Magnetostructural Characterization of a Monohydroxo-bridged, 1,1,2,2-Tetrakis(2-pyridyl)ethylene-bridged Copper(II) Dimer†

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The molecular structure of $[Cu_2(dpm)_2L(OH)][ClO_4]_3 \cdot 2H_2O$ [dpm = di(2-pyridyl)methane; L = 1,1,2,2-tetrakis(2-pyridyl)ethylene] has been determined by single-crystal X-ray diffraction: triclinic, space group $P\bar{1}$, $a = 11.685(3)$, $b = 14.569(2)$, $c = 15.509(4)$ Å, $\alpha = 87.97(2)$, $\beta = 73.34(2)$, $\gamma = 74.15(1)°$ and $Z = 2$. The copper co-ordination geometry can be described as a square-based pyramid with the two copper(II) centres bridged by two groups, N–C–C=C–C–N from L and the hydroxide ion. The bridging angle Cu–O–Cu is 137.9(4)° and the copper centres are separated by 3.663(3) Å. Magnetic susceptibility data collected as a function of temperature (5–400 K) are indicative of a relatively strong antiferromagnetic interaction ($2J \approx -360$ cm^{-1}).

There exists a prolific literature on the magnetic interactions in binuclear copper(II) complexes.[1–3] However, interest remains owing to the fact that the conceptual understanding of magnetic coupling, in terms of the interactions of magnetic orbitals, continues to evolve.[4,5]

Among the complexes that are less well understood are the unsymmetrically dibridged systems, *e.g.* the copper(II) azide and nitrite complexes with the binucleating ligand *N,N,N′,N′*-tetrakis(1-ethylbenzimidazol-2-yl)-2-hydroxy-1,3-diaminopropane. The azide complex was found to be completely diamagnetic at room temperature ($2J > -1100$ cm^{-1}),[6] while the nitrite complex is a less strong antiferromagnet ($2J \approx -278$ cm^{-1}).[7] Both complexes have a co-ordination stereochemistry that is close to trigonal bipyramidal with a d_{z^2} ground state. Therefore they differ magnetically much more than might be expected on the basis of their isostructural d_{z^2} interactions. Another complex having a comparably large coupling *via* d_{z^2} magnetic orbitals is the axially monobridged $[Cu_2(\mu\text{-}OH)(bipy)_4][ClO_4]_3$ (bipy = 2,2′-bipyridine) for which $2J = -322$ cm^{-1}.[8] Other single hydroxo-bridged complexes have an approximately square-pyramidal stereochemistry and show strong antiferromagnetic exchange between the copper(II) centres. All of them contain additional ligand bridges, varying in number from two to four.[9–20]

An approximately linear correlation between the hydroxo-bridge angle and the 2*J* values was observed for binucleating tetradentate (N_4) phthalazine and pyridazine complexes. The hydroxide group has been shown to act as an important super-exchange bridge. However the diazine bridges also contribute to the total exchange, with pyridazine being more efficient than phthalazine. Other unrelated systems were shown to approximate this correlation.[9]

In the present study we report the molecular structure and magnetic properties for $[Cu_2(dpm)_2L(OH)][ClO_4]_3 \cdot 2H_2O$, where dpm = di(2-pyridyl)methane and L = 1,1,2,2-tetrakis(2-pyridyl)ethylene. The ligand L is the condensation product of the reaction of dpm and di(2-pyridyl) ketone, catalysed by copper(II) ions.

