Substituted pyridazines as ligands in homoleptic (fac and mer) and heteroleptic Ru(II) complexes†

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This article reports the preparation of a range of phenyl, pyridyl and pyrazinyl substituted pyridazines via the inverse electron demand [2 + 4] Diels–Alder reaction between 3,6-di(2-pyridyl)-1,2,4,5-tetrazines (bptz) and 3,6-di(2-pyrazinyl)-1,2,4,5-tetrazines (bpztz) and suitable dienophiles including acenaphthalene. The resulting polyaromatic compounds vary systematically in the number of aromatic substituents and the number and position of N-heteroatoms. For four of these compounds, the effect of the molecular changes on the solid-state structures were investigated using single crystal X-ray crystallography. The pyridazines were used as bidentate ligands in \{M(II)(bipy)\} and tris(homoleptic) complexes (M = Fe, Ru). The optical and electrochemical properties of these complexes reflect the electron accepting character of the new ligands. The facial and meridional isomers of the tris complexes could be separated by column chromatography (on silica), thus allowing a spectral comparison of their absorption and emission properties. The solid-state structures of several of the metal complexes are discussed, including that of the facial isomer of the tris Ru(II) complex of 3,6-bis(2-pyridyl)-4,5-bis(4-pyridyl)pyridazine—a potential preformed geometric motif for the predirected construction of supramolecular assemblies.

Introduction

This work forms part of a long-standing interest in N-containing polyphenylenes both as synthons in the formation of heteroatomic graphenes and as ligands in co-ordination chemistry. In our synthetic development of N-containing polyaromatic compounds we have established protocols for the [2 + 4] cycloaddition of appropriately substituted alkynes and nitriles to cyclopentadienone derivatives. In order to introduce higher levels of N-doping in the resulting systems our attention has turned to substituted tetrazines as precursors to pyridazines. Such compounds were attractive because tetrazines, particularly 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (bptz) have been used as dienes in inverse electron demand Diels–Alder reactions for many years. Indeed pyridazine-derived assemblies generated synthetically in this manner have been used previously by the authors to demonstrate the importance of C–H···π, π···π and numerous weak C–H···N interactions in the stabilisation of supramolecular architectures.4

Another favourable aspect of this chemistry is the retention of the rich co-ordination chemistry of the tetrazine4 in the resulting pyridazine-derivatives, thus providing access to a variety of transition metal complexes8 and a useful set of systematic building blocks for the construction of supramolecular systems.7–9 3,6-Di(2-pyridyl)pyridazine, for example, is a popular bidentate chelating ligand in coordination chemistry, and complexes a wide range of metals including iridium and palladium.10,11 As highly adaptable ligands, pyridazines have also been used for the construction of supramolecular frameworks containing silver and copper.12,13 Constable and co-workers have prepared pyridazyl-centred ligands by reacting bptz with a variety of substituted alkynyl dienophiles; reporting the supramolecular self-assembly of some of these pyridazyl ligands with silver salts.14

The work herein describes the synthesis of both homoleptic ruthenium and iron and heteroleptic ruthenium bis(bipyridine) complexes of the form [Ru(L)(bpy)]+2. Such systems possess valuable chemical and spectral properties, e.g. metal to ligand charge transfer (MLCT) in the visible region, and long lived excited states. The inertness of the Ru(II) centre also allows the study of redox behaviour without complications arising from ligand substitution or exchange.15 The tris(homoleptic) complexes of the systems presented offer considerable possibilities as supramolecular building blocks due to the ease with which multiple secondary coordination sites can be built into the ligand. However, ideally in order to exploit this potential, the separation of the meridional and facial isomers should be demonstrated.
The presence of only one isomer leads to a more predictable geometric platform on which to build supramolecular structures. In general, fac isomers of coordination complexes have proven most valuable in this regard due to their inherent C₃ symmetry, which gives greater directional control in the formation of assemblies such as helicates. Unfortunately the formation of fac isomers in tris complexes is statistically disfavoured, and fac selective syntheses have only been achieved via tethering the chelating groups, as demonstrated by Weizman et al.¹⁶ and further developed by Fletcher.¹⁷

The separation of facial and meridional isomers is a challenging undertaking, and consequently few examples are found in the literature. Of the reported methods for such isomeric separation (including sublimation,¹⁸ HPLC¹⁹ and ion-exchange assisted Sephadex chromatography²⁰,²¹), it was found that conventional preparative chromatography was sufficient to effect the separation of the mer and fac isomers reported herein.

