

Structural and spectroscopic studies on 36-membered ring arrays formed by copper(II) halides with 1-(4-picolyl)pyrrolidin-2-one†

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Reaction of 1-(4-picolyl)pyrrolidin-2-one (ppo) with hydrated copper(II) chloride or bromide in methanol affords the compounds $[\text{Cu}(\text{ppo})_2\text{X}_2]$ ($\text{X} = \text{Cl}$ or Br). A single-crystal X-ray diffraction study of $[\text{Cu}(\text{ppo})_2\text{Br}_2]$ **1** shows that the ppo molecule acts as a bridging ligand with the formation of *all trans*- $\text{CuBr}_2\text{N}_2\text{O}_2$ units linked to produce sheets of contiguous 36-membered rings. The EPR spectra of **1** and its chloride analogue give well resolved rhombic-type spectra. The EPR and electronic spectra of $[\text{Cu}(\text{ppo})_2\text{X}_2]$ ($\text{X} = \text{Cl}$ or Br) are analysed in terms of angular-overlap bonding parameters. X-Ray studies show that the compound $[\text{Cu}_4\text{OCl}_6(\text{ppo})_4]$ comprises a $\text{Cu}_4(\mu_4\text{-O})\text{Cl}_6$ core with an N-bonded ppo ligand co-ordinated to each Cu atom.

As part of a programme aimed at the design of extended¹ and interpenetrating networks,² we have previously shown that 1-(4-picolyl)pyrrolidin-2-one (ppo) can form very large ring heterometallic framework complexes by virtue of its ability to bind its pyridine nitrogen atom and the lactam oxygen atom to dissimilar metal ions.³ During further studies aimed at making heterometallic copper(II)-lanthanide(III) complexes with ppo we obtained instead the compounds $[\text{Cu}(\text{ppo})_2\text{X}_2]$ ($\text{X} = \text{Cl}$ or Br) and $[\text{Cu}_4\text{OCl}_6(\text{ppo})_4]$. As X-band EPR measurements on $[\text{Cu}(\text{ppo})_2\text{X}_2]$ ($\text{X} = \text{Cl}$ or Br) gave very well resolved spectra of the type expected for a rhombic copper(II) environment we have determined the structure of $[\text{Cu}(\text{ppo})_2\text{Br}_2]$ **1**. This provides a firm basis for the analysis of the spectra and comparison of the derived parameters with those of related copper(II) systems.^{4,5} We also report the structure of the methanol solvate of the compound $[\text{Cu}_4\text{OCl}_6(\text{ppo})_4]$ **2**.

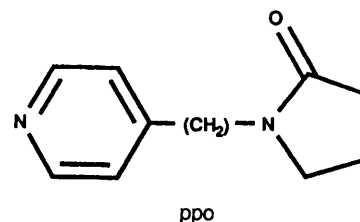
Experimental

Preparation of compounds

$[\text{Cu}(\text{ppo})_2\text{X}_2]$ ($\text{X} = \text{Cl}$ or Br). These were obtained on mixing methanolic solutions of 1-(4-picolyl)pyrrolidin-2-one⁶ (1 mmol) and the respective hydrated copper(II) salt (0.25 mmol) in a total of *ca.* 2 cm³ of methanol. Individual details are given below (microanalytical results are by the Microanalytical Laboratory, Imperial College). $[\text{Cu}(\text{ppo})_2\text{Cl}_2]$, blue-green microcrystals, 90% yield (Found: C, 49.1; H, 4.9; N, 11.4. $\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{CuN}_4\text{O}_2$ requires C, 49.4; H, 5.0; N, 11.5%); $[\text{Cu}(\text{ppo})_2\text{Br}_2]$ **1**, green crystals, 87% yield (Found: C, 41.5; H, 4.1; N, 9.6. $\text{C}_{20}\text{H}_{24}\text{Br}_2\text{CuN}_4\text{O}_2$ requires C, 41.7; H, 4.2; N, 9.7%).

$[\text{Cu}_4\text{OCl}_6(\text{ppo})_4]$ **2**. Methanolic solutions of copper(II) chloride dihydrate (0.24 mmol in 7 cm³) and 1-(4-picolyl)pyrrolidin-2-one (0.24 mmol in 5 cm³) were mixed and allowed to stand at room-temperature. The brown crystals which formed over several days were characterised by X-ray diffraction.