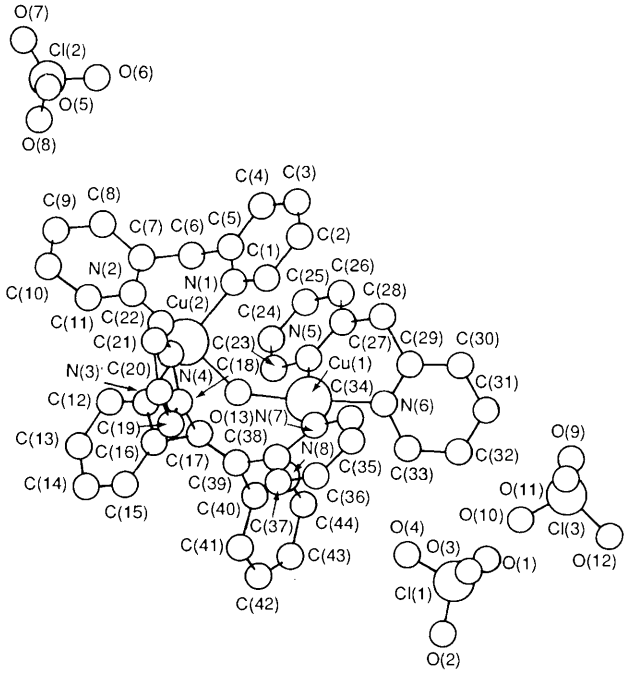

Fig. 1 The structure of complex $[Cu_2(dpm)_2L(OH)][ClO_4]_3 \cdot 2H_2O$

Results and Discussion

The dimeric species $[Cu_2(dpm)_2L(OH)][ClO_4]_3 \cdot 2H_2O$ contains di(2-pyridyl)methane ligands and two bridging ligands,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.
Non-SI unit employed: Oe = 10^3 A m^{-1}.

Table 1 Positional parameters and their estimated standard deviations for $[Cu_2(dpm)_2L(OH)][ClO_4]_3{\cdot}2H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	0.6942(1)	0.2759(1)	0.6338(1)	C(10)	0.174(1)	0.294(1)	1.092(1)
Cu(2)	0.4574(1)	0.2752(1)	0.8479(1)	C(11)	0.276(1)	0.265(1)	1.019(1)
Cl(1)	0.8657(4)	0.2046(3)	0.1940(3)	C(12)	0.267(1)	0.1809(9)	0.8312(9)
Cl(2)	−0.0414(4)	0.6353(3)	1.2555(3)	C(13)	0.229(1)	0.103(1)	0.814(1)
Cl(3)	1.3257(4)	0.2375(3)	0.2844(3)	C(14)	0.318(2)	0.0174(9)	0.7824(8)
O(1)	0.853(2)	0.291(2)	0.155(2)	C(15)	0.442(2)	0.014(1)	0.766(1)
O(2)	0.875(2)	0.118(2)	0.150(2)	C(16)	0.472(1)	0.096(1)	0.7805(8)
O(3)	0.983(2)	0.178(2)	0.226(2)	C(17)	0.605(1)	0.101(2)	0.760(1)
O(4)	0.804(2)	0.194(2)	0.290(2)	C(18)	0.636(1)	0.092(1)	0.8534(9)
O(5)	0.054(2)	0.574(2)	1.283(2)	C(19)	0.716(2)	0.011(1)	0.873(1)
O(6)	0.002(2)	0.693(2)	1.185(2)	C(20)	0.747(2)	0.011(1)	0.951(1)
O(7)	−0.154(2)	0.705(2)	1.312(2)	C(21)	0.695(2)	0.091(1)	1.008(1)
O(8)	−0.095(2)	0.599(2)	1.196(2)	C(22)	0.611(1)	0.165(1)	0.9843(9)
O(9)	1.263(2)	0.314(2)	0.295(2)	C(23)	0.444(1)	0.390(1)	0.6425(9)
O(10)	1.262(2)	0.168(2)	0.312(2)	C(24)	0.350(1)	0.470(1)	0.647(1)
O(11)	1.405(2)	0.214(2)	0.336(2)	C(25)	0.372(1)	0.559(1)	0.645(1)
O(12)	1.413(2)	0.213(2)	0.185(2)	C(26)	0.491(1)	0.563(1)	0.635(1)
O(13)	0.5926(7)	0.2253(5)	0.7379(5)	C(27)	0.581(1)	0.4819(9)	0.6332(8)
N(1)	0.5052(9)	0.3951(7)	0.8586(6)	C(28)	0.716(1)	0.479(1)	0.6220(9)
N(2)	0.3090(9)	0.3250(7)	0.9542(7)	C(29)	0.805(1)	0.4217(9)	0.5405(8)
N(3)	0.3885(8)	0.1747(7)	0.8144(6)	C(30)	0.880(1)	0.461(1)	0.4742(9)
N(4)	0.582(1)	0.1666(7)	0.9076(6)	C(31)	0.962(1)	0.405(1)	0.401(1)
N(5)	0.5604(8)	0.3949(7)	0.6385(6)	C(32)	0.959(1)	0.313(1)	0.3943(9)
N(6)	0.8061(9)	0.3310(7)	0.5353(7)	C(33)	0.881(1)	0.277(1)	0.4622(9)
N(7)	0.8380(8)	0.1737(7)	0.6509(6)	C(34)	0.952(1)	0.1810(9)	0.6393(9)
N(8)	0.6476(8)	0.1744(7)	0.5575(6)	C(35)	1.049(1)	0.103(1)	0.642(1)
C(1)	0.625(1)	0.3894(9)	0.8537(8)	C(36)	1.026(2)	0.018(1)	0.659(1)
C(2)	0.659(1)	0.470(1)	0.8629(9)	C(37)	0.911(2)	0.009(1)	0.673(1)
C(3)	0.574(1)	0.555(1)	0.876(1)	C(38)	0.817(1)	0.089(1)	0.6704(9)
C(4)	0.452(1)	0.561(1)	0.8857(9)	C(39)	0.690(1)	0.081(1)	0.684(1)
C(5)	0.418(1)	0.4789(8)	0.8762(8)	C(40)	0.656(1)	0.0913(9)	0.5957(8)
C(6)	0.288(1)	0.477(1)	0.8880(9)	C(41)	0.652(1)	0.013(1)	0.552(1)
C(7)	0.244(1)	0.4154(9)	0.9610(9)	C(42)	0.632(1)	0.020(1)	0.473(1)
C(8)	0.140(1)	0.450(1)	1.033(1)	C(43)	0.617(1)	0.105(1)	0.4339(9)
C(9)	0.104(1)	0.388(1)	1.097(1)	C(44)	0.626(1)	0.1816(9)	0.4800(8)

