups bound along the groove of the DNA helix.

It is believed that non-covalent interactions of these types take place in at least three distinct modes, ie. binding along the outside of the helix, binding along the major and/or minor grooves, and intercalation of a planar molecule or a planar aromatic ring system between base pairs. Identifying which of the above interaction modes is operative for the molecule concerned, as well as which is predominant among the series of weak interactions, is essential in designing new

drugs and DNA-probe molecules. The different types of interactions (Figure 1.23) will be examined in detail.

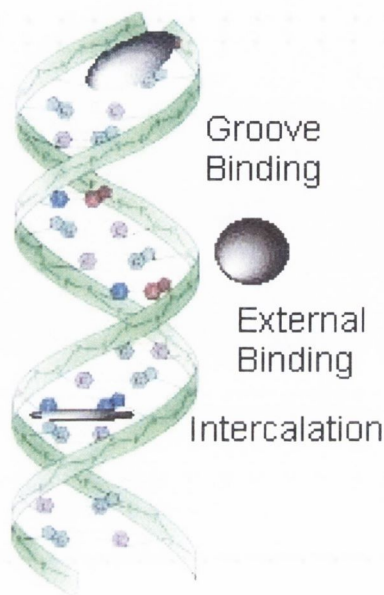


Figure 1.23: Schematic diagram illustrating the three modes of binding to DNA.

Typical modes of interaction between small molecules and DNA are:

Electrostatic interactions: Being a polyanion, DNA will attract any cationic species, the negative charge being on the phosphate groups.

A typical group of molecules that display a high affinity for DNA and other double-stranded polynucleotides consists of organic cations, such as the dyes ethidium and acridine³², which bear an extended heteroaromatic system. Methylene blue is also well known to bind in this way. These species are illustrated below in Figure 1.24. In addition they bind DNA by intercalation since the flat dye slides between the hydrophobic base pairs and is stabilized by a π -stacking interaction³³

Hydrogen bonds: the bases of DNA can form H-bonds with molecules situated in the major-groove or minor groove. An example is represented by DAPI, which is a neutral molecule, used as a fluorescent DNA stain, which binds in the minor groove³⁴.

Van der Waals Forces: these play an important role in the affinity of certain molecules with DNA. These forces can favour a specific interaction, ie. they can

mark only certain sequences of bases. An example is represented by distamycin which shows a particular affinity for some nucleotide rich portions in AT sequences.

Intercalation: Flat aromatic molecules, as exemplified by the dye methylene blue, can access an apparently even more hydrophobic environment by intercalation, ie. insertion into the base pair stack³⁵ where they are stabilized by π -stacking. The gap thus opened between two basepairs will be referred to as an intercalation pocket. Upon intercalation, the DNA is lengthened and the helix partially unwound. The distinction between intercalative and groove binding modes is relevant for small molecules, but loses some importance in complex molecules, where both intercalation and interactions with the groove are likely to determine the characteristics of the drug-DNA adducts.

An important aspect of non-covalent binding to DNA that distinguishes it from binding of drugs to receptors or enzymes, especially for compounds that do not have a very specific base sequence as a target, is the fact that DNA is a linear polymer of putative binding sites, and that the binding of one site will inevitably affect the neighbouring binding sites. This neighbouring interaction may discourage binding to the nearby binding site (anti-cooperativity), favour binding (cooperativity) or do neither (non-cooperativity binding). Even in the last case, more subtle properties of the bound molecules, such as kinetic or spectroscopic properties, can be affected by the presence or absence of neighbours.

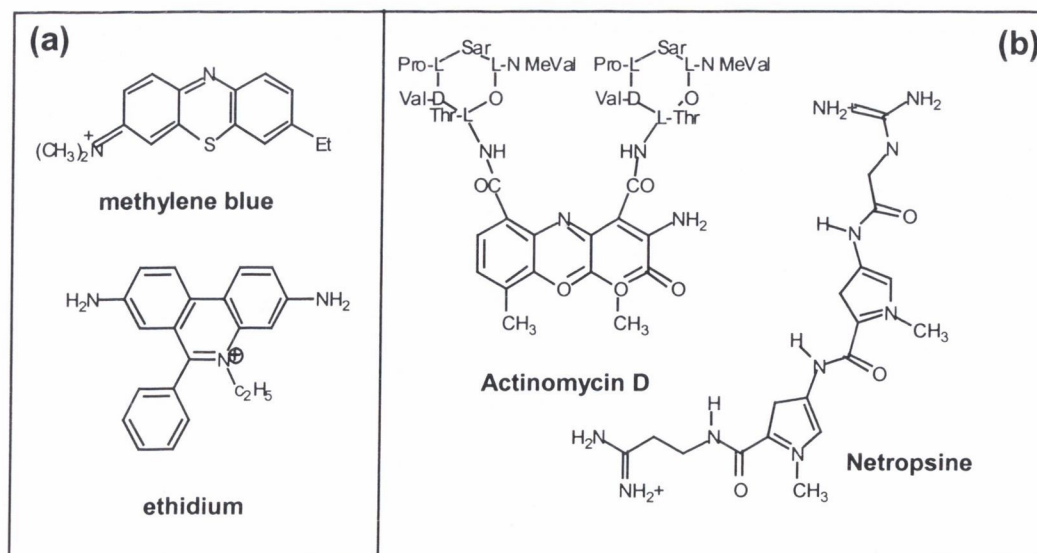


Figure 1.24: Examples of DNA a) intercalators, b) groove-binders

1.3.3. Reactions between small molecules and DNA

Reactions in the dark will be considered separately from those under illumination. As a general rule, the reactions described here produce a variation inside the structure of DNA, *in vivo*, or perturbations of the replication process of the DNA or of the gene expression.

Cleavage of the DNA

A great variety of compounds, ranging from heterocyclic molecules to metal transition complexes, can induce a cleavage of the bond between the sugar and the phosphate.

We can have:

- (i) cleavage in the absence of light;
- (ii) cleavage in the presence of light (photocleavage).

Formation of adduct with DNA

Irreversible formation of a covalent bond between certain components of DNA and the reactive molecule has been observed. These types of reaction are of great interest because these can be utilized as luminescent tracers of DNA.

In this case also we can distinguish:

- (i) formation of adduct in presence of light (photoaddition);
- (ii) formation of adduct in absence of light.

1.3.4. Interactions between polypyridyl complexes and DNA

The interaction of metal complexes with DNA and RNA is a fascinating area of supramolecular chemistry, which has great potential in the fields of biological diagnostic and chemical therapeutics.³⁶ Considerable interest also relies in DNA-mediated electron transfer.^{37,38}

Since the pioneering work of Lippard³⁹ on the interaction of *cis*-Pt(II) complexes with DNA an exponential number of complexes have been designed to investigate specific local DNA conformations or used as site-specific reagents, for example for conformation specific cleavage of the DNA helix. The photophysical and

photochemical properties can be useful for the above purposes as shown by a vast and growing literature in the subject.^{40,41,42} Among the various octahedral complexes that can be used in these studies, those containing polypyridyl ligands have received particular attention. In particular Ru(II) polypyridyl complexes have been studied extensively either as structural probes or as mediators of DNA cleavage reactions

Spectroscopy and photo physics

When Ru(II)-polypyridyl complexes interact with DNA, more or less noticeable changes occur in their spectroscopic and photophysical properties. In general, the metal-to-ligand charge-transfer bands in the visible region decrease in intensity and their maxima undergo blue or red shifts. The degree of hypochromism and the spectral shift generally correlate well with the overall binding strength. The hypochromicity data for complexes $[\text{Ru}(\text{bipy})_2(\text{LL})]^{2+}$ show that the interaction decreases along the ligand series $\text{HAT} > \text{biq} = \text{DIP} > \text{phen} > \text{bipy}$, indicating again that the dimensions of the ligand play an important role. No effect is observed for the neutral $\text{Ru}(\text{phen})_2(\text{CN})_2$ complex, indicating that ion-pair interaction is necessary for the stability of the adducts.

The luminescence of Ru(II)-polypyridyl complexes is also affected by interaction with DNA. In most cases, the emission intensity increases (by a factor of 2 or 3), the bandwidth decreases, and the band maximum is shifted. Furthermore the luminescence decay is strongly affected and becomes quite complicated. The red or blue shift of the emission band in the mixed-ligand complexes depends on whether or not the lowest (luminescent) excited state involves CT to the intercalated ligand. Time-resolved emission experiments show at least two emitting species are present. The reduction in the luminescence intensity and the very short-lived (< 20 ns) component observed for $[\text{Ru}(\text{TAP})_3]^{2+}$ in the presence of DNA are related to the excited-state quenching by a redox process. Protection from oxygen quenching plays a major role in increasing the lifetime of the intercalated complexes. Luminescence and quenching experiments have demonstrated that the enantiomeric form of $[\text{Ru}(\text{phen})_3]^{2+}$ possesses a quite different affinity for the right-handed B-form of DNA. The same specific

interaction is observed with $[\text{Ru}(\text{DIP})_3]^{2+}$. This enantiomeric specificity of binding can be understood in terms of the intercalation model and of its steric requirements. While most work has been concentrated on Ru(II) complexes, lately some attention has been devoted to a new class of complexes which seem to be very promising as potential anti-cancer drugs. In fact, Cr(III) polypyridyl complexes would appear to combine several of the attractive features of both the Ru(II) and Rh(III) complexes, in view of their long-lived room temperature emission and strong excited-state oxidizing power.⁴³

Recent papers by Kane-Maguire^{44,45} reported the quenching of the emission for the correspondent $[\text{Cr}(\text{phen})_3]^{3+}$ and related complexes in aqueous solution when DNA was added to them.

Polymetallic polypyridyl complexes have recently been examined showing a much higher binding affinity to DNA than most mononuclear complexes.⁴⁶

Photochemistry

Drug-dependent damage of DNA is a sensitive marker of binding, not only of the number of bound sites but also of their location along the strand. Since electron transfer reactions offer a pathway for oxidative cleavage of the DNA strand, redox-active metal complexes are very useful in the design of specific cleaving agents. Ferrous ions can activate O_2 to yield radicals or iron-bound oxygen species which can cleave the sugar phosphate backbone.

It was also realized that light-induced redox reactions of metal complexes could be used for DNA cleavage. It was shown that $[\text{Co}(\text{phen})_3]^{3+}$ is a DNA cleaver, and that the cleavage by $[\text{Co}(\text{DIP})_3]^{3+}$ is enantiospecific. The photoinduced cleavage of DNA by metal complexes is not limited to complexes which intercalate. $[\text{Rh}(\text{phen})_3]^{3+}$ and a variety of Ru(II) complexes are able to cause light-induced cleavage, whereas $[\text{Cr}(\text{phen})_3]^{3+}$ is inactive.

The variety of photoactive metal complexes and of the excited states involved points to the presence of different reaction mechanisms. A series of experiments based on the effect of D_2O and quenchers indicate that one possible mechanism is the sensitized production of singlet oxygen by the bound complexes which have a

long-lived excited state. Cleavage is also very efficient for complexes like $[\text{Ru}(\text{bipy})_3]^{2+}$ in the presence of the radical precursor $\text{S}_2\text{O}_8^{2-}$.

Another mechanism is direct photooxidation of a DNA base by the photoexcited complex. This is the case for $[\text{Ru}(\text{TAP})_3]^{2+}$ which is the most efficient cleaver among the Ru(II) complexes examined by Kelly's group. Evidence for this mechanism comes from the following:

On the basis of the same evidence it has been suggested that the same mechanism can occur in the $\text{Cr}(\text{phen})_3^{3+}$ complex.

The formation of photo-adduct has also been shown by a binuclear Ru(II) complex containing a multifunctional poly-aza aromatic ligand⁴⁷. Under steady-state illumination the complex gives rise to a photoadduct in the presence of denaturated CT-DNA, but not with non-denaturated CT-DNA. These results suggest that light-active polynuclear metal compounds could be used as molecular tools to target and mark irreversibly portions of important deformations along the double-helix.

1. 4. Photochemical molecular devices

Supramolecular species have the potential of performing specific functions, i.e. to behave as molecular devices. Particularly interesting molecular devices are those which use light to achieve their function. Molecular devices which perform light induced functions are called photochemical molecular devices (PMD). Luminescent and redox-active polynuclear complexes can play a role as PMDs operating by photoinduced energy and electron transfer processes.

In polynuclear complexes it is possible to identify components which can undergo photoexcitation independently from one another. The excited component can then give rise to intercomponent energy- or electron-transfer processes, in competition with intracomponent decay. For most of the components which we are discussing, the lifetime of the lowest excited state is long enough to allow the occurrence of energy or electron transfer to nearby components when suitable energetic and electronic conditions are satisfied. This is not the case for upper excited states, which decay very rapidly to the lowest excited state within each component. These processes are very important for the design of devices capable of performing useful light-induced functions.

1.4.1. Antenna systems

Electronic energy transfer in polynuclear transition metal complexes can be exploited for light harvesting (antenna effect). Generally speaking, an artificial antenna is a multicomponent system (Figure 1.25) in which several molecular components absorb the incident light and channel the excitation energy to a common acceptor component.

In the development of artificial antenna systems based on transition metal complexes, one trend is to assemble very large numbers of molecular components in more or less statistical ways. For example, photon-harvesting polymers are being developed in which rapid energy migration among pendant chromophoric groups is observed under certain conditions. Among the most interesting are porphyrin-based antenna arrays. Through systematic control of the position of the various components in the supramolecular arrays, a gradient can be created for energy transfer in a predetermined direction. For example, cyano-bridged

complexes with d^6 metal complexes have been used in the design of small antenna systems, in which solar energy can be converted into electricity.

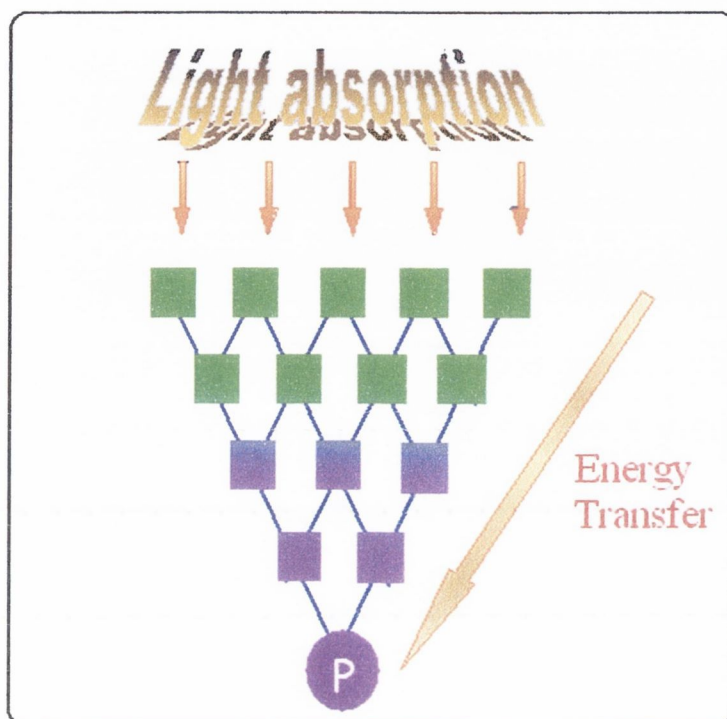


Figure 1.25: Schematic representation of an artificial antenna for light harvesting (courtesy of S. Campagna, TMR meeting, Contract N. ERBMRXCT98-0226).

1.4.2. Dendrimers and Arborols

An interesting example of an antenna system is represented by dendrimers or arborols, so called because of their shape.

The word "*dendrimer*" comes from the greek *δενδρον*, tree. Dendrimers are hyperbranched molecules, composed of a central core, to which repetitive branches are attached.

These branches are synthesized from identical building blocks via an iterative synthetic strategy.

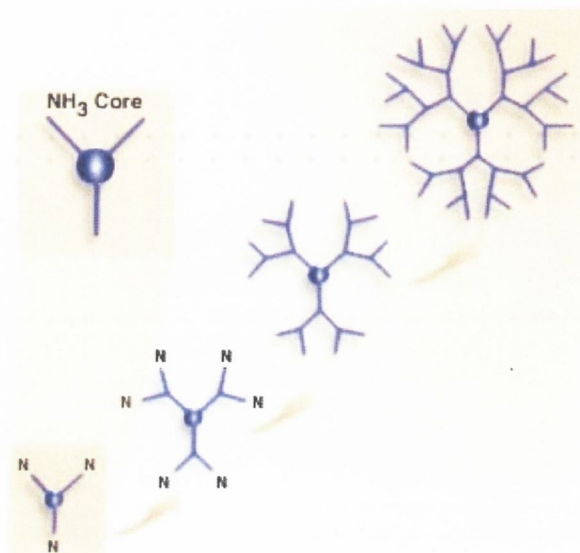


Figure 1.26: Representation of a dendrimer

By careful choice of the building blocks to be used and specific functionalization in the periphery, the molecular weight, monodispersity, size, shape, chirality, density, viscosity, polarity, solubility, flexibility and surface chemistry of the resulting macromolecules can be controlled. This leads to new materials with great potential for future applications.

Dendrimers based on polypyridyl complexes

Quite interesting for their potential application as light-harvesting units have been dendrimers based on transition metal complexes. These have been synthesized and studied by the groups of Campagna and Balzani. Complexes containing up to 22 metal-centres have been synthesised using 2,3-dpp and/or 2,5-dpp as bridging ligands, Ru(II) and/or Os(II) as metal centres, and bipy or 2,2'-biquinoline (biq) as terminal ligands. (Figure 1.27)

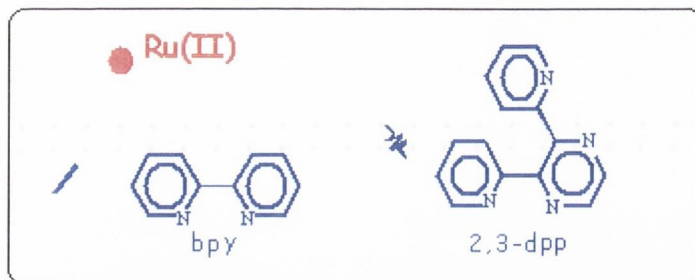


Figure 1.27: Schematic representation of some of the metal centres, bridging ligands and terminal ligands, and their symbols, used in the construction of dendrimers.

The strategy used to build up these species is called "complexes as metal/complexes as ligands", i.e. one uses complexes (building blocks) in place of the metal (M) and/or the ligands (L). The place of M can be taken by mono- or oligonuclear complexes that possess easily replaceable ligands, so that they can give rise to species with unsaturated metal coordination sites - "complex metals"- and the place of L can be taken by oligonuclear complexes which contain free chelating sites: "complex ligands"

Dendrimers can be constructed by two different approaches: one is convergent or "outside in" construction, whereby preformed branched arms are attached to a more or less large core⁴⁸, see Figure 1.28:

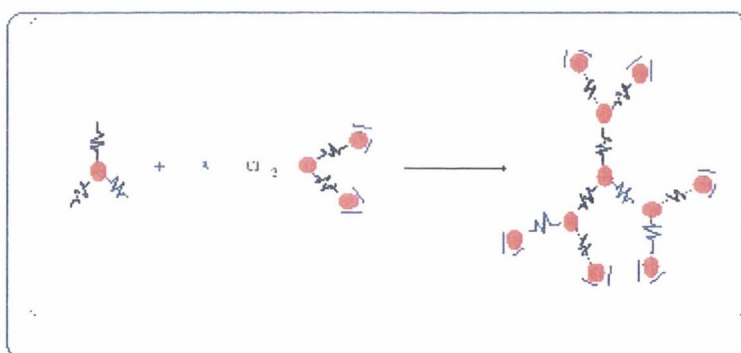


Figure 1.28: Convergent approach for the formation of a decanuclear dendritic species.

An alternative and more general strategy is called divergent (or "inside out")⁴⁹.

The latter is an iterative procedure which starts with an initial core containing n reactive sites. To this core (0^{th} generation of the dendrimers), n units (building blocks) can be connected. This produces the first generation of the dendrimer. If the peripheral units of the dendrimer so obtained still contain reactive sites, the process can be iterated, yielding a second generation dendrimer, and so on (Figure 1.29).

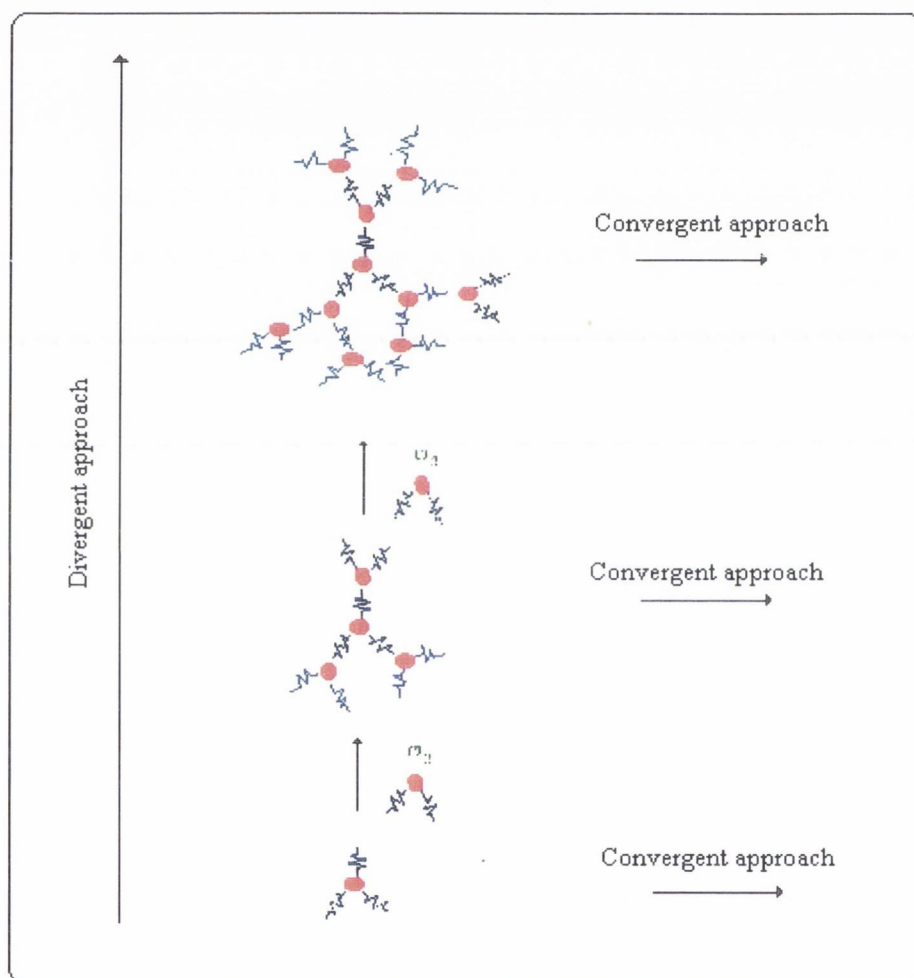


Figure 1.29: Divergent synthetic strategy to obtain polynuclear metal complexes of dendrimer shape. Each compound of the divergent synthetic approach can be used as a core in a convergent synthetic process.

The divergent iterative approach requires the availability of bifunctional species. In dealing with coordination compounds, such species have to be complexes capable of behaving both as a ligand and as a metal. A simple example is $[\text{Ru}(2,3\text{-dpp})_2 \text{Cl}_2]$ shown in Figure 1.30.

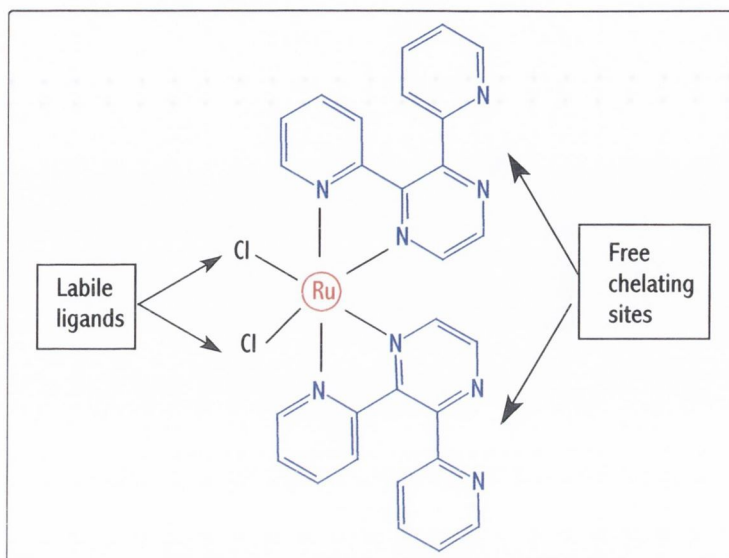


Figure 1.30: Schematic representation of the bifunctional $[Ru(2,3-dpp)_2Cl_2]$ complex.

Such polynuclear complexes can be obtained with a high degree of synthetic control in terms of the nature and position of the metal centres, bridging ligands and terminal ligands. A decanuclear Ru(II) complex is represented in Figure 1.31

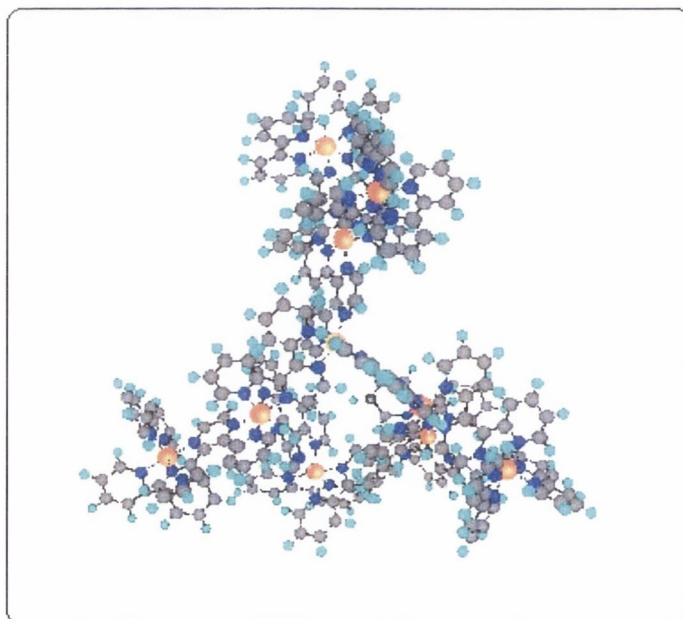


Figure 1.31: Structure of a decanuclear Ru(II) dendrimer (courtesy of S. Campagna, TMR meeting, Contract N. ERBMRXCT98-0226).

The energy of the lowest metal-to-ligand charge transfer (MLCT) excited state of each unit depends on metals and ligands in a well-known and predictable way. Thus, the synthetic control translates into a high degree of energy flow within the species.

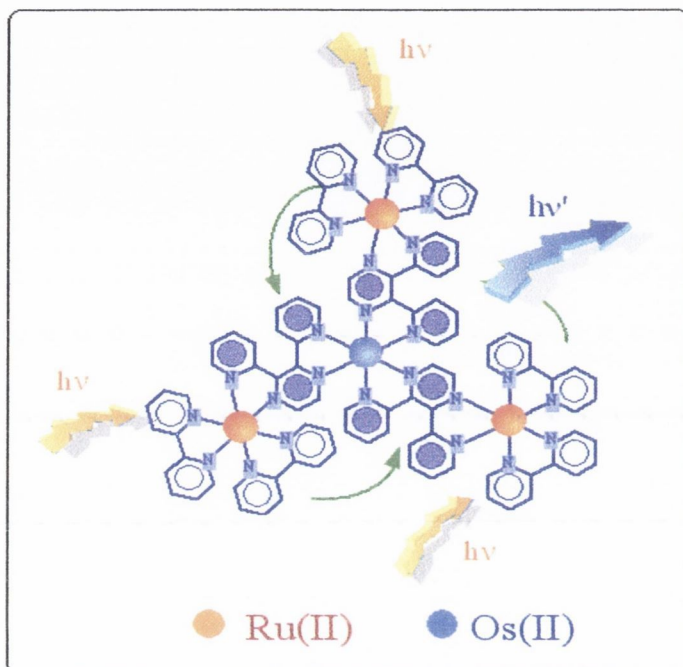


Figure 1.32. Schematic view of the structure of the tetranuclear compound containing Ru and Os metal centres (courtesy of S. Campagna, TMR meeting, Contract N. ERBMRXCT98-0226).

In the case of the tetranuclear compounds containing both Ru and Os, all the four possible energy migration patterns, shown in Figure 1.33, have been obtained.

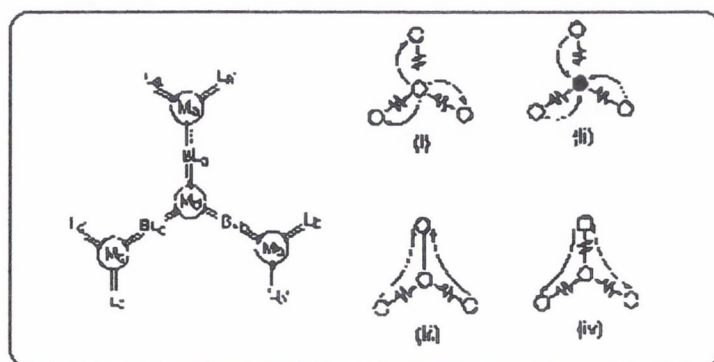


Figure 1.33: Energy-migration patterns in tetranuclear compounds.

Several other synthetically predetermined energy migration patterns have been obtained in similar decanuclear species, simply by using different combinations of metals and ligands (Figure 1.34).

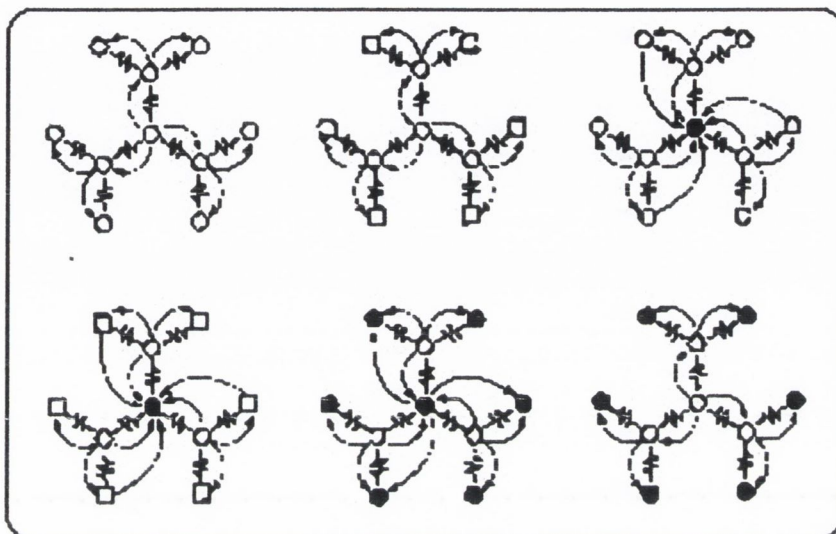


Figure 1.34: *Schematic representation of the energy-transfer processes in decanuclear compounds.*

The “complex as metals/complex as ligands” synthetic approach can be extended to obtain even larger dendrimers. Most of the work present in the literature has focused on compounds containing Ru and Os metal centers. However, synthetic control of energy gradients in larger structures, in order to obtain energy transfer according to predetermined patterns, will probably require the use of more than two different metals. This is a difficult task since for each family of metals, specific types of ligands must be chosen in order to ensure chemical stability and to confer the desired excited state and redox-properties.

1.4.3. Magneto-Optical Devices

In 1845, Faraday found that when plane-polarized light was transmitted through glass in a direction parallel to that of an applied magnetic field, the plane of polarization was rotated. This effect constituted the first demonstration of the connection between magnetism and light, and the origin of magneto-optics. Since Faraday’s original discovery, magneto-optics has become a highly competitive

and fascinating field of research, which is of great importance from both the basic science and applications point of view.⁵⁰

Multicomponent systems made of photo-active metal centres and paramagnetic components give rise to magnetic systems whose properties can be switched on or off by light (Figure 1.35).

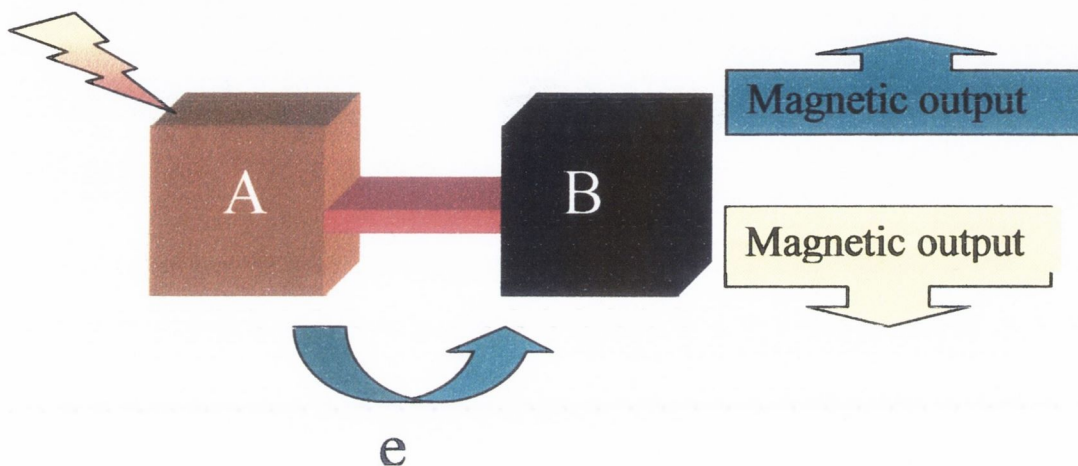


Figure 1.35: *Schematic representation of a magneto-optical device.*

Such heterometallic molecular materials may be expected to exhibit tunable spontaneous magnetization in addition to specific photophysical behaviour. The combination of these properties may play an important role in the development of magneto-optical devices, in that the control of the magnetic phase transition of these molecular magnetic materials might be governed by either optical or electronic stimuli, a goal yet to be achieved by any conventional magnet.

1.5. Why polypyridyl complexes based on Cr(III) and Ru(II) metal centres?

Among all the transition metal centres, Cr(III) and Ru(II) are those whose photochemistry has been most extensively studied.^{51,52} Cr(III) also presents interesting magnetic properties.

1.5.1. Chromium(III) polypyridyl complexes

Chromium(III) polypyridyl complexes are the most interesting after those of Ruthenium(II). The spectra of a very large number of such complexes have been studied. The spin forbidden bands of Cr(III), the so-called “Ruby” lines, are very well known and are of importance in the development of optical lasers.

Structure

Chromium is a first row transition metal and belongs to the VI group, with a configuration $[\text{Ar}] 3d^5 4s^1$. Almost all the Cr(III) complexes are hexacoordinate, with only a few exceptions. Therefore they adopt an octahedral geometry. Cr(III) has a d^3 configuration, with three electrons which are singlet independent of the ligand field strength present. Hence, the magnetic properties of these complexes are easily understood. Their magnetic moments have been calculated for a large number of mononuclear complexes and they all have values close to 3.88 BM. Cr(III) is the most stable state, the Cr(II) being easily oxidized by air.

The main characteristic of these complexes is their kinetic inertness in aqueous solutions. This is the reason why many thermodynamically unstable complexes can be isolated. Ligand substitutions and rearrangement reactions are slow, with the result that the preparation of different, solid, isomeric forms of a compound as a means of establishing stereochemistry is frequently possible. For the same reason, however the preparation of these complexes is not always straightforward. Cr(III) complexes undergo slow ligand replacement reactions. This behaviour maybe rationalized in terms of the valence bond and crystal field theory. The activation energy for a number of aquation and anation reactions has been found to vary between 20 and 30 Kcal/mol. As far as the mechanism of the aquation

reaction is concerned, there are conflicting claims. It has been suggested that the aquation reactions of Cr(III) complexes proceed via an intermediate with an enhanced coordination number, and that the probable geometry of the intermediate is either pentagonal bipyramidal or the trapezoidal octahedron. The aquation reaction of Cr(III) complexes is catalysed by strong oxidizing agents. The suggested mechanism involves oxidation to Cr(IV) which is expected to be labile to substitution, followed by reduction back to Cr(III). A parallel catalysing effect is noted in the presence of reducing agents. Cr(II) species are in fact also expected to be labile.

Some alternative routes, which avoid the formation of pre-formed inert complexes are:

- (i) Oxidation of Cr(II)
- (ii) Reduction of Cr(VI)

Absorption spectra and electronic transitions.

A typical absorption spectrum of a Cr(III) complex having practically octahedral microsymmetry is sketched in Figure 1.36.

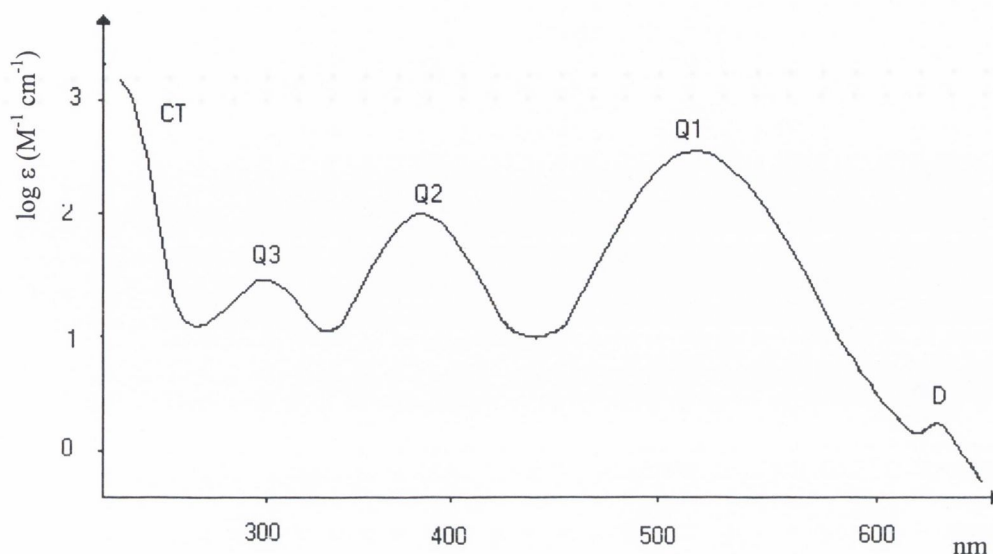


Figure 1.36: Schematic absorption spectrum of a Cr(III) complex having octahedral symmetry.

One observes three bands (Q1, Q2 and Q3 in order of decreasing wavelength) with molar extinction coefficients of 10 to $100 \text{ M}^{-1} \text{ cm}^{-1}$ and half-widths of 1500 to 2000 cm^{-1} . In most cases the band Q3 is covered by the tail of a very intense band whose maximum is often inaccessible. In addition, in the range $650\text{--}750 \text{ nm}$ there occurs a very sharp, weak band D, with molar extinction coefficient 1 and half-width of 100 to 200 cm^{-1} . This band usually exhibits a vibrational structure. The attribution of the bands D, Q1, Q2 and Q3 can be given using the ligand field theory. The system of energy levels for the d^3 configuration in octahedral symmetry is shown in Figure 1.37.

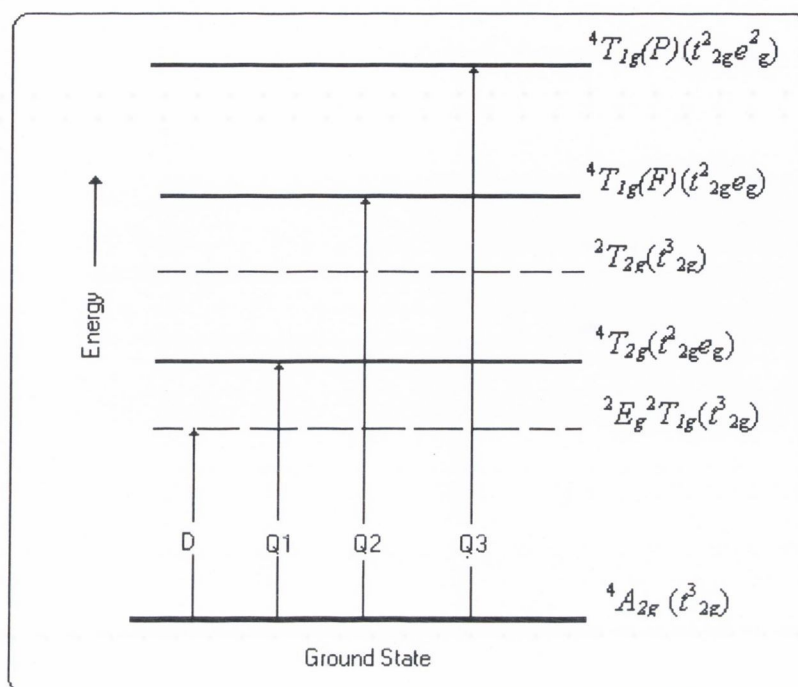


Figure 1.37: Energy levels for the d^3 configuration in octahedral symmetry. (Schematic graph).

The ground state is a quartet state (${}^4A_{2g}$), which corresponds, in the strong-field parentage, to the one-electron configuration t^3_{2g} ; the one-electron configurations of the lower excited states are shown on the right hand-side of the figure. Band D corresponds to the transition from the quartet ground state ${}^4A_{2g}$ to the lowest doublet states 2E_g and ${}^2T_{1g}$ which in a pure octahedral field and in the absence of spin-orbit interactions are degenerate. This transition is characterized by the following features: firstly, it is a parity-forbidden—as well as spin-forbidden, so that the corresponding band must be weak; secondly, it consists of a spin pairing within the non-bonding t_{2g} sub-shell; therefore the 2E_g excited state must have almost the same metal-ligand bond distances as the ground state and thus the absorption band is very sharp; thirdly, the energy difference between the 2E_g and ${}^4A_{2g}$ levels is independent of the ligand field parameter Dq , and thus, the position of the band is relatively insensitive to the type of ligand.

The bands Q1, Q2 and Q3 correspond to the parity-forbidden spin-allowed transitions from the ground state to the excited quartet states ${}^4T_{2g}$, ${}^4T_{1g}$ (F) and ${}^4T_{1g}$ (P) respectively:



These transitions consist of electron promotions from the non-bonding or slightly π -antibonding t_{2g} orbital to σ -antibonding e_g orbitals; therefore, the equilibrium distances in the excited states are larger than those in the ground state and thus, the corresponding absorption bands are broad. The actual spectral positions of the quartet-quartet bands depend on the type of ligand since the energy differences between the quartet excited states and the ground state depend on the ligand field strength. In the case of complexes of lower symmetry than O_h , the octahedral states split and the corresponding bands are also expected to split.

While the ligand field bands of Cr(III) complexes have been extensively investigated, little information exists concerning their charge transfer bands. Besides the more common ligand $\Rightarrow e_g$ (metal) transitions, the occurrence of vacancies in the metal t_{2g} orbitals would make ligand $\Rightarrow t_{2g}$ (metal) transitions possible.

Emission spectra

The emission spectra of Cr(III) complexes have been thoroughly studied, especially by Forster⁵³, Porter⁵⁴, Sartori⁵⁵ and Kirk.⁵⁶ At low temperature in rigid media, the Cr(III) complexes show phosphorescence in red due to emission from the lowest doublet state 2E_g . The emission occurs at the same positions as the corresponding absorption band, in agreement with the fact that the ground state and the lowest doublet state are expected to have about the same geometry. Some chromium complexes exhibit fluorescent emission with or without simultaneous phosphorescence. The fluorescent emission, which is attributed to the $^4T_{2g} \Rightarrow ^4A_{2g}$ transition, is broad and considerably shifted to the red with respect to the corresponding absorption band. This confirms that the $^4T_{2g}$ state is strongly distorted with respect to the ground state geometry. Both phosphorescence and fluorescent emission decrease rapidly as the temperature increases. The phosphorescence quantum yield is generally independent of excitation wavelength.

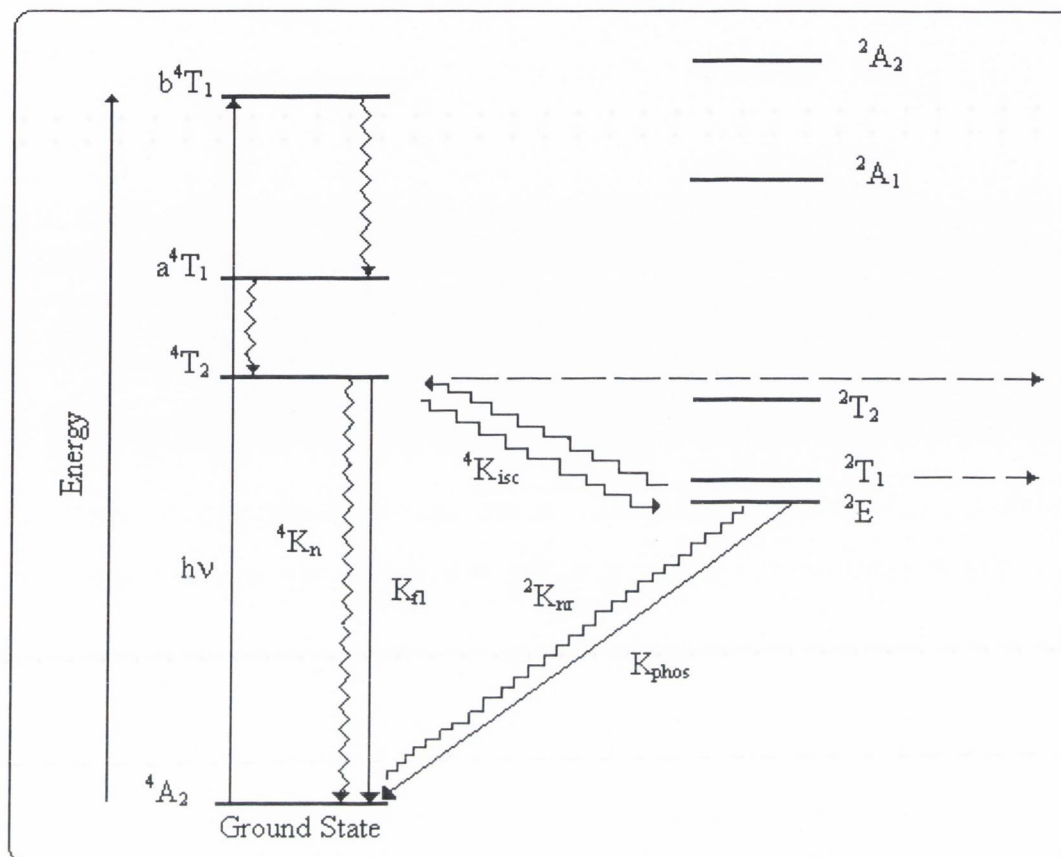


Figure 1.38: Schematic relative energy level diagram for the lowest excited states of $[\text{Cr}(\text{LL})_3]^{3+}$ complexes ($\text{LL} = \text{bipy}$ and related ligands). ($\text{fl} = \text{fluorescence}$, $\text{phos} = \text{phosphorescence}$, $\text{nr} = \text{non-radiative}$, $\text{isc} = \text{intersystem-crossing}$)

1.5.2. Ruthenium (II) polypyridyl complexes

Ruthenium(II) polypyridyl complexes are, among transition metal polypyridyl complexes, the most extensively studied. Their chemical stability and the presence of characteristics such as luminescence in solution, long excited state lifetime and ability to undergo energy and electron transfer processes contribute to their success and also to the development of inorganic photochemistry. Since the first ruthenium complex $[\text{Ru}(\text{bipy})_3]^{2+}$ synthesized, in 1936 by Burstall their number has grown exponentially and a recent review counts more than 286 ligands employed and 400 different complexes⁵⁷.

Structure

Ruthenium(II) with coordination number six adopts an octahedral configuration. They form low-spin octahedral complexes with strong-field ligands such as bipyridine and phenanthroline. The stability of these complexes is presumably enhanced by the symmetrical t_{2g}^6 configuration.

The coordinative bond between the metal centre and the ligands originates from six hybrid orbitals d^2sp^3 of the ruthenium with six sp^2 orbitals containing the lone-pair electrons on the nitrogen of the ligand. The partial delocalization of the metal electrons (of the orbital t_{2g}) on the orbital π^* of the ligands represents the retrocoordinative component of the bond.

Absorption spectra and electronic transitions

In the absorption spectrum of $[\text{Ru}(\text{bipy})_3]^{2+}$, the most studied and best understood complex from the photophysical point of view, the high energy bands at 185 nm and 285 nm have been assigned to ligand centred $(\pi-\pi)^*$ transitions (LC). The twin bands at 238 and 250 nm and the visible light absorption band at 452 nm have been assigned to MLCT $d-\pi^*$ transitions. The shoulders at 322 and 344 nm might be due to charge transfer or to d-d (MC) transitions. In Figure 1.39 the energy levels relative to the transition seen in the absorption spectrum of $[\text{Ru}(\text{bipy})_3]^{2+}$ are presented.

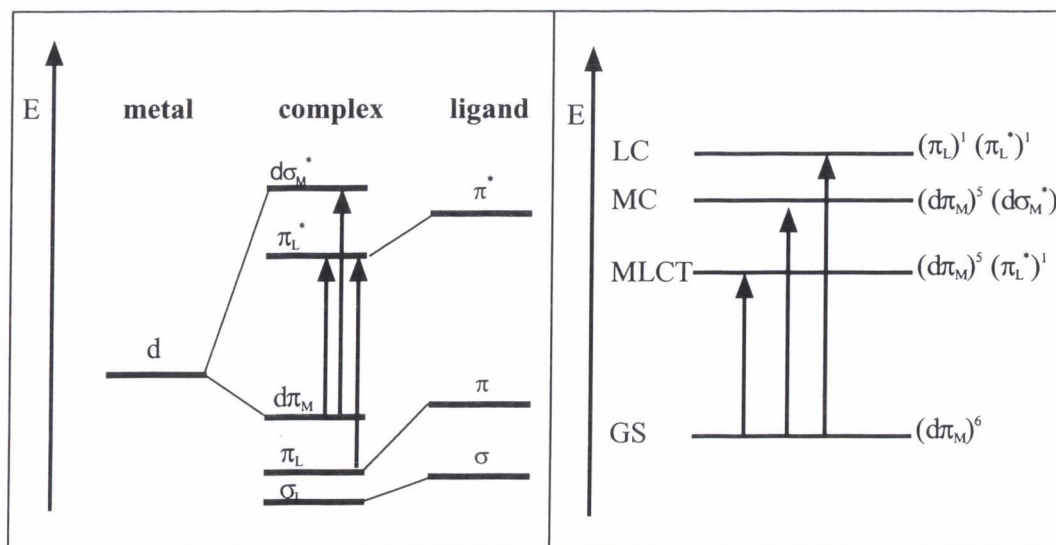


Figure 1.39: Energy levels for $[\text{Ru}(\text{LL})_3]^{2+}$ (where LL = bipy or phen)

Emission spectra

Excitation of $[\text{Ru}(\text{bipy})_3]^{2+}$ in any of the absorption bands leads to a single emission band with a maximum at about 602 nm. In degassed aqueous solutions, the emission is fairly long-lived.

The Figure 1.40 presents schematically an energy level diagram for the various low-lying excited states and the related photophysical processes.

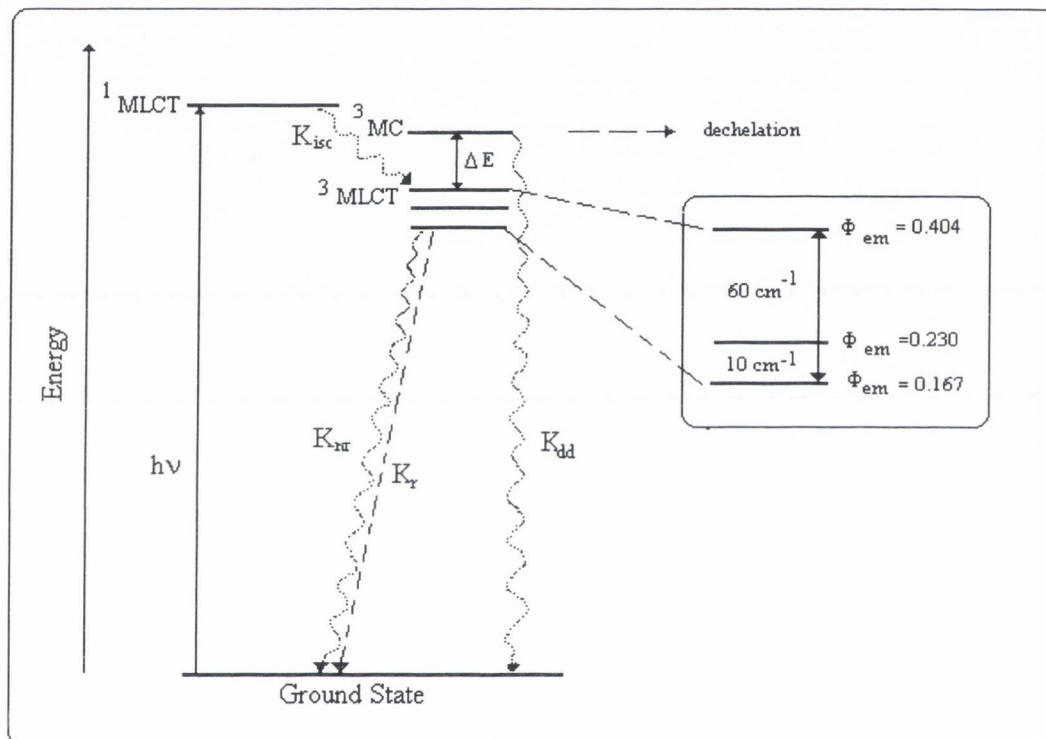


Figure 1.40: Photophysical scheme of the excited states of $[\text{Ru}(\text{bipy})_3]^{2+}$.

The singlet excited state $^1\text{MLCT}$, obtained by absorption of light, $h\nu$, is soon converted (< 1 ps) to the triplet state $^3\text{MLCT}$. This internal conversion singlet-triplet has a quantum yield of 1. It is possible to distinguish the three states which have very close energies $^3\text{MLCT}$ only at low temperature < 77 K. This excited state, $^3\text{MLCT}$ can deactivate radiatively (k_r) and non-radiatively (k_{nr}) or via thermal activation to a fourth state $^3\text{MLCT}$ or to the ^3MC state.

The radiative decay to the ground state with spontaneous emission of a photon gives rise to the luminescence of these complexes. This deactivation contributes less than 10% to the total deactivation of the $^3\text{MLCT}$ state.

The radiationless decay corresponds to the internal interconversion and to energy lost in the form of heat. This is the major deactivation of the excited states and controls the lifetimes of the $^3\text{MLCT}$. The lifetimes vary with the complexes and are usually between ns and μs .

The excited state ^3MC , which is thermally populated, will rapidly deactivate radiationlessly to the ground state or will repopulate the $^3\text{MLCT}$. This MC or d-d excited state, $(d\pi)^5(d\sigma^*)^1$ is strongly distorted with respect to the ground state geometry (involving promotion of a largely non-bonding electron to an antibonding σ orbital). Hence it undergoes very fast radiationless decay, which includes ligand substitution and racemization reactions.

1.6. Conclusions

The general topics discussed in this introduction have been concerned with:

- (i) developing new techniques to synthesize and characterize nanometer size systems and to study the interactions of metal complexes with DNA molecules;
- (ii) developing methods to build up configurationally-controlled photo-active polynuclear nanometer size metal complexes;
- (iii) the design of multinuclear systems capable of performing specific functions:
 - (i) photoinduced energy migration and charge separation on a large distance for photochemical energy conversion purposes;
 - (ii) stereospecific probes and markers for DNA sites;
 - (iii) photochemical molecular devices.

1.7. Aims of this thesis

Bearing in mind the general topics discussed in this introduction we will focus our efforts on:

- (i) the synthesis of mononuclear polypyridyl complexes made up of luminescent and/or paramagnetic metal centres, in particular Cr(III) metal centres which bear both characteristics. This synthetic approach will be extended to incorporate other paramagnetic metal centres (Cu(II), Co(II), Co(III) and Fe(II)).
- (ii) the synthesis of novel binuclear and tetranuclear bimetallic polypyridyl complexes made up of Cr and/or Ru based units which contain polypyridyl ligands, as the coupling of Cr(III) and Ru(II) is potentially interesting to study the energy transfer processes between these two metal centres.
- (iii) mononuclear Cr(III) complexes will be separated into their enantiomers. These enantiomeric pure building blocks could be used to build up configurationally pure supramolecular species.
- (iv) studying the photophysics of some racemic Cr(III) polypyridyl complexes in the absence and presence of DNA
- (v) studying the magnetic properties of the mononuclear complexes synthesized.

1.8. References

- ¹ <http://nano.med.umich.edu/Dendrimers.html>
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Chapter 2

Mononuclear polypyridyl complexes of Cr(III): Synthetic methods, structural characterization and resolution.

E' lo spirito che doma la materia non e' vero?[...] Mi buttai sul lavoro con lo stesso animo con cui in un tempo non lontano, attaccavamo le pareti di roccia; e l'avversario era ancora quello, il non-io, il Gran Curvo, la Hyle: la materia stupida, neghittosamente nemica, come e' nemica la stupidita' umana e come quella forte della sua ottusita' passiva. Il nostro mestiere e' condurre e vincere questa interminabile battaglia: e' molto piu' ribelle, piu' refrattaria al tuo volere una vernice impolmonita che un leone nel suo impeto insano; pero', via, e' anche meno pericolosa

Primo Levi, *Cromo, Il sistema periodico*.

2.1. Introduction

Tris-polypyridyl complexes with chromium (III) are of significant interest due to their potential use as light harvesting units and as DNA therapeutic agents. These complexes are a stronger photo oxidant than the more intensively studied Ru(II) polypyridyl complexes. Tris-polypyridyl complexes of Cr(III) have been known for a long time: the first Cr(III)(bipy)₃ complex was synthesized by Nyholm in 1952, by reducing Cr(III) to Cr(II) with Zn.¹

Photophysical studies of Cr(III) polypyridyl complexes have been performed by Serpone and Hoffmann^{2,3,4} and by Porter and Kirk⁵ but although their photophysical behaviour is well known and they have played a central role in the development of transition metal photochemistry,⁶ nevertheless the number of complexes studied is limited. The reason for this scarcity is most probably

associated with the synthetic difficulty of attaching the third diimine ligand to a Cr(III) via a Cr^{3+} precursor complex, due to the kinetic inertness of Cr(III).⁷ A few $[\text{Cr}(\text{polypyridyl})_3]^{3+}$ homoleptic compounds have been reported, but the synthetic approach has usually involved first generating the more substitutionally labile Cr(II) species, followed by subsequent oxidation to the Cr(III) state.

The three steps reported in the literature are:

- (i) initial reduction of Cr(III) to Cr(II);
- (ii) ligand addition;
- (iii) reoxidation of the product.

This method is quite tedious and requires particular care.

Of particular interest is also the isolation and characterization of heteroleptic Cr(III) polypyridyl complexes, as these may have DNA binding constants bigger than the correspondent homoleptic complexes, this behaviour having been shown already for the related Ru(II) complexes where, for example, $[\text{Ru}(\text{phen})_2(\text{dppz})]^{2+}$ has a DNA binding constant at least three orders of magnitude larger than $[\text{Ru}(\text{phen})_3]^{2+}$. This dramatic increase results from intercalation, where the planar aromatic dppz ring inserts itself between the stacked base pairs of double helical DNA. Although heteroleptic $[\text{M}(\text{diimine})_3]^{n+}$ species are quite common for ruthenium(II), rhodium(III), osmium(II), the synthesis of heteroleptic polypyridyl complexes of chromium(III) has not, in contrast, been well established. For these reasons more attention has been paid to the synthesis and characterization of tris-heteroleptic species, namely $[\text{Cr}(\text{III})(\text{LL})_2(\text{dppz})]$ and $[\text{Cr}(\text{III})(\text{LL})_2(\text{tpphz})]$ where LL = bipy or phen, because of the potentially intercalating behaviour of dppz (dipyrido[3,2-a:2',3'-c]phenazine) and tpphz (tetrapyrdo[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine). These compounds are in fact used as a molecular 'light switch' for DNA⁸ or for the study of fast electron transfer through DNA.⁹ It has been shown that intercalation of the planar dppz ligand between the base pairs of DNA protects the dppz nitrogen from proton transfer quenching. The same behaviour has been found¹⁰ for $[\text{Ru}(\text{bipy})_2(\text{tpphz})]^{2+}$ and can be interpreted in the same way. Upon irradiation in the MLCT band, the first charge transfer gives the excited state $^*\text{Ru}^{\text{III}}(\text{bipy})_2(\text{tpphz}^\cdot)$. In this state, the electron on the reduced tpphz is located in an orbital with high MO coefficients on the non-coordinating

phenazine nitrogen atoms; this should significantly increase their basicity and then allow proton transfer or H-bond formation. However, the access of electrophiles to these basic centres is partially impeded by steric crowding, which is even more significant for tpphz than for dppz. Only small electrophiles, such as H^+ , can access the nitrogen atoms buried in this hydrophobic environment, and this access is even more difficult for tpphz than for dppz. In hydrophobic media, or when the complex is intercalated in DNA, the tpphz nitrogen atoms are fully shielded from water, preventing the proton quenching.

To better understand the behaviour of these complexes in the presence of DNA the first aim of our study was to synthesize both homoleptic and heteroleptic tris-polypyridyl complexes of Cr(III), starting from the synthetic methods described in the literature.

Lee *et al.*¹¹ prepared $[Cr(phen)_3](ClO_4)_3$ in 1966 starting from $Cr(II)SO_4 \cdot 5H_2O$. Cr(II) sulfate was prepared either by dissolving pure chromium metal in dilute sulfuric acid or by reducing an acidic solution of $Cr_2(SO_4)_3 \cdot nH_2O$ in a Jones reductor, adding the resulting Cr(II) solution to cold, concentrated sulfuric acid, and collecting the $CrSO_4 \cdot 5H_2O$ in a sintered glass filter. All these reactions were performed in an inert atmosphere as the Cr(II) easily oxidizes back to Cr(III). In fact, the reduction of the metal centre to Cr(II) enhanced its reactivity but could lead to other complications. For the preparation of Cr(III) heteroleptic complexes this method is excluded *a priori* because if such a synthetic strategy were adopted for mixed diimine systems, scrambling of the diimine ligands in the final Cr(III) product would almost certainly result, due to the rapid equilibration in the Cr^{2+} state (ie. the composition of the mixed $[Cr(diimine)_3]^{3+}$ product may not reflect the stoichiometry used for the mixed diamine reactants, but match instead the relative thermodynamic stabilities of the various possible Cr-diimine precursor species).

Goswami *et al.*¹² report the synthesis of heteroleptic Cr(III) complexes of bidentate polypyridyl ligands. $[Cr(LL)_2Cl_2]^+$, an unusually substitutionally inert compound¹³, has been used as a starting material. They described a simple

metathesis reaction where a silver complex, $[\text{Ag}(\text{LL})_2]^+$ was acting as both the source of polypyridyl ligand and as a source of Ag^+ for abstracting the halide.

When we started our work no other approaches were available for the formation of homoleptic and heteroleptic complexes, therefore we followed the methods described in the literature.

Kane-Maguire *et al.*¹⁴ in 2001 reported a new route to the synthesis of Cr(III) polypyridyl complexes. They used the good leaving properties of the triflate group to achieve the desired complex, $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$

2.2. Results and Discussion

2.2.1. Synthetic Methods used for the preparation of Cr(III) complexes

A number of synthetic routes were attempted in the current study for the preparation of Cr(III) complexes .

These include:

- (i) addition of three equivalents of the desired ligands to a Cr(III) starting material using high boiling point solvents;
- (ii) reduction of Cr(III) to Cr(II) and the subsequent oxidation to Cr(III) after the addition of the ligand;
- (iii) functionalization of the ligand starting from known tris-chelate complexes;
- (iv) reaction of bis-polypyridyl bis-chloride complexes with a silver-polypyridyl species;
- (v) formation of the ligand labile triflate-polypyridyl species followed by reaction with the desired ligand;
- (vi) assembling precoordinated complexes with other ligands.

The methods reported in this chapter can be distinguished from those for the preparation of homoleptic complexes and those for the preparation of heteroleptic. Methods (i)-(iii) were used for the preparation of homoleptic complexes and methods (iv) –(vi) for the preparation of heteroleptic complexes.

These methods will be discussed below.

Method (i) Initially we followed the methods used for the formation of tris-chelated complexes which are in general applied to several transition metal complexes, such as Ru(II), Fe(II), Co(II), Os(II). The general procedure for the formation of mononuclear complex is described below where metal ion (M) and free ligands (L) are mixed together, in an appropriate solvent:



Scheme 2.1: *Synthesis of mononuclear complexes*

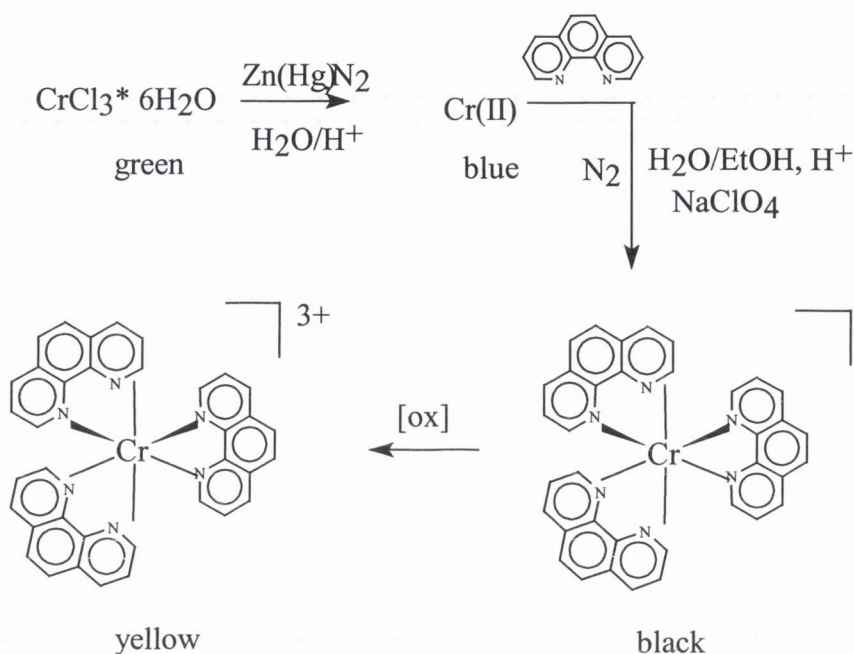
In order to achieve the direct synthesis of our compounds, without having to pass via the Cr(II) intermediate, several experimental conditions were used:

- (a) different solvents (from Ethanol to Ethylene Glycol)
- (b) a range of temperatures (from 100 to 180 °C)
- (c) longer reaction times (from 1 day to 7 days)
- (d) different ligands (from pyridine to bipy to phen)

We hoped that using high boiling point solvents such as ethylene glycol and refluxing for several days we could have overcome the kinetic inertness of the Cr(III) metal centre and achieved the synthesis of the desired product.

However, this method could not be applied to synthesizing Cr(III) tris-polypyridyl complexes. Although a wide range of conditions was attempted none of them proved successful and only a bis(polypyridyl) species could be isolated.

Method (ii) However, the synthesis of Cr(III) tris-polypyridyl complexes has been well known in the literature since the work of Nyholm¹ and of Baker and Metha¹⁵. The reduction to Cr(II) has been used by several research groups which slightly modified the original method. Thus, we decided to follow the modified method of Kane-Maguire *et al.*¹⁶, which is described in Scheme 2.2 for the synthesis of [Cr(phen)₃]³⁺.



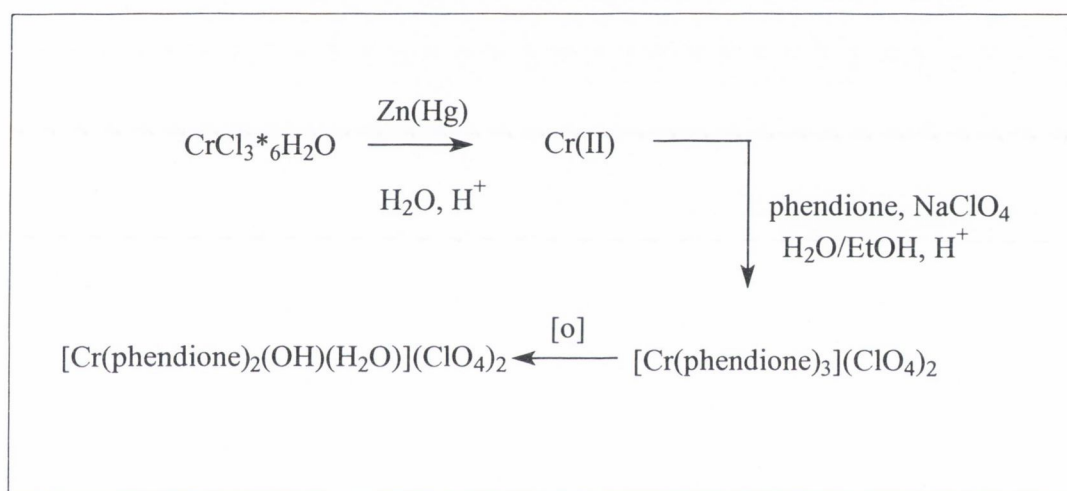
Scheme 2.2: Synthesis of $[Cr(phen)_3](ClO_4)_3$

The synthetic approach involves first the generation of the more substitution labile $Cr(II)$ species, then addition of the ligand to the sky-blue solution generates a black precipitate of $Cr(II)$ tris-polypyridyl, which is followed by subsequent oxidation by air to the $Cr(III)$ state. The compound is precipitated as a bright yellow perchlorate salt.

Following this method the ligands 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridine (Me_2bipy) and 4,7-dimethyl-1,10-phenanthroline (Me_2phen) were added to the $Cr(II)$ solution. This route was applied successfully to the preparation of $[Cr(bipy)_3](ClO_4)_3$, $[Cr(phen)_3](ClO_4)_3$, $[Cr(4,4'-dimethyl-bipy)_3](ClO_4)_3$, $[Cr(4,7-dimethyl-1,10-phen)_3](ClO_4)_3$.