† A more systematic name for this compound is *N*-[(4-pyridyl)methyl]pyrrolidin-2-one.



Spectroscopic measurements

EPR measurements were made at X-band frequency on polycrystalline samples at room temperature using a Varian E12 spectrometer and also at *ca.* 6 K with a Bruker ESP-300E spectrometer at Q-band frequency.

Electronic spectra were measured on powdered samples by the diffuse reflectance method, at room temperature using a Beckmann DK2 spectrometer, and at 298 K and *ca.* 15 K on a mull in Dow Corning high vacuum grease using a Cary 5A spectrophotometer with the sample cooled by a Cryodyne model 21 cryostat.

Crystal structure determinations

A summary of the crystal data, data collection, and the structure solution and refinement parameters for compounds **1** and **2** is given in Table 1. The data were collected at 293(2) K on a Siemens P4PC diffractometer using Cu-K α radiation ($\lambda = 1.54178$ Å) and ω scans.

There was no significant decay in the three standard reflections during the period of data collection. The data were corrected for Lorentz and polarisation effects but not for absorption. The structures were solved by the heavy-atom method and refined by full-matrix least-squares based on F^2 . Refinement was anisotropic except for the disordered oxygen atom in one of the methanol molecules of solvation in **2**. One of the pyrrolidone rings in **2** is disordered leading to two positions for the exocyclic oxygen atom due to a *ca.* 180° rotation of the ring about the linking C–N bond. The hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$, and allowed to ride on their parent atoms. Computations were performed using the

Table 1 Details of the crystal data collection and refinements

Compound	1	2·1.75 MeOH
Empirical formula	C ₂₀ H ₂₄ Br ₂ CuN ₄ O ₂	C ₄₀ H ₄₈ Cl ₆ Cu ₄ N ₈ O ₅ · 1.75 MeOH
Colour, habit	Green 'cube'	Brown needle
<i>M</i>	575.79	1242.03
Crystal size/mm	0.41 × 0.35 × 0.23	0.81 × 0.20 × 0.20
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	7.713(2)	10.330(3)
<i>b</i> /Å	9.912(2)	10.971(2)
<i>c</i> /Å	16.617(5)	23.022(4)
α /°	90.0	96.91(2)
β /°	103.23(2)	99.25(2)
γ /°	90.0	91.96(2)
<i>U</i> /Å ³	1088(1)	2553(1)
<i>D_c</i> /g cm ⁻³	1.758	1.616
<i>Z</i>	2	2
<i>F</i> (000)	574	1264
μ /mm ⁻¹	5.917	5.214
2 θ Range/°	4.0–120.0	3.0–110.0
Independent reflections	1615	6389
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	1535	5691
No. of parameters refined	134	614
<i>R</i> ₁ (<i>wR</i> ₂)	0.0344 (0.0864)	0.0382 (0.1019)
Mean, maximum Δ / σ ratio	0.001, 0.058	0.073, 0.289
Largest difference peak, hole/e Å ⁻³	0.388, -0.712	0.739, -0.387

Table 2 Bond lengths (Å) and angles (°) for compound **1**

Br–Cu	2.4210(6)	Cu–N(1)	1.986(4)
Cu–O(13) ⁱⁱ	2.932(3)		
N(1)–Cu–N(1) ⁱ	180.0	N(1)–Cu–Br ⁱ	89.39(1)
N(1)–Cu–Br	90.61(1)	Br ⁱ –Cu–Br	180.0
N(1)–Cu–O(13) ⁱⁱ	91.1(2)	N(1)–Cu–O(13) ⁱⁱ	88.9(2)
Br ⁱ –Cu–O(13) ⁱⁱ	91.02(7)	Br–Cu–O(13) ⁱⁱ	88.98(7)
O(13) ⁱⁱ –Cu–O(13) ⁱⁱⁱ	180.0		

Symmetry transformations used to generate equivalent atoms: i –*x*, –*y* + 2, –*z* + 2; ii *x* – ½, –*y* + ½, *z* – ½; iii –*x* + ½, *y* – ½, –*z* + ½.

SHELXTL PC system version 5.03.⁷ Selected bond lengths and angles for **1** and **2** are listed in Tables 2 and 3 respectively.

Atomic coordinates, thermal parameters, and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/254.

