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Copper(I) and silver(I) complexes of a new tetrahedrally-enforcing ligand containing two bipyridyl binding sites linked by a diphenyl disulfide bridge

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Conversion of the amino group of 6-(2-aminophenyl)-2,2′-bipyridine to a thiol resulted not in the expected N,N,S-terdentate chelating ligand HL [6-(2-sulfhydryl)-2,2′-bipyridine] but in the oxidised disulfide 2,2′-bis-[6-(2,2′-bipyridyl)]diphenyldisulfide, L–L. This ligand contains two bipyridyl arms linked by a diphenyl disulfide bridge in such a way that they cannot be coplanar, but tend to co-ordinate to a single metal ion with a substantial dihedral angle between the two ligand planes giving a pseudo-tetrahedral geometry. The crystal structure of L–L·$0.5C_6H_5CH_3$ shows the presence of near-linear N · · · S–S interactions (non-bonded N · · · S; 2.75 Å) in which the pyridyl lone pair interacts with the σ* orbital of the disulfide fragment. The complexes [Cu(L–L)][PF_6] and [Ag(L–L)][PF_6] were prepared and are isostructural, both having a distorted four-co-ordinate metal co-ordination environment in which the two chelating bipyridyl fragments have dihedral angles of between 70 and 80 °C between them (*i.e.* nearly mutually perpendicular). The electronic spectrum of the Cu^I complex [Cu(L–L)][PF_6], and the EPR spectrum of its one-electron oxidised product $[Cu(L–L)]^{2+}$, both confirm that the rigidity of the ligand donor set does not permit much variation in the co-ordination environment about the copper ion. The ligand therefore imposes a relatively rigid pseudo-tetrahedral geometry on the metal centres.

Ligands which can impose a tetrahedral or (more usually) a pseudo-tetrahedral geometry on metal ions are of interest for a variety of reasons.[1–5] These include ligands for selective metal-ion extraction,[1] models for mononuclear copper proteins,[2,3] and the study of the relationship between structure and properties of transition-metal complexes.[4] Amongst these examples copper complexes are especially prominent, largely because the differing geometries normally adopted by Cu^I and Cu^{II} complexes mean that their interconversion is accompanied by a pronounced structural change; consequently, imposition of a particular geometry on the metal allows control of the copper(I)–copper(II) redox couple.[2]

We describe here the synthesis of a new ligand 2,2′-bis-[6-(2,2′-bipyridyl)]diphenyldisulfide (L–L) which contains two chelating bipyridyl fragments attached to a diphenyl disulfide bridge. The steric properties of the bridging group are such that the two bipyridyl (bipy) fragments cannot co-ordinate to a metal ion in a coplanar manner, but must be mutually twisted such that there is a substantial dihedral angle between them and a tetrahedrally-distorted geometry is therefore imposed on the metal. The free ligand and its complexes [Cu(L–L)][PF_6] and [Ag(L–L)][PF_6] were prepared and crystallographically characterised; electrochemical and spectroscopic studies were also performed on the complexes.

Experimental

General

The compounds [Cu(MeCN)$_4$][PF_6][6] and 6-(2-aminophenyl)-2,2′-bipyridine[7] were prepared as described. Instrumentation used for routine spectroscopic and electrochemical studies has been described previously.[8] The EPR spectra were recorded at 77 K with a Bruker ESP-300E instrument.