Therefore we thought of following the same method to prepare other tris-chelate species, such as $[Cr(phendione)_3](ClO_4)_3$, $[Cr(dpq)_3](ClO_4)_3$, $[Cr(dppz)_3](ClO_4)_3$ and $[Cr(tpphz)_3](ClO_4)_3$ (where phendione = 1,10-phenanthroline-5,6-dione; dpq = dipyrido (3,2-d: 2', 3'-f)quinoxaline, dppz = dipyrido (3,2-a:2',3' -c) phenazine and tpphz = (tetrapyrido[3,2-a: 2',3'-c: 3'', 2''-h: 2'''-3'''-j]phenazine)). However, even working with an excess of ligand, the tris-chelate species were never isolated and the formation of the bis-chelate species was found to be

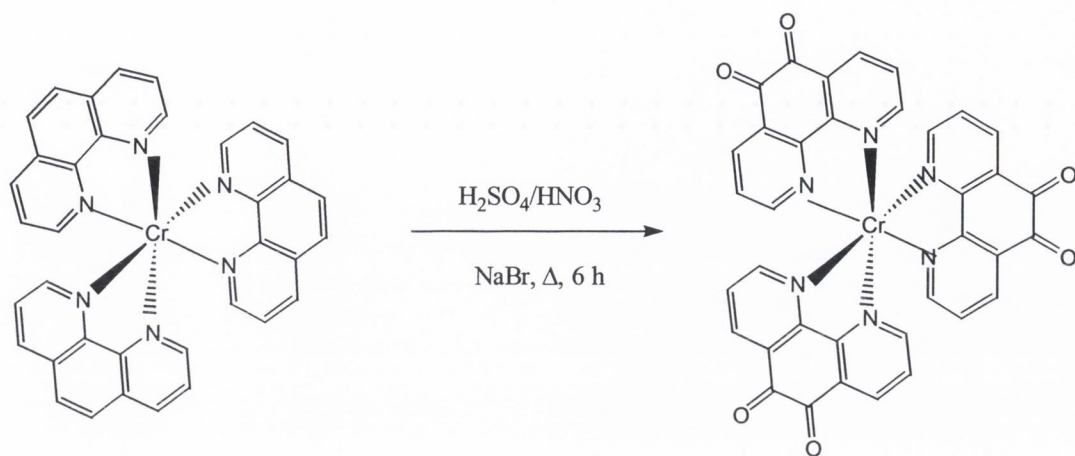
predominant. In fact the reaction of Cr(II) with phendione led to the isolation of a bis-aqua species instead of the expected tris-phendione complex. As these reactions are carried out in an aqueous environment, we have proven that water is a much stronger ligand than the polypyridyl ligands which therefore is impossible to remove. This method thus failed when we tried to attach a bulky, more aromatic or more π -acidic ligand. The reaction scheme for the bis-aqua-species formed is outlined below (Scheme 2.3). This complex will be discussed in detail later in this Chapter (Section 2.2.3).



Scheme 2.3: Synthesis of $[\text{Cr(phendione)}_2(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$

Another method must be proposed for the synthesis of the tris-chelate complex.

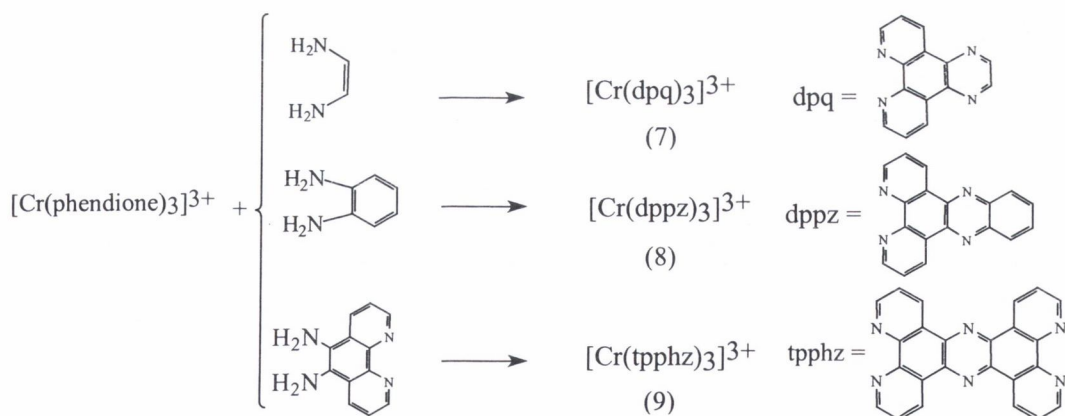
Method (iii) $[\text{M(phen)}_3]^{n+}$ complexes where $\text{M} = \text{Co (III)}$ or Ru(II) have already been successfully employed as precursors for the synthesis of $[\text{M(phendione)}_3]^{n+}$. The method proposed uses the nitric/sulfuric acid mixture and NaBr as a catalyst to achieve the oxidation of the phenanthroline in position 5 and 6. The method described by Gillard¹⁷ and MacDonnell¹⁸ could also be applied to the corresponding $[\text{Cr(phen)}_3]^{3+}$ complex. Following the same reaction conditions previously described we ended up with the desired Cr tris-phendione (Scheme 2.4).



Scheme 2.4: *Synthesis of $[\text{Cr}(\text{phendione})_3](\text{ClO}_4)_3$*

The preparation of the Cr tris-(phendione) species was a good starting point for the synthesis of three other tris(polypyridyl) complexes: $[\text{Cr}(\text{dpq})_3]^{3+}$, $[\text{Cr}(\text{dppz})_3]^{3+}$ and $[\text{Cr}(\text{tpphz})_3]^{3+}$ and it can be used as a building block for the synthesis of supramolecular species as will be shown in the following chapters.

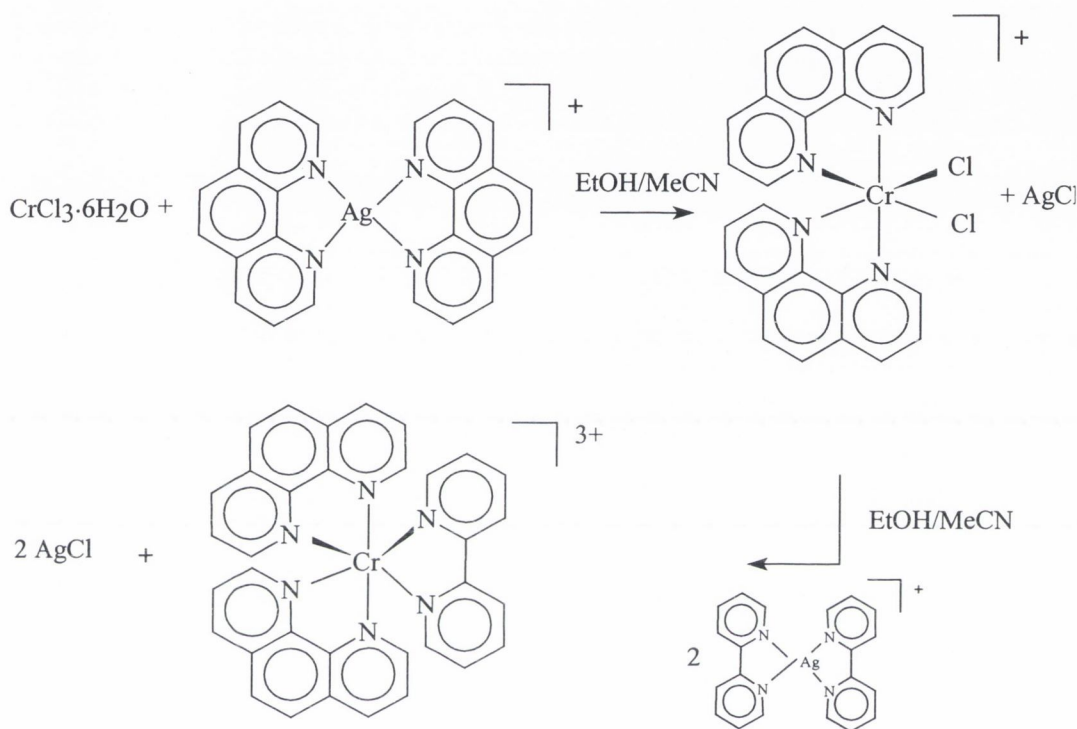
Scheme 2.5 shows the syntheses of the mentioned compounds.



Scheme 2.5: *Synthesis of tris-polypyridyl Cr(III) compounds.*

Method (iv) The synthesis of heteroleptic chromium(III) complexes was first reported by Goswami and co-workers.¹¹ This method consists of refluxing the $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in CH_3CN with two equivalents of $[\text{Ag}(\text{LL})_2](\text{X})$ (where LL = bipy or phen and $\text{X} = \text{BF}_4^-, \text{ClO}_4^-, \text{PF}_6^- \dots$) as the source of diimine ligand to end up

with the bis-polypyridyl species, $[\text{Cr}(\text{LL})_2\text{X}_2]^{n+}$. This species can further react with another equivalent of $\text{Ag}(\text{LL}')_2(\text{X})$ where $\text{LL} = \text{LL}'$ or $\text{LL} \neq \text{LL}'$ to end up with homoleptic or heteroleptic complex. The reaction scheme is outlined below (Scheme 2.6):



Scheme 2.6: *Synthesis of heteroleptic species*

This mechanism of employing a silver salt to remove the Cl^- ligands has been employed successfully elsewhere. Chromium(III) is usually substitutionally inert, thus the use of silver complexes of strong π -acceptors makes it possible to achieve the direct synthesis of chromium(III) bis-polypyridyl complexes. The silver halide metathesis reaction is ubiquitous in coordination chemistry and is used to generate vacant sites on metal fragments in a variety of transition metal mediated processes. Typically, weakly- or non-coordinating counterions are employed in such syntheses, leading to a rapid rate of metathesis. Silver is useful in this respect as it may be used for halide abstraction even from an inert metal chloride, producing an insoluble salt which may be easily removed from the reaction. The selection of an appropriate solvent is an important issue as, for example, chromium complexes are stable and unreactive towards acetonitrile but may be

reduced by alcohols. It was also observed that hydroxide formation occurs with alcoholic solutions containing as little as 10 % water, at neutral pH.

If the same procedure is repeated, by an appropriate choice of the chromium precursor complex and the silver complex, it should be possible to end up with both homoleptic and heteroleptic polypyridyl complexes.

Problems were encountered, however, when we attempted the synthesis of chlorine free chromium(III) complexes, largely due to the unusual inertness of the chloride to substitution reactions. Even using high boiling point solvents (such as DMSO or ethylene glycol) or refluxing for more than 5 days, no result was ever achieved.

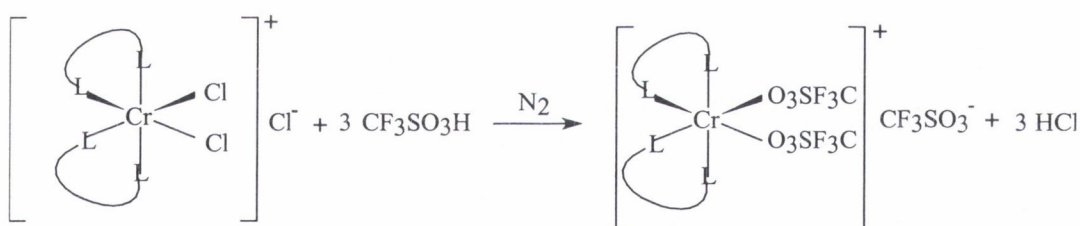
The same method was further reported in a recent paper by Kane-Maguire¹⁴, who also argued that this method gave low yields and in most of the cases scrambling of the ligands, so that it was not really possible to produce heteroleptic complexes following this method. In our case we have to report that following the same conditions described above, no reaction was ever observed apart from the formation of the bis(polypyridyl)Cr species.

Method (v) An alternative method was therefore used through which it was possible to obtain both homoleptic and heteroleptic complexes with no scrambling of the ligand and therefore with better yields. The method reported takes advantage of the excellent leaving group characteristics of the trifluoromethanesulfonate (triflate) ligand, CF_3SO_3^- .

Trifluoromethanesulfonic acid (triflic acid) and its organic esters have found considerable use in organic chemistry. The desirable qualities of these compounds include a high thermal stability and excellent leaving-group properties of the CF_3SO_3^- group. Its use in synthetic inorganic chemistry has been somewhat hampered by the lack of convenient routes for the preparation of the desired complexes. Despite this, the excellent leaving-group properties of the triflate ligand were established a decade ago by Scott and Taube.¹⁹ More recently, Dixon *et al.*²⁰ have developed a method that involves heating chloro complexes in neat triflic acid, followed by precipitation of the resultant complex by diethyl ether. This procedure has been applied successfully to Co(III), Ir(III), Cr(III), Ru(III)

and Os(III), i.e. substantially inert compounds²¹. The triflate complexes have many desirable properties once formed. The most useful property in synthesis is the relatively high lability of the triflate group, which is substituted at a rate comparable to the best leaving groups known, including the perchlorate and fluoromethansulfonato ligand. This feature combined with a high solubility in most polar organic solvents, high thermal stability, relatively low reactivity with atmospheric moisture, and simple and high yielding preparative routes from readily available starting materials, makes these complexes extremely versatile synthetic intermediates for a large variety of important classes of transition metal complexes.

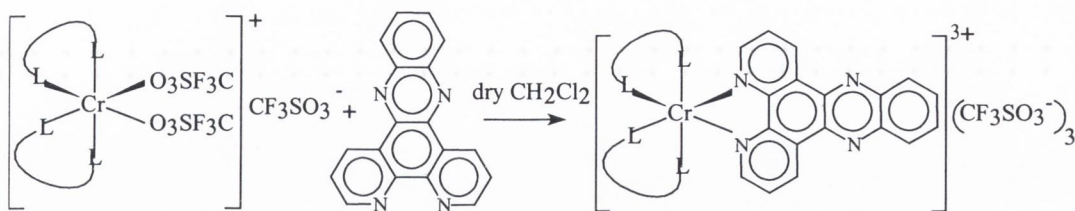
The general procedure described by Ryu and Endicott,²² for the formation of the precursor Cr(III)(triflate) complex, consists of dissolving the chloro complexes, $[\text{Cr}(\text{LL})_2\text{Cl}_2]\text{Cl}$ (1 g) in 5 ml of vacuum distilled triflic acid under nitrogen, and stirring at room temperature for 24 h, till no traces of HCl are present (monitored by passing the vapours through a solution of AgNO_3). The compound is further precipitated with diethyl ether and dried under vacuum.



Scheme 2.7: Synthesis of $[\text{Cr}(\text{LL})_2(\text{CF}_3\text{SO}_3)_2](\text{CF}_3\text{SO}_3)$ where $\text{LL} = \text{bipy}$ or phen

Kane-Maguire *et al.*¹⁹ thus reported the following method for the preparation of the desired heteroleptic Cr(III) complex, $[\text{Cr}(\text{phen})_2(\text{dppz})](\text{CF}_3\text{SO}_3)_3$.

The reaction scheme proposed consisted of refluxing the desired ligand with the triflate precursor in dry CH_2Cl_2 (Scheme 2.8):

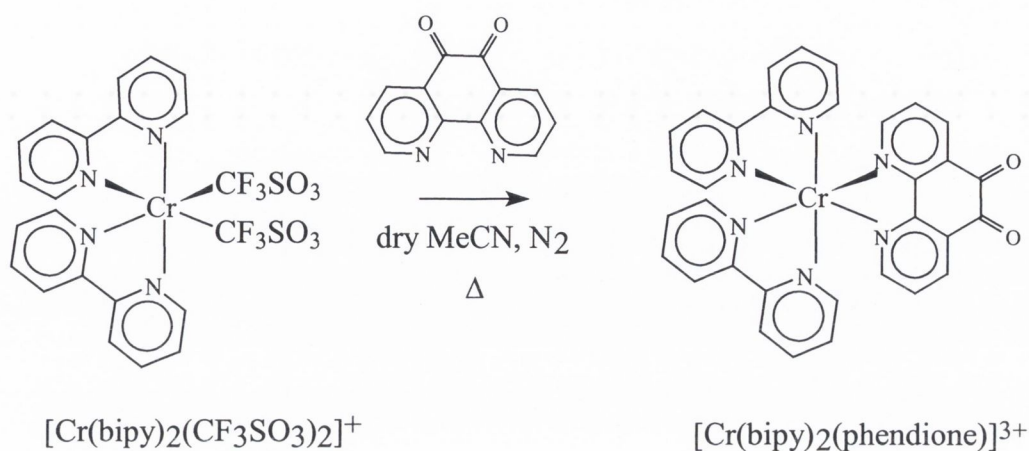


Scheme 2.8: Synthesis of $[\text{Cr}(\text{LL})_2(\text{dppz})]^{3+}$ where $\text{LL} = \text{bipy}$ or phen

In our case this method worked well for small polypyridyl ligands such as bipy or phen and their methylated analogues, so that we formed $[\text{Cr}(\text{phen})_2(\text{bipy})]^{3+}$, $[\text{Cr}(\text{phen})_2(\text{Me}_2\text{bipy})]^{3+}$, $[\text{Cr}(\text{phen})_2(\text{Me}_2\text{phen})]^{3+}$ and $[\text{Cr}(\text{phen})_2(\text{Ph}_2\text{phen})]^{3+}$.

No reaction was observed by directly adding dppz or any other π -acidic ligands, such as dpq or tpphz, to the starting material. This may be due to the low solubility of these ligands in CH_2Cl_2 .

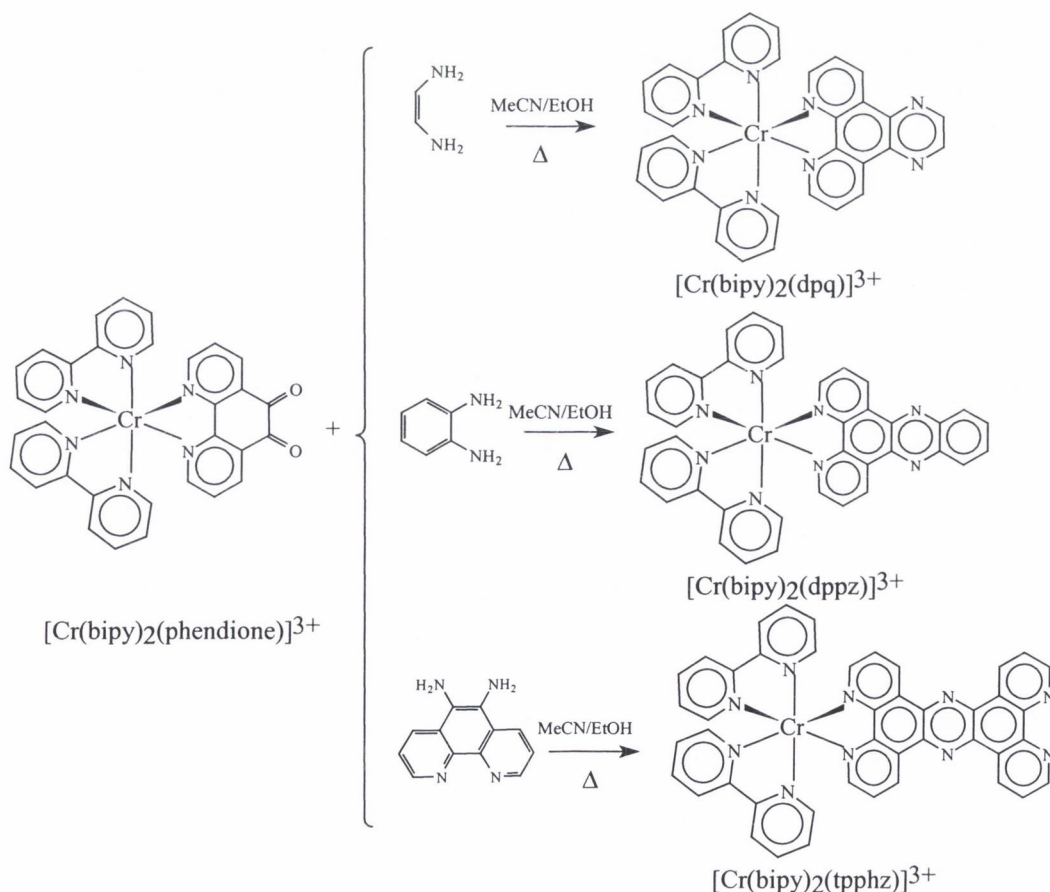
Method (vi) Hence we wish to report a modified synthetic route which starting from the same precursor complex, $[\text{Cr}(\text{LL})_2(\text{CF}_3\text{SO}_3)_2](\text{CF}_3\text{SO}_3)$, gave the possibility of synthesizing the whole family of $\text{Cr}(\text{LL})_2$ polypyridyl ligands in high yields and with good quality. The method is described in the scheme below (Scheme 2.9). The first difference is the choice of the solvent used. We found that better yields were achieved using dry MeCN instead of CH_2Cl_2 . The second difference was to first add the phendione ligand to form the $[\text{Cr}(\text{LL})_2(\text{phendione})]^{3+}$ to which, after extraction and purification of the newly formed complex, a series of ligands may be added.



Scheme 2.9: Synthesis of $[\text{Cr}(\text{LL})_2(\text{phendione})]^{3+}$ where LL: bipy or phen

Reported below is the reaction Scheme 2.10 for the $\text{Cr}(\text{III})(\text{bipy})_2(\text{LL})$ polypyridyl family where LL= dpq, dppz, tpphz.

The same method was followed for the corresponding $[\text{Cr}(\text{phen})_2(\text{LL})]^{3+}$ complex.



Scheme 2.10: Synthesis of $[\text{Cr}(\text{bipy})_2(\text{LL})]^{3+}$ complexes, where LL= dpq, dppz, tpphz

This method provides a good means of preparing heteroleptic complexes.

In conclusion, we have developed and applied successfully two different methods which can be applied to the preparation of homoleptic and/or heteroleptic complexes depending on the conditions used:

- (ii) and (iii) could be used for the preparation of homoleptic complexes;
- (vi) can be used for the preparation of both heteroleptic and homoleptic complexes;
- (v) was partially successful;
- (i) and (iv) were unsuccessful.

These results are summarized in the flow-chart in Figure 2.1:

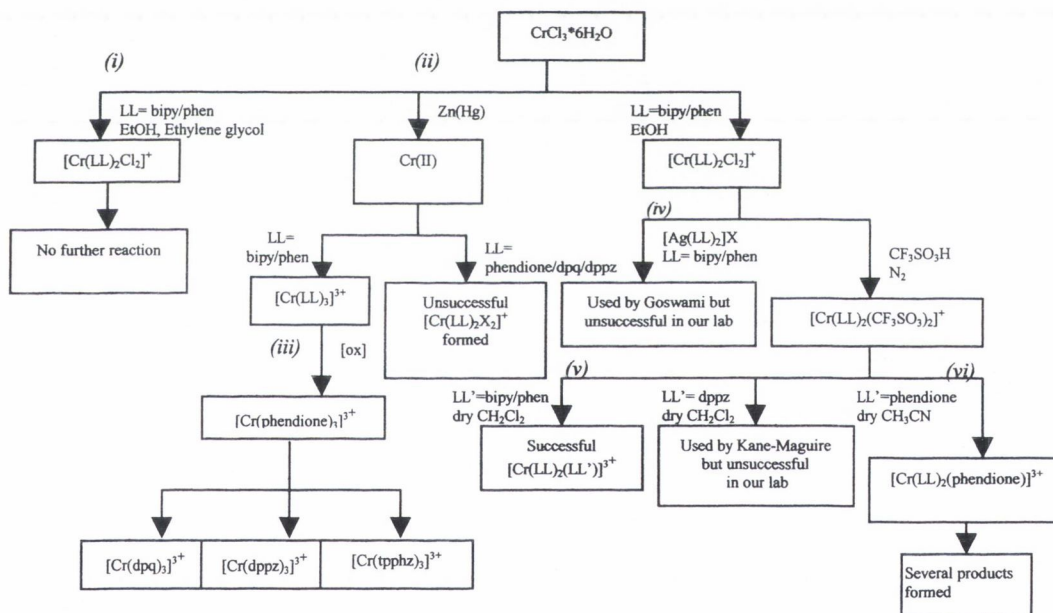


Figure 2.1: Flow-chart representing the synthetic methods used for the synthesis of $[Cr(LL)_3]^{3+}$ complexes

2.2.2. Cr(III) bis-polypyridyl complexes

Synthesis

In order to determine the utility of complexes of formulation $[\text{Cr}(\text{LL})_2\text{Cl}_2]\text{X}$ as starting materials for the synthesis of homoleptic and heteroleptic polypyridyl chromium complexes, different complexes were obtained where $\text{LL} = \text{bipy}$, phen or phendione and $\text{X} = \text{Cl}^-$, BF_4^- or PF_6^- and the solid structures of some of these complexes were obtained.

The complexes, $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$ and $[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$, have been known for many years and indeed Pfeiffer and Werdelmann²³ prepared cations of the type $[\text{Cr}(\text{LL})_2\text{Cl}_2]^+$ where $\text{LL} = \text{phen}$ and bipy , in 1950.

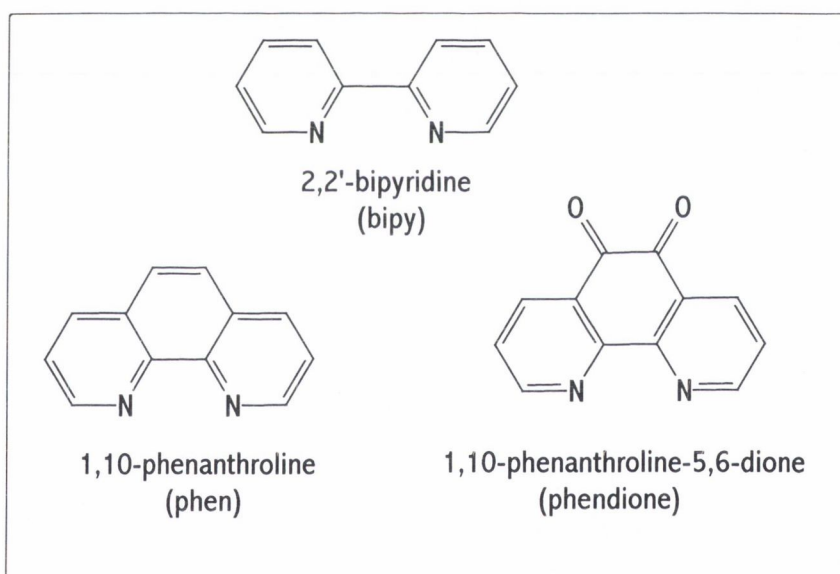


Figure 2.2: The ligands *bipy*, *phen* and *phendione* used in the synthesis of precursors complexes

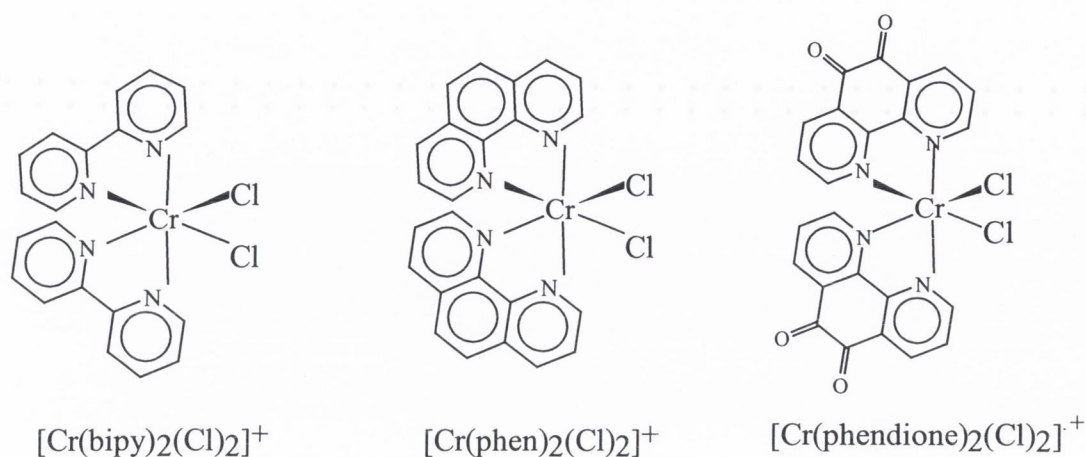


Figure 2.3. Structures of the bis-polypyridyl complexes synthesized.

The complexes with Cl^- as counterion can be prepared as described by Nyholm *et al.*¹ by reacting CrCl_3 with bipy or phen in EtOH and using traces of Zn powder as catalyst. The reaction is violent and a green precipitate of the dehydrated compound, $[\text{Cr}(\text{LL})_2\text{Cl}_2]\text{Cl}$, is formed

Following instead the procedure described by Goswami¹¹, the synthesis of dichloro complexes from $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ requires removal of one Cl^- associated with coordination of two moles of LL to the metal ion. Thus, the reaction of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ with an equimolar amount of $[\text{Ag}(\text{LL})_2]\text{X}$ where LL= bipy and phen and $\text{X} = \text{BF}_4^-, \text{PF}_6^-, \text{ClO}_4^-, \text{NO}_3^-$, led to the formation of $[\text{Cr}(\text{LL})_2\text{Cl}_2]\text{X} \cdot n\text{H}_2\text{O}$. We isolated the complexes as brown crystalline compounds. The change between the hydrated and non hydrated species has been already discussed by Hancock *et al.*²⁴ In general the anhydrous salts and lower hydrates are green to brown whereas higher hydrates or acid hydrates are violet to red.

Following these methods we also prepared the $[\text{Cr}(\text{phendione})_2\text{Cl}_2]\text{X}$ complex, isolated as a brown compound.

All the complexes synthesized were characterized by IR, UV/Vis, mass spectrometry and microanalysis.

UV/Vis absorption spectra

The absorption spectra of these complexes were determined in water and ethanol, to see any differences associated with the change of solvent. In Figure 2.4. are reported the UV/Vis spectra of the three complexes, $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$, $[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$ and $[\text{Cr}(\text{phendione})_2\text{Cl}_2]^+$ in water.

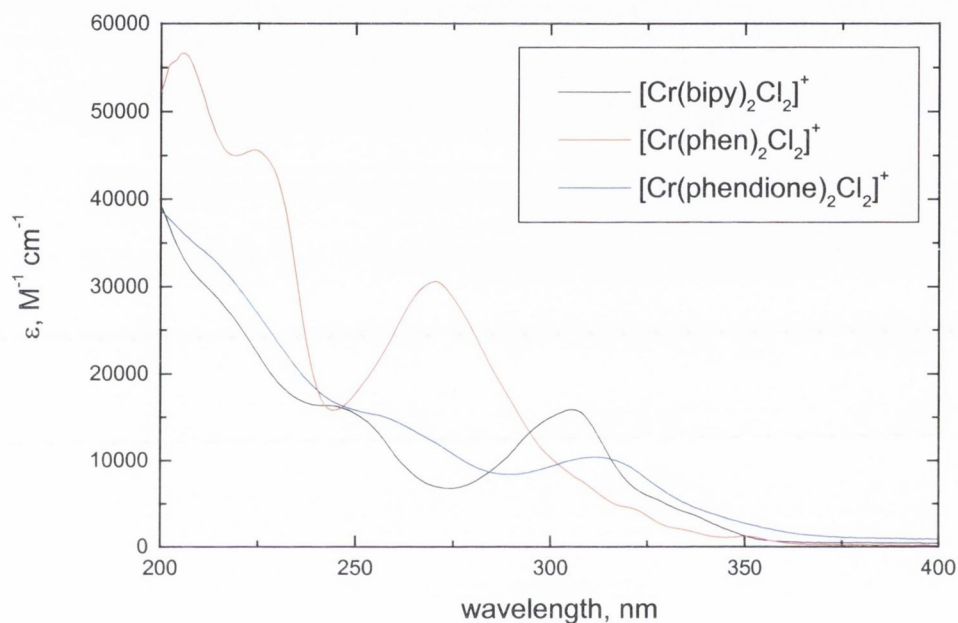


Figure 2.4: Absorption spectra of $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$, $[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$ and $[\text{Cr}(\text{phendione})_2\text{Cl}_2]^+$ in water.

The results are reported in Table 2.1.

Table 2.1: Spectral data characterising the compounds

Compound	Solvent	λ_{max}, nm ($\log \epsilon, M^{-1} cm^{-1}$)	λ_{max}, nm ($\log \epsilon, M^{-1} cm^{-1}$)
$[Cr(bipy)_2Cl_2]^+$	H ₂ O	213 (4.46), 245 (4.21), 305 (4.20), 393 (2.33), 417 (2.20), 447 (1.83), 550 (1.53)	^a 445 (1.95), 474, 553, (H ₂ O or 0.1 M HCl) ^b 444(1.94), 475 (1.34), 552 (1.65), (0.1M HCl)
	EtOH	221 (4.46), 254 (4.19),306 (4.19), 391 (3.05), 416 (3.02)	
$[Cr(phen)_2Cl_2]^+$	H ₂ O	205(4.75), 224 (4.65), 270 (4.48), 393 (2.38), 422 (2.19), 549 (1.65)	^a 478 (4.24), 558 in H ₂ O or 0.1 M HCl ^a
	EtOH	205(4.80), 225 (4.72),271 (3.57), 333 (3.39), 350 (3.26), 413 (2.55), 576 (2.18)	
$[Cr(phendione)_2Cl_2]^+$	H ₂ O	257 (4.17), 313 (4.17), 412 (2.96), 526 (2.67)	
	EtOH	275 (4.21), 306 (4.16), 417 (3.30)	

^a from Hancock *et al*, *Acta Chemica Scandinava*,1976, *A30*, 79-97 ; ^b from Kharmawphlang *et al*, *Inorg. Chem.*, 1995, *34*, 3826-3828

For each complex, there appears to be no significant difference in the position observed for the bands in different environments. As can be seen, in each case the extinction coefficients are higher in ethanol than in water. The spectrum of $[Cr(bipy)_2Cl_2]^+$ is characterized by a peak at 250 nm and a stronger peak at about 305 nm. The spectrum of $[Cr(phen)_2Cl_2]^+$ has three peaks at 210, 225 and 260 nm. The spectrum of $[Cr(phendione)_2Cl_2]^+$ has a weak band at 260 nm and a stronger band at 325 nm. In the region 350-650 nm, represented in Figure 2.5, the *d-d* bands of Cr(III) are clearly visible. In all the cases the extinction coefficients of

$[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$ are higher than those of $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$ and $[\text{Cr}(\text{phendione})_2\text{Cl}_2]^+$, which are similar.

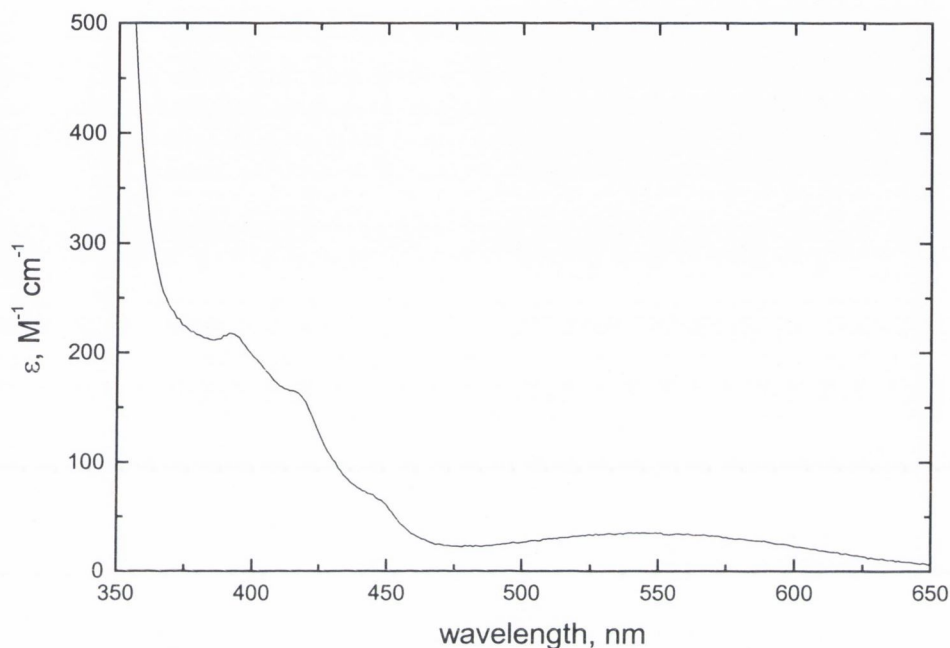


Figure 2.5: Absorption spectrum of $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$ in water, region 350-650 nm, $C = 4.4 \times 10^{-4} \text{ M}$.

X-Ray diffraction experiments

The solid state structures of starting materials, $[\text{Cr}(\text{bipy})_2\text{Cl}_2](\text{BF}_4)$ and $[\text{Cr}(\text{phen})_2\text{Cl}_2](\text{PF}_6)$ have been obtained.* Single crystals were obtained by slow evaporation of acetonitrile solutions of the two compounds. The crystallographic data for these complexes are reported in Appendices A and B. These crystal structures are new.

The X-ray crystal structures for the two molecules are reported in Figures 2.6 and 2.7. We have obtained exclusively the *cis*-forms. They both have a distorted octahedral geometry. The $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$ was crystallized as BF_4 salt. The structure was refined with a final R1 value of 0.0738. The quality of the data and refinement is good, however there is some disorder of anions and solvent molecules. It crystallized in a monoclinic $P2(1)/n$ space group. The $[\text{Cr}(\text{phen})_2\text{Cl}_2]$

crystallized as PF_6 salt. The structure was refined with a final R_1 value of 0.0497. $[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$ crystallize in a monoclinic $C2/c$ space group. They both crystallized in non-chiral space groups and this can be seen in the unit cell where, both enantiomers, Δ and Λ , are presents, but in Fig 2.6 and 2.7 only one of the two enantiomers is shown.

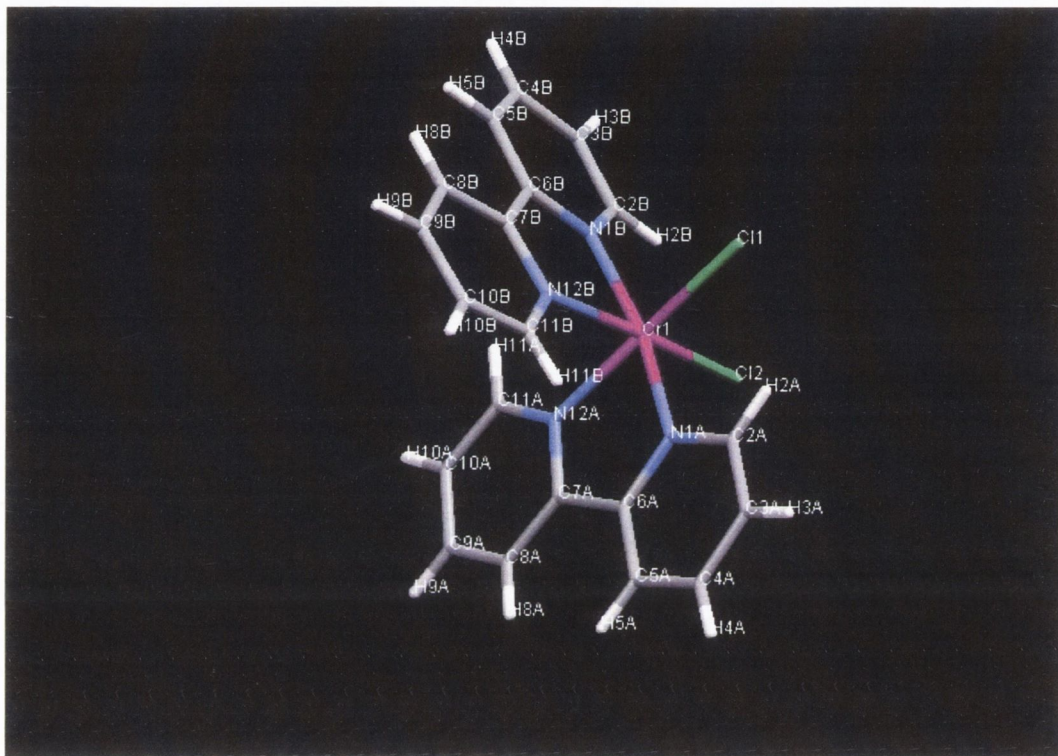


Figure 2.6: X-ray crystal structure of $[\text{Cr}(\text{bipy})_2\text{Cl}_2](\text{BF}_4) \cdot \text{CH}_3\text{CN}$ (counterion and solvent molecules omitted for clarity).

* The author gratefully acknowledges the assistance of Dr. Phil Mackie in the purification and crystallization of these samples.

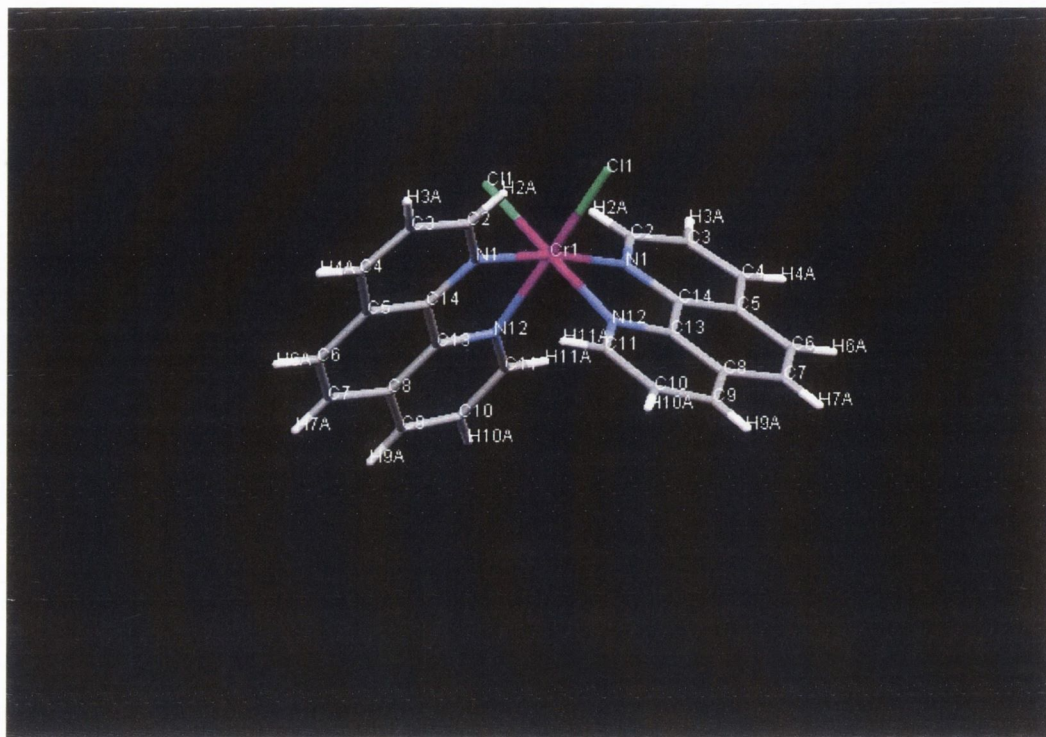


Figure 2.7: X-ray crystal structure of $[\text{Cr}(\text{phen})_2\text{Cl}_2](\text{PF}_6) \cdot \text{CH}_3\text{CN}$ (counterion and solvent molecules omitted for clarity).

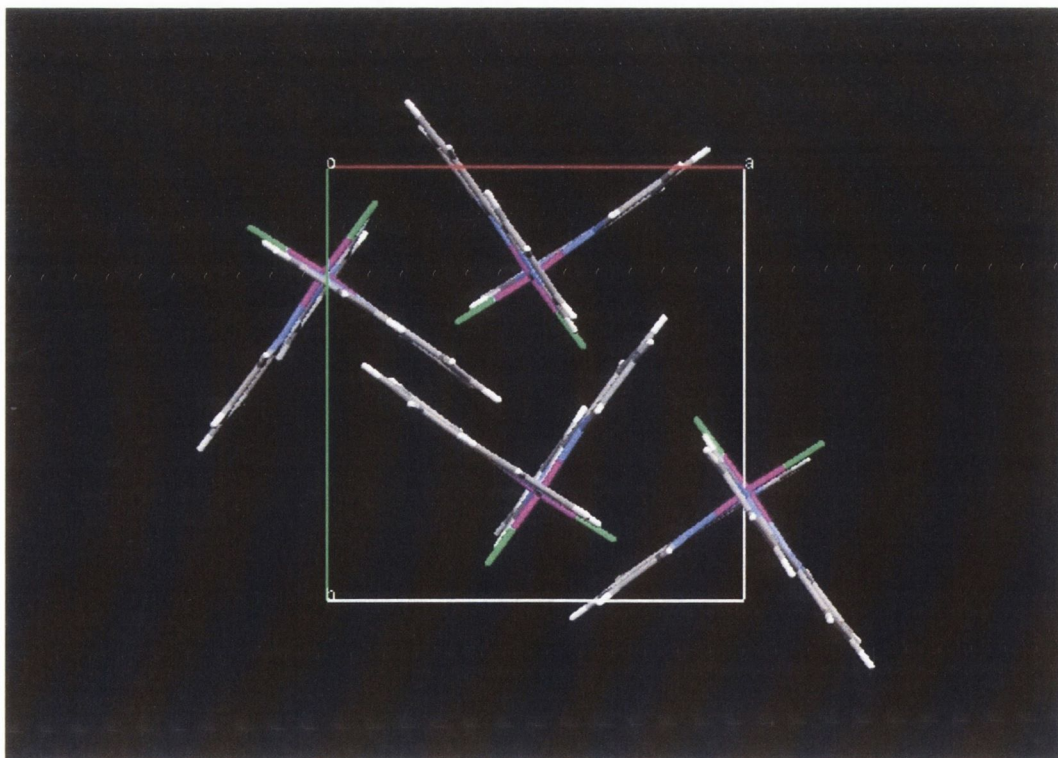


Figure 2.8: Packing of $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$ molecules in the crystal viewed approximately down the c axis.

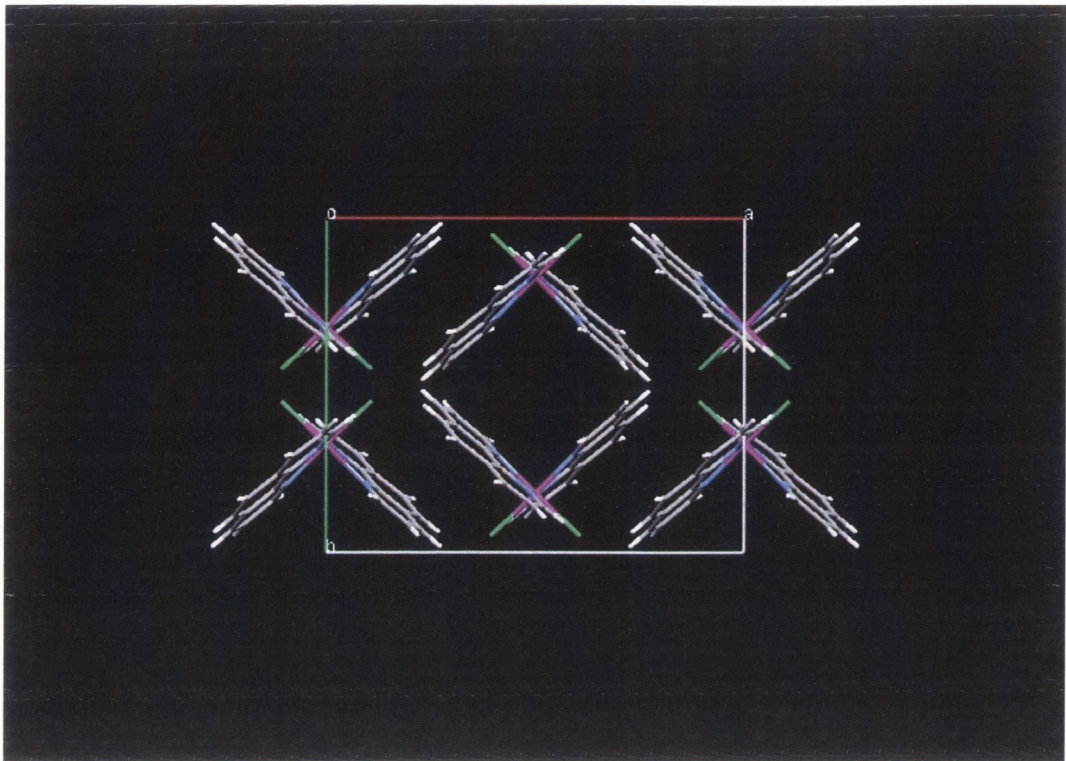


Figure 2.9: Packing diagram of the $[Cr(phen)_2Cl_2]^+$ molecules in the crystal along the c axis.

The packing diagrams show that for the phen complex π - π interactions are more present than in bipy complex (Fig. 2.8 and 2.9).

Selected bond distances (Å) and bond angles (°) are reported in Tables 2.2 and 2.3 respectively.

Table 2.2: Selected bond lengths for $[Cr(bipy)_2Cl_2]^+$ and $[Cr(phen)_2Cl_2]^+$

Bonds	Distances (Å) for $[Cr(bipy)_2Cl_2]^+$	Bonds	Distances (Å) for $[Cr(phen)_2Cl_2]^+$
Cr1-N1A	2.066 (3)	Cr1-N1	2.074(2)
Cr1-N1B	2.072(3)	Cr1-N1	2.074(2)
Cr1-N12A	2.056 (3)	Cr1-N12	2.066(2)
Cr1-N12B	2.057(3)	Cr1-N12	2.066(2)
Cr1-Cl1	2.2967(11)	Cr1-Cl1	2.2910(8)
Cr1-Cl2	2.2966(11)	Cr1-Cl1	2.2910(8)

Table 2.3: Selected bond angles for $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$ and $[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$

Bonds	Bond angles ($^\circ$) for $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$	Bonds	Bond angles ($^\circ$) for $[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$
N12B-Cr1-N1B	79.03(14)	N12-Cr1-N1	93.85(8)
N12A-Cr1-N1A	79.05(13)	N12-Cr1-N1	79.86(8)
Cl1-Cr1-Cl2	93.84(4)	Cl1-Cr-Cl1	93.42(4)

The $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$ and $[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$ are isostructural. The coordination geometry is for both structures that of a distorted octahedron, but for the $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$ is remarkably more evident in the bond length and bond angles. This can be due to the narrower bite of the bipy ligand compared to the phen. The bond lengths and bond angles of these two complexes can be compared with those of analogous first row transition metal complexes such as $[\text{Ni}(\text{bipy})_2\text{Cl}_2]$, $[\text{Fe}(\text{bipy})_2\text{Cl}_2]^+$, $[\text{Co}(\text{bipy})_2\text{Cl}_2]^+$.²⁵

2.2.3. Cr(III) homoleptic complexes

Synthesis and purification

The syntheses of the following complexes were attempted following the methods described in Section 2.2.1.

Table 2.4: Cr(III) homoleptic complexes (yields are reported in brackets)

Model Complexes			
$[\text{Cr}(\text{bipy})_3]^{3+}$	(1) (63 %)	$[\text{Cr}(\text{phen})_3]^{3+}$	(2) (80%)
$[\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$	(3) (72 %)	$[\text{Cr}(\text{dpq})_3]^{3+}$	(7) (31 %)
$[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$	(4) (95 %)	$[\text{Cr}(\text{dppz})_3]^{3+}$	(8) (60 %)
$[\text{Cr}(2,9\text{-Me}_2\text{phen})_3]^{3+}$	(5) (0 %)	$[\text{Cr}(\text{tpphz})_3]^{3+}$	(9) (12 %)
$[\text{Cr}(\text{phendione})_3]^{3+}$	(6) (51 %)		

The parent complexes (1) and (2) were synthesized following Kane-Maguire and Hallock.¹⁴ Following the same procedure, complexes (3) and (4) were synthesized, yielding bright yellow compounds (Scheme 2.2).

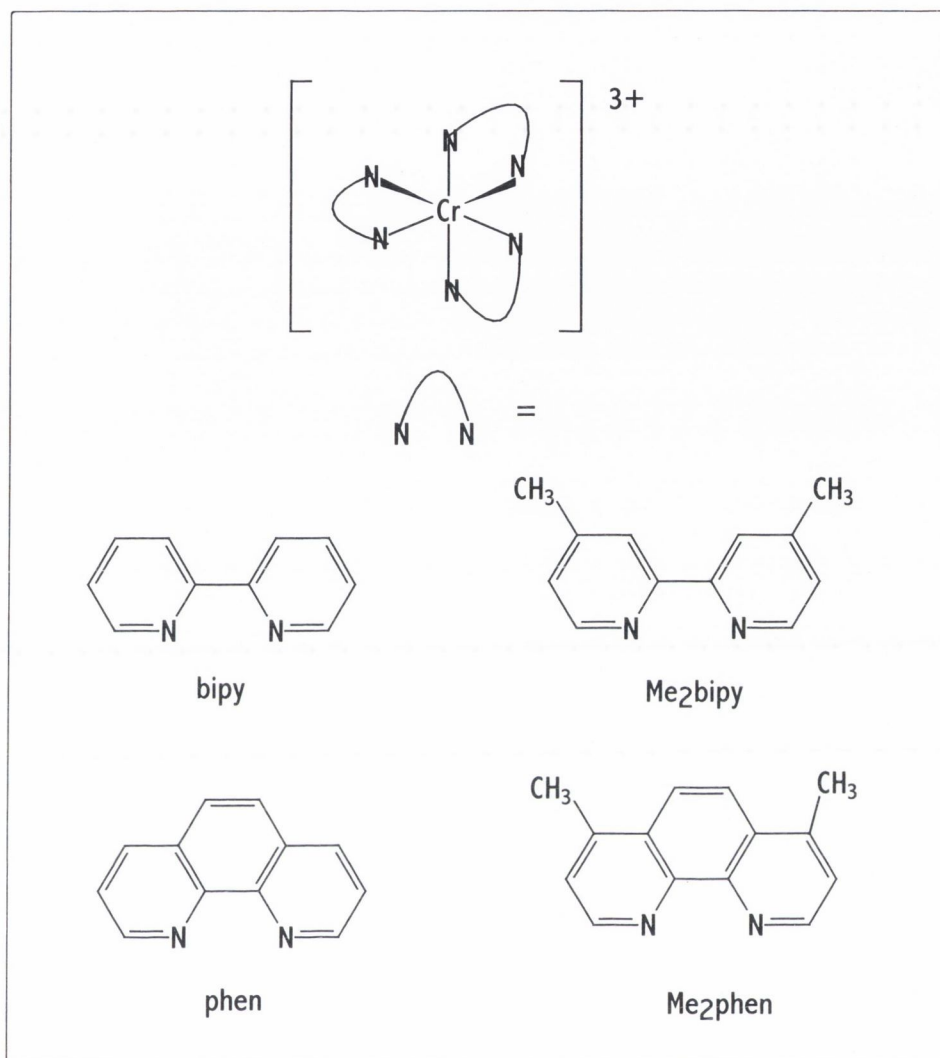


Figure 2.10. Structure of the $[\text{Cr}(\text{LL})_3]^{3+}$ complexes synthesized by method (ii)

Complexes (1) and (2) were synthesized and purified according to the procedure described. Crystals of both complexes were grown by diffusion of ether into a concentrated solution of the compound. The X-ray crystal structure of $[\text{Cr}(\text{bipy})_3]^{3+}$ was already known in the literature²⁶, while that of the $[\text{Cr}(\text{phen})_3]^{3+}$ was published²⁷ several months after we had obtained it.

The $[\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$ was synthesized as described and no purification was necessary. Crystals were grown from diffusion of ether into acetonitrile solutions, but these degraded very quickly during X-ray data collection.

The compound $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ was synthesized following the same procedure as for $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{phen})_3]^{3+}$ but purification with Sephadex LH-20 (using acetonitrile as eluent) followed by Sephadex-SP-C25 (using 0.5 M NaCl

acetone/water (5:3)) were necessary to remove an orange band from the yellow complex. Orange crystals were grown by slow evaporation of water solution, and these were characterized as an hydroxo-bridged complex, which is represented in Figure 2.11. The yellow purified product was precipitated as PF_6 salt. Crystals were grown from acetonitrile/ether solutions. The crystal structure of this complex is presented and discussed later.

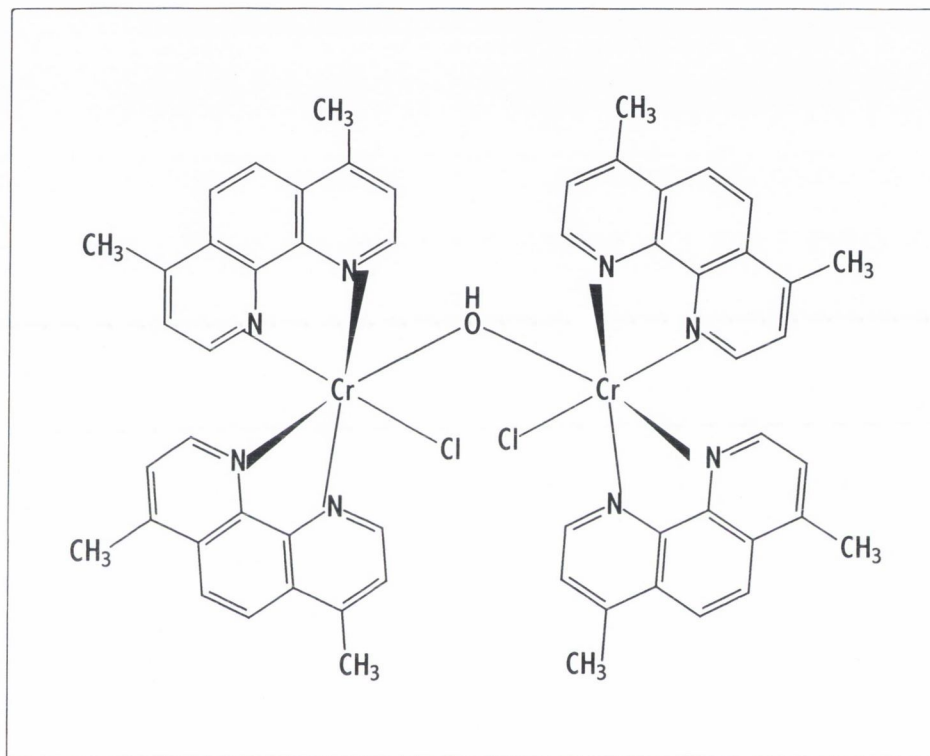


Figure 2.11: Structure of the binuclear-hydroxo-bridged Cr(III) complex.

Attempts to synthesize the complexes (5) and (6) using this method failed. In fact, during the synthesis of $[\text{Cr}(\text{2,9-Me}_2\text{phen})_3]^{3+}$, where 2,9-Me₂phen is the the ligand 2,9-dimethyl-1,10-phenanthroline, one of the nitrogens on the ligand 2,9-Me₂phen is protonated at the low pH at which the reaction is carried out and this prevents any possibility of coordinating the metal centre. The X-ray of the protonated ligand is presented in Figure 2.12. Crystallographic data for the ligand are reported in Appendix M.

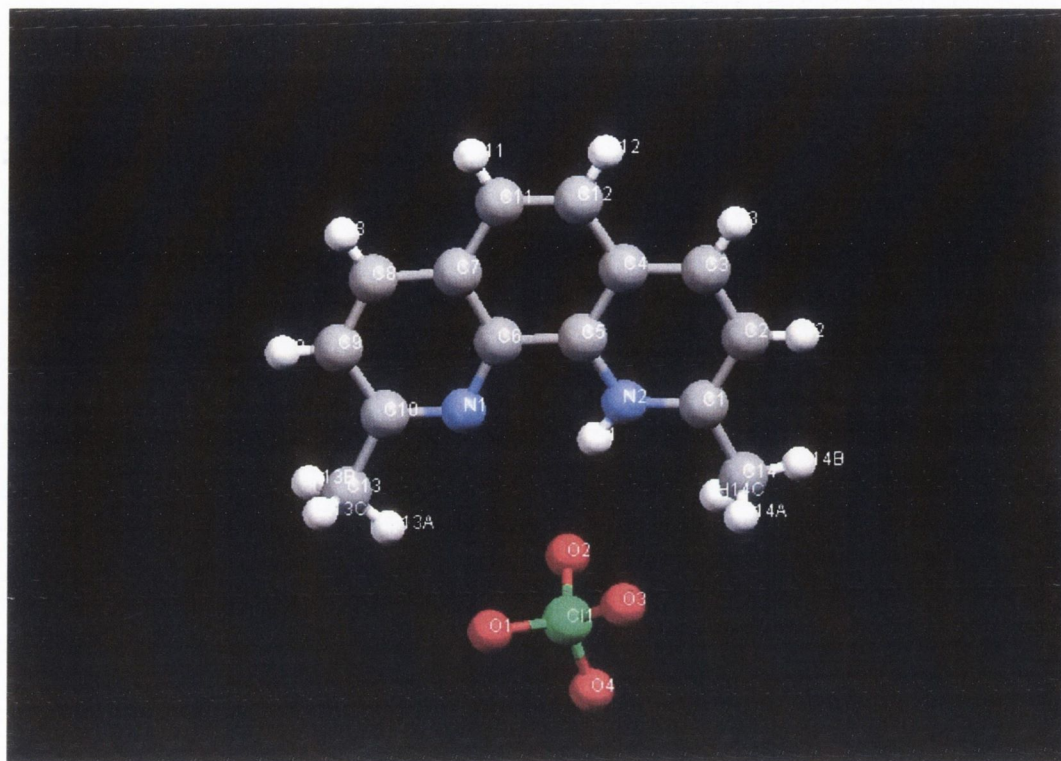


Figure 2.12. X-ray crystal structure of the ligand $2,9\text{-Me}_2\text{phenH}^+ \text{ClO}_4^-$

Similar behaviour was previously found in our lab for the ligand 2,3-dpq.²⁸ Attempts to synthesize $[\text{Cr}(\text{phendione})_3]^{3+}$ via the Cr(II) precursors gave a yellow compound, but this was characterised as the aquo-hydroxo species, $[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$, whose crystal structure is presented later in this Chapter.

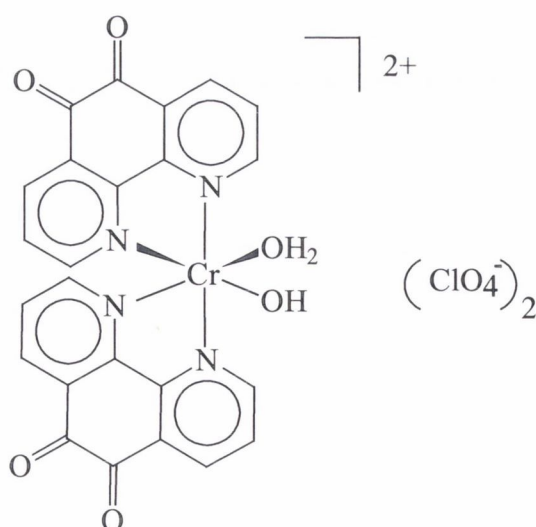


Figure 2.13: Structure of the $[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$

Complex (6), the starting material for all the other complexes (7) to (9), was prepared following the method developed by Gillard and subsequently by MacDonnell, which consists of oxidising the phenanthroline part of the complex using a nitric/sulfuric mixture in presence of NaBr as catalyst (Scheme 2.4). Complexes (7) to (9) were prepared by refluxing the $[\text{Cr}(\text{phendione})_3]^{3+}$ in MeCN/EtOH with the appropriate ligand. They were purified by crystallization from MeCN/ether.

In conclusion, in order to synthesize these complexes, method (ii) was used in the preparation of complexes (1) to (4), while method (iii) was used to synthesize complexes (7)-(9) (Scheme 2.5)

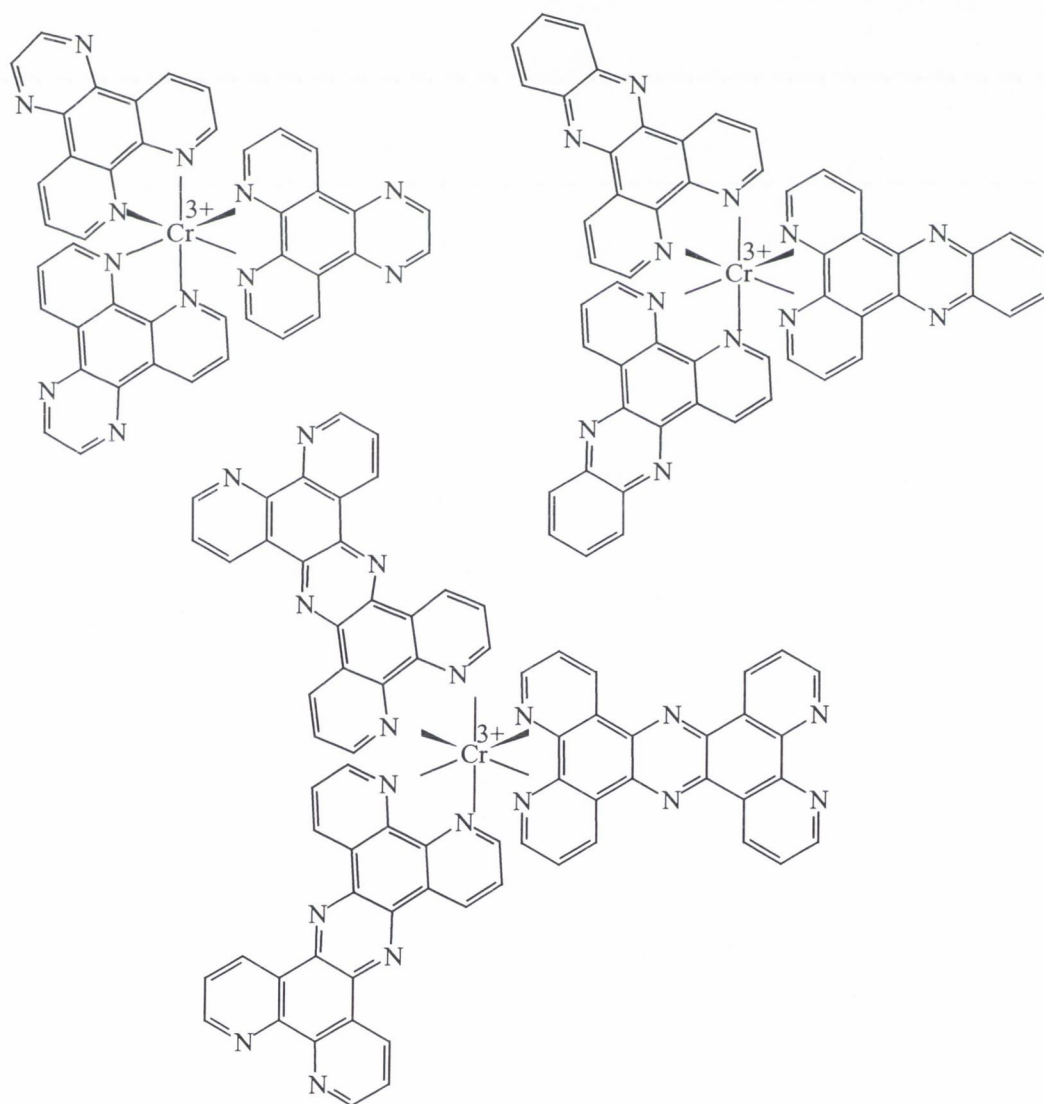


Figure 2.14: Structures of the complexes synthesized by method (iii)

All the complexes were isolated as the ClO_4^- salt and converted, when necessary, to the Cl^- salt using an anion exchange resin (DEAE-Sephadex), stirring the complex in water for more than one hour until complete dissolution. They were converted to the PF_6^- salt by addition of a saturated NH_4PF_6 solution. All these Cr(III) complexes were characterized by NMR spectroscopy, UV/Vis, IR and elemental analysis (C, H, N and Cr). All the compounds analysed in this chapter and further in this thesis were all subject to Electrospray Mass Spectrometer (ESMS) analysis both in our Department and in the laboratories of Prof. Alain van Doersselaer in Strasbourg. However it proved to be very difficult to analyse our compounds with ESMS and in only a few cases were we able to determine the parent ion. In fact a high degree of fragmentation was always found in the mass spectra but in any case we could not understand the reason. Maybe high temperature mass spec would have been useful.

Absorption spectra for the $[\text{Cr}(\text{LL})_3]^{3+}$ complexes where $\text{LL} = \text{bipy}$ and phen .

To assess the effect, if any, of the solvent medium, counter-ion induced changes and substituents (CH_3 positions in the bipy and phen ligand) the UV/Vis absorption spectra of the free ligands and their complexes were recorded in a variety of solvents. The extinction coefficients (ϵ_{max}) were obtained from Beer-Lambert's law, $A = \epsilon lc$, where A is the absorption, l is the pathlength and c is the concentration, and determined for at least two dilution factors at the wavelength corresponding to the maximum absorption (λ_{max}) for each peak in the spectrum. Where data were available from the literature, the values were in good agreement. The UV/Vis electronic spectra of the homoleptic complexes, $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{phen})_3]^{3+}$, were recorded in a variety of solvents to examine the effect of the solvent media. The results are tabulated in Table 2.5 and representative UV/Vis spectra are shown in Figure 2.15. The values found are good in agreement with those reported by Serpone *et al.*² and König and Herzog.²⁹

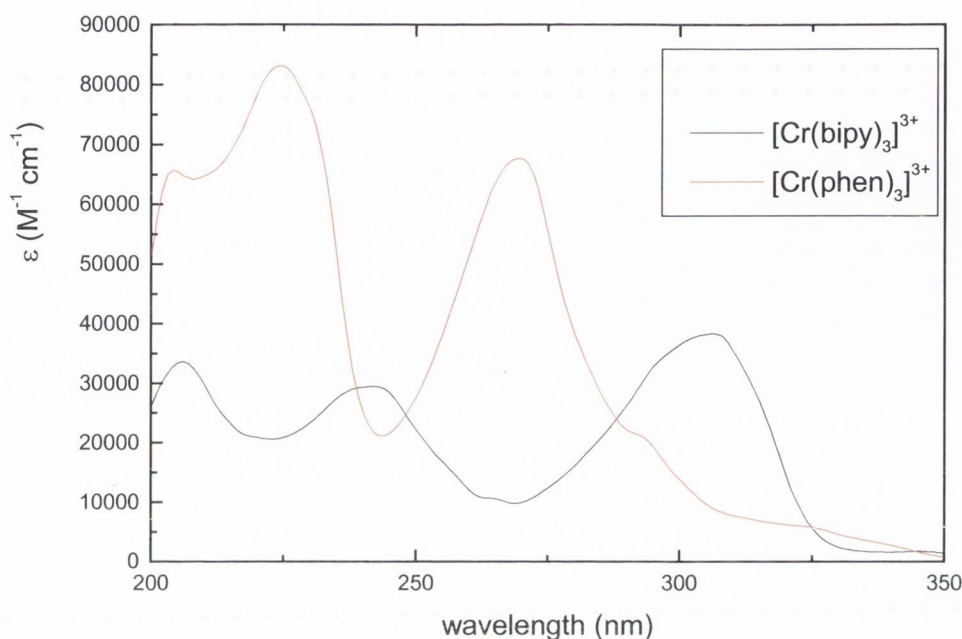


Figure 2.15: Absorption spectra of $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{phen})_3]^{3+}$ complexes in MeCN solutions.

The UV/vis spectra are dominated by ligand centred transitions with two strong peaks at around 225 nm and 275 nm. There is then a steep drop in absorption in the 350-400 nm region. The first ligand field band often appears as two or three unresolved shoulders on the low-energy side of the very intense intraligand band. This makes it difficult to assess the positions and the intensities of the ligand field bands. According to König and Herzog²⁹, the lowest energy multicomponent band of the complexes is assigned to the ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ transition. From this band they calculated the value of the ligand field parameter, Δ , which is $23.4 \cdot 10^3 \text{ cm}^{-1}$. The three vibrational components of the octahedral ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition can be seen clearly in Figure 2.16 where the region 350-500 nm is represented for the $[\text{Cr}(\text{bipy})_3]^{3+}$ complex.