X-Ray powder photographs showed that the compounds [Cu(ppo)₂X₂] (X = Cl or Br) are not isomorphous.

Results and Discussion

Our interest in these compounds was initially prompted by observation of the formation of mixtures of green (or blue-green) and brown products during attempts to produce heterometallic complexes of 1-(4-picolyl)pyrrolidin-2-one with copper(II) chloride or bromide and an oxophilic metal ion such as neodymium(III). Analogous reactions using only the copper(II) halides and ppo showed essentially similar behaviour and also that the products formed depended on Cu^{II}–ppo ratio employed. The compounds [Cu(ppo)₂Cl₂] (blue-green) and [Cu(ppo)₂Br₂] (green) were obtained in good yield (ca. 90%) by mixing concentrated methanolic solutions of 1-(4-picolyl)pyrrolidin-2-one and the appropriate copper(II) salt, provided that an excess of the organic ligand was used. Use of lower ppo–Cu^{II} ratios favoured the formation of the brown

product, later shown, in the case of the chloride, to be [Cu₄OCl₆(ppo)₄] (see below).

The X-band EPR spectra of microcrystalline samples of [Cu(ppo)₂Cl₂] and [Cu(ppo)₂Br₂] are very similar and comprise three very well resolved bands at *g* values of 2.020, 2.122 and 2.263 (chloride) and 2.026, 2.135 and 2.229 (bromide). Identical *g* values were observed at ca. 6 K at Q-band frequency. These are indicative of copper(II) in a rhombic ligand environment. The electronic spectra of mulls of [Cu(ppo)₂Br₂] and [Cu(ppo)₂Cl₂] at ca. 15 K are also very similar (Fig. 1). In each case there is a band centred at 12 000 cm⁻¹ with a marked shoulder at ca. 13 500 cm⁻¹ and a distinct asymmetry to higher energy. The corresponding spectra at room temperature and by reflectance were similar to those at ca. 15 K, though slightly less well resolved. The only significant difference in the spectra of the two compounds is the markedly lower energy of the intense absorption in the near ultraviolet region in the bromide complex. This may be assigned to a ligand → metal charge-transfer transition, which is expected at lower energy for the less electronegative halogen.

The close similarity of the EPR spectra and the bands due to the 'd–d' transitions in the electronic spectra suggests that the co-ordination geometry of the two complexes is very similar despite the lack of isomorphism shown by the X-ray powder patterns. Because of the variability in co-ordination geometry displayed by copper(II),⁸ we have determined the structure of [Cu(ppo)₂Br₂] by X-ray methods to provide a structural basis for the analysis of the spectra.

Crystal structure of [Cu(ppo)₂Br₂] **1**

The X-ray analysis of **1** reveals each copper to be bound to the pyridine nitrogen atoms of two ppo ligands and two bromine atoms in a *trans*-C₁ symmetric arrangement (Fig. 2). The distortions from strict orthogonal planar geometry are small, with a maximum departure of 0.6°. The Cu–Br and Cu–N distances (2.421 and 1.986 Å) are unexceptional (Table 2).

Within each ppo ligand the pyridine and pyrrolidone rings are oriented approximately orthogonal to each other (88° between their mean planes), the C(7)–N(8) bond being rotated by only 14° out of the plane of the pyridine ring which, in turn, is inclined by 76° to the CuBr₂N₂ co-ordination plane. A consequence of the orthogonal relationship between the pyridine and pyrrolidone rings is an enlargement⁹ from tetrahedral of the angle at C(7) to 114.7°. There is a small pyramidalisation at N(1), the nitrogen atom lying 0.037 Å out of the plane of its substituents.

The pyrrolidone oxygen atom of each ppo ligand is positioned orthogonally with respect to the CuBr₂N₂ co-ordination planes of adjacent symmetry-related copper centres thus occupying the 'vacant' octahedral co-ordination sites (Fig. 3). The result of this secondary, long-range Cu...O interaction (2.932 Å) is the creation of an extended two-dimensional array of contiguous, self-filling, 36-membered macrocycles each containing four Cu atoms and four ppo ligands (Fig. 4). Within these macrocycles the shortest Cu...Cu distances are 8.94 and 9.94 Å {*cf.* Ni...Nd 8.81–10.36 Å observed³ for [NiNd(ppo)₄(NCS)₂(NO₃)₃]_{*n*}}. Adjacent sheets stack in the crystallographic *a* direction. The pyridine rings within each sheet are directed alternately above and below the sheet plane and interleave with those of the neighbouring sheets.

