Synthesis and photochemical studies of Cu(I) complex with 1,4-bis(3,5-dimethylpyrazol-1yl)tetrazine ligand

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1.   INTRODUCTION

Nitrogen-rich compounds are unique very reactive substances which have high heats of formation. Pyridine is one of the most well known aromatic cycles where a CH is replaced by a nitrogen atom, but the pyridine ring is only one member of the azine heterocycles, in which one or more CH group of benzene is replaced by π-accepting and σ-donating nitrogen atoms, proceeding from diazines (pyridazines, pyrazine), triazines and up to tetrazines. Tetrazines are typical representatives of nitrogen rich heterocyclic compounds. They have a range of applications such as explosives,[1] propellants and pyrotechnic ingredients,[2] biological agents for recognition of anion[3] and precursors for drug development. [4,5]

Self-assembly of metal cations with nitrogen heterocyclic bridging ligands is a central theme in supramolecular chemistry aimed at developing assemblies of electronically coupled metal centres.[6] These ligands can be used to bridge metal centres in various ways, allowing electron and charge transfer processes in the structures. 1,2,4,5-Tetrazines also have very interesting redox-behaviour, which are similar to quinones.[7] The very low-lying π^* orbital localised at the four nitrogen atoms in tetrazines might allow intense low-energy charge valence transfer absorptions, electrical conductivity of coordination polymers, unusual stability of paramagnetic radicals or mixed valence intermediates. The ability of tetrazine π-ligand systems is well documented,[1,11a] double coordination of metal fragments to such binucleating ligands are known to cause a particularly strong perturbation of the ligand π system as is evident from pronounced spectroscopic effects.[8]

1,2,4,5-tetrazines and its 3,6-disubstituted derivatives exhibit interesting coordination chemistry, characterised by electron and charge transfer and by the ability of these nitrogen-rich ligands to bridge metal centres in various ways. Tetrazines also have a rich organic chemistry involving cycloaddition reactions, that makes them valuable organic reagents. Here we consider some aspects of coordination chemistry of known 3,6-disubstituted tetrazines.

The presence of at least four nitrogen donor atoms in the tetrazine derivatives allows for a potentially rich coordination chemistry. Tetrazines have a very low lying π^* molecular orbital, replacement of the four CH groups in the 1,2,4,5-positions of benzene by the more electronegative nitrogen atoms results in particular stabilisation of the unoccupied a_u orbital, making tetrazines very reducible.[9] Their anion radical and 3,6-dihydro forms are often more stable than the 'aromatic' parent molecule. 1,2,4,5-tetrazines can also be readily reduced to 3,6-dihydro derivatives.[10]

There has been only a little work done on the unsubstituted parent tetrazine due to the difficulties with its synthesis and stability. In contrast the chemistry of 3,6-substituted tetrazines and its derivatives has been studied quite extensively.[11] There are various examples of metal complexes for these substituted tetrazine derivatives.

2,2'- Bptz (3,6-bis(2-pyridyl)tetrazine) has also been used in the preparation and characterisation of paramagnetic Cu(I) dimers that can be described as anion radical complexes of binucleating α-diimines or α-iminoketones.[12] Interest in the former species stems from the assertion that the emitting state of the electron-transfer-active (α-dimmine) Cu(I) complexes may be described as resulting from the Metal-to-Ligand Charge Transfer (MLCT), i.e. involving the anion radical of the ligand. Complexes of the type $Cu(NN)_2^+$, where NN represents diimine ligands (i.e. bipyridine, tetrazine and their substituted derivatives), exhibit strong absorption bands in the near UV and visible range, due to MLCT transitions. The MLCT state gives rise to a rich variety of photophysical processes that have been studied in the past. For these reasons Cu(I) complexes with the various disubstituted tetrazines are of great interest.[13], [14]

Here we report synthesis and photochemical studies of 3,6-Bis(3,5-dimethylpyrazol-1-yl)-tetrazine ligand (dmptz)and its Cu(I) complex.

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2. RESULTS AND DISCUSSION

2.1 Synthesis and characterisation of 3,6-Bis(3,5-dimethylpyrazol-1-yl)-tetrazine

3,6-Bis(3,5-dimethylpyrazol-1-yl)-tetrazine (dmptz) has some structural similarities to the well known bppz and bptz ligands which have been used as bridging ligands in transition metals,[15] however the chemistry of dmptz is very poorly developed. The structure of dmptz allows for two metal centres to be attached and interlinked, which will result in the formation of new interesting poly-metallic complexes.