Table 2 Selected bond distances (Å) and angles (°) in the $[Cu_2(dpm)_2L(OH)][ClO_4]_3{\cdot}2H_2O$ complex

Cu(1)–O(13)	1.963(7)	Cu(2)–O(13)	1.962(6)
Cu(1)–N(5)	1.979(9)	Cu(2)–N(1)	1.999(11)
Cu(1)–N(6)	2.007(10)	Cu(2)–N(2)	2.003(9)
Cu(1)–N(7)	1.993(9)	Cu(2)–N(3)	1.999(11)
Cu(1)–N(8)	2.195(11)	Cu(2)–N(4)	2.211(10)
O(13)–Cu(1)–N(5)	93.0(3)	O(13)–Cu(2)–N(1)	94.9(3)
O(13)–Cu(1)–N(6)	174.6(5)	O(13)–Cu(2)–N(2)	174.9(5)
O(13)–Cu(1)–N(7)	86.0(3)	O(13)–Cu(2)–N(3)	83.2(4)
O(13)–Cu(1)–N(8)	83.1(3)	O(13)–Cu(2)–N(4)	81.0(3)
N(5)–Cu(1)–N(6)	88.1(4)	N(1)–Cu(2)–N(2)	87.9(4)
N(5)–Cu(1)–N(7)	166.1(5)	N(1)–Cu(2)–N(3)	165.1(4)
N(5)–Cu(1)–N(8)	103.1(4)	N(1)–Cu(2)–N(4)	104.2(5)
N(6)–Cu(1)–N(7)	91.6(4)	N(2)–Cu(2)–N(3)	93.0(4)
N(6)–Cu(1)–N(8)	101.7(4)	N(2)–Cu(2)–N(4)	102.3(4)
N(7)–Cu(1)–N(8)	90.6(4)	N(3)–Cu(2)–N(4)	90.2(4)

hydroxide and 1,1,2,2-tetrakis(2-pyridyl)ethylene, a condensation product of dpm with di(2-pyridyl) ketone. The structure of the complex is illustrated in Fig. 1, with the atom labelling used. Positional parameters, bond lengths and angles are given in Tables 1 and 2. The molecule comprises a binuclear copper trication in which the metal centres are separated by 3.663(3) Å and form a bridging angle Cu(1)–O(13)–Cu(2) of 137.9(4)°. Three perchlorate anions together with two hydration water molecules complete the asymmetric unit.