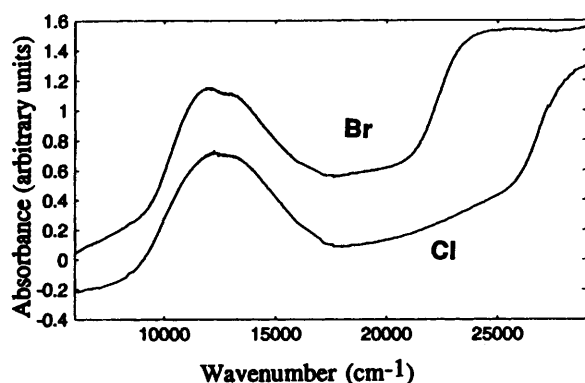
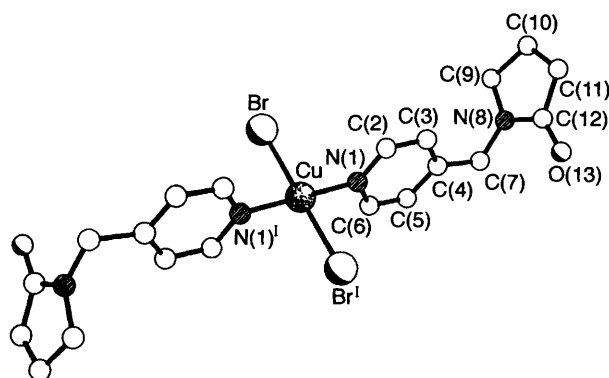
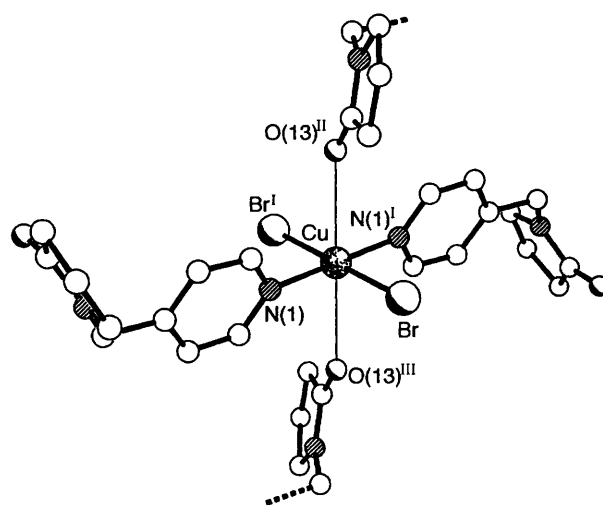
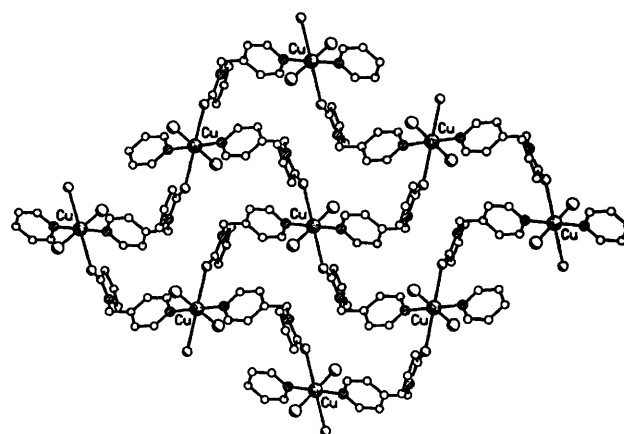
There is very little angular distortion (maximum 1.1°) of the '4 + 2' tetragonally distorted six-co-ordinate geometry about each copper atom. The CuBr₂N₂ co-ordination planes of adjacent copper centres are inclined by 56°.