The dmptz ligand was synthesised according to published procedure.[16] The preparation follows a four step process (Scheme 1) resulting in a high yield (87%) of dmptz with one by-product being formed in situ.

3,6-bis(3.5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine

3,5-dimethy-1-1H-pyrazole hydrochloride

3,6-Bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine
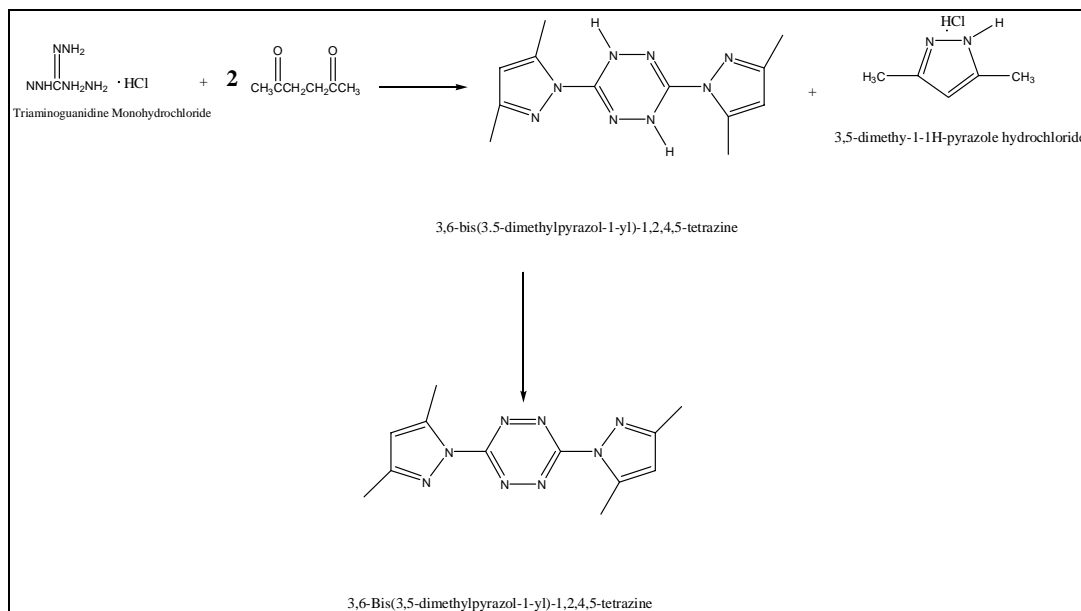
Scheme 1: Synthesis of 3,6-Bis(3,5-dimethylpyrazol-1-yl)-tetrazine (dmptz).

The by-product 3,5-dimethy-1-1*H*-pyrazole hydrochloride can be easily separated due to its high solubility in water, leaving the product dmptz, as a red precipitate.

The target product, dmptz, was characterised by melting point, elemental analysis, MS ES, NMR, FTIR spectroscopy and X-ray single crystal diffraction from crystals formed. The melting point of the ligand was determined to be 224 $^{\circ}$C [lit. 225 $^{\circ}$C].[16] A ^{1}H NMR (400MHz 298K) spectrum in CDCl$_3$ contained characteristic peaks of 3,6-bis(3,5-dimethylpyrazol-1-yl)-tetrazine at 2.39, 2.72, and 6.20 ppm with appropriate integration. ^{13}C-NMR spectrum showed peaks of the symmetric compound at 13.21 (CH$_3$), 18.36 (CH$_3$), 104.98(CH), 143.76 (pyrazol), and 169.67 (C, pyrazol). A ES^{+} mass spectrum of dmptz in CH$_3$CN showed M^{+} peak at 270 with appropriate fragmentation of the molecule.