Preparations

2,2′-Bis[6-(2,2′-bipyridyl)]diphenyldisulfide (L–L). This procedure is based on a published method for conversion of amino groups into thiols.[9] The compound 6-(2-aminophenyl)-2,2′-bipyridine (3.09 g, 12.5 mmol) in water (10 cm^3) and concentrated hydrochloric acid (2 cm^3) was cooled to 0 °C and diazotised by adding $NaNO_2$ (1.20 g, 17.4 mmol) in small portions over 20 min. This solution of the diazonium salt was added over 30 min to a solution of potassium *O*-ethyl dithiocarbonate (5.0 g, 31.2 mmol, excess) in water (30 cm^3) at 60 °C, and stirring was then continued at this temperature for a further 45 min. On cooling, the resulting oil was extracted with CH_2Cl_2 and the organic extracts were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The oil was added to ethane-1,2-diamine (15 cm^3) and stirred under nitrogen at room temperature for 16 h. The reaction mixture was quenched with water (50 cm^3) and neutralised by careful addition of concentrated HCl. The crude product was extracted with CH_2Cl_2, and the organic extracts were dried ($MgSO_4$) and reduced to an oil. Column chromatography on alumina (Brockmann grade approximately 3) eluting twice with CH_2Cl_2–hexane (1 : 1) eventually afforded 2,2′-bis[6-(2,2′-bipyridyl)]diphenyldisulfide (L–L), which followed an initial fast moving yellow impurity. Removal of the solvent *in vacuo* afforded L–L as a white powder (1.22 g, 37%), which could be recrystallised from hot toluene affording crystals suitable for an X-ray diffraction study. Electron impact (EI) mass spectrum: *m/z* 263 (263) $[L]^+$. Fast atom bombardment (FAB) mass spectrum: *m/z* 527 ($[L–L + H]^+$, 10) and 263 ($[L]^+$, 100%) (Found: C, 74.3; H, 4.3; N, 9.9. Calc. for $C_{32}H_{22}N_4S_2\cdot 0.5C_6H_5CH_3$: C, 74.4; H, 4.6; N, 9.8%). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.68 (m, 2 H, $H^{3'}$, $H^{6'}$), 8.44 (dd, 1 H, H^3), 7.93 (m, 2 H, H^4, $H^{3'' \text{ or } 6''}$), 7.81 (ddd, 1 H, $H^{4'}$), 7.63 (m, 2 H, H^5, $H^{6'' \text{ or } 3''}$) and 7.31 (m, 3 H, $H^{5'}$, $H^{4''}$, $H^{5''}$).

[Cu(L–L)][PF_6]. The salt [Cu(MeCN)$_4$][PF_6] (0.038 g, 0.101 mmol) in methanol (20 cm^3) was added to a solution of L–L (0.053 g, 0.102 mmol) in dichloromethane (5 cm^3). The resulting brown solution was stirred at room temperature for 5 min. Excess aqueous KPF_6 was then added, and the solution was reduced in volume to afford a brown precipitate, which was collected by filtration and purified by reprecipitation from

Table 1 Summary of crystal parameters, data collection and refinement for the three crystal structures

Compound	$L{-}L{\cdot}0.5C_6H_5CH_3$	$[Cu(L{-}L)][PF_6]$	$[Ag(L{-}L)][PF_6]$
Formula	$C_{35.5}H_{26}N_4S_2$	$C_{32}H_{22}CuF_6N_4PS_2$	$C_{32}H_{22}AgF_6N_4PS_2$
M	572.72	735.17	779.50
System, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Monoclinic, $C2/c$
a/Å	10.775(2)	14.675(3)	14.715(2)
b/Å	11.1679(10)	17.730(2)	17.947(4)
c/Å	12.041(2)	12.387(2)	12.672(2)
α/°	83.535(9)		
β/°	85.320(11)	113.080(11)	115.494(14)
γ/°	79.904(10)		
U/Å^3	1414.6(3)	2965.1(8)	3020.6(9)
Z	2	4	4
D_c/g cm^{-3}	1.345	1.647	1.714
μ/mm^{-1}	0.222	1.001	0.927
F(000)	598	1488	1560
Crystal size/mm	0.75 × 0.75 × 0.5	0.2 × 0.25 × 0.65	0.4 × 0.15 × 0.15
Reflections collected: total, independent, R_{int}	9023, 6203, 0.0171	9174, 3357, 0.0184	6884, 3129, 0.0312
Data, restraints, parameters	6197, 0, 388	3357, 0, 209	3129, 0, 209
Final $R1$, $wR2$ [a,b]	0.0347, 0.1024	0.0269, 0.0769	0.0428, 0.1144
Weighting factors [b]	0.0502, 0.6009	0.0477, 0	0.0689, 0
Largest peak, hole/e Å^{-3}	+0.311, −0.272	+0.348, −0.340	+0.896, −0.959

