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Double-helical dinuclear copper(I) and mononuclear copper(II) complexes of a compartmental tetradentate bridging ligand: crystal structures and spectroscopic properties

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Reaction of 3-(2-pyridyl)pyrazole with α,α′-dibromoxylene affords a new tetradentate ligand L having two bidentate pyridyl-pyrazole compartments linked by an *o*-$CH_2C_6H_4CH_2$ spacer. With Cu^I, L forms a dinuclear double helicate $[Cu_2L_2][PF_6]_2$ in which both ligands are bridging both pseudo-tetrahedral metal ions, which are 5.05 Å apart. However L does not support a double helical architecture with Cu^{II}. Reaction of L with $CuCl_2$ affords [CuLCl][BF_4] which is trigonal bipyramidal both in the solid state (by X-ray crystallography) and in solution (by EPR spectroscopy). Reaction of L with $Cu(MeCO_2)_2{\cdot}H_2O$ affords $[Cu_2L_3][BF_4]_4$ which was characterised by mass spectroscopy and elemental analysis. By analogy with the (known) nickel(II) analogue, this complex has one ligand acting as a bis-bidentate bridge between two $\{CuL\}^{2+}$ fragments in which L acts as a terminal tetradentate chelating ligand. Recrystallisation of this afforded a few crystals of the decomposition product [CuL(MeOH)][CuL(SiF_6)][BF_4]$_2$, which contains trigonal-bipyramidal [CuL(MeOH)]$^{2+}$ and six-co-ordinate [CuL(SiF_6)] fragments, the latter displaying the first known example of the hexafluorosilicate anion acting as a bidentate chelating F,F-donor.

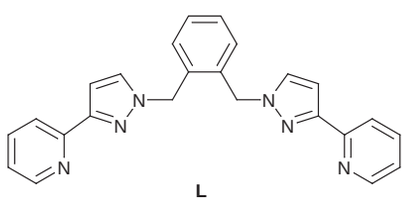
Of all the commonly studied transition metals, copper has a particular appeal because of the different stereoelectronic preferences of its two common oxidation states.[1] The Cu^I/Cu^{II} interconversion is often accompanied by a pronounced geometric change, and if the conversion is reversible this structural change may be the basis of an allosteric effect in which the geometric change at the metal alters the properties of a more remote site in the complex.[2] Conversely, control of the geometric environment around copper centres allows control of the redox potential of the Cu^I–Cu^{II} couple. This is in part the basis of the redox properties of type 1 copper proteins[3] and many synthetic analogues,[4] where the rigidity of a carefully designed ligand environment can impose a geometry on the metal which is anywhere between the extremes preferred by Cu^I and Cu^{II} and thereby control the redox potential.

In this paper we describe the synthesis of the tetradentate ligand L, containing two bidentate chelating pyridyl-pyrazolyl fragments linked by a flexible *o*-$CH_2C_6H_4CH_2$ spacer, and its co-ordination behaviour with Cu^I and Cu^{II}. This ligand is a new member of a class of ligand which we have been studying recently in which two bidentate pyridyl-pyrazolyl fragments are linked to a variety of spacer groups such as $\{BH_2\}^-$,[5] $\{CH_2\}$[6] and $\{PO_2\}^-$,[7] to give flexible ligands which can either co-ordinate to a single metal ion as a tetradentate chelate, or can co-ordinate each bidentate arm to a separate metal centre to give bridged polynuclear species. The results presented here show that L can bridge two metal ions to give a double helicate with Cu^I, but acts as a tetradentate chelate to a single metal centre in its structurally characterised complexes with Cu^{II}. There are other examples in the literature of pairs of copper-(I) and -(II) complexes in which the co-ordination mode of a tetradentate ligand is similarly dependent on the stereoelectronic preferences of the metal centre.[8]

Experimental

General details

Instrumentation used for routine spectroscopic and electrochemical studies has been described in previous papers. 3-(2-Pyridyl)pyrazole was prepared as previously described.[9]