Table 2.5: UV/Vis spectroscopic data for $[\text{Cr}(\text{LL})_3]^{3+}$ where LL= bipy and phen

Complex	Solvent	λ_{max} , nm ($\log \epsilon, M^{-1} \text{ cm}^{-1}$)	λ_{max} , nm ($\log \epsilon, M^{-1} \text{ cm}^{-1}$)
$[\text{Cr}(\text{bipy})_3]^{3+}$	CH_3CN^a	205 (4.52), 241 (4.46), 305 (4.57), 345 (3.5), 354 (3.40), 402 (2.92), 428 (2.80), 460 (2.40)	^d 458(2.43), 430(2.82), 402 (2.97)
	EtOH	236 (4.47), 284 (4.45), 308 (4), 349 (3.35)	
	H_2O^b	233 (4.58), 282 (4.48), 295 (4.45), 307 (4.39), 345 (3.56), 358 (3.41)	^e 235 (4.62), 265 (4.24), 276 (4.22), 305 (4.36), 313 (4.40), 346 (3.95), 360(3.76), 402 (2.97), 428 (2.83), 458 (2.43)
$[\text{Cr}(\text{phen})_3]^{3+}$	CH_3CN	204 (4.81), 224 (4.92), 269 (4.82), 293 (sh) (4.35), 323 (3.90), 354 (3.36), 407 (2.90), 432 (2.74). 4.54 (2.50)	^c 426 (2.58) ^d 455 (2.50), 434(2.77), 405 (2.94)
	EtOH	224 (4.87), 270 (4.66), 293 (4.22)	
	H_2O^b	222 (5.11), 268 (4.98), 292 (4.52), 429 (2.63),	^e 225 (4.93), 269 (4.81), 285 (4.57), 323 (4.10), 342 (3.90), 358 (3.61), 405 (2.93), 435 (2.77), 454 (2.51)

^a using ClO_4^- salts; ^b using Cl^- salts; ^c in water, using ClO_4^- salt, from Broomhead *et al*, *Inorg. Chem.*, 1968, 7, 1388; ^d in 0.1 M HCl, from Kharmawphlang *et al*, *Inorg. Chem.*, 1995, 34, 3826-3828; ^e using 1M HCl, from Serpone *et al*, *J. Am. Chem. Soc.*, 1979, 101, 2907

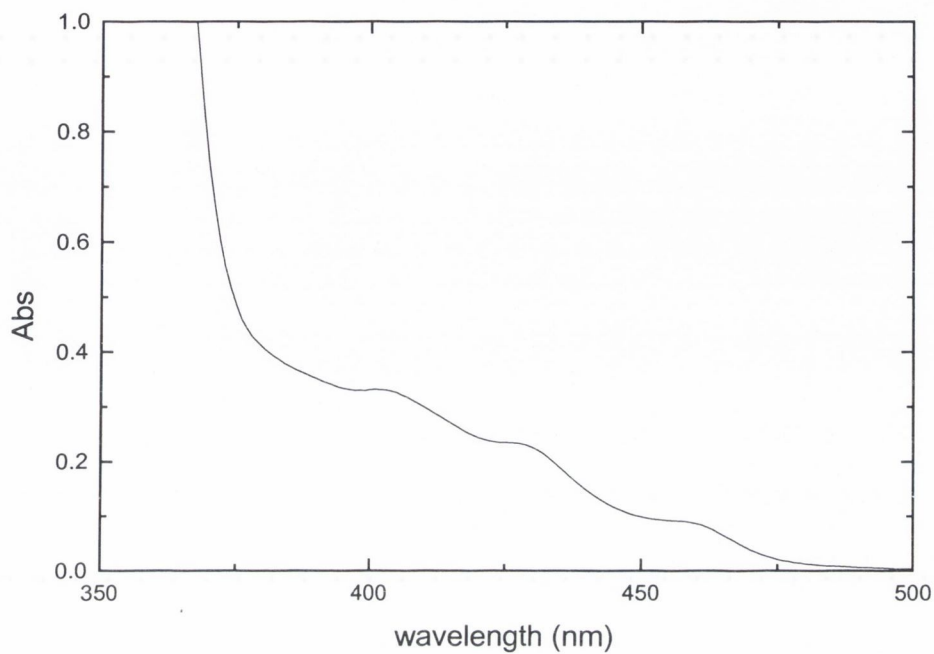


Figure 2.16: Region 380 nm-500 nm of the UV/Vis spectra of $[Cr(bipy)_3]^{3+}$ in MeCN, ($C = 10^{-3} M$).

In general the extinction coefficients for the phen complex are higher than those of the corresponding bipy compound.

Effects of substituents on the absorption spectra of the free ligands and complexes

In order to evaluate the effect of the substituents on the optical properties of these complexes, the absorption spectra for the free ligands, bipy, 4,4'-Me₂bipy, phen, 2,9-Me₂phen, Me₂phen, which are represented in Figure 2.17, were measured in CH₃CN, EtOH and water at room temperature, and are presented in Figures 2.18-2.20. The absorption data listings are summarized in Table 2.6.

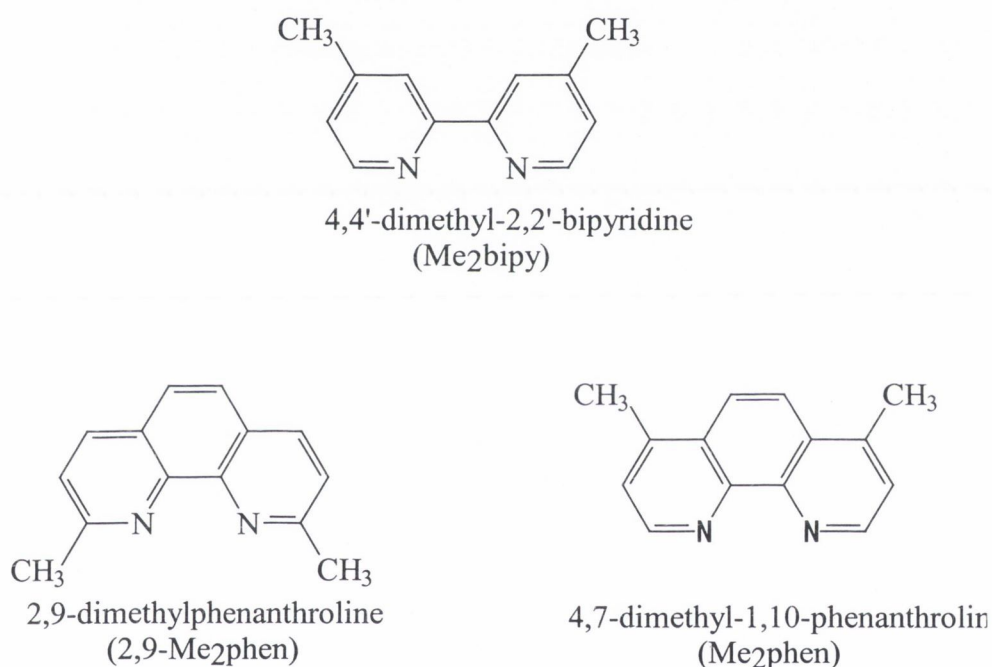


Figure 2.17: The ligands used in this study are represented together with their abbreviations

Table 2.6: Absorption spectra of the ligands in different solvents.

Ligands	Solvent	λ_{max} , nm ($\log \epsilon M^{-1} cm^{-1}$)
bipy	EtOH	201 (4.15), 235 (3.98) 242 (sh) (3.9), 281 (4.08),
	MeCN	236 (4.07), 243 (4.01), 281(4.17)
	H ₂ O	233 (3.99), 279 (4.09)
phen	EtOH	225 (4.52), 264 (4.40), 323(2.70)
	MeCN	226 (4.58), 262 (4.42), 276 (4.10), 309(sh)(2.95), 322(sh)(2.74),
	H ₂ O	226 (4.43), 264 (4.31), 289 (3.82)
Me ₂ bipy	EtOH	201 (4.38), 203 (4.40), 240 (3.92), 249(sh)(3.85), 281 (4.05)
	MeCN	200 (4.18), 241 (3.61), 248 (3.58), 280 (3.71)
	H ₂ O	237, 279 (very poor solubility)
2,9-Me ₂ phen	EtOH	203 (4.18), 228 (4.52), 269 (4.35)
	MeCN	202 (4.22), 229 (4.64), 268(4.46), 313 (3.02), 327 (2.78)
	H ₂ O	203 (4.24), 227 (4.53), 270 (4.39), 292 (3.99)
Me ₂ phen	EtOH	203 (4.19), 231 (3.99), 237 (4), 264(4.05), 300 (3.34)
	MeCN	202 (4.40), 231 (4.51), 237 (4.54), 263 (4.54), 278 (sh) (4.09), 297 (3.85), 325 (2.83)
	H ₂ O	204 (4.30), 231 (4.27), 265 (4.37), 301 (3.65)

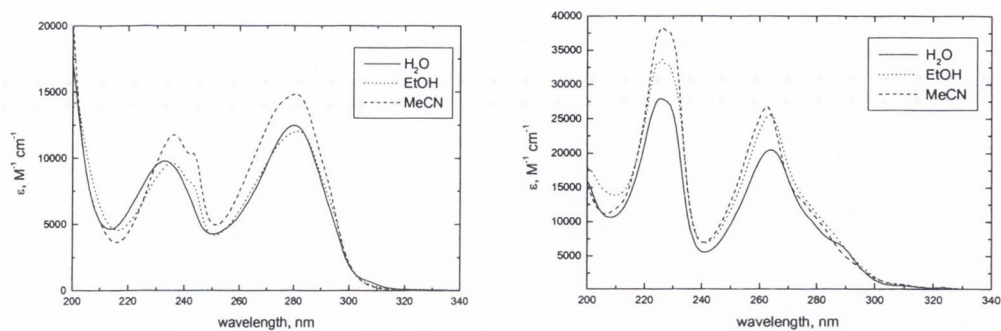


Figure 2.18: UV/Vis absorption spectra of the ligands bipy and phen (left and right respectively)

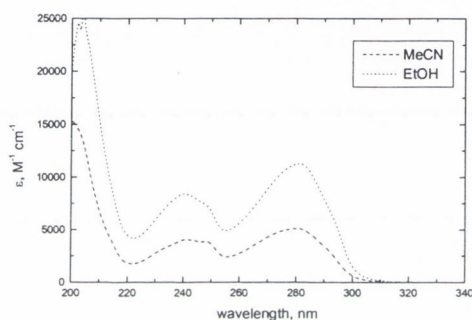


Figure 2.19: UV/Vis absorption spectra of the ligand Me_2bipy .

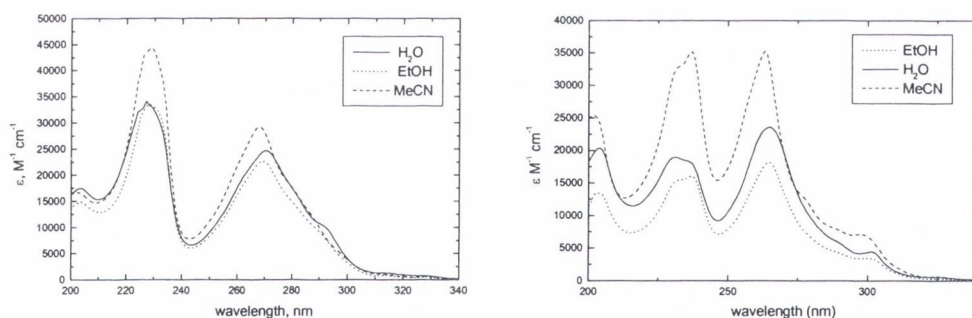


Figure 2.20: UV/Vis absorption spectra of the ligands $2,9\text{-Me}_2\text{phen}$ and Me_2phen (left and right respectively).

All the spectra show two intense bands at ~ 230 and ~ 280 nm, which are shifted to the red for the methylated complexes. The phen ligands have bigger extinction coefficients than the bipy. The extinction coefficients for all the ligands are much higher in acetonitrile than in water and ethanol, where their extinction coefficients are about the same.

The results for the corresponding complexes are reported in Table 2.7 The absorption spectra have been recorded in MeCN and H₂O.

The spectra of the two species have been compared to those of Cr(III)(bipy)₃ and Cr(III)(phen)₃ (Figures 2.21 and 2.22)

Table 2.7: UV/vis spectroscopic data of [Cr(Me₂bipy)₃]³⁺ and [Cr(Me₂phen)]³⁺ in different solvents.

Compound	Solvent	λ_{max} , nm (log ϵ , M ⁻¹ cm ⁻¹)
[Cr(Me ₂ bipy) ₃] ³⁺	MeCN	205 (4.84), 239 (4.59), 304 (4.50), 345 (3.52)
	H ₂ O ^a	238 (4.78), 280 (4.53), 300 (4.59), 340 (3.83), 390 (2.83), 416 (2.62), 443 (2.14)
	EtOH	240 (4.52), 283 (4.34), 307 (4.08), 345 (3.48)
	1M HCl ^b	240 (4.78), 278 (4.38), 307 (4.44), 342 (3.96), 354 (3.86), 394 (2.97), 418 (2.80), 446 (2.43) ^b
[Cr(Me ₂ phen) ₃] ³⁺	MeCN	208 (4.94), 227(4.81), 270 (4.88), 305 (4.36), 352 (3.72)
	H ₂ O ^a	223 (4.60), 266 (4.64)
	EtOH	236 (4.76), 266 (4.74), 302 (4.21), 354 (3.44)
	MeOH ^c	230 (4.86), 237 (4.80), 269 (4.85), 308 (4.40), 340 (3.94), 357 (3.77), 402 (3.02), 424 (2.95), 450 (2.70) ^c

^a as Cl⁻ salts, ^b and ^c data are from Serpone *et al*, *J. Am. Chem. Soc.*, 1979, 101, 2907.

The two absorption spectra are qualitatively similar. Methyl substituents on the bipy and phen ligands slightly blue-shift the low energy bands, while the band at 269 nm of [Cr(Me₂phen)₃]³⁺ is slightly shifted to the red (~1 nm). The fact that there are only minor shifts suggests that substitution in the positions 4,4' and 4,7 does not significantly alter the electron density in the bipy and phen ligands, respectively.

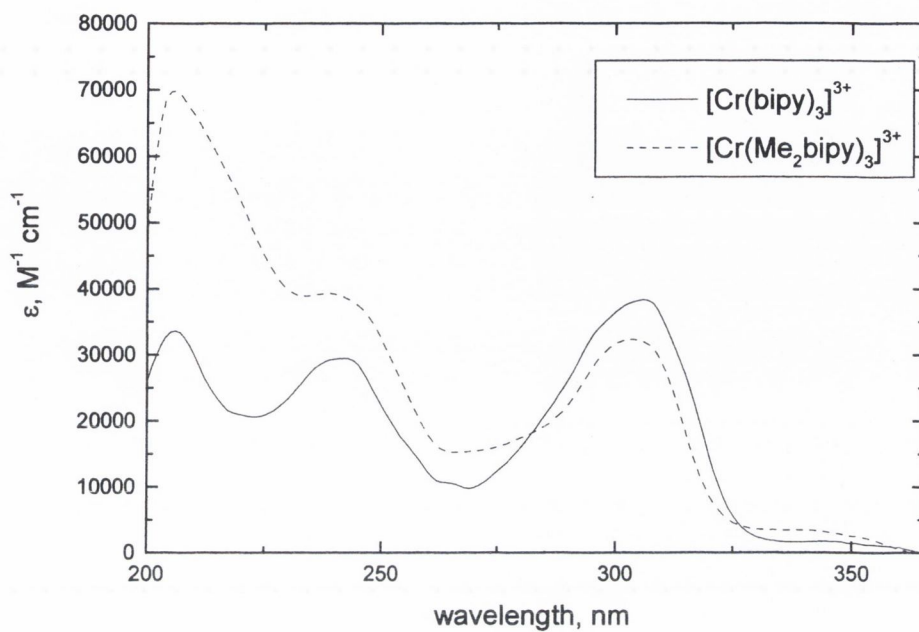


Figure 2.21: Absorption spectra of $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$ in MeCN.

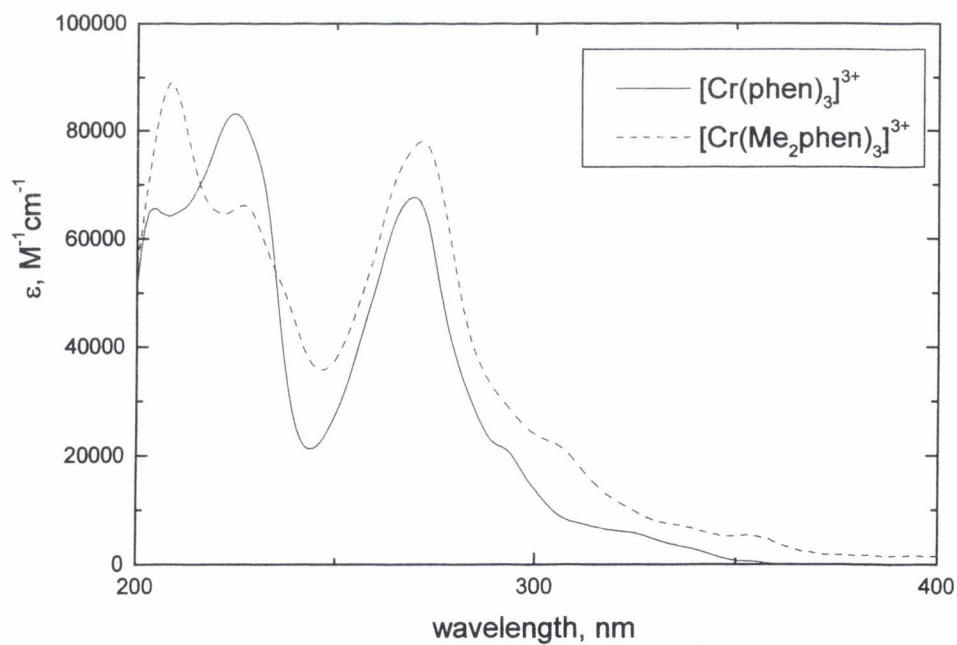


Figure 2.22: Absorption spectra of $[\text{Cr}(\text{phen})_3]^{3+}$ and $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ in MeCN.

Absorption spectra of $[Cr(phendione)_2(OH)(H_2O)](ClO_4)_2$

The UV/Vis spectrum of $[Cr(phendione)_2(OH)(H_2O)](ClO_4)_2$ was recorded in MeCN and water and is shown in Figure 2.23. The spectral data are collected in Table 2.8 below.

Table 2.8: Spectral data for $[Cr(phendione)_2(OH)(H_2O)](ClO_4)_2$

<i>Solvent</i>	<i>λ_{max} , nm (log ϵ, $M^{-1} cm^{-1}$)</i>
MeCN	203 (4.61), 248(4.62), 281(4.14), 300 (4.17), 312(4.18), 349 (3.25), 373 (3.12), 476 (1.67)
H ₂ O	233 (4.59), 253 (4.68), 296 (4.21), 309 (4.11), 353 (2.91)

The spectra are characterized by a strong peak at about 250 nm, a weaker peak at 275 nm and two peaks at 300 and 310, which are clearly visible in MeCN. The peak at 250 nm is due to ligand centred transitions. The two peaks at 300 and 310 nm are due to ligand localized π - π^* transitions on the phendione ligands. The spectrum in water shows a shoulder at 233 nm, and there is a red shift (~ 4 nm) in the peak at 250 nm. There are no longer two distinct peaks at 300-310 nm but they appear as a structured single band which is slightly shifted to the blue. This effect can be attributed to the high polarity strong H-bonding properties of water, which may lead to aggregation of the complex.

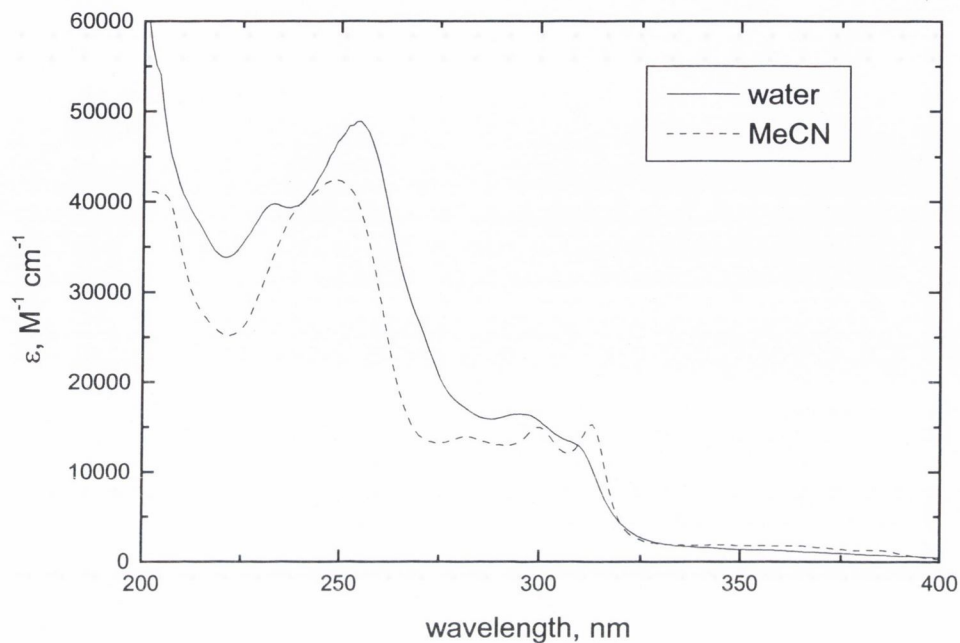
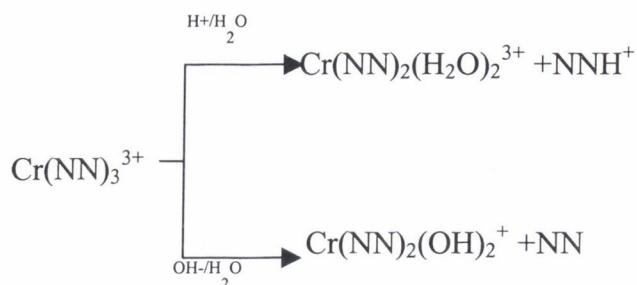


Figure 2.23: Absorption spectra of $[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$ in MeCN and water ($C \sim 10^{-5} \text{ M}$).

UV/Vis spectra of the complex were recorded in aqueous solutions at different pHs. The UV/Vis of the compound is dramatically affected by variation in the pH of the solution as can be seen in Figure 2.24. At acidic pH the curve is almost the same as at pH 7 while it changes completely at pH = 11.

Maestri *et al.*³⁰ have studied the pH dependencies of Cr(III) polypyridyl complexes and they have proposed that Cr(III) polypyridyl complexes lose one ligand at both acid and basic solutions (Scheme 2.11):



Scheme 2.11: Hydrolysis of Cr(III) polypyridyl complexes.

At $\text{pH} < 6$ the hydrolysis reaction is very slow, while it is faster at basic pH. Hence Maestri suggested the existence of monodentate complexes at $\text{pH} > 10.5$.

In the case of $[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$ the analysis of the absorption spectra shows that at basic pH something has occurred but at the same time no evidence is present to justify that hydrolysis has happened. In fact the UV/Vis is markedly affected and there is no evidence of the presence of the free ligand in solution. Therefore no hypothesis can be advanced and further studies are necessary to clarify what species are present.

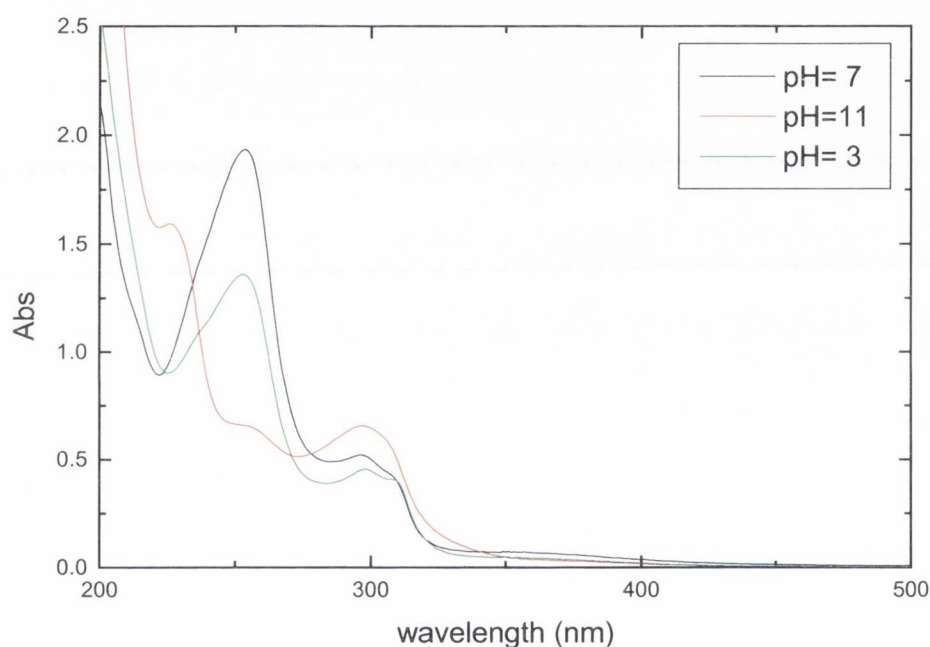


Figure 2.24: Effect of the pH in the absorption spectra of $[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$ ($C = 3.68 \times 10^{-5}$).

Absorption spectra of $[Cr(LL)_3]^{3+}$ complexes where $LL =$ phendione, dpq, dppz and tpphz.

Absorption spectra for the complexes synthesized are presented in Figure 2.26 and the λ_{max} and extinction coefficients are listed in Table 2.9 and 2.10 for the free ligands and the complexes respectively.

The ligands used are shown in Figure 2.25 below.

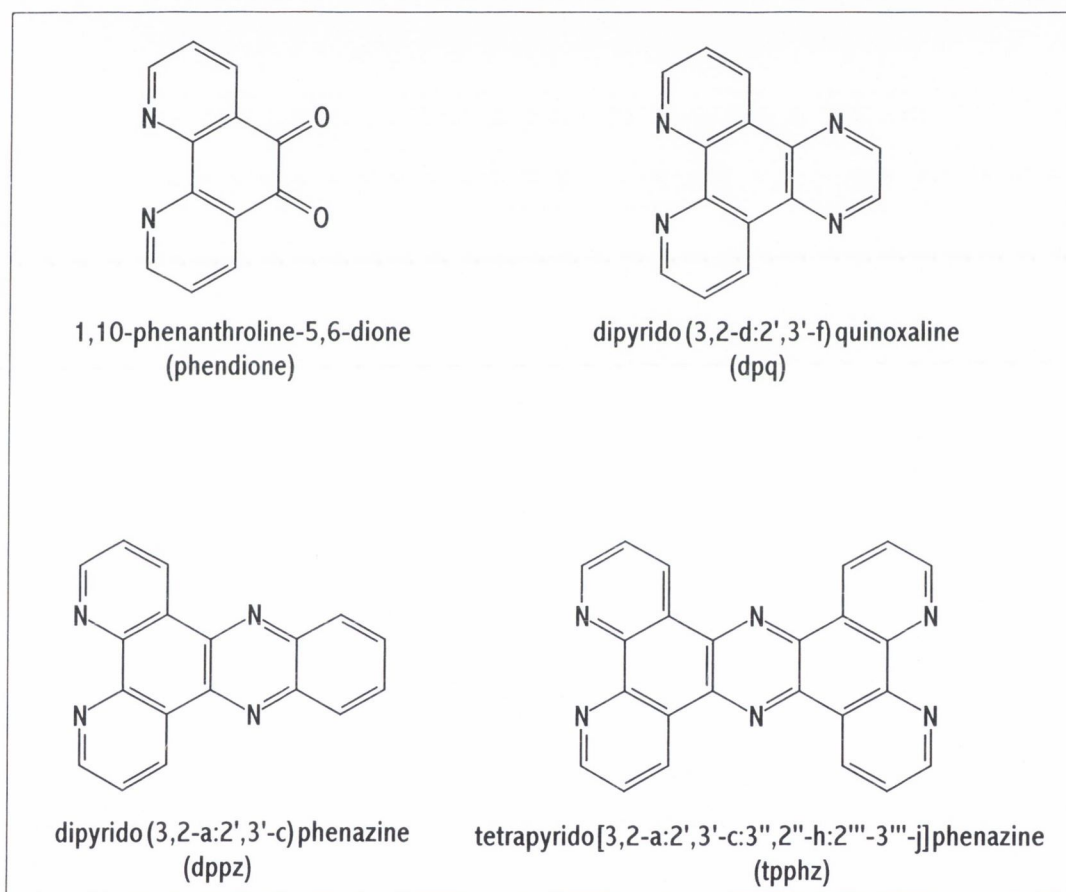


Figure 2.25: Ligands used in this study together with their abbreviations.

Table 2.9: Spectral data of the ligands used in EtOH and MeCN.

Ligands	$\lambda_{\max}$, nm ($\log \epsilon$, $M^l \text{ cm}^{-l}$)	$\lambda_{\max}$, nm ($\log \epsilon$, $M^l \text{ cm}^{-l}$)
	EtOH	MeCN
phendione	234 (4.06), 255 (4), 292 (3.56), 361 (2.31)	255 (4.21), 292 (3.42), 362 (2.56)
dpq	230 (4.21), 252 (4.48), 285 (3.94), 323 (3.45), 339 (3.33)	230 (4.45), 251 (4.64), 282 (4.11), 301(4.05), 325 (3.65), 339 (3.63)
dppz	239 (4.48), 294 (4.30), 333 (3.74), 341 (3.85), 349 (3.93), 357 (4.07), 365 (4.02), 376 (4.10)	210 (4.32), 239 (4.40), 268 (4.68), 291 (4.22), 333 (3.70), 342 (3.82), 349 (3.88), 358 (4.02), 367 (3.95), 377 (4.05)
tpphz	221 (3.91), 246 (4.05), 274 (4.33), 305 (3.92), 322 (3.80), 349 (3.60), 359 (3.63), 367 (3.80), 378 (3.76), 387 (3.99)	Poorly soluble

Table 2.10: Absorption data of $[\text{Cr}(\text{LL})_3]^{3+}$ complexes in MeCN

Complex*	$\lambda_{\max}$, nm ($\log \epsilon$, $M^l \text{ cm}^{-l}$)
$[\text{Cr}(\text{phendione})_3]^{3+}$	209 (4.78), 248 (4.89), 302 (4.41), 287 (4.48), 305 (4.52), 316 (4.51), 475 (2)
$[\text{Cr}(\text{dpq})_3]^{3+}$	222 (4.81), 229 (4.86), 251 (5.04), 278 (4.56), 299 (4.49), 325 (4.11), 339 (4.02), 450 (2.9)
$[\text{Cr}(\text{dppz})_3]^{3+}$	208 (4.93), 238 (4.8), 269 (5.07), 283 (4.99), 340 (4.47), 348 (4.48), 358 (4.55), 365 (4.5), 376 (4.53), 427 (3.90), 453 (3.88), 485 (3.82)
$[\text{Cr}(\text{tpphz})_3]^{3+ \text{ a}}$	274 (5.22), 367 (4.60), 379 (4.59), 387 (4.68)

* as ClO_4^- salts; ^a as PF_6^- salt.

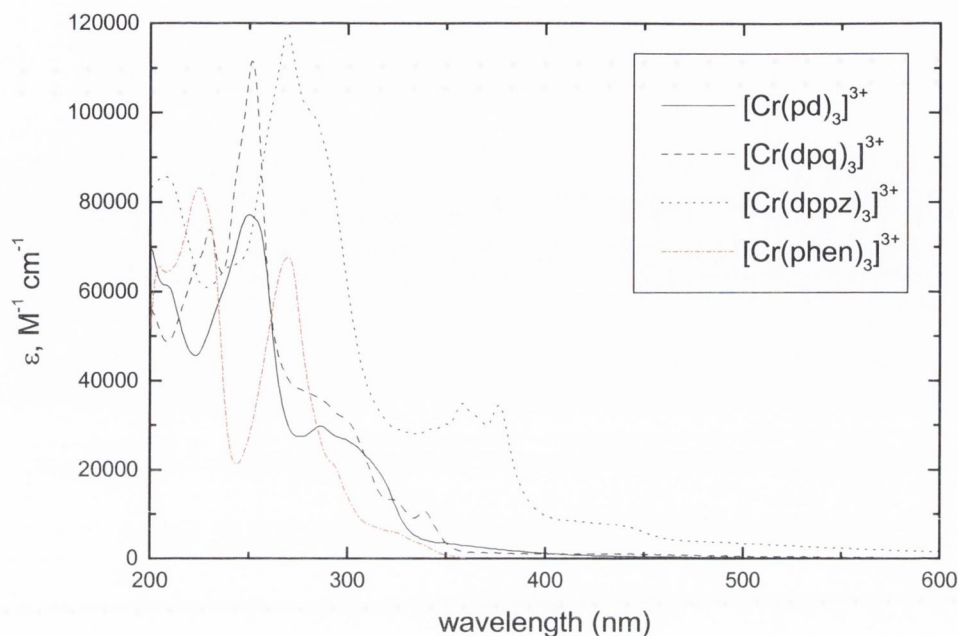


Figure 2.26: *UV/Vis of homoleptic Cr(III) complexes.*

In these spectra the electronic transitions of these peaks are ligand centred. The spin-allowed transitions of Cr(III) are buried under the more intense transitions of the ligand and cannot be seen. On going from phen to dppz and tpphz, the peaks are shifted to the red. In the region 375-400 nm the bands characteristic of the dppz and tpphz ligands are present, whereas the latter are stronger and more shifted to lower energy values.

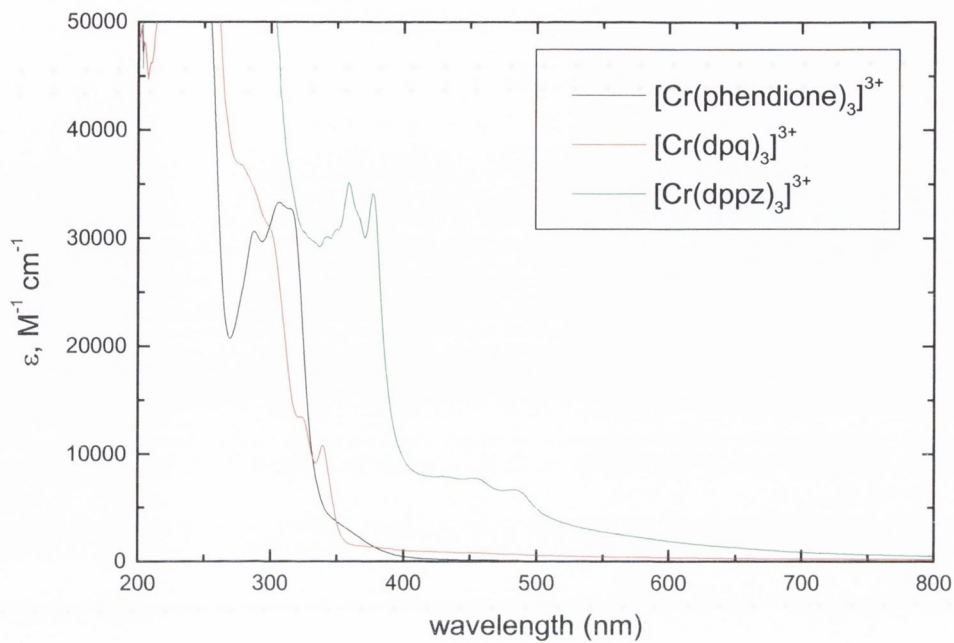


Figure 2.27: *UV/Vis spectra of the complexes in the range 250-800 nm*

X-ray diffraction experiments

Crystals suitable for X-ray diffraction experiments were obtained for a number of compounds containing Cr(III) as the metal centre by diffusion of ether into concentrated acetonitrile solutions.

The crystal and molecular structures of $[\text{Cr}(\text{phen})_3]^{3+}$ and $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ were obtained of the two compounds. The $[\text{Cr}(\text{phen})_3]^{3+}$ is presented in Figure 2.28.

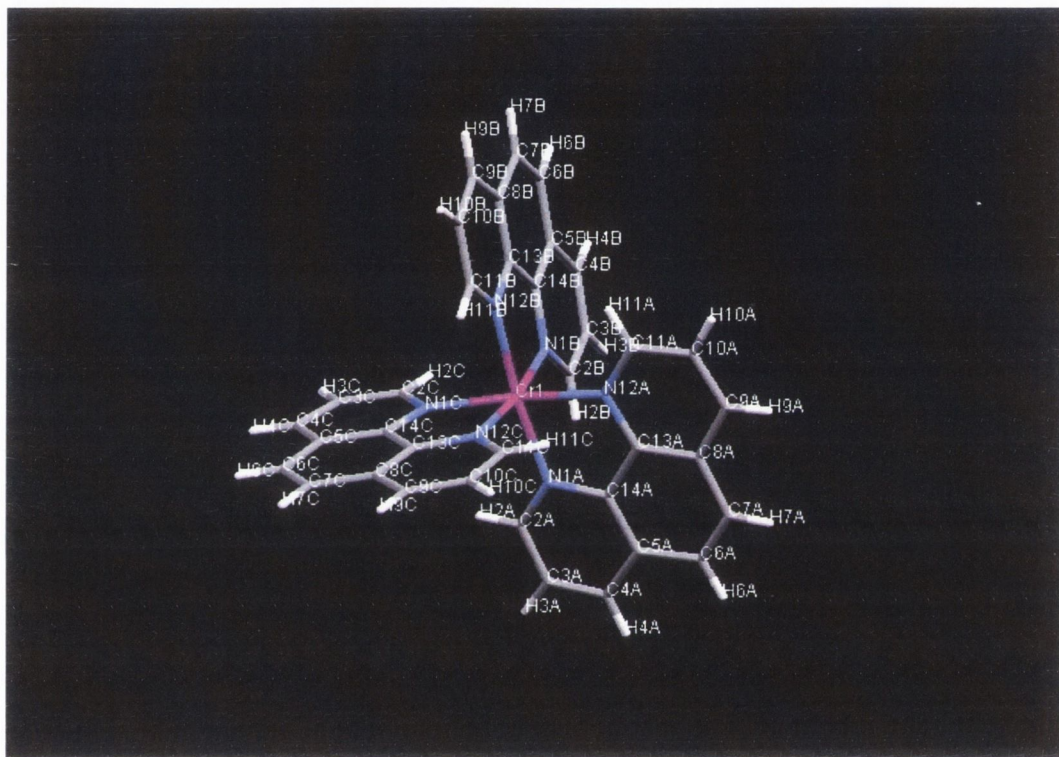


Figure 2.28: Molecular structure of $[\text{Cr}(\text{phen})_3](\text{ClO}_4)_3 \cdot 3.75\text{MeCN} \cdot 0.5\text{H}_2\text{O}$ (solvent molecules and counterion are omitted for clarity)

$[\text{Cr}(\text{phen})_3]^{3+}$ was crystallized as perchlorate salt. The structure was refined with a final R1 value of 0.0843. The quality of the data and refinement is good, however there are some disordered solvent molecules and a partially occupied water molecule. Each of the perchlorate anions are slightly disordered over two positions with the central chloride atom being coincident to each. The disorder has been modelled at 80:20 occupancy. Some of the acetonitrile molecules are disordered throughout the lattice. One of them (about C1sb) is positionally disordered over two sites with two water molecules (O1wb and O2wb). C4sa is disordered over two sites (with 54:46 occupancy) such that C4sa and C1sa are

coincident. C1sa is likewise disordered over two positions with 54:46 occupancy. Further refinement of this structure was not undertaken because a low temperature molecular structure has been obtained subsequent to submission by Luck *et al.*²⁶ This author saw close contacts indicative of H-bonding between the water and the oxygen atoms of the perchlorate. Similar interactions were evident in the structure presented here but were not investigated further. It is worth noting however that in our case the structure was crystallized in a triclinic space group.

$[\text{Cr}(\text{phen})_3]^{3+}$ consists of the two enantiomers, Δ and Λ . These can be seen in the diagram of the unit cell shown in Figures 2.29. The presence of both enantiomers results in the centrosymmetric nature of the unit cell.

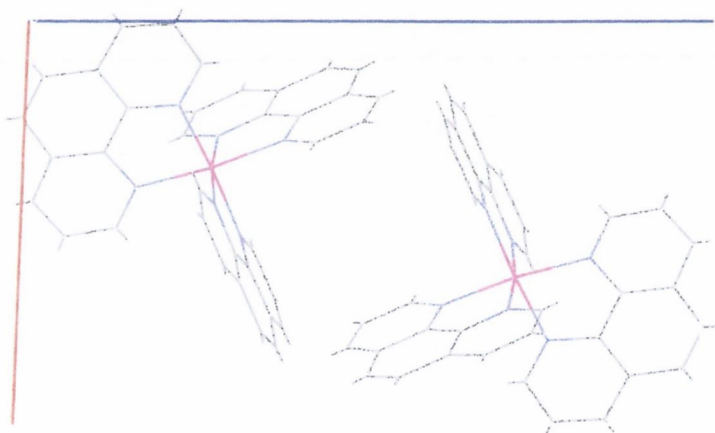


Figure 2.29: Packing diagram for $[\text{Cr}(\text{phen})_3]^{3+}$ viewed along the *b* axis.

The crystal structure of $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ is of poor quality ($R_1=0.18$). This is because the crystals were thin plates and weakly diffracting. The only useful comparison that can be made using the data are comparisons involving the geometry of the central metal ion. It is worth noting that this structure crystallized in a monoclinic space group with two molecules in the asymmetric unit. In Figure

2.30 the X-ray crystal structure of one asymmetric unit of $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ is presented.

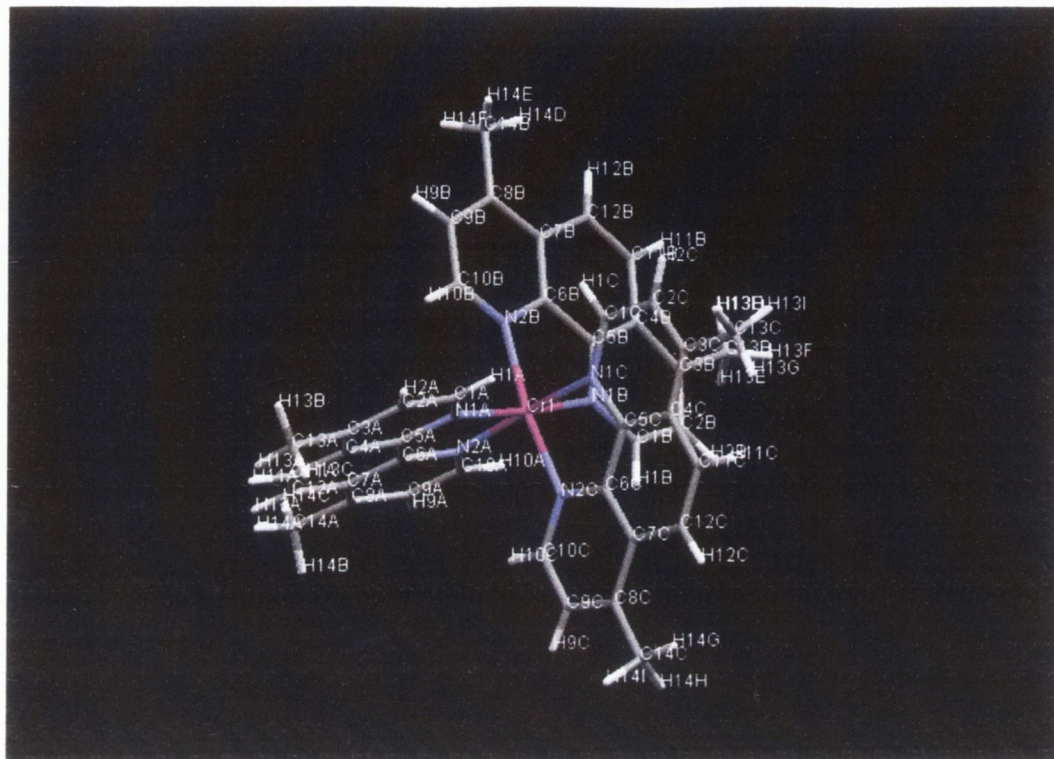


Figure 2.30: X-ray crystal structure of $[\text{Cr}(\text{Me}_2\text{phen})_3](\text{PF}_6)_3 \cdot 4\text{H}_2\text{O}$. One enantiomer is shown only (solvent molecules and counterion are omitted for clarity)

Selected bond lengths and bond angles for the two structures are compared in Tables 2.11-2.12 and 2. 13 respectively.

Table 2.11. Selected bond lengths (Å) for $[\text{Cr}(\text{phen})_3]^{3+}$

<i>Bonds</i>	<i>Distances (Å) for [Cr(phen)₃]³⁺</i>
Cr-N1A	2.053(3)
Cr-N1B	2.058(3)
Cr-N1C	2.067(3)
Cr-N12A	2.054(3)
Cr-N12B	2.059(3)
Cr-N12C	2.053(3)

Table 2.12. Selected bond lengths (Å) for the two enantiomers of $[Cr(Me_2phen)_3]^{3+}$

Bonds	Distances (Å) for $[Cr(Me_2phen)_3]^{3+}$	
Cr1-N2C (Cr2-N1D)	2.038 (10)	2.036 (10)
Cr1-N2B (Cr2-N2E)	2.054 (10)	2.040 (8)
Cr1-N1C (Cr2-N2F)	2.060 (9)	2.034 (9)
Cr1-N1A (Cr2-N2D)	2.065 (9)	2.059 (9)
Cr1-N2A (Cr2-N1F)	2.065 (9)	2.062 (10)
Cr1-N1B (Cr2-N1E)	2.076 (9)	2.073 (9)

Table 2.13. Selected bond angles (°) for $[Cr(phen)_3]^{3+}$ and $[Cr(Me_2phen)_3]^{3+}$

Bonds	Angles (°) for $[Cr(phen)_3]^{3+}$	Angles (°) for $[Cr(Me_2phen)_3]^{3+}$
N1A-Cr-N12A	80.93(13)	80.7(3)
N1B-Cr-N12B	80.48(14)	79.7(4)
N1C-Cr-N12C	80.39(13)	79.8(4)

$[Cr(phen)_3]^{3+}$ and $[Cr(Me_2phen)_3]^{3+}$ are isostructural. The three phen and Me₂phen around one metal centre form a propeller-like trigonal arrangement. The coordination geometry is within error that of a distorted octahedron. This is due to the narrow bite of each 1,10-phenanthroline ligand (on average the bite angle at the metal is ~81°). The average length of the Cr-N bonds is very similar to that observed in other phenanthroline complexes.

The $[Cr(Me_2phen)_3]^{3+}$ crystallizes in a monoclinic P2(1)/c space group. The packing diagram is shown below, and illustrates the layered nature of the structure.

Figure 2.31: Packing diagram for $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ viewed along the c axis

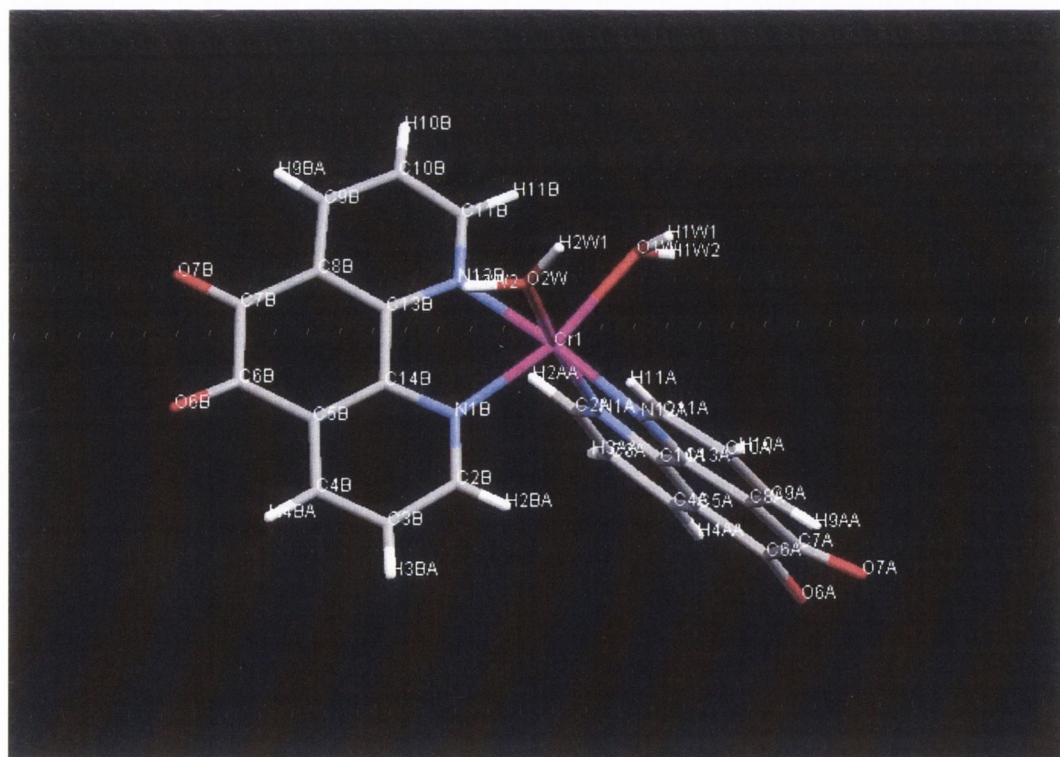


Figure 2.32: *Molecular structure of $[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (counterions omitted for clarity)*

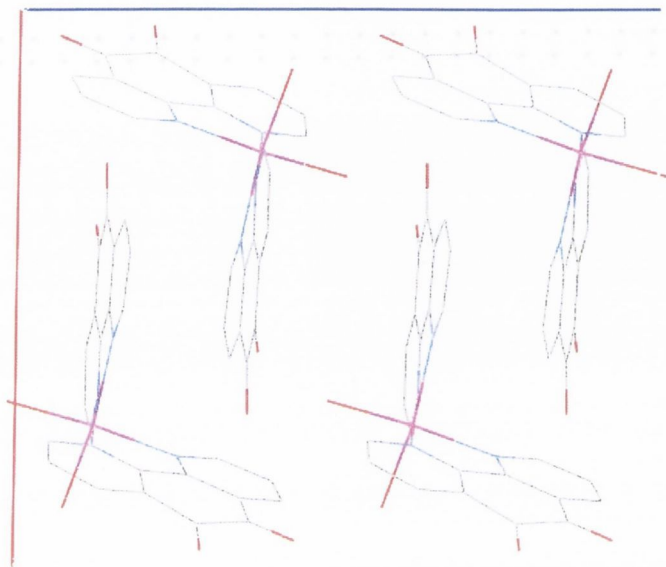


Figure 2.33: Packing diagram of $[Cr(phenadione)_2(OH)(H_2O)]^{2+}$ along the *b* axis

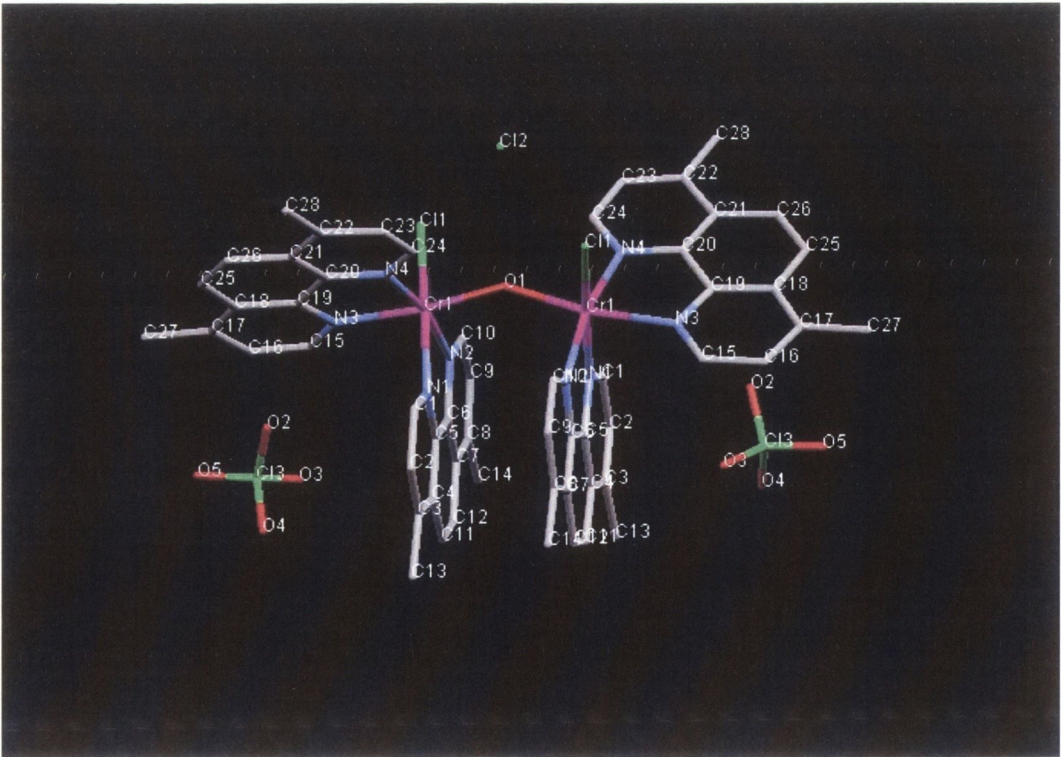


Figure 2.34. X-ray crystal structure of $[(Cr(Me_2phen)_2)(\mu-OH)Cl_2](Cl)(ClO_4)_2 \cdot 7H_2O$ (water molecules omitted for clarity)

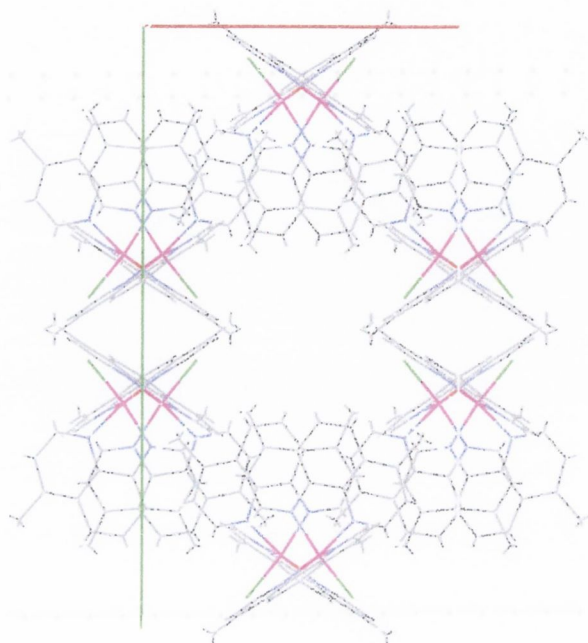


Figure 2.35: View of the packing diagram of $[(\text{Cr}(\text{Me}_2\text{phen})_2)(\mu\text{-OH})\text{Cl}_2]^{2+}$ along the c axis.

The two complexes, $[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$ and the binuclear Cr complex, presented in Figures 2.32 and 2.34, both have an O moiety, so we can compare the bond lengths and bond angles of the mononuclear against the binuclear. The mononuclear complex crystallizes in a monoclinic $P2(1)/c$ space group, with a final R1 factor of 0.0743. The dinuclear complex crystallize in a monoclinic $C2/c$ space group, with a final R1 factor of 0.1014. In both cases the data was collected at 153 K. The poor refinement of the binuclear complex comes in part from the plate-like morphology of the crystals. Also the Me_2phen ligand is a σ -donor while the phendione is a strong π -acceptor so we can compare how the bond lengths are affected by the presence of two ligands having different electronic character. The different electronic character of the bidentate ligand is illustrated by comparison of the Cr-N bond lengths which in the binuclear complex average about 2.06 Å nonuclear complex average 2.14 Å. The dinuclear complex crystallizes in an open lattice which allows to accomodate seven water molecules per dimer.

Table 2.14: Selected bond lengths (Å) for $[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$ and $[(\text{Cr}(\text{Me}_2\text{phen})_2)_2(\mu\text{-OH})\text{Cl}_2]^{3+}$

$[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$	$[(\text{Cr}(\text{Me}_2\text{phen})_2)_2(\mu\text{-OH})\text{Cl}_2]^{3+}$
2.101(4) (Cr1-O2W)	1.964(2) (Cr1-O)
2.112(4) (Cr1-N1A)	2.053(6) (Cr1-N1)
2.115(4) (Cr1-N1B)	2.060(6) (Cr-N2)
2.164(4) (Cr1-N12A)	2.079(5) (Cr-N3)
2.186(4) (Cr1-N12B)	2.057(5) (Cr-N4)

Table 2.15: Selected bond angles (°) for $[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$ and $[(\text{Cr}(\text{Me}_2\text{phen})_2)_2(\mu\text{-OH})\text{Cl}_2]^{3+}$

$[\text{Cr}(\text{phendione})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$	$[(\text{Cr}(\text{Me}_2\text{phen})_2)_2(\mu\text{-OH})\text{Cl}_2]^{3+}$
85.54(16)	88.53(18)
(O2W-Cr1-O1W)	(O1-Cr1-Cl1)
	148.7(4)
	(Cr1-O1-Cr1)

2.2.3. Cr(III) heteroleptic complexes

The starting materials for these syntheses, $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ and $[\text{Cr}(\text{bipy})_2(\text{phendione})]^{3+}$, are prepared by refluxing the precursor complexes $[\text{Cr}(\text{III})(\text{bipy})_2(\text{CF}_3\text{SO}_3)_2]$ and $[\text{Cr}(\text{III})(\text{phen})_2(\text{CF}_3\text{SO}_3)_2]$ in presence of an excess of phendione in dry MeCN (Scheme 2.9). The same reaction in dry CH_2Cl_2 did not produce the desired compound. As discussed in Section 2.21, the desired complexes can therefore be synthesized by condensation of ethylenediamine, *o*-phenylenediamine or 5,6-diamino-1,10-phenanthroline with the precoordinated phendione complex, $[\text{Cr}(\text{LL})_2(\text{phendione})]^{3+}$ (Scheme 2.10). Reaction of the ligands dppz and tpphz with the starting materials $[\text{Cr}(\text{LL})_2(\text{CF}_3\text{SO}_3)_2]$ (where LL= bipy or phen) in refluxing CH_2Cl_2 or MeCN does not give the expected products. In fact, the low solubility of dppz and of tpphz in most solvents prevents efficient synthesis of the mononuclear complexes.

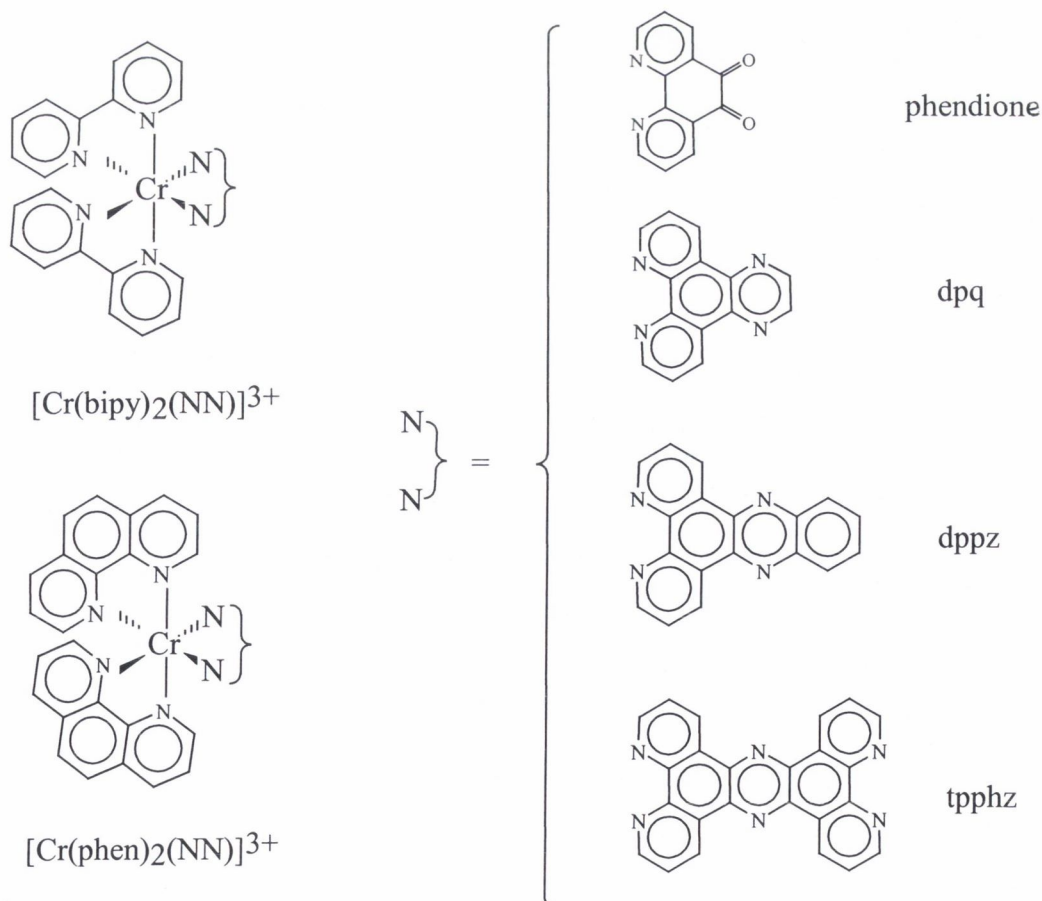


Figure 2.36: Structure of the Cr(III) complexes prepared in this study.

It must be emphasized that, due to the deactivating effect of the tpphz phenazine part, this condensation reaction is significantly slower (> 12 h) than that of *o*-phenyldiamine (only 6 h).

This synthetic route allows the synthesis of monometallic complexes bearing very, or even fully, insoluble ligands without formation of dimetallic species.

All these complexes have been obtained as PF_6^- salts and purified by chromatography using a Sephadex LH-20 column with acetonitrile as eluent. They have been characterized by IR, UV/Vis and elemental analysis. As reported before the ESMS of these compounds showed only fragmentation of the product and no parent ion was found.

UV/Vis absorption spectra

The UV/Vis spectra of the compounds synthesized are reported in Figure 2.37.

The λ_{max} and extinction coefficients of all the complexes are summarized in the table below (Table 2.15). The UV region is dominated by LC π - π^* transitions of the ligands. For the $[\text{Cr}(\text{phen})_2\text{dppz}]^{3+}$ complex a shoulder at 425 nm was assigned by Kane-Maguire¹⁴ to *d-d* transitions ($4A_{2g} \rightarrow 4T_{2g}(\text{Oh})$) while strong intraligand π - π^* absorption bands characteristic of the dppz chromophore are present in the 360-380 nm region. These bands are usually found for the tpphz ligand as well but are shifted to the red when the ligand is tpphz.

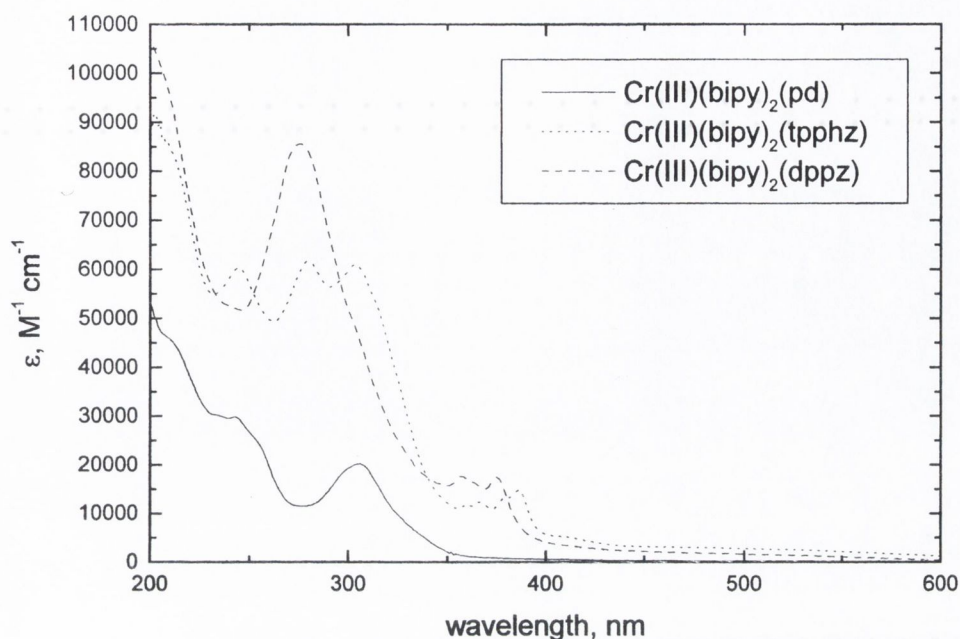


Figure 2.37: UV/Vis spectra of $[\text{Cr(III)(bipy)}_2\text{LL}]$ (where $\text{LL} = \text{phendione, dpq, dppz, tpphz}$) in MeCN

No great difference exists between the spectra of $[\text{Cr(bipy)}_2(\text{LL})]^{3+}$ and $[\text{Cr(phen)}_2(\text{LL})]^{3+}$ complexes. The molar extinction coefficients values are greater for the bis-phen species.

The literature value of $\epsilon_{430} = 1050 \text{ M}^{-1} \text{ cm}^{-1}$ (in water) for the complex, $[\text{Cr(phen)}_2(\text{dppz})]^{3+}$, reported by Kane-Maguire¹⁴ is quite low compared to our result of $2971 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 417 \text{ nm}$. This low value will be explained in one of the next subsections where we compare the absorption spectra of $[\text{Cr(phen)}_2(\text{dppz})]^{3+}$ in different solvents (see pag.122).

Table 2.16: Absorption data of heteroleptic Cr(III)(LL) species where LL = bipy or phen, in MeCN

Compound ^a	λ_{max} , nm (log ϵ , M ⁻¹ cm ⁻¹)
[Cr(bipy) ₂ (phendione)] ³⁺	210 (4.66), 243 (4.46), 305 (4.30), 481 (2.59)
[Cr(phen) ₂ (phendione)] ³⁺	227 (5.03), 257 (4.95), 273 (4.86), 299 (4.49), 311 (4.36), 349 (3.65)
[Cr(bipy) ₂ (dpq)] ³⁺	221 (4.80), 252 (4.94), 299 (4.53), 376 (3.39), 449 (3.13)
[Cr(phen) ₂ (dpq)] ³⁺	229 (5.25), 263 (5.07), 290 (4.56), 307 (4.13), 322 (3.95), 339 (3.70), 388 (3.14), 420 (3.12)
[Cr(bipy) ₂ (dppz)] ³⁺	276 (4.93), 357 (4.24), 363 (4.22), 375 (4.23), 497 (3.31)
[Cr(phen) ₂ (dppz)] ³⁺	202 (5.03), 223 (4.96), 271 (4.99), 347 (4), 356 (4.03), 363 (3.99), 374 (4), 417 (3.47), 499 (3.31)
[Cr(bipy) ₂ (tpphz)] ³⁺	208 (4.93), 244 (4.77), 279 (4.78), 303 (4.78), 358 (4.06), 367 (4.09), 378 (4.11), 381 (4.17), 411 (3.69), 490 (3.44)
[Cr(phen) ₂ (tpphz)] ³⁺	224 (4.82), 272 (4.84), 302 (4.46), 320 (4.17), 348 (3.88), 367 (3.94), 377 (3.93), 388 (4.04), 412 (3.75), 521(sh) (3.46)

^a as PF₆ salts

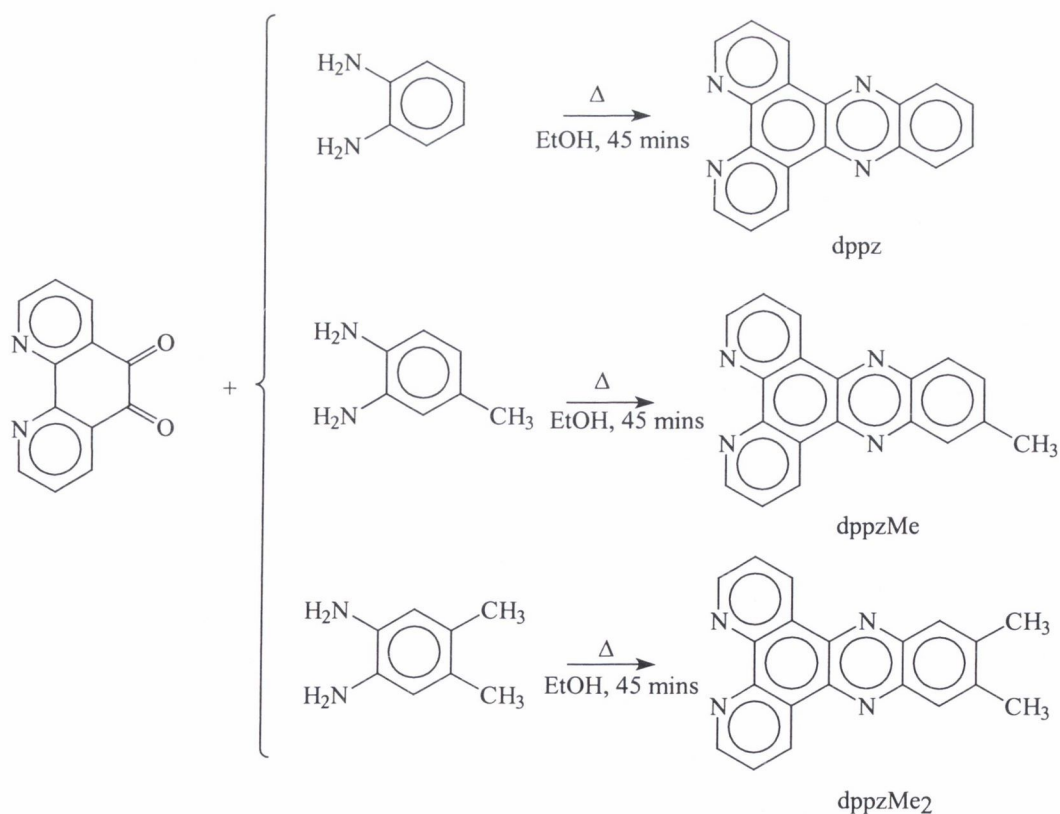
Effect of the substituents on the absorption spectra of the free ligands $dppzR_2$ and $[Cr(LL)_2(dppzR_2)]^{3+}$ (where $LL = bipy$ or $phen$ and $R_1 = R_2 = H$ or Me or $R_1 \neq R_2 = H$ and Me)

For the complexes $[Cr(bipy)_2(dppz)]^{3+}$ and $[Cr(phen)_2(dppz)]^{3+}$ the effect of the methyl groups on the $dppz$ ligand was investigated by observing any changes in the absorption spectra of the free ligands and complexes.

The ligands were prepared by condensation of 1,10-phenanthroline-5,6-dione with the appropriate phenyldiamine:

- (i) 1,2-diaminobenzene;
- (ii) 4-methyl-1, 2-diaminobenzene;
- (iii) 4,5-dimethyl-1, 2-diaminobenzene.

as illustrated in Scheme 2.12 where the orthodiamines are presented from top to bottom.



