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FULL PAPER

Copper(II/I) complexes of a bulky tris(pyrazolylmethyl)amine ligand

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The ligand tris[3-(4-methoxyphenyl)-5-methylpyrazol-1-ylmethyl]amine (L), the copper(II) complexes [$CuLCl_2$] **1**, [CuLCl][SbF_6] **2** and [$CuL(H_2O)$][SbF_6]$_2$ **3**, and the copper(I) complex [CuL][CF_3SO_3] **4** have been prepared. Complexes **1**–**3** are reduced by [BPh_4]$^-$ ion in a range of solvents to afford [CuL]$^+$. The [CuL]$^+$ ion does not react with dioxygen nor carbon monoxide but does react with chloride ion. Physicochemical and cyclic voltammetry data are reported for **1**–**4**, along with crystal structure analyses of **1**–**3** and [CuL][$CuCl_2$]. There are some notable differences between the structures and properties of these copper complexes and those reported for analogues with pyridyl- or imidazolyl amine ligands.

Introduction

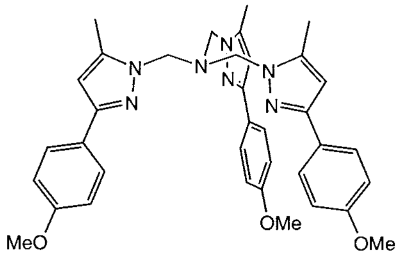
Investigations of copper complexes of tris(2-pyridylmethyl)amine (tpa) and substituted derivatives of this ligand have contributed greatly to understanding of the binding of dioxygen to copper(I) centres.[1–20] For example, reaction of [Cu(tpa)(MeCN)]$^+$ with dioxygen afforded the first X-ray crystallographically characterised copper–dioxygen adduct, [$Cu(tpa)_2(\mu\text{-}O_2)$]$^{2+}$.[2] This research has been extended to copper complexes of bulkier, substituted tpa derivatives,[3–12] to dicopper complexes with linked tpa units,[13–15] and to copper complexes of tripodal ligands based on the tpa core but with one or more of the pyridyl rings replaced by other donor groups.[16–21] We targeted copper complexes with phenol substituents as models for biological copper centres with proximal tyrosine groups.[22] Pyrazoles are arguably the most easily derivatised N-heterocycles[23,24] and readily afford tris(pyrazolylmethyl)amine analogues of tpa.[25] Dioxygen-binding copper(I) complexes with pyrazolyl donor groups,[20,26,27] including of pyrazolylmethylamine ligands,[20,27] are well known. Therefore, we prepared and describe herein the copper complexes of a new tris(pyrazolylmethyl)amine ligand with *p*-methoxyphenyl substituents (as potential precursors to phenol substituents).

Results and discussion

Ligand preparation

The targeted tripodal ligand for this study was tris[3-(4-methoxyphenyl)-5-methylpyrazol-1-ylmethyl]amine (L). The substituted pyrazole, 3-(4-methoxyphenyl)-5-methylpyrazole **I**, the precursor to L, was prepared by a slight modification of a method reported by Trofimenko *et al.*[23] as follows. The diketone from condensation of 4-methoxyacetophenone with ethyl acetate using sodium methoxide in toluene was treated with hydrazine to afford **I** in 42% overall yield. Treatment of **I** with aqueous formaldehyde[28] gave 1-hydroxymethyl-3-(4-methoxyphenyl)-5-methylpyrazole **II** as a white, microcrystalline powder in 46% yield. The addition was regioselective occurring entirely at N^1; conjugation with the methoxyphenyl ring makes this the favoured position for the addition. Reaction of **II** with ammonium acetate in methanol[28] afforded L in near quantitative yield (97%).

The new, potentially tetradentate ligand L was characterised by elemental analysis and by ^1H NMR, ^1H–^1H NOESY and mass spectroscopies. Notably, the ^1H NMR spectrum is simple revealing two phenyl doublets at δ 7.71 and 6.92 and singlets at δ 6.27, 5.24, 3.84 and 2.06 for the pyrazolyl ring, methylene, methoxy and methyl protons respectively. These data confirm the equivalence of all three pyrazolyl groups and their phenyl substituents. The regiochemistry of L is revealed by its ^1H–^1H NOESY NMR spectrum which shows a strong cross-peak between the methylene and methyl groups.



L

Copper complexes

Green, crystalline [$CuLCl_2$] **1** precipitated on mixing a solution of L in the minimum of dichloromethane (dcm) with a solution of copper(II) chloride dihydrate (one equivalent) in the minimum of methanol. To abstract the chloro co-ligands and so increase the likelihood of co-ordination of all three pyrazolyl “arms” to the copper centre, **1** in dcm solution was treated with successive equivalents of silver(I) hexafluoroantimonate. With one equivalent, the anticipated complex [CuLCl][SbF_6] **2** crystallised following removal of the precipitate of silver chloride and equilibration of the dcm solution with diethyl ether vapour. Reactions with two equivalents of silver hexafluoroantimonate to abstract both of the chloro co-ligands afforded, after removal of the precipitated silver chloride, dark green solutions. Solid product was not obtained when these were equilibrated with up to four volumes of anhydrous diethyl ether. However, when the ether saturated solutions were opened to the air and allowed slowly to evaporate, shiny, dark blue crystals of **3** formed. Partial elemental analyses of the crystals are consistent with “$CuL(H_2O)(SbF_6)_2$” as the formulation of **3**, and an X-ray structural analysis (see below) reveals that it is the aqua complex, [$CuL(H_2O)$][SbF_6]$_2$. The aqua ligand must have been introduced in the preparation of **3** when the diethyl ether

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Table 1 Selected bond lengths (Å) and bond angles (°) for [CuLCl$_2$] **1**

Cu–Cl1	2.238(1)	Cl1–Cu–Cl2	155.0(1)	Cl2–Cu–N3	90.8(1)
Cu–Cl2	2.268(1)	Cl1–Cu–N1	90.8(1)	Cl2–Cu–N7	104.8(1)
Cu–N1	2.024(4)	Cl1–Cu–N3	94.9(1)	N1–Cu–N3	158.3(1)
Cu–N3	2.043(4)	Cl1–Cu–N7	100.2(1)	N1–Cu–N7	78.1(1)
Cu–N7	2.355(3)	Cl2–Cu–N1	92.7(1)	N3–Cu–N7	80.3(1)

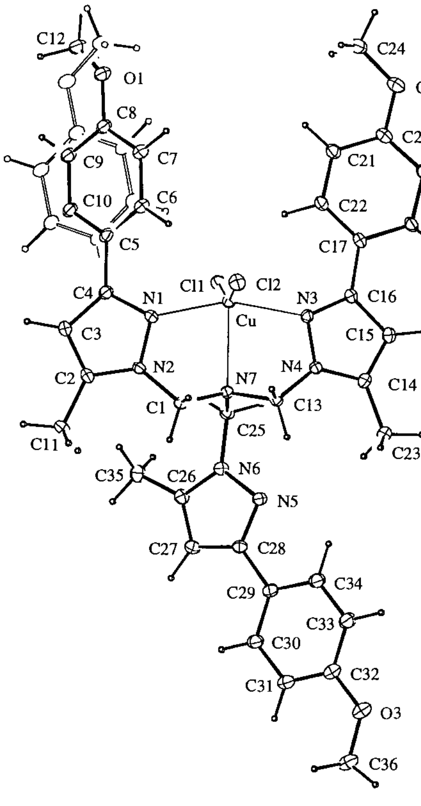

Fig. 1 View of [CuLCl$_2$] **1** showing 10% thermal ellipsoids at 294 K (as for all structures here).

saturated solution containing the complex was left to evaporate as water had been rigorously excluded up to this point. It may be that the aqua co-ligand is necessary for crystallisation of the complex. In this regard, Vahrenkamp reports that zinc(II) complexes of weakly co-ordinating anions and analogous tripodal ligands could not be obtained water-free.[29]

The copper(I) complex [CuL][CF$_3$SO$_3$] **4** was prepared by mixing equivalent amounts of L and [Cu(CH$_3$CN)$_4$][CF$_3$SO$_3$] in anhydrous, deoxygenated tetrahydrofuran. The white powdery product was recrystallised from dcm–diethyl ether to afford the colourless clear crystals of **4** which are stable in dry air. The [CuL]$^+$ cation could also be obtained by reduction of the copper(II) complexes, **1**–**3**, for example with tetraphenylborate anion (see below).