L

Preparations

Ligand L. A mixture of α,α′-dibromoxylene (5.50 g, 20.8 mmol), 3-(2-pyridyl)pyrazole (6.40 g, 44.1 mmol), NBu^n_4OH (25 drops of 40% aqueous solution), aqueous NaOH (10 M, 35 cm^3) and toluene (200 cm^3) was heated with stirring to 85 °C for 24 h. After cooling, the organic layer was washed with water and then dried over $MgSO_4$. Removal of the solvent *in vacuo* afforded a pale yellow oil which afforded a white powder on recrystallisation from CH_2Cl_2–Et_2O (6.7 g, 82%). EI mass spectrum: *m*/*z* 392 (M^+, 5%), 246 (loss of one bidentate pyridyl-pyrazolyl arm, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (2 H, d, *J* 4.8, pyridyl H^6), 7.94 (2 H, d, *J* 8.0, pyridyl H^3), 7.68 (2 H, td, *J* 7.8, 1.7, pyridyl H^4), 7.33 (2 H, d, *J* 2.3, pyrazolyl H^4 or H^5), 7.30 (2 H, m, phenyl), 7.17 (4 H, m, phenyl and pyridyl H^5), 6.91 (2 H, d, *J* 2.3; pyrazolyl H^5 or H^4) (Found: C, 73.0; H, 5.1; N, 21.3. $C_{24}H_{20}N_6$ requires C, 73.5; H, 5.1; N, 21.4%). X-Ray quality crystals were grown by slow diffusion of diethyl ether vapour into a concentrated CH_2Cl_2 solution of L.

$[Cu_2L_2][PF_6]_2$. Under an atmosphere of N_2, a solution of L (0.139 g, 0.35 mmol) in dry CH_2Cl_2 (7 cm^3) was added dropwise to a solution of [Cu(MeCN)$_4$][PF_6] (0.132 g, 0.35 mmol) in dry CH_2Cl_2 (10 cm^3) to afford an orange solution. After stirring at room temperature for 2 h, the solution was reduced in volume and hexane added to precipitate a yellow solid which was filtered off and dried *in vacuo* (yield: 0.20 g, 95%). Electrospray MS: *m*/*z* 1657.6 [7%, $\{Cu_3L_3(PF_6)_2\}^+$], 1449.5 [4%, $\{Cu_2L_3(PF_6)\}^+$], 1056.7 [12%, $\{Cu_2L_2(PF_6)\}^+$], 455.0 [100%, $\{Cu_2L_2\}^{2+}$] (Found: C, 47.5; H, 3.5; N, 13.6. $C_{48}H_{40}Cu_2F_{12}N_{12}P_2$

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Table 1 Crystallographic data for the four crystal structures[a]

Compound	L	$[Cu_2L_2][PF_6]_2\cdot 0.5CH_2Cl_2$	$[CuLCl][BF_4]$	$[CuL(MeOH)][CuL(SiF_6)][BF_4]_2$
Formula	$C_{24}H_{20}N_6$	$C_{24.5}H_{21}ClCuF_6N_6P$	$C_{24}H_{20}BClCuF_4N_6$	$C_{49}H_{44}B_2Cu_2F_{14}N_{12}OSi$
M	392.46	643.43	578.26	1259.75
System, space group	Monoclinic, $P2_1/c$	Tetragonal, $P4_32_12$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a/Å	10.1831(10)	16.3084(14)	16.333(2)	10.135(2)
b/Å	24.930(3)	16.308(2)	8.492(2)	18.355(4)
c/Å	8.1034(7)	19.627(2)	17.002(2)	27.362(5)
β/°	102.111(6)	90	90.423(9)	99.284(14)
U/Å^3	2011.4(3)	5220.1(10)	2358.1(6)	5024(2)
Z	4	8	4	4
D_c/g cm^{-3}	1.296	1.637	1.629	1.666
μ/mm^{-1}	0.081	1.071	1.099	0.976
F(000)	824	2600	1172	2552
Crystal size/mm	0.6 × 0.3 × 0.3	0.5 × 0.3 × 0.1	0.3 × 0.2 × 0.1	0.3 × 0.2 × 0.1
Reflections collected: total, independent, R_{int}	11 978, 4566, 0.0334	33 732, 6003, 0.0426	23 437, 5371, 0.0471	50 899, 11 519, 0.1098
Data, restraints, parameters	4563, 0, 271	6003, 0, 357	5371, 0, 371	11 517, 111, 749
Final $R1$, $wR2$[b,c]	0.0524, 0.1464	0.0535, 0.1576	0.0362, 0.1078	0.0628, 0.1247
Weighting factors[c]	0.0596, 0.9333	0.0893, 4.5299	0.0573, 0.0708	0.0296, 8.9760
Largest peak, hole/e Å^{-3}	+0.325, −0.373	+0.684, −0.682	+0.429, −0.489	+0.755, −0.603

[a] Details in common: temperature for data collection, 173 K; upper 2θ limit for data collection, 55°. [b] 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 $F \geqslant 4\sigma(F)$. [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

requires C, 48.0; H, 3.3; N, 14.0%). X-Ray quality crystals were grown by slow diffusion of diethyl ether vapour into a concentrated CH_2Cl_2 solution of $[Cu_2L_2][PF_6]_2$.