2.2 Spectroscopic studies

A UV-Visible spectrum and a photoluminescence spectrum of the dmptz in spec-grade acetonitrile are presented in Figure 1 and Figure 2 respectively. The UV-Visible spectrum shows absorption with maxima at 290 nm corresponding to π-π absorption of dmptz. Since there is no available information on the luminescence properties of disubstituted tetrazines, dmptz was investigated by photoluminescence spectroscopy. The photoluminescence, PL, spectrum of dmptz (1×10^{-8} M) in spec-grade acetonitrile have shown a luminescence band at 320-350 nm, after excitation at 280 nm, Figure 2.
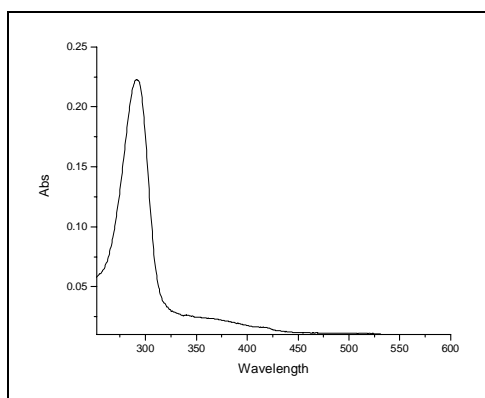
Figure 1: A UV-vis spectrum of dmptz (1×10^{-8} M) in acetonitrile.
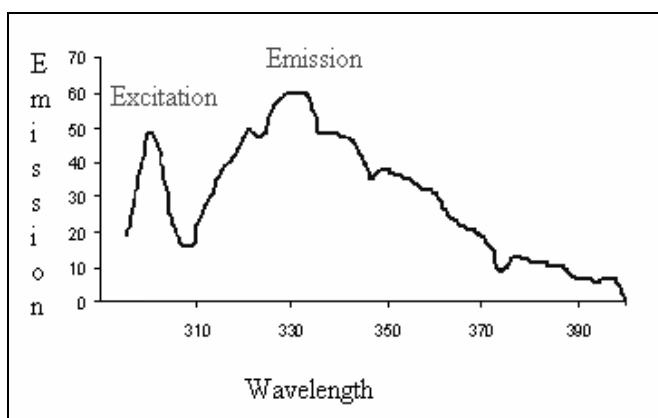

Figure 2: PL excitation and emission (when excited at 280nm) spectra of dmptz in acetonitrile.

Cu(I) diimines are known as the first row-transition metal compounds with excited state properties that are at all comparable to Ru^{II}(bpy) complexes. Cu(I) diimine complexes generally absorb UV–vis light over the range of 350–650 nm with relatively high extinction coefficients ($\varepsilon \sim 10^{3}$–10^{4} M^{-1}cm^{-1}). The most suitable comparisons is the phenanthroline ligands that possess alkyl or aryl subsitutents in the 2- and 9- positions, the MLCT excited states are emissive with 10^{-9}–10^{-7} s lifetimes at room temperature.[17] Copper is less toxic, less expensive, and less environmentally hazardous than Ruthenium. Therefore new photoluminescent Cu(I) complexes present a great research and commercial interest. The synthesis of the Cu(I)dmptz complex was carried out as a one step process by reaction of tetrakis(acetonitrile)copper(I) hexafluorophosphate with the dmptz in acetonitrile-THF mixture (Scheme 2). Due to the low solubility of the product it was precipitated from the reaction mixture as a deep violet powder, **1**, in 76% yield.
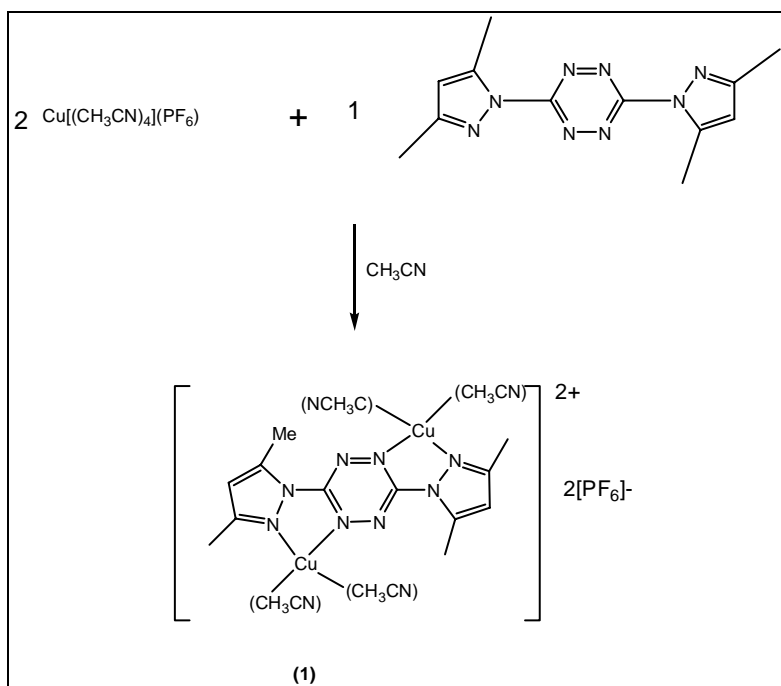
Scheme 2: Preparation of [{Cu(CH₃CN)₂}₂dmptz][PF₆]₂ (**1**).