The co-ordination sphere of each copper can be described as a square-based pyramid where the basal plane is formed by three imine nitrogens and one oxygen. Two nitrogen atoms are provided by the chelating dpm ligand and the other one by the condensed ligand L, which bridges the two metal centres. This basal plane is completed by one oxygen from the bridging hydroxide. The apical copper–nitrogen bond is formed by an imine nitrogen provided by the ethylenic ligand.

The two sets of copper–ligand bonds are quite similar: Cu(1)–N(5) 1.979(9), Cu(2)–N(1) 1.999(11); Cu(1)–N(6) 2.007(10), Cu(2)–N(2) 2.003(9); Cu(1)–N(7) 1.993(9), Cu(2)–N(3) 1.999(11); Cu(1)–O(13) 1.963(7), Cu(2)–O(13) 1.962(6) Å. The apical distances are Cu(1)–N(8) 2.195(11) and Cu(2)–N(4) 2.211(10) Å respectively.

The weighted mean plane through the four donor atoms N(5), N(6), N(7) and O(13) shows a lack of planarity with displacement of −0.076, 0.076, −0.078 and 0.079 Å respectively. The Cu(1) atom is displaced from this plane by 0.158 Å, in the direction of the apical N(8) atom, which is 2.317 Å away from the same plane. These values are comparable with the values of the other pyramid, which defines the first co-ordination sphere of the Cu(2) atom. The displacements of the donor atoms N(1), N(2), N(3) and O(13) from the mean plane are in this case 0.097, −0.097, 0.103 and −0.102 Å. The Cu(2) atom is displaced by 0.160 Å in the direction of the apical atom N(4), which is found at 2.321 Å from this basal plane. The dihedral angle between the two basal planes is 65.1°. Some tetrahedral distortion from coplanarity is evident from the dihedral angle (15.1°) formed between the planes through Cu(2), N(1), N(2) and Cu(2), N(3), O(13). A similar distortion is present (14.1°) between the plane through Cu(1), N(5), N(6) and through Cu(1), N(7), O(13).

In both dpm ligands the angle defined by the methylene carbon and the adjacent carbons of the pyridine rings is 113(1)°. In the case of the condensed bridging ligand L the angle C(18)–C(17)–C(16) is 106(1)° and for C(40)–C(39)–C(38) is 82.01°. The two dpm ligands have different dihedral angles between the two pyridine rings, 84.07° for the ligand bonded to

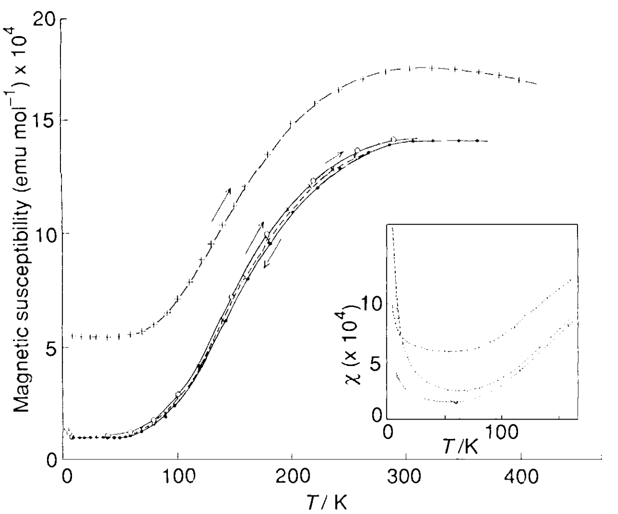

Fig. 2 Corrected magnetic susceptibility *vs.* temperature for two samples of $[Cu_2(dpm)_2L(OH)][ClO_4]_3$ at 1 (sample 1, +) and 10 kOe (sample 1, ○; 2, ×, ●). Inset: uncorrected experimental data at lower temperature

Cu(2) and 58.12° for that bonded to Cu(1). For the bridging ligand L the dihedral angle between the pyridine rings of the moiety bonded to Cu(2) is 82.01°, while that for the fragment bonded to Cu(1) is 69.93°.