[a] Structure was refined on F_o^2 using all data; the value of $R1$ is given for comparison with older refinements based on F_o with a typical threshold of $F \geqslant 4\sigma(F)$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{\frac{1}{2}}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

aqueous acetonitrile. The salt $[Cu(L{-}L)][PF_6]$ was obtained as a brown powder (0.064 g, 86%). Red-brown crystals suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex. FAB mass spectrum: *m/z* 589 $\{[Cu(L{-}L)]^+\}$ (Found: C, 52.6; H, 2.9; N, 7.7. Calc. for $C_{32}H_{22}CuF_6N_4PS_2$: C, 52.3; H, 3.0; N, 7.6%). ^1H NMR (CD_3CN, 300 MHz): δ 8.64 (ddd, 1 H, $H^{6'}$), 8.33 (dd, 1 H, $H^{3'}$), 8.15 (m, 2 H, $H^{3\text{ or }5}$, $H^{4'}$), 7.98 (dd, 1 H, H^4), 7.65 (ddd, 1 H, $H^{5'}$), 7.54 (dd, 1 H, $H^{5\text{ or }3}$), 7.35 (dd, 1 H, $H^{3''\text{ or }6''}$), 7.11 (dd, 1 H, $H^{6''\text{ or }3''}$), 6.98 (ddd, 1 H, $H^{4''\text{ or }5''}$) and 6.41 (ddd, 1 H, $H^{5''\text{ or }4''}$).

$[Ag(L{-}L)][PF_6]$. This was prepared as for the Cu^I complex above, except that $AgBF_4$ (0.020 g, 0.103 mmol) was used in place of $[Cu(MeCN)_4][PF_6]$. Following reprecipitation from aqueous acetonitrile with excess NH_4PF_6, $[Ag(L{-}L)][PF_6]$ was obtained as a very pale brown powder (0.061 g, 77%). Crystals suitable for an X-ray crystallographic study were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex. FAB mass spectrum: *m/z* 635 $[Ag(L{-}L)]^+$ (Found: C, 49.3; H, 2.7; N, 7.1. Calc. for $C_{32}H_{22}AgF_6N_4PS_2$: C, 49.3; H, 2.8; N, 7.2%). ^1H NMR (CD_3CN, 300 MHz): δ 8.78 (ddd, 1 H, $H^{6'}$), 8.33 (dd, 1 H, $H^{3'}$), 8.16 (m, 2 H, $H^{3\text{ or }5}$, $H^{4'}$), 8.00 (dd, 1 H, H^4), 7.65 (ddd, 1 H, $H^{5'}$), 7.52 (dd, 1 H, $H^{5\text{ or }3}$), 7.31 (m, 2 H, $H^{3''}$, $H^{6''}$), 6.91 (ddd, 1 H, $H^{4''\text{ or }5''}$) and 6.41 (ddd, 1 H, $H^{5''\text{ or }4''}$).

Crystallography

Suitable crystals were quickly transferred from the mother-liquor to a stream of cold N_2 at −100 °C on a Siemens SMART diffractometer fitted with a CCD-type area detector. In all cases data were collected at −100 °C to a 2θ limit of 55° using graphite-monochromatised Mo-Kα radiation. A detailed experimental description of the methods used for data collection and integration using the SMART system has been published.[10] Table 1 contains a summary of the crystal parameters, data collection and refinement. In all cases the structures were solved by conventional heavy atom or direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL 5.03 package[11] on a Silicon Graphics Indy computer. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters.

In crystals of $L{-}L{\cdot}0.5C_6H_5CH_3$, the asymmetric unit contains an entire molecule of the ligand and half of a molecule of toluene which is disordered across an inversion centre. Some atomic positions are common to both components of the disorder. The two disordered components could be satisfactorily resolved; the thermal parameters for these solvent atoms are rather higher than those of the (well ordered) ligand. The compounds $[Cu(L{-}L)][PF_6]$ and $[Ag(L{-}L)][PF_6]$ are isostructural, and in both cases the complex molecule lies on a C_2 axis such that only half of the molecule is in the asymmetric unit. Solution and refinement of these two structures presented no problems.