Scheme 2.12: *Synthesis of the $dppz$ derivatives and the ligand abbreviations*

The UV/Vis absorption spectra for the free ligands, dppz, Medppz and Me₂dppz were measured in CH₃CN and EtOH at room temperature and are presented in Figure 2.38 in the region 300-450 nm. The spectral data for these ligands are summarized in Table 2.17.

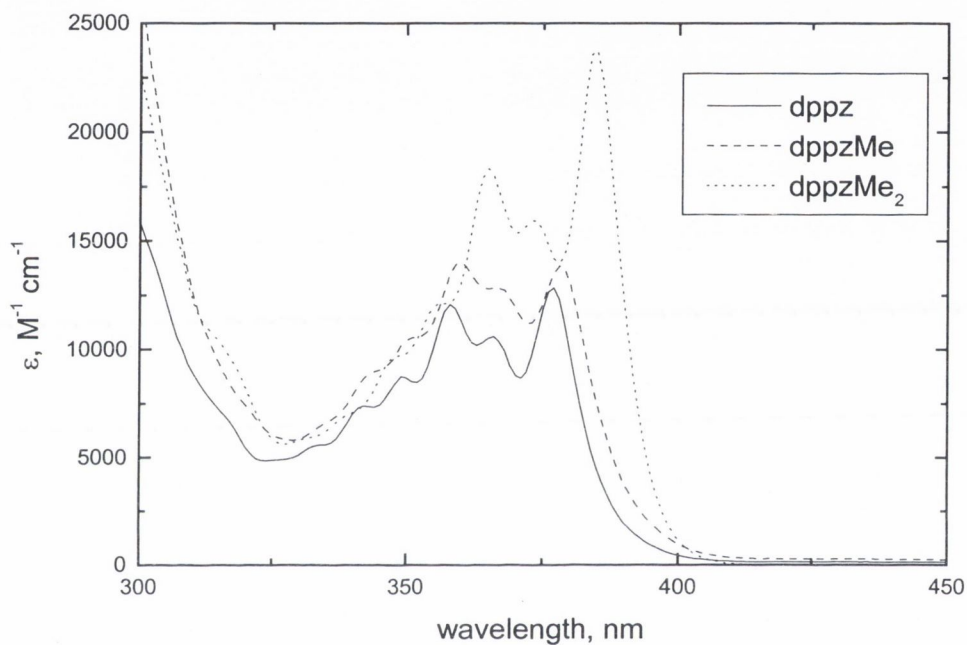
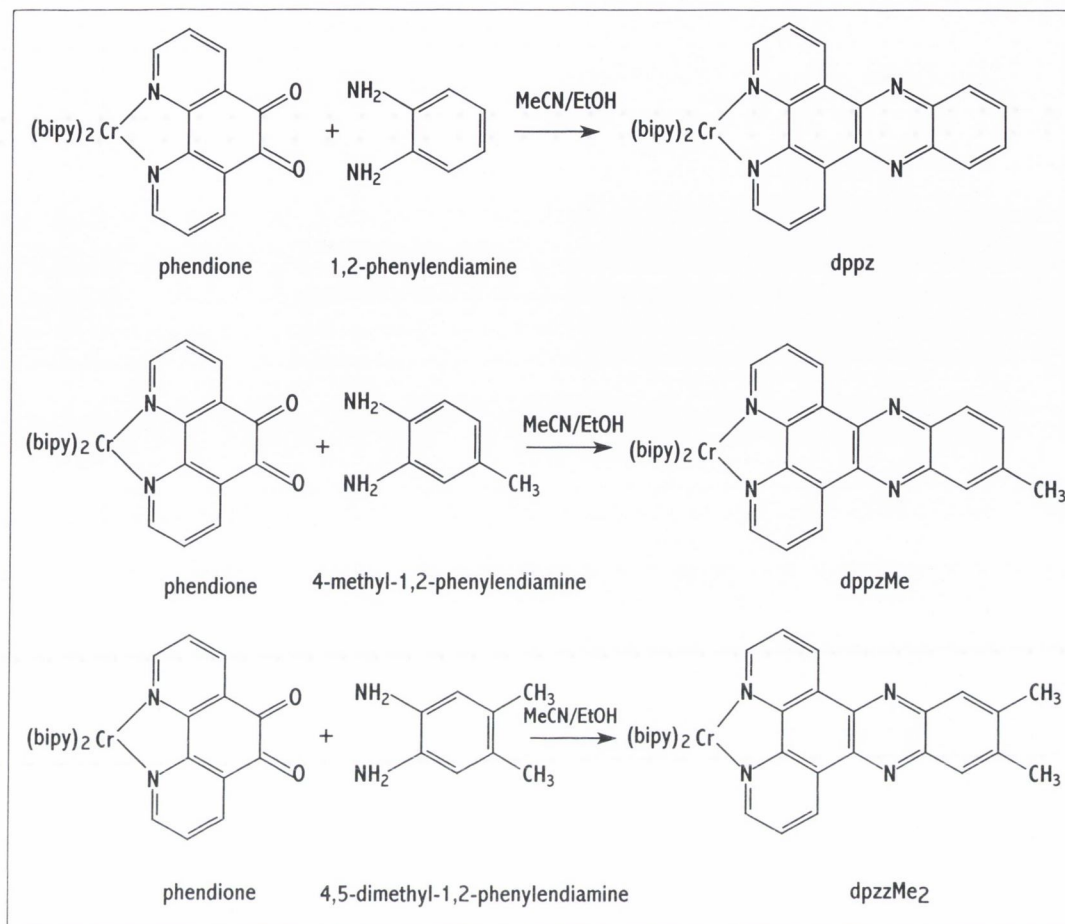


Figure 2.38: UV/Vis spectra of the ligands in EtOH, $C \sim 10^{-4}$ M.

Table 2.17: Absorption spectra of the ligands $dppzR_2$ in MeCN and EtOH.

Ligand	λ_{max} , nm (log ϵ , M ⁻¹ cm ⁻¹),		λ_{max} , nm (log ϵ , M ⁻¹ cm ⁻¹),	
	MeCN		EtOH	
Dppz	210 (4.32), 239 (4.40), 268 (4.68), 291 (4.22), 333 (3.70), 342 (3.82), 349 (3.88), 358 (4.02), 367 (3.95), 377 (4.05)		239 (4.48), 294 (4.3), 333 (3.74), 341 (3.85), 349 (3.93), 357 (4.07), 365 (4.02), 376 (4.10)	
Medppz	213 (4.59), 240 (4.56), 273 (4.76), 297(4.43), 343 (3.90), 350(3.97), 360(4.11), 366 (4.07), 379 (4.11)		239 (4.48), 297 (4.35), 333 (3.80), 342 (3.93), 349 (3.93), 359 (4.14), 367 (4.1), 377 (4.13)	
Me ₂ dppz	Poorly soluble		239 (4.48), 300 (4.36), 338 (3.83), 347 (3.98), 355 (4.08), 364 (4.26), 373 (4.20), 385 (4.37)	

The complexes $[\text{Cr}(\text{bipy})_2(\text{dppzMe})]^{3+}$ and $[\text{Cr}(\text{bipy})_2(\text{dppzMe}_2)]^{3+}$ were synthesized following the method described before for the synthesis of the $[\text{Cr}(\text{bipy})_2\text{dppz}]^{3+}$, but using the 4-methyl-*o*-phenyldiamine and the 4,5-dimethyl-1,2-phenyldiamine in the condensation with the precoordinated complex, $[\text{Cr}(\text{bipy})_2(\text{phendione})](\text{PF}_6)_3$. The reaction scheme (Scheme 2.13) is presented below. The syntheses of the corresponding $[\text{Cr}(\text{phen})_2(\text{dppzR})]^{3+}$ complexes is carried out in the same way.



Scheme 2.13: Synthesis of $[Cr(bipy)_2(LL)]^{3+}$ where $LL = dppz, dppzMe, dpzzMe_2$.

The UV/Vis spectra of the six species are compared in Figures 2.39 and 2.40, while Tables 2.18 and 2.19 list λ_{max} and extinction coefficients of the complexes.

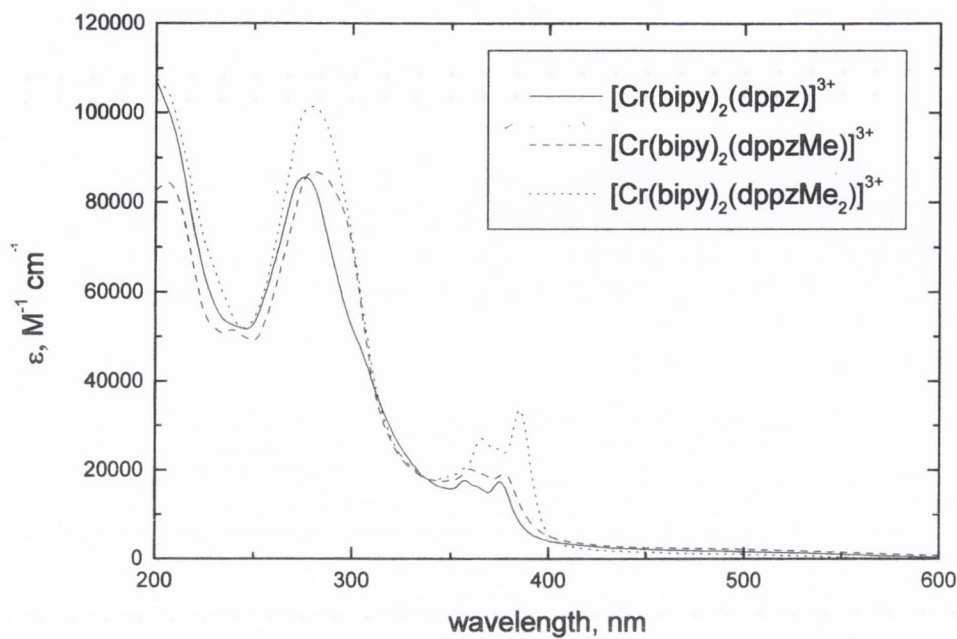


Figure 2.39: Absorption spectra of complexes $[Cr(bipy)_2(dppzR_2)]^{3+}$ as their PF_6 salt in acetonitrile solution at room temperature.

Table 2.18: Spectral data for $[Cr(bipy)_2(dppzR_2)]^{3+}$ in MeCN, $T = 298\text{ K}$.

Compounds	$\lambda_{max}, nm (\log \epsilon, M^l cm^{-l})$						
$[Cr(bipy)_2(dppz)]^{3+}$		276	356	363	374		497
—————		(4.93),	(4.25),	(4.22),	(4.24),		(3.31)
$[Cr(bipy)_2(dppzMe)]^{3+}$	239	280	358	366	377	467	
-----	(4.71)	(4.93)	(4.46)	(4.27)	(4.28)	(3.37)	
$[Cr(bipy)_2(dppzMe_2)]^{3+}$		279	366	374	384		492
.....		(5)	(4.42)	(4.39)	(4.52)		(3.22)

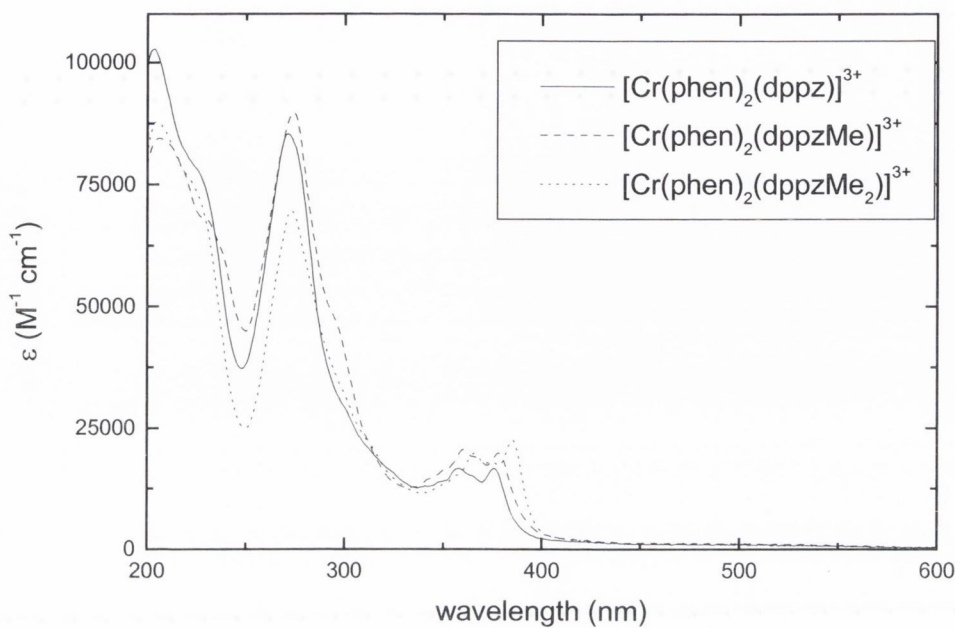


Figure 2.40: Absorption spectra of $[Cr(phen)_2(dppzR_2)]^{3+}$ in MeCN.

Table 2.19: Spectral data for $[Cr(phen)_2(dppzR_2)]^{3+}$ in MeCN, $T= 298\text{ K}$

Compounds	$\lambda_{max}, nm (\log \epsilon, M^{-1} cm^{-1})$
$[Cr(phen)_2(dppz)]^{3+}$	203 (5.01), 227 (4.88), 271 (4.93), 339 (4.11), 347 (4.14), 358 (4.21), 364 (4.18), 376 (4.21), 500 (3)
$[Cr(phen)_2(dppzMe)]^{3+}$	206 (4.92), 229 (4.83), 273 (4.95), 342 (4.12), 351 (4.22), 360 (6.30), 367 (4.27), 378 (4.28), 498 (3.09)
$[Cr(phen)_2(dppzMe_2)]^{3+}$	205 (4.94), 223 (4.87), 273 (4.84), 346 (4.10), 354 (4.16), 366 (4.22), 374 (4.18), 385 (4.31), 500 (3.13)

We observe that the spectra are qualitatively similar. The band at high energy can be assigned to LC bands on the bipy and dppz ligands. Going to lower energies (350- 390 nm) the bands characteristic of the dppz ligand are found (π - π^*). The peak at 377 nm observed in the free dppz ligand has been assigned to the $n \rightarrow \pi^*$ transition of the phenazine (phz) part of the dppz ligand. A shoulder of $d-d$ origin ($^4A_{2g} \rightarrow ^4T_{2g} (Oh)$) is observed above 450 nm.

Comparing the spectra of the three complexes the differences are: a red-shift in the intraligand bands (~ 10 nm) on going from the dppz to the Me_2dppz complex, and a blue shift in the MC transitions. This behaviour has been observed previously for methyl substituents on the phen ligand.² Also it can be observed that the molar extinction coefficients of $[\text{Cr(III)(bipy)}_2(\text{dppzMe}_2)]$ are bigger than the other two complexes.

Effect of the solvents in the absorption spectra of $[\text{Cr(phen)}_2\text{dppz}]^{3+}$

In order to observe any differences induced by the solvent we have analysed the absorption spectra of $[\text{Cr(phen)}_2(\text{dppz})]^{3+}$ in MeCN, MeOH, DMF and phosphate buffer pH= 7.

The spectra are shown in Figure 2.41 in the region 300-500 nm.

The spectrum in phosphate buffer at pH= 7 has the most dramatic effect, losing the characteristic intraligand bands of the dppz. The extinction coefficients decrease in the order $\text{DMF} > \text{MeCN} > \text{MeOH} > \text{buffer}$.

The spectra in buffer and in DMF are red shifted ($\sim 2\text{nm}$) with respect to the two spectra in MeCN and MeOH. The shape of the spectra in water is flat and broad compared to the other three solvents, and this can be maybe attributed to the high polarity, strong H-bonding properties of water.

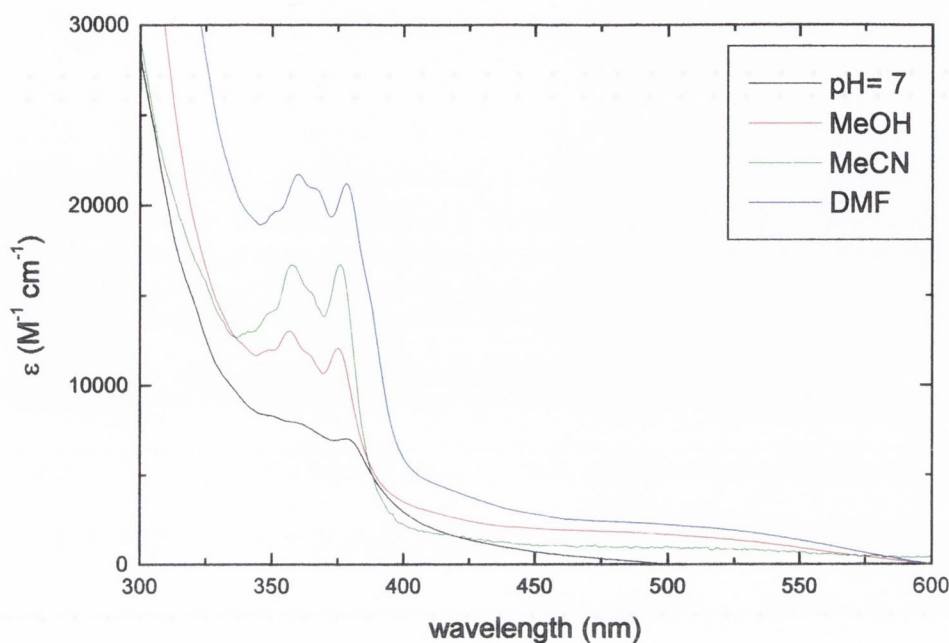


Figure 2.41: Effect of the solvents on the UV/Vis spectra of $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$

2.2.5. Preparation of enantiomerically pure Cr(III) complexes

Cr(III) complexes are configurationally stable and therefore these complexes can be resolved into enantiomers.

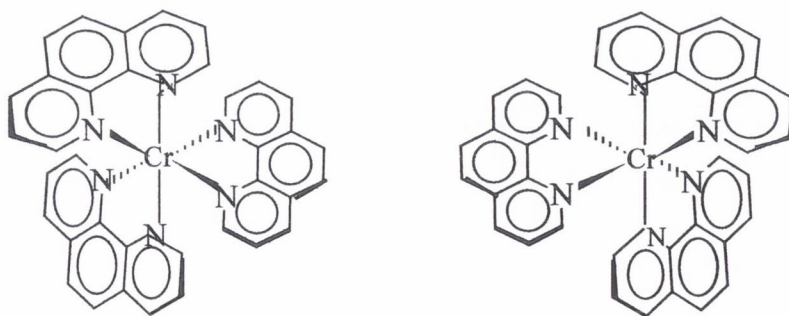


Figure 2.42: Structure of Δ and Λ $[\text{Cr}(\text{phen})_3]^{3+}$ (charges and counterion omitted)

The resolution of $[\text{Cr}(\text{bipy})]^{3+}$ and $[\text{Cr}(\text{phen})]^{3+}$ has been reported previously and utilized the classical method of fractional precipitation with silver-antimonyl d-tartrate or with (+) D-tris(1-cysu)cobaltate(III) (where cysu= cysteinesulfinato(2-)

SN) as the anionic resolving agents. These methods have been reported by Lee *et al.*¹¹, Kane-Maguire *et al.*¹⁶ and Dollimore *et al.*³¹ Two other methods are available for the resolution of tri-polypyridyl complexes and they have been applied mainly to Ru(II) species.

The first, which has been applied successfully by MacDonnell *et al.*^{18,32}, involves the assembly of enantiomerically pure complexes.

The other technique involves absorption on an optically active column, followed by extraction with an optically active solvent.³³

Method used for chiral resolution of Cr(III) complexes

The method described here is a cationic exchange chromatography method developed for the resolution of tris-(bidentate)Ru(II) complexes. This method has been largely used by Keene *et al.*³⁴

The separation of the enantiomers of $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{phen})_3]^{3+}$ was carried out by Dr. Nick Fletcher, Queen's University of Belfast. This method is based on the differential association of the enantiomeric forms with a chiral organic counterion, and discriminates according to (i) charge and (ii) size.

In a typical experiment, the Cr-tris(polypyridyl) complexes were resolved on a column of Sephadex SP C-25 cation exchanger using 0.2 mol dm⁻³/0.09 M(-)-O-O'-dibenzoyl-L-tartrate solution as the eluent, which contained 5% acetone to maintain complex solubility. The column was sealed enabling the complex to be recycled several times down its length with the aid of a peristaltic pump. Two distinct bands were observed after three days. The two bands of the two products, the Δ and Λ enantiomers of both $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{phen})_3]^{3+}$ however could not be precipitated as PF_6^- salt, as usually carried out for the Ru(II) species. This is due to the strong water-like soluble complexes separated. Several counterions have been tried but at the moment none has been successful. Hence the characterization of these enantiomers remains still unresolved.

We hope that the other two complexes $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ and $[\text{Cr}(\text{phen})_2(\text{tpphz})]^{3+}$ which are to be separated in the near future will precipitate more easily because they are bulkier.

2.3. Conclusions

The synthesis and characterization of a wide range of Cr(III) bis- and tris-polypyridyl species have been described. The reactions presented here investigated a wide range of synthetic methodologies and achievements and limitations of each method are presented.

The separation of the enantiomers of $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{phen})_3]^{3+}$ has been achieved with the use of a chiral column. The next step will be the separation of the $\text{Cr}(\text{LL})_2$ -dppz and -tpphz species.

The features seen in the crystal and molecular structures of the complexes studied here can be used to construct models for the binding of DNA that are consistent with chemical and spectroscopic observations (see Chapter 4).

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Chapter 3

Synthesis and characterization of Fe(II), Co(II), Co(III) and Cu(II) tris-polypyridyl complexes

If what one finds is made of pure matter, it will never spoil.

Paulo Coelho, *The Alchemist*

3.1. Introduction

Polypyridine complexes of Fe(II) are highly coloured. The red complexes are widely employed as the redox indicator 'ferroin'.

It is worth noting that addition of phenanthroline to an aqueous solution of Fe(II) leads almost entirely to the formation of the tris-phen complex rather than the mono or bis, even though the Fe is initially in great excess.

Tris-chelated iron(II) complexes have a d^6 electronic configuration. They can form both high-spin and low-spin complexes. Therefore their magnetic moments range from 0 to 5BM. These complexes serve as an example of high-spin/low-spin transitions within the same compound.¹

The absorption spectra of $[\text{Fe}(\text{bipy})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ have been subject to detailed analysis.² While the lowest excited state of Ru(II) is MLCT in character, the lowest excited state of $[\text{Fe}(\text{bipy})_3]^{2+}$ is of ligand field type. $[\text{Fe}(\text{LL})_3]^{2+}$ complexes do not luminesce in absolute ethanol at room temperature or at 80 K. Excited state lifetimes of several Fe(II) polypyridyl complexes have been determined in aqueous solution at room temperature using picosecond transient absorption methods. The excited state lifetime is ligand insensitive.

Unlike ruthenium complexes, there are fewer reports on the synthesis of Fe complexes (II) containing phen and its derivatives, although it has been shown that these complexes can bind to DNA in the same way as their Ru(II) counterparts.^{3,4,5,6,7}

Unfortunately, the interaction of both iron(II) and ruthenium(II) tris-phen complexes with DNA is relatively weak and their binding modes are still controversial.⁸

In order to get a deeper understanding of the interaction of these complexes with DNA we have synthesized tris-chelate complexes of iron(II) containing the dpq, dppz and tpphz ligands, to investigate the effect of the ligand planarity on the interaction with DNA.

Complexes of Fe(II), Co(II), Cu(II) and Co(III) transition metals with phendione ligand have been synthesized because they can be used as building blocks to construct tetranuclear species (Chapter 6). Phendione has been known for many years,^{9,10} it is a quite interesting ligand as it has the ability to form stable complexes with a variety of metal ions.¹¹ It can directly bridge one or two metal centres¹² having a diimine and a catecholate unit. This dual chelating ability was first reported by Balch in 1975.¹³

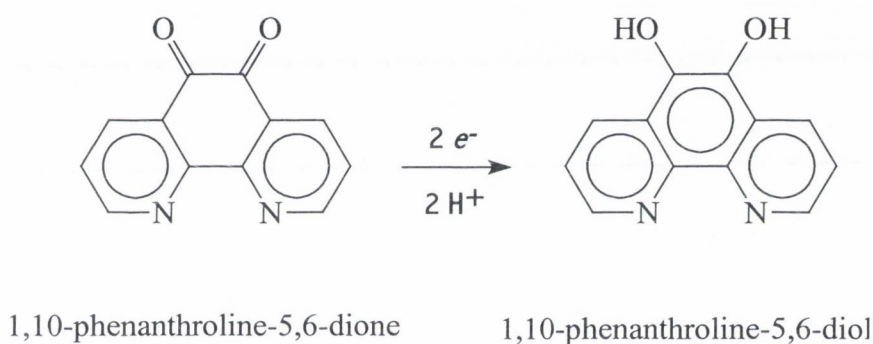


Figure 3.1. Structures of the oxidized and reduced forms of the phenanthroline-dione used in this study.

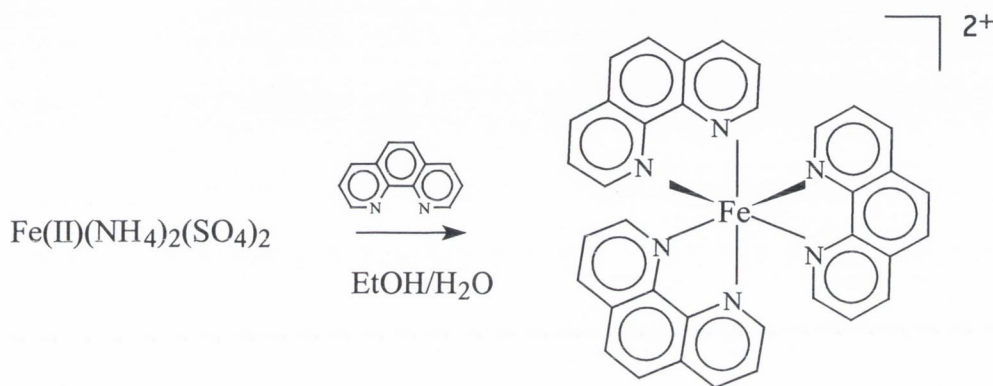
The electrochemical activity of phendione complexes has been investigated.^{6,14,15} Metal complexes of this ligand potentially allow for the variation and control of redox properties over a wide range as well as the fine-tuning of potentials through pH changes.¹⁶

3.2. Results and Discussion

3.2.1. Fe(II) tris-polypyridyl complexes

Synthesis and Purification

The compounds were prepared quite easily by addition of the ligand to a solution of $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$ (Scheme 3.1).



Scheme 3.1: *Synthesis of $[\text{Fe}(\text{phen})_3]^{2+}$ (isolated as PF_6 salt)*

As the solubility of the ligand decreases in the order $\text{phen} \sim \text{phendione} > \text{dpq} > \text{dppz} > \text{tpphz}$, we noticed that better yields were obtained following the method used for the Cr(III) complexes in Scheme 2.5.

The red compounds were usually precipitated as ClO_4^- salt or PF_6^- salt. They were purified by recrystallization from an acetonitrile/ether solution. The $[\text{Fe}(\text{phendione})_3]^{2+}$ was purified by passing through a column of Sephadex LH-20 using MeCN as eluent. Their purity was assessed by ^1H NMR and microanalysis. They were also characterized by UV/Vis and IR. Crystals of $[\text{Fe}(\text{phendione})_3]^{2+}$ and $[\text{Fe}(\text{dpq})_3]^{2+}$ were grown by diffusion of a solution of ether into acetonitrile. The crystal structure of $[\text{Fe}(\text{phendione})_3]^{2+}$ has been solved while the data for the crystal structure of the $[\text{Fe}(\text{dpq})_3]^{2+}$ have not been collected at the time of writing.

UV/Vis spectra of Fe(II) tris-polypyridyl family

The absorption spectra of the compounds synthesized are presented in Figure 3.2 and the results are summarized in Table 3.1.

The UV region of the spectra is characterized by ligand localized π to π^* transitions (ILT). The same transitions are usually found for the free ligands, but upon coordination these bands are usually shifted to longer wavelengths by at least 5 nm.

The intense visible absorption band of the iron(II) complexes in the region 375-600 nm region is mainly due to a metal-to-ligand charge transfer (MLCT) transition involving the promotion of electrons from the filled d orbital of the iron to the vacant π^* orbital of the ligand ($d-\pi^*$). The λ_{max} of the complexes in the visible region gives rise to a regular red shift (*ca* 5-7 nm) as the aromatic system becomes more extended except for the tris(phendione) complex where there is a blue shift in the maximum wavelength of absorption. In fact it has a maximum absorption at 472 nm as compared to the tris(phenanthroline) complex, whose wavelength of maximum absorption is 508 nm. This effect essentially reflects the enhanced π acidity of the phendione ligand relative to that of the phenanthroline and the other ligands.

The intensity of the bands, as indicated by the value of its extinction coefficient (ϵ), is almost the same for all the complexes.

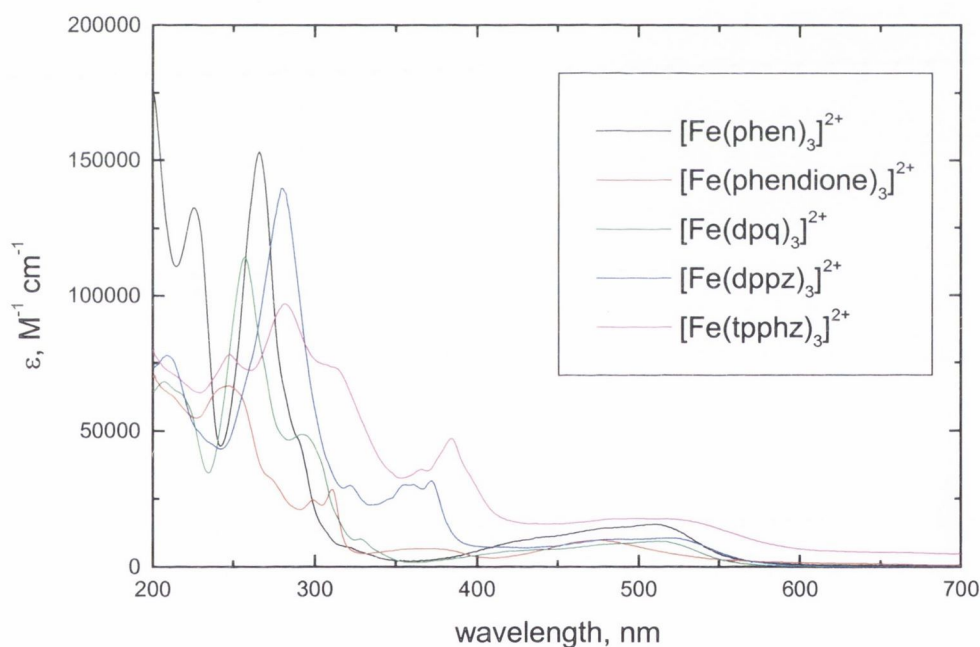


Figure 3.2: Absorption Spectra of $[\text{Fe}(\text{LL})_3]^{2+}$ where $\text{LL} = \text{phen}, \text{phendione}, \text{dpq}, \text{dppz}$ and tpphz .

Table 3.1: Spectroscopic data of Fe(II) complexes in MeCN.

Complex	λ_{max} , nm ($\log \epsilon$, $M^{-1} cm^{-1}$)	λ_{max} , nm ($\log \epsilon$, $M^{-1} cm^{-1}$)
$[Fe(phen)_3]^{2+}$	225 (4.19), 265 (5.18), 290 (4.67), 423 (3.97), 472 (4.12), 508 (4.18)	^a 268, 510 (4.07)
$[Fe(phendione)_3]^{2+}$	246 (4.82), 272 (4.51), 297 (4.38), 310 (4.44), 367 (3.83), 472 (3.98)	^b 252 (4.88), 300 (4.37), 312 (4.42), 368 (3.88), 472 (3.97)
$[Fe(dpq)_3]^{2+}$	207 (4.83), 256 (5.05), 292 (4.68), 329 (4.01), 424 (3.77), 476 (3.91), 513 (3.98)	
$[Fe(dppz)_3]^{2+}$	208 (4.88), 280 (5.14), 321 (4.47), 357 (4.48), 371 (4.49), 481 (4), 520 (4.02)	
$[Fe(tpphz)_3]^{2+}$	248(5.19), 281 (5.28), 312 (5.16), 363 (4.85), 383 (4.97), 500 (4.54)	

^a from Mudasir *et al*, *Transition Metal Chem.*, 1999, 24, 210-217 ; ^b Goss, C., Abruna, H.D., *Inorg.Chem.*, 1985, 24, 4263

Vibrational spectra

In general the IR spectra of the iron(II) tris-polypyridyl complexes are similar and there are no major differences in their vibrational frequencies. The results are not surprising as they have the same valence and the same number of coordinated ligands. However, more detailed examination shows that the spectra of iron(II) can be easily distinguished from those of the free ligands thus providing a satisfactory method for identifying them.

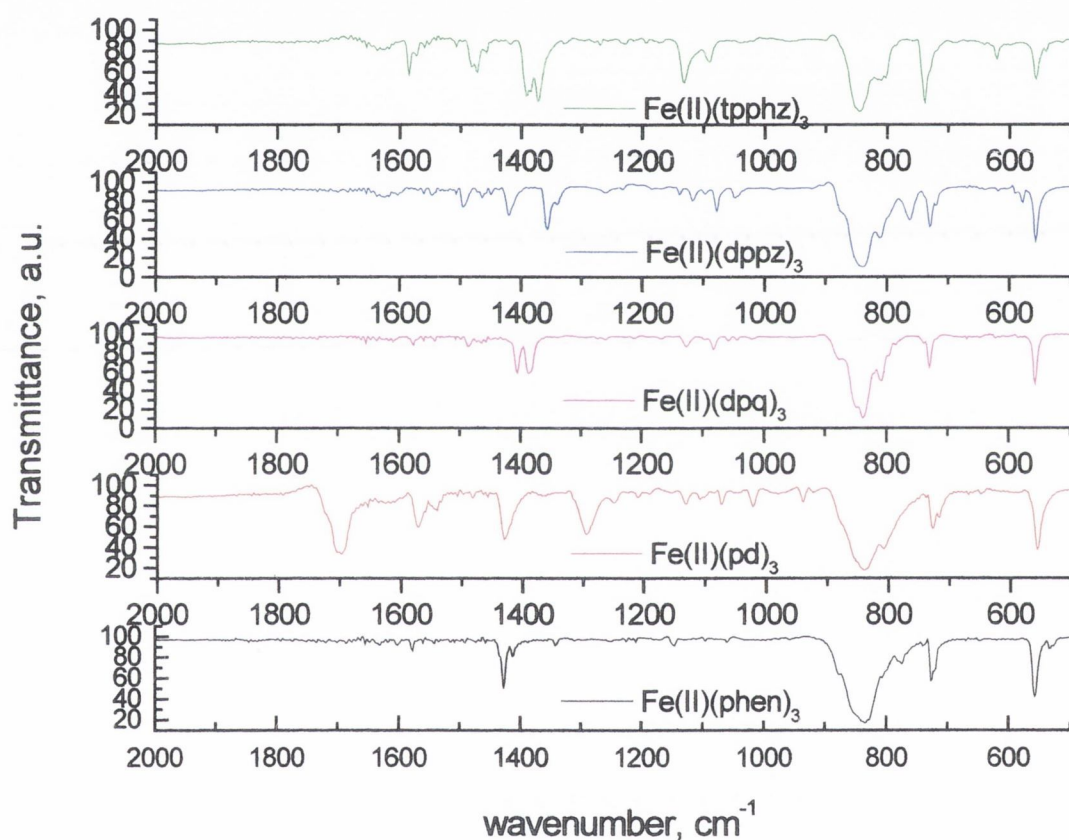


Figure 3.3: IR spectra of *Fe(II)* tris-polypyridyl complexes in *KBr*.

In general, the spectra of the tris-complexes are simpler than those of the free ligands especially in the 600-900 cm^{-1} region, which is associated with the ring deformation of the ligands.^{17,18,19} Hexafluorophosphate bands which appear at *ca.* 846 cm^{-1} belong to an ionic species²⁰. This means that the hexafluorophosphate ion is not involved in the metal to ligand coordination and only acts as a counter ion. The 1400-1650 cm^{-1} region which is concerned with the ring modes (ν_{CC} and ν_{CN}), consists of three

three rather less intense bands; one close to 1510 cm^{-1} , the second in the neighbourhood of 1600 cm^{-1} and the third at ca 1420 cm^{-1} . The region $500\text{-}900\text{ cm}^{-1}$ exhibits two intense bands at ca. 725 cm^{-1} and at ca. 845 cm^{-1} assigned to the out-of-plane motion of the hydrogen atoms on the heterocyclic rings (the latter is buried under the more intense band of the PF_6^-).

The bands associated with the carbonyl stretch are the most relevant. By comparison of the spectra of the metal complexes with those of phendione and phenanthroline, it was determined that the bands centered at about 1700 and 1300 cm^{-1} are carbonyl stretches on the phendione ligand. It must be emphasized that the carbonyl band at 1685 cm^{-1} of the free phendione, moves to 1700 cm^{-1} upon coordination. In general, the carbonyl stretches are relatively insensitive to changes in the metal centre and the coordination environment has only a secondary effect on the carbonyl stretch.

On going from the IR spectra of phendione to those of dpq, and dppz, the most striking effect is the loss of the strong band at 1700 cm^{-1} , indicating that the reaction was successful.

^1H NMR spectra

The ^1H NMR data of the iron(II) complexes in MeCN-d_3 are presented in Table 3.2 together with those of their corresponding free ligands for comparison.

The spectra of both free ligands and tris-complexes exhibit three, four or five distinct resonance patterns owing to the symmetrical structure of the molecules. The assignment of the various peaks to the proton is either straightforward or analogous to those of ruthenium complexes which have been extensively studied. The multiplet structure arises entirely from ^1H - ^1H couplings. The exact appearance of each multiplet is determined by the magnitudes of the coupling constants which are $J_{\text{ortho}} > J_{\text{meta}} > J_{\text{para}}$.

For the $[\text{Fe}(\text{phen})_3]^{2+}$ a AMX spin system can be assigned to the H_a , H_b and H_c protons. Therefore the splitting consists of two doublets, H_a and H_c , and one doublet of doublets, H_b , with coupling constants of $8.65(J_{\text{H}_a\text{H}_b})$, 8.03 and $5.28(J_{\text{H}_a\text{H}_b}, J_{\text{H}_b\text{H}_c})$ and $5.02(J_{\text{H}_b\text{H}_c})$ Hz respectively. Also one singlet is present and is assigned to the proton H_d . The same spin system AMX is also found for $[\text{Fe}(\text{pd})_3]^{2+}$ and the other two following complexes, $[\text{Fe}(\text{dpq})_3]^{2+}$ and $[\text{Fe}(\text{dppz})_3]^{2+}$. The splitting consists of one doublet of doublets and two doublets ($J_{\text{meta}} \ll J_{\text{ortho}}$). A singlet is present for the $[\text{Fe}(\text{dpq})_3]^{2+}$ and an AX spin system which gives rise to two doublets is present in the $[\text{Fe}(\text{dppz})_3]^{2+}$.

A general chemical shift (δ) downfield in the protons occurs upon chelation of the ligand to iron(II) ion except for the H_a protons. This deshielding effect can be attributed to a decrease in electron density at the individual carbon nuclei as a result of the interaction with the positive iron(II) ion. Unlike the other protons, the H_a protons show a dramatic upfield shift upon chelation of the ligand to the Fe(II). The magnitude of the upfield shift is between 0.49 ppm in the phen, and 1.56 ppm in the dpq. These protons lie within the shielding cone of the heterocyclic ring of the adjacent ligand. This is called the diamagnetic anisotropic effect of the aromatic ring of the adjacent ligand. Furthermore, upon coordination of the ligands to the iron(II) ion, the electron density of the aromatic rings is reduced. The protons in close proximity to the N-coordination sites are most affected.

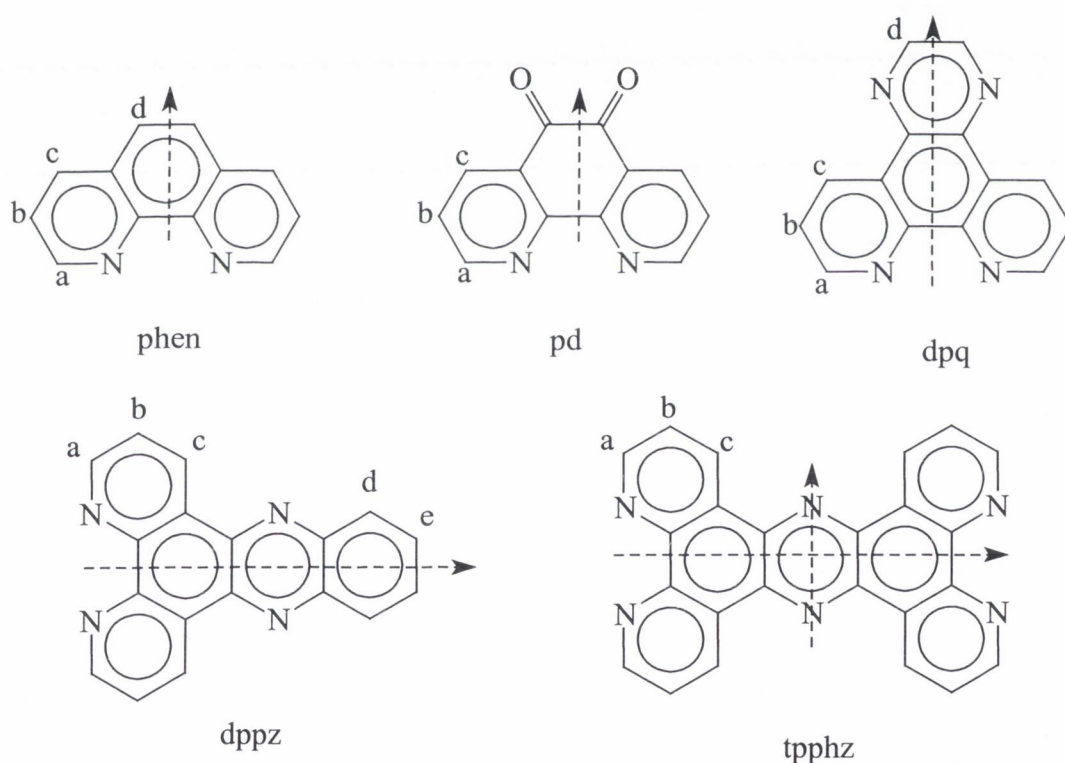


Figure 3.4: Structures of the ligands with their abbreviations and the proton assignments.

Table 3.2: ^1H NMR Chemical shift (δ_{H} , ppm), 400 MHz, MeCN- d_3 , SiMe $_4$.

Compounds	Ha	Hb	Hc	Hd	He
<i>phen</i>	9.13 (2H, dd)	7.80 (2H, m)	8.52 (2H, dd)	8.02 (2H, s)	
<i>pd</i>	8.52 (2H, dd)	7.60 (2H, dd)	9.13 (2H, dd)		
<i>dpq</i>	9.50 (2H, d)	7.81 (2H, dd)	9.30 (2H, d)	8.99 (2H, s)	
<i>dppz</i>	9.29 (2H, dd)	7.82 (2H, dd)	9.68 (2H, dd)	7.95 (2H, dd)	8.35 (2H, m)
<i>tpphz</i>	9.68 (4H, dd)	7.86, (4H, dd),	9.36 (4H, dd)		
$[\text{Fe}(\text{phen})_3]^{2+}$	8.64 (6H, d)	7.62 (6H, dd)	7.68, (6H, d)	8.29 (6H, s)	
$[\text{Fe}(\text{pd})_3]^{2+}$	7.82 (6H, d)	7.72 (6H, dd)	8.65 (6H, d)		
$[\text{Fe}(\text{dpq})_3]^{2+}$	7.94 (6H, d)	7.80 (6H, dd)	9.57 (6H, d)	9.24 (6H, s)	
$[\text{Fe}(\text{dppz})_3]^{2+}$	8.00 (6H, d)	7.86 (6H, dd)	9.74 (6H, d)	8.52 (6H, dd)	8.18 (6H, dd)
$[\text{Fe}(\text{tpphz})_3]^{2+}$	Not soluble				

3.2.2. $[M(\text{phendione})_3]^{n+}$ complexes: building blocks for supramolecular species

Synthesis and purification

The synthesis of a series of phendione compounds has been carried out following published procedures with transition metal centres of the first-row: Fe, Co, Cu.¹¹ In the case of Co(III), an inert complex like Cr(III), we cannot add the phendione directly to the Co(II) and oxidize it to Co(III) using $\text{H}_2\text{O}_2/\text{HCl}$ as oxidising agent, as described for $[\text{Co}(\text{phen})_3]^{3+}$ previously by Lee *et al*.²¹ The Co(III) phendione was produced by the method of Gillard and Hill²² starting from a preformed Co(III)phen and oxidising the ligand with a sulfuric/nitric mixture in presence of NaBr as catalyst. All the complexes were precipitated as PF_6^- salt. The complexes were characterized by UV/Vis, IR, NMR and microanalysis. The X-ray single crystal structures of these complexes were determined. The most interesting result is that the Cu(II) is tris-chelated whereas Goss reported a bis-chelated complex.¹¹

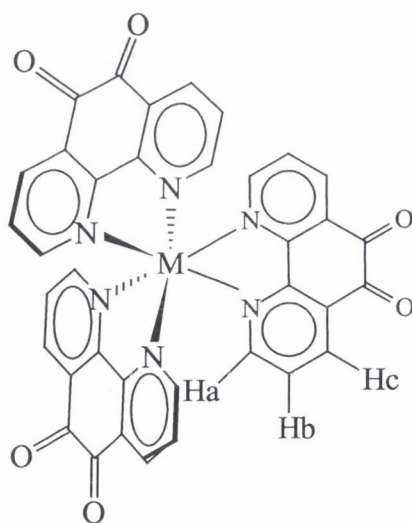


Figure 3.5: Structure of $[M(\text{phendione})_3]^{n+}$ complex

UV/Vis spectra

The UV/Vis spectra of the compounds synthesized are reported in Figure 3.6 and the results are summarized in Table 3.3. $[\text{Cr}(\text{phendione})_3]^{3+}$ and $[\text{Ru}(\text{phendione})_3]^{2+}$ are reported for comparison. The spectra are all qualitatively and quantitatively similar below 370 nm. The UV/Vis spectra are dominated by $\pi-\pi^*$ transitions at about 250 nm. The lowest energy band peaks at around 300-310 nm are typical of a carbonyl group. These bands are of lower intensities and are due to $n-\pi^*$ transitions, symmetry

forbidden, and are caused by excitation of an oxygen lone-pair electron to the antibonding π -orbital of the carbonyl group. Above 400 nm the MLCT bands can be found for the ruthenium and the iron species.

Table 3.3: Spectral data for tris-phendione complexes, $C \sim 10^{-5} M$, in MeCN

Complex	$\lambda_{max}, nm (log \epsilon, M^l cm^{-l})$	$\lambda_{max}, nm (log \epsilon, M^l cm^{-l})$
phendione	234 (4.06), 255 (4), 292 (3.56), 361 (2.31)	256 (4.60), 292 (3.65), 370 (2.71) ^b
[Cr(phendione) ₃] ³⁺	209 (4.78), 248 (4.89), 302 (4.41), 287 (4.48), 305 (4.52), 316 (4.51), 475 (2)	
[Ru(phendione) ₃] ²⁺	252 (4.71), 270 (3.69), 368 (4.12), 428 (4.01)	245(4.86), 295 (4.50), 305 (4.54), 344 (4.10), 550 (3.41) ^a
[Fe(phendione) ₃] ²⁺	246 (4.82), 272 (4.51), 297 (4.38), 310 (4.45), 367 (3.83), 472 (3.98)	252(4.88), 300(4.37), 312(4.46), 368(3.88), 472 (3.97) ^b
[Cu(phendione) ₃] ²⁺	250 (4.91), 301(4.33), 313 (4.30), 350 (4.91)	734 (2.20) ^{b, c}
[Co(phendione) ₃] ²⁺	249 (5.95), 300 (4.42), 309 (4.41)	254 (4.96), 300 (4.33), 312 (4.32) ^b

^a from MacDonnell *et al*, *Inorg. Chim. Acta*, 1999, 293, 37-43; ^b from Goss, C., Abruna, H.D., *Inorg.Chem.*, 1985, 24, 4263; ^cfor [Cu(phendione)₂]²⁺

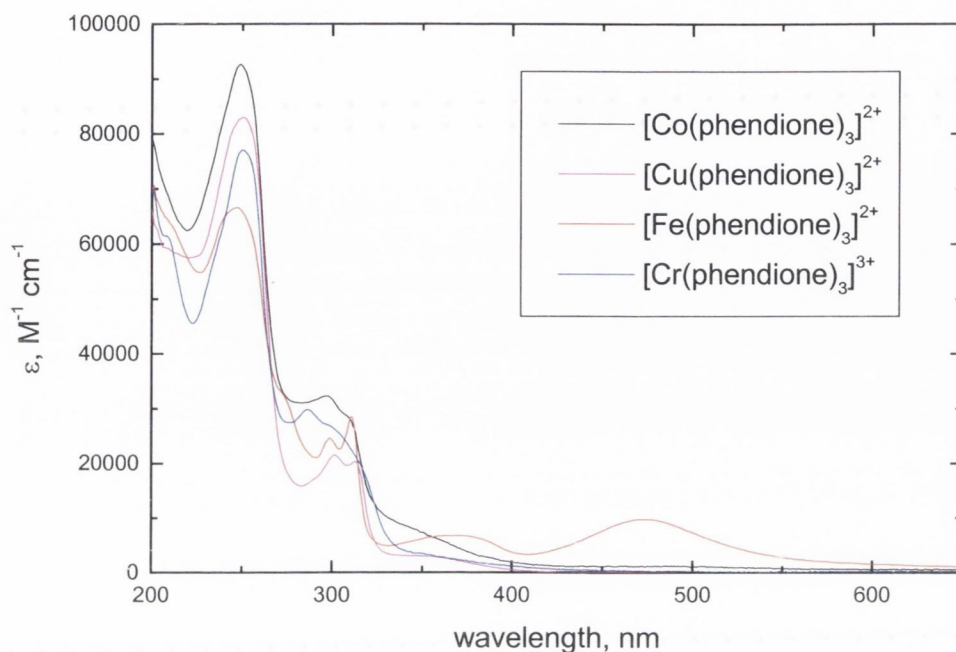


Figure 3.6: UV/Vis spectra of tris-phendione complexes.

¹H NMR spectra

The ¹H NMR of [Fe(phendione)₃]²⁺, [Co(phendione)₃]³⁺ and [Cr(phendione)₃]³⁺ were compared to check for difference in the chemical shift due to the metal centre.

[Ru(phendione)₃]²⁺ values of chemical shifts are reported for comparison.²³

[Cu(phendione)₃]²⁺ and [Co(phendione)₃]²⁺ show quite a broad NMR.

Table 3.4: ¹H NMR shift of [M(phendione)₃]³⁺ complexes in MeCN-d

Complex	Ha	Hb	Hc
[Ru(pd) ₃] ²⁺	8.51(d)	7.71 (dd)	9.03(d)
[Fe(pd) ₃] ²⁺	7.82(d)	7.72(dd)	8.66(d)
[Co(pd) ₃] ³⁺	7.66(d)	8.13(dd)	9.01(d)
[Cr(pd) ₃] ³⁺	10.27(d)	9.54(dd)	10.47(d)

The splitting consists of one double doublet and two doublets. The proton assignment is reported in Figure 3.4. The most noticeable effect is the isotropic shift downfield of the protons on the Cr(III) complex compared to those on other complexes. This effect has been examined earlier.^{24,25,26}

During the development of nuclear magnetic resonance as a spectroscopic tool for structure determination, attempts to observe the nmr spectra of paramagnetic species in solution under high-resolution conditions were occasionally unsuccessful, or at best gave broad featureless signals whose line widths rather than chemical shifts were the important characteristics. Such observations were no doubt responsible for numerous cases in the literature in which the nmr spectra of metal complexes were not recorded for the reason, stated or implied, that the complexes were paramagnetic. The proton resonance spectra of several paramagnetic complexes in solution have been reported.²⁷ The spectra of these complexes revealed the isotropic shift phenomenon in the form of large displacements of resonance frequencies upfield and downfield from their nominal diamagnetic positions, with retention of narrow line widths. For proton signals at ambient temperature these displacements, ie isotropic shifts, cover in some cases a 310 ppm range, from -170 (downfield) to +140 ppm (upfield). Well resolved spectra are obtained only in those cases in which the electronic relaxation times are very short. The nmr spectra of complexes containing Mn(II), Fe(III) (sextet), Cu(II) whose relaxation times are relatively long, are in general very poorly resolved or undetectable. Conversely, the spectra of complexes derived from V(III), Cr(II), and Ni(II) are in general well resolved.^{26, 27}

Analysis of X-Ray crystallographic data for the complexes $[M(\text{phendione})_3]^{2+}$ where $M = \text{Fe(II)}, \text{Co(II)}$ and Cu(II) .

Single crystals of the three complexes were grown by diffusion of ether in acetonitrile solutions. The crystal structures of the three complexes, $[\text{Fe}(\text{phendione})_3]^{2+}$, $[\text{Co}(\text{phendione})_3]^{2+}$ and $[\text{Cu}(\text{phendione})_3]^{2+}$ have been determined and are shown in Figures 3.7-3.9. The author gratefully acknowledges the assistance of Dr. Phil Mackie in the purification and crystallization of $[\text{Fe}(\text{phendione})_3](\text{PF}_6)_2$. Each complex crystallizes with hexafluorophosphate as counterion. The structures consist of a central metal atom with three phendione ligands arranged in distorted octahedral symmetry. All three structures crystallized in a monoclinic P2(1) space group with two molecules in the asymmetric unit. In fact the unit cell consists of only one of the enantiomers, this being a chiral space group. This result is interesting because it is an example of chiral resolution by crystallography. Although H-bonding is observed between the oxygens of the phendione and the solvents, the disorder of the solvents molecules makes discussion of this inappropriate.

In the case of the $[\text{Fe}(\text{phendione})_3]^{2+}$ the structure was refined with a final R1 value of 0.0883. The anions and solvent molecules were refined isotropically.

The structure for $[\text{Co}(\text{phendione})_3]^{2+}$ was refined with a final R1 value of 0.0726. The anions and solvent molecules are highly disordered. There was partial occupancy of some of the solvent molecules. Subsequent to the submission of this thesis crystallographic data on the same compound but as its perchlorate salt has been published. In this case the compound crystallizes in an orthorhombic space group whereas we obtained a monoclinic space group. Maybe the counterion has a significant influence on crystal packing. Each of the hexafluorophosphate anions centered on P1 and P2 are slightly rotationally disordered over two positions such that the phosphorous atoms are coincident to each. The disorder in each case has been modelled at 36:64 occupancy. The acetonitrile molecule centred on C9 is disordered over two positions and has been modelled at 42:58 occupancy.

The structure for $[\text{Cu}(\text{phendione})_3]^{2+}$ was refined with a final R1 value of 0.0958. The geometry about the Cu(II) centre is distorted because of Jahn-Teller effects. The Cu---N1C and Cu---N12A bonds are over 0.04 Å longer than the other metal-nitrogen bonds. Subsequent to the submission of this thesis the same compound has been crystallized at room temperature, crystallographic data indicates that the compound crystallize in an orthorhombic $P2(1)2(1)2(1)$ (chiral) space group. The counterion is different but the number of acetonitrile molecules is identical in this thesis with that of the literature.²⁸

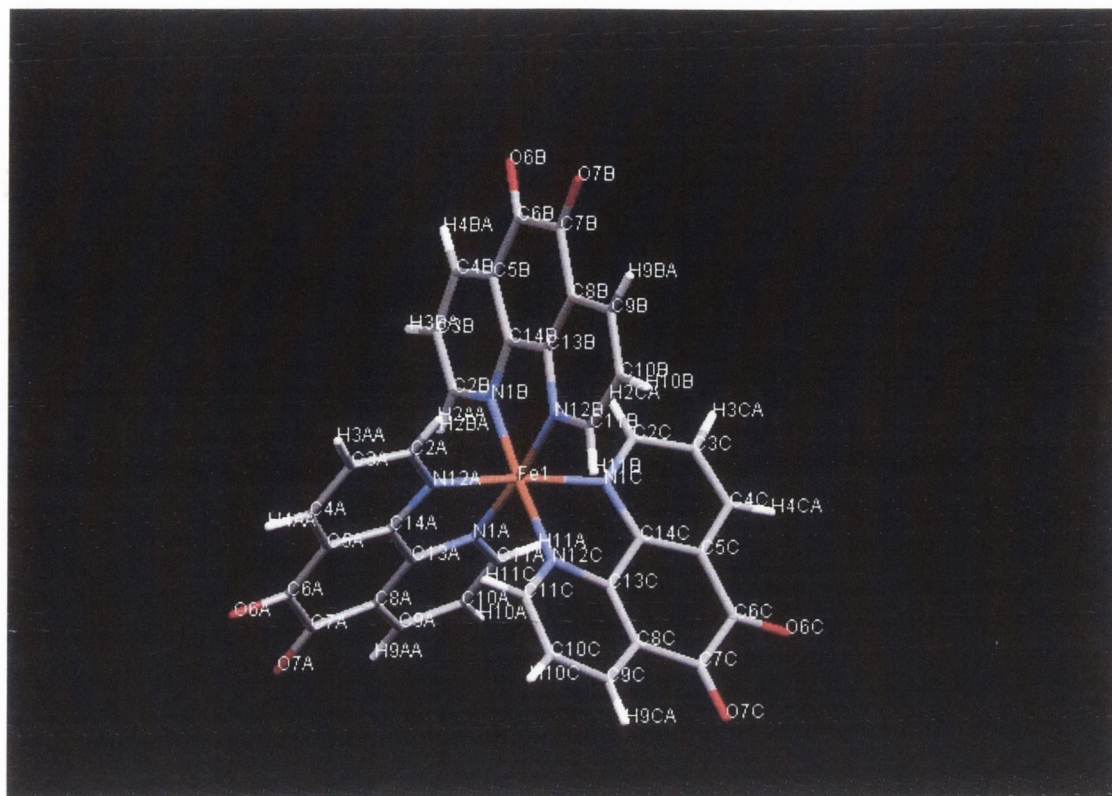


Figure 3.7: X-ray crystal structure of $[\text{Fe}(\text{phendione})_3](\text{PF}_6)_2 \cdot 3\text{MeCN}$ (counterion and solvent molecules omitted for clarity).

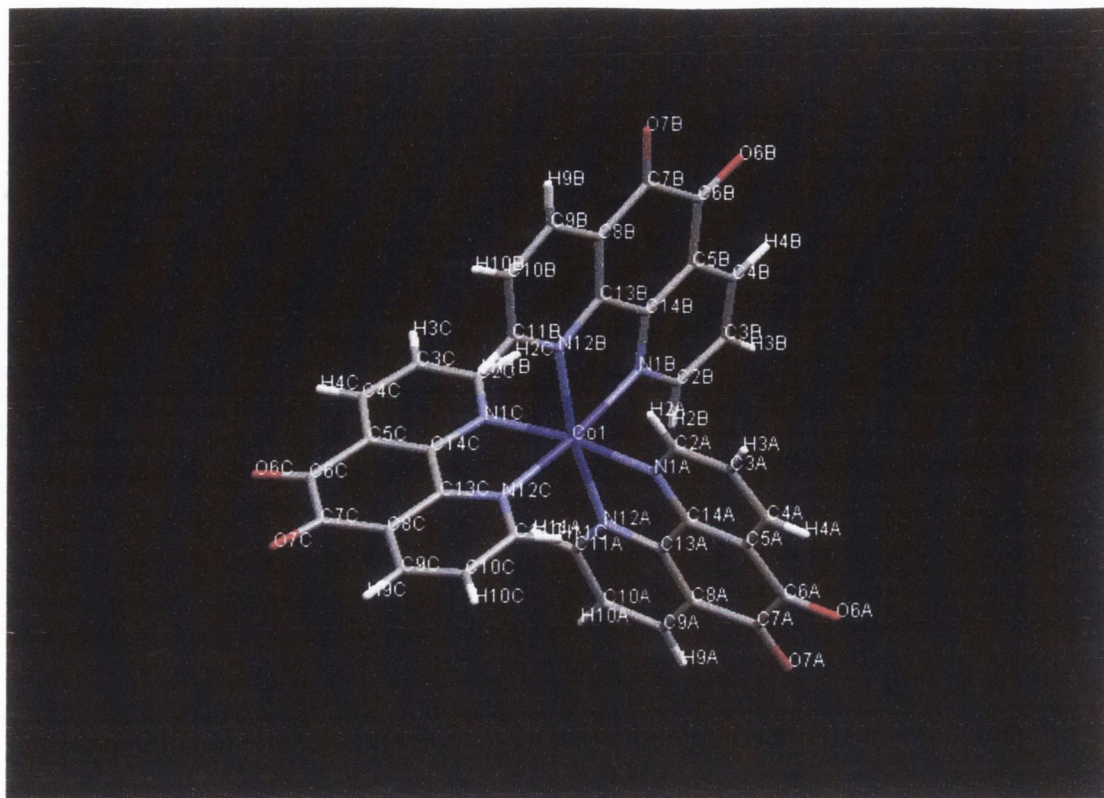


Figure 3.8: X-ray crystal structure of $[\text{Co}(\text{phendione})_3](\text{PF}_6)_2 \cdot 3\text{MeCN}$ (counterion and solvent molecules omitted for clarity).

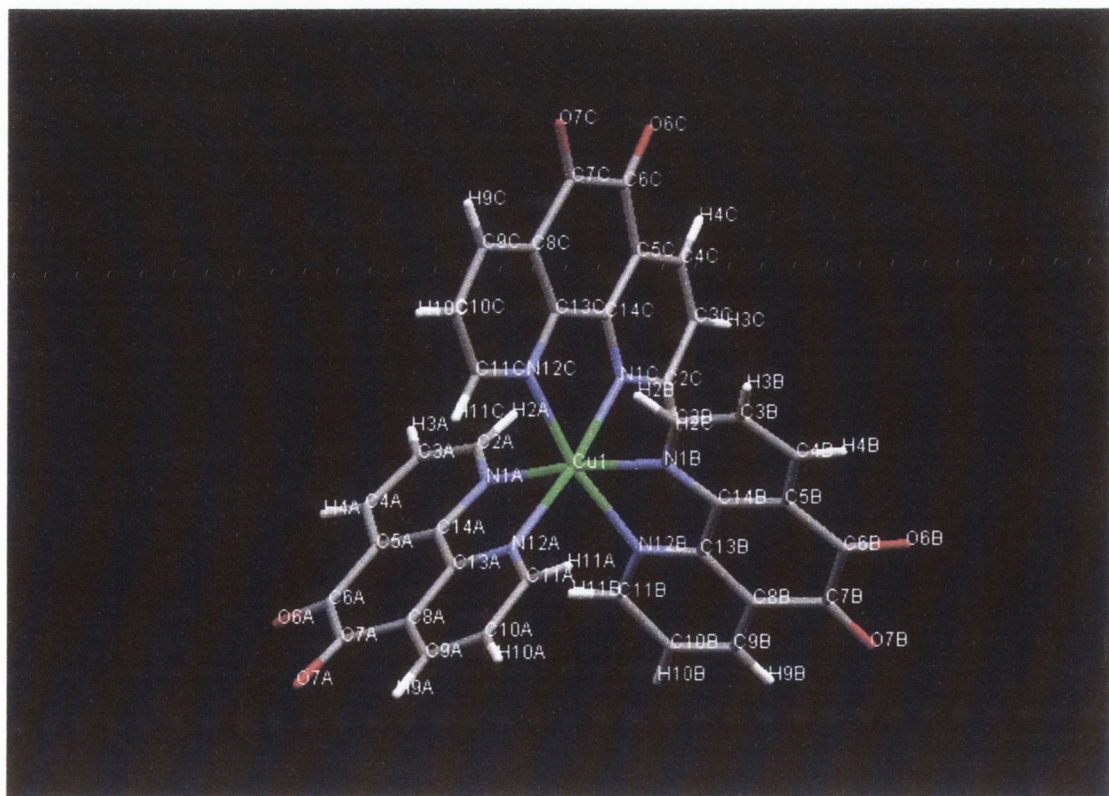


Figure 3.9: X-Ray crystal structure of $[\text{Cu}(\text{phendione})_3](\text{PF}_6)_2 \cdot 2\text{MeCN}$ (counterion and solvent molecules omitted for clarity).

Significant bond lengths and bond angles for the three complexes are listed below in Tables 3.5 and 3.6.

Table 3.5: Selected bond lengths (Å) for the three complexes

Bonds	[Fe(phendione) ₃](PF ₆) ₃	[Co(phendione) ₃](PF ₆) ₃	[Cu(phendione) ₃](PF ₆) ₃
M-N1A	1.968(8)	2.128(4)	2.079(8)
M-N1B	1.951(8)	2.142(4)	2.104(8)
M-N1C	1.979(8)	2.128(4)	2.196(8)
M-N12A	1.966(8)	2.122(3)	2.204(8)
M-N12B	1.965(8)	2.155(3)	2.162(6)
M-N12C	2.006(8)	2.119(4)	2.107(7)

A comparison of the iron and cobalt set of data shows that the average bond lengths increase going from Fe to Co. We would have expected instead that bond lengths to increase in the order Co(II) (d^7)< Fe(II) (d^6) on the bases of the ionic radius. Assuming the magnetic susceptibility data obtained for these compounds (pag.245 and 247) are correct then the fact that Fe(II) has the shortest bond length can be explained on the grounds that it is in a low-spin configuration and thus with its t_{2g} orbital completely filled it shows a decrease in the bond lengths, while the Co(II) is in a high-spin configuration ($t^5_{2g} e^2_g$) and because the e_g orbitals have anti-bonding character this will cause an increase in the bond lengths .

Table 3.6: Selected bond angles (°) for the three complexes

Bonds	[Fe(phendione) ₃] ²⁺	[Co(phendione) ₃] ²⁺	[Cu(phendione) ₃] ²⁺
N1A-M-N12A	82.5(3)	77.63(16)	78.7(3)
N1B-M-N12B	82.0(3)	77.81(14)	76.6(3)
N1C-M-N12C	82.7(3)	76.58(14)	76.4(3)

3.3. Conclusions

In this chapter Fe(II) complexes with phen, dpq and dppz ligands have been prepared and characterized. Phendione complexes with Fe(II), Co(II) and Cu(II) have been prepared and their crystal structures determined. These complexes will be analyzed in Chapter 4 as DNA probes, while the tris-phendione species will act as building blocks to construct dendritic species (Chapter 5).

3.4. References

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Chapter 4

Spectroscopic studies of Cr(III) and Fe(II) polypyridyl complexes in absence and in presence of DNA

“...the most beautiful X-ray photograph of any substance ever taken..”

J.D. Bernal, *Nature*, 1958, 182, 154

4.1. Introduction

The role of metal ions in the structure, stability and reactivity of double-helical DNA is well documented and it has been recognised that nucleic acids in general could not exercise their biological functions without the participation of metal ions that are involved in replication, transcription and translation processes. These facts have stimulated extensive research on the interactions between metal ions and complexes with nucleic acids.^{1,2} Important research now centres on the development of transition metal complexes for use in medicine and in biological applications, i.e., as spectroscopic probes, artificial nuclease, chemotherapeutic agents etc.³

We saw before that transition metal complexes can interact with DNA by intercalation, groove binding, or external electrostatic binding (“outer-sphere” interactions) as well as by direct coordination to nucleic acids.^{4,5,6}



Figure 4.1: Computer generated model of the binding of ruthenium complexes to B-DNA. $[Ru(bipy)_3]^{2+}$ (green) represents simple electrostatic binding to the helix,; $\Delta-[Ru(phen)_3]^{2+}$ (yellow) is shown intercalating from the major groove and $\Lambda-[Ru(phen)_3]^{2+}$ (red) illustrates surface binding against the minor groove. (from *Acc. Chem. Res.* 24, 1991, 332)

The design and construction of small complexes with polypyridyl ligands for use as structural probes or artificial nuclease has been an active area of research during the last 20 years or so.⁷

A particular attraction of metal complexes is their three-dimensional nature, which makes them excellent candidates for spatial probes of DNA. The most intriguing possibility has been that of stereoselective/stereospecific binding for chiral metal complexes. This was first noted for the binding of $[\text{Fe}(\text{bipy})_3]^{2+}$ complex to DNA by Norden and Tjerneld⁸. Subsequently, others have investigated stereoselective binding of metal complexes with different structural motifs^{9,10}. In addition to changing the DNA binding properties, the chemical, photophysical and photochemical properties of metal complexes can be radically altered by modifications of the ligands, by changing the metal ions or just by changing its oxidation state.^{11,12,13}

Coordination complexes can be used to probe the nature of microenvironments (e.g. hydrophobicity and microviscosity) by varying their ligands and thus their physical and photophysical properties.¹⁴

We have been interested in knowing the effect of variation of metal ion and also the ability to bind DNA for a variety of ligand complexes containing the phenanthroline family of ligands.

Although DNA investigations of a number of $[\text{M}(\text{LL})_3]^{n+}$ type complexes have appeared in the literature, mainly based on ruthenium(II) metal complexes,¹⁵ relatively little attention has been paid to systematic investigations inquiring into the effects brought about by changing M and LL in such complexes. In fact only a few reports are present on the interaction of chromium(III)^{16,17} and iron(II)^{18,19,20} complexes with DNA. In this study we compare the DNA binding characteristics of a number of Cr(III) and Fe(II) complexes, using different polypyridyl ligands.

Various physical-chemical and biochemical techniques will be employed to probe the nature of these complexes with the duplex.

A wide range of techniques will be employed:

- (i) Steady-state isotropic absorption and emission;
- (ii) Circular dichroism spectroscopy;
- (iii) Dialysis experiments;
- (iv) Melting curves.

In order to elucidate the nature of the interaction between polypyridyl complexes and DNA we want to investigate the effect of metal ion, ligands and charge on the binding affinity of DNA.

It must be noted that no techniques can be used alone to determine the binding mode, but a judicious combination of optical and hydrodynamic techniques can be seen to provide a strong basis for characterizing the interactions of metal complexes with DNA.

4.1.1. Tools to characterize the interaction between metal complexes and DNA

Steady State Isotropic Absorption and Emission

Absorption and emission spectroscopy are routinely used to monitor interactions of dyes with nucleic acids because these optical properties tend to be quite sensitive to environment and easily measured. Both intercalation and electrostatic interaction can induce changes in the electronic spectra of molecules binding to DNA.

Intercalation has the more marked effect. In general intercalation is accompanied by a redshift (usually attributed to a change of solvent polarity) and hypochromism (due to the π - π stacking interactions with the nucleobases) in the dye absorption spectra. Spectroscopic studies may be used to determine the strength of binding, the effect of ionic strength, and whether binding shows any base-specificity.