Spectroscopic studies and bonding parameters

As mentioned previously, the X-band EPR spectra of [Cu(ppo)₂Br₂] and [Cu(ppo)₂Cl₂] are characteristic of highly rhombic *g* tensors. The X-band spectra of a crystal of **1** at

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

Cu(1)–O(11)	1.897(3)	Cu(1)–N(20)	1.971(3)
Cu(1)–Cl(10)	2.3805(12)	Cu(1)–Cl(9)	2.4082(13)
Cu(1)–Cl(8)	2.4626(12)	Cu(2)–O(11)	1.916(3)
Cu(2)–N(44)	1.975(3)	Cu(2)–Cl(8)	2.3658(13)
Cu(2)–Cl(6)	2.4156(14)	Cu(2)–Cl(7)	2.4248(13)
Cu(3)–O(11)	1.909(3)	Cu(3)–N(32)	1.968(3)
Cu(3)–Cl(7)	2.3762(12)	Cu(3)–Cl(5)	2.3962(13)
Cu(3)–Cl(9)	2.4130(13)	Cu(4)–O(11)	1.906(3)
Cu(4)–N(56)	1.978(3)	Cu(4)–Cl(6)	2.3912(13)
Cu(4)–Cl(5)	2.4076(13)	Cu(4)–Cl(10)	2.4366(13)
O(11)–Cu(1)–N(20)	175.53(13)	O(11)–Cu(1)–Cl(10)	84.88(8)
N(20)–Cu(1)–Cl(10)	96.59(10)	O(11)–Cu(1)–Cl(9)	85.58(8)
N(20)–Cu(1)–Cl(9)	96.85(10)	Cl(10)–Cu(1)–Cl(9)	126.66(5)
O(11)–Cu(1)–Cl(8)	84.43(8)	N(20)–Cu(1)–Cl(8)	91.21(10)
Cl(10)–Cu(1)–Cl(8)	120.97(5)	Cl(9)–Cu(1)–Cl(8)	110.05(5)
O(11)–Cu(2)–N(44)	176.05(13)	O(11)–Cu(2)–Cl(8)	86.76(8)
N(44)–Cu(2)–Cl(8)	97.13(10)	O(11)–Cu(2)–Cl(6)	83.95(8)
N(44)–Cu(2)–Cl(6)	93.15(11)	Cl(8)–Cu(2)–Cl(6)	125.89(5)
O(11)–Cu(2)–Cl(7)	83.55(8)	N(44)–Cu(2)–Cl(7)	95.12(10)
Cl(8)–Cu(2)–Cl(7)	119.37(5)	Cl(6)–Cu(2)–Cl(7)	112.30(5)
O(11)–Cu(3)–N(32)	176.66(13)	O(11)–Cu(3)–Cl(7)	85.06(8)
N(32)–Cu(3)–Cl(7)	95.93(11)	O(11)–Cu(3)–Cl(5)	85.29(8)
N(32)–Cu(3)–Cl(5)	91.52(11)	Cl(7)–Cu(3)–Cl(5)	124.00(5)
O(11)–Cu(3)–Cl(9)	85.20(8)	N(32)–Cu(3)–Cl(9)	97.30(11)
Cl(7)–Cu(3)–Cl(9)	113.87(5)	Cl(5)–Cu(3)–Cl(9)	120.03(5)
O(11)–Cu(4)–N(56)	177.38(13)	O(11)–Cu(4)–Cl(6)	84.84(8)
N(56)–Cu(4)–Cl(6)	92.76(11)	O(11)–Cu(4)–Cl(5)	85.03(8)
N(56)–Cu(4)–Cl(5)	95.47(11)	Cl(6)–Cu(4)–Cl(5)	123.40(5)
O(11)–Cu(4)–Cl(10)	83.13(8)	N(56)–Cu(4)–Cl(10)	99.04(11)
Cl(6)–Cu(4)–Cl(10)	121.88(5)	Cl(5)–Cu(4)–Cl(10)	111.83(5)
Cu(3)–Cl(5)–Cu(4)	80.33(4)	Cu(4)–Cl(6)–Cu(2)	81.21(4)
Cu(3)–Cl(7)–Cu(2)	81.40(4)	Cu(2)–Cl(8)–Cu(1)	79.91(4)
Cu(1)–Cl(9)–Cu(3)	79.80(4)	Cu(1)–Cl(10)–Cu(4)	81.10(4)
Cu(1)–O(11)–Cu(4)	110.89(13)	Cu(1)–O(11)–Cu(3)	108.70(13)
Cu(4)–O(11)–Cu(3)	108.62(12)	Cu(1)–O(11)–Cu(2)	108.86(12)
Cu(4)–O(11)–Cu(2)	109.86(13)	Cu(3)–O(11)–Cu(2)	109.89(12)