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Results and Discussion

Synthesis and structure of L–L

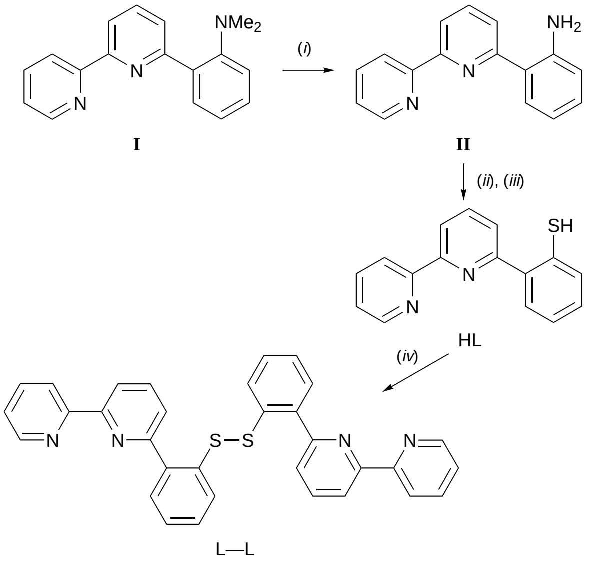
Our initial aim had been to prepare the N,N,S-terdentate chelating ligand HL as part of a general programme to study the co-ordination chemistry of new mixed-donor polydentate ligands. We recently described the synthesis and co-ordination behaviour of the bidentate N,S-donor ligand 2-(2-pyridyl)benzenethiol,[8] and were interested to prepare HL as a higher homologue. Demethylation of 6-(2-dimethylaminophenyl)-2,2′-bipyridine (Scheme 1, **I**)[12,13] afforded 6-(2-aminophenyl)-2,2′-bipyridine (Scheme 1, **II**);[7] both of these are interesting ligands in their own right and their syntheses and co-ordination chemistry has been described. Conversion of the amino group of **II** to a thiol followed the published route[8,9] in 37% yield. However, as with the preparation of the smaller homologue 2-(2-pyridyl)benzenethiol, we found that facile oxidation to the disulfide occurred during the (aerobic) work-up to give L–L, a 'protected' form of HL. In the case of 2-(2-pyridyl)benzenethiol we found that reduction of the disulfide *in situ* allowed isolation of complexes of the bidentate anionic ligand. For L–L this may also be possible, but we concentrate in this paper on the use of the disulfide as a tetradentate N-donor ligand in its own right.

The crystal structure of L–L (as its toluene solvate) is shown in Fig. 1; selected bond lengths and angles, and inter-ring dihedral angles, are in Table 2. The torsion angle about the S–S bond [C(32)–S(1)–S(2)–C(41)] is 86.3°, allowing the phenyl substituents to avoid one another. The bipyridyl fragments are essentially *trans* coplanar. A significant feature of the structure

Table 2 Selected bond lengths (Å) and angles (°) for L–L·$0.5C_6H_5CH_3$

S(1)–C(31)	1.8036(14)	S(1)–S(2)	2.0628(5)
S(2)–C(41)	1.7934(13)		
C(42)–S(2)–S(1)	104.34(5)	C(31)–S(1)–S(2)	104.37(5)
C(42)–C(41)–S(2)	120.47(10)	C(32)–C(31)–S(1)	120.45(11)
C(51)–N(3)–C(55)	118.90(12)	C(21)–N(2)–C(25)	118.86(12)
C(15)–N(1)–C(11)	117.65(13)	C(65)–N(4)–C(61)	117.5(2)
Rings 1/2	176.2*	Rings 4/5	29.3
Rings 2/3	29.1	Rings 5/6	173.2

* Dihedral angles between mean planes of aromatic rings. The rings are numbered according to the first digit used for the carbon atoms in that ring; thus, the ring containing N(3) and C(51)–C(55) is ring 5.