Results and discussion

The Diels–Alder reaction of bptz and bpztz (synthesised according to literature procedures²⁴,²⁵) and suitable dienophiles gave rise to novel pyridazine centred ligands (Scheme 1). In the reaction of 2-acetyl pyridine with bptz, the ketone functional group was activated using a 10% methanolic solution of KOH, allowing for an 80% yield of 1a. Diels–Alder reactions involving acetylene-derived dienophiles required more extreme reaction conditions: 5-ethynylpyrimidine and bptz were refluxed for 24 h in toluene to give a 65% yield of 2a. In both reactions the products were purified by column chromatography.

In the case of alkene-derived dienophiles, the resulting dihydropyridazinyl Diels–Alder adduct must be oxidized to furnish the aromatic pyridazine product. The reactions of bptz with trans-stilbene, 1,2-di(4'-pyridyl)ethene and 3,3',5,5'-tetramethoxy stilbene led to yields of 92%, 75% and 61%, respectively. After purification by column chromatography these were oxidised using nitrous oxide gas to yield the pyridazine-derived ligands 3a, 4a and 5a in yields of 74%, 50%, and 75%, respectively. 6 has been reported elsewhere⁶ and 3a has been synthesised previously from diphenylacetylene by Constable and co-workers.¹⁴

The same procedures were used to generate compounds 1b–4b. The yields of these reactions were generally lower and their metal complexes deviate little from their bptz-derived counterparts.

Heteroleptic complexes [Ru(1a–6)(bpy)₂][PF₆]₂

The ruthenium(II) bis(bpy) complexes of 1a–6 were prepared by refluxing the ligands with [Ru(bpy)₂Cl₂] in ethylene glycol and water for 4–6 h (Scheme 2). The complexes were isolated in good yield as their PF₆ salts and purified by column chromatography.

Ruthenium(II) and iron(II) tris(homoletic) complexes

The ruthenium(II) tris(homoletic) complexes of 3a, 4a and 5a were prepared on reflux with RuCl₃ and N-ethyl morpholine in ethylene glycol for 72 h. Following precipitation with saturated KPF₆, the two geometric isomers were separated using preparative TLC plates. The particularly low yield of the complex [Ru(5a)₃][PF₆]₂ (mer 5%, fac 3%) arose as a result of the need to further purify the mer isomer via preparative TLC.

Scheme 1 Synthesis of pyridazine derivatives. (i) Stirred at R.T. in THF with KOH; (ii) toluene, reflux overnight; (iii) nitrous oxide gases, CH₂Cl₂.

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Dalton Trans., 2011, 40, 8206–8212 | 8207

The iron(II) tris complexes were prepared from 3\textit{a}, 4\textit{a} and 5\textit{a} with an excess of Fe(BF\textsubscript{4})\textsubscript{2} in acetonitrile. The \textit{mer} and \textit{fac} isomers were again separated by column chromatography and/or TLC plates. (Reaction conditions summarised in Scheme 3.)