Solid-state crystal structures of complexes 1–3 and [CuL][CuCl$_2$]

Dark green crystals of complex **1** and lustrous dark blue-black crystals of **2** and **3** were obtained by recrystallisation from dcm–diethyl ether solutions. Colourless crystals of [CuL]-[CuCl$_2$] were obtained by reduction of **1** with Na[BPh$_4$] (see below) and recrystallisation of the product from dcm–methanol. Key bond length and bond angle data from the crystal structures of **1**–**3** and [CuL][CuCl$_2$] are listed in Tables 1–4.

[CuLCl$_2$] 1. The crystal structure analysis of complex **1** (Fig. 1) reveals the copper(II) ion to be co-ordinated by the amine and two of the pyrazolyl groups of L (*i.e.* L acts as a tridentate, not a tetradentate, ligand) and by two chloro co-ligands. The third pyrazolyl group remains unbound and sits away from the copper ion. One of the methoxyphenyl substituents is disordered (see Fig. 1) and refined with site occupancies of 0.63 and 0.37 for the two disorder components. Whereas [Cu(tpa)-Cl]Cl exhibits a tetradentate tpa ligand,[30] [Cu(Me$_3$tpa)Cl$_2$] [Me$_3$tpa = tris((6-methyl-2-pyridyl)methyl)amine] adopts a similar structure to that of **1**, with the failure of all three pyridyl arms to co-ordinate to the copper, in this case, being attributed to the bulkiness of the Me$_3$tpa ligand.[9]

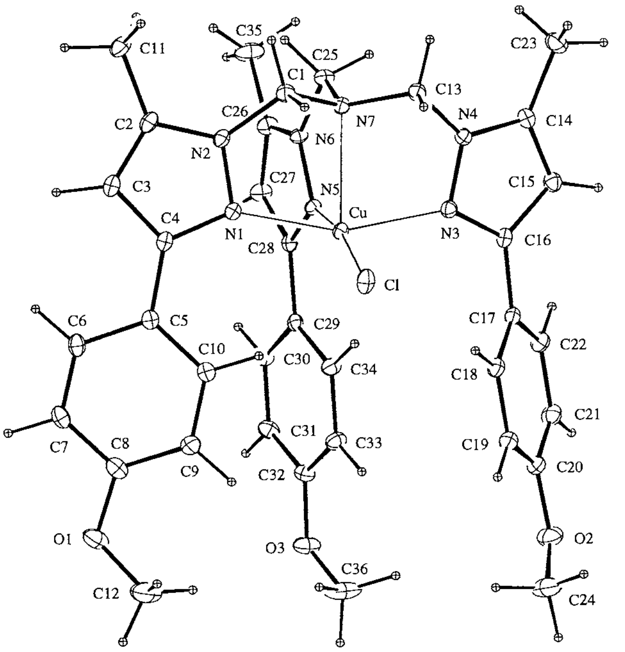

Fig. 2 View of the [CuLCl]$^+$ cation **2**.

Complex **1** has a trigonality (τ) index of 0.06 indicative of near perfect square pyramidal stereochemistry about the copper(II) ion [$\tau = (\alpha - \beta)/60$ where α and β are the largest and next-largest bond angles about the central atom; τ is 0 for a perfect square pyramid and 1.0 for a perfect trigonal bipyramid[31]]. The basal plane comprises the two co-ordinated pyrazolyl groups of L and the two chloro co-ligands. The four basal donors are not located in the basal plane which exhibits slight tetrahedral distortion: the two pyrazolyl nitrogen atoms are constrained by the ligand design above the basal plane towards the apex (α: N1–Cu–N3 158.3°), while the two chloro ligands sit on the other side of the basal plane (β: Cl–Cu–Cl 155.0°). The apex of the square pyramid is taken by the tertiary amine nitrogen atom, N7, at a distance of 2.355 Å from the copper ion. The Cu–N$_{\text{basal}}$ bond lengths are 1.95–2.04 Å, about 0.35 Å shorter than the Cu–N$_{\text{apical}}$ bond length.

[CuLCl][SbF$_6$] 2 and [CuL(H$_2$O)][SbF$_6$]$_2$·MeOH 3. Fig. 2 displays the molecular structure of the cation in complex **2**. Immediately apparent is that L is now tetradentate; a chloro co-ligand and the tertiary amino and the three pyrazolyl nitrogen atoms of L bind the copper(II) ion. The cation in **3** (Fig. 3) is isostructural with that in **2** with the chloro co-ligand in the latter cation replacing an aqua co-ligand in the former. A molecule of lattice methanol lies hydrogen bonded to the aqua ligand in **3** with an O···O distance of 2.8 Å. The hexafluoroantimonate anions in both structures are well separated from the cations.

The cations **2** and **3** exhibit square pyramidal co-ordination geometries (the τ indices are 0.16 and 0.17, respectively). The tertiary amino nitrogen atom occupies the apical position in the structures. The basal planes of **2** and **3** are tetrahedrally distorted similarly to that of **1**, with the pyrazolyl nitrogen atoms constrained above the basal plane to the same side as the copper

Table 2 Selected bond lengths (Å) and bond angles (°) for [CuLCl]-[SbF$_6$] **2**

Cu–Cl	2.200(1)	Cl–Cu–N1	92.5(1)	N1–Cu–N5	88.3(1)
Cu–N1	2.063(3)	Cl–Cu–N3	94.0(1)	N1–Cu–N7	79.8(1)
Cu–N3	2.062(3)	Cl–Cu–N5	167.8(1)	N3–Cu–N5	89.7(1)
Cu–N5	2.034(3)	Cl–Cu–N7	113.0(1)	N3–Cu–N7	79.0(1)
Cu–N7	2.296(3)	N1–Cu–N3	158.7(1)	N5–Cu–N7	79.1(1)

Table 3 Selected bond lengths (Å) and bond angles (°) for [CuL-(H$_2$O)][SbF$_6$]$_2$·MeOH **3**

Cu–N1	2.017(6)	N1–Cu–N3	96.5(3)	N3–Cu–N7	80.8(2)
Cu–N3	1.983(6)	N1–Cu–N5	158.5(3)	N3–Cu–OW	168.8(3)
Cu–N5	2.020(7)	N1–Cu–N7	79.0(2)	N5–Cu–N7	80.8(3)
Cu–N7	2.280(6)	N1–Cu–OW	87.4(3)	N5–Cu–OW	92.4(3)
Cu–OW	1.952(6)	N3–Cu–N5	87.7(3)	N7–Cu–OW	110.3(2)