Scheme 1 (*i*) Pyridine–HCl, 200 °C; (*ii*) $NaNO_2$, HCl; (*iii*) potassium *O*-ethyl dithiocarbonate; (*iv*) work-up in air

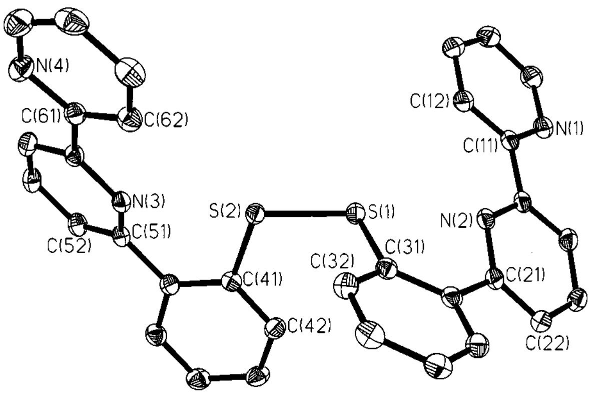


Fig. 1 Crystal structure of L–L

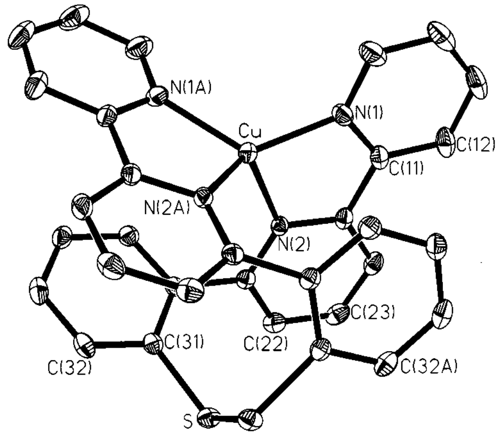


Fig. 2 Crystal structure of [Cu(L–L)][PF_6]

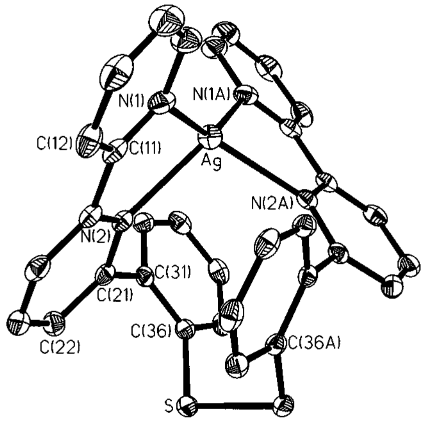


Fig. 3 Crystal structure of [Ag(L–L)][PF_6]

is the close N(3)···S(2) and N(2)···S(1) contacts (both 2.75 Å), which arise from the interaction of the N lone pair with the S–S σ^* orbital.[8,14] Ideally the N···S–S fragments would therefore be linear, but this is not sterically possible here; nevertheless the angles N(3)–S(2)–S(1) and N(2)–S(1)–S(2) are 172.4 and 176.5° respectively, both close to linearity. Similar behaviour was observed in the disulfide of 2-(2-pyridyl)-benzenethiol.[8]

It is clear from this structure that the two bipyridyl fragments cannot be coplanar and co-ordinate to the same metal ion; instead, tetrahedrally distorted structures are more likely to occur in which the two (planar) co-ordinated bipyridyl fragments have a substantial dihedral twist between them. We accordingly prepared complexes of L–L with Cu^I and Ag^I which commonly occur in distorted N_4 co-ordination geometries.

Synthesis and structures of [Cu(L-L)][PF_6] and [Ag(L–L)][PF_6]

These complexes were readily prepared in good yield by reaction of the ligand with 1 equivalent of [$Cu(MeCN)_4$][PF_6] in the former case, or with $AgBF_4$ followed by anion metathesis in the latter case. Both complexes could be recrystallised to give X-ray quality crystals of compounds whose mass spectra and elemental analyses were exactly consistent with 1 : 1 metal : ligand formulations. Their ^1H NMR spectra both indicated 11 proton environments in the aromatic region, indicating that the two halves of each ligand are equivalent in solution; full assignments (Experimental section) were made with the aid of two-dimensional correlation spectroscopy (COSY) spectra.