Characterization of [Ru(1a–6)(bpy)]\textsubscript{2}[PF\textsubscript{6}]:

In order to facilitate NMR characterisation of the ruthenium(II) \textit{bis}(bipyridyl) complexes of 1\textit{a}, 2\textit{a}, 3\textit{a} and 4\textit{a}, [Ru(1a–4a)(bpy)]\textsubscript{2}\textsuperscript{2+}, the analogous deuterated bipyridine (bpy\textsubscript{d8}) complexes were synthesised. As illustrated in Fig. 1 for [Ru(2a)(bpy\textsubscript{d8})\textsubscript{2}][PF\textsubscript{6}]	extsuperscript{2-}, the removal of the bipyridine signals vastly simplifies the 1\textit{H} NMR spectra. The two 2-pyridyl ring systems were differentiated on the basis of nOe experiments. These indicated a through-space interaction between the proton at C13 on the pyridazine ring in 1\textit{a} and 2\textit{a}, (see Scheme 1 for atom labelling) and the adjacent proton on the co-ordinated pyridyl ring. Full assignment was achieved using a range of 2-D TOCSY NMR experiments.

The 1\textit{H} NMR spectrum of [Ru(6)(bpy)]\textsubscript{2}\textsuperscript{2+} was well resolved, allowing satisfactory characterisation without resorting to the use of bpy\textsubscript{d8}. Analysis of the 1\textit{H}–1\textit{H} COSY showed two three-spin systems (arising from the fluoranthene portion) and six four-spin systems (the pyridyl portions of bpy\textsubscript{s} and 6). ROESY experiments revealed a single interaction between a fluoranthene and a pyridyl spin system—indicating H3\textsuperscript{¢} of the co-ordinated (fixed) pyridine of 6 (ring A) and its closest neighbouring proton, a\textsuperscript{¢} on ring E (see Scheme 1). Further evidence supporting this assignment was obtained by inversion recovery experiments—five of the four-spin systems (excluding ring C) recovered from inversion within 0.8 s. The remainder took over 2.5 s and was assigned as the non-coordinated ring C, the only ring which could not recover through the relaxation pathways provided to the other rings by the co-ordinated metal centre. Signals within each spin system were again assigned using selective TOCSY experiments. The 1\textit{H} NMR spectrum of [Ru(5a)(bpy)]\textsubscript{2}\textsuperscript{2+} was assigned similarly.

UV-Vis spectroscopy

The UV-Vis absorption spectra of the [Ru(1a–5a)(bpy)]\textsubscript{2}[PF\textsubscript{6}]: complexes are shown in Fig. 2. They are quite similar to that of [Ru(bpy)]\textsubscript{3}\textsuperscript{2+}, though the absorbance in the visible region is broader, consisting of two MLCT bands. The most red-shifted of these (\(\approx \lambda 485\) nm) arises from the pyridazine derived ligand (dp → p\textsubscript{1*}). The other band (\(\approx \lambda 428\) nm) is ascribed to an MLCT of the bpy ligands, or to a HOMO–SLUMO (second lowest unoccupied molecular orbital) transition (dp → p\textsubscript{2*}). The absorption maximum at \(\approx \lambda 280\) nm is a ligand-centred transition and varies only slightly from one complex to another. The spectrum of [Ru(6)(bpy)]\textsubscript{2}[PF\textsubscript{6}]: is different from the others: the introduction of the aromatic fluoranthene to the molecule causes some structured ligand-centred absorptions to be observed.
at ~ λ 350 nm and the highest energy 1MLCT band is less intense. Enhanced aromaticity also lowers the energy of the ligand’s π* orbitals, resulting in the most red shifted 1MLCT-pyridazine absorption in the series.

The emission spectra of complexes [Ru(1a–6)(bpy)2][PF6]2 are shown in Fig. 3, excitation into either of the two MLCT absorption maxima exhibited by these compounds, results in the same red emission. Complexes of ligands 3a and 5a emit at a slightly shorter wavelength (λem = 670 nm for both) than those of 1a, 4a and 6 (λem = 700 nm, 710 nm and 710 nm, respectively). The lower energy emission of the latter may be due to the electron-withdrawing character of nitrogen-rich substituents on 1a and 4a, and is a consequence of the aromaticity of the fluoranthene portion of 6.