$[CuLCl][BF_4]$. A solution of L (0.146 g, 0.37 mmol) in MeOH (8 cm^3) was added to a solution of $CuCl_2$ (0.050 g, 0.37 mmol) in MeOH (6 cm^3). The mixture was stirred at room temperature for 1 h and then filtered to remove traces of unidentified insoluble material. Addition of an aqueous solution of $NaBF_4$ to the dark green solution afforded a precipitate of the product which was filtered off and dried *in vacuo* (yield: 0.10 g, 50%). Fast-atom bombardment MS: *m/z* 490 [40%, $\{CuLCl\}^+$], 455 [100%, $\{CuL\}^+$] (Found: C, 49.5; H, 3.5; N, 14.6. $C_{24}H_{20}BClCuF_4N_6$ requires C, 49.8; H, 3.5; N, 14.5%). X-Ray quality crystals were grown by slow diffusion of diethyl ether vapour into a concentrated solution of $[CuLCl][BF_4]$ in MeCN–acetone (1 : 1).

$[Cu_2L_3][BF_4]_4$. A solution of L (0.090 g, 0.23 mmol) in MeOH (5 cm^3) was added dropwise to a solution of $[Cu(MeCO_2)_2]\cdot H_2O$ (0.030 g, 0.15 mmol) in MeOH (5 cm^3). After stirring the mixture at room temperature for 1 h to give a clear solution, the product was precipitated by addition of aqueous $NaBF_4$ to give a blue-green solid which was filtered off and dried *in vacuo* (yield: 0.10 g, 74%). Fast-atom bombardment MS: *m/z* 1542 (100%); see Results and Discussion section for interpretation. Electrospray MS: *m/z* 1171.5 [1%, $\{Cu_2L_2(BF_4)_3\}^+$], 825.6 [1%, $\{Cu_2L_3(BF_4)_4\}^{2+}$], 455.4 [100%, $\{CuL\}^+$] (Found: C, 50.9; H, 3.7; N, 15.1. $C_{24}H_{20}BClCuF_4N_6\cdot 2H_2O$ requires C, 51.2; H, 3.8; N, 14.9%). Recrystallisation by slow diffusion of diethyl ether vapour into a concentrated solution of $[Cu_2L_3][BF_4]_4$ in acetone–MeOH (1 : 1) afforded X-ray quality crystals of what proved to be $[CuL(MeOH)][CuL(SiF_6)][BF_4]_2$ (see Results and Discussion for explanation).

X-Ray 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, and data were in all cases 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 direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL 5.03 package on a Silicon Graphics Indy computer.[11] Absorption corrections were applied using SADABS.[12] Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atom.

The structural determinations of L and $[CuLCl][BF_4]$ were straightforward and presented no problems. In $[Cu_2L_2][PF_6]_2\cdot 0.5CH_2Cl_2$ the carbon atom of the half-molecule of CH_2Cl_2 in the asymmetric unit lies astride a twofold axis. The space group is chiral, indicating that spontaneous resolution of the helicates occurs on crystallisation; the Flack parameter was zero within experimental error, indicating a correct assignment of the absolute configuration. In $[CuL(MeOH)][CuL(SiF_6)][BF_4]_2$ one of the $[BF_4]^-$ anions was disordered over two orientations. These could be resolved successfully, but similarity restraints were applied to the bonded B–F distances and non-bonded F···F separations to keep the geometries of the disordered components reasonable.

CCDC reference number 186/992.

See http://www.rsc.org/suppdata/dt/1998/2047/ for crystallographic files in .cif format.

Results and Discussion

Synthesis and crystal structure of the ligand L

The new ligand L was simply prepared in high yield by reaction of 2 equivalents of 3-(2-pyridyl)pyrazole with α,α′-dibromoxylene under phase-transfer conditions. Satisfactory ^{1}H NMR and mass spectral data confirmed the formulation of the product. As mentioned in the introduction a particular advantage of using chelating fragments with terminal pyrazol-3-yl groups is the ease with which several of these groups can be linked to a common spacer *via* deprotonation of the pyrazolyl N^1 position. We can easily envisage extension of this general route to the preparation of multinucleating ligands in which several chelating arms are linked to central spacers such as 1,3,5-tris-(bromomethyl)benzene, $C(CH_2Br)_4$, and so on.

The crystal structure of L is in Fig. 1. The two pyridyl-pyrazolyl arms are approximately *trans* coplanar, with angles of 6° between the mean planes of rings 6 and 7 [where ring 6