The crystal structures are in Figs. 2 and 3 respectively; selected bond lengths, angles, and inter-ring dihedral angles, are collected in Table 3. The structures are essentially identical, with the metal ion in each case co-ordinated by two bipyridyl fragments which are linked by a diphenyl disulfide bridge. The metal atom and the centre of the S–S bond lie on a C_2 axis, so the two ligand halves are equivalent (*cf.* the solution ^1H NMR spectra). The ligand has helical chirality. The dihedral angle θ between the two MN_2 planes is 76.9° in [Cu(L–L)][PF_6] and 72.3° in [Ag(L–L)][PF_6]. For planar (local D_{2h}) geometry θ would be 0°, and for pseudo-tetrahedral (local D_{2d}) geometry θ would be 90°; the metal ions are therefore in geometries that are much closer to pseudo-tetrahedral than planar. The metal–ligand bond distances are in the expected range for bis(diimine) complexes of these metal ions. The C–S–S–C torsion angles are 77.5 and 76.5 °C respectively for the Cu and Ag structures, a

Table 3 Selected bond lengths (Å) and angles (°) for [Cu(L–L)][PF$_6$] and [Ag(L–L)][PF$_6$]

	Cu	*Ag*
M–N(1)	2.0124(14)	2.276(3)
M–N(2)	2.0640(13)	2.381(3)
N(1A)–M–N(1)	125.56(8)	141.8(2)
N(1A)–M–N(2)	131.74(6)	135.12(10)
N(1)–M–N(2)	80.97(6)	71.40(11)
Rings 1/2 *	0.8	6.7
Rings 2/3	63.4	61.2

* Ring numbering as described in Table 2.

decrease compared to the value of 86.3° in free L–L, which has permitted the two bipyridyl substituents to approach one another sufficiently to be able to co-ordinate to the same metal ion.

In Cu$^{\mathrm{I}}$ complexes of various bidentate diimine ligands the value of θ between the two CuN$_2$ planes is typically 70–80° in the solid state,[12,15] the slight compression away from 90° occurring usually as a result of ubiquitous intermolecular aromatic π-stacking interactions in the crystals.[16] In solution removal of this constraint allows θ to be 90°.[17] Simple mononuclear Ag$^{\mathrm{I}}$ complexes with the same ligands are much rarer, but they have basically the same type of slightly flattened pseudo-tetrahedral geometry for the same reasons.[16] With ligands bearing aromatic substituents at the positions *ortho* to the nitrogen atoms of the co-ordinating pyridyl rings, there is generally an additional intramolecular π-stacking interaction between the aromatic substituent of one ligand and the co-ordinated bipyridyl or phenanthroline fragment of the other,[12,15] and this can also contribute to the distortion of the structures away from D_{2d} geometry. Such an interaction is evident in both [Cu(L–L)][PF$_6$] and [Ag(L–L)][PF$_6$], with the phenyl ring pendant from one bipy fragment stacking with the pyridyl rings of the other bipy fragment. The interacting π-systems are not parallel due to the steric constraints of the ligand (for example, the mean planes of the phenyl ring and the pyridyl ring with which it is stacked have an intersection angle of about 12° in the Cu$^{\mathrm{I}}$ complex and about 14° in the Ag$^{\mathrm{I}}$ complex), but the separations between the overlapping segments lie in the range 3.3–4 Å in both complexes, which is typical of such π-stacking interactions.

In [Cu(L–L)][PF$_6$] and [Ag(L–L)][PF$_6$] therefore the geometry about the metal is much the same as that which would be adopted if there were no constraining linkage between the two bipy fragments. It appears that the peculiar steric limitations of L–L are ideally matched to metal ions such as Cu$^{\mathrm{I}}$ and Ag$^{\mathrm{I}}$ that require pseudo-tetrahedral geometries.