![Fig. 3 Normalised emission spectra of the complexes [Ru(1a–6)(bpy)2][PF6]2 (2 × 10−4 M in CH3CN).](image)

Electrochemistry

The redox potentials associated with [Ru(1a–6)(bpy)2][PF6]2 are shown in Table 1. The first ligand reduction in each case was assigned to the pyridazine-centred ligand, as their lower energy shown in Table 1. The first ligand reduction in each case was assigned to the pyridazine-centred ligand, as their lower energy π* orbitals (compared to bpy) ensure that these are more easily reduced.27 The second and third highly consistent reductions are assigned to the bpy ligands, though there are pyrimidyl complexes known where the second reduction is thought to occur preferentially on the non-bpy ligand.28 The values of the oxidation potentials indicate the effect of the pyridazine-centre on the electrochemistry of the complexes; its lower pKa (an indicator of lower σ-bonding strength) relative to pyridine results in higher Ru(II/III) oxidation potentials. The final column in Table 1 provides the ΔE1 values of each of the six complexes, calculated by subtracting the first reduction potential of each complex from its oxidation potential. These values give an indication of the HOMO–LUMO energy gap and correlate with the position of the MLCT emissions. [Ru(5a)(bpy)2][PF6]2 has the highest energy emission (λmax 670 nm) and the largest ΔE1 (2.51 V). Similarly [Ru(6)(bpy)2][PF6]2, having the lowest energy emission, λmax 710 nm, has the smallest ΔE1 value (2.22 V). Although ΔE1 values can have error values of up to ± 20 mV, the results were found to be highly reproducible.

![Fig. 4 The 1H-NMR spectrum of fac-[Ru(3a)3][PF6]2 (CD3CN, RT, 600 MHz).](image)

Ruthenium(II) tris(homoleptic) complexes of ligands 3a–5a

The 1H NMR spectra of the mer isomers of the ruthenium(II) tris complexes of ligands 3a, 4a and 5a consisted of many overlapping signals and only the most highly shielded and deshielded signals could be assigned (see ESI†). 2D-NMR experiments and the C1 symmetry of the fac isomers aided spectral assignments. The 1H-NMR spectrum of fac-[Ru(3a)3][PF6]2 is shown colour coded in Fig. 4. The H3 protons are expected to be shielded by the neighbouring ring current; H3 of ring A experiences this effect to the greatest extent as it has no freedom to rotate. On this basis the two 2-pyridyl rings were differentiated using 2-dimensional NMR TOCSY experiments. The two phenyl rings give rise to two separate sets of signals, TOCSY NMR experiments show that one ring exhibits three sharp peaks whereas the other displays two broad signals which sharpen and shift at higher temperatures. Full details of the NMR assignments of these complexes are given in the ESI†.

UV-Vis spectroscopy

The UV-Vis absorption spectra of both isomers of [Ru(3a–5a)3][PF6]2 are shown in Fig. 5. The absorption maxima are bathochromically shifted (~λ 20 nm) relative to [Ru(bpy)3]2+ due
The UV-Vis absorption spectra of the fac and mer isomers of [Ru(3a–5a)]₂[PF₆]₂ (2 × 10⁻⁵ in CH₃CN).

to the increased electron withdrawing character of the pyridazine ring. The most interesting feature of the spectra is the small but consistent bathochromic shift of the mer isomers relative to their fac counterparts. This is as a result of the reduced symmetry associated with the mer isomer, and the loss of degeneracy in the ligands’ π* orbitals.

The emission spectra of [Ru(3a–5a)]₂[PF₆]₂ are shown in Fig. 6. These spectra reflect a pattern similar to that of the absorption spectra: there is a small consistent bathochromic shift in the emission maxima wavelength for each mer isomer relative to its fac counterpart. This difference is most apparent for the complex of ligand 3a, where the maximum of the mer isomer is red-shifted 27 nm compared to the fac isomer. The fac isomer of the complex [Ru(4a)]₂[PF₆]₂ has the lowest energy emission of the three fac isomers (λ 638 nm), probably due to the lower energy of the π* orbitals arising from the electron-withdrawing effect of the 4-pyridyl substituents.