The positional disorder of the oxygen atoms of the three perchlorate anions is clearly detectable from different electron-density maps based on accurately refined co-ordinates for the rest of the molecule.

The square-pyramidal geometry around each copper(II) centre is in accord with electronic spectra.[20] The solid visible reflectance spectrum of the dimeric complex presents one major absorption with a low-energy shoulder (17 550 and 11 430 cm^{-1}). The same features are observed in acetonitrile solution [17 700 cm^{-1}, ε = 180 dm^3 mol^{-1} cm^{-1}; 11 765(sh) cm^{-1}].

Since in the dimeric complex an obtuse Cu(1)–O(13)–Cu(2) angle of 137.9(4)° was obtained a magnetic study was undertaken in order to obtain the 2*J* value. Dimeric copper(II) complexes with a wide range of singlet–triplet separations are known.[20]

The magnetic properties of the studied complex are shown in Fig. 2. Susceptibility measurements were performed at both low and high magnetic fields since non-linearities of the magnetization were observed. No remanent magnetization was observed after a field cycle, which precludes any interpretation of such non-linearities as magnetically ordered impurities. The inset of Fig. 2 shows the experimental susceptibility data at fields of 1 and 10 kOe: the susceptibility increase below 50 K follows a Curie variation, and may be accounted for by the presence of small amounts of monomeric impurities, estimated to be 0.6–2% depending on the sample.

Fig. 2 also shows the corrected susceptibility after subtraction of the magnetic impurities contribution. The shape of the susceptibility curve reveals a behaviour typical of a strongly antiferromagnetically coupled binuclear compound with a maximum at a temperature higher than 300 K. A flat temperature-independent susceptibility is observed below 50 K at both 1 and 10 kOe, with χ_0 values of the order of 550 × 10^{-6} and 100 × 10^{-6} emu mol^{-1} respectively. It is important to notice that at 10 kOe both samples 1 and 2 obey the same susceptibility behaviour, independent of the amount of monomeric impurities initially present in the samples, indicating that the χ_0 values (at $T = 0$) must be an intrinsic parameter of this compound.

The corrected susceptibility data were fitted with the Bleaney–Bowers equation (1). Least-squares fitting of the χ'_M *vs.* *T* yielded

$$\chi'_M = \frac{2N\beta^2 g^2}{kT}\left|3 + \exp\left(\frac{-2J}{kT}\right)\right|^{-1} \qquad (1)$$

$g = 2.01$ and $J = -181$ cm^{-1} (1 kOe), $g = 2.15$ and $J = -185$ cm^{-1} (10 kOe) for sample 1, and $g = 2.14$ and $J = -182$ cm^{-1} (10 kOe) for sample 2.

The copper ion ground state for the studied dimer is $d_{x^2-y^2}$ associated with the square-pyramidal geometry. Limited distortions from an idealized square-pyramidal geometry do not seem to disrupt the effective ground-state situation. The presence of the bridging OH group in both basal planes of the binuclear unit allows good overlap of the corresponding orbitals with the $d_{x^2-y^2}$ orbitals of both copper atoms, thus increasing the antiferromagnetic interaction. The large Cu–O(H)–Cu angle, 137.9°, should also increase the antiferromagnetic interaction.[4] However the obtained 2*J* value of −360 cm^{-1} for $[Cu_2(dpm)_2L(OH)]^{3+}$ is not as large as could be expected, considering the value of the Cu–O(H)–Cu angle (Table 3). It is similar to those for two monohydroxo-bridged dicopper(II) complexes, $[Cu_2(bipy)_4(OH)][ClO_4]_3$ ($J = -161$ cm^{-1})[8] and $[Cu_2(tren)_2(OH)]X_3$ (tren = tris(2-aminoethyl)amine; X = PF_6, $J = -350$ cm^{-1}; X = ClO_4, $J = -380$ cm^{-1}).[21] However, these values cannot be compared as the studied complex has square-pyramidal geometry, while the bipy complex has trigonal-bipyramidal copper centres. No structural data are available for the $[Cu_2(tren)_2(OH)]^{3+}$ cation.

