Crystal Structure and Magnetic Properties of 1-Aqua-μ-hydroxo-1,2,2-tris(perchlorato)-1,2-bis(2,2′;6′,2″-terpyridine)dicopper(II) †

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The crystal and molecular structure of $[Cu_2(terpy)_2(OH)(OH_2)(ClO_4)_3]$ (terpy = 2,2′;6′,2″-terpyridine) has been determined by *X*-ray diffraction methods. It crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions a = 8.825(5), b = 10.391(10), c = 19.258(8) Å, α = 88.24(2), β = 99.27(3), γ = 96.63(4)°. Least-squares refinement of 3 590 reflections with $I > 2.5\sigma(I)$ and 353 parameters gave a final R' = 0.052. The structure consists of discrete dimeric molecules where the two copper(II) ions are bridged by only a single hydroxide anion with a Cu–O–Cu angle of 145.7(3)°, the resulting copper–copper distance being 3.642(1) Å. No crystallographic symmetry is imposed on the binuclear entities. The co-ordination geometry around each copper ion is approximately elongated tetragonal octahedral with the bridging hydroxide ion occupying an equatorial site. The apical sites are occupied by a perchlorate oxygen atom and a water oxygen atom for Cu(1), and by two perchlorate oxygen atoms for Cu(2). The tetragonal distortion is greater for Cu(2) due to the longer Cu–O apical distances. Magnetic susceptibility measurements performed from 295 to 5 K show relatively strong antiferromagnetic exchange interaction between the copper(II) ions ($2J = -303$ cm^{-1}, g = 2.07, and ρ = 0.019). The strength of the exchange interaction is discussed on the basis of the structural features and correlated with published magneto-structural data on similar single hydroxide-bridged copper(II) complexes.

As a part of our studies in the search for new exchange-coupled copper(II) complexes we have examined the magneto-structural chemistry of a wide variety of compounds containing the entity $[Cu(L_{III})X]$, where L_{III} is a tridentate rigid quasi-planar ligand such as terpy (2,2′;6′,2″-terpyridine), pyridine-2-carbaldehyde 2′-pyridylhydrazone, 2,4,6-tris(2-pyridyl)-1,3,5-triazine, or *N*-2′-pyridylcarbonyl-2-pyridinecarboximidate anion, and X = halide, pseudohalide, or one half of a doubly charged bridging anion such as oxalate or chloranilate (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinonate).[1–10] Up to now, the structures of these kinds of systems have shown a typical parallel stacking of square-planar $[Cu(L_{III})X]$ moieties bridged by the X groups to give dimers or more extended magnetic lattices (linear or ladder-like chains). In general, due to the poor effective overlap between the magnetic orbitals determined by this geometry, weak exchange interactions (around 0.05—3 cm^{-1}) have been observed.[1–10]

We report here the crystal structure and magnetic characterization of a new binuclear terpy-containing copper(II) complex bridged by only a single hydroxide anion, $[Cu_2(terpy)_2(OH)(OH_2)(ClO_4)_3]$. The unusual geometry adopted by this dimer has given rise to the first terpy-containing compound exhibiting strong exchange interactions. In addition, this compound represents one of the scarce examples of monohydroxo-bridged copper(II) complexes.[11,12] The exchange interactions observed for this kind of complex will be discussed in the light of structural features such as the bridging angle and the co-ordination geometries around the copper(II) ions.

Experimental

Preparation of the Complex.—A solution of terpy (1 mmol) in acetone (10 cm^3) was added, with stirring, to an aqueous solution (15 cm^3) containing $Cu(ClO_4)_2\cdot6H_2O$ (1 mmol). To the resulting blue solution was added NaOH (*ca.* 6 mmol) dissolved in water (0.5 cm^3), with stirring, and the solution turned blue greenish. After mild heating to remove acetone, the resulting solution was allowed to stand at *ca.* 80 °C for several hours. The dark blue crystals which appeared were filtered off, washed with acetone, and stored in a desiccator over silica gel (Found: C, 38.9; H, 2.7; Cu, 13.7; N, 9.1. $C_{30}H_{25}Cl_3Cu_2N_6O_{14}$ requires C, 39.0; H, 2.8; Cu, 13.7; N, 9.1%).