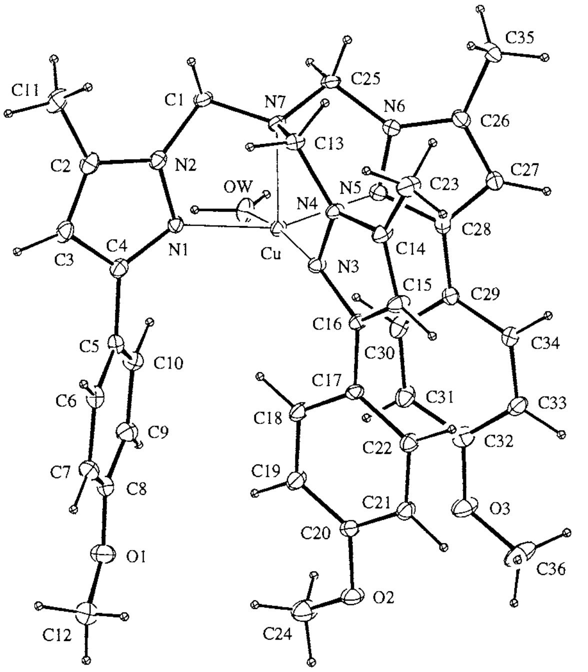

Fig. 3 View of the [CuL(H$_2$O)]$^{2+}$ cation **3**.

ion (N_{apical}–Cu–N_{basal} angles average 79.5 ± 0.5° for **2** and 80.2 ± 1.2° for **3**), while the chloro (**2**: N_{apical}–Cu–Cl is 113.0°) or aqua (**3**: N_{apical}–Cu–OW is 110.3°) co-ligands lie to the other side. The *trans* N_{basal}–Cu–N_{basal} angles in **2** and **3** (at 158.7° and 158.5° respectively) are very similar to that for **1** (158.3°). The Cu–N_{basal} bond lengths average 2.053 Å for **2** and 2.007 Å for **3**, about 0.24 and 0.27 Å respectively shorter than the Cu–N_{apical} distance. The significant shortening of the Cu–N_{apical} bonds in **2** [2.296(3) Å] and **3** [2.280(6) Å] compared to **1** [2.355(3) Å] is reasonably attributed to co-ordination of the third pyrazolyl "arm" in these cations.

The square pyramidal co-ordination geometries of complexes **2** and **3** distinctly contrast with the trigonal bipyramidal structures found for [Cu(tmima)Cl]$^+$ {tmima = tris[2-(1-methylimidazolyl)methyl]amine},[16] [Cu(tpa)X]$^{n+}$ (X = Cl, n = 1; X = H$_2$O, n = 2)[9,30] and [Cu(Ph$_3$tpa)(MeCN)]$^{2+}$ {Ph$_3$tpa = tris[(6-phenyl-2-pyridyl)methyl]amine}.[10,11] Given that the phenyl substituents to the six-membered pyridyl rings in the latter complex are likely to be more crowded together than the methoxyphenyl substituents to the five-membered pyrazolyl rings in **2** or **3**, the main factor(s) dictating the different structures is not obvious.

[CuL][CuCl$_2$]. The molecular structure of the [CuL]$^+$ cation (Fig. 4) reveals tetradentate co-ordination of L with no other ligands to the copper(I) ion. The three pyrazolyl groups form the basal plane of a trigonal pyramid (as was implicated by the NMR data for the complex—see below), with the tertiary amino nitrogen adopting the axial position. The copper(I) ion is centrally located slightly below the trigonal basal plane, *i.e. away* from the apical amine nitrogen atom such that the N_{basal}–Cu–N_{apical} angles average 80.8 ± 1.2°, very similar to the comparable angles in **1**–**3**. It may well be that the ligand confines the copper(I) ion below the basal plane. Although the Cu–N_{basal} bond lengths for [CuL]$^+$ are not significantly different from those of **2** and **3**, the Cu–N_{apical} distance of 2.338 Å is longer than 2.296 and 2.280 Å for **2** and **3**, respectively. The structure of [CuL]$^+$ resembles that found for [Cu(Ph$_3$tpa)]$^+$.[10,11] Finally, the linear [CuCl$_2$]$^-$ ions are sited on two independent centres of symmetry in the crystal structure well isolated from the [CuL]$^+$ ions.

Table 4 Selected bond lengths (Å) and bond angles (°) for [CuL]-[CuCl$_2$]

Cu3–N1	1.987(3)	N1–Cu3–N3	120.9(1)	N3–Cu3–N7	79.6(1)
Cu3–N3	2.000(3)	N1–Cu3–N5	119.2(1)	N5–Cu3–N7	81.4(1)
Cu3–N5	2.032(3)	N1–Cu3–N7	81.4(1)		
Cu3–N7	2.338(4)	N3–Cu3–N5	112.4(1)		

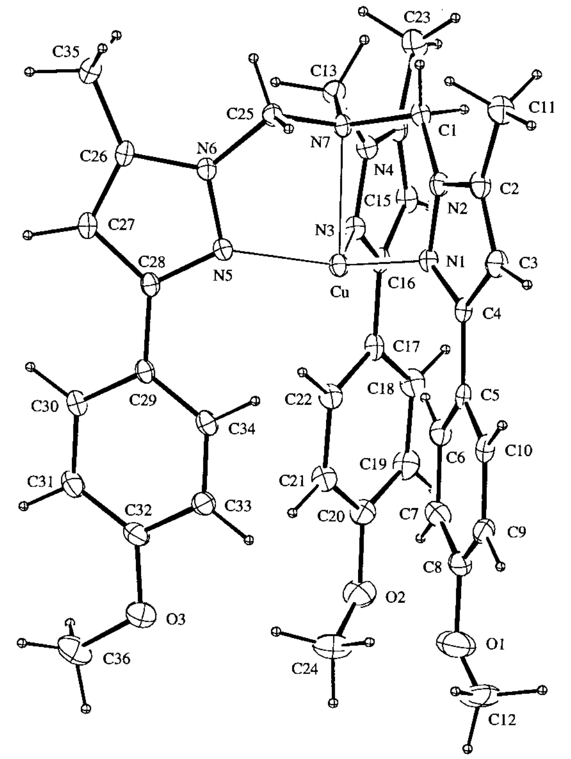

Fig. 4 View of the [CuL]$^+$ cation **4**.