Changes in the emission properties of a dye such as spectral shifts and intensity changes can also accompany different types of binding interaction: ethidium (intercalator) and DAPI (minor groove binder) both experience large fluorescence enhancements on binding to DNA.²¹ Luminescence quenching on binding to DNA tends to occur due to electron transfer reactions with the nucleotides, as seen for thionine.²²

Steady State Polarized Absorption: Circular Dichroism (CD) Spectroscopy

Metal complexes are usually achiral, being synthesized as a racemic mixture, but when they bind to DNA they acquire an induced CD (ICD) that is characteristic of their interaction. If the ligand transitions occur in the DNA region of the spectrum we take the ICD to be the total CD of the system minus that of the DNA at the same

concentration. This means that any DNA conformational changes that alter the DNA CD or any ICD of the DNA itself are included in the net ICD of the interaction.

Changes in these spectroscopic properties can also be analysed to provide quantitative binding data. However these techniques are more powerful than isotropic spectroscopies since they provide additional qualitative information about the nature of the binding mode.

Although CD spectroscopy is very sensitive, it is also very difficult to interpret CD changes in a qualitative way. Large induced-CD signals are expected for groove-binding and smaller signals for intercalation. However, small induced-CD signals are also predicted for groove binders in certain positions.^{23,24} Furthermore the sign of the induced CD signal is very sensitive to the exact orientation of the bound dye, making it dangerous to use induced CD for more than a diagnosis of interaction. However, for characterizing the interactions of chiral metal complexes with DNA, CD has proven extremely useful since it allows the enantioselectivity to be very sensitively monitored. For an inversion stable complex, dialysis of the racemate against DNA results in the dialyzate being depleted of the favoured enantiomers, resulting in a net CD spectrum; on the other hand, if the complex is inversion-labile, a net CD will result in a solution of the complex and DNA resembling that of the favoured enantiomers.²⁵

Dialysis experiments

For quantitative purposes techniques that separate bound and free dye provide the most reliable data for determination of binding parameters. The concentration of free and bound dye is determined independently. However, these techniques are time and material consuming; hence fewer data are usually collected than with spectroscopic titrations.

Dialysis is the most widely applied separation technique, but one problem is that moderately high salt concentrations (~ 50 mM Na^+) are generally required to avoid Gibbs-Donnan effects; lower ionic strengths are generally required to favour binding of low-affinity species. Thus dialysis can be less useful than absorption or emission spectroscopy which requires low ionic strength.

Binding Constants

Spectroscopic data can be analysed quantitatively to obtain binding affinities and site sizes.

The simplest measure of the binding strength between two molecules (such as a DNA binding ligand and DNA) is the equilibrium binding constant,

$$K = L_b / L_f S_f \quad (4.1)$$

for the equilibrium



where L_f is the concentration of free ligands, and S_f is the free site concentration and L_b is the concentration of the bound ligand. The total site concentration, S_{tot} , is given by

$$S_{tot} = C_M / n \quad (4.3)$$

where C_M is the macromolecule concentration and n is the number of bases in a binding site

It is common practise to present binding data as a Scatchard plot²⁶, rearranging equation (5.1) as follow:

ie r/L_f vs. r from the Scatchard equation

$$r/L_f = K/n - rK \quad (4.4)$$

where $r = L_b/C_M$. Thus the binding data should yield a linear plot with slope = $-K$ and intercept $y = K/n$.

The problem with the Scatchard plot is that we need to know the value of L_f and L_b . Therefore Rodger²⁷ developed the Intrinsic Method (IM) where the equation (5.1) is rearranged to give:

$$K = \alpha \rho / (S_{tot} - \alpha \rho) (L_{tot} - \alpha \rho) \quad (4.5)$$

where $\alpha = \rho/L_{tot}$ and ρ is the CD signal at a chosen wavelength and α (which is a function of wavelength) is a constant over the range of binding ratios being considered.

Thus a plot of $y = (L_{tot}^k - L_{tot}^j) / (\rho^k - \rho^j)$ versus $x = [(L_{tot}^k / \rho^k) - (L_{tot}^j / \rho^j)] / (\rho^k - \rho^j)$ should give a straight line with slope $C_M / n\alpha$ and intercept α .

Nonlinearity of the binding plot may arise from several effects which are difficult to distinguish: overlap of binding sites, cooperative effects, existence of two different binding sites or dye aggregation in solution.

A more rigorous model developed by McGhee and von Hippel²⁸ which can be applied to binding to homogeneous lattices describes for noncooperative binding the Scatchard plot as

$$r/L_f = K(1-r/n)\{(n-r)/(n-[1-n]r)\}^{1/n-1} \quad (4.6)$$

This equation reduces to the Scatchard equation when $n=1$ ie there is no possible overlap of potential sites. The McGhee/von Hippel treatment is also valid for cooperative effects.

4.2. Results and Discussion

4.2.1. Cr(III) tris-polypyridyl complexes in absence of DNA

Photophysical properties

All the complexes synthesized exhibit emission at room temperature in aqueous solution (phosphate buffer, pH=7) in the 730 region, characteristic of Cr(III) polypyridyl complexes. A representative emission spectrum is shown in Figure 5.2. for the $[\text{Cr}(\text{bipy})_3]^{3+}$ (excitation wavelength = 324 nm).

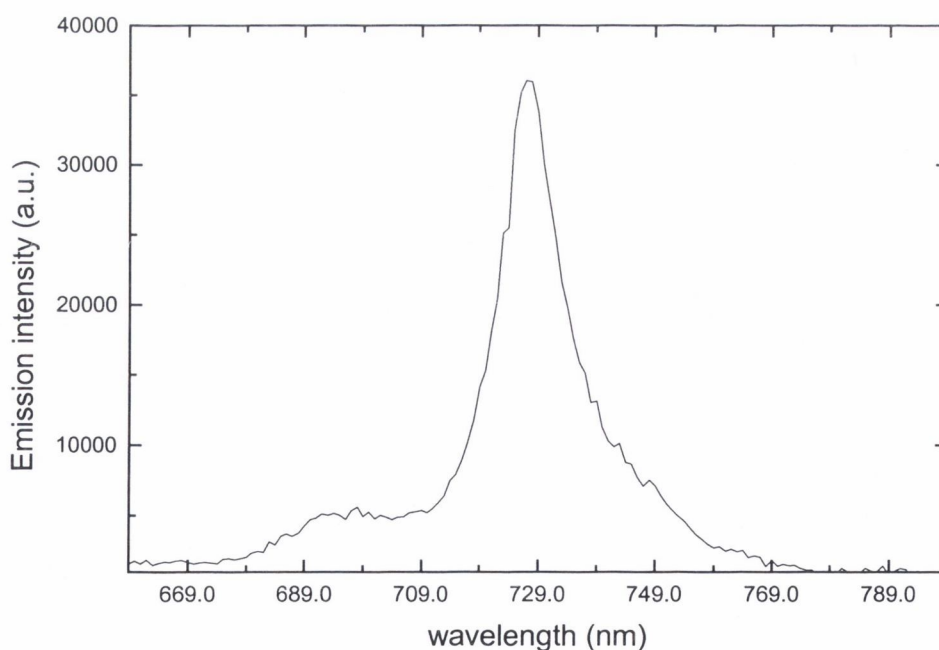


Figure 4.2: Steady-state emission spectrum of $[\text{Cr}(\text{bipy})_3]^{3+}$ in aerated phosphate buffer solution (pH=7).

Emission wavelength maxima data at room temperature in aqueous and MeCN solution, aerated, are presented in Table 4.1.

Table 4.1: Emission maxima in 10 mM phosphate buffer and MeCN (aerated)

Complex	$\lambda_{\text{max}},(\text{nm});$	$E_{0-0},10^{-3}\text{ cm}^{-1}$	$\lambda_{\text{max}},\text{nm}$	$\lambda_{\text{max}},\text{nm}$
	(buffer)	(buffer)	(MeCN)	(1M HCl)
				ref. 29
$[\text{Cr}(\text{bipy})_3]^{3+}$	727	13.75	728	730
$[\text{Cr}(\text{phen})_3]^{3+}$	728	13.74	728	732
$[\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$	730	13.71	730	732
$[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$	734	13.62	735	735
$[\text{Cr}(\text{phen})_2(\text{pd})]^{3+}$	730	13.71	-----	-----
$[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$	728	13.74	-----	-----

The wavelength maxima for the dominant ${}^2E_g \rightarrow {}^4A_{2g} (O_h)$ emission component for the homoleptic systems correspond closely to the literature values²⁹. Our N₂-purged lifetime for $[\text{Cr}(\text{phen})_3]^{3+}$ of 500 ns (in MeCN) is shorter than the literature result of 0.33 ms (extrapolated value to infinite substrate dilution in deaerated 1M HCl)³⁰ but these values are very sensitive to the composition of the solution medium due to the lowering of the population of the 2E state in presence of non-aqueous solvents which results from a decrease in the ${}^4T_2 \rightarrow {}^2E/{}^2T_1$ intersystem crossing efficiency.³¹ The emission maxima of $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ and $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ in MeCN could not be determined. This could be due to the quenching by oxygen of these two long-lived species.

Redox potential in the ground and in the excited states

The redox potentials of the complexes under study were determined in 0.05 M TBAPF₆ acetonitrile solutions and in 0.1 M LiCl aqueous solutions. The results of our studies together with the literature values are reported in Table 4.2. As an example, we report the CV of $[\text{Cr}(\text{phen})_3]^{3+}$ in 0.05 M TBAPF₆ (tetrabutyl ammonium hexafluorophosphate) MeCN in Figure 4.3.

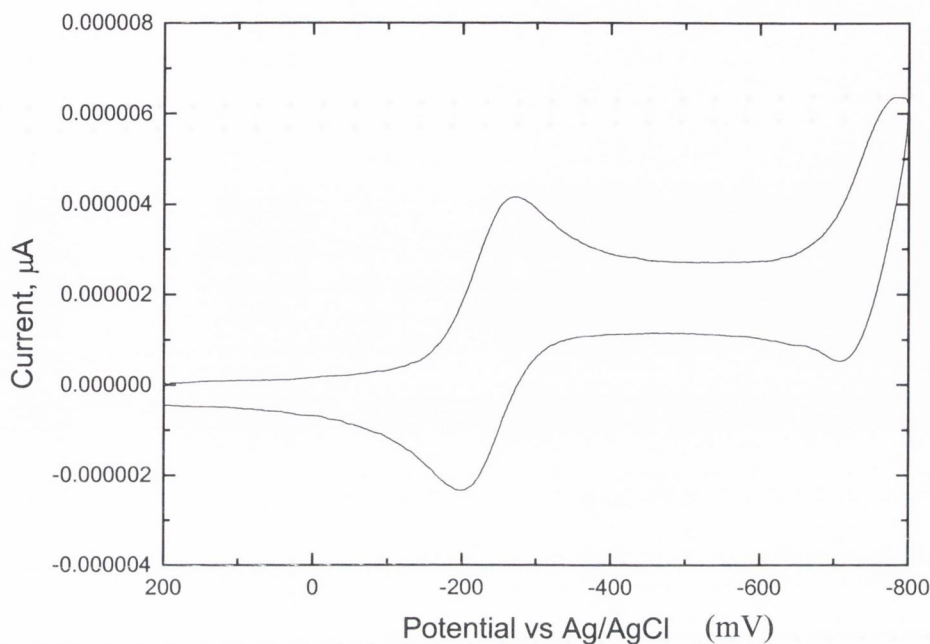


Figure 4.3. Cyclic voltammogram of $[Cr(phen)_3]^{3+}$ in 0.05 M TBAF₆ MeCN.

In Figure 4.3 the first peak is assigned to the reduction $Cr(III) \rightarrow Cr(II)$; the second reduction wave is due to the reduction of $Cr(II) \rightarrow Cr(I)$

Table 4.2: Standard reduction potentials vs NHE

Complex	$E^{\circ}Cr^{3+}/Cr^{2+}$, V	$E^{\circ}Cr^{3+}/Cr^{2+}$, V	$E^{\circ}Cr^{3+}/Cr^{2+}$, V ^a
	(0.1 M LiCl)	(0.05 M TBAPF ₆)	1 M LiCl
$[Cr(bipy)_3]^{3+}$	-0.24	-0.25	-0.26
$[Cr(phen)_3]^{3+}$	-0.23	-0.23	- 0.28
$[Cr(Me_2bipy)_3]^{3+}$	-0.36	-0.42	-0.45
$[Cr(Me_2phen)_3]^{3+}$	-----	-0.39	-0.45
$[Cr(phen)_2(phenadione)]^{3+}$	-----	irreversible	-----
$[Cr(phen)_2(dppz)]^{3+}$	-----	-0.20	-0.17

^a from ref.32 and 33

The values match those reported by Sutin³² and Kane-Maguire³³ considering the different conditions used in the experiments. The irreversible behaviour of $[Cr(phen)_2(phenadione)]^{3+}$ was similarly found for $[Ru(phen)_2(phenadione)]^{2+}$.³⁷

When the Stokes shift between the ground-state absorption and excited state emission is very small, and the changes in shape, size and solvation between the two states are also small, the entropy differences between the ground and excited states may be neglected. Hence the redox potential of the excited state can be estimated from equations (5.7) for chromium(III) polypyridyl species.

$$E\left({}^*Cr^{3+}/Cr^{2+} \right) = E\left(Cr^{3+}/Cr^{2+} \right) + E_{0-0}\left(Cr^{3+}/{}^*Cr^{3+} \right) \quad (4.7)$$

where $E_{0-0}\left(Cr^{3+}/{}^*Cr^{3+} \right)$ is the one-electron potential corresponding to the zero-zero spectroscopic energy of the excited state which we assume is equal to the energy emission expressed in V.

From the difference between the emission energy and standard reduction potential in acetonitrile, we have estimated the excited-state redox potentials, which are presented in Table 4.3.

Table 4.3: Redox-potentials of the excited-states of chromium(III) complexes

Complex	$E^o\left({}^*Cr^{3+}/Cr^{2+} \right), V$	$E^o\left({}^*Cr^{3+}/Cr^{2+} \right), V^a$
$[Cr(bipy)_3]^{3+}$	+1.45	+1.44
$[Cr(Me_2bipy)_3]^{3+}$	+1.28	+ 1.25
$[Cr(phen)_3]^{3+}$	+1.47	+1.42
$[Cr(Me_2phen)_3]^{3+}$	+1.30	+1.23
$[Cr(phen)_2(dppz)]^{3+}$	+1.50	+ 1.53

^afrom ref.26 and ref. 27

These results are in agreement with the reported literature data. The validity of this procedure has been verified in the case of the MLCT state of $[Ru(bipy)_3]^{2+}$ ³⁴ for which the estimated value of −0.84 V for the $E_0\left(Ru^{3+}/Ru^{2+} \right)$ is in accordance with the value of −0.81 V for the couple $[Ru(bipy)_3]^{3+}/[{}^*Ru(bipy)_3]^{2+}$ in acetonitrile. For some chromium(III) complexes, Balzani and co-workers³⁵ have experimentally verified the estimation of the redox-potentials of various polypyridyl complexes using a series of quenchers of graded potential.

A comparison of the ground and excited state redox potentials in Tables 5.2 and 5.3 reveals that the latter state are indeed better oxidants than their respective ground states.

4.2.2. Cr(III) tris-polypyridyl complexes in presence of DNA

The complexes analysed were $[\text{Cr}(\text{LL})_3]^{3+}$ where LL= 1-10-bipyridine (bipy), 4-4'-dimethyl,1-10-bipyridine (Me_2bipy), 1-10-phenanthroline (phen) and 4-7-dimethyl-1-10-phenanthroline (Me_2phen) as our aim was to investigate the binding differences arising from the presence of two methyl groups on those ligands. In each case crystals of the compounds were taken for these measurements. In the case of $[\text{Cr}(\text{phen})_3]^{3+}$ the relevant space group is centrosymmetric P-1 and in $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ is achiral P2(1)/(c).

The Figure 4.4 below represents the structures of the $[\text{Cr}(\text{LL})_3]^{3+}$ type complexes investigated in this study.

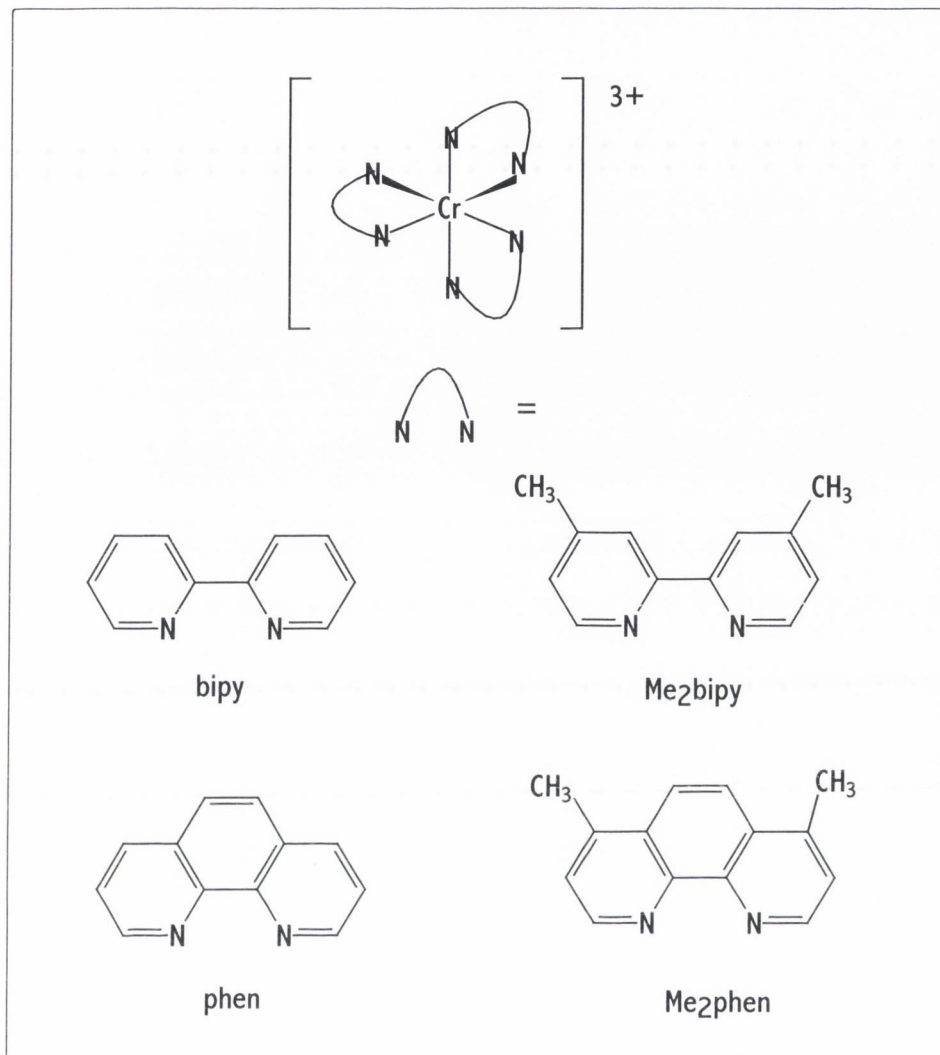


Figure 4.4: Structure of the $[\text{Cr}(\text{LL})_3]^{3+}$ type complexes investigated in this study.

Preliminary studies were also conducted on Cr(III) heteroleptic complexes to investigate the difference in binding modes with DNA due to the ligand planarity. The complexes investigated were mixed ligand complexes of chromium (III), $[\text{Cr}(\text{phen})_2(\text{LL})]^{3+}$ where LL is a modified phenanthroline ligand, 1-10-phenanthroline-5-6-dione (phendione) and dipyridophenazine (dppz). The interactions between these complexes and DNA were compared to those of $[\text{Cr}(\text{phen})_3]^{3+}$.

The structures of the complexes investigated in this study are presented in Figure 4.5. below.

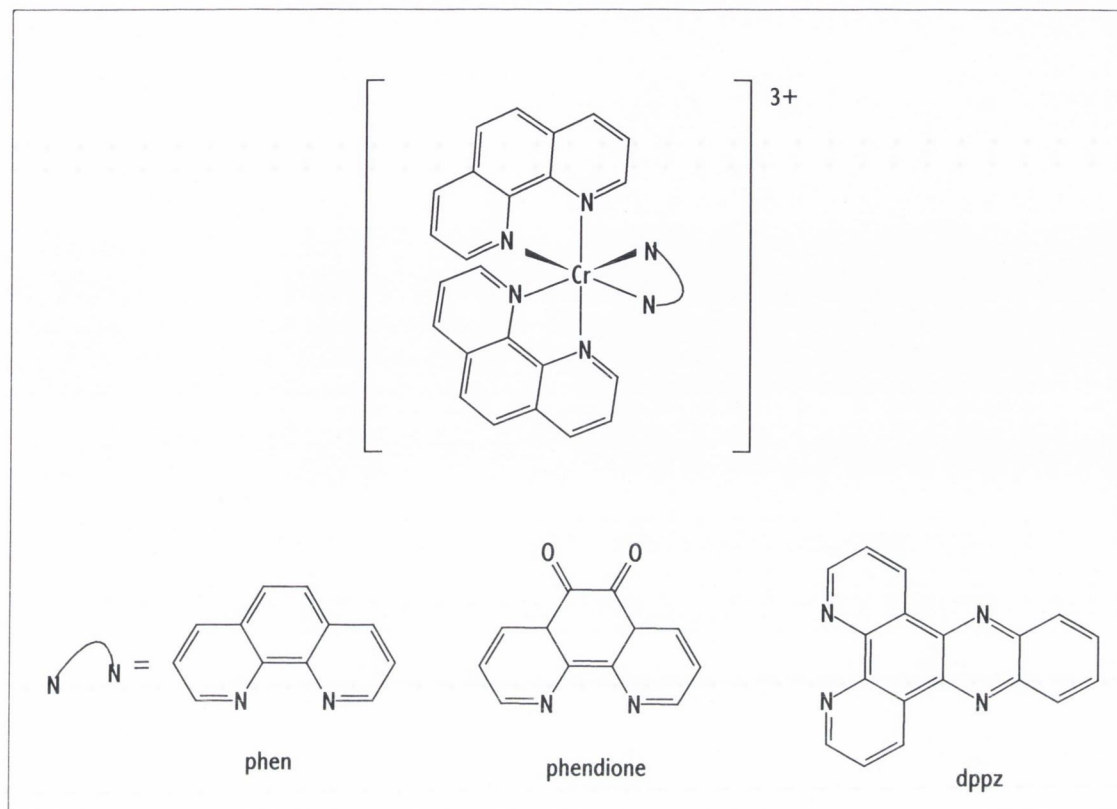


Figure 4.5: Structures of some chromium (III) complexes investigated

Thermal denaturation studies

Previous studies also conducted in our group have shown that the melting behaviour of DNA is affected by intercalators and in particular by metal complexes.^{36, 37}

We have studied the effects of the chromium polypyridyl complexes on the melting of CT-DNA. Thermal denaturation curves for DNA in the presence and absence of the complexes at a ratio of P/D = 20 are given in Figure 4.6 and the relevant data for all the complexes investigated in this study are summarized in Table 4.4.

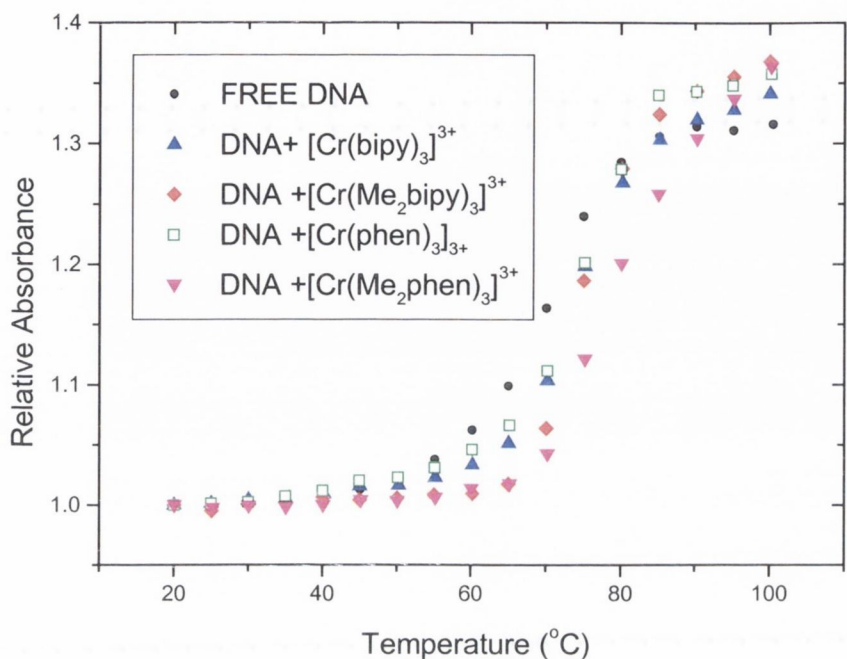


Figure 4.6: Melting curves for DNA alone and in presence of different Cr(III) complexes at $P/D= 20$. $[DNA]= 150\ \mu M$, $[Complex]= 7.5\ \mu M$ and 10 mM phosphate buffer was used in these experiments.

The T_m (melting temperature) of CT-DNA in 10 mM phosphate buffer is 70 °C, calculated by a derivative method. The results reported here are not in agreement with the previous reported data^{36, 37} in which a value of 60 °C was determined for the CT-DNA melting. This temperature is increased by 5 °C in the presence of $P/D = 20$ for all the chromium homoleptic complexes except for the $[Cr(Me_2phen)_3]^{3+}$ where there is an increase of 10 °C. Similar results, but for different complexes were found by Maiya *et al.*³⁶ who also found that a larger temperature increase was observed in the presence of intercalators.

Table 4.4: Results of thermal denaturation, T_m , studies, $[DNA]/[complex]=P/D = 20$

Complex	T_m °C
CT-DNA	70
$[Cr(bipy)_3]^{3+}$	75
$[Cr(Me_2bipy)_3]^{3+}$	75
$[Cr(phen)_3]^{3+}$	75
$[Cr(Me_2phen)_3]^{3+}$	80

The effects on the melting curves show clearly that these complexes bind to DNA. The larger effect noted for the $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ is suggesting that this complex binds in an intercalative mode.

Absorption titrations studies

The UV/Vis spectra of the complexes under study have been examined before in Chapter 2.

Owing to the lack of a strong absorption band above 300 nm, a wavelength up to which DNA itself absorbs, the binding affinities of the bipy, phen and phendione complexes of Cr(III) could not be investigated by the absorption titration method, while the corresponding $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ having the characteristic dppz intraligand bands between 340-350 nm can be investigated by absorption titration. However, for comparison the spectrum of $[\text{Cr}(\text{phen})_3]^{3+}$ when titrated with CT-DNA is also reported even though we cannot obtain any quantitative data. The results presented here are qualitative

The visible spectra of $[\text{Cr}(\text{phen})_3]^{3+}$, $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ and $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ are shown in Figure 4.7.

Slight changes were observed in the visible spectrum of $[\text{Cr}(\text{phen})_3]^{3+}$ on addition of CT-DNA (calf thymus-DNA), in 10 mM phosphate buffer. The general behaviour is a decrease in absorption from 300 to 500 nm. An isosbestic point is observed at 450 nm. Hypochromism measured at 325 nm is 0.27.

In the UV/Vis spectrum of $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ a decrease in absorbance is seen until $P/D = 5$, but no major differences are seen on further addition of CT-DNA. An isosbestic point is found at 327 nm. A strong hypochromism is found at 383 nm of about 0.17.

The spectrum of $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ on addition of CT-DNA loses the characteristic band of the dppz ligand ($\pi \rightarrow \pi^*$) in the region 350-380 nm. Two isosbestic points are found at 315 and 385 nm. There is not much difference in the spectra at $P/D = 5$ and $P/D = 40$, indicating that at a ratio $P/D = 5$ all the metal complex has been bound to DNA. The hypochromism at 376 nm is not very strong, only 0.03 in both cases, even at high binding ratio, and in contrast to what was reported by Kane-Maguire for this species.

Hypochromism and red shift have been correlated to intercalation in the base-pairs of DNA.³⁸ Similar observations have also been reported for other platinum(II),³⁹^{40,41,42} copper(I)^{43,44}, ruthenium (II)^{45,,46,47,48,49,50,51,52,53} osmium(II)⁵⁴ and rhenium(I)⁵⁵ metallointercalators.

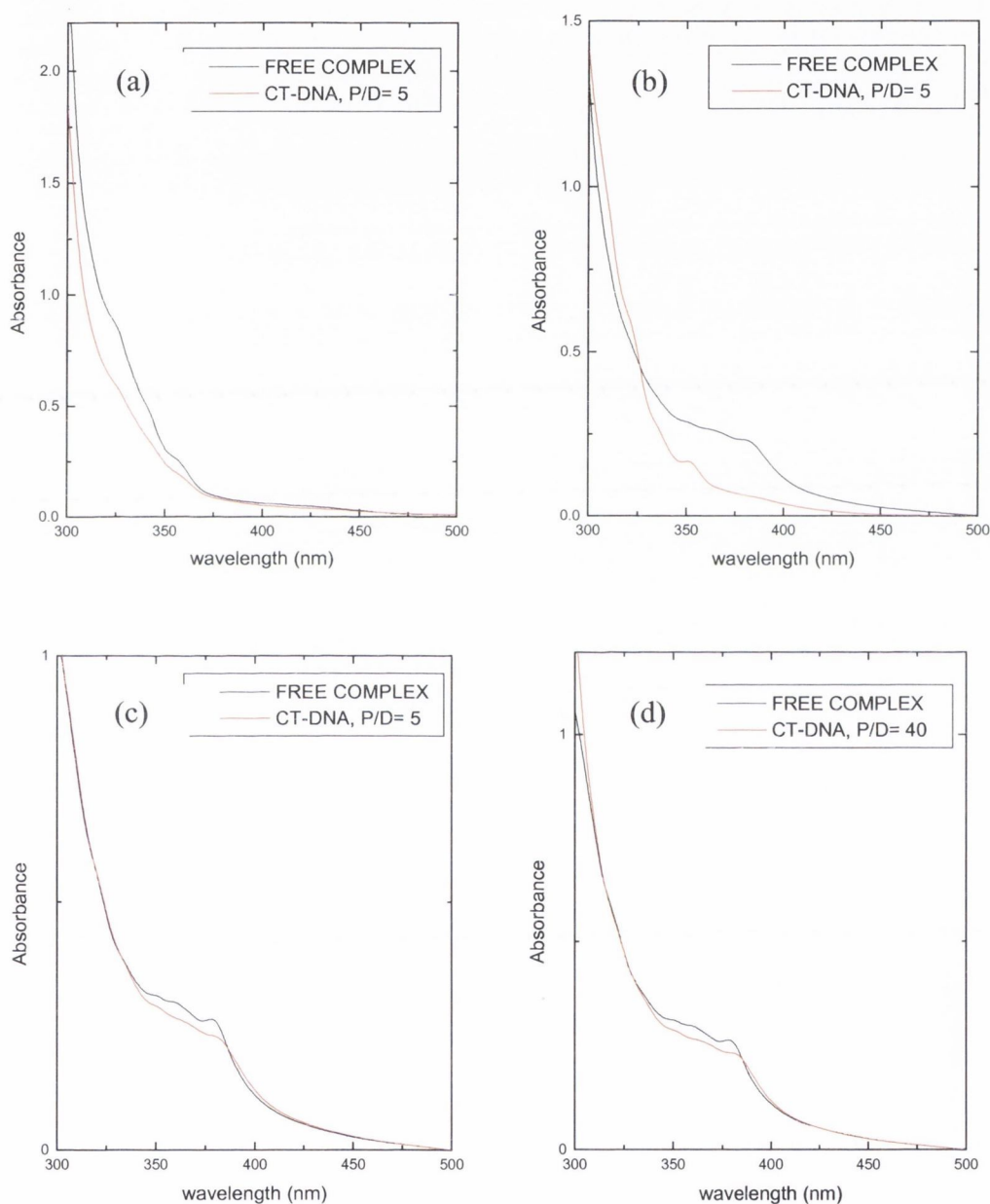


Figure 4.7: The effect on the absorption spectra of (a) $[\text{Cr}(\text{phen})_3]^{3+}$, (b) $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ and (c-d) $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ of CT-DNA in 10 mM phosphate buffer (pH=7). The two spectra in the absence (—) and in the presence (—) of CT-DNA are shown for comparison for each compound. Dye concentrations are: (a) $2 \cdot 10^{-4}$ M, (b) $1.30 \cdot 10^{-4}$ M and (c-d) $3.75 \cdot 10^{-5}$ M.

Emission titrations

The fluorescence spectra of the Cr(III) polypyridyl complexes are markedly affected by the CT-DNA. The general behaviour is a quenching of the emission at ca. 728 nm, but while the quenching for $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{phen})_3]^{3+}$ is total, for the other two complexes the quenching is only partial. As the excited state potential of the complexes $[\text{Cr}(\text{phen})_3]^{3+}$ and $[\text{Cr}(\text{bipy})_3]^{3+}$ (+ 1.45-1.47 V) is more than the oxidation potentials of guanine (1.20 V)⁵⁶, quenching of its emission by redox interaction with the purine bases is expected.^{57,58} At the time of writing, the emission behaviour of $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ and $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ in the presence of DNA has not been investigated. We report in Figure 4.8-4.9 the emission spectra of the compounds investigated in the presence of increasing concentrations of DNA.

As can be seen in Figure 4.10 the degree of quenching decreases going from $[\text{Cr}(\text{bipy})_3]^{3+} > [\text{Cr}(\text{phen})_3]^{3+} > [\text{Cr}(\text{Me}_2\text{phen})_3]^{3+} > [\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$

The quenching of the emission has been suggested as due to an electron transfer mechanism involving guanine base oxidation,¹⁶ having an oxidising power of +1.4 V versus NHE, they are thermodynamically capable of oxidising guanine in DNA, while oxidation of other DNA bases is improbable. This behaviour is similar to other ruthenium(II) complexes with HAT and TAP ligands for which oxidation of the nucleobase guanine has been conclusively demonstrated.^{45,59}

The results found for the two methylated chromium(III) complexes, $[\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$, are in agreement with those found by Kane-Maguire¹⁶ for the related $[\text{Cr}(\text{TMP})_3]^{3+}$, where TMP is the 3,4, 7,8-tetramethyl, 1,10-phenanthroline, complex where no quenching was found, while we observed a partial quenching in the emission of these two species. In fact, the redox-oxidation potential of the excited states for those species (+1.28-1.30 V) is intermediate between that of $[\text{Cr}(\text{phen})_3]^{3+}$ (+1.47 V) and that of $[\text{Cr}(\text{TMP})_3]^{3+}$ (+1.1 V).

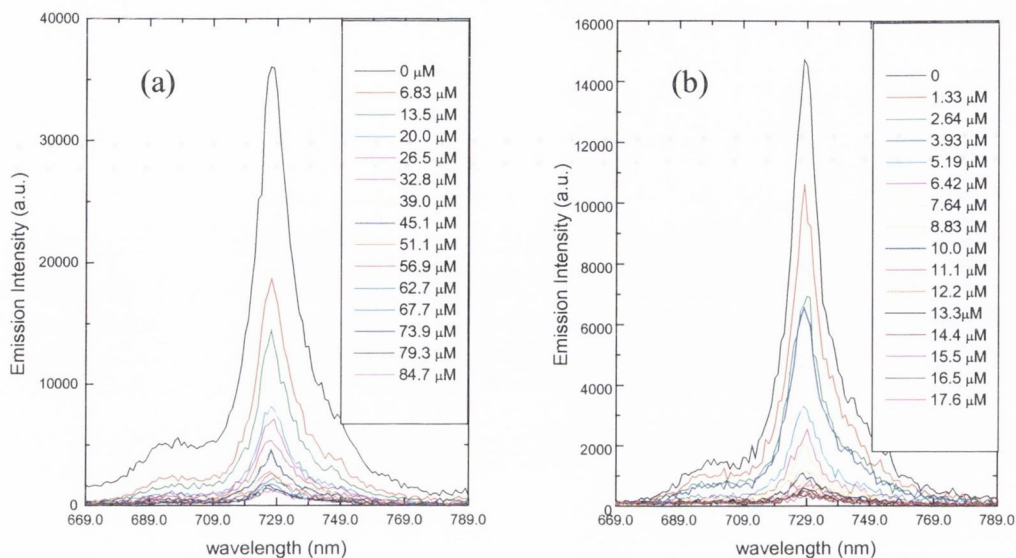


Figure 4.8: Steady-state emission spectrum of an air-saturated (a) $2 \times 10^{-4} \text{ M}$ solution of $[\text{Cr}(\text{bipy})_3]^{3+}$ and (b) $1.46 \times 10^{-5} \text{ M}$ of $[\text{Cr}(\text{phen})_3]^{3+}$ in 10 mM phosphate buffer (pH= 7) in the presence of different concentrations of CT-DNA (shown in the window). $\lambda_{\text{exc}} = 324 \text{ nm}$, $T = 25^\circ \text{C}$.

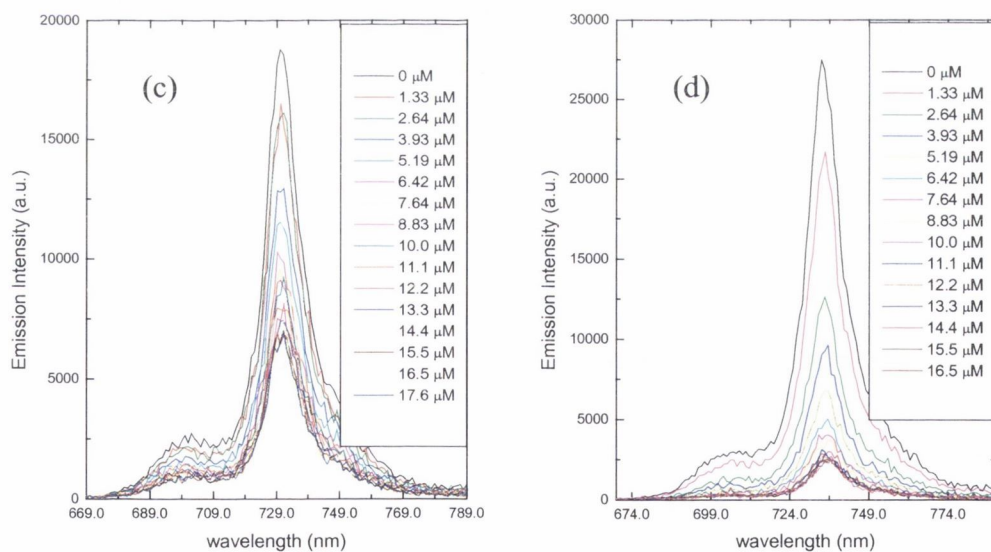


Figure 4.9: Steady state emission quenching of a solution of (c) $1.88 \times 10^{-5} \text{ M}$ $[\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$ and (d) $1.74 \times 10^{-5} \text{ M}$ $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ at various DNA concentrations (in box) in 10 mM phosphate buffer, $\lambda_{\text{exc}} = 324 \text{ nm}$, $T = 25^\circ \text{C}$.

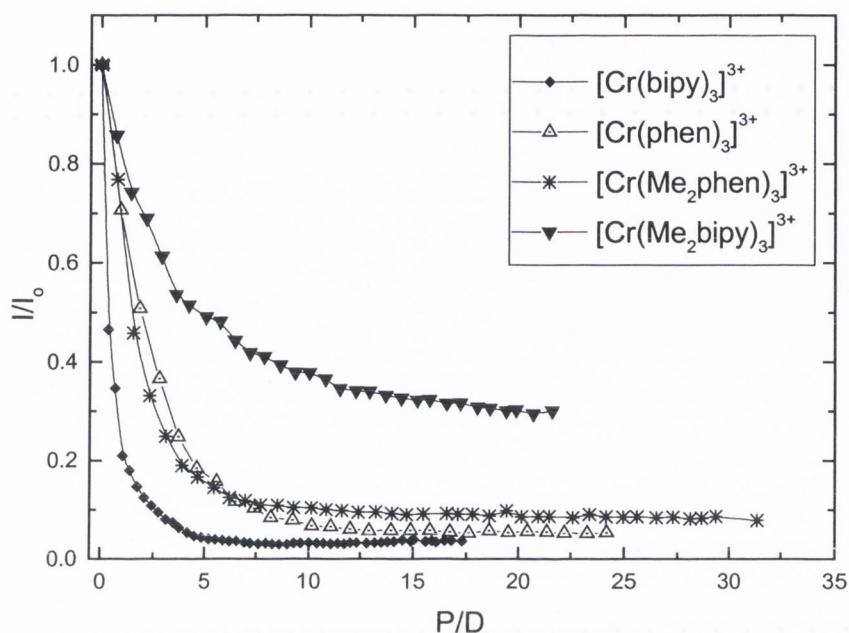


Figure 4.10: The effect of CT-DNA on the emission intensity of $[\text{Cr}(\text{bipy})_3]^{3+}$, $[\text{Cr}(\text{phen})_3]^{3+}$, $[\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$, I/I_0 is the ratio of the area under the curve, P/D is $[\text{DNA}]/[\text{complex}]$.

Equilibrium dialysis studies

Equilibrium dialysis experiments with $[\text{Cr}(\text{phen})_3]^{3+}$ were carried out in the presence of calf-thymus DNA, but no information could be gathered from the CD spectra of the dialyzed species as the optical activity was too weak. Therefore binding affinities could not be determined.

Circular Dichroism titrations

The ICD spectra for the complexes $[\text{Cr}(\text{phen})_3]^{3+}$ and $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ are reported in Figure 4.12 and Figure 4.14. The $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$ complexes showed no ICD and are not reported. For comparison a spectrum of CT-DNA is given in Figure 4.11 in the region of absorbance where we perform our measurements (210–500 nm).

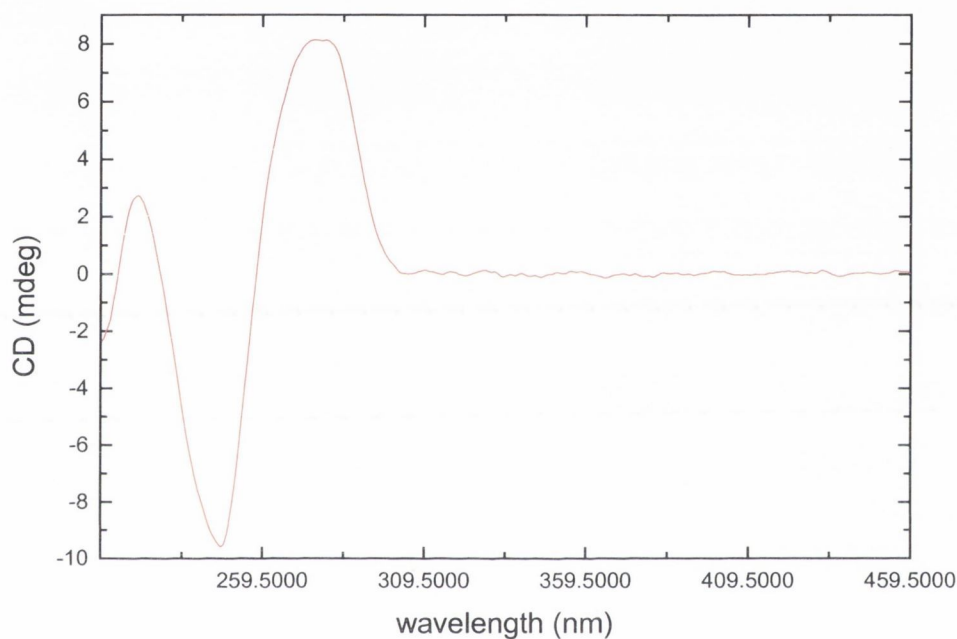


Figure 4.11: CD spectrum of CT-DNA in 10 mM phosphate buffer solution, $[\text{DNA}] = 1 \times 10^{-4} \text{ M}$.

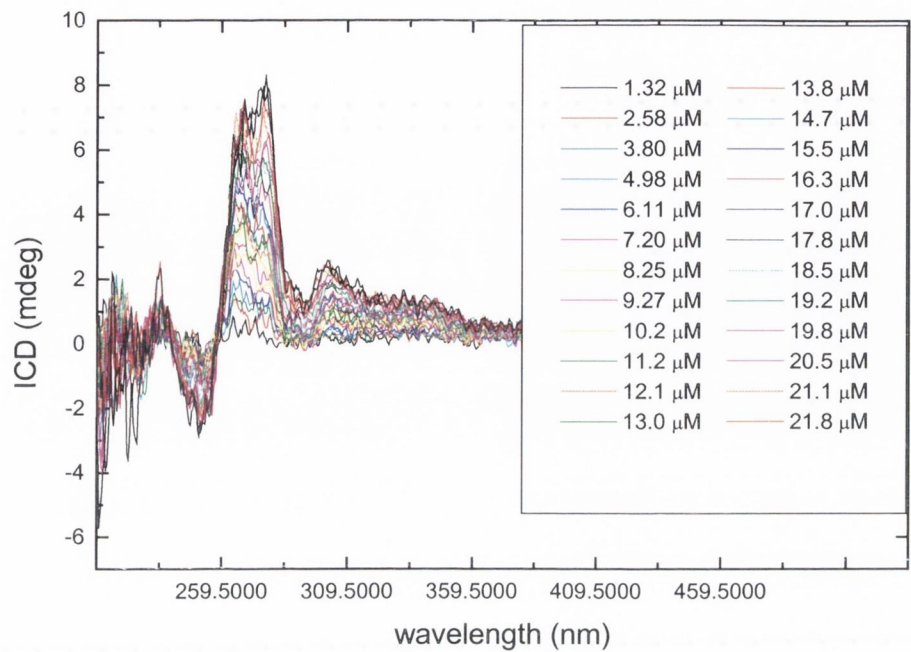


Figure 4.12: ICD spectra of $[\text{Cr}(\text{phen})_3]^{3+}$ at various concentrations in 10 mM phosphate buffer, $[\text{DNA}] = 100 \mu\text{M}$, $R = [\text{complex}]/[\text{DNA}]$, $0 < R < 0.22$, $T = 25^\circ\text{C}$.

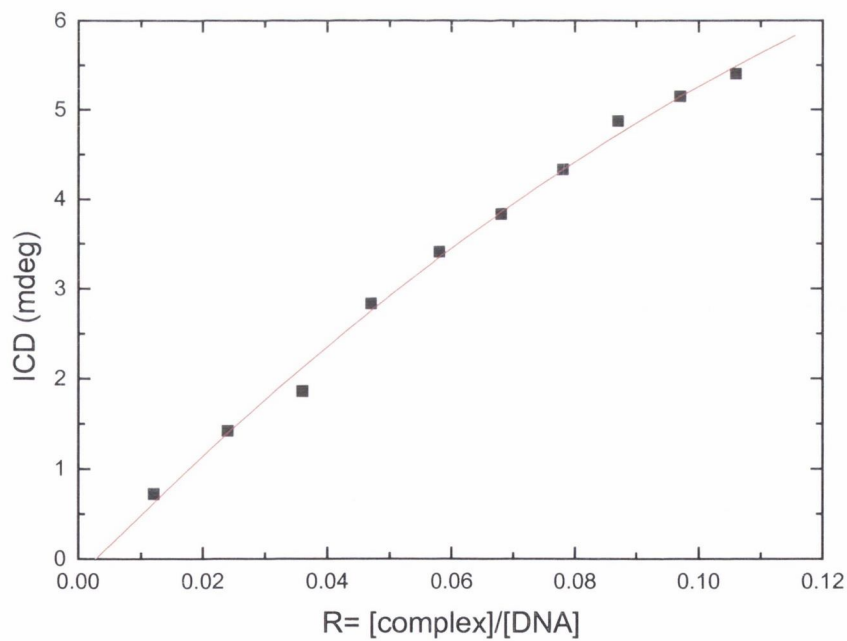


Figure 4.13: ICD at 259 nm of $[\text{Cr}(\text{phen})_3]^{3+}$ versus $R = [\text{complex}]/[\text{DNA}]$, $0 < R < 0.1$.

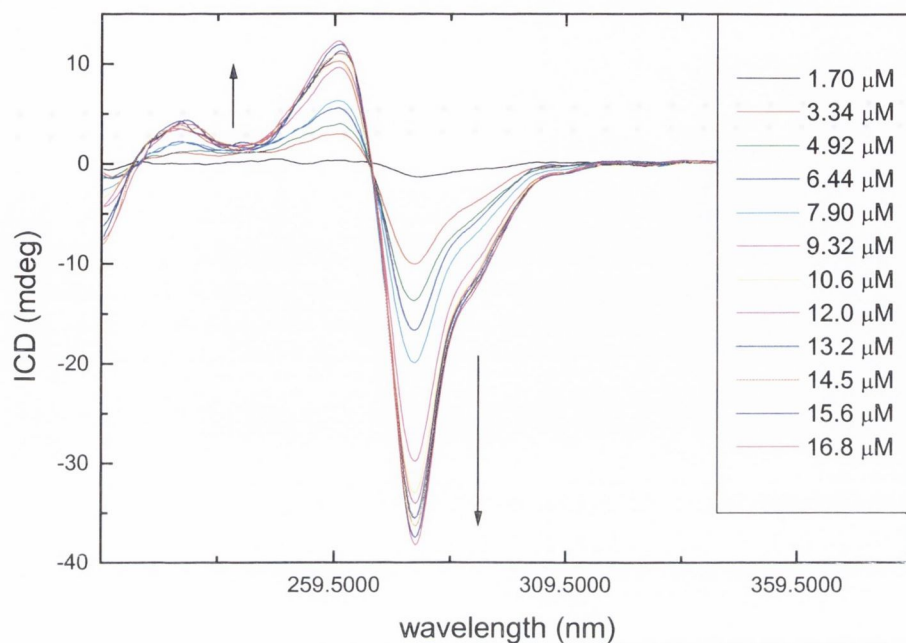


Figure 4.14: ICD spectra of $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ at various concentrations in 10mM phosphate buffer, $[\text{DNA}] = 108 \mu\text{M}$, $0 < R < 0.15$, $T = 25^\circ\text{C}$.

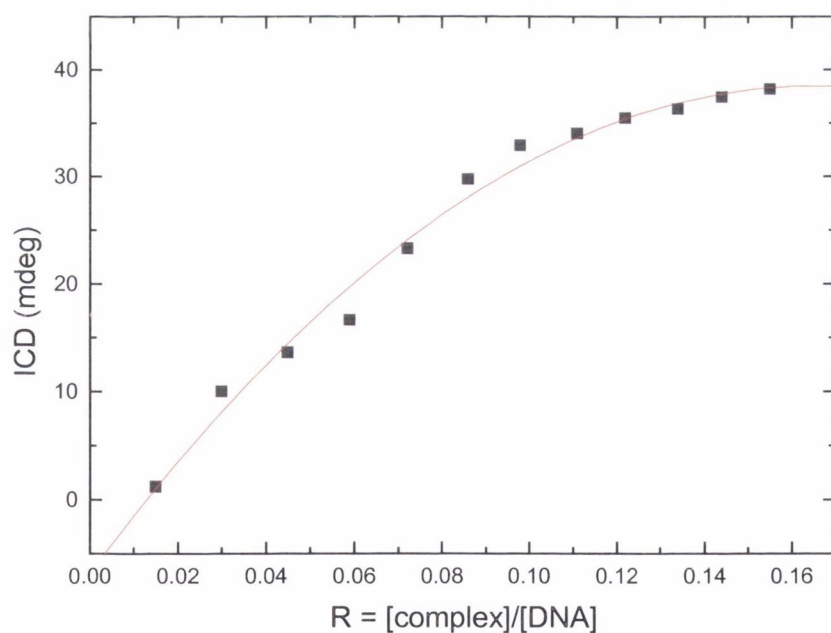


Figure 4.15: ICD at 276 nm of $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ versus $R = [\text{complex}]/[\text{DNA}]$

The ICD spectra for the two complexes are substantially different. The ICD spectra of the $[\text{Cr}(\text{phen})_3]^{3+}$ show two negative maxima at 250 nm and 280 nm, while a strong positive maximum is present at 275 nm. Three other small positive maxima are present at 307, 325 and 345 nm.

The ICD spectrum of $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ has instead a very strong negative maximum at 277 nm and two positive maxima at 225 and 261.

As expected no CD is developed in the visible region, due to the fact that these complexes do not absorb above 350 nm.

The bands between 210-300 nm are due to intra-ligand transitions of the phenanthroline-type ligands on the central atom and are assigned to the A_2 and E transitions. The bands at about 300-350 nm are probably due to the $d-d$ transitions of the chromium atom.

In the spectra of the $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ we noticed that the CD intensity increases but the shape of the spectrum remains the same during each experiment. This indicates that only one binding mode is present for the complex, while the CD spectra of $[\text{Cr}(\text{phen})_3]^{3+}$ shows a change in shape as the concentration of the metal complex increases. Changes in the form of the ICD spectra are indicative of multiple binding modes and are observed for the spectra of $[\text{Cr}(\text{phen})_3]^{3+}$. The shape of the spectra changes at a mixing ratio $[\text{complex}]/[\text{DNA}] = 0.1$ where the peak at 267 nm disappears while another at longer wavelength appears (276 nm).

This change is usually due to occupancy of more than one binding site as the drug load on the DNA increases, but may also be due to changes in the DNA conformation or to ligand-ligand interactions.^{60,61} As there is no evidence of excitonic Cr-Cr interactions, this suggests that there is more one than one binding mode and, at higher complex concentrations, less favourable sites or modes are vacated.

Table 4.5: Circular Dichroism (CD) data on binding of Cr(III) complexes to CT-DNA at $T= 25\text{ }^{\circ}\text{C}$.

Complex	λ_{max}, nm (ICD , mdeg)
$[\text{Cr}(\text{phen})_3]^{3+}$	250 (-2.15), 275 (5.38), 280 (-1.32), 307 (1.33), 325(1.33), 345 (1.10)
$[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$	225 (4.23), 261 (12.18), 277 (-37.48)

Applying the exciton theory, for the $[\text{Cr}(\text{phen})_3]^{3+}$, the ICD spectra developed can be assigned to the Λ enantiomers of the complex.

Rehmann and Barton⁶² on studies of the oligonucleotide d(GTGCAC)₂ in the presence of [Cr(phen)₃]³⁺ have shown that the Λ isomer binds preferentially in the minor groove, while weak evidence was found for the Δ isomer binding in the major groove. Kane-Maguire¹⁶ found through capillary electrophoresis (CE) studies that the Λ binds preferentially and that two binding modes are present, intercalative and surface binding and they both occur in the minor groove. Rehmann and Barton⁶² also found that increasing complex charge is an additional factor favouring surface binding over partial intercalation. Our results shows two binding modes are present which is in agreement with previous results, and also that there is a preferential binding of the Λ over the Δ enantiomers. The second binding mode also seems to be concentration dependent. This result seems to be in agreement with the related [Ru(phen)₃]²⁺ complex where two binding modes also seem present.^{1,10}

The ICD spectra of [Cr(Me₂phen)₃]³⁺ can be assigned to the Δ enantiomers. The bands of these spectra are stronger than those of [Cr(phen)₃]³⁺, indicating that a different kind of interaction occurs. Usually stronger ICD signals are due to groove binding. For a similar ruthenium(II) complex, the [Ru(TMP)₃]²⁺, with methyl groups that preclude intercalative stacking, it has been shown that it associates with the duplex primarily in a surface-bound mode.^{63,64}

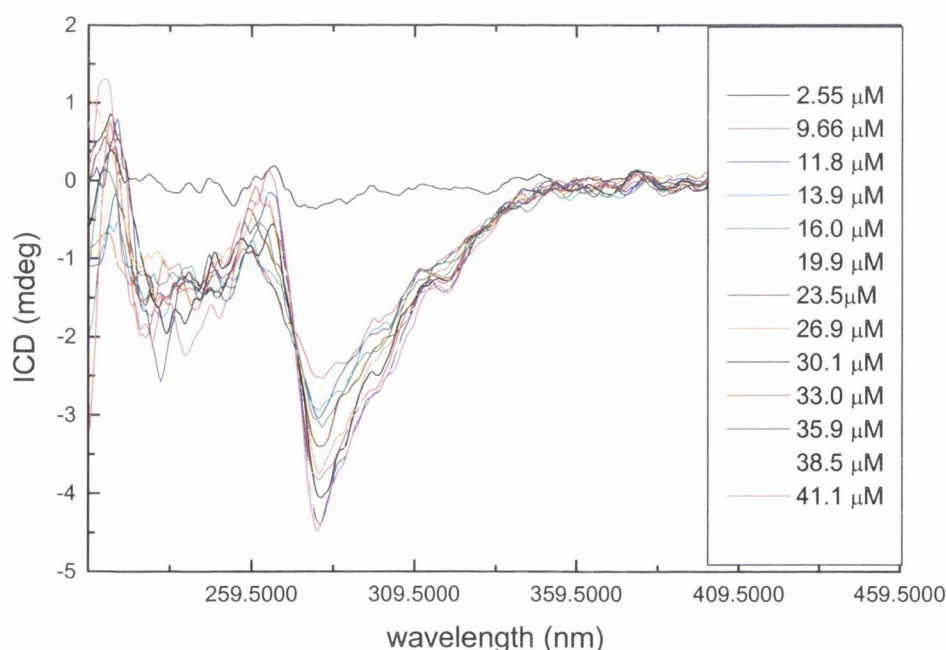


Figure 4.16: ICD spectra of [Cr(phen)₂(phendione)]³⁺ at various concentrations, $T = 25\text{ }^{\circ}\text{C}$, [DNA] = 100 μM .

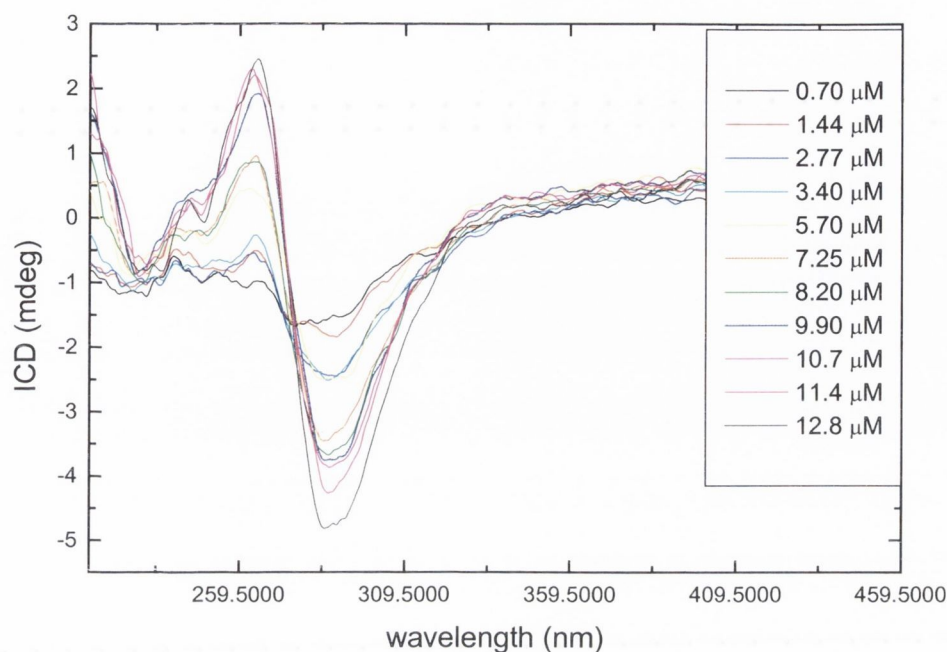


Figure 4.17: ICD spectra of $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ at various concentrations, $T = 25^\circ\text{C}$, $[\text{DNA}] = 100\ \mu\text{M}$.

The ICD spectrum of $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ is qualitatively different from the previous two complexes. The ICD bands are all in the negative regions with peaks at about 225 and 265 nm.

For the $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ complex, a negative peak was observed at about 275 nm in the phenanthroline region ($\pi-\pi^*$) and a positive peak at 260 nm, while a slight positive curvature is present between 300 and 500 nm. Applying the exciton theory⁶⁵ the signal can be assigned to the Δ -enantiomer. The CD developed is very similar to that presented by Kane-Maguire, which was obtained from dialysis of a solution of $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ in presence of CT-DNA. According to the author, assigning the spectra of the dialyzed to the Δ -enantiomer, the Λ -enantiomer is binding to DNA. Our experiments show instead an opposite behaviour where the Δ -enantiomer seems to interact with DNA. Future experiments with the two resolved enantiomers of $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$, which have been planned, are necessary to clarify this point. Previous studies on ruthenium (II) complexes have shown that for intercalation in the right-hand helix, both enantiomers bind to DNA with comparable binding strengths.⁶⁶ According to the previous study on DNA binding of $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ we expect the binding mode to be intercalative.

Temperature dependence studies on the CD spectra of $[\text{Cr}(\text{phen})_3]^{3+}$

The ICD data for $[\text{Cr}(\text{phen})_3]^{3+}$ were also determined at 20 and 30 °C to see any effect of the temperature on the binding affinities. The two spectra at 20 and 30 °C are shown in Figure 4.18-4.19.

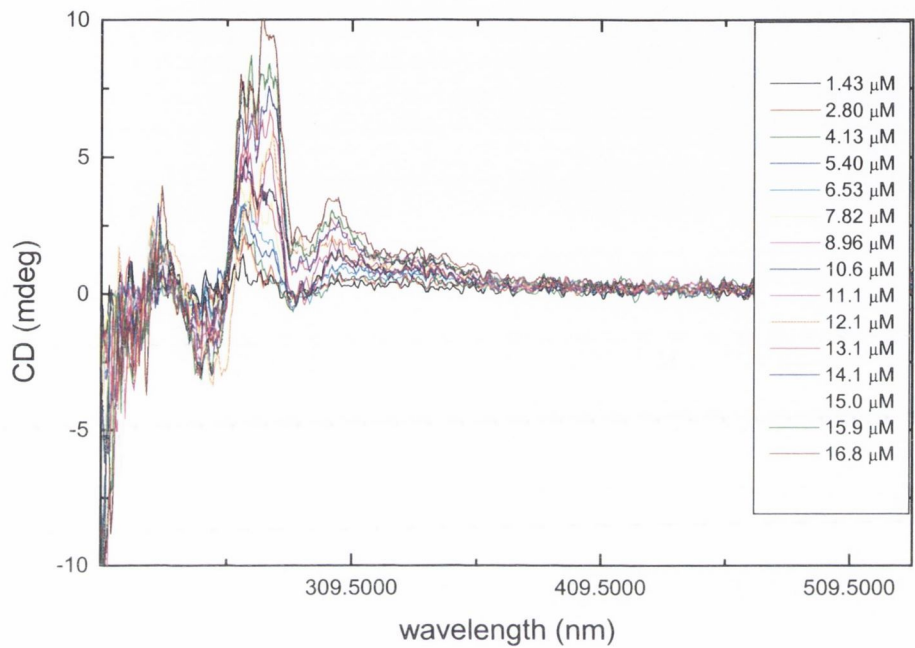


Figure 4.18: ICD spectra of $[\text{Cr}(\text{phen})_3]^{3+}$ at various concentrations, $[\text{DNA}] = 149 \mu\text{M}$, $0 < R < 0.12$, $R = [\text{complex}]/[\text{DNA}]$, $T = 20^\circ\text{C}$.

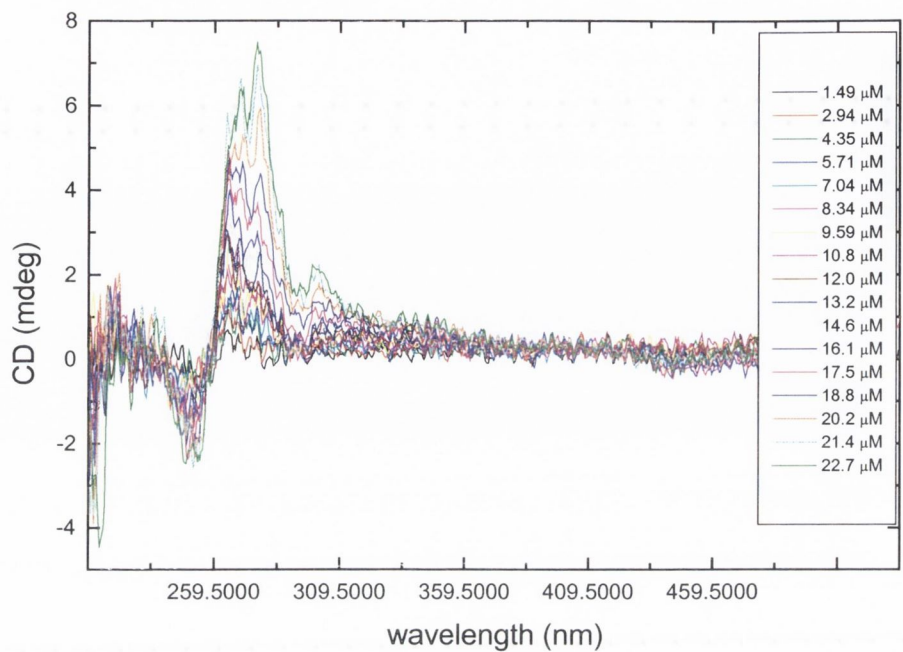


Figure 4.19: ICD spectra of $[Cr(phen)_3]^{3+}$ at various concentrations at $T= 30\text{ }^{\circ}\text{C}$, $[DNA] = 100\text{ }\mu\text{M}$, $0 < R < 0.22$.

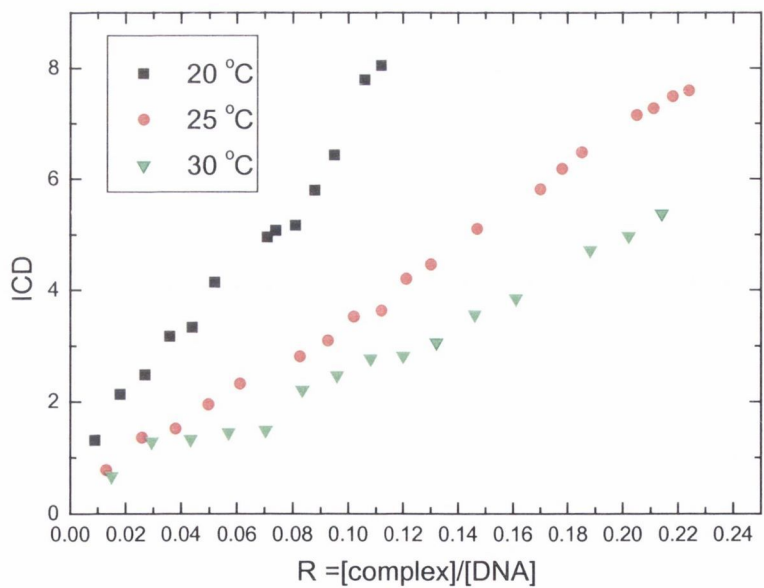


Figure 4.20: ICD versus R at different temperature for the complex $[Cr(phen)_3]^{3+}$.

From the data presented we can see that at the same ratio, the ICD at 20 °C is greater than that at 30 °C.

Equilibrium binding constants from CD

The equilibrium binding constants for the complexes studied were calculated from the experimental values found using the intrinsic method (IM).²⁷ For the $[\text{Cr}(\text{bipy})_3]^{3+}$ and $[\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$ complexes, in the absence of data from CD, binding constants could not be determined, while for the $[\text{Cr}(\text{phen})_3]^{3+}$, $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ they were determined using the CD data. Those of $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ and $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ have not yet been determined because of lack of time.

For all the complexes, IM calculations were carried out using data from regions where the form of the ICD spectra are independent of R ($= [\text{complex}]/[\text{DNA}]$). Plots of $([\text{complex}]_i - [\text{complex}]_k)/\rho_i - \rho_k$ versus $([\text{complex}]_i/\rho_i - [\text{complex}]_k/\rho_k)/(\rho_i - \rho_k)$ where (i,k) equals all pairs of spectra in the series, were linear with slope $[\text{complex}]_{\text{tot}}/\alpha$ and intercept $n\alpha$ and are shown in Figure 4.20.

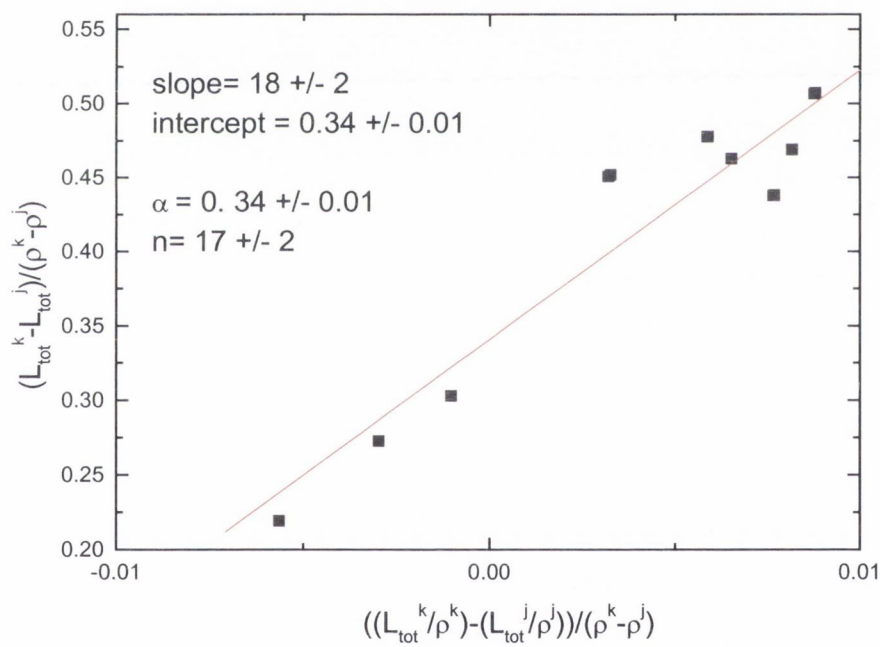


Figure 4.21: Intrinsic method determination of α and n for the binding of $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ to CT-DNA (108 μM in base, in 10 mM phosphate buffer).

The equilibrium binding association constants, K , for the equilibria

$$\text{Free ligand} + \text{free binding site} \leftrightarrow \text{bound ligand}$$

and effective binding sites size n (i.e. the number of phosphates or bases per bound metal complex) may be determined using a Scatchard plot. The results are shown in Table 4.6.