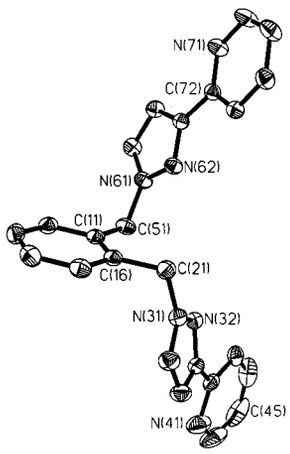

Fig. 1 Crystal structure of the new ligand L

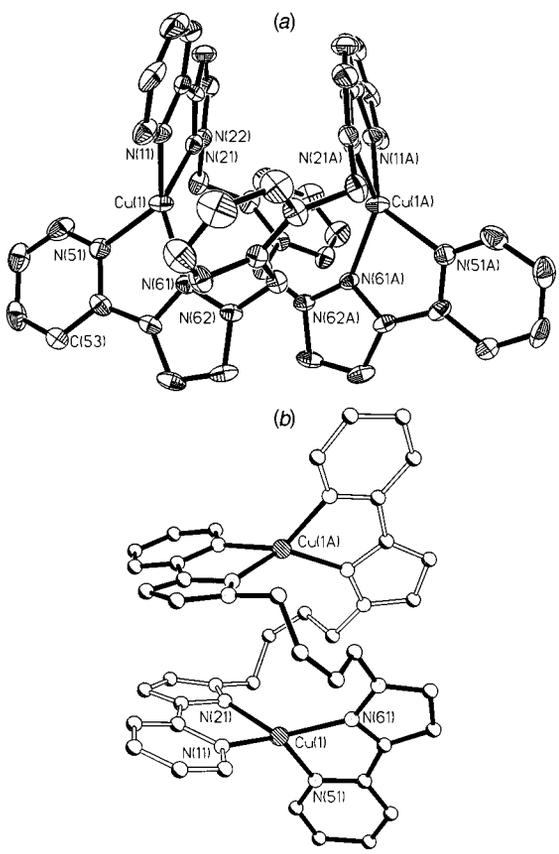

Fig. 2 Two views of the crystal structure of the dication of $[Cu_2L_2][PF_6]_2$: (*a*) the entire structure showing the labelling scheme; (*b*) a simplified view emphasising the helical geometry (four of the atoms on the central phenyl ring of each ligand have been omitted for clarity)

denotes atoms N(61)–C(65), *etc.*], and 20° between rings 3 and 4. The bond lengths and angles within the molecule are unremarkable. There are close intermolecular contacts in the range 3.2–3.6 Å between overlapping phenyl rings of adjacent molecules. From the conformation of the molecule in the crystal structure it is apparent that the two CH_2 hinges allow a substantial degree of flexibility, such that the two bidentate fragments can vary their separation, which will be of significance for determining the mode of co-ordination of the ligand (see later).

Synthesis and crystal structure of $[Cu_2L_2][PF_6]_2$

Reaction of L with 1 equivalent of $[Cu(MeCN)_4][PF_6]$ afforded a yellow compound whose elemental analysis indicates the stoichiometry $[CuL][PF_6]$, *i.e.* a 1:1 metal:ligand ratio as would be expected for a complex between a ligand with four donor atoms and a metal ion with a preference for four-co-ordination. The mass spectral data showed the complex to be dimeric, *i.e.* $[Cu_2L_2][PF_6]_2$, and the crystal structure (Fig. 2, Table 2) showed it to be a dinuclear double helicate[13] with both ligands bridging both metal ions.

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu_2L_2][PF_6]_2 \cdot 0.5CH_2Cl_2$

Cu(1)–N(11)	2.022(4)	Cu(1)–N(51)	2.050(4)
Cu(1)–N(61)	2.028(4)	Cu(1)–N(21)	2.049(4)
N(11)–Cu(1)–N(61)	123.4(2)	N(11)–Cu(1)–N(51)	134.7(2)
N(11)–Cu(1)–N(21)	81.3(2)	N(61)–Cu(1)–N(51)	80.5(2)
N(61)–Cu(1)–N(21)	134.3(2)	N(21)–Cu(1)–N(51)	110.1(2)

The complex dication lies on a C_2 axis, such that both metal ions are equivalent. The Cu^I ion has the usual pseudo-tetrahedral co-ordination with an angle of 71.5° between the two $Cu(NN)_2$ mean planes. Aromatic π-stacking interactions are evident between the ligands: specifically, the near-planar pyridyl-pyrazolyl fragment comprising rings 1 and 2 stacks with its symmetry-related equivalent, with separations of 3.3–4.1 Å between the atoms of one fragment and the mean plane of the other; similarly, the pyrazolyl ring N(61)–C(65) overlaps with its symmetry-related equivalent N(61A)–C(65A), with a separation of *ca.* 3.4 Å. Such interactions are common in double helicates with aromatic ligands, and the structure of $[Cu_2L_2][PF_6]_2$ is generally typical of double helicates of Cu^I with bis-bidentate ligands.[13] The metal–metal separation is 5.051(3) Å which reflects the length and flexibility of the *o*-$CH_2C_6H_4CH_2$ spacer group. It is clearly not possible for the two bidentate sites of one ligand to co-ordinate to a single metal ion in such a way that the two CuN_2 planes are mutually perpendicular, which would confer the required pseudo-tetrahedral geometry on the metal in a mononuclear complex. This is in contrast to some related ligands described recently containing two bipyridyl fragments with a large and flexible spacer between them, which are capable of forming mononuclear pseudo-tetrahedral complexes in this way.[14]

In solution the ^1H NMR spectrum, although rather broad, was consistent with the presence of four-fold symmetry such that eight aromatic and one aliphatic ($-CH_2-$) proton environments were present. Electrochemical studies revealed no evidence for a Cu^I–Cu^{II} couple at the potentials accessible with our combination of solvent and base electrolyte.