Physicochemical properties

Gouy magnetic moment measurements of the powdered complexes at 295 K gave values [**1** (μ_{expt}/μ_B: 1.89); **2** (μ_{expt}/μ_B: 1.91); **3** (μ_{expt}/μ_B: 1.83)] typical for mononuclear copper(II) centres. EPR and electronic absorption spectra of **1**–**3** were recorded in two solvents, dcm and dmf. In dcm glasses at 77 K each complex displays an axial spectrum with $g_{\parallel}$ (≈2.23) ≫ $g_{\perp}$ (≈2.05) > 2.03 and $A_{\parallel} \approx 150$ G, indicative for a $d_{x^2-y^2}$ ground state characteristic of a tetragonal environment for all three complexes.[32,33] The EPR spectra and data are typical of those exhibited by other copper(II) complexes of tetradentate tripodal ligands, closely related to L, with square pyramidal structures.[9,19,30–33] The electronic absorption spectra of **1**–**3** ground in KBr disks (the solid state) and in dcm solutions exhibit an intense band at ≈350–400 nm that is not observed in the spectrum of the ligand L nor in that of the copper(I) complex **4**. As each chloro co-ligand is abstracted on going from **1** to **3** the band shifts slightly to lower

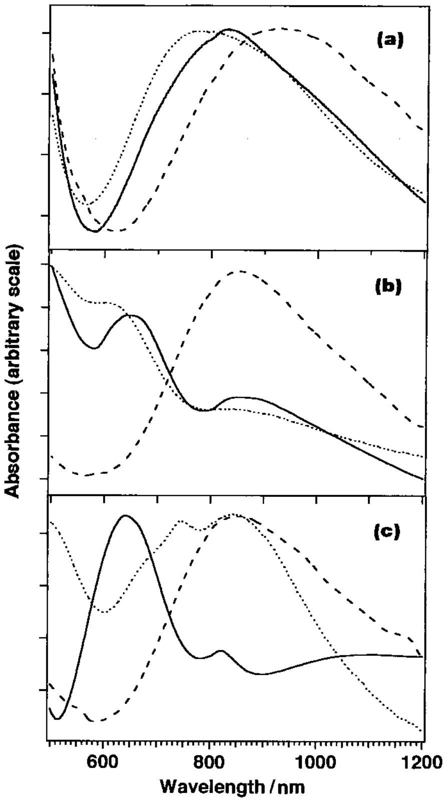

Fig. 5 Electronic absorption spectra of complexes **1** (a), **2** (b) and **3** (c) in the solid state (——) and in dcm (• • • • • •) and dmf (----) solution.

energy and drops in intensity. This band is ascribed to a ligand-to-metal charge transfer transition. Ligand-field bands are observed to lower energy and for **1** and **2** are similar in the solid state and in dcm solution, Fig. 5, suggestive for the solid-state structures being retained in dcm solution. However, the electronic absorption spectra of **3** in the solid and in dcm differ, Fig. 5, implying that there are changes from the solid to solution.

Likewise, the EPR and electronic absorption spectra of complexes **1**–**3** in dmf solution differ from those for each in the solid state or in dcm solution. The EPR spectra of **1**–**3** in dmf glasses at 77 K exhibit signals with sharpened features at $g_{\parallel} \approx 2.39$ ($A_{\parallel} \approx 120$ G) $\gg g_{\perp}$ ($\approx$2.08) characteristic for tetrahedrally distorted copper(II) centres,[32–34] *e.g.* Fig. 6(b). In spectra of **1**–**3** at highest resolution splitting of the low field peak into at least five peaks can be discerned. This is attributed to nitrogen superhyperfine ($A_n \approx 11.5$ G) coupling suggesting two or more nitrogen donor groups are bound to the copper(II) ion. The electronic absorption spectra of the complexes in dmf show broad peaks with low energy tails, at 930 ($\varepsilon = 110$) for **1**, 860 (160) for **2** and 860 nm (135 M^{-1} cm^{-1}) for **3**. For comparison, EPR and electronic absorption spectra of $CuCl_2$ and $Cu(ClO_4)_2 \cdot 6H_2O$ in the same dmf as used to prepare solutions of **1**–**3** were recorded. In dmf at 77 K, $CuCl_2$ displays inverted axial EPR signals with $g_{\perp}$ 2.15 ($A_{\perp}$ 81 G) and $g_{\parallel}$ 2.02 ($A_{\parallel}$ 106 G) characteristic for a trigonal bipyramidal copper(II) centre, whereas $Cu(ClO_4)_2 \cdot 6H_2O$ shows a typical tetrahedral EPR spectrum with $g_{\parallel}$ 2.40 ($A_{\parallel}$ 121 G) and $g_{\perp}$ 2.08. The electronic absorption spectrum of $CuCl_2$ exhibits a single visible band at 960 nm ($\varepsilon = 85$ M^{-1} cm^{-1}) whereas that of $Cu(ClO_4)_2 \cdot 6H_2O$ in dmf has a visible band at 805 nm ($\varepsilon = 32$ M^{-1} cm^{-1}). The tetrahedral EPR spectra for **1**–**3** imply that some ligand N-donor groups no longer bind to the copper ion in dmf solution, whereas a comparison of the electronic absorption spectra of **1**–**3** and $CuCl_2$ and $Cu(ClO_4)_2$ in dmf reveals that the ligand (L) is not completely lost; at least some of the N-donor groups remain bound to the copper ion. Since dmf is notoriously difficult to dry, it may be that the unbound N-donor groups have been protonated and dmf or water is likely also co-ordinated to the copper(II) centres.

Table 5 Molar conductivity data from measurements on 1.0 mM solutions of the complexes at 298 K; values are ±15%

Compound	Δ_M/S cm^2 mol^{-1}	
	dcm	dmf
1	0	17
2	5	56
3	14	111
4	16	62
$[Bu^n_4N][PF_6]$	25	66

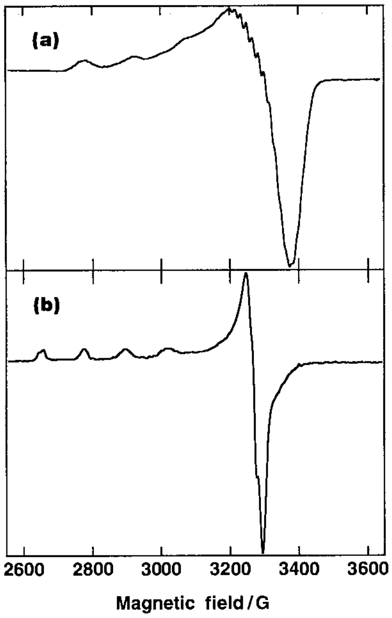

Fig. 6 X-Band EPR spectra at 77 K of $[CuL(H_2O)][SbF_6]$ **3** in dcm (a) and dmf (b); ν/GHz = 9.502.

The ^1H NMR spectrum of complex **4** was measured in $CDCl_3$, CD_2Cl_2 and in $(CD_3)_2NCDO$. Each spectrum has a similar pattern of peaks to that of L, but with altered chemical shifts [for example, in $CDCl_3$ $\Delta\delta$ {$=\delta_H(\mathbf{4}) - \delta_H(L)$}is -0.11 and -0.18 for the phenyl protons, and 0.14 and 0.31 for the methylene and methoxy protons respectively]. The spectra indicate the pyrazolyl groups in the $[CuL]^+$ cation to be equivalent (on the NMR timescale) in all three solvents. This is consistent with the crystallographically determined trigonal pyramidal structure for the $[CuL]^+$ cation being maintained in the solutions, although fast equilibration between isomers with unbound N-donor groups can not be discounted.

Values for the molar conductivities measured for complexes **1**–**4** are given in Table 5. Conductivities of copper complex salts in non-aqueous solvents are complicated by counter anion co-ordination and ion-pairing phenomena[33,35] and the data reflect this. We attribute the low molar conductivities in dcm solution to ion pairing, as models indicate that there is insufficient space for uptake of a sixth ligand and certainly not the bulky $[SbF_6]^-$ anion. In agreement with this conclusion, **4** exhibits a higher molar conductivity in dcm than **2** consistent with less ion pairing for the less polarising copper(I) ion. The higher values for the conductivity in dmf solution indicate weaker ion pairing, which is expected because of the higher relative permittivity for dmf. The values for **2** and **3** in dmf are slightly less than expected for 1 : 1 and 2 : 2 electrolytes, respectively. For **2** this suggests that there is little solvolysis of the chloro co-ligand.