The complex $[Cu_2(dpm)_2L(OH)]^{3+}$ does not follow the trend of complexes of diazine ligands, even though the geometry is similar. The magnitude of the exchange for the latter was found to vary in a linear way with the hydroxide bridge angle for a related series of complexes in which the $N_4Cu_2(OH)$ binuclear fragment remains intact and the copper ions have $d_{x^2-y^2}$ ground states. This observation reflects the fact that strong antiferromagnetic coupling exists between the copper(II) centres in complexes of this sort, and that the exchange occurs *via* a superexchange mechanism with the hydroxide bridge acting as the primary pathway for exchange, while the other bridges also contribute significantly. The fact that the studied complex has a relatively less strong antiferromagnetic interaction can be explained by the inability of the additional ligand L to contribute to the exchange mechanism.

The antiferromagnetic coupling observed for most mono-bridged hydroxo complexes is larger than found for di-μ-hydroxo-dicopper(II) complexes with square-pyramidal structures and *J* values between +86 and −255 cm^{-1}, depending on the Cu–O(H)–Cu bridge angles which range from 96 to 104°.[22] A critical change from ferromagnetic to antiferromagnetic behaviour is observed for a Cu–O(H)–Cu angle of approximately 97.5°.

Experimental

The reagents were obtained from Aldrich Chemical Company and used as received, with the exception of di(2-pyridyl)methane which was prepared following the procedure described by Leetle and Marion.[23]

Preparation of the Dimer, $[Cu_2(dpm)_2L(OH)][ClO_4]_3 \cdot 2H_2O$.—Dark blue crystals of the dimeric complex were obtained by treating copper(II) perchlorate dissolved in methanol with a mixture of dpm and di(2-pyridyl) ketone. They were recrystallized from a methanol–water solution.

The condensation product, 1,1,2,2-tetrakis(2-pyridyl)ethylene, is only obtained in the presence of copper(II) ions and for short periods of reaction at room temperature. If the reaction mixture is heated for 60 min then a monomeric complex is obtained $[Cu(dpm)L][ClO_4]_2 \cdot MeOH$ where L is $R_2CHCR_2(OH)$ (R = pyridyl).[24]

Crystal-structure Determination.—Crystal data. $C_{44}H_{37}Cl_3Cu_2N_8O_{15}$, *M* = 1252.36, mean crystal dimensions 0.23 × 0.25 × 0.58 mm, triclinic, space group $P\bar{1}$, $a = 11.685(3)$, $b = 14.569(2)$, $c = 15.509(4)$ Å, $\alpha = 87.97(2)$, $\beta = 73.34(2)$,

Table 3 Magnetic and structural data for some dimeric copper(II) complexes with single hydroxide bridges

Compound[a]	$-2J$/cm^{-1}	Cu–Cu/Å	Cu–O–Cu/°	Geometry[b]	Ref.
$[Cu_2L^1(OH)Cl_3]\cdot 1.5H_2O$	201	3.001	100.1	*SP*	12
		2.972	101.8		
$[Cu_2L^1(OH)Br_3]\cdot 1.5H_2O$	186	3.010	101.3	*SP*	12
		2.986	102.9		
$[Cu_2L^1(OH)(IO_3)_3]\cdot 4H_2O$	290	3.165	113.8	*SP-TBPY*	9
	335				12
$[Cu_2L^1(OH)Cl(SO_4)]\cdot 2H_2O$	532	3.211	115.6	*SP*	11
$[Cu_2L^2(OH)(H_2O)_2(NO_3)_2]NO_3$	497	3.138	115.3	*DOH*	11
$[Cu_2L^3(OH)Cl_3(H_2O)]\cdot 0.8H_2O$	898	3.454	116.4	*SP*	17
$[Cu_2L^3(OH)Br_3(H_2O)]\cdot 0.6H_2O$	915	3.413	118.9	*SP*	17
$[Cu_2L^4(OH)(NO_3)_2(H_2O)]NO_3\cdot H_2O$	750	3.338	119.3	Planar	16
$[Cu_2L^5(OH)Br_3(H_2O)]\cdot H_2O$	Diamagnetic	3.420	124.9	*SP*	17
$[Cu_2L^5(OH)Cl_3(H_2O)]\cdot H_2O$	800	3.425	126.2	*SP*	9
$[Cu_2L^6(OH)]^{3+}$	820	3.384	132.2	*DSP*	13
$[Cu_2(dpm)_2L(OH)]^{3+}$	360	3.663	137.9	*SP*	This work
$[Cu_2L^7(OH)]^{3+}$	240	3.570	141.7	*SP*	15
$[Cu_2L^8(OH)(ClO_4)]^{2+}$	1000	3.642	143.7	*DSP*	14