Synthesis and crystal structure of $[CuLCl][BF_4]$

Reaction of L with $CuCl_2$, followed by treatment of the solution with $NaBF_4$, afforded a material with empirical formula (from elemental analysis) $[CuLCl][BF_4]$. In this case however the mass spectral data were also consistent with a monomeric complex rather than a dimeric one, and this was confirmed crystallographically (Fig. 3, Table 3). The ligand L is now acting as a tetradentate chelate, co-ordinating all four donor atoms to the single metal centre which has an approximately trigonal-bipyramidal geometry. According to the method of Addison *et al.* for classifying five-co-ordinate geometries intermediate between square pyramidal (C_{4v}) and trigonal bipyramidal (D_{3h}),[15] the parameter τ is 0.63 (where a value of 1 denotes perfect trigonal-bipyramidal symmetry and 0 denotes perfect square pyramidal symmetry) indicating an intermediate structure but one that lies more towards the trigonal bipyramidal limit. The three equatorial ligands are therefore Cl, N(41) and N(71); the two axial ligands are N(51) and N(61), and the four atoms Cu(1), Cl, N(41) and N(71) are almost exactly coplanar (maximum deviation from mean plane, 0.006 Å). The principal distortion from ideal trigonal-bipyramidal geometry arises from a distortion in the equatorial plane, which has an

Table 3 Selected bond lengths (Å) and angles (°) for $[CuLCl][BF_4]$

Cu(1)–N(61)	1.996(2)	Cu(1)–N(41)	2.141(2)
Cu(1)–N(51)	2.014(2)	Cu(1)–Cl	2.2878(8)
Cu(1)–N(71)	2.090(2)		
N(61)–Cu(1)–N(51)	171.74(9)	N(71)–Cu(1)–N(41)	109.72(8)
N(61)–Cu(1)–N(71)	79.73(8)	N(61)–Cu(1)–Cl	96.21(6)
N(51)–Cu(1)–N(71)	95.45(8)	N(51)–Cu(1)–Cl	91.96(7)
N(61)–Cu(1)–N(41)	96.06(8)	N(71)–Cu(1)–Cl	133.95(6)
N(51)–Cu(1)–N(41)	79.17(8)	N(41)–Cu(1)–Cl	116.31(6)

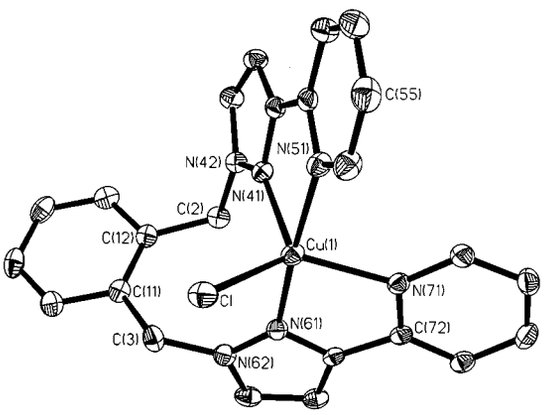

Fig. 3 Crystal structure of the cation in $[CuLCl][BF_4]$

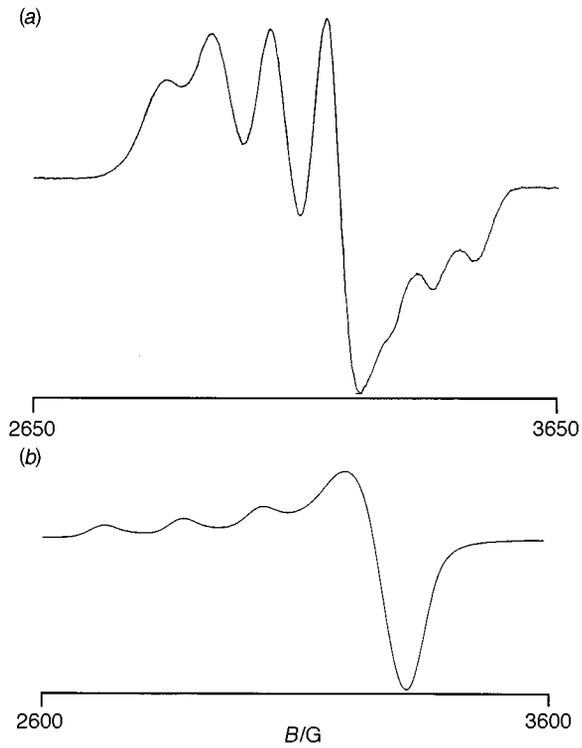

Fig. 4 X-Band EPR spectra of (*a*) $[CuLCl][BF_4]$ and (*b*) $[Cu_2L_3][BF_4]_2$ as frozen glasses at 77 K