Reactivity studies

Some reactions of the complexes are worthy of mention. First, in an initial attempt to obtain $[CuLCl]^+$, we treated a solution of **1** in dcm with sodium tetraphenylborate in methanol. The reaction mixture initially turned inky black and then within *ca.* 10 seconds (with excess of sodium tetraphenylborate) to 1 minute (with 1.0 equivalent of sodium tetraphenylborate) cleared to colourless. Transparent, colourless crystals deposited when the solutions were left to evaporate for several days. Examination of the crystals showed two sets with distinct habits. One set rapidly clouded and turned to powder on removal from the mother liquor; ES-mass and ^1H NMR spectra of the powder showed peaks for $[CuL]^+$ and for $[BPh_4]^-$ ions. The other set were transparent and stable, and were shown to be $[CuL][CuCl_2]$ by X-ray structural analysis (see above). Subsequent reactions revealed that **1**–**3** are also reduced by tetraphenylborate ion in acetonitrile, acetone or tetrahydrofuran solution to afford $[CuL]^+$ and that biphenyl was always a product. The fate of the borate species was not determined. Although tetraphenylborate ion is generally considered an innocent counter ion, it is not necessarily so[36] and can reduce transition metal species.[37] Of particular relevance here, it has previously been noticed without comment that some other copper(II) complexes with tetradentate, tripodal ligands are also reduced by tetraphenylborate ion.[11,38] Eqns. (1) and (2) (:E = Lewis base)

$$Ph_4B^- \longrightarrow Ph_4B^\bullet + e^- \qquad (1)$$

$$Ph_4B^\bullet + :E \longrightarrow Ph_2B\text{–}E + Ph\text{–}Ph + e^- \qquad (2)$$

describe appropriate half-equations for tetraphenylborate ion acting as a reducing agent.[37]

The reactivity of the copper(I) complex **4** towards dioxygen, carbon monoxide and chloride ion was investigated because of the possible biological relevance of such reactions. We found that **4** does not react with dioxygen: the solid is completely stable, as are the clear, colourless solutions containing **4**, even when flushed with dioxygen for several hours at either room temperature or −80 °C. Likewise, no reaction was observed when solutions of **4** were bubbled with carbon monoxide. The structures of **2** and **3** suggest that five-co-ordinate carbonyl, peroxo or superoxo complexes with a similar structure would be relatively free from steric strain. In contrast, a reaction was observed upon addition of 1 equivalent chloride ion [as the bis(triphenylphosphoranylidene)ammonium salt] to **4** in deuteriochloroform, leading over several minutes to complete break up of the complex and the ligand (L). The differing reactivity of **4** towards the three reagents is possibly related to their charge.

Several attempts were made to obtain 4-phenol-substituted analogues of L or $[CuLCl_2]$ by treatment with reagents that cleave arylmethyl ethers.[39] All of these reactions failed. For example, treatment of L with sodium sulfide in dmf caused complete fragmentation of the ligand and reactions of $[CuLCl_2]$ with BBr_3 or Me_3SiI in dichloromethane resulted in decomplexation and destruction of the ligand. The methylene linkages between the amine and pyrazolyl groups appear to be much weaker than the C(Me)–O bonds and therefore do not survive in these reactions. The originally targeted 4-phenol-substituted analogues will only be made by starting from 4-phenolpyrazoles protected by more easily removed groups. Moreover, the break up of L in these reactions serves to highlight the fragility of pyrazolylmethylamine ligands.

Electrochemistry

The electrochemical behaviour of complexes **1**–**4** was examined by cyclic voltammetry. Unfortunately the cyclic voltammograms in dcm solutions showed only broad, ill defined and poorly reproducible peaks. However, the voltammetric behaviour in dmf solution was clearly defined and reproducible (Fig. 7). In dmf solution complex **1** exhibits a quasi-reversible process at −0.04 V [$i_{pa}/i_{pc} = 1.0$ and $\Delta E_p \approx 100$ mV *cf.* $\Delta E_p(Fc^+–Fc) \approx 75$ mV] attributed to the $Cu^{II}–Cu^{I}$ couple. The couple broadens but remains quasi-reversible at faster scan rates up to 10 V s^{-1}. The structures of **1** in dmf solution and in the crystal differ (see above), and so the observed $Cu^{II}–Cu^{I}$ couple is for a solution species of unknown structure.

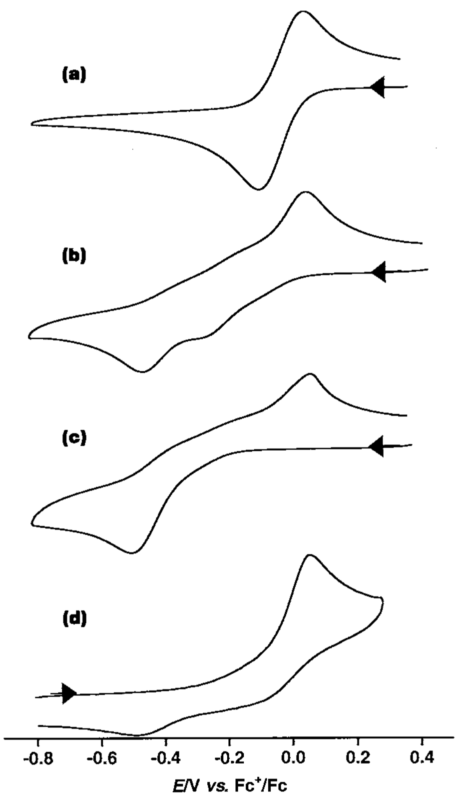

Fig. 7 Cyclic voltammograms of complexes **1** (a), **2** (b), **3** (c) and **4** (d) in dmf solution. Conditions: freshly polished platinum disc electrode, scan rate = 100 mV s^{-1}, temperature = 296 K.

Only irreversible electrochemical processes are seen in cyclic voltammograms of complexes **2**–**4** in dmf solution. These processes remained irreversible and no new peaks were observed as the scan rate was varied from 20 mV s^{-1} to 10 V s^{-1}. For **2**, two cathodic peaks are observed at −0.29 and at −0.50 V [see Fig. 7(b)]. Provided the −0.29 V peak is traversed, a daughter anodic peak is found at ≈+0.08 V in the reverse positive scan. Cyclic voltammograms of **3** [see Fig. 7(c)] only show the cathodic peak at −0.50 V which again gives rise to the anodic peak at ≈+0.08 V upon scan inversion. The two processes remained irreversible as the scan rate was varied from 20 mV s^{-1} to 10 V s^{-1}. The copper(I) complex **4** shows the same two redox processes as **3**, but now the oxidation is the parent process; that is the irreversible oxidation at +0.08 V in the forward positive sweep gives rise to a cathodic peak at −0.50 V in the reverse (negative) sweep. As for **3**, the voltammetric response of **4** did not change as the scan rate was varied between 20 mV s^{-1} and 10 V s^{-1}.

Since the voltammograms of complexes **3** and **4** show common peaks and the chemical reductions of **1**–**3** produce **4** (see above), the cathodic peak at −0.50 V is attributed to one-electron reduction of **3** to give **4** and the anodic peak at +0.08 to oxidation of **4**. The electrochemical irreversibility of the $Cu^{II}–Cu^{I}$ couples is ascribed to the electron transfer processes being accompanied by rate-limiting structural changes, possibly with concomitant protonation of one or more ligand N-donor groups (the structures of **2** and **3** in dmf are uncertain, see above). The cathodic peak at −0.29 V in the cyclic voltammogram of **2** is assigned to the reduction of **2** to **4**. The observation of the cathodic peak at −0.50 V for reduction of **3** in the voltammogram of **2** suggests pre-equilibration of **2** and **3**.