[a] L^1 = 1,4-Di(2′-pyridylamino)phthalazine; L^2 = 1,4-di(4′-methyl-2′-pyridylamino)phthalazine; L^3 = 3,6-bis(pyrazol-1-yl)pyridazine; L^4 = 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine; L^5 = 1,4-di(1′-methylimidazol-2-yl)phthalazine; L^6 = 1,4-bis[(1-oxa-4,10-dithia-7-azacyclododecan-7-yl)methyl]benzene; L^7 = macrocycle derived from condensation of 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine; L^8 = sexadentate macrocycle. [b] *SP* = Square pyramidal, *TBPY* = trigonal bipyramidal, *DOH* = distorted octahedral and *DSP* = distorted square pyramidal.

$\gamma = 74.15(1)°$, $U = 2443(7)$ Å^3, $Z = 2$, $D_c = 1.711$ g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 11.22 cm^{-1}, $F(000) = 635$.

Three-dimensional X-ray diffraction data were collected in the range $6.11 < 2\theta < 50°$ on a Nonius CAD-4 four-circle diffractometer by the ω–2θ scan technique, scan width $(1.0 + 0.35 \tan \Theta)$. Of a total of 9196 reflections, 4280 independent reflections for which $F^2 > 3\sigma(F^2)$ were corrected for Lorentz and polarization effects; no absorption and no time-decay corrections were applied. The structure was solved by standard Patterson and Fourier techniques,[25] and refined by full-matrix least squares using 601 parameters based on F_0; weights based on counting statistics, $1/w = \sigma^2(F) = \frac{1}{4}\{[\sigma^2(I) + (0.04I)^2]/I\}$.[26] The final electron-density difference synthesis showed electron density of -0.74 to $+0.67$ e Å^{-3}. Two alternative, and mutually incompatible, sites were found for partial-occupancy oxygen atoms of the three perchlorate anions; occupancies of 0.50 were assigned to each. The hydrogen atom positions, with the exception of that located on the oxygen which bridges the copper atom, were calculated and then positional parameters were refined ($B = 5$ Å^2). Refinement converged at $R = 0.076$ and $R' = 0.081$, with allowance for anisotropic thermal motion of all non-hydrogen atoms, with exception of the partial occupancy perchlorate oxygens. Table 1 lists the atomic positional parameters with estimated standard deviations. Atomic scattering factors for neutral atoms were taken from ref. 27. Programs used were from Enraf-Nonius, as described by Frenz.[28]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Magnetic Measurements.—Crystals were crushed and samples were used as powders for magnetic susceptibility measurements. Magnetic susceptibilities were obtained between 5 and 400 K using a SHE 906 SQUID magnetometer, at field strengths of 1 and 10 kOe. Magnetization measurements, as a function of field, were also performed at different temperatures under magnetic fields up to 40 kOe. Pascal's constants were used to estimate the correction for diamagnetism of the sample (-555.5×10^{-6} emu mol^{-1}) and the temperature-independent paramagnetism contribution for the copper atom was taken as 60×10^{-6} emu mol^{-1}.

Because the low-temperature susceptibilities suggested the presence of a small amount of paramagnetic impurity in each sample, corrections for these impurities were estimated from the experimental results. The corrected magnetic data were fitted to the Bleaney–Bowers equation by a least-squares process. The function minimized was $\Sigma|(\chi_{obs} - \chi_{calc})/\chi_{obs}|^2$.

Spectroscopy.—UV–visible absorption spectra were recorded on a Carl Zeiss DMR 22 spectrophotometer with a ZR 21 accessory for reflectance measurements.

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