expanded angle Cl–Cu(1)–N(71) [133.95(6)°] and a compressed N(41)–Cu(1)–N(71) angle [109.72(8)°]. This could arise in part from the steric bulk of the chloride ligand and from the geometric constraints inherent in co-ordination on all four donor atoms of L to a single metal centre. However Hathaway *et al.* have recently shown for a wide variety of five-co-ordinate CuN_4X complexes that geometries along the pathway between regular trigonal-bipyramidal and square-based pyramidal geometries can occur by a vibronic coupling mechanism,[16] and the geometry observed for the $[CuLCl]^+$ cation is exactly consistent with this. The mean planes of the two bidentate pyrazolyl-pyridyl arms are inclined at an angle of 71° to one another. It is clear from this structure that the *o*-$CH_2C_6H_4CH_2$ linking group of L is sufficiently flexible to allow the two bidentate arms to chelate to one metal ion, as well as bridging two metal ions as we saw in the double helicate with Cu^I.

We used EPR and electronic spectroscopy to examine the complex in solution. The frozen solution X-band EPR spectrum of $[CuLCl][BF_4]$ [Fig. 4(*a*)] is characteristic of a complex with a d_{z^2} ground state arising from a predominantly trigonal bipyramidal geometry,[17,18] with parameters of $g_{\|} = 2.00$, $g_{\perp} = 2.19$, $A_{\|} = 78$ G and $A_{\perp} = 109$ G (G = 10^{-4} T). Even in a good donor solvent therefore the five-co-ordinate structure is retained, as solvation would inevitably lead to a six-co-ordinate structure with a $d_{x^2-y^2}$ ground state and a quite different spectrum. The electronic spectrum (dmf solution) shows the d–d transition at $\lambda_{max} = 825$ nm ($\varepsilon = 240$ dm^3 mol^{-1} cm^{-1}) and a strong ligand-centred transition at 291 nm ($\varepsilon = 26\,300$ dm^3 mol^{-1} cm^{-1}); the relatively low energy and high intensity of the d–d transition is indicative of a non-tetragonal geometry and therefore also consistent with the solid-state structure.[18]

Synthesis of $[Cu_2L_3][PF_6]_2$ and the crystal structure of $[CuL(MeOH)][CuL(SiF_6)][BF_4]_2$

It seemed possible that formation of the relatively simple mononuclear complex $[CuLCl][BF_4]$ arose in part from the presence of the co-ordinated chloride ligand. We therefore investigated the reaction of L with copper(II) acetate in MeOH, and following precipitation of the complex as its $[BF_4]^-$ salt isolated a material whose elemental analysis was consistent with formation of a dinuclear complex $[Cu_2L_3][BF_4]_2$. The dinuclear formation was confirmed by the electrospray mass spectrum, which showed (very weak) peaks corresponding to the fragments $\{Cu_2L_2(BF_4)_3\}$ and $\{Cu_2L_3(BF_4)_4\}$. Because of the weakness of this spectrum we also investigated the FAB mass spectrum of $[Cu_2L_3][BF_4]_2$ and obtained a very strong signal at *m*/*z* 1542. There are two possible interpretations for this. The fragment $\{Cu_3L_3(BF_4)_2\}$ has the most intense peak of its isotope envelope at *m*/*z* 1541, and the fragment $\{Cu_2L_3(BF_4)(noba)\}$ has the most intense peak of its isotope envelope at *m*/*z* 1543 (Hnoba is the matrix 3-nitrobenzyl-alcohol used in the spectrum, and it is not uncommon to find molecules of deprotonated noba co-ordinating to complex fragments to give adducts of this sort). The isotopic patterns of these two possible assignments are not sufficiently different for it to be obvious which is the correct assignment, although the latter (with a Cu_2L_3 ratio) is in agreement with the ES mass spectrum and the elemental analysis. We can envisage two possible structures for the $\{Cu_2L_3\}$ stoichiometry. The first is a triple helicate, in which each of three ligands bridges both metal ions.[19] The second is a structure in which each one ligand is wholly co-ordinated to each metal ion {as in $[CuLCl][BF_4]$ above}, and one ligand bridges the two copper(II) centres. We recently structurally characterised $[Ni_2L_3][PF_6]_4$ and found it to be of this second structural type, which suggests that the copper(II) complex may follow suit,[20] and the crystallographic evidence described below indirectly supports this.