Electrochemical and spectroscopic studies on [Cu(L–L)][PF$_6$]

The electronic spectrum of [Cu(L–L)][PF$_6$] in MeCN at room temperature shows a copper(I)-to-bipyridine metal-to-ligand charge transfer (MLCT) band at 462 nm ($\varepsilon = 4800$ dm^3 mol^{-1} cm^{-1}), with a pronounced shoulder at 530 nm whose intensity is about 0.25 times that of the MLCT band maximum. The position of the 462 nm maximum may be compared with the spectrum of 'unconstrained' [Cu(bipy)$_2$]$^+$, which has $\lambda_{\max} = 440$ nm for the MLCT band. The significant red shift of the MLCT transition in [Cu(L–L)][PF$_6$] compared to [Cu(bipy)$_2$]$^+$ may be ascribed principally to the different geometries of the two metal centres.

In solution the *inter*molecular crystal packing effects which lead to the reduction of θ from 90° are assumed to be absent, and the spectra of (for example) Cu$^{\mathrm{I}}$ complexes with simple phenanthroline derivatives are readily interpretable in terms of a D_{2d} structure with θ = 90°.[17] In contrast, the *intra*molecular π-stacking interactions between ligands with aromatic substituents, which can also result in distortions from D_{2d} geometry, can be maintained in solution.[12,17] Distortion away from pseudo-tetrahedral geometry towards planarity (reduction of θ) has been shown to result in a red shift of the MLCT maximum in [Cu(L′)$_2$]$^+$ complexes (L′ = bidentate diimine) because the greater spread of d orbital energies that arises from the reduced symmetry of the ligand field results in raising of the highest-energy d orbitals nearer to the ligand π* orbitals.[17,18] Since [Cu(bipy)$_2$]$^+$ ($\lambda_{\max} = 440$ nm) can be assumed to have a D_{2d} structure in solution,[17] it follows that in solution the structure of [Cu(L–L)][PF$_6$] ($\lambda_{\max} = 462$ nm) is flattened with θ < 90°, indicating that the structure observed in the crystalline state is retained in solution. It is apparently not capable of 'relaxing' to give local D_{2d} geometry because of a combination of the steric constraints imposed by the linkage between the two bipy fragments, and the presence of intramolecular π-stacking within L–L. Additional support for this comes from the low energy and high intensity of the shoulder at ≈530 nm. In strict D_{2d} geometry this transition is weak, but with the reduction in symmetry that occurs on distortion it moves to lower energy and becomes more intense.[12,17]

Cyclic voltammetry of [Cu(L–L)][PF$_6$] in CH$_2$Cl$_2$ revealed a chemically reversible, one-electron couple at $E_{\frac{1}{2}} = +0.13$ V *vs.* the ferrocene–ferrocenium couple, Fc–Fc$^+$. The voltammetric wave was symmetric (cathodic and anodic peak currents equal at scan rates between 20 and 500 mV s^{-1}), and the peak–peak splitting ΔE_p was 90 mV at a scan rate of 200 mV s^{-1}, identical to that of the ferrocene–ferrocenium couple under the same conditions. This we assign to the Cu$^{\mathrm{I}}$–Cu$^{\mathrm{II}}$ couple. There are also two fully irreversible reductions (no return waves) with peaks at −1.69 and −2.15 V *vs.* Fc–Fc$^+$ on the outward scan, of which it is likely that one will be a metal-based Cu$^{\mathrm{I}}$–Cu^0 couple and the other ligand-based but we cannot tell which is which.