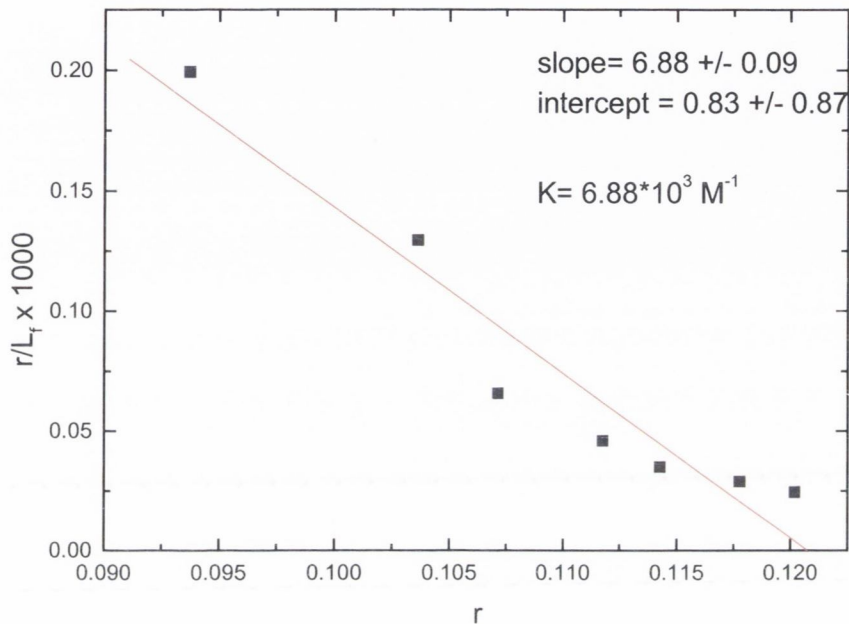


Figure 4.22: Scathard plot for the binding of $[Cr(Me_2phen)_3]^{3+}$ to DNA, using data from the final seven points in Figure 5.15, where the relationship between CD and the total ligand concentration is not a straight line through the origin.

Table 4.6: Results of binding data in 10 mM phosphate buffer at $T= 25\text{ }^{\circ}C$, equilibrium binding constants K_b and effective binding sites, n (ie number of DNA bases per metal complex)

Complex	$K_b\text{ (M}^{-1}\text{)}$	n
$[Cr(phen)_3]^{3+}$	$(8.6\pm 0.1) * 10^3\text{ M}^{-1}$	10
$[Cr(Me_2phen)_3]^{3+}$	$(6.8\pm 0.1) * 10^3\text{ M}^{-1}$	17

These values of binding constants for $[Cr(phen)_3]^{3+}$ and $[Cr(Me_2phen)_3]^{3+}$ are comparable to those reported by Barton and co-workers⁶⁷ for $[Ru(phen)_3]^{2+}$ 5500 M^{-1} at 25°C and that of 7100 M^{-1} for $[Fe(phen)_3]^{2+}$ ⁶⁸ although lower than those measured for the proven classical intercalators involving the complete insertion of the planar molecules between the base-pairs (ethidium-DNA $2*10^5\text{ M}^{-1}$)⁶⁹ even though these values have been measured in different buffers.

The binding constants of the complex $[\text{Cr}(\text{phen})_3]^{3+}$ were also determined in a range of temperature 20-30 °C and are listed in Table 4.7. They were studied in an attempt to study the thermodynamic parameters of DNA binding. A plot of the variation of the ICD change with temperature is shown in Figure 4.18.

The experimental results show that the K_b values of the complex increase with the temperature.

Table 4.7: Results of binding data for $[\text{Cr}(\text{phen})_3]^{3+}$ at different temperatures

T (°C)	<i>n</i>	K_b (M ⁻¹ base)	K_b (M ⁻¹ base pairs)
20 °C	(15.83-9.02)	4330	2165
25 °C	(10.03 –4.24)	8610	4305
30 °C	(8.76 -3.7)	12670	6335

Thermodynamic parameters

Measurements of thermodynamic parameters such as enthalpy, free energy and entropy changes, upon binding of the metal complexes to DNA are exceptionally rare. In the present study we have obtained the binding constants of the $[\text{Cr}(\text{phen})_3]^{3+}$ complex at various temperatures (see Table 4.7). This approach provides a good means of determining indirectly the thermodynamic parameters of DNA binding of the complex by using the van't Hoff plots of $\ln K_b$ versus $1/T$ in the temperature range 20-30 °C. Therefore ΔH° is obtained from the slope ($= -\Delta H^\circ/R$) under the assumption that ΔH° is independent of temperature over the range of employed temperatures. $T\Delta S$ is calculated from the Gibbs equation. ΔG° is calculated from the equation:
$$\Delta G^\circ = -RT \ln K_b \text{ (R= 8.315 joule/K mol)}$$

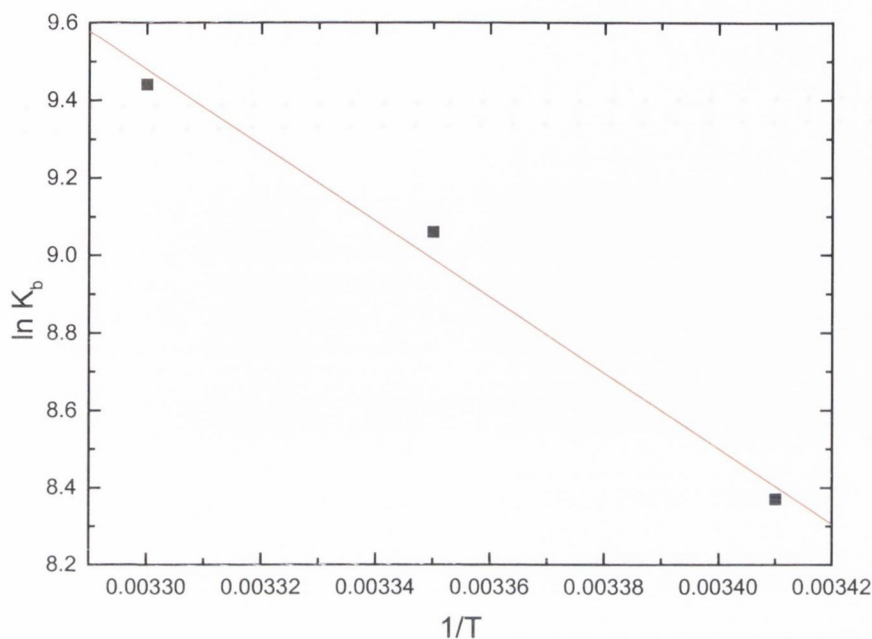


Figure 4.23. *Van't Hoff plot of $\ln K_b$ vs $1/T$ for $[\text{Cr}(\text{phen})_3]^{3+}$.*

The values found are reported in Table 4.8 and are compared with those of $[\text{Ru}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ and other DNA-binding ligands. It is understood that changes in the experimental conditions used to obtain these data will have an influence on the validity of this comparison.

Table 4.8: *Comparison of thermodynamic parameters for the racemic Cr(III) complex and other DNA-binding ligands (temp in K).*

Binding ligands	K_b (10^3 M^{-1})	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	$T\Delta S^\circ$ (kJ mol^{-1})
$[\text{Cr}(\text{phen})_3]^{3+}$	4.3 bp^{-1}	-22.45	+81.36	+103
$[\text{Ru}(\text{phen})_3]^{2+ \text{ a}}$	10 bp^{-1}	-22.8	+10.9	+33.9
$[\text{Fe}(\text{phen})_3]^{2+ \text{ b}}$	4.68 bp^{-1}	-19.7	+32.2	+54.4
Ethidium ^a	1250 bp^{-1}	-32.2	-36.8	-4.6
Daunomycin ^a	6430 bp^{-1}	-37.7	-43.5	-5.86

^a data from ref. 73; ^b data from ref 19

The enthalpy change and the entropy are both positive. These results are in agreement with what was found for the $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+19,70,71}$. Inspection of Table 4.8 shows that the DNA binding of proven intercalators like ethidium and daunomycin is driven by a large negative enthalpy value.⁷² The $[\text{Cr}(\text{phen})_3]^{3+}$ binding is entropically driven like that of the $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ but its value is larger. Therefore this confirms that there is a difference between metal centres or it maybe that the charge on the metal ion has an effect on the DNA binding. Chaires studies on the thermodynamic parameters of drug-DNA interactions revealed that for all intercalators except actinomycin, the binding enthalpy changes are large and negative.⁷³ This supports an intercalation mode of $[\text{Cr}(\text{phen})_3]^{3+}$. The value of ΔG at 25 °C is, however, 10KJ/mol less than that of proved intercalators like ethidium and daunomycin.

The molecular interaction which stabilizes the binding of the $[\text{Cr}(\text{phen})_3]^{3+}$ complex to DNA is assessed by examining the relative magnitude of the characteristic thermodynamic parameters of the DNA binding. In general electrostatic interactions exhibit small enthalpy and positive entropy changes. Hydrophobic interactions are generally indicated by positive enthalpy and entropy changes and by negative heat capacity changes. Hydrogen bonding and van der Waals interactions are usually characterized by negative standard enthalpies and entropy of interaction,⁷¹ the favourable binding free energy coming from a large $T\Delta S$ term. We observe that the pattern of the thermodynamic profile (positive enthalpy, positive entropy) is typical of that observed for “hydrophobic” interactions, in which nonpolar groups are buried and rendered inaccessible to solvent. Intercalation of the phen moiety certainly would be consistent with such a phenomenon. Disruption of bound water would be expected to contribute an unfavourable positive enthalpy but a favourable positive entropy. The signs of ΔH and ΔS are consistent with the removal of water from either the ligand or DNA or both upon binding. We conclude that entropically driven binding of $[\text{Cr}(\text{phen})_3]^{3+}$ to DNA results primarily from changes in hydration and “hydrophobic” interactions resulting from the transfer of the phen ligands from the aqueous solvents into the interior of the DNA helix.

Binding Models

While we have the thermodynamic parameters for the $[\text{Cr}(\text{phen})_3]^{3+}$ which helped in the understanding of the binding mode to DNA for that complex, for the other complexes we have to base our conclusions on the binding modes from the results available and on comparison with other complexes.

The binding mode of $[\text{Cr}(\text{Me}_2\text{phen})_3]^{3+}$ is surface bounded like the relative $[\text{Ru}(\text{TMP})_3]^{3+}$ and $[\text{Ru}(\text{DIP})_3]^{3+}$ because the two methyl groups will not favour an intercalative mode even though melting studies suggested a possible intercalative mode. As concerns the $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ we do not have sufficient data available to understand the binding mode. We can expect that the $[\text{Cr}(\text{phen})_2(\text{dppz})]^{3+}$ binding mode is intercalative by comparison with other dppz complexes. As little information is present at the moment for those complexes a more detailed study must be conducted.

4.2.3. $[\text{Fe(II)(LL)}_3]^{2+}$ complexes in absence and in presence of DNA.

The interactions of $[\text{Fe(LL)}_3]^{2+}$ complexes, where LL= dpq and dppz, represented in Figure 4.24, was studied by using UV/vis and circular dichroism (CD) spectroscopy and the results were compared with those of the parent complex, $[\text{Fe(phen)}_3]^{2+}$.

Polypyridyl complexes of Fe(II) have been previously studied by Mudasir *et al.*^{18,19}

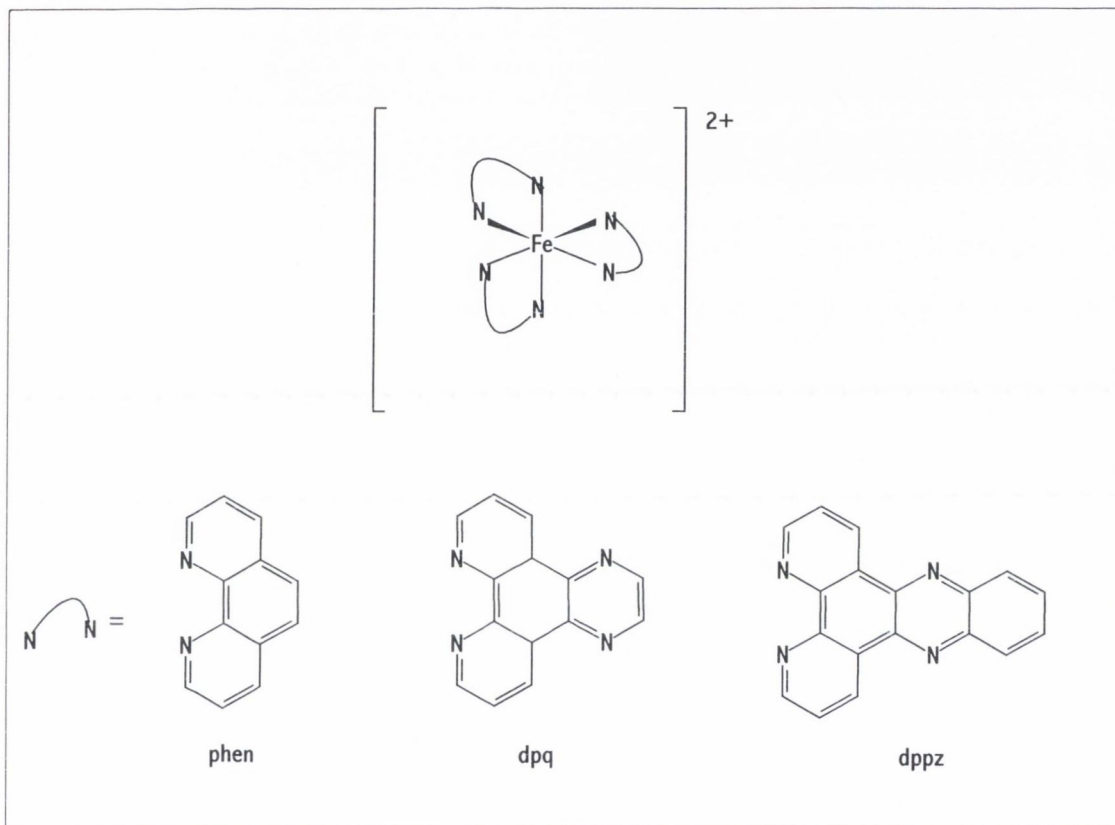


Figure 4.24: Structure of the iron(II) complexes used in this study.

Absorption titrations

The absorption spectral features of the interaction of racemic $[\text{Fe(phen)}_3]^{2+}$, $[\text{Fe(dpq)}_3]^{2+}$ and $[\text{Fe(dppz)}_3]^{2+}$ with CT-DNA in 10 mM phosphate buffer, was studied using the absorption titration method. The intense $d \rightarrow \pi^*$ MLCT bands of the iron (II) observed were measured as a function of added CT-DNA. The absorption spectra of the three complexes are reported in Figures 4.25-4.27.

Table 4.9.: Hypochromicity and red shifts for binding of iron (II) complexes to DNA.

Complex	Hypochromicity	Hyperchromicity	Red shift (nm)
[Fe(phen) ₃] ²⁺	0.02		1
[Fe(dpq) ₃] ²⁺	0.035	0.02	3
[Fe(dppz) ₃] ²⁺		0.01 –0.03	5

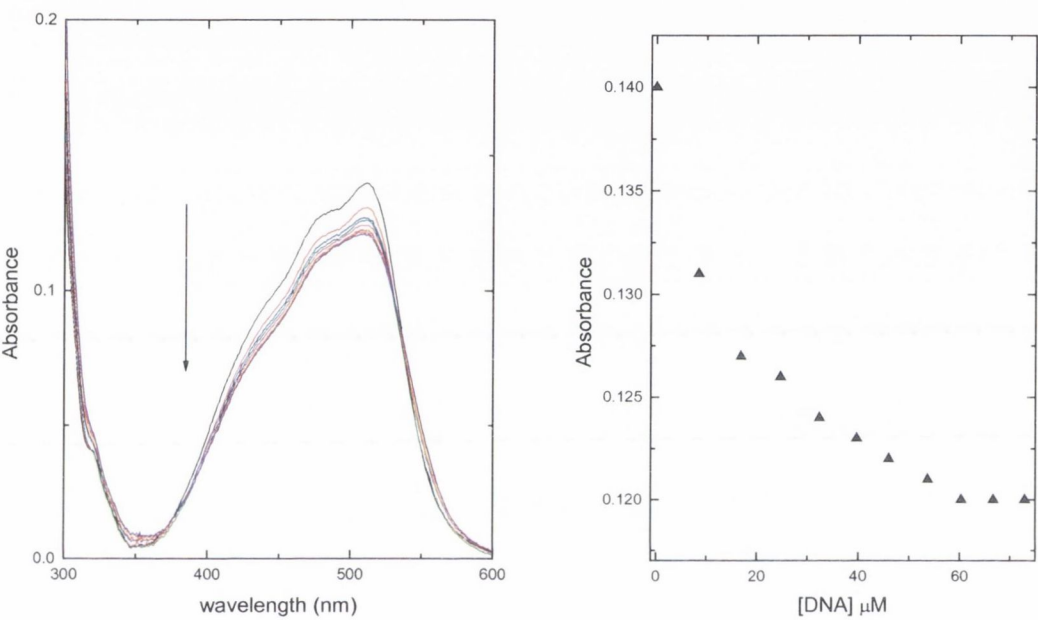


Figure 4.25: The effect of CT-DNA on the absorption spectra of a solution of [Fe(phen)₃]²⁺, 6.54*10⁻⁶ M.

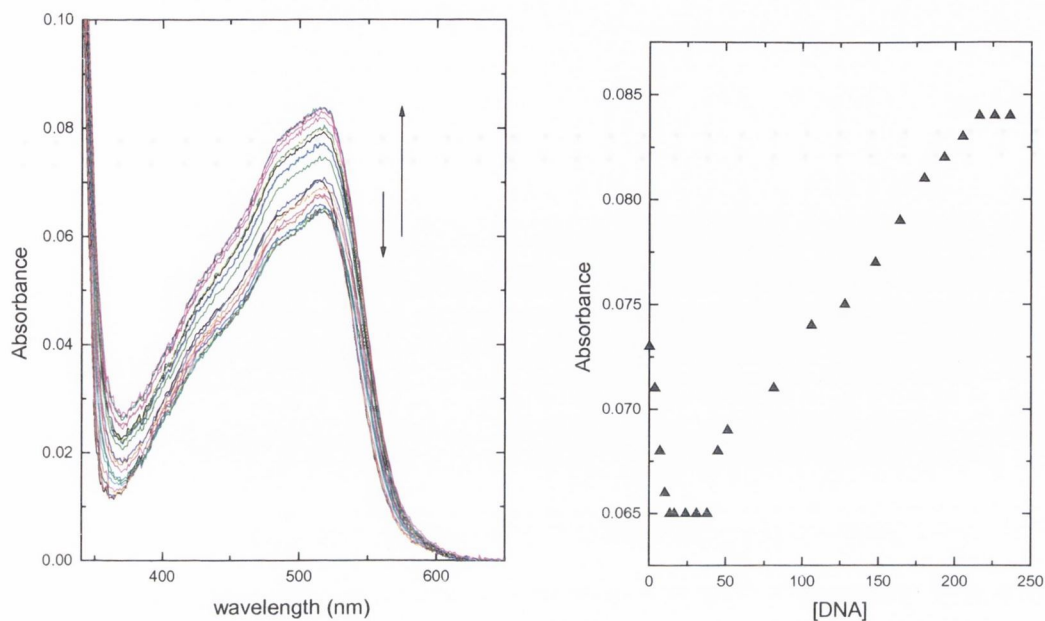


Figure 4.26: The effect of CT-DNA on the absorption spectra of $[Fe(dpq)_3]^{2+}$ 1.43×10^{-5} M in 10 mM phosphate buffer.

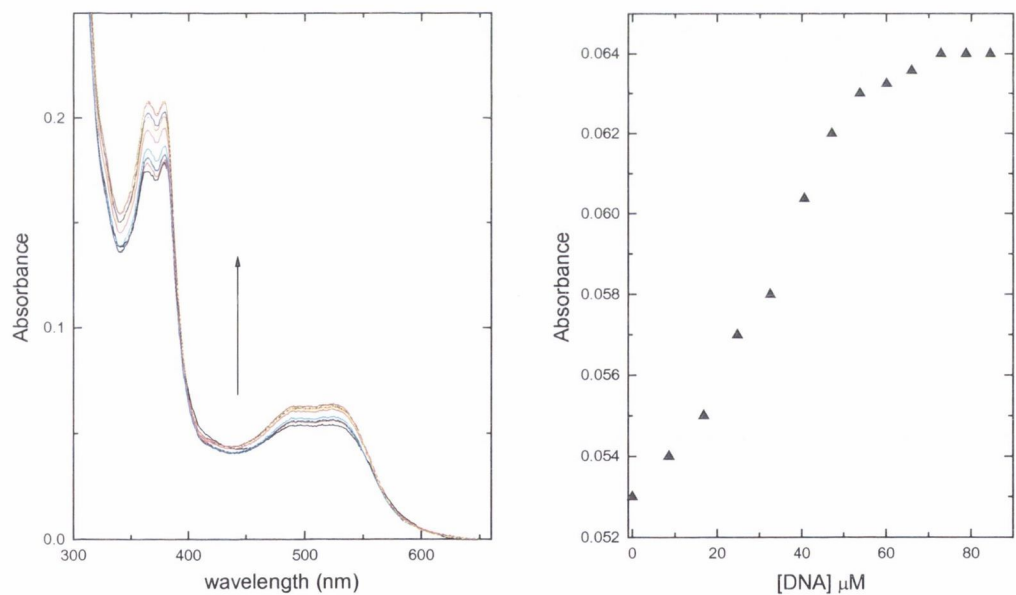


Figure 4.27: The effect of CT-DNA on the absorption spectra of $[Fe(dppz)_3]^{2+}$, 8.43×10^{-6} M.

Upon binding of the complexes to DNA three different behaviours are observed. In the UV/vis spectra of the $[Fe(phen)_3]^{2+}$ there is a decrease in absorbance, the $[Fe(dppz)_3]^{2+}$ shows an increase in absorbance while the $[Fe(dpq)_3]^{2+}$ has an intermediate behaviour, the absorbance first decreases and then increases to reach a

maximum of absorbance. A small bathochromic shift is observed for all the compounds. Isosbestic points are observed at 377 nm and 535 nm for the $[\text{Fe}(\text{phen})_3]^{2+}$ species while three isosbestic points at 396 nm, 431 and 563 nm are present for the dppz complex. It has been suggested that these characteristics, already noted for ruthenium(II) tris-chelated complexes can be attributed to a stacking interaction of the aromatic chromophore with the base-pairs of DNA. It is certain that two different binding modes are present for the $[\text{Fe}(\text{dpq})_3]^{2+}$ complex, one at low binding ratio and one at a higher binding ratio. Without any doubt the increase in size and in hydrophobicity of the latter two complexes with respect to the $[\text{Fe}(\text{phen})_3]^{2+}$ prevents any intercalations between the base pairs of DNA.

CD titrations

A strong CD develops in the UV and visible region upon addition of CT-DNA to the solution of the racemic iron(II) complexes. Figures 4.28-4.30 show the ICD spectra of the three complexes under investigation, $[\text{Fe}(\text{phen})_3]^{2+}$, $[\text{Fe}(\text{dpq})_3]^{2+}$ and $[\text{Fe}(\text{dppz})_3]^{2+}$.

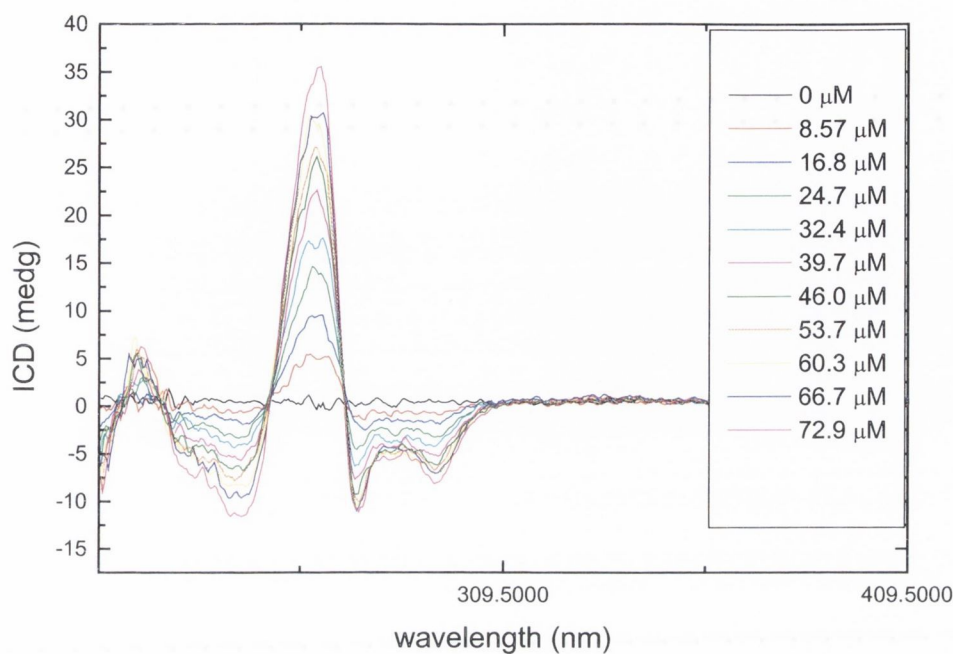


Figure 4.28: ICD spectra of a solution of $[Fe(phen)_3]^{2+}$ $6.58 \times 10^{-6} M$ upon interaction with CT-DNA at different concentration (reported in box), in 10 mM phosphate buffer.

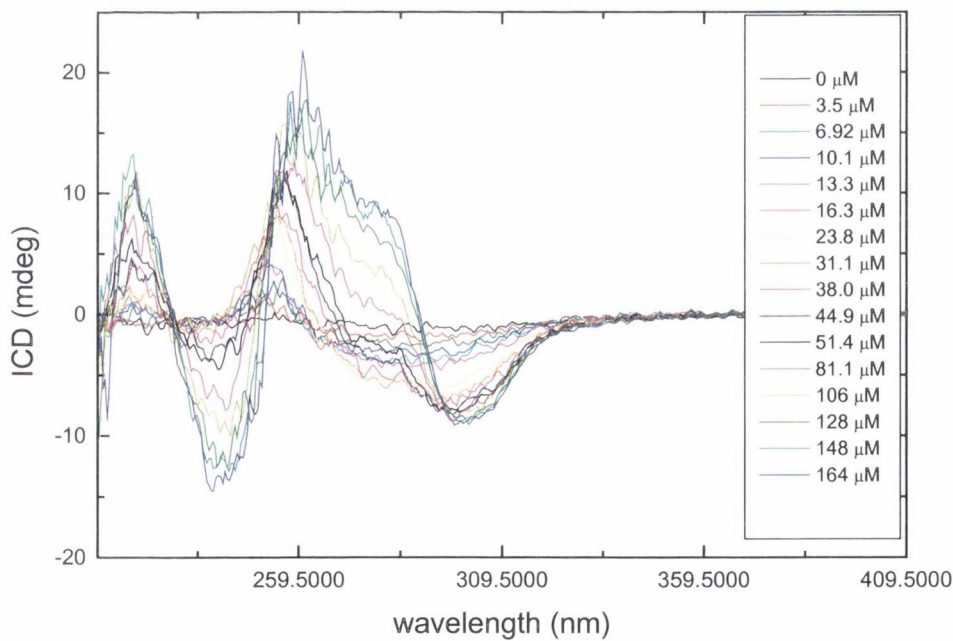


Figure 4.29: ICD spectra of $[Fe(dpq)_3]^{2+}$ $1.43 \times 10^{-5} M$ upon interaction with CT-DNA at different concentration (reported in box), in 10 mM phosphate buffer.

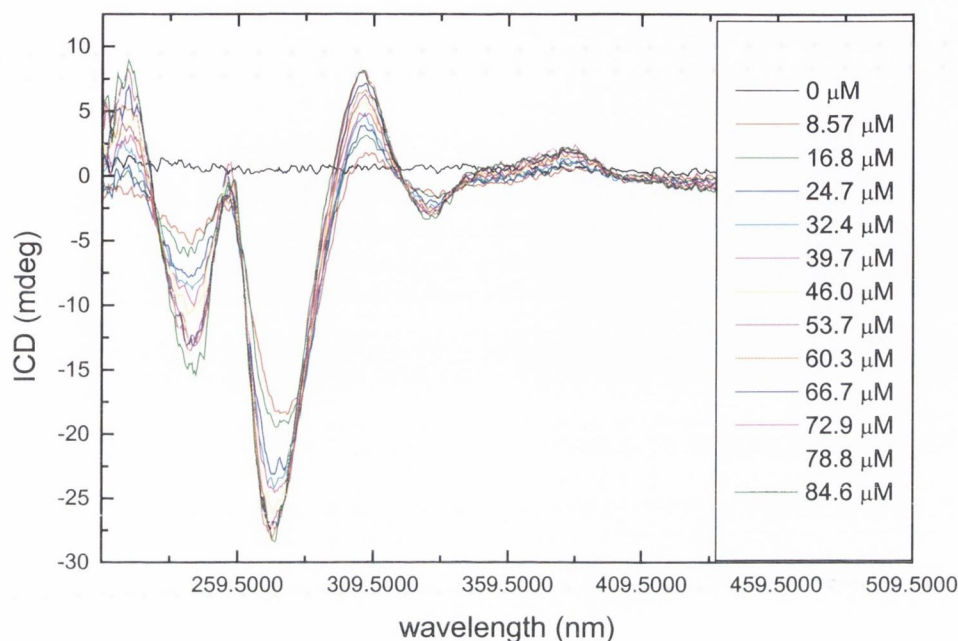
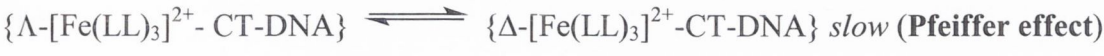


Figure 4.30: ICD spectra of $[Fe(dppz)_3]^{2+}$ $8.43 \cdot 10^{-6}$ M upon interaction with CT-DNA at different concentrations (listed in box), in 10 mM phosphate buffer.

The CD spectra of $[Fe(phen)_3]^{2+}$ have been examined previously. Our spectra look very similar to those reported by Mudasir et al.^{18,19} They show a positive peak at 263 and negative peaks at 244 and 272 nm. The spectrum was assigned to the Δ -enantiomer of the complex. The other two spectra shown are both quite strong. The intensity of the peaks is presented in Table 4.10.

We were not able to assign the spectra developed to either of the two enantiomers. This can be achieved only if the spectra of the two enantiomers are compared with the spectra developed. Iron(II) complexes are labile species, therefore the development of the CD spectra suggests that an enrichment of one of the complex-DNA diastereoisomers occurs in the solution, probably owing to a shift in the diastereoisomeric equilibria (*Pfeiffer effect*). This has revealed that a shift in the diastereoisomeric equilibrium takes place in the solution to yield an excess of one of the DNA-complex diastereoisomers. Of course no CD spectra are observed in the UV and visible regions for the free racemates. When CT-DNA is added to the racemic solution of the iron(II) complexes, it is assumed that the following equilibria take place in solution:



This effect has not been noted for the inversion stable $[\text{Ru(phen)}_3]^{2+}$, where no rearrangement process of the DNA-bound complexes from Λ to Δ -form after binding can occur. Thus the development of the CD spectra should be correlated not with the binding process but with the racemization of DNA-bound complex.

Table 4.10: Results of CD data on binding of iron (II) complexes to CT-DNA

Complex	λ_{max} (nm) ($\Delta\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)
$[\text{Fe(phen)}_3]^{2+}$	220 (29021), 244(-53036), 263(164068), 272 (-45942), 291 (-34445), 460(-602), 543 (1019)
$[\text{Fe(dpq)}_3]^{2+}$	217 (25867), 239 (-28792), 260 (25230), 299 (-18552)
$[\text{Fe(dppz)}_3]^{2+}$	219(32297), 242(-52223), 272(-101928), 304(28629), 328 (-12012), 345(1150), 380 (7445)

Equilibrium binding constants

The equilibrium binding constants for the developed CD of the iron(II) complexes were calculated using the methods previously reported. The results are reported in Table 4.11 below. The results show a binding constant for $[\text{Fe(phen)}_3]^{2+}$ of 1500 M^{-1} , quite low compared to that reported in the literature ($4600\text{-}7100 \text{ M}^{-1}$). Surprisingly low are the other two binding constants for the tris-dpq and tris-dppz complexes (one order of magnitude lower). It is possible that a different method must be used to determine the binding constants. These results must be examined better in future experiments.

Table 4.11: Results of binding data for the iron(II) complexes, $T= 25\text{ }^{\circ}\text{C}$

Complex	n	$K_b\text{ (M}^{-1}\text{)}$
$[\text{Fe(phen)}_3]^{2+}$	7.11	$1.5\cdot 10^3$
$[\text{Fe(dpq)}_3]^{2+}$	4.	$0.14\cdot 10^3$
$[\text{Fe(dppz)}_3]^{2+}$	4.07	$0.10\cdot 10^3$

4.3. Conclusions

In this chapter we have examined briefly the interactions of some chromium(III) and iron(II) complexes with DNA using mainly absorption spectroscopy and CD measurements.

$[\text{Cr(phen)}_3]^{3+}$ binds to DNA in two binding modes, while $[\text{Cr(Me}_2\text{phen)}_3]^{3+}$ has only one binding mode. The binding constants have been determined from CD data for the two homoleptic chromium(III) complexes. The constants of the two complexes are in agreement with literature values. Strong CD spectra are developed for all the three iron(II) complexes and this has been assigned to the Pfeiffer effect. The binding strength decreases in the order $\text{phen}>\text{dpq}\approx\text{dppz}$. The behaviour of $[\text{Fe(phen)}_3]^{2+}$ must be similar to that of the related chromium(III) and ruthenium(II), where a partial intercalation must be possible. At least two binding modes are present for the $[\text{Fe(dpq)}_3]^{2+}$. For the dppz complex the results did not allow us to reach any conclusion except that due to steric factors the latter two complexes will not intercalate, and they can possibly bind only in an electrostatic fashion.

We could not determine by CD the binding constants of $[\text{Cr(bipy)}_3]^{3+}$ and $[\text{Cr(Me}_2\text{bipy)}_3]^{3+}$ and we intend to do so in future experiments. Luminescence studies and lifetime measurements and also experiments with the enantiomers of such complexes are necessary to better clarify the binding models.

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Chapter 5

Synthesis of a novel rigid family of Cr(III)-Ru(II) and other metals for the investigation of electron and energy transfer

La scienza, come la poesia, si sa che sta a un passo dalla follia.

Leonardo Sciascia, *La scomparsa di Majorana*

5.1. Introduction

The synthesis and physical properties of polymetallic ligand-bridged molecular assemblies have been a topic of particular interest, motivated by their possible application to photochemical molecular devices.¹ In the last few years increasing interest in photoinduced energy and electron transfer processes in supramolecular systems has led to important progress in the design and preparation of new bridging ligands and in the development of versatile and selective synthetic strategies for the assembly of mononuclear complexes in supramolecular structures. Among polynuclear polypyridyl complexes, *metal-based dendrimers* are particularly interesting for several reasons: (i) the topography of the dendritic assembly is well-defined, an aspect which is relevant for preparing species with made-to order properties and functions; (ii) the dendritic structure allows the incorporation of a large number of metal-based subunits in a limited space, employing relatively few synthetic steps. Moreover, these systems are interesting as they are able to perform *light-induced functions*. Thus of particular interest are supramolecular species which contain chromophores and/or luminophores. The antenna-like structure of the dendrimer provides an ideal organization for such chromophores and redox centres to work in synergistic ways.

Particularly good building blocks for the construction of such supramolecular species have been polypyridyl ruthenium (II) and osmium (II) complexes because of their favourable photophysical and redox characteristics. To our knowledge, no reports

exist on Cr(III) and Ru(II) polypyridyl complexes linked together in the same supramolecular structure. The only complex in which Cr(III) and Ru(II) are present in the same molecule is a $[\text{Ru}(\text{bipy})_2(\text{CN})-\text{NC}-\text{Cr}(\text{CN})_5]^{2-}$ which has been investigated by the group of Scandola *et al.*² to perform spectral sensitisation. Spectral sensitisation is important when the light absorption properties of a potentially luminescent or photoreactive species do not permit excitation in a desired wavelength range. In this case the visible light absorption by the $[\text{Ru}(\text{bipy})_2]^{2+}$ chromophoric unit causes luminescence from the colourless $[\text{Cr}(\text{CN})_6]^{3-}$ luminophore. The device is shown in Figure 5.1 below:

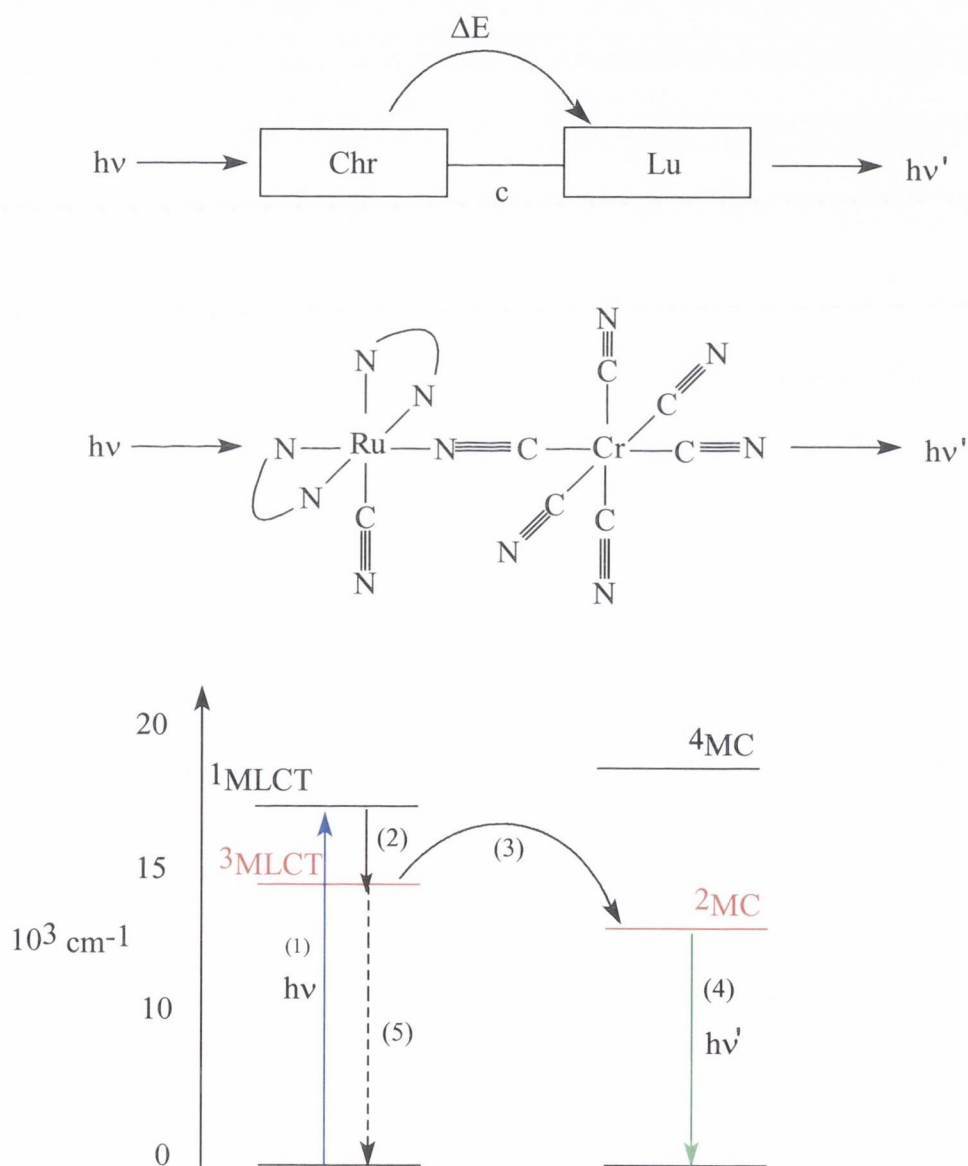


Figure 5.1: Block diagram, schematic molecular structure and energy level diagram for the $[\text{Ru}(\text{bipy})_2(\text{CN})-\text{NC}-\text{Cr}(\text{CN})_5]^{2-}$ diad performing spectral sensitization.

The steps involved are:

- (i) light excitation in the intense spin-allowed charge transfer ($^1\text{MLCT}$) bands of the Ru-based chromophore;
- (ii) complete energy conversion to the lowest spin forbidden charge transfer ($^3\text{MLCT}$) level;
- (iii) energy transfer to the metal-centred doublet (^2MC) state of the Cr-based luminophore;
- (iv) phosphorescence from the luminophore.

The energy transfer process, which occurs by an exchange mechanism, has unit efficiency and is fast enough ($k > 10^9 \text{ s}^{-1}$) to prevent radiative and radiationless deactivation within the Ru-based chromophore (step 5). It should also be noted that the efficiency of ^2MC population in the Chromophore-Luminophore device is twice that obtainable upon direct excitation of the spin-allowed quartet metal-centred (^4MC) level in the free Luminophore (L) because the $^4\text{MC} \rightarrow ^2\text{MC}$ intersystem crossing process is only 50% efficient. Furthermore, the device is photostable whereas the free L is highly photolabile because of the ^4MC reactivity. In conclusion this system provides an example not only of spectral sensitisation and bathochromic luminescence shift, but also of the antenna effect and photoprotection. The antenna effect was discussed earlier and consists of an enhanced light-sensitivity obtained by an increase in the overall cross-section for light absorption. To achieve this result, energy should be conveyed from several Chromophores to a common component that represents the interface towards use. We would expect that the same behaviour would be observed for a **Ru₃Cr** complex where the photon energy collected by the peripheral Ru-containing chromophores is conveyed to the central Cr-containing luminescent core. This device will mimic some of the features of natural photosynthetic antenna. This behaviour is well known for its Ru-Os polypyridyl complexes.³

Thus, polypyridyl complexes based on Cr(III) and Ru(II) will be very promising for their light harvesting properties which will make ideal candidates to construct antenna-like systems. Also, because the Cr(III) are paramagnetic, we would expect them to potentially behave as magneto-optical devices.

So far, the lack of synthetic routes to the formation of Cr(III) tris-chelate complexes has not allowed these metal centres to be used as building blocks for such supramolecular species.

As part of our project involving the synthesis and the study of mixed-metal chromium-ruthenium polypyridyl complexes, we have prepared polypyridyl complexes based on the fully conjugated bridging ligand *tpphz*. Most of the systems studied up to now are linear molecules in which the two remote electrophore or chromophore sites are linked by extended bridging spacers such as alkenes, alkynes or polyphenyls. However the main drawback of such bridging spacers is the possible rotation around the σ -bonds, which decreases the long-distance electronic coupling between the terminal sites by loss of coplanarity of the π -electrons or aromatic parts. The various bridging functions provide different degrees of conformational flexibility, chemical stability, and electronic communication between the metal centres. For electronic communication (energy transfer applications) and conformational stability (molecular recognition applications) the phenazine bridge has distinct advantages.

In this work we report the synthesis and characterization of three Cr(III)-Ru(II) dimers and six nanoscopic -tetramers, made up of Ru(II)-Cr(III), Ru(II)-Fe(II), Ru(II)-Co(II), Ru(II)-Co(III) and Ru(II)-Cu(II) metal centres. These complexes represent the first mixed-metal polypyridyl complexes containing both Cr(III) and Ru(II) metal centres.

Before discussing the results we will review (i) the synthetic strategies that can be employed for constructing dimers and tetramers which represent the ‘core’ of our molecules and (ii) the strategies used to extend the core and construct ‘dendritic’ species.

5.1.1.Synthetic strategies

The synthetic strategy most frequently adopted for the synthesis of dendrimers is the so-called “ complex as ligands and complex as metals” strategy, which allowed the synthesis of the luminescent and redox-active dendrimers containing the largest number of metal subunits.⁴

The ligands used are the 2,3-dpp (2,3-bis(2-pyridyl)pyrazine) and 2,5-dpp (2,5-bis(2-pyridyl)pyrazine) which are quite interesting bridging units, since they can coordinate luminescent and redox-active ML_2 building blocks ($M = Ru(II)$ or $Os(II)$; $L =$ bipyridine-type ligands). Furthermore, coordination of dpp to Ru or Os gives rise to additional chromophoric and redox centres and the homo- and heterooligometallic complexes so obtained can be used as building blocks to design larger supramolecular

species. This approach has also been used to prepare oligonuclear assemblies based on the planar-trigonally symmetric (D_{3h}) tritopic ligand HAT.⁵

Using this strategy, metal-dendrimers can be synthesized via a divergent or convergent approach. All the divergent syntheses rely on an iterative coupling of subunits and require the availability of a species carrying two types of functional groups. The divergent and convergent approaches have been discussed in the introduction.

In general, the “complexes as metals/ complexes as ligands” strategy is quite easy and straightforward. If the target is the preparation of a dinuclear homometallic complex, the synthesis is particularly easy: it is sufficient to react a complex-metal with a bridging ligand in stoichiometric ratio, as illustrated in Figure 5.2 (a).

To obtain a binuclear heterometallic complex, the usual approach involves two steps, Figure 5.2 (b): first reacting a metal precursor with an excess of ligand performs the preparation of a mononuclear complex-ligand. During this step binuclear homometallic by-products are unavoidably formed, but the desired mononuclear complex-ligand can be isolated by column chromatography. In a following step, the second metal is added, so that only the binuclear heterometallic species can be obtained.

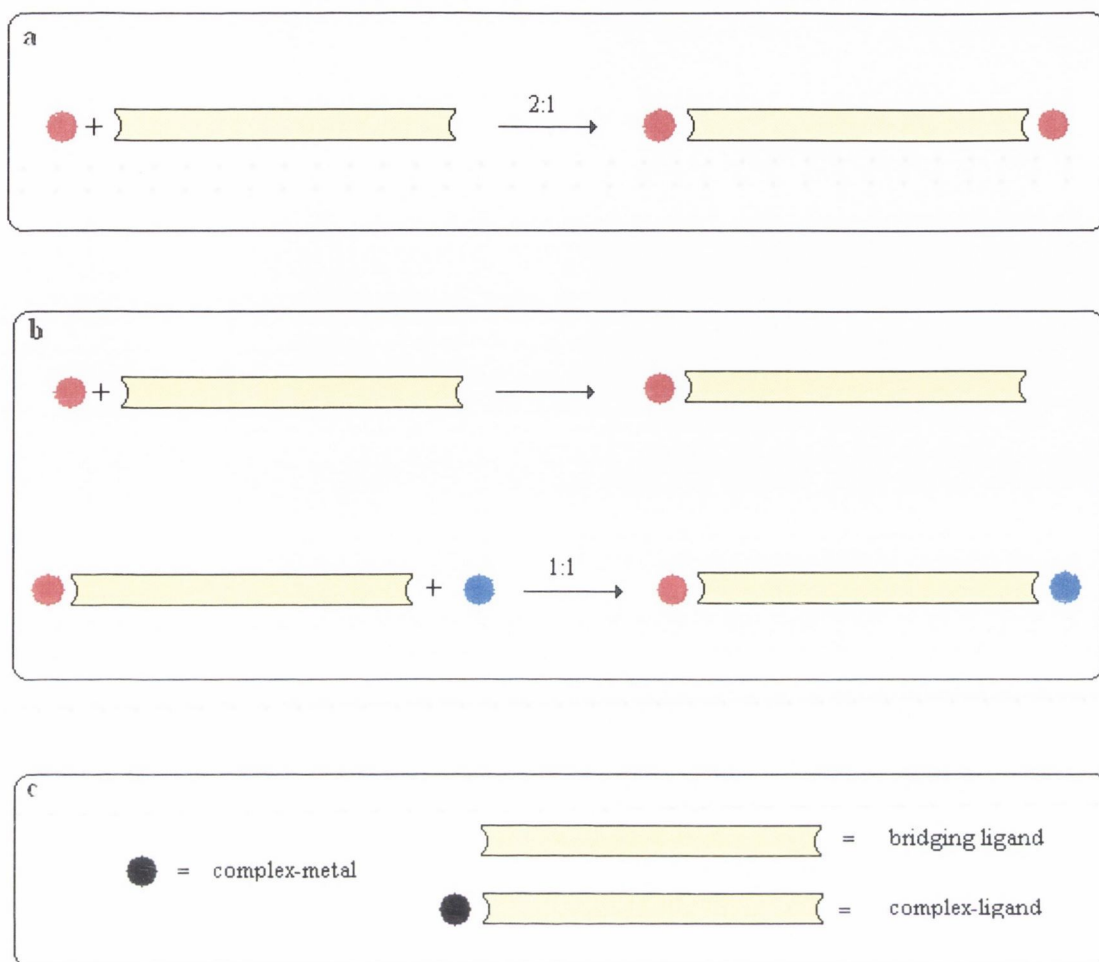


Figure 5.2: Schematic representation of the synthetic strategy used to prepare homonuclear (a), heterodinuclear complexes (b) and the symbols used to represent them (c).

Following this mechanism it was possible to synthesize species with up to 22 metal centres.

Another approach consists of reacting Ru(II) containing polypyridine ligands substituted with reactive sites and directly coupling these modules by means of high yielding organic reactions on the coordinated ligands. In this way the bridging ligand is formed during the reaction. This approach is schematised in Figure 5.3.

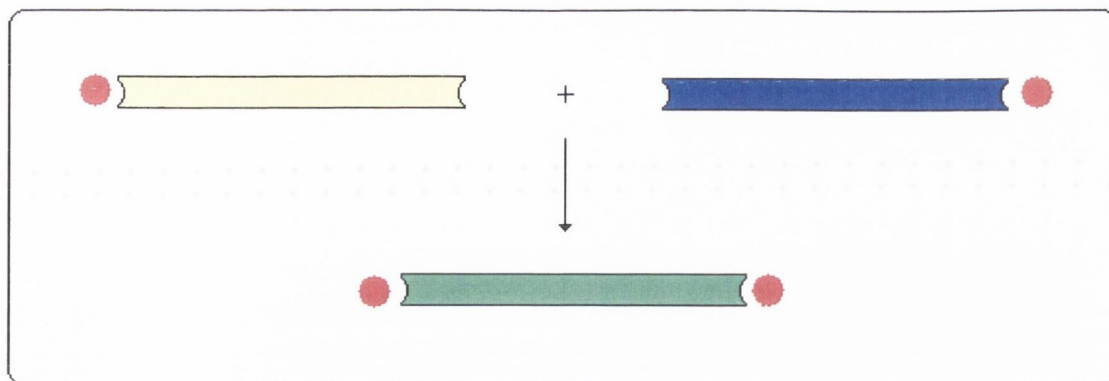


Figure 5.3: Schematic representation of the approach of connecting preformed homo-metals systems by coupling of complementary ligands.

Metallodendrimers based on tridentate polypyridine ligands, like terpy, have been prepared using this alternative strategy by Constable *et al.*^{6,7}

So, for example, the ring-forming condensation reaction between the 1,10-phenanthroline-5,6-dione and the 1,10-phenanthroline-5,6-diamine leads to a symmetric, rigid, and planar tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2'',3''j]phenazine (tpphz) bridge which has been used to link Ru(II) and Os(II) metal-centres in dinuclear complexes.⁸ In fact, it has been seen that the direct reaction of tpphz with a metal centre is very slow and the yields are low.

This method has also been employed by MacDonnell *et al.*^{9,10} for the synthesis of stereoisomerically pure Ru(II) dendrimers of the first and second generation, since the reaction takes place with retention of configuration at the metal centres and the new bridging ligand generated by the reaction does not introduce further chirality elements into the final species. The 'core' of these dendrimers was represented by binuclear and tetranuclear complexes. Thus, if we want to synthesize the binuclear species **Ru₂** we need to couple the [Ru(phen)₂(phendione)]²⁺ with the [Ru(phen)₂(phendiamine)]²⁺ as can be seen in Figure 5.4.

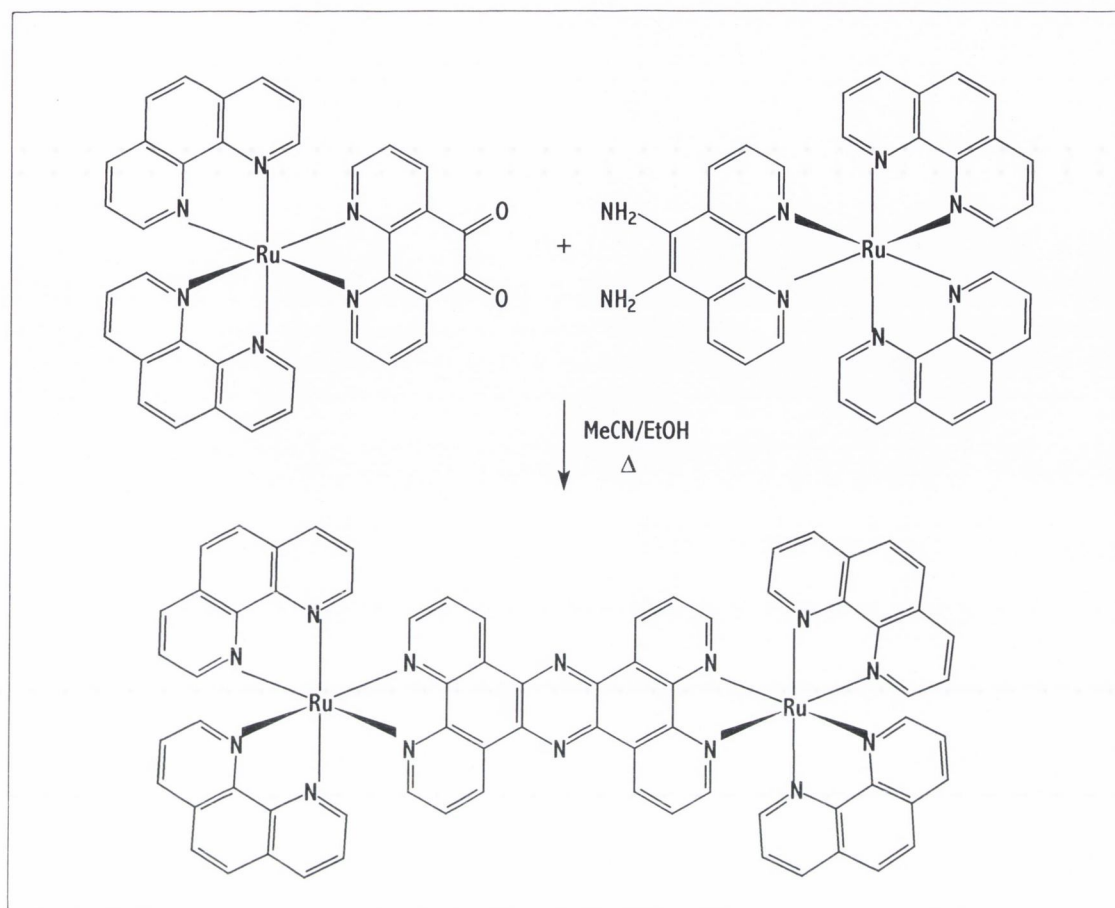


Figure 5.4: Schematic diagram of the synthesis of $[\text{Ru}_2(\text{phen})_4(\text{tpphz})]^{4+}$ (charges omitted)

In the same way, coupling of 1 equivalent of $[\text{Ru}(\text{phendione})_3]^{2+}$ with 3 equivalents of $[\text{Ru}(\text{phen})_2(\text{phendiamine})]^{2+}$ gives the tetranuclear species represented in Figure 5.5:
 $[\{\text{Ru}(\text{phen})_2(\text{tpphz})\}_3\text{Ru}]^{8+}$ (**Ru₄**)

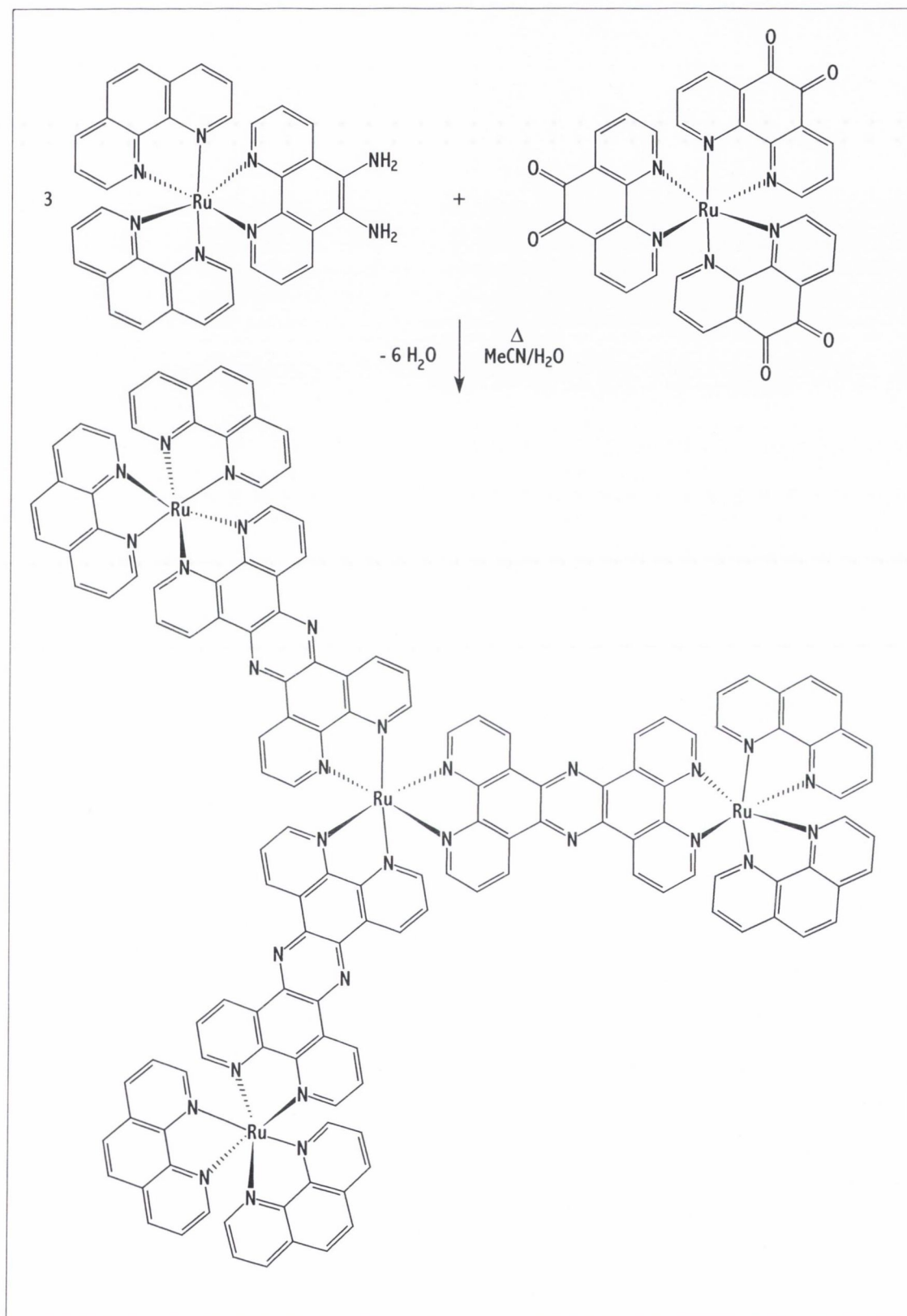


Figure 5.5: Schematic diagram of the synthesis of $[\{\text{Ru}(\text{phen})_2(\text{tpphz})\}_3\text{Ru}]^{8+}$ (charges omitted)

5.1.2. Dimers and tetramers as core molecules for dendrimers

To expand the dendrimer, we need to add further layers to the core, in a divergent way. All the divergent syntheses of dendrimers rely upon an iterative coupling of subunits and require the availability of a species carrying two types of functional groups. In the “complex as metal/complex as ligand” approach this requires a species that can behave as a complex metal or as a complex ligand. Typical dendritic syntheses utilize protecting groups at certain growth sites to prevent cross-linking reactions during generational growth reactions.¹¹

In order to build larger structures from the ‘core’ structure of dimers and tetramers used by MacDonnell and co-workers, the terminal phenanthroline groups of these molecules must be further functionalized. In fact, the unfunctionalized phenanthroline ligands can act as protected phendione which are ‘deprotected’ by selective oxidation. So, oxidation of the dimer by a mixture of sulphuric acid- nitric acid and NaBr catalyst selectively converts the 5 and 6 positions on all four 1,10-phenantrolines to form coordinated 1,10-phenanthroline-5,6-diones as shown below (Figure 5.6.)

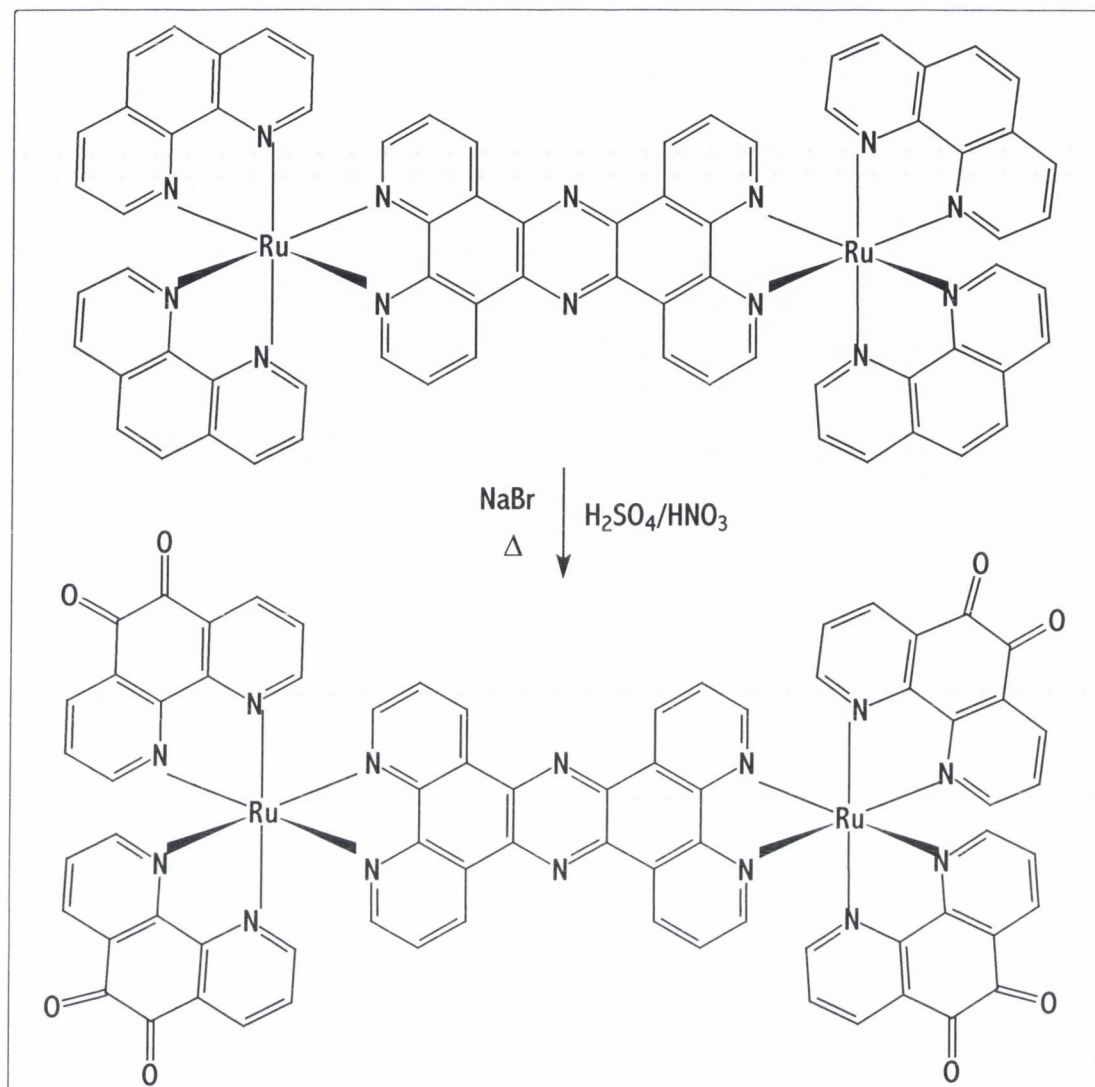


Figure 5.6: Schematic diagram showing the synthesis of $[Ru_2(phendione)_4(tpphz)]^{4+}$

Oxidation of the tetramers under similar conditions yield the $[(phendione)_2 Ru(tpphz))_3 Ru]^{8+}$ (**Ru₄**)

The oxidized dimer **Ru₂** and tetramers **Ru₄** can react with a slightly stoichiometric excess (3.4 equivalents) of $[Ru(phen)_2(phendiamine)]^{2+}$ to give the hexanuclear **Ru₆** and the decanuclear **Ru₁₀** and so we can construct bigger dendrimers.

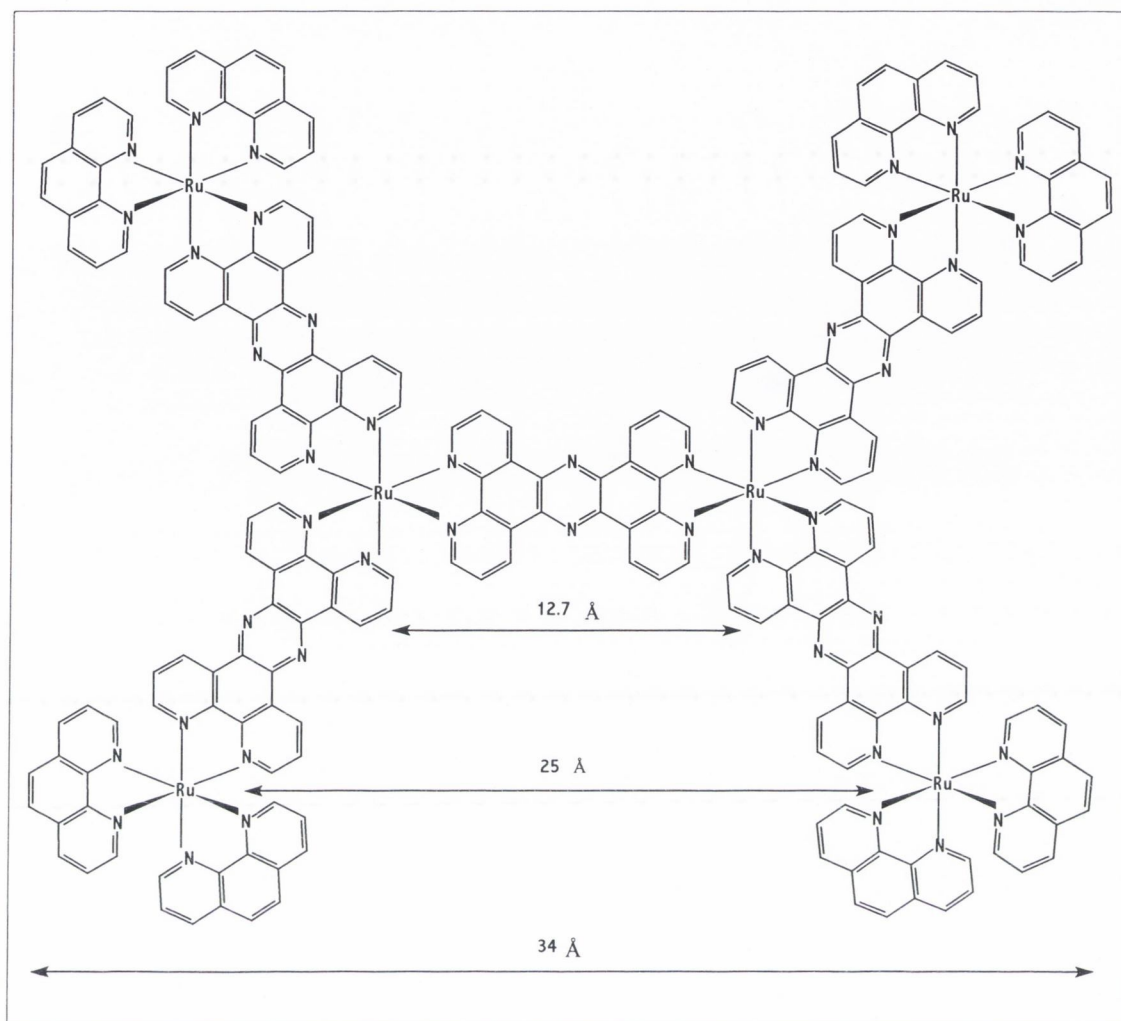


Figure 5.7: Drawing of a hexamer (charges omitted).

The advantages of using this strategy are now clear: (i) a complex of higher nuclearity is prepared in a single step by taking advantage of the complementary functionality of the reaction partners; (ii) the topography of the final structure is fully controlled, in the sense that: we can decide which metal centre to have in the central position (Mc) and in the peripheral positions (Mp) so that we can have: (i) a mixed-metal species with a central Cr(III) core and Ru(II) in the peripheral positions; or (ii) *viceversa*, a Ru(II) in the centre and Cr(III) as the peripheral metal; (iii) the third possibility will be to have all Cr(III) metal centres as both Mc or Mp. So we can decide each time which metal to include in the structure and in which order. It must be pointed out that the prerequisite for the application of this method is that ligand scrambling does not occur. In fact, both the Ru(II) and the Cr(III) polypyridine linkages are quite stable under the experimental conditions used.

5.1.3. Aims of this work

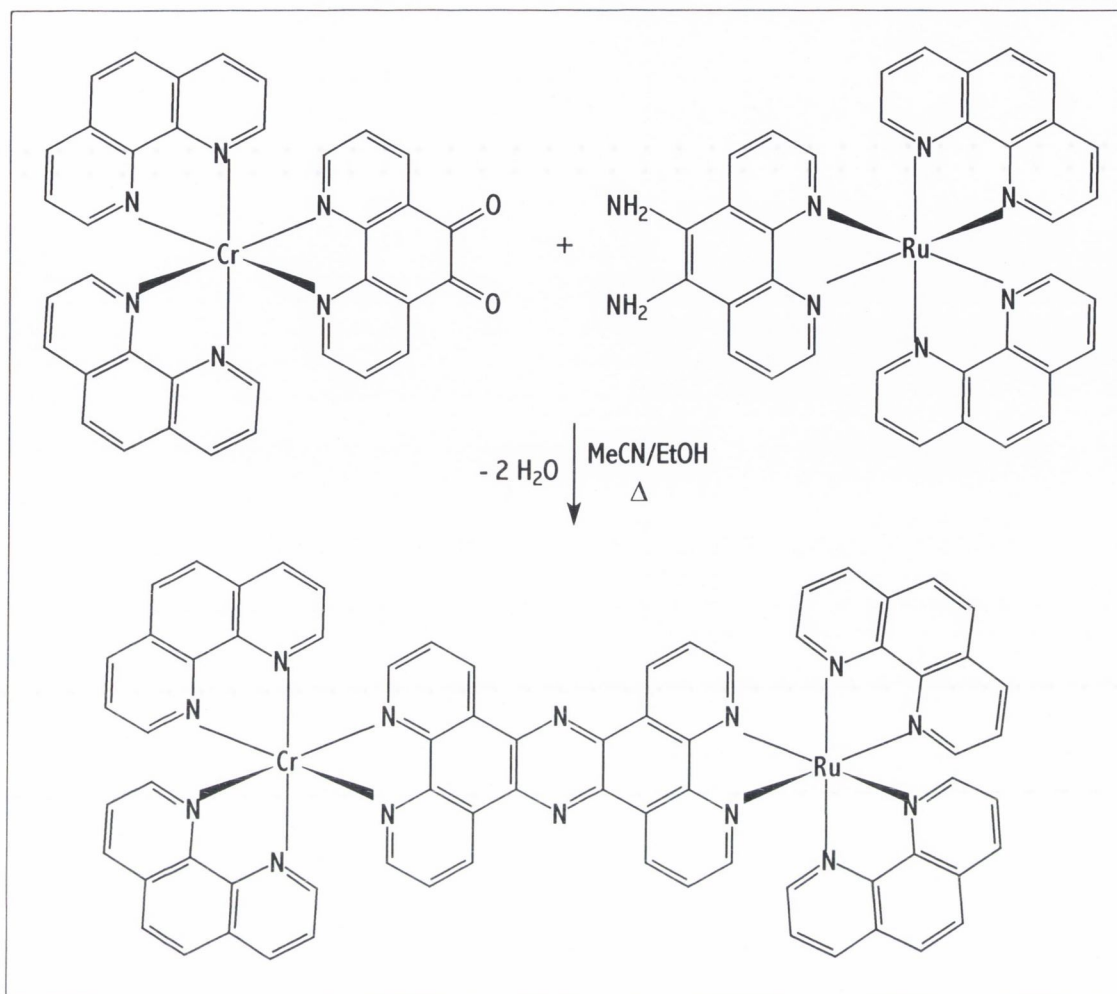
In this work, our aims were to synthesise and study binuclear and tetranuclear metal complexes where the various metal centres used are linked through the *tpphz* ligand. This will favour some degree of electronic communication between the various chromophores and redox centres with the overall structure and, because the intermetallic distance is known, will allow the determination of the rate constants of electron and energy transfer processes.