The electronic spectrum of $[Cu_2L_3][BF_4]_2$ in MeCN showed the expected d–d transition at 759 nm ($\varepsilon = 160$ dm^3 mol^{-1} cm^{-1}), with a second transition visible as a shoulder at about 900 nm. Intense ligand-centred transitions occur at 303 and 252 nm ($\varepsilon = 31\,000$ and $72\,000$ dm^3 mol^{-1} cm^{-1} respectively). The frozen solution EPR spectrum [thf–MeCN (1:1) at 77 K], shown in Fig. 4(*b*), has the parameters $g_{\|} = 2.28$, $g_{\perp} = 2.07$, $A_{\|} = 156$ G which are characteristic of a basically tetragonal geometry with a $d_{x^2-y^2}$ ground state.[1] There is no evidence in the EPR spectrum for any interaction between the metal centres, but this is not surprising given the likely large separation between them; in $[Ni_2L_3][BF_4]_2$ the metal–metal separation

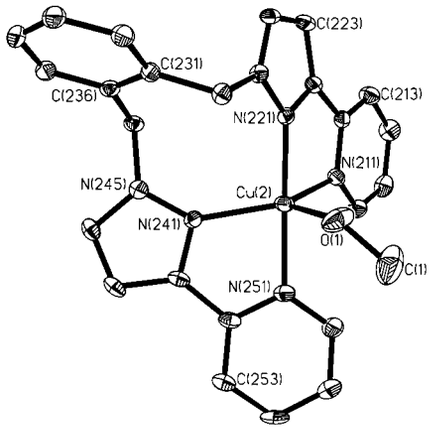

Fig. 5 Crystal structure of the $[CuL(MeOH)]^{2+}$ fragment of $[CuL(MeOH)][CuL(SiF_6)][BF_4]_2$

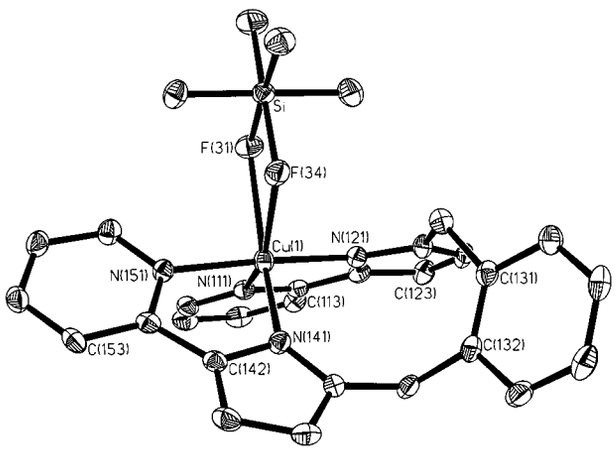

Fig. 6 Crystal structure of the $[CuL(SiF_6)]$ fragment of $[CuL(MeOH)][CuL(SiF_6)][BF_4]_2$

is 9.36 Å. Significantly however there is no evidence for dissociation of the complex into mononuclear $\{CuL(solv)\}^{2+}$ (solv = solvent) fragments, which {*cf.* the crystal structure below, and the structure above of $[CuLCl]^+$} would be trigonal bipyramidal and have a quite different EPR spectrum.

Recrystallisation of pale green $[Cu_2L_3][BF_4]_2$ by slow diffusion of diethyl ether vapour into a concentrated solution of the complex in acetone–MeOH (1:1) afforded a large amount of pale green powder, which was unchanged $[Cu_2L_3][BF_4]_2$, and a small number of dark green crystals which on investigation proved to be the decomposition product $[CuL(MeOH)][CuL(SiF_6)][BF_4]_2$ (Figs. 5 and 6, Table 4). It is reasonable to suppose that if $[Cu_2L_3][BF_4]_2$ has the structure proposed above, with two terminal ligands and one bridging, dissociation of the bis-bidentate bridging ligand would liberate mononuclear $\{CuL\}^{2+}$ fragments which would fill their co-ordination spheres with whatever ligands are available in the reaction mixture.

The $[CuL(MeOH)]^{2+}$ fragment (Fig. 5) is approximately trigonal bipyramidal with the axial ligands being N(221) and N(251), and the equatorial ligands being O(1), N(211) and N(241). The τ value is 0.68, with the principal distortion from trigonal-bipyramidal geometry arising from a distortion in the trigonal plane where the three angles are 134.1(2), 100.9(2) and 115.0(2)°, resulting in a distortion towards a square-pyramidal geometry in which O(1) would be the apical ligand. Apart from differences arising from the different steric bulk of the MeOH ligand compared to chloride, this complex has a similar structure to that of $[CuLCl]^+$.