The potential of the Cu$^{\mathrm{I}}$–Cu$^{\mathrm{II}}$ couple of [Cu(L–L)][PF$_6$] is similar to those of various Cu$^{\mathrm{I}}$ complexes with sterically hindering bipyridine or phenanthroline derivatives that also tend to impose tetrahedral geometry on the metal, *i.e.* 2,9-disubstituted phenanthroline derivatives and 6,6′-disubstituted bipyridine derivatives.[19] Ligands of this type tend to stabilise (pseudo-tetrahedral) Cu$^{\mathrm{I}}$ and destabilise (planar) Cu$^{\mathrm{II}}$ complexes, because the substituents which stabilise the Cu$^{\mathrm{I}}$ state by forming an interlocked structure when the ligands are mutually perpendicular tend to interfere sterically with one another when the ligands move towards coplanarity in the Cu$^{\mathrm{II}}$ state. For this reason the Cu$^{\mathrm{I}}$–Cu$^{\mathrm{II}}$ couples are at rather anodic potentials compared to those of the parent unsubstituted ligands, and from the electrochemical results L–L confers similar properties on the metal centre to ligands such as 2,9-diphenyl-1,10-phenanthroline.[17]

One-electron oxidation of [Cu(L–L)][PF$_6$] to the Cu$^{\mathrm{II}}$ form was achieved by treatment of the complex with 1 equivalent of the outer-sphere one-electron oxidant [Ru(bipy)$_3$][PF$_6$]$_3$ in MeCN.[20] The X-band EPR spectrum of the oxidised complex was recorded in a frozen glass at 77 K. The spectrum was a typical axial spectrum with the following parameters: $g_{\parallel} = 2.24$, $g_{\perp} = 2.08$ and $A_{\parallel} = 147 \times 10^{-4}$ cm^{-1}. The EPR spectra of Cu$^{\mathrm{II}}$(L′)$_2$ complexes are sensitive to the angle θ between the two CuL′ planes and this provides a useful indication of the geometry.[12,21–23] Specifically, in pseudo-tetrahedral (θ = 90°; D_{2d}) geometries the value of $g_{\parallel}$ is high (>2.3) and the value of $A_{\parallel}$ is low. As the geometry changes towards planar (θ = 0°; D_{2h}) the value of $g_{\parallel}$ decreases and that of $A_{\parallel}$ increases. In general it is the value of $A_{\parallel}$ that is most sensitive to θ, with Cu$^{\mathrm{II}}$N$_4$ chromophores having $A_{\parallel}$ values that vary between about (100 and 200) × 10^{-4} cm^{-1} as θ changes from 90 to 0°.

The cation [Cu(bipy)$_2$]$^{2+}$, the most sensible comparison for [Cu(L–L)]$^{2+}$, has in the solid state a geometry exactly mid-way between planar and pseudo-tetrahedral (θ = 44.6°).[23] Its *g* values (as a polycrystalline powder, in which it is safe to assume that the geometry observed in the crystal structure is retained) are very similar to those of $[Cu(L{-}L)]^{2+}$ but, more importantly, its value of $A_{\parallel}$ (176 × 10^{-4} cm^{-1}) is significantly higher, indicating that $[Cu(L{-}L)]^{2+}$ has a more tetrahedral geometry than $[Cu(bipy)_2]^{2+}$. Comparison with the EPR spectra of several $[Cu(L')_2]^{2+}$ complexes in the literature[21,22] shows that the parameters of $[Cu(L{-}L)]^{2+}$ are consistent with a θ value of 60–70°, not very different from that observed in the crystal structure of the Cu^{I} complex. Oxidation of $[Cu(L{-}L)]^{+}$ therefore does not result in the usual substantial flattening towards planarity that is observed with less constrained ligands. Clearly, isolation and structural characterisation of Cu^{II} complexes of L−L will be of interest, and work towards this is in progress.

Conclusion

The new ligand L−L, containing two bipy-type co-ordinating arms linked by a diphenyl disulfide spacer, has been prepared. The structures of the Cu^{I} and Ag^{I} complexes show that it imposes a pseudo-tetrahedral geometry on metal ions in which the two ligand planes are at an angle of 76.9° (Cu) or 72.3° (Ag) respectively. The electronic spectrum of $[Cu(L{-}L)][PF_6]$, and the EPR spectrum of the one-electron oxidised form $[Cu(L{-}L)]^{2+}$, both indicate that there is little scope for the geometry about the metal centre to vary either with removal of crystal packing interactions in solution, or with change in the metal oxidation state, because of the steric constraints of the ligand.

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