The complex was characterised by elemental analyses, ^{1}H NMR, ^{13}C NMR, FTIR, and ESI mass spectroscopy. The results of the elemental analysis were in perfect agreement with the formula [{Cu(CH$_3$CN)$_2$}$_2$(dmptz)][PF$_6$]$_2$. A ^{1}H NMR of the complex in CD$_3$CN has shown characteristic peaks of one dmptz ligand at 2.25(Me), 2.30(Me), 6.32(pyrazol) with appropriate integration. ^{13}C NMR spectrum of **1** contained peaks at 193.13 ppm, 142.95 ppm, 102.58 ppm, 12.51 ppm, 12.48 ppm, that were assigned to the Cu(I)dmptz complex.

ESI$^+$ MS spectrum of the compound in an acetonitrile-methanol mixture has shown the maximum mass-peak at 605 ([Cu$_2$dmptz(CH$_3$OH)$_2$PF$_6$]$^+$) and fragments that can be attributed to the different Cu(I)dmptz species. IR bands show peaks at 723, 1091, 1239, 2726 and 3365 cm^{-1} characteristic of the dmptz ligand.

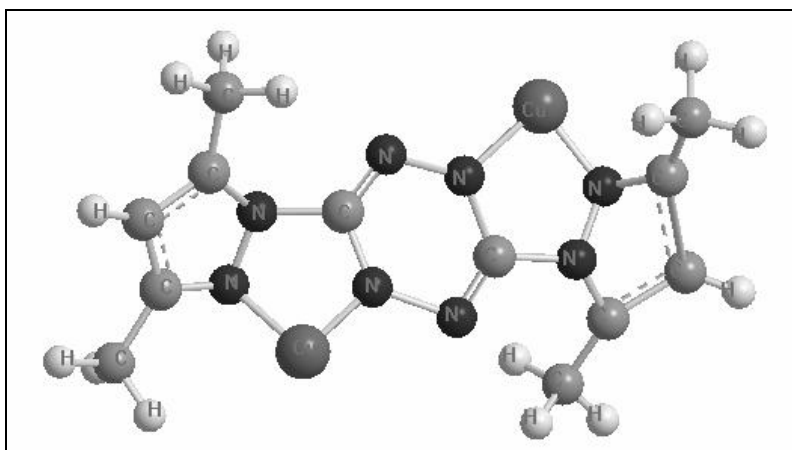Based on the results obtained the dinuclear dmptz-bridged structure shown in Figure 3 was suggested.

Figure 3: Computer-simulated 3D structure of [{Cu(CH$_3$CN)$_2$}$_2$(dmptz)][PF$_6$]$_2$ (**1**). PF$_6$

anions and CH$_3$CN ligands are omitted for clarity)

A UV-Visible spectrum (Figure 4) of the complex in acetonitrile contained broad bands of at 290 nm(dmptz) and 530 nm (MLCT).
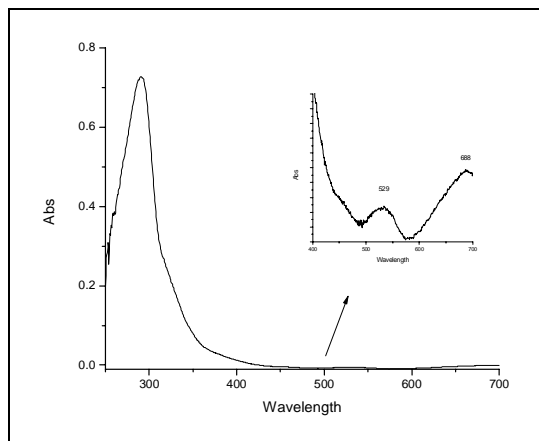

Figure 4: UV Vis spectrum of copper complex **1**.

Surprisingly all our attempts to prepare a Cu(I) complex with 1:1 Cu:dmptz ratio using an excess of the ligand resulted only in formation of 2:1 complex $[\{Cu(CH_3CN)_2\}_2(DMPTZ)][PF_6]_2$. Presumably this is due to the competitive coordination of acetonitrile molecules and the presence of methyl-subsitutents in the ligand. The methyl subsitutents make the dmptz ligand quite sterically demanding, which prevents the coordination of the second dmptz ligand to the same metal centre in this case.