The synthesis of binuclear and tetranuclear mixed-metal species made of Cr(III) and Ru(II) was our first target and these compounds are examined here in detail. Coupling reactions between Ru(II) and other first row transition metal centres have also been carried out.

5.2. Results and Discussion

5.2.1. Synthesis

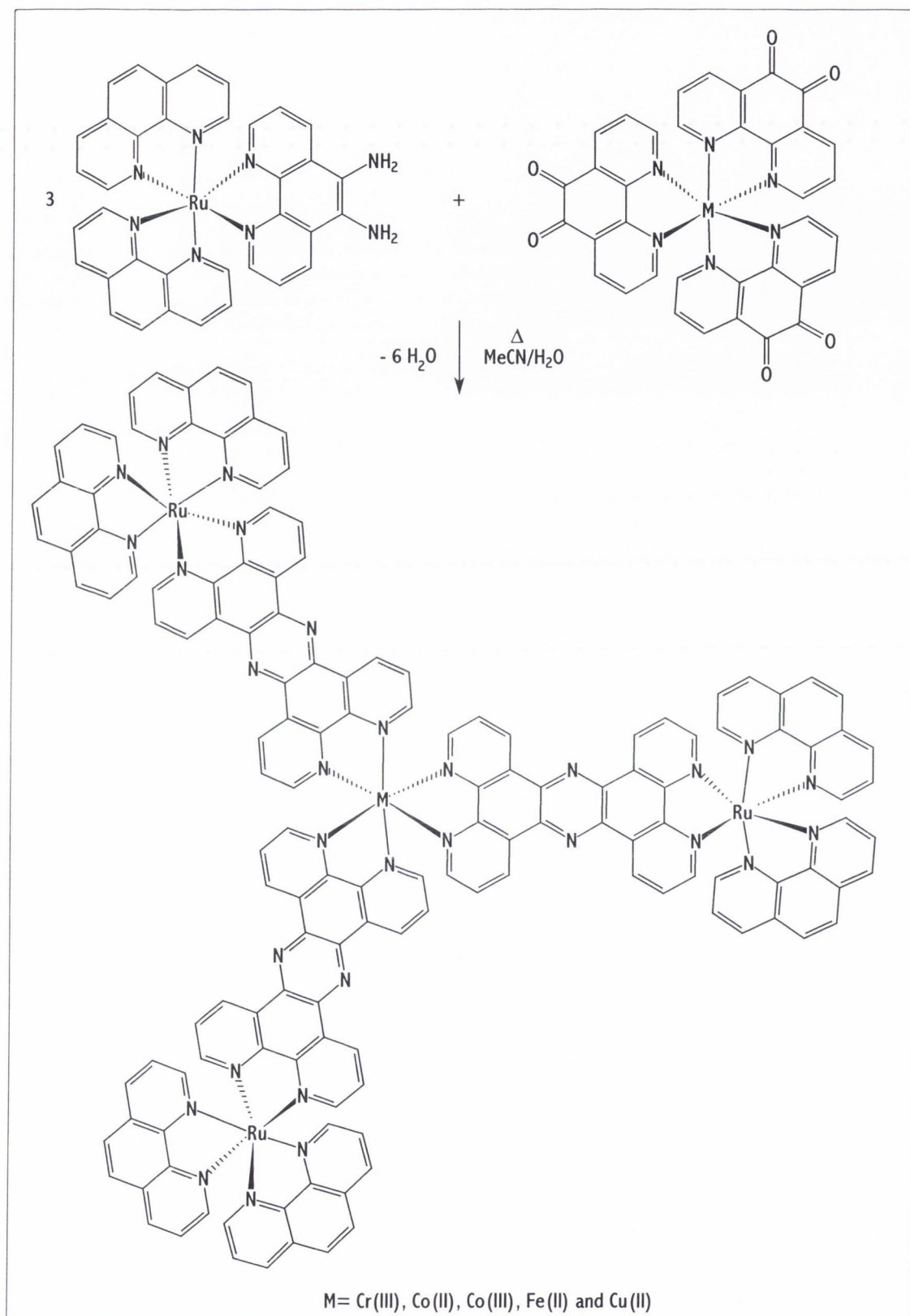
Binuclear complexes were made of Cr(III) and Ru(II) building blocks, whereas the tetranuclear complexes included both Cr(III) and Ru(II) or Ru(II) and other first row transition metal centres, namely Fe(II), Co(II), Co(III), and Cu(II). The synthetic strategy developed by MacDonnell and co-workers allows the synthesis of a wide range of ‘dendritic-type’ complexes. This strategy can be applied with extreme feasibility using preformed building blocks bearing a phendione ligand and a phendiamine ligand. A coupling reaction takes place between these two species in a mixture of MeCN/EtOH with elimination of water. For the synthesis of the binuclear complexes the starting materials were: $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$, $[\text{Cr}(\text{bipy})_2(\text{phendione})]^{3+}$ complexes, whose syntheses have been described in the experimental part, and $[\text{Ru}(\text{phen})_2(\text{phendiamine})]^{2+}$ and $[\text{Ru}(\text{bipy})_2(\text{phendiamine})]^{2+}$. The syntheses are described in Scheme 5.1:



Scheme 5.1: Synthesis of a binuclear complex, $[(\text{phen})_2\text{Cr}(\text{tpphz})\text{Ru}(\text{phen})_2]^{5+}$ (**CrRu**) (charges omitted)

The synthesis represented above is only one of the three carried out. The other two binuclear **CrRu** products obtained are: the symmetric complex $[(\text{bipy})_2\text{Cr}(\text{tpphz})\text{Ru}(\text{bipy})_2]^{5+}$ obtained by reaction of $[\text{Cr}(\text{bipy})_2(\text{phendione})]^{3+}$ with $[\text{Ru}(\text{bipy})_2(\text{phendiamine})]^{2+}$ and the asymmetric $[(\text{bipy})_2\text{Cr}(\text{tpphz})\text{Ru}(\text{phen})_2]^{5+}$ by coupling the $[\text{Cr}(\text{bipy})_2(\text{phendione})]^{3+}$ with $[\text{Ru}(\text{phen})_2(\text{phendiamine})]^{2+}$. A planar tpphz ring is formed along the C_2 axis between the two metal centres. These complexes have a maximum of 2^2 isomers. Two D_2 $\Lambda\Lambda$ and $\Delta\Delta$ enantiomers and the C_{2h} *meso* $\Lambda\Delta$ complex can be formed for the symmetric complex. The asymmetric complex has an additional $\Delta\Lambda$ isomer. As these complexes were synthesized from racemic starting material, the final products consist of a statistical mixture of all the isomers. All the products were precipitated as PF_6^- salts.

The synthesis of the tetranuclear complexes is described in Scheme 5.2.



Scheme 5. 2: Synthesis of tetranuclear 'dendritic-type' species (charges omitted)

In this case, the metal complex-building blocks, $[M(\text{phendione})_3]^{3+}$, where M = Cr(III), Fe(II), Co(II), Co(III) and Cu(II), and 3.2 equivalents of $[\text{Ru}(\text{phen})_2(\text{phendiamine})](\text{PF}_6)_2$, or $[\text{Ru}(\text{bipy})_2(\text{phendiamine})](\text{PF}_6)_2$, synthesized as

described in the experimental part, are linked along the 2-fold axes of the complexes using condensation reactions between the *o*-diamine and *o*-dione functions to form a pyrazine ring between complexes. The result is a rigid D_3 -symmetric trigonal-propeller-shaped molecule. Theoretically, the product has a maximum of 2^4 isomers which in this case is lowered to 8 due to the trigonal symmetry. The complexes are obtained as a statistical mixture of isomers, i.e. the racemic product was obtained from reaction of the racemic starting materials. Because the ring formation gives a planar-symmetric (D_2) tpphz ligand the symmetry of the monomer's 2-fold axes is maintained and rotational and conformational motion is restricted.

Each phenazine-coupling reaction is 95 % efficient. The crude products are relatively pure and usually reprecipitation from MeCN/Ether was sufficient to purify the binuclear species, the main impurity of the tetranuclear species being the appearance of the dimer which is known to be a side product in this type of reactions.⁹ This product has been explained by oxidative formation of $[\text{Ru}(\text{phen})_2(\text{phendiamine})]^{2+}$ which couples with itself to give the dimer $[\text{Ru}(\text{phen})_4(\text{tpphz})]^{4+}$ and NH_3 . In this case it was not possible to purify the tetramers by standard chromatography (silica or alumina); however, they were purified by size exclusion chromatography using lipophilic Sephadex LH-20 column with acetonitrile as eluent. After purification the isolated yields are typically between 50 and 60 %. The products are soluble in acetonitrile and acetone as the hexafluorophosphate salt and in water, methanol and ethanol as the choride salt.

All the products have been characterized by IR, UV/Vis, microanalysis and NMR, where possible.

5.2.2. Absorption spectra

All the complexes were stable in the solvents used as confirmed by the fact that the absorption spectra were constant within one week.

The absorption spectra of some representative complexes studied are represented in Figure 5.8 and Figure 5.9. The absorption bands in the visible can be assigned to spin-allowed MLCT transitions, whereas the absorption bands in the UV are assigned to LC transitions. The spectra shapes are qualitatively similar to those of the corresponding binuclear and tetranuclear Ru(II) complexes studied by Campagna *et al*¹². Such assignments are based on the energies and intensities of the bands when compared to the other MLCT and LC bands of Ru(II) polypyridine complexes. In particular, the two sharp absorption peaks in the region 350-380 nm which are present in the compound containing tpphz can be assigned to transitions centered on this ligand, namely $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions^{8,13} (such bands are in fact absent from the spectra of $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ and $[\text{Ru}(\text{phen})_2(\text{phendiamine})]^{2+}$, in agreement with results reported for other tpphz-containing complexes. The MLCT bands contain different transitions, also owing to the heteroleptic nature of most of the complex, so that a detailed discussion of the contributions to this band is also prevented. Usually these are due to the $\text{Ru} \rightarrow \text{phen}$ and $\text{Ru} \rightarrow \text{tpphz}$. The spin-allowed bands typical of Cr(III) are obscured under the intense LC bands. A weak band is also present at around 705 nm, which can be assigned to interligand transitions.

Within the tpphz-series of complexes, the extinction coefficients throughout the whole UV and visible region increases with the number of metal based chromophores while the profiles of the absorption spectra are quite similar, as can be seen comparing the spectra of Figures 5.8 and 5.9 (Tables 5.1 and 5.2). Peak molar extinction coefficients for these complexes approximate the values anticipated simply by adding up the extinction values for four independent chromophores. For example, the molar extinction coefficient at 434 nm for the binuclear complex $[(\text{phen})_2\text{Cr}(\text{tpphz})\text{Ru}(\text{phen})_2]^{5+}$ is $21000 \text{ M}^{-1} \text{ cm}^{-1}$ while for the tetranuclear $[\text{Cr}\{\text{Ru}(\text{phen})_2(\text{tpphz})\}_3]^{9+}$ it is $60000 \text{ M}^{-1} \text{ cm}^{-1}$, ie the value is proportional to the number of Ru(II) centres present. This is in agreement with what was observed by MacDonnell *et al*¹² and with the corresponding value of $19700 \text{ M}^{-1} \text{ cm}^{-1}$ for $[\text{Ru}(\text{phen})_2(\text{tpphz})]^{2+}$ while for $[\text{Cr}(\text{phen})_2(\text{tpphz})]^{3+}$ $\epsilon_{434} \sim 2000 \text{ M}^{-1} \text{ cm}^{-1}$.

This demonstrates that each chromophore contributes with its own properties to the overall absorption and hence that cross absorption increases with the number of chromophores, as is usual in multimetallic systems featuring little interaction between subunits.

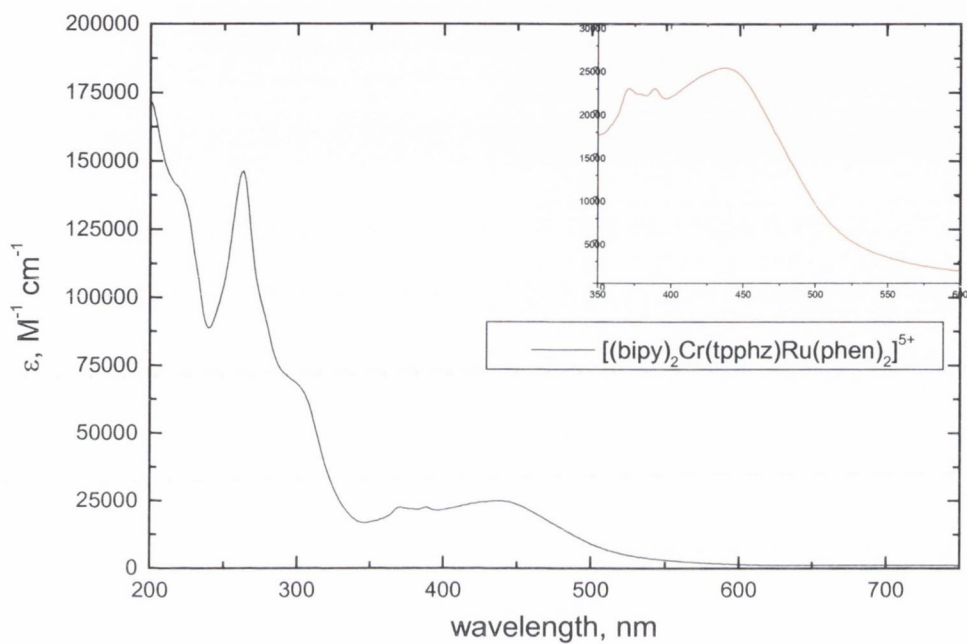


Figure 5.8: *UV/Vis of a binuclear complex, [(bipy)₂Cr(tpphz)Ru(phen)₂]⁵⁺ in MeCN solution.*

Table 5.1: *Absorption data of binuclear species in MeCN.*

Compound ¹	$\lambda_{max}, nm (log\epsilon, M^{-1} cm^{-1})$
$[(phen)_2Cr(tpphz)Ru(phen)_2]^{5+}$	223 (5.11), 263 (5.14), 377(4.26), 437 (4.32), 710 (3)
$[(bipy)_2Cr(tpphz)Ru(phen)_2]^{5+}$	221 (5.14), 262 (5.16), 303 (4.81), 370 (4.35), 388 (4.33), 436 (4.39), 707 (3.05)
$[(bipy)_2Cr(tpphz)Ru(bipy)_2]^{5+}$	243 (4.76), 285 (4.76), 305 (4.63), 373 (4.023), 435 (4.04)

¹ as PF₆⁻ salt

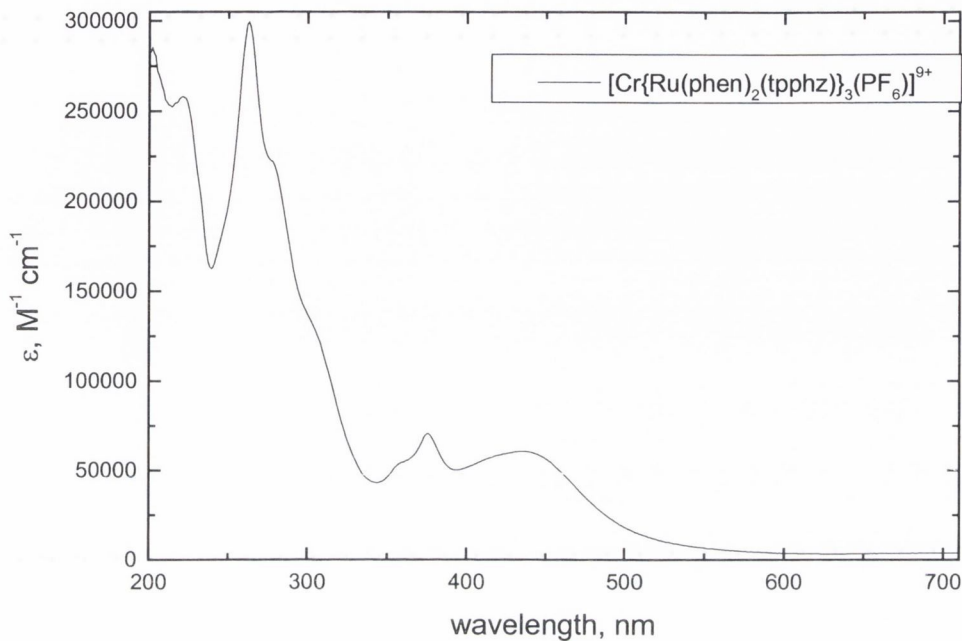


Figure 5.9: UV/Vis spectra of tetranuclear species, $[Cr(III)\{Ru(phen)_2(tpphz)\}_3]^{9+}$ as PF_6^- salt in MeCN.

Table 5.2: Absorption data of tetranuclear complexes in MeCN.

Compounds ¹	λ_{max} , nm (log ϵ , $M^{-1} cm^{-1}$)
$[Cr(III)\{Ru(phen)_2(tpphz)\}_3]^{9+}$	202 (5.45), 221 (5.41), 262 (5.47), 278 (5.34), 304 (5.11), 375 (4.84), 434 (4.78), 702 (2.84)
$[Fe(II)\{Ru(phen)_2(tpphz)\}_3]^{8+}$	223 (5.38), 261 (5.47), 291 (4.97), 308 (4.76), 376 (4.57), 437 (4.72), 746 (2.89), 779 (2.79)
$[Co(II)\{Ru(phen)_2(tpphz)\}_3]^{8+}$	222 (5.45), 263 (5.51), 371 (4.56), 437 (4.72), 718 (3.45)
$[Co(III)\{Ru(phen)_2(tpphz)\}_3]^{9+}$	222 (5.45), 261 (5.53), 306 (4.92), 377 (4.65), 436 (4.75)
$[Cu(II)\{Ru(phen)_2(tpphz)\}_3]^{8+}$	221 (5.36), 261 (5.47), 304 (4.85), 373 (4.58), 436 (4.70), 691 (3.22)
$[Cr(III)\{Ru(bipy)_2(tpphz)\}_3]^{9+}$	244 (5.14), 252 (5.13), 284 (5.32), 306 (4.95), 439 (4.69), 748 (3.15), 778 (3.06)

¹ as PF_6^- salt

5.2.3. NMR studies

The ^1H and ^{13}C NMR were examined for the complexes formed. As can be seen from the ^1H NMR in Figure 5.10 for the **CrRu₃** complex the signals are quite broad because of the paramagnetism of chromium(III) which has a d^3 electronic configuration. Therefore a clear interpretation of this spectrum seems impossible.

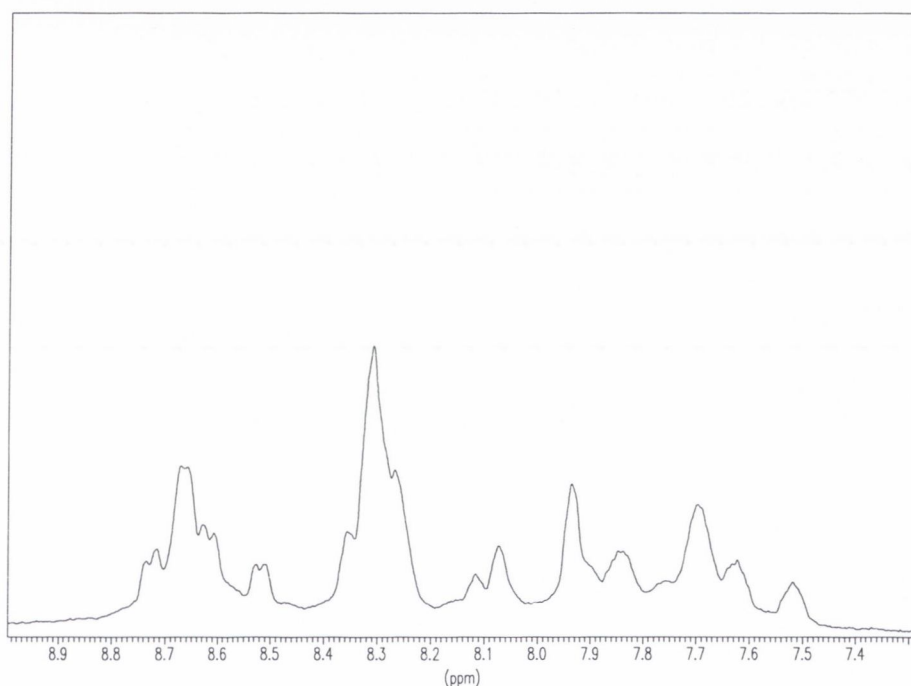


Figure 5.10. ^1H NMR of $[\text{Cr(III)}\{\text{Ru}(\text{phen})_2(\text{tpphz})\}_3](\text{PF}_6)_9$ (400 MHz, CD_3CN)

Among all the complexes synthesized, Co(III) and Fe(II) have a d^6 electronic configuration and, being in a low spin configuration, are not paramagnetic. The 1D and 2D ^1H NMR of the **Co(III)Ru₃** and **Fe(II)Ru₃** complexes can be analysed (only that of Co(III) is shown). The 1D and 2D COSY NMR are provided in Figures 5.11 and 5.12. The D_3 symmetry for the compound is clearly evident in the NMR data. Of the 84 H atoms in the structure, only 14 are symmetrically inequivalent and only 10 are magnetically inequivalent. The proton assignments, shown in Figure 5.11, are based on the coupling patterns established by COSY spectra and by comparison with related compounds.

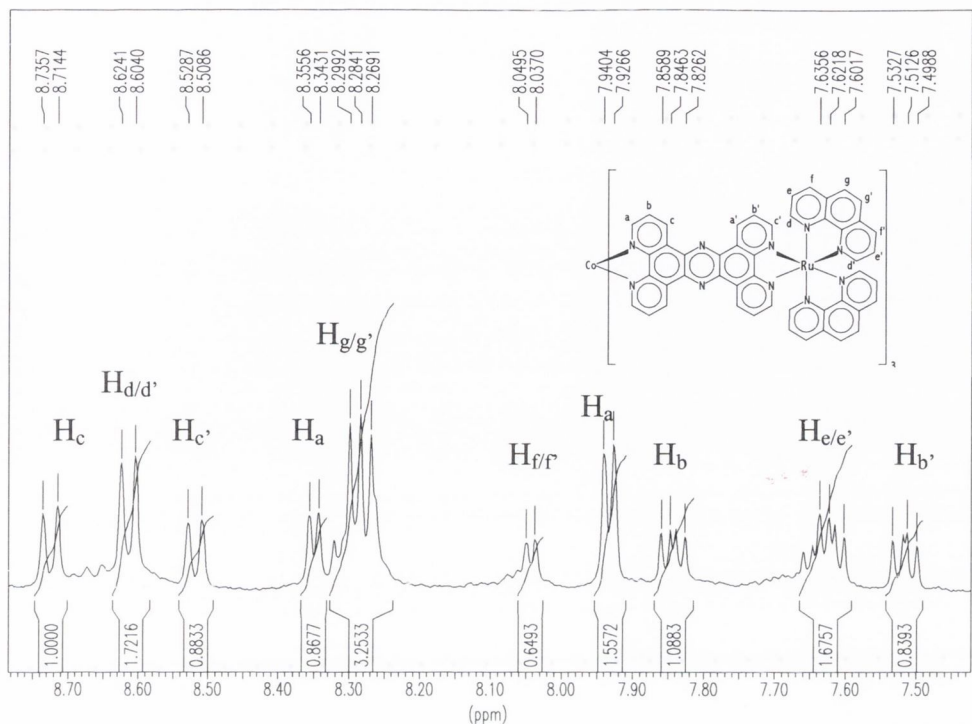


Figure 5.11: ^1H NMR of $[\text{Co(II)}\{\text{Ru(phen)}_2(\text{tpphz})\}_3](\text{PF}_6)_8$

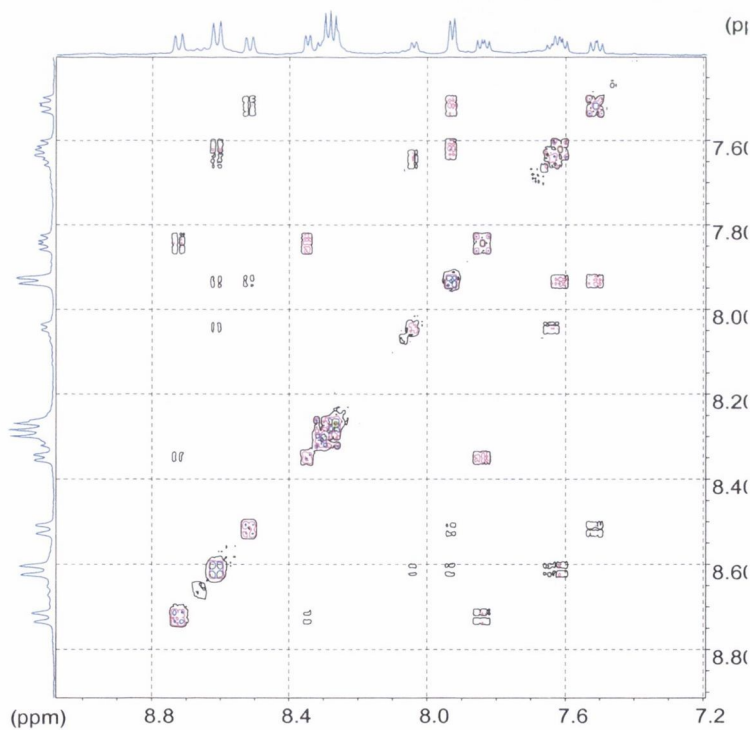


Figure 5.12: ^1H , ^1H COSY NMR of $[\text{Co}\{\text{Ru(phen)}_2(\text{tpphz})\}_3](\text{PF}_6)_9$

The tpphz inner (H_a , H_b , H_c) and outer protons ($\text{H}_{a'}$, $\text{H}_{b'}$, $\text{H}_{c'}$) are examined first. COSY data reveal two AMX-coupled sets, with peaks respectively at δ 8.72 (d), 8.34 (d), 7.84 (dd), and at 8.51(d), 8.28 (d) and 7.53 (dd) ppm. In general, the doublets

furthest downfield can be attributed to the protons H_c and $H_{c'}$, followed by H_a and $H_{a'}$ and upfield we can find the H_b and $H_{b'}$. My assignments were supported by coupling constants. The integration of $H_{a'}$ at δ 7.94 ppm is the only inconsistency with this assignment. The assignment of the phen protons is more complicated. The doublet at 8.28 ppm does not couple with any other proton and can be definitely attributed to the protons H_g and $H_{g'}$ which are known to couple as an AB doublet in related systems. There is a broad doublet or triplet under the signal at 8.34 ppm. Another AMX-coupled set has peaks respectively at 8.61 (d), 8.03 (d) and 7.62 (m) and must correspond to the protons $H_{d/d'}$, $H_{f/f'}$ and $H_{e/e'}$. In order to do a full assignment we would need a TOCSY or a nOe.

5.2.4. Molecular modelling studies

Molecular modelling studies have been carried out for the binuclear $[(\text{phen})_2\text{Cr}(\text{tpphz})\text{Ru}(\text{phen})_2]^{5+}$ (**CrRu**) and for the tetranuclear $[\text{Cr}\{\text{Ru}(\text{phen})_2(\text{tpphz})\}_3(\text{PF}_6)_9]$ (**Ru₃Cr**) (shown in Figures 5.13 and 5.14) and also for the hexanuclear and decanuclear second-generation complex, which can be formed by adding another layer to the formed ‘core’ molecules (Figures 5.15 and 5.16). These models were built starting from the crystal structures of $[\text{Cr}(\text{phen})_3]^{3+}$ and $[\text{Ru}(\text{phen})_3]^{3+}$, and using the Hyperchem program to assemble the structure and to perform a semi-empirical energy minimization.

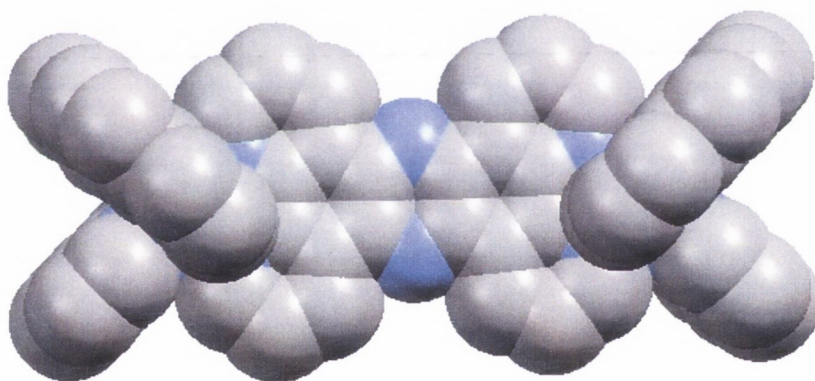


Figure 5.13: *Computer generated molecular model of the binuclear complex CrRu*

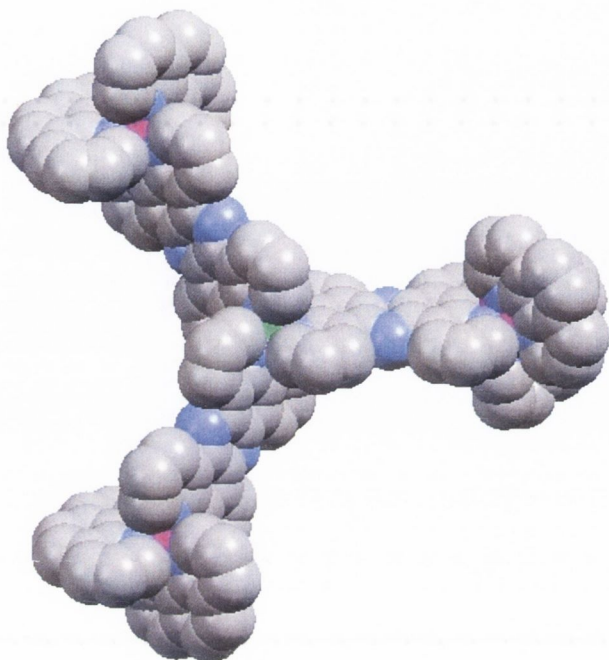


Figure 5.14: Computer generated molecular model of the tetranuclear complex **CrRu₄**. (*Ru_{terminal}* are displayed in red, Cr in green, N in blue).

The Cr-Ru distance in the binuclear complex (**CrRu**) is 12.52 Å against a distance of 12.7 Å calculated for the Ru-Ru distance by MacDonnell. For the tetranuclear complex **CrRu₃** the distance between Ru_{terminal}-Ru_{terminal} is 21.45 Å against 23 Å calculated by MacDonnell for the **Ru₄** tetramer. Therefore these molecules are truly nanoscopic.

Some slight bending and twisting of the tpphz bridge was observed which gives the tetranuclear complex a quite marked propeller shape.

Some considerations can be also made of the stereochemistry of these molecules.

Metallo-dendrimers constructed of D_3 -symmetric $[M(\text{diimine})]^{2+}$ units exhibits tremendous stereochemical complexity arising from the local chirality (Δ or Λ) of each metal centre.⁹

As seen before, in Scheme 5.1, coupling between the $[\text{Cr}(\text{phen})_2(\text{phendione})]^{3+}$ and $[\text{Ru}(\text{phen})_2(\text{phendiamine})]^{2+}$ gives a dimer. By using enantiopure synthons, the two D_2 symmetric $\Lambda\Lambda$ and $\Lambda\Delta$ enantiomers and the C_{2h} symmetric meso complex, $\Delta\Lambda$ can be synthesized directly.

Coupling between three $[\text{Ru}(\text{phen})_2(\text{phendiamine})]^{2+}$ and $[\text{Cr}(\text{phendione})_3]^{3+}$ yields the tetranuclear structure also shown in Scheme 5.2. Because all three C_2 axes of the $[\text{Cr}(\text{phendione})_3]^{3+}$ are symmetrically substituted the dendritic tetramer captures the full symmetry of the building blocks. The four diastereoisomers, $\Delta_3\Delta$, $\Delta_3\Lambda$, $\Lambda_3\Delta$, and $\Lambda_3\Lambda$ represent all of the D_3 symmetric isomers possible for the tetramer.

Stereochemical composition is expected to result in large changes in the topochemistry of these products which can be revealed by molecular modelling calculations. It is shown that adjacent metal centres, like chromium and ruthenium in our case, must have an alternating Δ and Λ stereochemical composition to keep the molecule approximately planar. But, from the molecular models for both the hexamer and the decamer complex, if the molecule remains planar then steric crowding may prevent further dendritic growth. By inspections, it is obvious that both the hexamer and the decamer have deep molecular clefts which are defined by the dendritic arms of the complex. In fact, due to the structure both complexes have multiple molecular clefts which are topologically identical and due to the rigid structure precisely defined. Ultimately, it is hoped that these molecular clefts may serve as 'binding pockets' or 'endoreceptor sites' for chiral recognition.

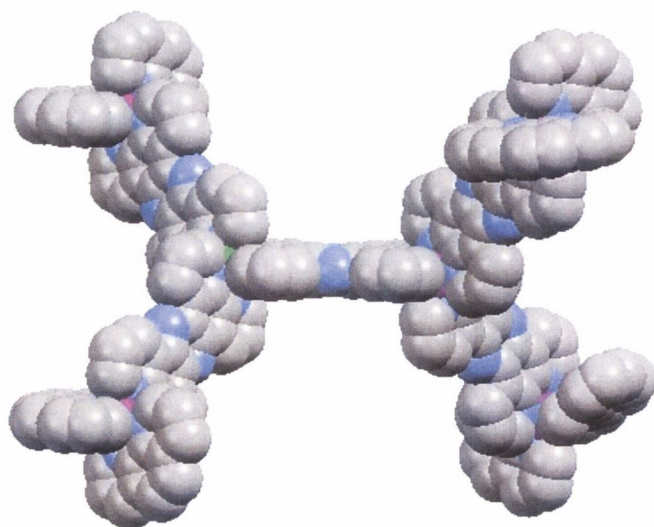


Figure 5.15. Computer generated model of second-generation dendrimer (**CrRu5**).

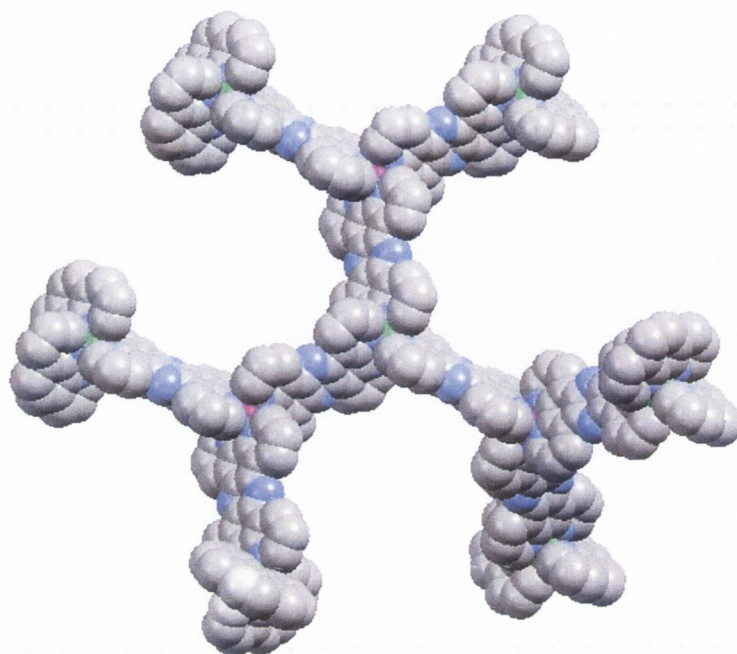


Figure 5.16: *Computer generated molecular model of Cr-Ru of next generation dendrimers (Ru₃Cr₇).*

5.3.Conclusions

The syntheses described here demonstrate the possibility of using coupling reactions between coordinated ligands to achieve the synthesis of multinuclear metal complexes. The advantages of this method are that the syntheses are quite simple, give high yield, the condensation reaction takes only a few hours to complete, the tpphz ligand formed is symmetrical, rigid and stable and provides an electronic conduit between metal centres and by a careful choice of the metal centres and the peripheral ligands used, allow the construction of a variety of species. By extending the pyrazine coupling reaction along all three axes of the homoleptic monomer [M(phendione)₃], the full D_3 symmetry is utilized, resulting in a nanoscopic product of exceptionally high symmetry. This approach permits easy access to most desired heterometallic structures and can be extended to the synthesis of higher nuclearity complexes, dendrimers and polymers. The photophysical properties of these complexes is at present being investigated by the group of Prof. Sebastiano Campagna and these studies will clarify whether energy and electron transfer occur in these complexes.

5.4. References

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Chapter 6

Design and synthesis of novel chromium (III) polypyridyl complexes with TPA ligand for future investigations

The chemistry of the future is anybody's guess...

Hugh W. Salzberg, *From Caveman to Chemist*

6.1. Introduction

In a desire to find new polypyridyl ligands that can coordinate our metal centres we have chosen the ligand TPA.

TPA is a tetrapodal polypyridyl ligand, which has been widely used in bioinorganic chemistry in order to understand the characteristics of metalloenzymes through their structural and functional modelling of dinuclear and mononuclear active sites which contain iron^{1,2,3,4} and copper^{5,6,7} sites as dioxygen activation centres.

The TPA ligand includes three π -acceptors (pyridyl group) and one σ -donor (tertiary amino group) and could provide thermodynamic stability to complexes formed by its tetradentate chelation. It has been a central issue to elucidate the π -back-bonding interactions from metal centre to pyridine derivatives, as such interactions play an indispensable role in a variety of interesting excited-state behaviour involving photoredox reactions, luminescence, photosubstitution and photoinduced electron transfer. For these purposes, bipy (2,2'-bipyridine), terpy (2,2':6',2''-terpyridyl), phen (1,10-phenanthroline) and their derivatives have been widely employed with a variety of metal centres, all of them act as bidentate π -acceptors. Cr(III)TPA complexes have not yet been reported, in contrast to both Ru(II)^{8,9} and Ru(III)^{10,11}TPA. It is, however, intriguing to explore the molecular structures and chemical properties of Cr(III) complexes with tightly bound tripodal pyridylamine ligands. In an attempt to construct a new category of Cr complexes with ligands with the π -acceptor and σ -

donor in the same molecule, we have embarked on studies of Cr complexes having TPA as ligand. We describe here the syntheses and characterization of novel Cr(III) complexes with TPA to establish the structures of those complexes and to understand their electronic characters.

6.2. Results and Discussion

6.2.1. The ligand TPA

The ligand TPA (tris(2-pyridylmethyl)amine) was synthesized by a published procedure¹² by reaction of 2-aminomethyl-pyridine and picolyl chloride·HCl and the yield was almost quantitative. Its structure is shown in Figure 7.1.

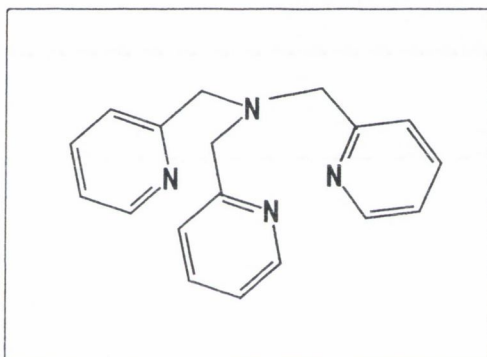
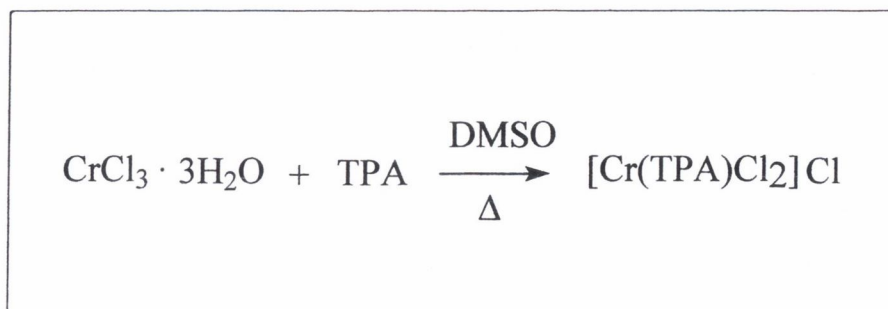


Figure 6.1: Structure of the ligand TPA

6.2.2. [Cr(TPA)Cl₂]Cl: a new precursor complex

The [Cr(TPA)Cl₂]Cl complex was synthesized as described in Scheme 6.1. below, using DMSO as solvent, refluxing for about three hours. The colour changes during this time were red → green → purple.



Scheme 6.1: Reaction scheme to the precursor complex

The reaction proceeded via ligand substitution between the three originally bound water molecules and one Cl⁻ ligand in the starting material CrCl₃·3H₂O and one

tetradentate ligand, TPA, due to its chelating effect. The structure of the complex is shown below in Figure 6.2.

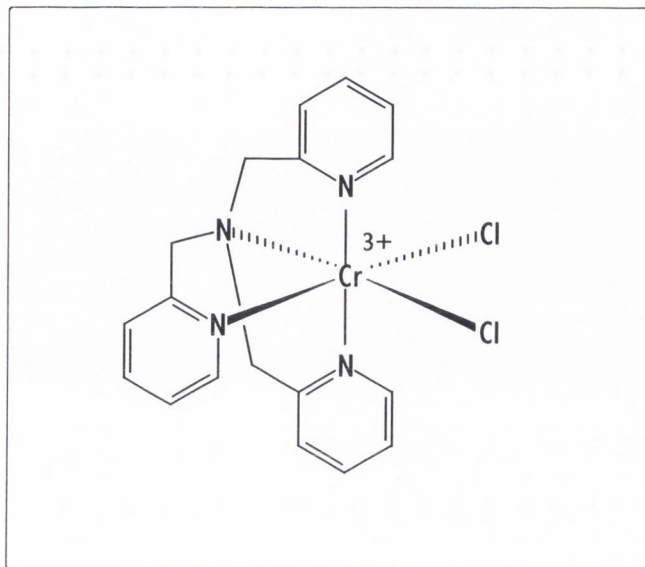


Figure 6.2: *Structure of the complex*

A single crystal of the complex was obtained by slow evaporation of a concentrated DMSO solution of the compound and the molecular structure was determined by X-ray crystallography. An ORTEP diagram is shown in Figure 6.3.

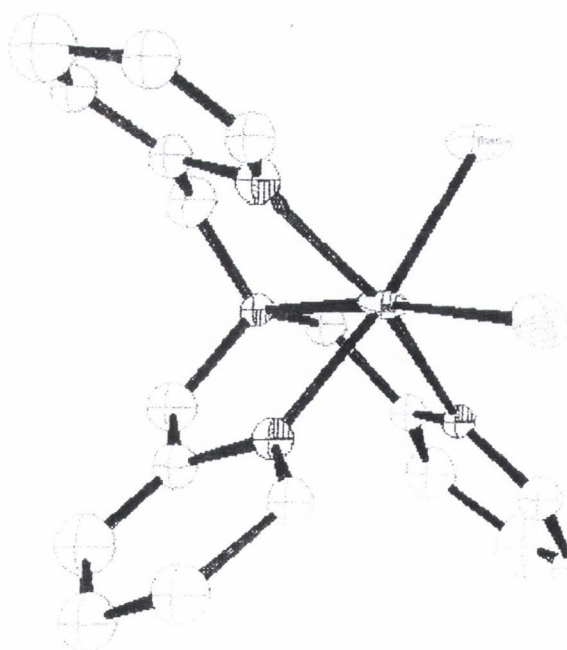
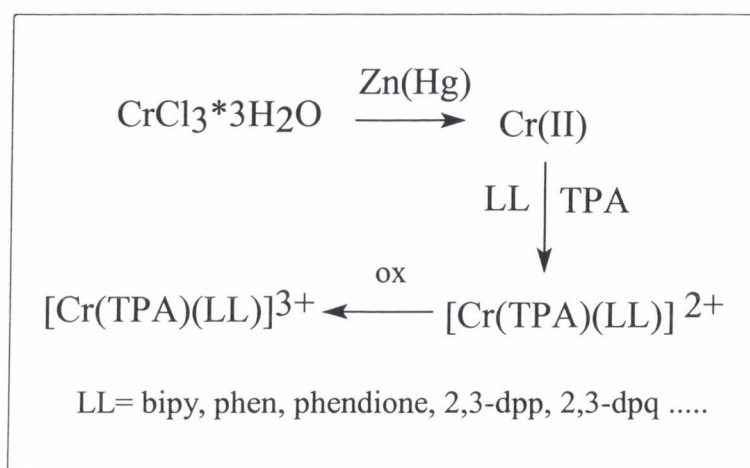


Figure 6.3: *X-ray crystal structure of $[Cr(TPA)Cl_2]Cl$. Thermal ellipsoid at 50% probability level. Hydrogen atoms, lattice anions and water molecules omitted for clarity.*

This is a preliminary structure only and the crystallographic data was obtained purely to confirm the coordination at the metal centre. The geometry around the Cr atom is a distorted octahedron. This is due to a stronger trans influence of pyridine than that of the tertiary amino group.¹³ The pyridine rings of TPA can be divided into *axial* (trans to each other) and *equatorial* (cis to one of the chlorides). Pyridine moieties of the TPA ligand showed remarkable differences between equatorial and axial pyridine. This steric constraint has been shown before for related Ru(II)TPA complexes¹⁴ and also in $[\text{Ru}(\text{bipy})_2\text{Cl}_2]^{15}$ and in $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^+$ in which the pyridine nitrogen trans to Cl^- has a shorter M-N bond distance than that of the pyridine trans to another pyridine¹⁶.

6.2.3. Towards Mononuclear and Binuclear Cr(III) TPA Complexes

$[\text{Cr}(\text{TPA})\text{Cl}_2]\text{Cl}$ can be considered a new precursor complex for the synthesis of mononuclear and binuclear complexes. The characteristics of the TPA ligand (π -back-bonding and σ -donor) will make it an ideal candidate for the construction of heteroleptic species because it can stabilize thermodynamically unstable complexes. On this assumption, we started the synthesis of mononuclear and binuclear Cr(III)TPA complexes. The starting point was again the reduction of the $[\text{Cr(III) Cl}_3]$ species with the Zn amalgam described before (Chapter 2). Addition of a second ligand should result in the heteroleptic complex, with no scrambling of the ligands. In fact the TPA, because of its strong σ -donor character will provide thermodynamic stability for the complexes. The reaction scheme is shown below.



Scheme 6.2. Synthesis of $[\text{Cr(III)TPA(LL)}]$ complexes.

Following the reaction scheme we attempted the synthesis of a mononuclear complex, $[\text{Cr}(\text{TPA})(\text{phen})](\text{ClO}_4)_3$ (in an equimolar ratio 1:1 between TPA and LL) and a binuclear complex, $[\text{Cr}(\text{TPA})]_2(2,3\text{-dpq})(\text{ClO}_4)_6$, (in an equimolar ratio 2:1 between the TPA and LL) whose structures are reported in Figure 6.4 and 6.5.

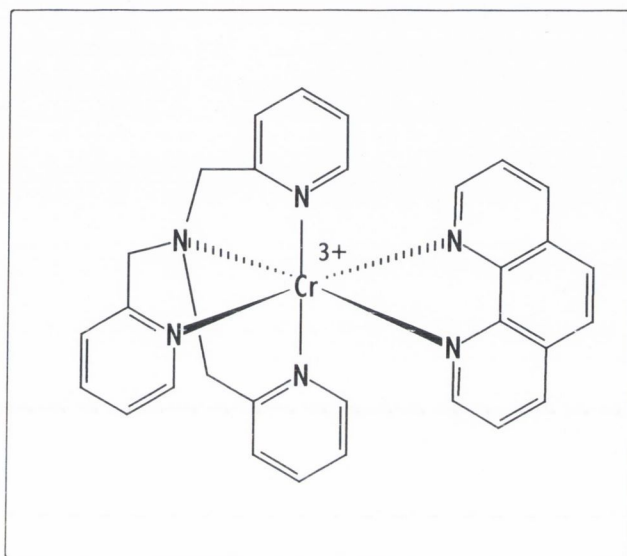


Figure 6.4. Proposed structure of the complex $[\text{Cr}(\text{TPA})\text{phen}]^{3+}$

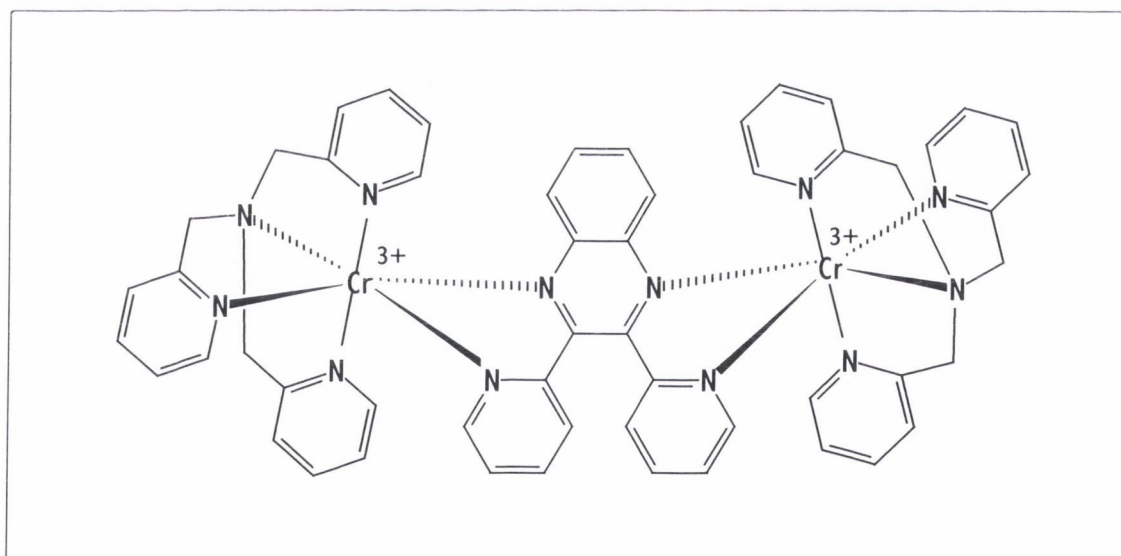


Figure 6.5. Proposed structure of the complex $[\text{Cr}(\text{TPA})]_2(2,3\text{-dpq})^{6+}$

These complexes have been synthesized as pink compounds. Crystals of these compounds were formed by slow evaporation of acetonitrile solutions but their crystal structures were impossible to solve.

Another method that could be followed is the preparation of the Cr(TPA)triflate as an intermediate as seen for the reaction of the previously synthesized heteroleptic Cr(III) complexes.

The synthesis of Ru(TPA)-polypyridyl complexes has also begun.

6.3. Conclusions and Perspectives

The synthesis and crystal structure of a new precursor complex, $[\text{Cr}(\text{TPA})\text{Cl}_2]\text{Cl}$, is described. We have presented the synthesis of Cr(III) monomers and dimers having TPA as ligand. The synthetic procedures described here, although at a preliminary stage, will contribute to versatile synthesis of novel chromium (III) and, also, of ruthenium(II) complexes. The π -back-bonding interaction and the σ -bonding interaction between the metal centres and pyridine moieties are cooperative, and this is an essential aspect in considering the properties and reactivity of Cr and Ru TPA complexes. Without any doubt what we described were novel complexes, and we hope that future investigations of those complexes will make them useful as new probes for DNA and as new sensitizers for solar energy storage and conversion.

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Chapter 7

Experimental Part

Today there is a beautiful experimental apparatus and people are looking for ideas on how to use it. We always had plenty of ideas and were only preoccupied with the lack of apparatus.

Carlo Cercignani, *Ludwig Boltzmann - the man who trusted atoms.*

This chapter describes the procedures used during the course of this work. The exact conditions used for each type of experiment are given in the section of the thesis where the results are reported.

7.1. Syntheses

7.1.1. Ligands

The syntheses of the ligands used in this thesis were performed as follows:

[1,10-phenantroline-5,6-dione] (phendione)

This ligand was prepared following the method of Paw and Eisenberg.¹

Yield: 3.8 g, 81 %

UV/Vis (CH₂Cl₂): $\lambda_{\text{max}}(\epsilon)$ 220, 256, 282, 370 nm

IR (KBr): 1685, 1563, 1415, 1295, 1207, 1118, 1014, 806, 738 cm⁻¹

¹H NMR (CDCl₃): δ 7.61 (dd, 2H, J=8, 4.45 Hz), 8.54 (dd, 2H, J=7.8, 1.5 Hz),

9.15 (dd, 2H, J= 7.0, 1.5 Hz) ppm

ESMS: M⁺ = 211 m/z

[dipyrido (3,2-d:2',3'-f) quinoxaline] (dpq)

This ligand was prepared by the method of Collins *et al.*²

Yield: 0.56 g, 50 %

¹H NMR (CDCl₃): δ 9.46 (dd, 1H, J= 8.0, 1.5 Hz), 9.26 (dd, 1H, 4.2, 1.5 Hz), 8.96

(s, 1H), 7.78 (dd, 1H, J= 8.0, 4.5 Hz) ppm

IR (KBr): 1571, 1467, 1391, 1304, 1260, 1190, 1119, 1078, 812, 740 cm^{-1} .

UV/Vis (CH_3CN): λ_{max} 230, 251, 284, 300, 324, 338 nm

ESMS: $\text{M}^+ = 233 \text{ m/z}$

[dipyrido [3,2-a: 2',3'-c] phenazine] (dppz)

The ligand was prepared following the preparation of Summers *et al.*³

Yield: 0.38g, 76 %

UV/Vis: (EtOH): λ_{max} 210, 239, 268, 291, 343, 350, 359, 377 nm

IR(KBr): 1573, 1488, 1413, 1360, 1337, 1125, 1073, 1032, 810, 759, 741 cm^{-1} .

^1H NMR (CDCl_3): δ 7.82 (dd, 2H, $J = 8.0, 4.5\text{Hz}$), 7.95 (dd, 2H, $J = 6.5, 3.5 \text{ Hz}$),

8.35 (m), 9.29 (dd, 2H, $J = 4.5, 2 \text{ Hz}$), 9.68 (dd, 2H, $J = 8.0, 1.5 \text{ Hz}$) ppm

ESMS: $\text{M}^+ = 283 \text{ m/z}$

[dipyrido [3,2-a: 2',3'-c] phenazine] (Medppz)

The ligand was prepared by a modification of the preparation of Summers *et al.*³ using 1,10-phenanthroline-5,6-dione and 3,4-diamminotoluene.

Yield: 0.40 g (65%)

UV/Vis (EtOH): λ_{max} ($\log \epsilon, \text{M}^{-1} \text{ cm}^{-1}$) 239 (4.48), 297 (4.35), 333 (3.80), 342 (3.93), 349 (3.93), 359 (4.14), 367 (4.1), 377 (4.13) nm

^1H NMR: no ^1H NMR spectrum was obtained for this ligand.

[dipyrido [3,2-a: 2',3'-c] phenazine] (Me_2dppz)

The ligand was prepared by a modification of the preparation of Summers *et al.*³ using 1,10-phenanthroline-5,6-dione and 1,2-dimethyl-4,5-phenylenediamine.

Yield: 0.44 g (70 %)

UV/Vis (EtOH): λ_{max} ($\log \epsilon, \text{M}^{-1} \text{ cm}^{-1}$) 239 (4.48), 300 (4.36), 338 (3.83), 347 (3.98), 355 (4.08), 364 (4.26), 373 (4.20), 385 (4.37)

^1H NMR: δ 9.28 (d, 2H, $J=4.5$ Hz), 7.81 (dd, 2H, $J=8, 4.5$ Hz), 9.66 (d, 2H, $J=8$ Hz), 8.13 (s), 2.64 (s) ppm

[5,6-diamino-1,10-phenantroline] (phendiamine)

This ligand was prepared by the method of MacDonnell.⁴

Yield: 0.126 g, 62 %

IR(KBr): 2362, 2343, 1609, 1561, 1486, 1437, 1282, 1110, 1071, 798, 732, 669, 623 cm^{-1} .

^1H NMR (MeOD): δ 7.67 (dd, 2H, $J=4.52, 8.57$ Hz), 8.51 (dd, 2H, $J=1.52, 8.56$ Hz), 8.86 (dd, 2H, $J=1.52, 4.52$ Hz) ppm. No record of NH_2 signals was obtained because these were obscured by water.

ESMS: $\text{M}^+=213$ m/z

[Tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2'''-3'''-j]phenazine] (tpphz)

The ligand is prepared by the method reported by Bolger et al.⁵

Yield: 0.95 g, 35.78 %

IR(KBr): 1575, 1475, 1390, 1375, 1132, 1089, 806, 750, 624, 431 cm^{-1} .

^1H NMR (CD_3CN): δ 10.23 (dd, 4H, $J=8.3, 1.6$ Hz), 9.49 (dd, 4H, $J=5.1, 1.4$ Hz), 8.43 (dd, 4H, $J=8.31, 5.1$ Hz) ppm

UV/Vis (MeOH): λ_{max} 379, 368, 317, 278, 245 nm

[Tris(2-pyridyl)methyl]amine (TPA)

The ligand was prepared following the preparation reported in *Inorganic Synthesis*⁶.

Yield: 11 g, 93.75 %

^1H NMR (CDCl_3): δ 8.55 (d, 3H, $J=4.52$ Hz), 7.66 (td, 3H, $J=2.0, 7.78$ Hz), 7.58 (d, 3H, $J=7.53$ Hz), 7.15 (t, 3H, $J=6.02$ Hz) ppm

UV/Vis (CH_3CN): λ_{max} 210, 261 nm

IR(KBr): 3079, 3052, 3013, 2923, 2878, 2817, 1670, 1628, 1474, 1436, 1365, 1310, 1242, 1153, 1123, 981, 772 cm^{-1} .

[2,3-bis(2-pyridyl)quinoxaline] (2,3-dpq)

This was prepared by the method of Goodwin and Lions.⁷

Yield: 2.52 g (60 %)

¹H NMR (CD_3Cl): δ 8.67 (1H, d), 8.26 (1H, d), 7.79 (1 H, m), 7.61 (1H, dd), 6.73 (2H, s) ppm

7.1.2. Precursors Complexes

The following complexes used as precursors in the experiments described in this thesis were prepared according to procedures described in the literature. All complexes were used as pure.

[Ag(bipy)₂](BF₄)⁸

AgBF₄ (1.39 g, 0.007 mol) and two-equivalents of bipy (2.21 g, 0.014 mol) were dissolved in 175 ml of water/ethanol mixture (1:1) and the solution was boiled for 5 minutes. The solution was allowed to cool down at room temperature and the resulting yellow needles of the product were collected and washed with a small volume of hot 50% aqueous ethanol solution and dried in vacuum.

Yield: 3.1 g, (87.52 %)

[Ag(phen)₂](BF₄)

This compound was prepared following the same method as above.

Yield: 1.46 g (80 %)

[Cr(bipy)₂Cl₂]Cl⁹

CrCl₃.6H₂O (1.5 g, 0.0056 moles) and 2,2'-bipy (4.7 g, 0.030 moles) in ethanol (50 ml) were mixed and heated to reflux after addition of a trace of zinc dust as

catalyst. The reaction mixture was stirred for 3 h. On cooling down a green precipitate was formed. It was filtered off and dried at 80 ° C under vacuum prior to use.

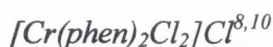
Yield: 1.77 g (53.32 %)

IR(KBr): 1602, 1564, 1496, 1470, 1448, 1315, 1244, 1160, 1107, 1031, 766, 729 cm^{-1} .

UV/Vis(EtOH): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$): 221 (4.46), 254 (4.19), 306 (4.19), 391 (3.05), 416 (3.02) nm

Paramagnetic susceptibilities: $R_0 = -76$, $R = 122$, $l = 2.1 \text{ cm}$, $m = 0.0421 \text{ g}$

$R_0 = -75$, $R = 128$, $l = 1.8 \text{ cm}$, $m = 0.0343 \text{ g}$



This complex was synthesized using the same method as above.

Yield: 6.3 g (81 %)

IR(KBr): 1628, 1604, 1582, 1519, 1427, 1341, 1310, 1225, 1147, 1108, 875, 849, 740, 723 cm^{-1}

UV/Vis (EtOH): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$): 205 (4.80), 225 (4.72), 271 (3.57), 333 (3.39), 350 (3.26), 413 (2.55), 576 (2.18) nm

Paramagnetic susceptibilities: $R_0 = -70$, $R = 40$, $l = 2.2 \text{ cm}$, $m = 0.0464 \text{ g}$

$R_0 = -70$, $R = 40$, $l = 1.9 \text{ cm}$, $m = 0.0387 \text{ g}$



This complex was prepared using the same method as above.

Yield: 0.83 g (38 %)

IR(KBr): 1703, 1577, 1486, 1427, 1375, 1299, 1254, 1208, 1131, 1073, 1043, 1026, 986, 818, 718 cm^{-1} .

UV/Vis (EtOH): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$): 275 (4.21), 306 (4.16), 417 (3.30) nm

Paramagnetic susceptibilities: $R_0 = -77$, $R = 126$, $l = 1.7 \text{ cm}$, $m = 0.0318 \text{ g}$

$R = 118$, $l = 1.6 \text{ cm}$, $m = 0.0296 \text{ g}$

[Cr(bipy)₂Cl₂](BF₄)¹¹

CrCl₃·6H₂O (2.36 g, 0.006 moles) was added to a solution of Ag(bipy)₂BF₄ (3.1 g, 0.006 mol) in CH₃CN (75 ml) and the mixture was stirred under reflux for 6 h. After this time the solution became brown coloured and the heat was removed. The AgCl precipitate was filtered off. The solution was concentrated and the crystals that separated were filtered off and dried under vacuum.

Crystals suitable for X-Ray diffraction were grown in CH₃CN by slow evaporation.

Yield: 38 % (1.197 g)

IR(KBr): 1604, 1446, 1319, 1160, 1098, 898, 767, 728, 647, 518 cm⁻¹.

UV/Vis (DMF): λ_{max} 394, 417, 576, 581, 586 nm

ESMS (MeCN): m/z = 436 (M-BF₄)⁺

Microanalysis: CrC₂₀N₄H₁₆Cl₂BF₄: Theory: C:46.01, H:3.09, N: 10.73; Cl: 13.58;

Found: C: 45.71, H: 3.86, N: 10.53, Cl: 13.73 %

[Cr(phen)₂Cl₂](PF₆)

CrCl₃·6H₂O (0.25 g, 0.94 mmol) was added to a solution of CH₃CN (25 ml) containing 0.57 g of [Ag(phen)₂](PF₆) (0.94 mmol). The solution was stirred under reflux for 6 h. The colour of the solution changed from green to brown. The solution was left to cool down and a white precipitate of AgCl was removed by filtration. The filtrate was concentrated to saturation and brown crystals separated which were collected and dried under vacuum..

Crystals of [Cr(phen)₂Cl₂](PF₆) suitable for X-Ray diffraction were obtained by slow evaporation from a CH₃CN solution.

The same complex was also prepared as the BF₄⁻ salt for which the microanalysis is given below.

Yield: 27 % (0.161 g)

UV/Vis (CH₃CN): λ_{max} 380, 480, 575 nm.

ESMS (MeCN): m/z = 484 [M-PF₆]⁺

Microanalysis CrC₂₄N₄H₁₆Cl₂BF₄·H₂O: Theory: C: 49.01, H: 3.08, N: 9.53,

Found: C: 49.15, H: 2.89, N: 9.49 %



Nitrogen was bubbled through a solution of $[Cr(phen)_2Cl_2]Cl \cdot 2H_2O$ (1 g) in 5 ml of freshly distilled CF_3SO_3H (TFMSH)¹³ at room temperature until the evolution of HCl gas had ceased (less than 1 day). The solution was then cooled in an ice-water bath, and ether was slowly added with vigorous stirring until the formation of the pink precipitate was complete. The precipitate was filtered out, washed several times with ether and dried under vacuum. This compound was used without further purification.

Yield: 100% (~1 g)



This complex was prepared using the same method described by Ruy and Endicott¹¹ for the corresponding complex $[Cr(phen)_2(TFMS)_2](TFMS)$.

Yield: 100 % (~1g)



$CrCl_3 \cdot 6H_2O$ (3.64 g, 13.65 mmol) was dissolved in DMSO (12 ml) and the mixture was refluxed for 1 h until the green colour of the initially formed solution turned to rose-red, indicating loss of water. After removal from heat a solution of TPA (2.22 g, 0.013 mmol) in DMSO (10 ml) was added slowly with stirring. After two hours of reflux, the solution changed its colour from deep red-brown to light green. It was left to cool at room temperature. The solution was reduced to half-volume under vacuum. The solution is left to evaporate slowly at room temperature. After a few days purple crystals were formed. They were collected, washed with ether and dried under vacuum.

Crystals grown by slow evaporation from a solution of DMSO were suitable for X-ray diffraction analysis.

Yield: 48 %

UV/Vis: λ_{max} 426, 474 nm

IR(KBr): 1610, 1510, 1436, 1286, 1056, 1050, 944, 842, 655 cm^{-1}

ESMS: $[\text{M}^+ - \text{Cl}] = 412 \text{ m/z}$

$[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$

This complex was prepared by the method of Evans *et al.*¹⁴

Yield: 2.05 g (87 %)

$[\text{Ru}(\text{bipy})_2\text{Cl}_2]$

This complex was prepared by the method of Meyer *et al.*¹⁵

Yield: 1.04 g, (44 %)

$[\text{Ru}(\text{phen})_2\text{Cl}_2]$

This complex was prepared following the same method described above.

Yield: 1.53 g, (59 %)

IR(KBr): 1426, 1406, 1260, 1095, 1018, 844, 799, 717 cm^{-1} .

7.1.3 Mononuclear Complexes

Unless otherwise stated all the reaction were performed under N_2 .

$[\text{Ru}(\text{bipy})_2(\text{phendione})](\text{PF}_6)_2$

This complex was prepared following the preparation by Goss and Abruna.¹⁶

Yield: 0.63 g (88 %)

$[\text{Ru}(\text{bipy})_2(\text{phendiamine})](\text{PF}_6)_2$

This complex was prepared used the method described by MacDonnell⁴ for the corresponding $[\text{Ru}(\text{phen})_2(\text{phendiamine})](\text{PF}_6)_2$

Yield: 0.088 g (17.6 %)

[Ru(phen)₂(phendione)](PF₆)₂

This complex was prepared following the procedure described by Goss and Abruna.

Yield: 0.65 g (93 %)

¹H NMR (CD₃CN): δ 8.72 (d, 2H, J = 7 Hz), 8.51 (d, 2H, J = 7.15 Hz), 8.34 (d, 4H, J = 4.52 Hz), 8.29 (s, 4H), 7.93 (d, 4H, J =), 7.84 (dd, 4H, J = 7, 4.52 Hz), 7.62 (dd, 2H, J = 7.15, 7 Hz) ppm

[Ru(phen)₂(phendiamine)](PF₆)₂

This complex was prepared following the procedure described by MacDonnell *et al.*⁴

Yield: 0.24 g (68 %)

¹H NMR (CD₃CN): δ 8.59 (d, 2H, 7.8 Hz), 8.48 (d, 4H, J = 8.02 Hz), 8.25(s, 4H), 8.01 (d, 4H, J = 7.28 Hz), 7.77 (d, 2H, J = 7.18 Hz), 7.63 (dd, 2H, J = 7.8 Hz, 7.18 Hz), 7.51 (dd, 4H, J = 8.02, 7.28 Hz) ppm

[Ru(phendione)₃](PF₆)₂

Ru(DMSO)₄Cl₂ (0.041 g, 8.46*10⁻⁵ mol) and phendione (0.075 g, 3.57*10⁻⁴ mol) were mixed together in EtOH/w (1:1) (20 ml) and kept under reflux for 3 h. The colour of the solution changed from yellow to orange-brown. The solvent was removed partially under vacuum. A solution of NH₄PF₆ was added to precipitate the compound. The product was filtered off and collected as a green compound.

Yield: 0.060 g (69.5 %)

IR (KBr): 1698, 1569, 1429, 1297, 846, 725, 559 cm⁻¹.

UV/Vis (MeCN): λ_{max} (log ε M⁻¹ cm⁻¹) 252 (4.71), 270 (3.69), 368 (4.12), 428 (4.01) nm.

^1H NMR (CD_3CN): δ 9.03 (d, 6H, $J = 7.20$ Hz), 8.51 (d, 6H, $J = 7$ Hz), 7.71 (dd, 6H, $J = 7, 7.20$ Hz) ppm

WARNING: ClO_4^- salts are potentially explosive!

“Cr(II) $\text{Cl}_2 \cdot n \text{H}_2\text{O}$ ”

All the complexes were prepared following the method of Kane-Maguire.¹⁸

A 100 ml 3 necked round bottom flask equipped with pressure equalising dropping funnel, nitrogen inlet/outlet and septum, was charged with the Zn(Hg) previously prepared. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (2.67 g, 0.01 mol) was dissolved in 50 ml 0.1 M HClO_4 and the green solution was added drop wise to the amalgam with stirring. A sky blue colour is seen after 30 minutes, but the solution is left stirring for another 2h until a persistent blue colour appears.

$[\text{Cr}(\text{bipy})_3](\text{ClO}_4)_3$

This compound was prepared following the method by Kane-Maguire *et al.*¹⁷

2,2'-bipyridine (4.7 g, 0.0295 mol) was dissolved in 200 ml of 0.01 M HClO_4 containing 40 g of NaClO_4 . Cr(II) solution (50 ml) was transferred in the flask containing the bipy solution via syringe. A purple-black precipitate was formed immediately. The solution was stirred for a further 10 minutes under N_2 before allowing the mixture to stir in air for 4 h. The brown compound was filtered off, and then on washing with ethanol went yellow. The residue was dissolved in 50 ml of 1M HClO_4 stirred for 10 minutes and then filtered off and dried.

Yield: 62.66 % (5.18 g)

IR (KBr): 1604, 1585, 1531, 1440, 1317, 846, 763, 622 cm^{-1} .