The electrochemical behaviour of complexes **1**–**4** makes an interesting comparison with other copper complexes of tetradentate tris(N-heterocyclic methylene)amine ligands, for example [Cu(R$_y$tpa)X]$^{n+}$ [R = 6-substituent to a pyridyl ring of tpa, *e.g.* Me, Ph or NHC(O)Bu^t; y = 0–3; X = co-ligand; n = 1 or 2], which typically are described as exhibiting (quasi)reversible Cu^{II}–Cu^{I} couples.[3–19,21] Many of the previously described complexes exhibit large shifts in the redox potentials for the Cu^{II}–Cu^{I} couples between solvents (up to 0.8 V) and/or large peak-to-peak separations (ΔE_p) between the cathodic and anodic peaks (peaks separated by 650 mV have been ascribed to quasi-reversible couples!). In these electrochemical studies a variety of solvents were employed with dmf the most common, and this was the reason for our use of it. Notably, the solvents used for electrochemical studies in the literature reports are often different from those employed for the spectroscopic and reactivity studies; account for the structure changing with the solvent most often has not been made with the geometry of a complex presumed to be that characterised in the solid state. We suggest that the large peak-to-peak separations for the Cu^{II}–Cu^{I} couples most probably result from rate-limiting conformational changes between the copper(II) and copper(I) states and, furthermore, that a large shift in the potential for a particular Cu^{II}–Cu^{I} couple between two solvents may indicate that the structure of the copper(II) complex changes between the two solvents. The structural changes may include changes to the conformation about the copper(II) ion, co-ordination by solvent or water, and may involve protonation of one or more of the N-donor groups. Structural/conformational changes in the copper(I) state are expected to exert less influence on Cu^{II}–Cu^{I} couples.[21]

Conclusion

A new, potentially tetradentate pyrazolyl ligand and its copper complexes, **1**–**4**, have been synthesized and characterised both in the solid state and in dcm and dmf solutions. Notable differences are observed between these complexes and previously described examples of copper complexes of other potentially tetradentate, tris(*N*-heterocyclic methylene)amine ligands. For example, the crystal structures of **1**–**3** reveal distorted square pyramidal copper(II) centres, whereas [Cu^{II}(tmima)X]$^{n+}$, [Cu^{II}(tpa)X]$^{n+}$ and [Cu^{II}(Ph$_3$tpa)X]$^{n+}$ complexes are typically trigonal bipyramidal. Although [Cu(Me$_n$tpa)Cl]$^+$ ions exhibit square pyramidal geometries, these have axial 6-methylpyridyl groups whereas in **1**–**3** the amine group is in the weakly bound axial position. These differences extend to the solution behaviour of **1**–**3**. For example, EPR and electronic absorption spectra of **1**–**3** in dmf solution differ from those found in the solid or in dcm solution, highlighting that tris(*N*-heterocyclic methylene)amine ligands may be co-ordinatively labile and that the structures of their copper(II) complexes may vary between solvents. The copper(I) complex **4** appears to retain the same structure in all solvents studied. Whereas [Cu(R$_n$tpa)Cl]$^+$ (R = H or Me, n = 0–3) and [Cu(Ph$_n$tpa)]$^{2+}$ complexes display (quasi)reversible Cu^{II}–Cu^{I} couples, **2**–**4** display irreversible electrochemical processes reasonably accounted for by rate-limiting structural changes accompanying electron transfer.

Experimental

Physical measurements

Microanalyses for C, H and N were performed by the Australian National University microanalytical service. Prior to analysis, samples were dried at 35 °C for 48 h under vacuum (0.2 mmHg) over phosphorus pentoxide. Quoted melting points are uncorrected. EI and ES mass spectra were recorded using a VG Quattro mass spectrometer; the carrier stream for ES-MS was 1% acetic acid in 1 : 1 acetonitrile–water. ^{1}H and ^{13}C NMR spectra were obtained in the designated solvents on a Bruker AC300F (300 MHz) instrument, EPR spectra on a Bruker EMX 10 EPR spectrometer. Room temperature magnetic moments were determined on a magnetic susceptibility balance using the Gouy method. Diamagnetic corrections were calculated from tabulated values of Pascal's constants. IR spectra were recorded as paraffin mulls on a Perkin-Elmer 580B spectrometer, electronic spectra using a CARY 5 spectrophotometer in the dual beam mode.

Electrochemical measurements were recorded using a Pine Instrument Co. AFCBP1 Bipotentiostat interfaced to and controlled by a Pentium computer. Data were transferred to a Power Macintosh computer for processing using the IGOR-PRO 2.0™ software.[40] For CV measurements, a standard three electrode configuration was used with a quasi-reference electrode comprised of a commercial Ag–AgCl mini-reference electrode (Cyprus Systems, Inc. EE008) but filled with the electrolyte solution to be used in the experiment [rather than AgCl saturated 3 M KCl(aq) solution], a freshly polished platinum disc (1 mm diameter) working electrode and a platinum wire as the auxiliary electrode. Freshly polished platinum working electrodes were prepared from commercial mini-electrodes (Cyprus Systems, Inc. EE041) by grinding with SiC emery paper (600 mesh), then successively polishing with 6 μm and 1 μm diamond slurries, and finally with 0.2 μm alumina slurry. Between each grinding and polishing step, and after final polishing, the electrode was sonicated in doubly distilled water for 5 min. The electrodes were then rinsed with the solvent to be used and thoroughly dried. The solvents used for electrochemical measurements, dcm and dmf, were highest quality anhydrous grade sealed under argon (Aldrich) and used as obtained. The support electrolyte was 0.1 M [NBu$^n_4$][PF$_6$]. Solutions were de-oxygenated by sparging with high purity nitrogen (presaturated with solvent) and then blanketed with a cover of nitrogen for the duration of the experiment. An electrochemical scan of the solvent electrolyte system was always recorded before the addition of the compound to ensure that there were no spurious signals. All potentials are quoted relative to the ferrocenium–ferrocene (Fc$^+$–Fc) couple which was measured *in situ* as an internal reference.

Preparations

Reactions were routinely carried out under an atmosphere of dry dinitrogen using standard Schlenk and cannula techniques. Solvents were distilled from the appropriate drying agent under dinitrogen immediately prior to use: dcm and acetonitrile from P$_2$O$_5$ and then from CaH$_2$; acetone from KMnO$_4$ and then from anhydrous B$_2$O$_3$; hexanes from sodium wire; diethyl ether and tetrahydrofuran from sodium–benzophenone; dmf was dried over calcium hydride and then twice distilled under reduced pressure; methanol and ethanol were distilled from magnesium turnings. Chemicals were obtained from commercial sources (usually Aldrich) and used as obtained.