**Fig. 1** The electronic spectra of mulls of $[\text{Cu}(\text{ppo})_2\text{Cl}_2]$ and $[\text{Cu}(\text{ppo})_2\text{Br}_2]$ at ca. 15 K**Fig. 2** The planar Cu co-ordination environment forming the basic structural unit in the polymeric structure of **1****Fig. 3** The '4 + 2' tetragonal geometry about each copper atom in **1** resulting from the long-range axial co-ordination of pyrrolidone oxygen atoms from adjacent $\text{Cu}(\text{ppo})_2\text{Br}_2$ units**Fig. 4** Part of one of the sheets of contiguous 36-membered rings in the structure of **1**

various orientations showed only a single signal, indicating that electron exchange between the two molecules in the unit cell is more rapid than the EPR timescale, so that the observed g values (2.026, 2.135 and 2.229 for **1**) refer to the crystal, rather than the molecular g tensors. The lowest molecular g value will be approximately parallel to the bonds involving the strongest ligand,¹⁰ in this case the amine. The Cu–N bonds of the two molecules in the unit cell are almost parallel (the angle between them is 10.4°) so that to a good approximation the smallest crystal g value corresponds to this molecular g value, *i.e.* $g_x = 2.026$. The middle and highest molecular g values, g_y and g_z , will be associated with the Cu–Br and long Cu–O bonds, respectively, and these may be derived from the middle two crystal g values g_2, g_3 via the relationships,¹¹ $g_2 = g_y \cos^2 \alpha + g_z \sin^2 \alpha$ and $g_3 = g_y \sin^2 \alpha + g_z \cos^2 \alpha$, where 2α is the angle of misalignment of the Cu–Br bonds of the two molecules in the unit cell, 56° (the Cu–O bonds are misaligned by the same amount). Substitution of the crystal g values $g_2 = 2.135, g_3 = 2.229$ yields the molecular g values $g_y = 2.098, g_z = 2.266$.

As the g tensors indicate a ligand field of approximate D_{2h} symmetry, four 'd–d' transitions are expected in the electronic spectrum but only two transitions were clearly resolved (Fig. 1). The bonding parameters of the complexes may therefore only be derived within rather broad limits. These were investigated using the computer program CAMMAG developed by Gerloch and co-workers,¹² which describes the bonding using the angular overlap model σ - and π -bonding parameters $e_\sigma, e_{\pi x}$ and $e_{\pi y}$. Initially, the calculations were performed using bonding