The low-lying π^* MO, a_u, of tetrazines are an excellent target orbital for low energy electronic transitions, therefore the copper metal complex exhibits large MLCT bands.[18,16a] This emission band can be seen in Figure 5.
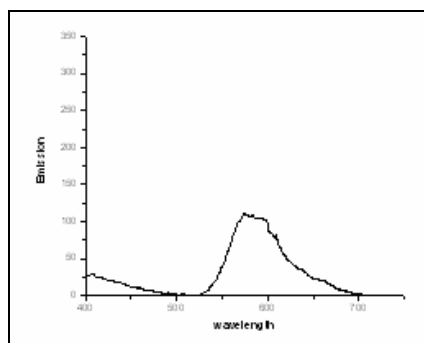

Figure 5: Cu(I) DMPTZ emission spectrum when excited at 300nm.

The copper(I) complex was excited at 256 and 260nm to study the shift in emission spectra for the copper, Figure 6. It can be seen that the emission λ_{max} occurs at 565 nm, when excited at 260nm. A glass filter is used to block harmonics.
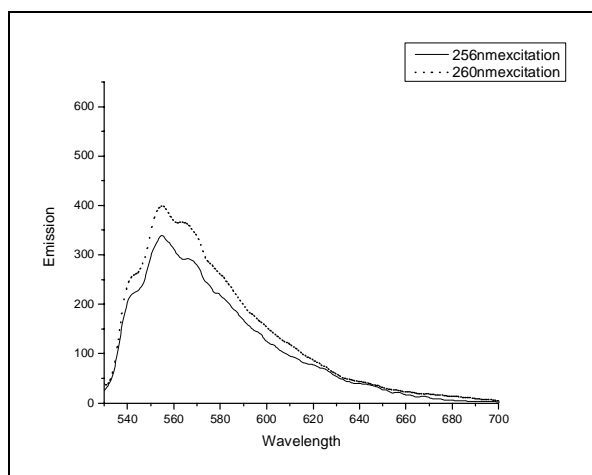
Figure 6: Emission spectra for the copper(I) dmptz complex (**1**).

It was found that changing the polarity of the solvents (acetonitrile, THF and toluene) would cause a small shift in λ_{max} of emission for the ligand. Emission bands in both spectra are due to transitions in the dmptz ligand and do not involve Cu-transitions, which should be observed at higher (over 800 nm) wavelengths, which was not possible with our equipment. The low-lying π^* MO(a_u of tetrazines is an excellent target orbital for low energy electronic transitions, therefore the copper metal complexes might also exhibit MLCT bands, often extending into the near IR region).[19]

3.   EXPERIMENTAL

3.1   Synthesis of Triaminoguanidine Monohydrochloride

Hydrazine monohydrate was added slowly to guanidine hydrochloride (19.1g, 0.020 moles) in 1,4-dioxane (100 ml) under stirring. The mixture was heated under reflux for two hours. The solution was then cooled to room temperature and the product was collected by Büchner filtration, washed with 1,4-dioxane and dried on the air. The product formed was triaminoguanidine monohydrochloride (25.2g, 98%). M.p. 229°C, (lit. 230 °C). ^{1}H NMR (400 MHz, CDCl$_3$, 298K) δ: 1.28(s, 4H, NH$_2$), 7.28(s, 2H NH$_2$), 2.2(s, 2H, NH). ^{13}C NMR (100 MHz, CDCl$_3$, 298K), δ: 154.82. IR (KBr, cm^{-1}): 723.2(w, CH) 966.16(m, C-H), 1604.49(m, NH$_2$), 2032.61, 2335.38(m, NH), 2726(m, NH).

3.2   Synthesis of 3,6-Bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine

2,4-Pentanedione (30.0g, 0.30 moles) was slowly added to triaminoguanidine monohydrochloride (21.09g, 0.15 moles) in water (150 ml) cooled in an ice-bath. The mixture was heated under reflux for four hours. During the experiment a yellow solid precipitated out of solution. The solution was cooled, the product was collected by filtration, washed with water, and dried to yield a yellow powder of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (17g, yield 83%). M.p. 150°C (lit. 152°C). ^{1}H NMR (400 MHz, CDCl$_3$, 298K) δ: 2.22(s, 6H, Me), 2.47(s, 6H, Me), 5.98 (s, 2H, CH), 8.12 (s, 2H, H-N).