3-(4-Methoxyphenyl)-5-methyl-1*H*-pyrazole I. A solution of 4-methoxyacetophenone (9.45 g, 63 mmol) in an excess of ethyl acetate (11.10 g, 126 mmol) was added dropwise to a suspension of sodium methoxide (3.42 g, 63 mmol) in dry toluene (200 cm^3) that was mechanically stirred. No apparent reaction took place until the mixture was heated gently with an oil bath, whereupon the sodium methoxide slowly dissolved. After all of the sodium methoxide had dissolved a beige solid suddenly precipitated out of the hot pale orange solution. The mixture was heated at reflux for an additional 1 h to ensure complete reaction. The resulting thick slurry was cooled and the solid collected by filtration, washed twice with hot toluene, then hexane and finally air-dried. The pale orange-beige solid was re-dissolved in methanol (150 cm^3) and treated with hydrazine dihydrochloride (6.6 g, 63 mmol) in water (50 cm^3). The solution became lighter yellow and more turbid as the addition proceeded. The mixture was then concentrated to half its original volume by rotary evaporation and water (100 cm^3) added. A fine solid flocculated and was extracted with dcm (3 × 50 cm^3). The combined extracts were washed with a saturated brine solution, dried over magnesium sulfate and filtered through a plug of alumina. The solvent was removed *in vacuo*, and the residue re-dissolved in hot isopropyl alcohol (50 cm^3) and treated with hydrazine hydrate (55%, 3.67 g, 63 mmol). The solution was refluxed for 1 h and then the solvent removed *in vacuo*. The crude solid was recrystallised from 1:2 chloroform–diethyl ether to afford the product as a white powder (4.97 g, 42%), mp 115–116 °C (Found: C, 69.71; H, 5.82; N, 15.10. $C_{11}H_{12}N_2O$ requires C, 71.06; H, 5.96; N, 14.63%); *m*/*z* (EI-MS) 188 (M^+, 70), 173 (80), 145 (100), 115 (98), 91 (60) and 69 (97); δ_H ($CDCl_3$) 7.91 (2 H, d, Ph), 7.02 (2 H, d, Ph), 6.44 (1 H, s, pz), 3.85 (3 H, s, OCH_3) and 2.58 (3 H, s, CH_3); ν/cm^{-1} (KBr disc) 3050m, 1614m, 1531s, 1513s, 1455m, 1280s, 1260s, 1181s, 1030s, 842m and 795m.

1-Hydroxymethyl-3-(4-methoxyphenyl)-5-methylpyrazole II. 3-(4-Methoxyphenyl)-5-methyl-1H-pyrazole (3.76 g, 20 mmol) was treated with a large excess of aqueous formaldehyde (40 cm^3, 34–38% w/w) and stirred at room temperature for 1 h and then heated to reflux for 6 h to yield a golden yellow solution. An off-white crystalline solid began to precipitate on cooling. The crude product was obtained by filtration and washed twice with water to remove residual formaldehyde. The resulting off-white powder was recrystallised from 1,2-dichloroethane to give the product as a white powder (2.0 g, 46%), mp 151–153 °C (Found: C, 66.01; H, 6.70; N, 13.18. C_6H_7NO requires C, 66.03; H, 6.47; N, 12.84%); *m*/*z* (EI-MS) 218 (M^+, 4%), 188 (100), 173 (65), 145 (36) and 115 (18); δ_H ($CDCl_3$) 7.66 (2 H, d, Ph), 6.92 (2 H, d, Ph), 6.29 (1 H, s, pz), 5.52 (2 H, s, CH_2), 3.83 (3 H, s, OCH_3) and 2.39 (3 H, s, CH_3); ν/cm^{-1} (KBr disc) 3173m, 2964m, 1611m, 1523s, 1434s, 1292m, 1250s, 1178m, 1057s, 1027m, 959m, 839m and 796m.

Tris[3-(4-methoxyphenyl)-5-methylpyrazol-1-ylmethyl]amine (L). A solution of 1-hydroxymethyl-3-(4-methoxyphenyl)-5-methylpyrazole (2.94 g, 13.5 mmol) and ammonium acetate (0.35 g, 4.5 mmol) in methanol (50 cm^3) was stirred at ambient temperature. White solid began to precipitate after 24 h. After 3 days of stirring the white solid was collected by filtration and the volume of filtrate reduced to ≈10 cm^3 and stirred for two days to afford more product. The solids were combined, washed twice with methanol and dried to yield the product as a white powder (2.8 g. 97%), mp 142–145 °C (Found: C, 69.88; H, 6.70; N, 16.02. $C_{36}H_{39}N_7O_3$ requires C, 70.00; H, 6.36; N, 15.88%); *m*/*z* (EI-MS) 617 (M^+, 16%), 430 (33), 242 (82), 228 (84), 201 (100), 188 (78), 160 (70) and 145 (39); δ_H ($CDCl_3$) 7.71 (6 H, d, Ph), 6.92 (6 H, d, Ph), 6.27 (3 H, s, pz), 5.24 (6 H, s, CH_2), 3.84 (9 H, s, OCH_3) and 2.06 (9 H, s, CH_3); ν/cm^{-1} (KBr disc) 2956w, 2835w, 1614m, 1525s, 1436s, 1289m, 1246s, 1173m, 1031m, 954m, 836m, 786m and 595m.

[$CuLCl_2$] 1. $CuCl_2\cdot 2H_2O$ (0.177 g, 1.04 mmol) was dissolved in the minimum amount of methanol and added to a solution of L (0.641 g, 1.04 mmol) in dcm (15 cm^3). A dark green solution formed immediately and a green crystalline precipitate on standing overnight. The solid was collected by filtration and the solution left in a diethyl ether atmosphere for two days to give more green crystalline precipitate (0.57 g total, 71%), mp 178 °C (decomp.) (Found: C, 56.01; H, 5.32; N, 12.73. $C_{36}H_{39}Cl_2CuN_7O_3\cdot H_2O$ requires C, 56.09; H, 5.32; N, 12.94%); *m*/*z* (ES-MS) 189 (100%), 438 and 219; λ_{max}/nm ($\varepsilon/M^{-1}\ cm^{-1}$) (dcm) 226 (19,300), 268 (70,700), 349 (1,750), 780 (164) and 900 (sh); EPR (dcm, 77 K) $g_\parallel$ 2.27, $A_\parallel$ 147 G, $g_\perp$ 2.04; (dmf, 77 K) $g_\parallel$ 2.40, $A_\parallel$ 125 G, $g_\perp$ 2.08; μ/μ_B (Guoy, 24 °C) 1.89.

[CuLCl][SbF_6] 2. Under a dinitrogen atmosphere, a dcm solution (1 cm^3) containing silver hexafluoroantimonate (0.085 g, 0.25 mmol) was added to a solution of complex **1** (0.19 g, 0.25 mmol) in dcm (10 cm^3). The green solution darkened on mixing and a white precipitate formed. The mixture was stirred for 10 min and filtered under dinitrogen through a bed of Celite to give a dark green solution. This was diluted with more dcm (10 cm^3) and placed under a diethyl ether atmosphere. Dark blue X-ray quality crystals formed over several days (0.15 g, 72%), mp 182 °C (decomp.) (Found: C, 45.26; H, 3.70; N, 10.10. $C_{36}H_{39}ClCuF_6N_7O_3Sb$ requires C, 45.35; H, 4.09; N, 10.29%); *m*/*z* (ES-MS) 438 (M^+, 25%), 219 and 189 (100); λ_{max}/nm ($\varepsilon/M^{-1}\ cm^{-1}$) (dcm) 226 (25,200), 262 (52,400), 368 (1,410), 605 (175) and 830 (sh); EPR (dcm, 77 K) $g_\parallel$ 2.28, $A_\parallel$ 151 G, $g_\perp$ 2.06; (dmf, 77 K) $g_\parallel$ 2.39, $A_\parallel$ 122 G, A_N 11 G, $g_\perp$ 2.07; μ/μ_B (Gouy, 24 °C) 1.91.