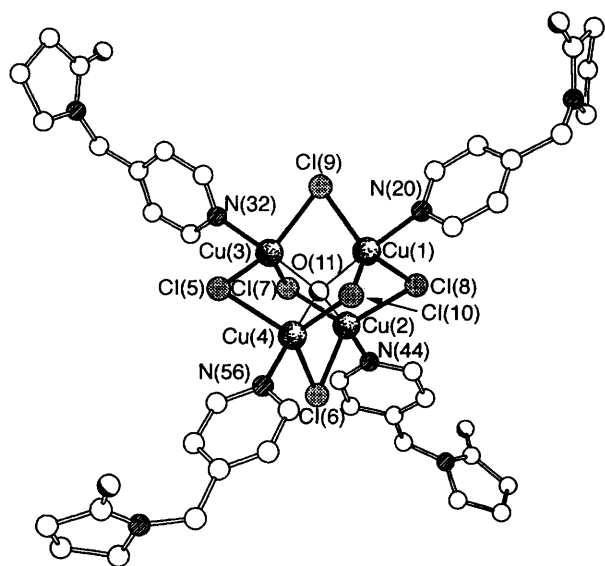


Fig. 5 The molecular structure of compound 2

parameters similar to those reported for complexes with similar ligands ($e_{\sigma} = 6500$, $e_{\pi x} = 0$, $e_{\pi y} = 1000$ cm^{-1} for the amine¹³ and $e_{\sigma} = 5000$, $e_{\pi x} = e_{\pi y} = 800$ cm^{-1} for the bromide ion in Cs_2CuBr_4 ,¹⁴ a slight correction being applied in the latter case for the marginally longer Cu–Br bond lengths in $[\text{Cu}(\text{ppo})_2\text{Br}_2]$). However, this yields calculated transition energies for the ${}^2\text{B}_{1g}(xy)$, ${}^2\text{B}_{3g}(yz)$ and ${}^2\text{B}_{2g}(xz)$ states, 13 900, 15 700 and 17 300 cm^{-1} , much higher than those observed experimentally. Agreement with experiment is obtained using the lower values $e_{\sigma} = 5750$, $e_{\pi x} = 0$, $e_{\pi y} = 875$ cm^{-1} for the amine and $e_{\sigma} = 4250$, $e_{\pi x} = e_{\pi y} = 675$ cm^{-1} for the bromide ion (calculated transition energies 12 100, 13 750 and 15 100 cm^{-1}). The first two transitions correspond to the peaks at 12 000 and 13 500 cm^{-1} , while the third may be the cause of the asymmetry on the high energy side of the peak (Fig. 1). The calculated molecular g values 2.028, 2.083 and 2.275 obtained using an isotropic orbital reduction parameter of 0.71 are also in satisfactory agreement with the experimental values (2.026, 2.098 and 2.266). The possibility that the rather low energies of the band maxima in the optical spectrum are due solely to a low ligand-field strength of the amine was considered. However, to produce the observed band positions this required similar ligand-field strengths for the amine and bromide ligands, which is incompatible with the highly rhombic g tensor of the complex.

The transition to the ${}^2\text{A}_g(z^2)$ state must also contribute to the band envelope centred at ca. 12 000 cm^{-1} . This transition, the energy of which has an insignificant effect on the g values, is influenced by the distant axial oxygen atoms at 2.931 Å, and the direct effect of these may be estimated by assuming that the bonding parameters vary inversely to about the fifth power of the metal–ligand bond length, as found in several studies.^{4,5,15} Applying this correction to the values reported for copper(II) hydrate complexes¹⁶ yields the estimates $e_{\sigma} \approx 600$, $e_{\pi x} = e_{\pi y} \approx 100$ cm^{-1} for the axial oxygen ligands in $[\text{Cu}(\text{ppo})_2\text{Br}_2]$. Calculations using these values suggest an energy of ca. 9 100 cm^{-1} for the transition to the ${}^2\text{A}_g(z^2)$ state, but no band is observed in this region. However, in complexes departing markedly from cubic symmetry this state is raised in energy because of mixing with the $a_g(4s)$ metal orbital,^{4,5,17} presumably moving the transition under the band at 12 000 cm^{-1} . This implies a shift of ca. 3000 cm^{-1} , which is similar to that noted by Deeth and Gerloch¹⁸ for highly tetragonally distorted complexes.

The reason why the bonding parameters in $[\text{Cu}(\text{ppo})_2\text{Br}_2]$ are lower than those in other complexes with similar ligands is not readily apparent. Possibly the differences in the substituents

of the pyridine groups may have an influence, but this does not explain why bromide apparently acts as a significantly weaker ligand in the present complex than in Cs_2CuBr_4 . It has been pointed out that it is not to be expected that metal–ligand bonding parameters will always be transferable from one complex to another,¹⁹ and the present example seems to support this conclusion.

Crystal structure of $[\text{Cu}_4\text{OCl}_6(\text{ppo})_4]$ 2

The X-ray characterisation of the brown compound 2 showed it to have the stoichiometry $[\text{Cu}_4\text{OCl}_6(\text{ppo})_4]$ and to contain the well known $\text{Cu}_4(\mu_4\text{-O})\text{Cl}_6$ unit²⁰ with a ppo ligand bonded to each Cu atom *via* the pyridine nitrogen atom (Fig. 5). The copper–chlorine, copper–nitrogen and copper–oxygen bond lengths and angles (Table 3) are typical of those observed for the $\text{Cu}_4(\mu_4\text{-O})\text{Cl}_6$ core. The geometries of the four independent ppo ligands are very similar, there being an approximately orthogonal relationship between the pyridine and pyrrolidone rings. Examination of the molecular packing reveals the presence of only weak intermolecular $\text{CH} \cdots \text{O}$ interactions involving the pyrrolidone oxygen atoms. As may be seen from Fig. 5, those oxygen atoms are well disposed geometrically to bind oxophilic metal ions and hence to form heterometallic networks.

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