Crystallography.—*Crystal data.* Blue prismatic crystals of $C_{30}H_{25}Cl_3Cu_2N_6O_{14}$, M = 926.4, triclinic, space group $P\bar{1}$, a = 8.825(5), b = 10.391(10), c = 19.258(8) Å, α = 88.24(2), β = 99.27(3), γ = 96.63(4)°, U = 1 731.1(9) Å^3, D_m(flotation) = 1.770 g cm^{-3}, Z = 2, D_c = 1.777 g cm^{-3}, $F(000)$ = 936, μ(Mo-K_α) = 14.9 cm^{-1}.

Data collection. Preliminary cell dimensions and the space group were obtained from Weissenberg and oscillation photographs. A well formed crystal of dimensions 0.13 × 0.20 × 0.33 mm was selected and mounted on a Phillips PW1100 diffractometer equipped with a graphite monochromator. The cell dimensions were obtained by least-squares refinement of 25 well centred reflections ($4 < 2\theta < 20°$) using Mo-K_α radiation (λ = 0.709 26 Å). The space group $P\bar{1}$ was assumed throughout the structure analysis and was confirmed by the successful refinement of the structure. Examination of three standard reflections, monitored after 2 h, showed no substantial intensity decay. A total of 5 816 reflections were measured ($2 < 2\theta < 50°$; $-9 < h < 9$, $-12 < k < 12$, $0 < l < 18$)

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates (× 10^4) for $[Cu_2(terpy)_2(OH)(OH_2)(ClO_4)_3]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	3 225(1)	1 537(1)	3 257(1)	C(20)	−476(8)	−616(6)	908(3)
Cu(2)	23(1)	1 593(1)	1 808(1)	C(21)	−1 573(7)	286(6)	590(3)
N(1)	4 344(6)	3 364(5)	3 226(3)	C(22)	−2 646(9)	87(8)	−3(4)
N(2)	5 184(6)	1 261(5)	3 807(3)	C(23)	−3 559(9)	1 068(9)	−228(4)
N(3)	2 782(6)	−334(5)	3 605(3)	C(24)	−3 431(8)	2 198(8)	154(4)
N(4)	495(6)	−160(5)	1 474(3)	C(25)	−2 346(7)	2 329(7)	753(3)
N(5)	−1 420(6)	1 398(5)	947(3)	C(26)	−2 043(7)	3 426(6)	1 245(4)
N(6)	−994(6)	3 259(5)	1 816(3)	C(27)	−2 778(8)	4 531(7)	1 134(4)
O(1)	1 261(5)	1 739(4)	2 717(2)	C(28)	−2 403(10)	5 483(8)	1 629(6)
C(1)	3 776(9)	4 432(7)	2 935(4)	C(29)	−1 336(10)	5 333(7)	2 222(5)
C(2)	4 618(11)	5 634(7)	3 008(5)	C(30)	−656(8)	4 190(7)	2 300(4)
C(3)	6 070(12)	5 725(8)	3 379(5)	Cl(1)	1 885(2)	3 350(2)	4 558(1)
C(4)	6 674(9)	4 666(8)	3 664(4)	Cl(2)	2 603(2)	3 934(2)	888(1)
C(5)	5 802(7)	3 470(7)	3 581(4)	Cl(3)	−3 115(2)	−904(2)	−2 324(1)
C(6)	6 325(7)	2 258(7)	3 865(4)	O(2)	4 203(8)	1 315(7)	2 166(3)
C(7)	7 792(9)	2 041(9)	4 179(5)	O(3)	1 901(7)	2 088(5)	4 284(3)
C(8)	8 074(10)	843(10)	4 422(5)	O(4)	3 424(6)	3 945(6)	4 724(3)
C(9)	6 898(10)	−162(8)	4 377(4)	O(5)	1 179(7)	3 212(6)	5 167(3)
C(10)	5 432(8)	91(7)	4 056(3)	O(6)	1 038(6)	4 069(5)	4 027(3)
C(11)	4 033(9)	−816(6)	3 967(4)	O(7)	2 177(9)	2 799(7)	1 233(4)
C(12)	3 931(12)	−2 070(8)	4 232(5)	O(8)	3 447(8)	3 698(8)	375(4)
C(13)	2 543(15)	−2 788(8)	4 136(6)	O(9)	1 078(8)	4 222(7)	505(4)
C(14)	1 285(12)	−2 304(9)	3 801(5)	O(10)	3 149(12)	4 984(8)	1 267(5)
C(15)	1 408(9)	−1 051(7)	3 517(4)	O(11)	−2 538(8)	425(5)	2 394(4)
C(16)	1 561(9)	−900(7)	1 777(4)	O(12)	−3 466(8)	−1 233(8)	1 608(3)
C(17)	1 630(10)	−2 140(8)	1 532(5)	O(13)	−4 408(7)	−1 195(6)	2 664(4)
C(18)	610(10)	−2 611(7)	972(5)	O(14)	−1 972(7)	−1 662(6)	2 633(4)
C(19)	−446(9)	−1 857(7)	659(4)				