[$CuL(H_2O)$][SbF_6]$_2$ 3. A solution of complex **1** (0.21 g, 0.28 mmol) in dcm (10 cm^3) was treated with silver hexafluoroantimonate (0.19 g, 0.56 mmol) in dcm (1 cm^3) under dinitrogen. The mixture was filtered under dinitrogen through a bed of Celite. The intensely dark green solution was placed under a diethyl ether atmosphere. No solid had deposited from the solution when it had approximately doubled in volume. The solution was then exposed to the atmosphere and slowly evaporated at room temperature. Shiny dark blue crystals of the product formed (0.22 g, 68%), mp 170 °C (decomp.) (Found: C, 36.85; H, 3.81; N, 8.16. $C_{36}H_{41}CuF_{12}N_7O_4Sb_2$ requires C, 36.90; H, 3.50; N, 8.37%); λ_{max}/nm ($\varepsilon/M^{-1}\ cm^{-1}$) (dcm) 226 (24,400), 258 (46,700), 347 (452), 846 (119) and 748 (sh); EPR (dcm, 77 K) $g_\parallel$ 2.27, $A_\parallel$ 156 G, $g_\perp$ 2.07, A_N 16 G; (dmf, 77 K) $g_\parallel$ 2.39, $A_\parallel$ 123 G, A_N 12 G, $g_\perp$ 2.08; μ/μ_B (Gouy, 24 °C) 1.83.

[CuL][CF_3SO_3] 4. Under a dinitrogen atmosphere, a solution of [$Cu(CH_3CN)_4$][CF_3SO_3] (0.096 g, 0.26 mmol) in THF (2 cm^3, deoxygenated) was added to a solution of L (0.16 g, 0.26 mmol) in THF (3 cm^3, deoxygenated). A white precipitate formed immediately which was collected by filtration under dinitrogen. Clear colourless crystals of the product were obtained by recrystallising the solid from dcm–diethyl ether (0.16 g, 74%) (Found: C, 52.18, H, 4.46; N, 11.42. $C_{37}H_{41}CuF_3N_7O_7S\cdot H_2O$ requires C, 52.37; H, 4.83; N, 11.56%; *m*/*z* (ES-MS) 439 (18), 230 (13) and 189 (100%); δ_H ($CDCl_3$) 7.60 (6 H, d, Ph), 6.74 (6 H, d, Ph), 6.26 (3 H, s, pz), 5.38 (6 H, s, CH_2), 3.88 (9 H, s, OCH_3) and 2.41 (9 H, s, CH_3); (d_7-dmf) 8.03 (6 H, d, Ph), 7.10 (6 H, d, Ph), 6.79 (3 H, s, pz), 5.68 (6 H, s, CH_2), 4.07 (9 H, s, OCH_3) and 2.59 (9 H, s, CH_3).

Reaction between [$CuLCl_2$] and Na[BPh_4]. A solution of Na[BPh_4] (0.089 g, 0.26 mmol) in dcm–methanol (5 cm^3, 1:1) was added in one portion to complex **1** (0.100 g, 0.13 mmol) in dcm–methanol (5 cm^3, 1:1). The initial green solution of **1** immediately darkened to grey-black before clearing to colourless (within 30 s). The solvent was removed and the white solid recrystallised from dcm–diethyl ether. A mixture of clear colourless crystals with two different habits was obtained. On standing one set of crystals turned to powder. The remaining set were determined by X-ray crystallography to be [CuL][$CuCl_2$] and exhibited a ^1H NMR spectrum similar to that of **4**: δ_H ($CDCl_3$) 7.74 (d, 6 H), 6.85 (d, 6 H), 6.29 (s, 3 H), 5.36 (s, 6 H), 3.86 (s, 9 H) and 2.40 (s, 9 H).

The above reaction was repeated several times with complexes **1**–**3** in different solvents (THF, dcm, CH_3CN and acetone). In each, the initial green of the complexes turned to colourless when the Na[BPh_4] was added. GC/EI-MS analysis of the reaction mixture in which **1** was used as the starting complex and THF as solvent showed a strong GC peak with *m*/*z* (%) 154 (27) and 77 (100) for biphenyl.

X-Ray crystallography

[CuLCl$_2$] 1. ($C_{36}H_{39}Cl_2CuN_7O_3$), *M* 752.2, monoclinic, space group $P2_1$, *a* 7.314(2), *b* 20.573(2), *c* 12.094(2) Å, *β* 104.575(8)°, *V* 1761.2(5) Å^3, D_c 1.42 g cm^{-3}, *Z* 2, μ_{Cu} 26.56 cm^{-1}, *T* 21(1) °C. 2922 reflections considered observed [$I > 3\sigma(I)$] out of 3580 unique data. Final residuals *R*, R_w were 0.033, 0.042 for the observed data. The enantiomer is confirmed, the alternative giving 0.039, 0.051. One of the methoxyphenyl groups is disordered, see Fig. 1, and the relative occupancies of the components of this disordered group refined to 0.63(1) and 0.37(1).

[CuLCl][SbF$_6$] 2. ($C_{36}H_{39}ClCuF_6N_7O_3$)Sb, *M* 952.5, triclinic, space group $P\bar{1}$, *a* 11.771(6), *b* 12.059(6), *c* 13.525(8) Å, *α* 89.76(3), *β* 87.17(3), *γ* 83.56(13)°, *V* 1905(2) Å^3, D_c 1.66 g cm^{-3}, *Z* 2, μ_{Mo} 14.16 cm^{-1}, *T* 21(1) °C. 5067 reflections considered observed [$I > 3\sigma(I)$] out of 6686 unique data. Final residuals *R*, R_w were 0.037, 0.051 for the observed data.

[CuL(H$_2$O)][SbF$_6$]·MeOH 3. ($C_{36}H_{41}CuF_{12}N_7O_4Sb_2 \cdot CH_4O$, *M* 1202.8, monoclinic, space group $P2_1/c$, *a* 11.044(7), *b* 14.300(5), *c* 28.578(20) Å, *β* 90.87(3)°, *V* 4513(5) Å^3, D_c 1.77 g cm^{-3}, *Z* 4, μ_{Mo} 17.60 cm^{-1}, *T* 21(1) °C. 5291 reflections considered observed [$I > 3\sigma(I)$] out of 7908 unique data, with R_{merge} 0.012 for 315 pairs of 0*kl* reflections. Final residuals *R*, R_w were 0.048, 0.077 for the observed data.

[CuL][CuCl$_2$]. $C_{36}H_{39}CuN_7O_3 \cdot CuCl_2$, *M* 815.8, triclinic, space group $P\bar{1}$, *a* 12.154(6), *b* 13.182(8), *c* 14.328(9) Å, *α* 113.03(4), *β* 91.98(4), *γ* 117.45(2)°, *V* 1809(2) Å^3, D_c 1.50 g cm^{-3}, *Z* 2, μ_{Cu} 31.87 cm^{-1}, *T* 21(1) °C. 2893 reflections considered observed [$I > 3\sigma(I)$] out of 3707 unique data. Final residuals *R*, R_w were 0.047, 0.069 for the observed data. One of the methoxy groups is disordered with two positions for the methyl carbon; the relative occupancies of the components of the disordered methyl group refined to 0.54(1), 0.46(1).

CCDC reference number 186/2109.

See http://www.rsc.org/suppdata/dt/b0/b005081o/ for crystallographic files in .cif format.

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