Iron(II) tris(homoleptic) complexes [Fe(3a–5a)]₂[PF₆]₂.

The meridional and facial isomers of the iron(II) complexes were similarly characterised by ¹H-NMR spectroscopy, mass spectrometry and UV-Vis spectroscopy. The ¹H-NMR spectra of the meridional isomers were complicated due to the lack of symmetry, however the methoxy protons were easily assigned, being the most shielded signals (ca. δ 3.6 ppm). The phenyl protons appear at δ 6.4 ppm, and the 2-pyridyl signals appear between δ 7.0 and 8.5 ppm. The fac isomer of [Fe(5a)]₂[PF₆]₂ is drawn colour-coded along with its assigned ¹H NMR spectrum in Fig. 7. The proton signals were identified using a range of 2D-NMR techniques. Of particular note are the phenyl signals appearing between δ 6.0–7.0 ppm. The spectrum is similar to that of its ruthenium counterpart, with broadening observed in the signals associated with the aryl substituents. Assignments of the ¹H-NMR spectra of the mer and fac isomer of [Fe(3a)]₂[PF₆]₂ and [Fe(4a)]₂[PF₆]₂ were also obtained and are provided in the ESI†

The UV-Vis absorption spectra of the fac and mer isomers of the three iron tris(homoleptic) complexes of ligands 3a, 4a and 5a are shown in Fig. 8. The high-energy region of the spectra in each case is dominated by a ligand-centred π→π* transition which, for comparison appears at λ 298 nm in [Fe(bpy)]⁺.³⁰ Again, the meridional isomer of each complex absorbs at slightly longer wavelength than its facial analogue. The electron-withdrawing effects of the 4-pyridyl and the electron-donating effect of the methoxy substituents is evident in the slight shift in the absorption

Fig. 5 The UV-Vis absorption spectra of the fac and mer isomers of [Ru(3a–5a)]₂[PF₆]₂ (2 × 10⁻⁵ in CH₃CN).

Fig. 6 The normalised emission spectra of the fac and mer isomers of [Ru(L)]₂[PF₆]₂ for ligands 3a, 4a and 5a in CH₃CN.

Iron(II) tris(homoleptic) complexes [Fe(3a–5a)]₂[PF₆]₂.

The meridional and facial isomers of the iron(II) complexes were similarly characterised by ¹H-NMR spectroscopy, mass spectrometry and UV-Vis spectroscopy. The ¹H-NMR spectra of the meridional isomers were complicated due to the lack of symmetry, however the methoxy protons were easily assigned, being the most shielded signals (ca. δ 3.6 ppm). The phenyl protons appear at δ 6.4 ppm, and the 2-pyridyl signals appear between δ 7.0 and 8.5 ppm. The fac isomer of [Fe(5a)]₂[PF₆]₂ is drawn colour-coded along with its assigned ¹H NMR spectrum in Fig. 7. The proton signals were identified using a range of 2D-NMR techniques. Of particular note are the phenyl signals appearing between δ 6.0–7.0 ppm. The spectrum is similar to that of its ruthenium counterpart, with broadening observed in the signals associated with the aryl substituents. Assignments of the ¹H-NMR spectra of the mer and fac isomer of [Fe(3a)]₂[PF₆]₂ and [Fe(4a)]₂[PF₆]₂ were also obtained and are provided in the ESI†

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maxima of the MLCT of complexes of 4a and 5a compared with the complexes of 3a.

Crystallographic studies

The single crystal X-ray structures of the ligands 1a, 2a, 3a and 6 are provided and discussed in the ESI.† The experimental and crystallographic data for the ruthenium complexes are detailed here and summarised in Table 2. Crystals of [Ru(2a)(bpy)]2+ were grown by slow evaporation of diethylether into an acetone solution of the complex. The asymmetric unit consists of the octahedral complex species along with two PF6− counter ions and three dichloromethane molecules.