UV/Vis (MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$) 205 (4.52), 241 (4.46), 305 (4.57), 345 (3.5), 354 (sh)(3.40), 402 (2.92), 428 (2.80), 460 (2.40) nm

Paramagnetic susceptibilities: $R_0 = -76$, $R = -13$, $l = 2.2$ cm, $m = 0.0595$ g

$R = -13$, $l = 2$ cm, $m = 0.0493$ g

[Cr(phen)₃](ClO₄)₃

This compound was prepared following the same method as published by Kane-Maguire.¹⁷

Yellow crystals suitable for X-Ray diffraction were grown by ether diffusion in acetonitrile solutions.

Yield: 7.1 g, (79.8 %)

UV/VIS (MeCN): $\lambda_{\max}$ (log ϵ , M⁻¹ cm⁻¹) 204 (4.81), 224 (4.92), 269 (4.82), 293(sh) (4.35), 323 (sh) (3.90), 354 (3.36), 407(2.90), 432 (2.74), 454 (2.50) nm

IR(KBr): 1624, 1583, 1424, 1338, 1142, 1102, 846 cm⁻¹

¹H NMR (MeCN-d): δ 9.23 (6H, d, J= 4.52 Hz), 8.98 (6 H, d, J= 8.54 Hz), 8.28 (6 H, s), 8.18 (6H, dd, J= 8.28, 4.52 Hz) ppm

Microanalysis: CrC₃₆H₂₄N₆Cl₃O₁₂ Theory: C: 45.76, H: 3.20, N: 8.89, Cl: 11.25,

Cr 5.50;

Found: C: 45.46, H: 2.70, N 8.68, Cl: 11.45,

Cr 5.09 %

Paramagnetic susceptibilities: Ro= -76, R= 3, l= 2.1 cm, m= 0.0575 g

Ro= -76, R= 6, l= 1.7 cm, m= 0.0482 g

[Cr(4,4'-dimethyl- 2,2'-bipyridine)₃](ClO₄)₃

This complex was synthesized using the same method as above.

Crystals suitable for X-ray diffraction were obtained by diffusion of ether into a solution of CH₃CN. During data collection the crystals degraded.

Yield: 1.30 g (72%)

IR(KBr): 1617, 1556, 1498,1440, 1309, 1298, 1249,1089, 927, 835,624, 576, 522, 420 cm⁻¹.

UV/Vis: $\lambda_{\max}$ (log ϵ , M⁻¹ cm⁻¹) 205 (4.84), 239 (4.59), 304 (4.50), 345 (3.52) nm

Microanalysis: CrC₃₆H₃₆N₆Cl₃O₁₂: Theory: C: 46.89, H: 3.94, N: 9.11

Found: C: 46.59, H: 3.88, N: 8.82 %

Paramagnetic susceptibilities: Ro= -78, R= -3, l= 2 cm, m= 0.0437g

R= -2, l= 1.8 cm, m= 0.0383 g

Attempt to synthesize $[Cr(2,9\text{-dimethyl-phen})_3](ClO_4)_3$

2,9- dimethyl-1,10-phenantroline hemidrate (1.3 g, 6 mmol) was dissolved in ethanol (10 ml) and then added to 10 ml of 0.01 M $HClO_4$ containing 10 g of $NaClO_4$ and the resulting solution was purged with N_2 .

10 ml of the Cr(II) stock solution (containing 2 mmol) were added to the previous solution via syringe. The colour went to orange-brown. The suspension was stirred for further 10 minutes before allowing air to go through. The final colour was light brown. The precipitate was collected and then dissolved partially in a solution 1M $HClO_4$, stirred while heating up for a few minutes and then cooled down. The light yellow precipitate, which separated, was filtered off and dried under vacuum.

Crystals suitable for X-Ray diffraction were grown by ether diffusion into a solution of CH_3CN . The X-ray crystal structure showed that we ended up with the protonated ligand instead of the desired complex.

Yield: 0.81 g

UV/Vis: λ_{max} (ϵ , $M^{-1} cm^{-1}$) 209 (sh) (86936), 221 (113199), 263 (sh)(48832) 274 (sh)(77147), 281 (88988), 320 (16355) nm

Microanalysis: $C_{14}H_{13}N_2ClO_4$, Theory: C: 54.47, H: 4.24, N: 9.07

Found: C: 53.98, H: 4.17, N: 8.89 %

 $[Cr(4,7\text{-dimethyl-1,10-phenanthroline})_3](ClO_4)_3$

This complex was obtained using the same procedure described before, using 0.31 g (0.002 mol) of $CrCl_3$ and 1.08 g (0.006 mol) of the ligand. The complex was precipitated as a bright yellow solid. It was purified by Sephadex LH-20 using acetonitrile as eluent and Sephadex SP-C25 using 0.5 M $NaCl$ water/acetone (5:3). The yellow band was separated from an orange by-product which was characterized as a binuclear species. The solvent was removed partially under vacuum and the yellow compound was precipitated as a ClO_4^- and characterized as the desired complex.

Yield: 1.86 g (95.5%)

UV/Vis (MeCN): $\lambda_{\max}$ (log ϵ , $M^{-1} \text{ cm}^{-1}$) 208 (4.94), 227(4.81), 270 (4.88), 305 (4.36), 352 (3.72) nm

Microanalysis: $\text{CrC}_{42}\text{H}_{36}\text{N}_6\text{Cl}_3\text{O}_{12}$; Theory C:51.73, N8.62, H: 3.72

Found: C:50.98, N:8.54, H: 3.90 %

Paramagnetic susceptibilities: $R_0 = -72$, $R = -32$, $l = 2.5 \text{ cm}$, $m = 0.052 \text{ g}$

[Cr(phendione)₂(OH)(H₂O)](ClO₄)₂

This complex was synthesized following the same procedure described for the $[\text{Cr}(\text{bipy})_3]^{3+}$. The residue was dissolved in 1M HClO_4 solution which was heated on a hotplate. The solution was left evaporating in air. After several days orange crystals were formed.

IR(KBr): 1699(s), 1578, 1479, 1433, 1305, 1115 cm^{-1} .

UV/Vis (MeCN): $\lambda_{\max}$ (log ϵ , $M^{-1} \text{ cm}^{-1}$): 203 (4.61), 248(4.62), 281(4.14), 300 (4.17), 312(4.18), 349 (3.25), 373 (3.12), 476 (1.67) nm

Mass Spec: $[\text{M}]^+ = 707 \text{ m/z}$

Microanalysis: $\text{CrC}_{24}\text{H}_{14}\text{O}_{14}\text{N}_4\text{Cl}_2$ Theory: C: 40.87, H: 2.00, N:7.94, Cl: 10.04

Found: C: 39.34, H: 2.13, N: 7.40, Cl: 10.03 %

[Cr(phendione)₃](ClO₄)₃

Finely powered $[\text{Cr}(\text{phen})_3](\text{ClO}_4)_3$ (1g, 0.0012 moles) was slowly added to 10 ml of cold (0 °C) concentrated sulphuric acid and allowed to stir for approximately 15 minutes, followed by addition of 0.5 g of NaBr. It was kept on ice for a further 5 minutes. Then 5 ml of concentrated HNO_3 were added during which the solution turned to orange and Br_2 gas evolved. The mixture was stirred under reflux for 6 h. When the heat was removed, and the solution was cooled down, NaClO_4 was added and the solution was left in the fridge overnight. Then the yellow precipitate formed was filtered through a sintered glass funnel and dried under vacuum.

Yield: 0.55 (51 %)

IR(KBr): 1706, 1577, 1490, 1430, 1384, 1299, 1253, 1089, 811, 721, 624 cm^{-1} .

UV/Vis: $\lambda_{\max}$ ($\log \epsilon$, $M^{-1} \text{ cm}^{-1}$): 209 (4.78), 248 (4.89), 302 (4.41), 287 (4.48), 305 (4.52), 316(4.51), 475(2) nm

^1H NMR (CD_3CN): δ 9.54 (dd, 6H, $J = 8.03$, 5.52 Hz), 10.27(d, 6H, $J = 8.03\text{Hz}$), 10.47 (d, $J = 5.02$ Hz) ppm

Mass Spec: $m/z = 980 [M^+]$, 683 $[M^+ - 3\text{ClO}_4]$.

Microanalysis $\text{CrC}_{36}\text{N}_6\text{H}_{18}\text{Cl}_3$: Theory: C: 44.08, H: 1.85, N: 8.57

Found: C: 43.79, H: 2.10, N: 8.43 %

Paramagnetic susceptibilities: $R_o = -73$, $R = 47$, $l = 2.1$ cm, $m = 0.0572$ g

$R_o = -73$, $R = 56$, $l = 2$ cm, $m = 0.0556$ g

$[\text{Cr}(\text{dpq})_3](\text{ClO}_4)_3$

0.100 g of $\text{Cr}(\text{phendione})_3(\text{ClO}_4)_3$ ($1.02 \cdot 10^{-4}$ moles) and 6 equivalents of ethylenediamine (0.020 g) were dissolved in a mixture 1:1 of MeCN/EtOH (20 ml) and the resulting solution was refluxed under stirring for 12 h. The solvent was removed partially under vacuum, and the precipitate was filtered off and dried. The final colour was orange-brown.

Yield: 0.033 g, (31 %)

IR(KBr): 1636, 1579, 1473, 1390, 1034, 806, 740, 624, 437 cm^{-1} .

UV/Vis: $\lambda_{\max}$ ($\log \epsilon$, $M^{-1} \text{ cm}^{-1}$) 222 (4.81), 229 (4.86), 251 (5.04), 278 (4.56), 299 (4.49), 325 (4.11), 339 (4.02), 450 (2.9) nm

Microanalysis: $\text{CrC}_{42}\text{H}_{24}\text{N}_{12}\text{Cl}_3\text{O}_{12}$, Theory: C: 48.18, H: 2.41, N: 16.05

Found: C: 47.97, H: 2.15, N: 15.45 %

Paramagnetic susceptibilities: $R_o = -73$, $R = -40$, $l = 0.8$ cm, $m = 0.0160$ g

$R = -43$, $l = 0.8$ cm, $m = 0.0149$ g

$[\text{Cr}(\text{dppz})_3](\text{ClO}_4)_3$

0.100 g of $[\text{Cr}(\text{phendione})_3](\text{ClO}_4)_3$ ($1.02 \cdot 10^{-4}$ mol) and 0.060 g of *o*-phenylenediamine were dissolved in a mixture of MeCN/EtOH (1:1) 20 ml, and refluxed overnight. The solution turned from yellow to red. The solvent was removed under vacuum and the precipitate was filtered off and dried.

Yield: 0.073 g (60%)

IR(KBr): 198, 1419, 1378, 1091, 1049, 813, 730, 624 cm^{-1} .

UV/Vis: λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$): 208 (4.93), 238 (4.8), 269 (5.07), 283 (4.99), 340 (4.47), 348 (4.48), 358 (4.55), 365 (4.5), 376 (4.53), 427 (3.90), 453 (3.88), 485 (3.82) nm

Microanalysis: $\text{CrC}_{54}\text{N}_{12}\text{H}_{30}\text{Cl}_3\text{O}_{12}$, Theory: C: 54.17, H: 2.53, N: 14.04

Found: C: 53.87, H: 2.79, N: 14.01 %

Paramagnetic susceptibilities: $R_0 = -79$, $R = -3$, $l = 2.2$ cm, $m = 0.0341$ g

$R = 7$, $l = 2$ cm, $m = 0.0299$ g

[Cr(tpphz)₃](ClO₄)₃

0.100 g of $[\text{Cr}(\text{phendione})_3](\text{ClO}_4)_3$ (1.02×10^{-4} mol) was dissolved in 10 ml of MeCN/EtOH (1:1) and mixed with 3 equivalents of phendiamine (0.063 g). The resulting mixture was refluxed for 24 h. The solvent was removed under vacuum and the precipitate was filtered off and dried.

Yield: 0.019 g (12.4 %)

IR(KBr): 1577, 1484, 1423, 1390, 1373, 1114, 813, 740, 624 cm^{-1}

UV/Vis (MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$) 274 (5.22), 367 (4.60), 379 (4.59), 387 (4.68) nm

Microanalysis: $\text{CrC}_{72}\text{N}_{18}\text{H}_{36}\text{Cl}_3\text{O}_{12}$ Theory: C: 57.52, H: 2.41, N: 16.77

Found: C: 57.34, H: 2.76, N: 17.01 %

[Cr(bipy)₂(phendione)](PF₆)₃

0.500 g of $[\text{Cr}(\text{bipy})_2(\text{TFMS})_2](\text{TFMS})$ and 0.20 g of phendione (a 2 molar equivalent excess) were mixed in dry acetonitrile and refluxed under N_2 for 6 h. The colour turned from yellow to brown. When the heat was removed the solvent was partially evaporated under vacuum and NH_4PF_6 (aq) was added to precipitate the product. The brown compound, which separated, was filtered off and dried.

Yield: 0.27 g (45 %)

IR(KBr): 1710, 1611, 1581, 1430, 1251, 1166, 1031, 846 cm^{-1} .

UV/Vis (MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$) 210 (4.66), 243 (4.46), 305 (4.30), 481 (2.59) nm

Microanalysis: $\text{CrC}_{32}\text{H}_{22}\text{N}_6\text{O}_2\text{P}_3\text{F}_{18}$, Theory: C: 38.08, H: 2.20, N: 8.33

Found: C: 37.27, H: 2.27, N: 8.24 %

$[\text{Cr}(\text{bipy})_2(\text{dpq})](\text{PF}_6)_3$

0.100 g of $[\text{Cr}(\text{bipy})_2(\text{phendione})](\text{PF}_6)_3$ and an equivalent of ethylenediamine (0.005 g) were mixed in 20 ml MeCN/Ethanol (1:1) and refluxed for 6 h. The solution went red. After six hours the heat was removed and the solvent was partially pumped out and the product was precipitated as PF_6 salt. The precipitate was collected and dried. The yellow-orange compound was purified by recrystallization from MeCN/Ether.

Yield: 0.025 g (24 %)

IR (KBr): 1637, 1579, 1475, 1402, 1120, 1079, 1045, 846, 740, 559 cm^{-1} .

UV/Vis(MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$) 221 (4.80), 252 (4.94), 299 (4.53), 376 (3.39), 449(3.13) nm

Microanalysis: $\text{CrC}_{34}\text{H}_{24}\text{N}_8\text{P}_3\text{F}_{18}$ Theory C: 39.59, H: 2.35, N: 10.86

Found: C: 40.77, H: 3.23, N: 15.20 %

$[\text{Cr}(\text{bipy})_2(\text{dppz})](\text{PF}_6)_3$

$[\text{Cr}(\text{bipy})_2(\text{phendione})](\text{PF}_6)_3$ (0.050 g) and o-phenylenediamine (0.030 g) were refluxed together in MeCN/Ethanol (1:1) 10 ml for 6 h. The solution turned to red. After the heating was removed, the solvent was partially removed under vacuum and the product was precipitated as PF_6 salt. The compound was filtered off and washed with water and dried. Passing the product through a SephadexLH-20 column and eluting with MeCN further purified it.

Yield : 37 % (0.020 g)

IR(KBr): 1605, 1579, 1381, 1496, 1075, 1448, 846, 558 cm^{-1} .

UV/Vis(MeCN): $\lambda_{\max}$ ($\log \epsilon$, $M^{-1} \text{ cm}^{-1}$) 276 (4.93), 357 (4.24), 363 (4.22), 375 (4.23), 497 (3.31) nm

Microanalysis $\text{CrC}_{38}\text{H}_{26}\text{N}_8\text{P}_3\text{F}_{18}$: Theory: C: 44.42, H: 2.84, N: 9.87

Found C: 43.20, H: 2.42, N: 10.36 %

[Cr(bipy)₂(Medppz)](PF₆)₃

$[\text{Cr}(\text{bipy})_2(\text{phendione})](\text{PF}_6)_3$ (0.100 g, $9.9 \cdot 10^{-5}$ mol) and a 3-fold excess of 4-methyl-*o*-phenylendiamine (0.012 g) were refluxed in 20 ml of MeCN/Ethanol (1:1), the flask was covered with aluminium foil and the reaction mixture was stirred under reflux for 16 h. After this time the colour went deep red. The solvent was removed partially under vacuum and the product was precipitate as PF_6 salt. It was then collected by filtration, washed with water and dried. It was further precipitated from MeCN/Ether and dried.

Yield: 0.040 g (37 %)

IR(KBr): 1604, 1579, 1498, 1448, 1423, 1400, 1376, 1099, 1074, 1035, 846, 771, 730, 557 cm^{-1} .

UV/Vis(MeCN): $\lambda_{\max}$ ($\log \epsilon$, $M^{-1} \text{ cm}^{-1}$) 239 (4.71), 280 (4.93), 358 (4.46), 366 (4.27), 377 (4.28), 467 (3.37) nm

Microanalysis: $\text{CrC}_{39}\text{H}_{28}\text{N}_8\text{P}_3\text{F}_{18} \cdot 2\text{CH}_3\text{CN}$: Theory: C: 44.46, H: 2.82, N: 12.67

Found: C: 45.49, H: 2.80, N: 11.18 %

[Cr(bipy)₂(Me₂dppz)](PF₆)₃

$[\text{Cr}(\text{bipy})_2(\text{phendione})](\text{PF}_6)_3$ (0.100 g, $9.9 \cdot 10^{-5}$ mol) and a 3-fold excess of 4,5-dimethyl-*o*-phenylendiamine (0.013 g) were mixed together with MeCN/ethanol (20 ml, 1:1). The flask was covered with aluminium foil and refluxed for 14 h. The solution was deep red in colour. The solvent was partially removed under vacuum, and NH_4PF_6 was added to precipitate the compound. The product was further purified from MeCN/Ether and dried under vacuum.

Yield: 0.040 g (36.4 %)

IR(KBr): 1606, 1579, 1496, 1473, 1448, 1405, 1376, 1361, 1076, 1035, 846, 730, 557 cm^{-1} .

UV/Vis (MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1}\text{cm}^{-1}$) 279 (5), 366 (4.42), 374 (4.39), 384 (4.52), 492 (3.22) nm

Microanalysis, $\text{CrC}_{40}\text{H}_{30}\text{N}_8\text{P}_3\text{F}_{18} \cdot 2\text{CH}_3\text{CN}$, Theory: C: 44.35, H: 3.04, N: 11.75

Found: C: 45.54, H: 3.08, N: 10.93 %

[Cr(bipy)₂(tpphz)](PF₆)₃

$[\text{Cr}(\text{bipy})_2(\text{phendione})(\text{PF}_6)_3]$ (0.100g, $9.9 \cdot 10^{-5}$ mol) and *o*-phenyldiamine (0.020 g, $9.9 \cdot 10^{-5}$ mol) were dissolved in 20 ml of MeCN/Ethanol (1:1), the flask was covered with aluminium foil and refluxed for 16 h. The solution after this time became deep red. The solvent was partially removed under vacuum and the product is precipitated as PF_6 salt. It was filtered off and then purified by recrystallization from MeCN/Ether

Yield: 0.033 g (28 %)

IR (KBr): 1606, 1448, 1376, 1074, 1035, 846, 769, 730, 559 cm^{-1} .

UV/Vis(MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$) 208 (4.93), 244 (4.77), 279 (4.78), 303 (4.78), 358 (4.06), 367 (4.09), 378 (4.11), 381 (4.17), 411 (3.69), 490 (3.44) nm

Microanalysis: $\text{CrC}_{44}\text{H}_{28}\text{N}_{10}\text{P}_3\text{F}_{18}$: Theory: C: 44.65, H: 2.38, N: 11.83

Found: C: 44.15, H: 2.40, N: 9.60 %

[Cr(phen)₂(bipy)](PF₆)₃

10 ml solution of CH_2Cl_2 containing 0.054 g of bipy ($3.4 \cdot 10^{-4}$ mol) and 0.100 g of $[\text{Cr}(\text{phen})_2(\text{TFMS})_2](\text{TFMS})$ ($1.16 \cdot 10^{-4}$ mol) were stirred together and refluxed for 4 h. After 3 h of reflux a yellow precipitate appeared. It was filtered off and collected. It was dissolved in water and a solution of NH_4PF_6 was added to precipitate the compound. It was collected, washed with water, ethanol and ether and dried.

Yield: 0.020 g (17 %)

IR(KBr): 1607, 1522, 1449, 1430, 846, 577 cm^{-1} .

UV/Vis (MeCN): 220, 267, 299, 308, 350 nm

Microanalysis: $\text{CrC}_{34}\text{H}_{24}\text{N}_6\text{P}_3\text{F}_{18}\cdot\text{H}_2\text{O}$ Theory: C: 39.96, H: 2.57, N: 8.23,

Found: C: 39.68, H: 2.25, N: 7.73 %

$[\text{Cr}(\text{phen})_2(\text{Me}_2\text{bipy})](\text{PF}_6)_3$

It was synthesized using the same method as above.

Yield: 0.048 g (40 %)

UV/Vis (MeCN): λ_{max} 224, 267, 300, 343 nm.

$[\text{Cr}(\text{phen})_2(\text{Me}_2\text{phen})](\text{PF}_6)_3$

It was synthesized using the same method as above.

Yield: 0.010 g (8 %)

UV/Vis (MeCN): λ_{max} 203, 225, 265, 300 nm

$[\text{Cr}(\text{phen})_2(\text{Ph}_2\text{phen})](\text{PF}_6)_3$

It was synthesized using the same method as above.

Yield: 0.020 g (14.6 %)

UV/Vis (MeCN): λ_{max} 219, 271, 316, 356 nm.

$[\text{Cr}(\text{phen})_2(\text{phendione})](\text{PF}_6)_3$

0.500 g of $[\text{Cr}(\text{phen})_2(\text{TFMS})_2](\text{TFMS})$ ($5.8 \cdot 10^{-4}$ moles) and 0.20 g of phendione about two molar equivalents were mixed in dry MeCN and refluxed under N_2 for 6 h.

The solution turned from yellow to brown-red. The solvent was concentrated under vacuum. $\text{NH}_4\text{PF}_6(\text{aq})$ was added to precipitate the product. It was then filtered off and washed with water and ethanol and dried with ether.

Yield: 68 % (0.419 g)

UV/Vis (MeCN): $\lambda_{\max}$ ($\log \epsilon$, $M^{-1} \text{ cm}^{-1}$) 227 (5.03), 257 (4.95), 273 (4.86), 299 (4.49), 311 (4.36), 349 (3.65) nm

IR(KBr): 1700.47 cm^{-1} .

Microanalysis $\text{CrC}_{36}\text{H}_{22}\text{N}_6\text{O}_2\text{P}_3\text{F}_{18}$. CH_3CN : Theory: C: 41.53, H: 2.29, N: 8.93,

Cr: 4.73

Found: C: 42.55, H: 2.02, N: 7.94,

Cr: 3.80 %

Paramagnetic susceptibilities: $R = -75$, $R = 29$, $l = 1.7 \text{ cm}$, $m = 0.0597 \text{ g}$

$R = -76$, $R = 22$, $l = 1.7 \text{ cm}$, $m = 0.0572 \text{ g}$

$[\text{Cr}(\text{phen})_2(\text{dpq})](\text{PF}_6)_3$

0.100 g of $[\text{Cr}(\text{phen})_2(\text{phendione})](\text{PF}_6)_3$ ($9.5 \cdot 10^{-5}$ moles) and 0.020 g of ethylenediamine were dissolved in MeCN/EtOH (20 ml) (1:1) and heated to reflux overnight. The solution turned from red to orange. NH_4PF_6 (aq) was added to precipitate the compound, which was then filtered off and dried. It was further recrystallized from MeCN/Ether and dried.

Yield: 0.060 g (58.5 %)

UV/Vis (MeCN): $\lambda_{\max}$ ($\log \epsilon$, $M^{-1} \text{ cm}^{-1}$): 229 (5.25), 263 (5.07), 290 (4.56), 307 (4.13), 322 (3.95), 339 (3.70), 388 (3.14), 420 (3.12) nm

IR(KBr): 1619, 1589, 1509, 1423, 1141, 1068, 838, 730, 557 cm^{-1} .

Microanalysis: $\text{CrC}_{38}\text{H}_{24}\text{N}_8\text{P}_3\text{F}_{18}$, Theory: C: 42.28, H: 2.24, N: 10.38

Found: C: 42.10, H: 2.46; N: 10.98 %

Paramagnetic susceptibilities: $R_0 = -76$, $R = -46$, $l = 1.7 \text{ cm}$, $m = 0.0335 \text{ g}$

$R = -47$, $l = 1.7 \text{ cm}$, $m = 0.0322 \text{ g}$

$[\text{Cr}(\text{phen})_2(\text{dppz})](\text{PF}_6)_3$

0.100 g of $[\text{Cr}(\text{phen})_2(\text{phendione})](\text{PF}_6)_3$ ($9.45 \cdot 10^{-5}$ moles) and 0.050 g of *o*-phenylenediamine were dissolved in MeCN/EtOH (1:1) 20 ml and heated to reflux for 6 hours. During this time the solution became redder. The compound was precipitated as PF_6^- salt and filtered off and dried. The final colour of the compound was pink.

The product was further purified in a Sephadex LH-20 column eluting with acetonitrile. A top yellow band stays on the top of the column while the compound is first eluted. The solvent was removed under vacuum and the compound was dried.

Yield: 0.028 g (24.3%)

IR(KBr): 1629, 1585, 1521, 1429, 1375, 1149, 1070, 1039, 838, 723, 557 cm^{-1} .

UV/Vis (MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$): 202 (5.03), 223 (4.96), 271 (4.99), 347 (4), 356 (4.03), 363 (3.99), 374 (4), 417 (3.47), 499 (3.31) nm

Microanalysis: $\text{CrC}_{42}\text{H}_{26}\text{N}_8\text{P}_3\text{F}_{18}$, Theory: C: 44.66, H: 2.32, N: 9.92, Cr: 4.60

Found: C: 46.20, H: 2.39, N: 9.51, Cr: 4.94 %

Paramagnetic susceptibilities: $R_0 = -74$, $R = -32$, $l = 1.9 \text{ cm}$, $m = 0.0274 \text{ g}$

$R = -20$, $l = 2 \text{ cm}$, $m = 0.0282 \text{ g}$

$[\text{Cr}(\text{phen})_2(\text{dppzMe})](\text{PF}_6)_3$

It was synthesized using the same method as above.

Yield: 0.028 g (27 %)

UV/Vis (MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$): 206 (4.92), 229 (4.83), 273 (4.95), 342 (4.12), 351 (4.22), 360 (6.30), 367 (4.27), 378 (4.28), 498 (3.09) nm

$[\text{Cr}(\text{phen})_2(\text{dppzMe}_2)](\text{PF}_6)_3$

It was synthesized using the same method as above.

Yield: 0.026 g (24%)

UV/Vis(MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$): 205 (4.94), 223 (4.87), 273 (4.84), 346 (4.10), 354 (4.16), 366 (4.22), 374 (4.18), 385 (4.31), 500 (3.13) nm

Microanalysis: $\text{CrC}_{44}\text{H}_{30}\text{N}_8\text{P}_3\text{F}_{18}$, Theory: C: 45.65, H: 2.61, N: 9.68

Found: C: 45.54, H: 3.08, N: 10.93 %

$[\text{Cr}(\text{phen})_2(\text{tpphz})](\text{PF}_6)_3$

0.100 g of $[\text{Cr}(\text{phen})_2(\text{phendione})](\text{PF}_6)_3$ ($9.4 \cdot 10^{-5}$ moles) and phendiamine (0.040 g, $1.9 \cdot 10^{-4}$ moles) were dissolved in acetonitrile/ethanol (20 ml) 50% and heated

to reflux overnight. A solution of NH_4PF_6 was added to precipitate the product. The solvent was removed under vacuum and the compound was filtered off and dried. The brown-orange product was purified by recrystallization from MeCN/Ether.

Yield: 0.085g (67.25 %)

UV/Vis(MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$): 224 (4.82), 272 (4.84), 302 (4.46), 320 (4.17), 348(7689), 367 (3.94), 377 (3.93), 388 (4.04), 412 (3.75), 521(sh) (3.46) nm

IR(KBr): 1635, 1427, 1392, 1375, 1132, 1072, 1037, 838, 740, 721, 559 cm^{-1} .

Microanalysis: $\text{CrC}_{48}\text{H}_{36}\text{N}_{10}\text{P}_3\text{F}_{18}$, Theory: C: 46.50, H: 2.93, N: 11.30, Cr: 4.22

Found: C: 46.12, H: 2.66, N: 11.94, Cr: 3.39 %

Paramagnetic susceptibilities: $R_o = -73$, $R = -11$, $l = 1.8 \text{ cm}$, $m = 0.0251$

$R = -11$, $l = 1.5 \text{ cm}$, $m = 0.0198$

$[\text{Cr}(\text{TPA})\text{phen}](\text{ClO}_4)_3$

5 ml of Cr(II) stock solution ($1 \times 10^{-3} \text{ mol}$) was mixed with a solution of TPA (0.27 g, $1 \times 10^{-3} \text{ M}$) and 0.18 g of phenanthroline ($1 \times 10^{-3} \text{ mol}$) in a solution of ethanol: 0.01 M HClO_4 (~20 ml) containing 3 g of NaClO_4 . The resulting mixture was stirred at room temperature for 30 minutes. After opening to air the colour changed from black to pink.

Yield: 20 %

$[\text{Cr}_2(\text{TPA})_2(\mu\text{-dpq})](\text{ClO}_4)_6$

This compound was synthesized using the same method as above, using an equimolar ratio of 2:1 between Cr(TPA) and the 2,3-dpq ligand.

Yield: 10 %

[Co(phendione)₃](PF₆)₂

CoCl₂ · 6H₂O (0.2 g, 8.4 · 10⁻⁴ mol) was dissolved in water and mixed with 0.6 g of phendione (a 3-fold excess) dissolved in EtOH (20 ml). A yellow compound was immediately formed, and it was precipitated as PF₆ salt. It was then filtered off, washed with water, ethanol and ether and dried. It was further purified by redissolving in acetonitrile and reprecipitated from ether. It was dried under vacuum.

Yield: 80 %, 0.65 g

IR (KBr): 1698, 1577, 1479, 1429, 1303, 1210, 1127, 1022, 935, 842, 733 cm⁻¹.

UV/Vis (MeCN): λ_{max} (log ε, M⁻¹ cm⁻¹) 249 (5.95), 300 (4.42), 309 (4.41) nm

ESMS: [M⁺] = 980 m/z

Microanalysis: CoC₃₆N₆H₁₈O₆P₂F₁₂; Theory: C: 44.15, H: 1.85, N: 8.58

Found: 42.99, H: 1.78, N: 8.29 %

Paramagnetic susceptibilities: R₀ = -78, R = 71, l = 1.5 cm, m = 0.0221 g

R = 80, l = 2.1 cm, m = 0.0223 g

[Co(III)(phendione)₃](ClO₄)₃

[Co(phen)₃](ClO₄)₃ (1g) was dissolved in 10 ml of con H₂SO₄ and mixed for 10 minutes to complete dissolution of the product. Then NaBr (0.5 g) was added and to this suspension 5 ml of HNO₃ conc. were further added. The solution was stirred under reflux at 100 °C for 3 h. The solution was then allowed to cool down. The compound was precipitated with NaClO₄ (aq) and left in the fridge for two hours. The yellow precipitate, which appeared, was filtered off in a sintered glass filter and dried under vacuum.

Yield: 0.7 g (64 %)

IR (KBr): 1708, 1608, 1577, 1523, 1432, 1292, 1249, 1078, 923, 821, 723, 622 cm⁻¹.

UV/Vis: (λ_{max}, log ε (M⁻¹ cm⁻¹)): 230 (5.47), 309 (4.06), 325 (4.05) nm

^1H NMR: δ 7.66 (d, 6H, $J = 5.52$ Hz), 8.13(dd, 6H, $J = 6.55, 7.03$ Hz), 9.01(d, 6H, $J = 8.03$ Hz) ppm

Paramagnetic susceptibilities: $R_o = -79$, $R = -74$, $l = 1.6$ cm, $m = 0.0430$ g

$R = -80$, $l = 1.8$ cm, $m = 0.0434$ g

[Cu(phendione)₃](PF₆)₂

CuSO_4 (0.12 g, 5.10^{-4} mol) dissolved in water was mixed with 0.32 g of phendione (a 3-fold excess) dissolved in EtOH. The solution turned to olive-green. The compound was precipitated as NH_4PF_6 salt and washed with water and ethanol and dried with ether.

Crystals suitable for X-ray diffraction were grown by diffusion of ether in MeCN solution

Yield: 72 %, 0.28 g

IR(KBr): 1706, 1575, 1427, 1314, 1122, 1034, 842 cm^{-1} .

UV/Vis (MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$): 250 (4.91), 301 (4.33), 313 (4.30), 350 (4.91) nm.

Microanalysis: $\text{CuC}_{36}\text{H}_{18}\text{N}_6\text{O}_6\text{P}_2\text{F}_{12}$, Theory: C: 43.94, H: 1.84, N: 8.54,

Found: C: 43.39, H: 2.04, N: 9.49 %

Paramagnetic susceptibilities: $R_o = -76$, $R = -56$, $l = 2.2$ cm, $m = 0.0382$ g

$R = -55$, $l = 1.6$ cm, $m = 0.0292$ g

[Fe(phen)₃](PF₆)₂

$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.20 g, 5.10^{-4} mol) and 1,10 phen (0.30 g, $1.5 \cdot 10^{-3}$ mol) were mixed together in water (20 ml). The solution turned immediately to red. The solution was stirred for further 10 minutes and then precipitated adding NH_4PF_6 (aq) and filtered off. The red compound was washed with water and ethanol and then dried with ether. It was purified by recrystallization from MeCN/Ether.

Yield: 0.37 g (83 %)

IR(KBr): 1575, 1427, 842 cm^{-1} .

UV/Vis(MeCN): $\lambda_{\max}$ ($\log \epsilon$, $M^{-1} \text{ cm}^{-1}$) 225 (4.19), 265 (5.18), 290 (4.67), 423 (3.97), 472 (4.12), 508 (4.18) nm

^1H NMR (MeCN- d): δ 8.65 (dd, 6H, $J = 7.73$, 1.5 Hz), 8.29 (s, 6H), 7.68 (dd, 6H, $J = 5.28$, 1.5 Hz), 7.63 (dd, 6H, $J = 8.03$, 5.02 Hz) ppm

Paramagnetic susceptibilities: $R_o = -77$, $R = -72$, $l = 1.8 \text{ cm}$, $m = 0.0381 \text{ g}$

$R = -85$, $l = 1.8 \text{ cm}$, $m = 0.0398 \text{ g}$

$[\text{Fe}(\text{phendione})_3](\text{PF}_6)_3$

$[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2] \cdot 6\text{H}_2\text{O}$ (0.15 g, $3.82 \cdot 10^{-4}$ moles) and 3-equivalent excess of phendione (0.29 g) dissolved in EtOH were mixed together with stirring. The solution turned immediately to red. The compound was precipitated as PF_6 salt and filtered off and washed with water and ethanol and dried. The red-black compound was purified by passing it through a Sephadex LH-20 column and eluting with MeCN.

Crystals were grown by diffusion of ether into a solution of MeCN.

Yield: 48.16 %, 0.18 g.

^1H NMR: δ 7.82 (6H, d, $J = 5.02 \text{ Hz}$), 7.72 (6H, dd, $J = 6.77$, 7.53 Hz), 8.65 (6H, d, $J = 7.53 \text{ Hz}$) ppm

UV/Vis(MeCN): $\lambda_{\max}$ ($\log \epsilon$ $M^{-1} \text{ cm}^{-1}$) 246 (4.82), 272 (4.51), 297 (4.38), 310 (4.44), 367 (3.83), 472 (3.98) nm

IR(KBr): 1703, 1572, 1429, 1295, 841, 722 cm^{-1} .

Microanalysis: $\text{FeC}_{36}\text{H}_{18}\text{N}_6\text{P}_2\text{F}_{12}\text{O}_6 \cdot \text{H}_2\text{O} \cdot \frac{1}{2} \text{PF}_6$:

Theory: C: 40.49, H: 1.86, N: 7.87;

Found: C: 40.80, H: 1.88, N: 7.89 %

Paramagnetic susceptibilities: $R_o = -72$, $R = -72$, $l = 1.4 \text{ cm}$, $m = 0.051 \text{ g}$

$R = -71$, $l = 1.6 \text{ cm}$, $m = 0.0592 \text{ g}$

$[\text{Fe}(\text{dpq})_3](\text{PF}_6)_2$

$[\text{Fe}(\text{phendione})_3](\text{PF}_6)_2$ (0.1 g, $1 \cdot 10^{-4}$ mol) was mixed with ethylenediamine in ethanol (10 ml). The solution was refluxed overnight, during which time the colour changed from red to purple. The solvent was partially removed under

vacuum and NH_4PF_6 was added to precipitate the compound. It was filtered off and washed with water and ethanol and dried. Crystals suitable for X-ray diffraction were grown by diffusion of ether into MeCN solution.

Yield: 33.5 %, 0.035 g.

IR(KBr): 1637, 1579, 1386, 1081, 846, 740, 557 cm^{-1} .

^1H NMR: δ 7.94(6H,d, J = 5.02 Hz), 7.80 (6H,dd, J = 7.78, 5.02 Hz), 9.57 (6H,d, J = 8.03 Hz), 9.24(6H, s) ppm

UV/Vis: λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$): 207 (4.83), 256 (5.05), 292 (4.68), 329 (4.01), 424 (3.77), 476 (3.91), 513 (3.98) nm

Microanalysis: $\text{FeC}_{42}\text{H}_{24}\text{N}_{12}\text{P}_2\text{F}_{12}$, Theory: C: 48.39, H: 2.32, N: 16.12,

Found: C: 47.43, H: 2.48, N: 15.03 %

Paramagnetic susceptibilities: R_0 = -73, R = -81, l = 1.6 cm, m = 0.0306 g

R = -82, l = 1.7 cm, m = 0.0332 g

$[\text{Fe}(\text{dppz})_3](\text{PF}_6)_3$

$[\text{Fe}(\text{phendione})_3](\text{PF}_6)_2$ (0.22 g, $2.25 \cdot 10^{-4}$ mol) in MeCN (10 ml) and to this solution a 3-fold excess of *o*-phenyldiamine (0.1 g) dissolved in ethanol was added and the resulting mixture was refluxed for 24 h. On mixing the colour of the solution went to red. The compound was precipitated with PF_6 salt, filtered off, washed with water and ethanol and dried with ether. It was recrystallized from MeCN/Ether.

Yield: 0.20 g (74.5%)

IR(KBr): 1421, 1357, 1078, 846, 763, 557 cm^{-1} .

UV/Vis(MeCN): λ_{max} ($\log \epsilon$, $\text{M}^{-1} \text{cm}^{-1}$) 208 (4.88), 280 (5.14), 321 (4.47), 357 (4.48), 371 (4.49), 481 (4), 520 (4.02) nm

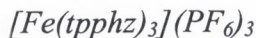
^1H NMR: δ 8.52(6H, dd, J = 6.27, 3.01 Hz), 8.18(6H, dd, J = 6.27, 3.01 Hz) 9.74(6H, d, J = 8.04 Hz) 8.00(6H, d, J = 5.02 Hz), 7.86(6H, dd, J = 8.03, 5.02 Hz) ppm

Microanalysis: $\text{FeC}_{54}\text{H}_{30}\text{N}_{12}\text{P}_2\text{F}_{12}$; Theory: C: 54.38, H: 2.54, N: 14.09

Found: C: 53.75, H: 2.48, N: 14.58 %

Paramagnetic susceptibilities: $R_0 = -78$, $R = -75$, $l = 2.2$ cm, $m = 0.0333$ g

$R = -85$ cm, $l = 1.6$ cm, $m = 0.0235$ g



Fe(II)(NH₄)₂(SO₄) · 6H₂O (0.101 g, $2.55 \cdot 10^{-4}$ moles) dissolved in water are added to a solution of tpphz (0.34 g, $8.9 \cdot 10^{-4}$ mol) in methanol. On mixing the two solutions a pink-red compound was formed. It was stirred for further 30 minutes under reflux. After this time, the compound was allowed to cool down and NH₄PF₆ was added to precipitate the compound. The precipitate was collected, washed with water, ethanol and dried with ether. It was precipitated a second time from MeCN/Ether.

Yield: 0.36 g, 94.3 %

IR (KBr): 1585, 1477, 1390, 1373, 1132, 846, 738, 557 cm⁻¹.

UV/Vis (MeCN): $\lambda_{\max}$ (log ϵ , M⁻¹ cm⁻¹) 248 (5.19), 281 (5.28), 312 (5.16), 363 (4.85), 383 (4.97), 500 (4.54) nm

7.1.4. Binuclear Complexes



0.050 g of [Cr(bipy)₂(phendione)](PF₆)₃ ($4.95 \cdot 10^{-5}$ moles) and [Ru(bipy)₂(phendiamine)](PF₆)₂ ($4.95 \cdot 10^{-5}$ moles) were dissolved in 20 ml of 1:1 MeCN/EtOH and refluxed under N₂ for 3 h. The colour changed from dark red to brown-yellow. The solvent was removed partially under vacuum. An excess of NH₄PF₆ aqueous was added to complete the precipitation of the compound and then it was filtered off and dried with ether. Some impurities were removed by passing the product through a Sephadex LH-20 column and eluting with acetonitrile.

Yield: 0.020 g (21.4 %)

IR(KBr): 1700, 1606, 1448, 838, 767, 730, 559 cm⁻¹.

UV/Vis: $\lambda_{\max}$ (ϵ , $M^{-1} \text{ cm}^{-1}$) 243 (57547), 285 (60000), 305 (43396), 373 (10566), 435 (11037) nm

Micronalysis: $\text{CrRuC}_{64}\text{N}_{14}\text{H}_{44}\text{P}_5\text{F}_{30}$, Theory: C: 40.74, H: 2.35, N: 10.39

Found: C: 39.55, H: 2.21, N: 9.89 %

$[(bipy)_2\text{Cr}(tpphz)\text{Ru}(\text{phen})_2](\text{PF}_6)_5$

This compound was prepared using the same method described above.

Yield: 0.025 g (26 %)

IR(KBr): 1072, 1033, 846, 557 cm^{-1} .

UV/Vis: $\lambda_{\max}$ (ϵ , $M^{-1} \text{ cm}^{-1}$) 221 (138709), 262 (146774), 303 (65322), 370 (22419), 388 (21774), 436 (25000), 707 (1129) nm

Microanalysis: $\text{CrRuC}_{68}\text{H}_{44}\text{N}_{14}\text{P}_5\text{F}_{30}$, Theory C: 42.21, H: 2.29, N: 10.13

Found: C: 42.95, H: 2.65, N: 9.55 %

$[(\text{phen})_2\text{Ru}(tpphz)\text{Cr}(\text{phen})_2](\text{PF}_6)_5$

$[\text{Cr}(\text{phen})_2(\text{phendione})](\text{PF}_6)_3$ (0.054 g, $5.1 \cdot 10^{-4}$ mol) and $[\text{Ru}(\text{phen})_2(\text{phendiamine})](\text{PF}_6)_2$ (0.49 g, $5.1 \cdot 10^{-4}$ mol) dissolved in MeCN/water (20 ml, 1:1) were mixed together and refluxed under N_2 for 3 h. The solution, deep red at the beginning, turned to orange brown. The solvent was partially removed under vacuum and the product was precipitated as PF_6 salt. It was filtered off, washed with water and ethanol and dried with ether.

Yield: 0.052 g (51.4%)

IR(KBr): 1698, 1627, 1579, 1429, 1261, 1072, 846, 723, 557 cm^{-1} .

UV/Vis: $\lambda_{\max}$ (ϵ , $M^{-1} \text{ cm}^{-1}$): 223 (131404), 263 (139669), 377 (18346), 437 (21074), 710 (1000) nm

Microanalysis: $\text{CrRuC}_{72}\text{H}_{44}\text{N}_{14}\text{P}_5\text{F}_{30}$, Theory C: 43.61, H: 2.24, N: 9.89, Cr: 2.62

Found: C: 43.68, H: 2.77, N: 8.27, Cr: 1.60 %

7.1.5. Tetranuclear complexes



$[Cr(phendione)_3](ClO_4)_3$ (0.040 g, $4.5 \cdot 10^{-5}$ moles) and $[Ru(phen)_2(phendiamine)](PF_6)_3$ (0.130 g, 3-fold equivalents) were dissolved in 20 ml water/MeCN (1:1). The reaction flask was covered with aluminium foil and refluxed under N_2 gas for 15 h.

The final colour of the solution was reddish. The solvent was removed under vacuum and the compound was precipitated as PF_6 salt. The product was purified by recrystallization from MeCN/Ether.

Yield: 0.010 g (56.7 %)

IR(KBr): 1700, 1577, 1427, 1373, 1132, 1097, 1072, 840, 721, 557 cm^{-1} .

UV/Vis: $\lambda_{\max}$ (ϵ , $M^{-1}\text{ cm}^{-1}$) 202 (283333), 221 (257843), 262 (298039), 278 (220588), 304 (129313), 375 (70784), 434 (60686), 702 (3823) nm

Microanalysis: $CrRu_3C_{144}N_{30}H_{108}P_9F_{54}$, Theory: C: 44.14, H: 2.78, N: 10.72

Found: C: 44.41, H: 2.57, N: 9.12 %



$[Cr(phendione)_3](ClO_4)_3$ (0.040 g, $4.5 \cdot 10^{-5}$ moles) and $[Ru(bipy)_2(phendiamine)](PF_6)_3$ (0.130 g) were dissolved in 20 ml water/MeCN (1:1) and the reaction flask was covered with aluminium foil and refluxed under N_2 for 24 h. The final colour of the solution was reddish. The solvent was removed under vacuum and the compound is precipitated as PF_6^- salt. The product was purified by recrystallization from MeCN/Ether.

Yield: 0.106 g (63 %)

IR(KBr): 1701, 1604, 1466, 1447, 1427, 1374, 1297, 1071, 841, 763, 729 cm^{-1} .

UV/Vis: $\lambda_{\max}$ (ϵ , $M^{-1}\text{ cm}^{-1}$) 244 (138134), 252 (134592), 284 (213105), 306 (89374), 439 (48996), 748 (1416), 778 (1157) nm

Microanalysis: $CrRu_3C_{132}N_{30}H_{84}P_9F_{54}$: Theory: C: 42.28, H: 2.26, N: 11.20

Found: C: 41.34, H: 2.25, N: 10.22 %



[Fe(phendione)₃](PF₆)₂ (0.050 g, 5.12.10⁻⁵ moles) and [Ru(phen)₂(phendiamine)](PF₆)₂ (0.150 g) were dissolved in 20 ml MeCN/H₂O and heated to reflux for 24 h, under N₂. The solvent was removed under vacuum and the compound was precipitated as PF₆ salt and filtered off. It was then recrystallized from MeCN/Ether and dried.

Yield: 0.130 g, (67 %)

IR(KBr): 1698, 1628, 1601, 1569, 1428, 1292, 841, 721 cm⁻¹.

UV/Vis: λ_{max} (ε, M⁻¹ cm⁻¹) 223 (242253), 261 (296244), 291 (93427), 308 (58215), 376 (37245), 437 (52895), 746 (782), 779 (625) nm.

¹H NMR (CD₃CN): 8.72 (d, J= 8.03 Hz), 8.61 (d, J= 8.03 Hz), 8.51 (d, J= 8.03 Hz), 8.35 (d, J= 5.02 Hz), 8.28 (t, J= 12.04, 6.02 Hz), 8.04 (d, J= 5.02 Hz), 7.93 (d, J= 5.02 Hz), 7.85 (dd, J= 13.05, 5.02), 7.62 (dd, J= 13.55, 5.02 Hz), 7.51 (dd, J= 13.55, 6.02 Hz) ppm.

Microanalysis: FeRu₃C₁₄₄N₃₀H₈₄P₈F₄₈: Theory, C: 46.08, H: 2.26, N: 11.20

Found: C: 46.78, H: 2.14, N: 10.57 %



[Cu(phendione)₃](PF₆)₂ (0.050 g, 5.12.10⁻⁵ moles) and [Ru(phen)₂(phendiamine)](PF₆)₂ (0.150 g) were dissolved in 20 ml MeCN/H₂O and heated to reflux for 24 h, under N₂. The solvent was removed under vacuum and the compound was precipitated with PF₆ salt, filtered off and dried.

Yield: 0.138 g (71.6%)

IR(KBr): 1700, 1577, 1428, 1368, 1299, 841, 721 cm⁻¹.

UV/Vis: λ_{max} (ε, M⁻¹ cm⁻¹) 221 (233557), 261 (296644), 304 (71140), 373 (38255), 436 (50469), 691 (1677) nm

Microanalysis CuRu₃C₁₄₄N₃₀H₈₄P₈F₄₈ Theory: C: 45.99, H: 2.25, N: 11.17

Found: C: 45.52, H: 2.06, N: 11.79 %



$[Co(phendione)_3](PF_6)_2$ (0.040 g, $4 \cdot 10^{-5}$ moles) and $[Ru(phen)_2(phendiamine)](PF_6)_2$ (0.117 g, $1.2 \cdot 10^{-4}$ mols) were dissolved in 20 ml MeCN/H₂O and heated to reflux for 24 h, under N₂. The compound was treated as described above.

Yield: 0.086 g, 55.5 %

IR(KBr): 1700, 1626, 1604, 1579, 1519, 1428, 839, 722 cm⁻¹.

UV/Vis: λ_{max} (ϵ , M⁻¹ cm⁻¹) 222(285937), 263(325468), 371(36718), 437(53046), 718(2812) nm

Microanalysis, CoRu₃C₁₄₄N₃₀H₈₄P₈F₄₈, Theory: C: 46.04, H: 2.25, N: 11.19

Found: C: 45.90, H: 2.32, N: 11.14 %



$[Co(phendione)_3](PF_6)_3$ (0.046 g, $4 \cdot 10^{-5}$ moles) and $[Ru(phen)_2(phendiamine)](PF_6)_2$ (0.115 g, $1.19 \cdot 10^{-4}$ mols) were dissolved in 20 ml MeCN/H₂O and heated to reflux for 24 h, under N₂.

During this time the colour went to orange. The compound was isolated and purified as described above.

Yield: 0.084 g, 54 %

IR(KBr): 1699, 1577, 1428, 1299, 838, 721 cm⁻¹.

UV/Vis (MeCN): λ_{max} (ϵ , M⁻¹ cm⁻¹) 222 (281250), 261 (345703), 306 (83984), 377 (44921), 436 (57226) nm.

¹H NMR (CD₃CN): δ 8.72 (d, JJ= 8.54 Hz), 8.61 (d, JJ= 8.03 Hz), 8.51 (d, JJ= 8.03 Hz), 8.34 (d, JJ= 5.02 Hz), 8.28 (t, JJ= 6.02 Hz), 8.03 (d, JJ= 5.02 Hz), 7.93 (d, JJ= 6.19 Hz), 7.84 (dd, JJ= 13.05, 5.02 Hz), 7.62 (m, JJ= 5.53), 7.52 (t, JJ= 5.52 Hz) ppm.

Microanalysis, CoRu₃C₁₄₄N₃₀H₈₄P₉F₅₄, Theory: C: 44.33, H: 2.17, N: 10.77

Found: C: 44.83, H: 2.13, N: 10.58 %

7. 2. Apparatus

All experiments were performed at room temperature unless otherwise stated.

7.2.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR Spectra were obtained on a Bruker DPX 400 instrument operating at 400.14 MHz for ^1H . Chemical shifts, δ , are expressed in ppm, using the solvent as an internal standard relative to TMS. The coupling constants, J , are expressed in Hz. As most of the complexes are hexafluorophosphate or perchlorate salts, $\text{CH}_3\text{CN}-d_3$ or $\text{DMSO}-d_6$ (both from Aldrich) are used as solvents. For the ligands CD_3Cl or CD_3OD are instead used.

7.2.2. Fourier Transform Infrared Spectroscopy (FT-IR)

IR spectral data were obtained with a Genesis II FT-IR spectrometer from Mattson, using samples (1%) in compressed KBr pellets.

7.2.3. UV/Vis Absorption Spectroscopy

The absorption spectra and optical density data were obtained with Pye-Unicam PV-800 spectrometers or with a Cary 300 (Varian) in Trinity College, or on a Kontron Uvikon 860 spectrophotometer (University of Messina). All these machines were interfaced to a PC for storage, printing and manipulation of spectra. The range used was 200-800 nm. λ_{max} is expressed in nm, while ϵ in $\text{M}^{-1}\text{cm}^{-1}$.

Molar extinction coefficients

The molar extinction coefficients were determined using a 1 cm pathway quartz cuvette. Concentrations of the solutions were of the order of 10^{-4} - 10^{-5} M in order to achieve a maximum absorption in the range 0-2.

7.2.4. Mass Spectrometry

Mass spectra were recorded with an Electro Spray Mass Spectrometer in Trinity College, Dublin, or in the laboratories of Prof. Alain van Dorsselaer in University Louis Pasteur, Strasbourg, France.

7.2.5. Circular Dichroism Spectroscopy

The instrument used was a Jasco-810 circular dichroism spectropolarimeter. All samples were recorded in 1 cm path quartz cuvette.

A150 W Xenon lamp was used as light source. This light, rendered monochromatic and linearly polarized by the monochromator, passes through a polarization modulator to the photo multiplier detector. The polarization modulator induces a periodic variation in the polarization of the light beam through all ellipticities from left circular through elliptical, and elliptical to right circular. During this cycle (at any fixed wavelength) the intensity of the light beam does not vary. The introduction of an optically active sample, which absorbs at this wavelength, sees a preferential absorption during one of the polarization periods, and the intensity of the transmitted light will now vary during the modulation cycle. This intensity variation is directly related to the circular dichroism of the sample at the specified wavelength. Successive detection at various wavelengths leads to the generation of the full CD spectrum. In a CD spectrum, the values of absorbance are measured in ellipticity, θ (measured in mdeg), while the values of $\Delta\epsilon$ are related to the molar ellipticity, $[\Theta] = \theta/cl$, whose units are degree.cm²

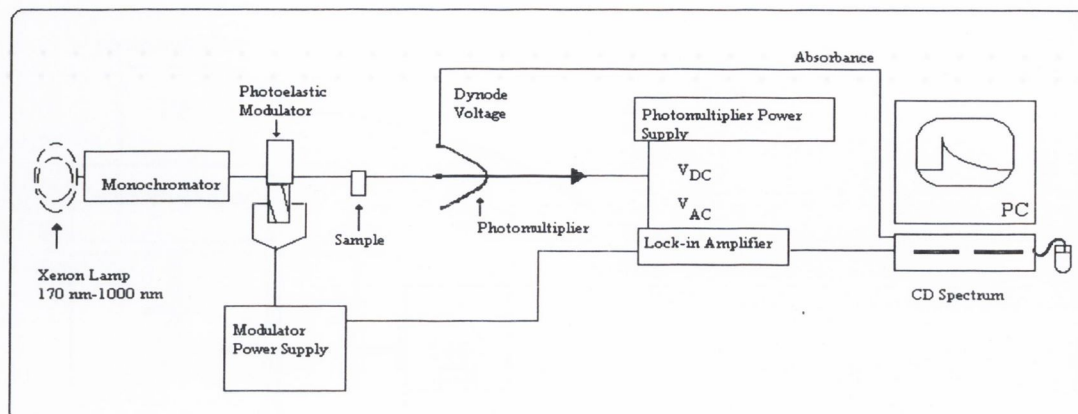


Figure 7.1: *Schematic Representation of a CD spectropolarimeter*

The parameters set for each experiments were: scanning speed: 100 nm/min; Sensitivity: low; Bandwidth: 1 nm; Response: 1 sec; data pitch: 0.5 nm; Accumulation: 3-5. The ICD was obtained by subtracting the CD spectrum of DNA to each spectrum formed at the appropriate concentrations.

7.2.6. Steady-State Emission Spectroscopy

Emission Spectra were obtained using a Edinburgh Instruments spectrofluorimeter. The excitation source was a 150 W Xenon Lamp. The excitation wavelength was selected by a monochromator (ion blazed holographic concave grating F/2.5). The excitation beam was focused on the centre of a 4-face spectroscopy cell containing the sample. The emission light was focused on a monochromator at a 90-degree angle to the excitation beam. For all of the emission measurements, suitable spectroscopic cut off filters were used in order to eliminate stray light. The emission signal was detected by a Hamamatsu R928 red sensitive photomultiplier tube.

All the emission spectra were recorded in air and nitrogen-purged solutions.

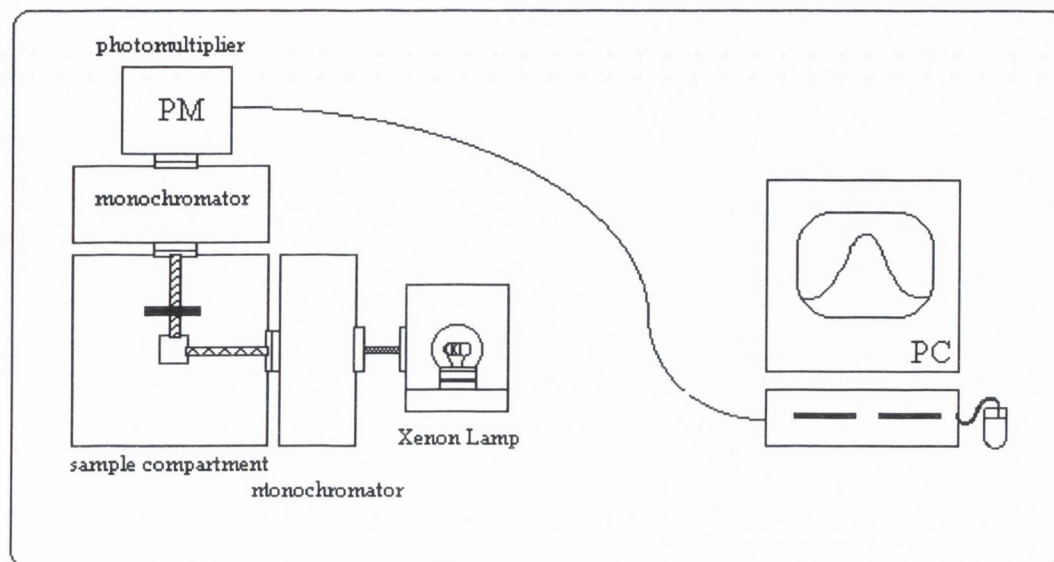


Figure 7.2: *Schematic representation of a spectrofluorimeter*

7.2.7. Life-time measurements: single photon counting (SPC)

Excited state lifetime measurements were carried out using an Edinburgh FL-900 single photon counting spectrometer in the laboratory of Prof. S. Campagna, University of Messina.

The instrument is equipped with a nitrogen-filled discharge lamp and a Peltier-cooled Hamamatsu R928 PM tube. The emission decay were analysed with the Edinburgh Instruments software based on non-linear least-square regression using Marquardt algorithms.

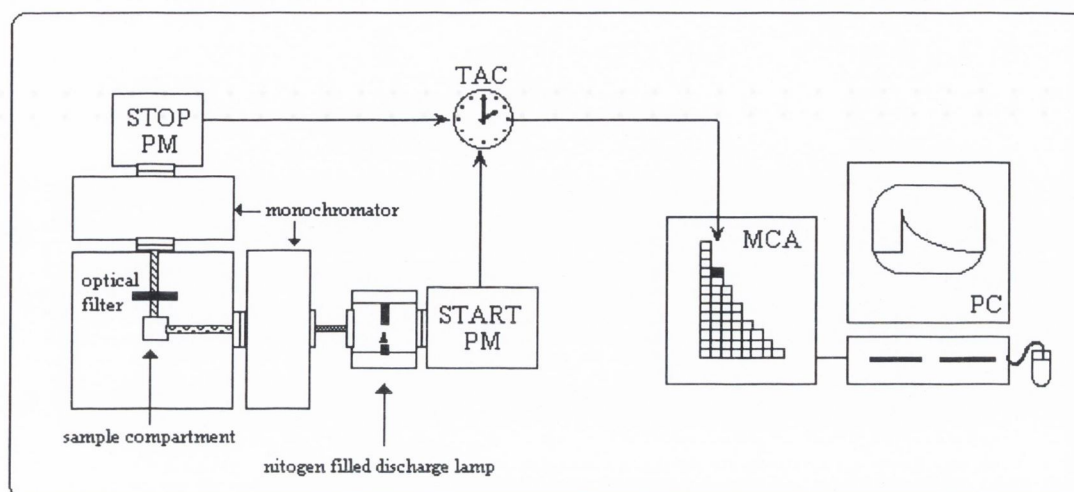


Figure 7.3: *Schematic Representation of the Single Photon Counting Instrument*

7.2.8. Atomic Absorption Spectroscopy

For Chromium analysis the Environmental Unit of Trinity College Dublin performed the measurement under the supervision of Prof. Norman Allott. Chromium quantification was performed by atomic absorption on a Perkin-Elmer 2380 air-acetylene flame atomic absorption spectrophotometer with a Perkin-Elmer chromium hollow cathode lamp-set at 357.9 nm, with a 0.7 mm slit width, gain of 75 and a 1:2 air-acetylene gas mixture. Chromium standards were prepared in 1% HCl from a 1000-ppm chromium standard solution supplied by Reagecon.

7.2.9. Elemental Analysis

The elemental analysis (C, H, N, Cl) of all compounds was performed at the Microanalytical Laboratories of UCD, Dublin, Ireland.

7.2.10. Cyclic Voltammetry

Cyclic Voltammetry experiments were performed on a CV-50W instrument interfaced with a PC in the laboratory of Dr. Mike Lyons (Trinity College Dublin). A Platinum-button working electrode, a platinum-wire counter electrode and a Ag/AgCl electrode (0.20 V) as reference electrode were employed.

Scan rates used were 10mA/V, 20 mA/V, 40 mA/V, 60 mA/V, 80 mA/V and 100 mA/V.

Solution 10^{-3} M of the sample to analyse as PF_6^- or ClO_4^- salts were prepared in dry acetonitrile, using 0.1 M Tetrabutylammonium hexafluorophosphate (Aldrich) (TBAPF_6) as supporting electrolyte or 0.1 M LiCl for water solutions when Cl⁻ salts of the compound were used. The solutions were degassed by bubbling N_2 for about 15 minutes.

7.2.11. X-Ray single crystal structure diffraction

X-Ray Structure Analysis of all compounds were performed at the Queen's University of Belfast, Northern Ireland, by Dr. Mark Nieuwenhuyzen (Appendix A-C and F-L) or at Trinity College Dublin, by Dr. Tom McCabe (Appendix M) or Dr. Paul Jensen (Appendix D-E) on a Bruker Smart APEX CCD four circle diffractometer using Mo-K α radiation except for the $[\text{Cr}(\text{bipy})_2\text{Cl}_2]^{2+}$ (Appendix) on a P₄ Siemens. The temperature at which the data were collected was 153 K. Data were processed and integrated using Bruker SMART and SAINTPLUS software. Absorption corrections were applied using SADABS. The structures were solved and refined using the SHELXTL suite of programs. Crystallographic data and data parameters are reported in the Appendices.

7.2.12. Magnetic susceptibility

Magnetic susceptibility measurements for solid samples of the complexes were carried out using a Sherwood Scientific Balance (Chemistry Department, Trinity College, Dublin) developed by Prof. D. F. Evans of Imperial College London. The instrument is calibrated using $\text{Co}(\text{Hg})(\text{SCN})_4$. Diamagnetic corrections to the apparent magnetic susceptibility values have been incorporated as specified.¹⁸

These data were not discussed in the text under the direction of my supervisors.

7.2.13. pH meter

The pH meter used is supplied by Methrom. It is calibrated with a pH 4 and 7 standard phosphate buffer solution (Aldrich)

7.2.14. Temperature control

The studies in function of temperature (at 20, 25 and 30 °C) were carried out using a peltier associated with the instrument under use.

7.2.15. Experimental errors

Experimental errors in the reported data are as follow: infrared bands $\pm 4 \text{ cm}^{-1}$; absorption maxima (λ_{max}) $\pm 2 \text{ nm}$, extinction coefficients ($\log \epsilon$) $\pm 10\%$, emission maxima $\pm 4 \text{ nm}$, emission lifetimes $\pm 10 \%$, ^1H NMR (δ) $\pm 0.1 \text{ ppm}$, magnetic susceptibilities (μ_{eff}) $\pm 10 \%$, redox potentials (V) $\pm 0.03 \text{ V}$, binding constants (K_b) $\pm 10 \%$, melting temperatures (T_m) $\pm 1 \text{ }^\circ\text{C}$

7.3. Materials and Methods

All chemicals and reagent grade products were obtained from Aldrich, Fluka, Merk or Lancaster and used, unless noted, without further purification.

7.3.1. Ligands

The ligands 1, 10-phenantroline (phen), 2,2'-bipyridine (bipy), 4,4'-dimethyl-2,2'-bipyridine (Me_2bipy), 4,7-dimethyl-1,10-phenanthroline (Me_2phen) and 2,9-dimethyl-1,10-phenanthroline (2,9- Me_2phen) were obtained from Aldrich. All the other ligands were synthesized as described before.

7.3.2. Complexes

$\text{RuCl}_3 \cdot 6\text{H}_2\text{O}$ [41.12 % Ru] was obtained from Johnson Matthey Materials Technology, UK. All the other complexes were obtained by Aldrich.

7.3.3. Calf- Thymus DNA

High molecular weight calf thymus DNA was obtained from Sigma and purified as follows. Approximately 1 gram of DNA was allowed to dissolve overnight in sterile water (500 ml) and then sodium dodecylsulphonate and NaCl added to make it 1% sodium dodecylsulphonate and 1 M NaCl. An equal volume of phenol/chloroform/isoamylalcohol (25:24:1) was added containing 0.5 %w/v of 8-hydroxyquinoline.

This mixture was shaken for 1 hour at 4 °C, and separated by centrifugation at 10,000 rpm. Protein impurities were trapped as a white film between the aqueous and organic layer. The aqueous DNA solution was removed, and the process repeated until it was protein free, usually 1 or 2 times. The DNA was precipitated using two volumes of ice-cold ethanol and spooled onto a glass rod. It was re-dissolved in water to a final concentration of about 3×10^{-3} M phosphate and then dialysed extensively against water and then 10 mM phosphate buffer to remove very low molecular weight DNA. The DNA was free of protein if the absorption ratio A_{260}/A_{280} nm was greater than 1.9. The CT-DNA was stored in sterile Eppendorf tubes at -20 °C, to prevent bacterial growth.

7.3.4. Zn amalgam¹⁹

Mercury chloride (3.67 g, 13.5 moles) was added to a 500 ml beaker containing water (35 ml). HCl (2.75 ml) was added with stirring, resulting in the complete dissolution of the mercury chloride. Zinc powder (18.3 g, 0.28 moles) was added and the mixture stirred for one and half hour. The resulting amalgam was filtered, washed with ethanol (50 ml), dried with diethyl ether (50 ml) and used immediately in the reduction of Cr(III) to Cr(II).

7.3.5. Solvents

All solvents were of the highest available commercial grade and where necessary were purified by distillation. Singly distilled water was deionised using a Millipore Mili-Q water purification system. For all experiments involving DNA, deionised water was sterilised by autoclave (courtesy of the Genetics Department, Trinity College, Dublin) before being used for sample preparation. Ethanol was stored over molecular sieves 4 Å to keep it dry.

Table 7.1. *Solvents used for spectroscopic measurements*

<i>Solvent</i>	<i>Supplier</i>	<i>Purity</i>
Water	University	Millipore
Acetonitrile	Riedel-de Haën	99.9%
Methanol	Riedel-de Haën	99.9 %
Ethanol	Riedel-de Haën	99 %
DMF	Riedel-de Haën	99 %

7.3.6. Buffers

For all DNA manipulation experiments buffers were prepared as specified in Maniatis.²⁰

Phosphate Buffer

Phosphate buffers consisted of solutions of equal concentrations of salt K_2HPO_4 and KH_2PO_4 in deionised water to give a total concentration of phosphate ion of 10 mM. All solutions were pH 7 unless otherwise specified.

7.3.7. Solution Degassing

Where degassing of samples was necessary, the sample was degassed by bubbling with water-saturated nitrogen solution for at least 30 minutes. Similarly where oxygenation was required the solutions were bubbled with water-saturated oxygen for 30 minutes.

7.3.8. Experimental Solution Preparations

Solutions were freshly prepared before each experiment from the stock solutions of accurately determined concentration. Experimental solutions were made up by volume using accurate calibrated micropipettes (Gilson, P20, P200, and P1000). Pipette tips, glasswear and solvent were autoclaved where the experiment involved the use of DNA.

7.3.9. Titration experiments

Titration experiments involved addition of CT-DNA to the metal complex solution or viceversa. The method of Rodger and Norden²¹, was used to avoid dilution effects. Considering a starting sample that has concentration x M of species X. Each time y μ L of Y is added, also y μ L of a $2x$ M solution of X are added. The concentration of X remains constant at x M. For all titrations, after each addition of CT-DNA to the buffered complex solution, the samples were stirred for 15 to 20 minutes in order to reach a thermodynamic equilibrium. Special attention was paid to keep the sample in the dark all the time and not exposed to illumination from the spectrophotometer or from external light, except for the actual measurements or during sample addition for the titrations.

7.3.10. Preparation of Dialysis tubing

The tubing were SPECTRA /POR-2 dialysis tubing, molecular weight cut-off 12000-14000 (SIGMA)

The tubing was cut into pieces of convenient length (10-20 cm) and boiled for 10 minutes in a large volume of 2% (w/v) sodium bicarbonate and 1 mM EDTA (pH8.0). The pieces were rinsed thoroughly in distilled water and then boiled again for 10 minutes in 1 mM EDTA (pH=8.0). The tubes were cooled down, and then stored at 4 °C. Before use the tubing was washed inside and outside with distilled water.

7.3.11. Chromatography

Thin Layer Chromatography

For Thin Layer chromatography (TLC) commercial Alumina (Aldrich) or Silica Plates (Merck) were used.

Size exclusion column (Sephadex LH-20)

Sephadex LH-20 (Fluka) was used as size exclusion resin. The compound, which was loaded on the top of the column, was eluted with acetonitrile. The compound

that is bigger in size elutes first, while the smaller compounds remain in the top of the column.

Anion-exchange column (Sephadex DEAE-Cl⁻ form)

Sephadex DEAE-Cl⁻ (Aldrich) form was used as anion exchange resin to convert the complexes from ClO₄⁻ salts into Cl⁻ salts. The compound was usually stirred in water together with the resin for about 30 minutes until the solution became coloured.

Cation-exchange column (Sephadex CM-C25 or Sephadex SP-C25)

Sephadex SP-C25 (Aldrich) was used as a cation exchange resin to separate the complexes by charge using a solution 0.5 M NaCl water/acetone. This resin was also used by Dr. Nick Fletcher (Queen's University of Belfast) for the resolution of the chromium complexes in enantiomers.

7.3.12. Thermal denaturation studies

DNA melting experiments were carried out by monitoring the absorption (260 nm) of CT-DNA (150 μM) at various temperature (from 20 to 100 °C), in both the absence and the presence of each investigated complex (P/D= 20) using the 'Thermal' program of the Cary 300 (Varian). The melting temperature (T_m) were calculated by derivative methods by the instrument itself after the completion of the experiment. Some of the metal complexes were seen to absorb at 260 nm, but control experiments suggested that this absorption is independent of temperature.

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