3.3   Oxidation to 3,6-bis(3.5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine

3,6-bis(3.5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine was prepared by oxidisation of 3,6-Bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine using a mixture of NO and NO$_2$ gases. NO/NO$_2$ gas was generated by slow addition of concentrated nitric acid onto iron filings in a reaction vessel (3-neck round bottom flask). A slow steady stream of argon gas was used to bubble the NO/NO$_2$ gas mixture through a series of tubes and a gas trap, into a solution of 3,6-Bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (13.2g) in 1-methyl-2-pyrrrolidinone(100 ml) for one hour. Upon oxidation the reaction mixture colour changed to deep red. Ice water (200 ml) was added to the mixture, and the red solid that precipitated out of solution was collected by filtration and washed with water. The final translucent red

product was crystallised from acetonitrile and dried in vacuum (12.3g, 99% yield). M.p. 224°C (lit 225°C). ^{1}H NMR (400 MHz, CDCl$_3$, 298K), δ: 2.39 (s, 6H, Me), 2.72 (s, 6H, Me), 6.20 (s, 2H, CH).
^{13}C NMR (100 MHz, CDCl$_3$, 298K). 13.21 (CH$_3$) 18.36 (CH$_3$) 104.98(CH), 143.76 (pyrazol), 169.67 (C, tetrazine ring).

3.4 Preparation of tetrakis(acetonitrile)copper (I) hexafluorophosphate

Cu[CH$_3$CN]$_4$](PF$_6$) was prepared according to published procedure.[20] Copper(I) oxide (4g, 0.028 moles) was mixed with acetonitrile (80ml) in a round bottom flask. HPF$_6$ (10ml, 60%, 113 mmole) was added slowly with constant stirring over a 30 minute period. After addition of all the HPF$_6$ the mixture was left stirring for a further 10 minutes, then the hot mixture was filtered removing any unreacted copper(I) oxide. The blue solution was then cooled to -10°C in a freezer and left overnight. A blue-white powder crystallised out of solution, which was collected by filtration, washed with diethyl ether and then recrystallised from CH$_3$CN. The pure tetrakis(acetonitrile) copper (I) hexafluorophosphate, was then dried in vacuum and stored under argon (6.9g, 72%). ^{1}H NMR (400 MHz, 298K,CDCl$_3$) δ: 2.15 (s, 12H, Me). Elem. Analysis found C, 26.02%, H, 3.31%, N, 15.72 %; required for CuC$_8$H$_{12}$N$_4$PF$_6$ C, 25.78; H, 3.25; N, 15.03.

3.5 Synthesis of Cu(I)-3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine complex (1)

Dmptz (0.015g, 5.37x10^{-5} moles) was dissolved in dry THF under argon. Cu[CH$_3$CN]$_4$](PF$_6$) (0.04g, 1.07x10^{-4} moles) was added slowly under constant stirring. Upon addition of the copper the solution colour changed from bright red to dark blue. The mixture was left stirring overnight, the solvent was then removed by canular filtration and the dark blue product was washed with dry THF and dried in vacuum to give the Cu(I) dmptz complex (0.038g, yield 76%). Elemental analysis, found %: C - 28.81, H - 3.02, N - 20.35.; Cu$_2$C$_{20}$H$_{26}$N$_{12}$P$_2$F$_{12}$ requires C - 28.17, H - 3.05, N - 19.72. ^{1}H NMR (400 MHz, 298K,CDCl$_3$) δ: 2.25 (s, 24H, Me), 2.3 (s, 24H, Me), 6.32 (s, 8H, ring). ^{13}C NMR(400 MHz, 298K,CDCl$_3$) δ: 193.13, 142.95, 102.58. MS ES$^+$ in acetonitrile: 605(Cu$_2$dmptz(CH$_3$OH)$_2$[PF$_6$])$^{+1}$, 547(Cu$_2$dmptz(CH$_3$CN)$_4$),- CH$_3$)]$^{+1}$, 334(Cu$_1$dmptz)$^{+1}$, 271(Dmptz)$^{+1}$. IR (KBr, cm^{-1}): 2844(s, CH$_3$), 1440 (m, NN), 1097 (s, CH), 842 cm^{-1} (m).

4. CONCLUSIONS

Dmptz was found to be an excellent bridging ligand for Cu(I) complexes. The Cu(I) complex has been shown to have a dinuclear structure where a single dmptz ligand links two metal centers. It is apparent that the methyl groups of dmptz have a large steric effect on the structure of the complexes preventing the formation of larger tetra- or penta- nuclear complexes reported in the literature for similar ligands (bptz). We have shown that Cu(I) dmptz complexes possess interesting luminescent properties, that might be potentially used to prepare new luminescent materials for sensing and energy conversion applications.

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