Table 2 Crystal data for complexes [Ru(bpy)2(1a)][PF6]2, [Ru(bpy)2(2a)][PF6]2, [Ru(bpy)2(6)][PF6]2 and [Ru(3a)][PF6]2.

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Fig. 9  Ortep representation of the crystal structure of [Ru(2a)(bpy)]2+[PF6]2, (ellipsoids shown at 50% probability), the host–guest interaction observed is illustrated on the right.

A crystal of fac-[Ru(3a)][PF6]2, suitable for single crystal X-ray diffraction was grown by slow diffusion of diethylether into an acetone solution of the complex (see Fig. 11). The complex crystallised in a P3 trigonal space group and the unit cell contains two complex molecules and two [PF6]2− equivalents. The ruthenium(n) metal centre occupies a crystallographic special position at the 3-fold centre of symmetry and the anions are distributed across three sites (see Figure S3†). The host-framework comprises a layered arrangement of the metal centres with the guest framework, with two acetone molecules and two PF6− anions occupying the void space (Fig. 9). The guest species is held to the host-framework through C–H···O (H···O, 2.42, 2.45 Å) and C–H···F (H···F distance varying from 2.31 to 2.53 Å) interactions. Unlike many such porous assemblies, the void space is not extended further to form a channel.

Crystals of [Ru(1a)(bpy)]2+ were grown by slow evaporation of diethylether into an acetone solution of the complex. The mixture yielded a complex, isostructural with that of [Ru(2a)(bpy)]2+ (space group P2₁/c).

Crystals of [Ru(6)(bpy)]2+ were obtained via recrystallisation from a dichloromethane/hexane mixture. The asymmetric unit consists of two PF6− counter ions and three dichloromethane molecules, crystallising in the monoclinic P2₁/c space group. The Ru–N bond lengths are typical, ranging from 2.03(5) Å to 2.074(5) Å. The crystal packing is presented in Fig. 10.

Fig. 10  Representations of the lattice structures of [Ru(6)(bpy)]2+[PF6]2.
Fig. 11 Left: Ortep representation of the crystal structure of \(\text{fac-}[\text{Ru}(3a)(bpy)]_2[\text{PF}_6]_2\). (ellipsoids shown at 50% probability, counterions removed for clarity). Right: A representation of the hexagonal packing arrangement (Ru(t) centres shown as turquoise octahedra. (Counterions removed for clarity.)

Anions lying in different planes. The bond lengths between the ruthenium metal and the pyridine and pyridazine nitrogen donor atoms are similar: 2.059(4) Å and 2.007(4) Å respectively. An ORTEP representation of the complex cation is shown in Fig. 11, alongside a representation of the packing arrangement observed down the c axis. The complex forms a porous assembly which is stabilised by weak intermolecular \(\pi \cdots \pi\) (3.481 Å) and C–H···F (2.546 Å–2.650 Å) interactions.

Conclusion

A family of substituted pyridazines, arising from inverse electron demand [2 + 4] Diels–Alder reactions between tetrazines and suitable dienophiles including acenaphthalene, have been structurally characterised and their crystal packing arrangements examined. The optical and electrochemical properties of these species as ligands in Fe(II) and Ru(II) complexes were shown to depend on the electron withdrawing nature of the pyridazine. The separation of both mer and fac isomers of the tris(homoleptic) complexes were shown to exhibit a slight but consistent red-shift in the absorption spectra. In one case the fac-isomer was structurally characterised revealing the potential of such symmetric complexes with multiple metal coordination modes in supramolecular frameworks. The work opens the possibility of using preformed geometrically separable isomers as predirecting supramolecular motifs.

Experimental section

Full experimental details are available in the ESI.† CCDC 812335–812342 contain the supplementary crystallographic data for this paper.†

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