The neutral fragment $[CuL(SiF_6)]$, containing a bidentate hexafluorosilicate anion, is more unusual (Fig. 6). Hexafluorosilicate anions can arise in compounds originally containing

Table 4 Selected bond lengths (Å) and angles (°) for $[CuL(MeOH)][CuL(SiF_6)][BF_4]_2$

Cu(1)–N(121)	1.952(4)	Cu(2)–N(221)	1.957(4)
Cu(1)–N(151)	1.982(4)	Cu(2)–N(251)	1.996(4)
Cu(1)–N(141)	2.089(4)	Cu(2)–N(241)	2.033(4)
Cu(1)–N(111)	2.100(4)	Cu(2)–N(211)	2.066(4)
Cu(1)–F(34)	2.203(3)	Cu(2)–O(1)	2.242(4)
Cu(1)–F(31)	2.355(3)		

N(121)–Cu(1)–N(151)	175.9(2)
N(121)–Cu(1)–N(141)	98.9(2)
N(151)–Cu(1)–N(141)	80.6(2)
N(121)–Cu(1)–N(111)	80.4(2)
N(151)–Cu(1)–N(111)	96.2(2)
N(141)–Cu(1)–N(111)	117.4(2)
N(121)–Cu(1)–F(34)	97.20(13)
N(151)–Cu(1)–F(34)	86.88(13)
N(141)–Cu(1)–F(34)	92.52(12)
N(111)–Cu(1)–F(34)	150.08(13)
N(121)–Cu(1)–F(31)	87.89(13)
N(151)–Cu(1)–F(31)	94.32(13)
N(141)–Cu(1)–F(31)	154.20(12)
N(111)–Cu(1)–F(31)	88.24(13)
F(34)–Cu(1)–F(31)	61.84(9)
N(221)–Cu(2)–N(251)	174.6(2)
N(221)–Cu(2)–N(241)	99.4(2)
N(251)–Cu(2)–N(241)	81.0(2)
N(221)–Cu(2)–N(211)	80.6(2)
N(251)–Cu(2)–N(211)	102.9(2)
N(241)–Cu(2)–N(211)	134.1(2)
N(221)–Cu(2)–O(1)	88.66(14)
N(251)–Cu(2)–O(1)	86.2(2)
N(241)–Cu(2)–O(1)	110.9(2)
N(211)–Cu(2)–O(1)	115.0(2)

$[BF_4]^-$ because partial hydrolysis in the presence of atmospheric moisture generates traces of HF which reacts with glassware (in this case the vial used for the recrystallisation),[21] and although not common there are a few examples in which the hexafluorosilicate ion is known to act as a bridging ligand by co-ordinating a fluorine atom to each of two different metal ions.[21,22] There are however no previously reported examples of the $[SiF_6]^{2-}$ anion acting as a bidentate chelating ligand to a single metal ion. The two Cu–F distances [Cu(1)–F(31) 2.355(3), Cu(1)–F(34) 2.203(3) Å; average 2.28 Å] are significantly longer than those observed with simple fluoride ligands (*ca.* 1.9–1.95 Å),[23] but significantly shorter than the 'semico-ordinate' distances of *ca.* 2.6 Å arising from weak interactions with *e.g.* $[BF_4]^-$ anions.[24] The geometry of the complex is further distorted by the four-membered chelate ring, with the angle F(31)–Cu(1)–F(34) being 61.84(9)° and the 'opposite' angle N(111)–Cu(1)–N(141) being correspondingly large at 117.4(2)°. This geometry is characteristic of a *cis*-distorted octahedron, typified by numerous complexes of the form $[Cu(chelate)_2(OO)]^+$, where 'OO' is a trigonal planar bidentate anion such as carboxylate or nitrate which also forms a four-membered chelate ring.[25] The inequivalence of the Cu–F distances involving the $[SiF_6]^{2-}$ ligand is typical of these *cis*-distorted octahedra and suggests a distortion towards a Jahn–Teller elongated geometry. Unfortunately only a few single crystals of this decomposition product appeared so further spectroscopic characterisation was not possible.

Conclusion

The new ligand L was simply prepared by reaction of 3-(2-pyridyl)pyrazole with α,α′-dibromoxylene; this is a potentially general route to a wide variety of new multinucleating ligands. Whereas L acts as a bridging ligand between two metal ions in the double helicate $[Cu^{I}_2L_2][PF_6]_2$, it is also capable of co-ordinating all four donor atoms to one metal centre in various five- and six-co-ordinate mononuclear copper(II)

complexes. Of these $[CuL(SiF_6)]$ is of particular interest as it contains the first example of a chelating hexafluorosilicate anion.

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