with the variable-speed ω—2θ technique, of which 3 590 were unique with $I > 2.5\sigma(I)$ and used in the determination of the structure. Lorentz and polarization corrections were applied, but not for absorption.

Structure solution and refinement. The positions of the two copper atoms were determined by direct methods (MULTAN 11/84).[13] The remaining non-hydrogen atoms were located from subsequent Fourier syntheses. The model obtained was refined with the SHELX 76 system[14] by weighted anisotropic full-matrix least-squares methods. After refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms, difference maps indicated the positions of all the hydrogen atoms (except those associated with the water molecule), and were included in the final refinement with common fixed isotropic thermal parameters ($U = 0.06$ Å^2). The final R values were $R = 0.051$ and $R' = 0.052$ (353 parameters refined); $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma^2(F_o) + 0.001\,036(F_o^{\,2})]$ with $\sigma^2(F_o)$ from counting statistics. It was apparent that the three perchlorate groups are undergoing considerable thermal motion and may indeed be disordered. However, examination of Fourier maps throughout the course of the analysis did not reveal any meaningful disordered model, and the best description of these anions appears to be that of roughly tetrahedral groups undergoing considerable libration. In the final difference map the residual maxima were less than 0.7 e Å^{-3} except for a peak of 1.19 e Å^{-3} near the Cl(2)–O(10) bond. Atomic scattering factors and corrections for anomalous dispersion for Cu and Cl atoms were taken from ref. 15. The geometrical calculations were performed with XANADU[16] and DISTAN[17] and molecular illustrations were drawn with PLUTO.[18]

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

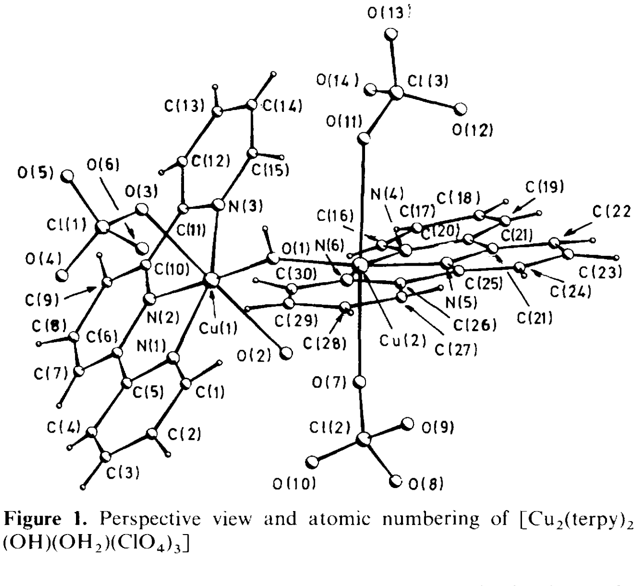

Figure 1. Perspective view and atomic numbering of $[Cu_2(terpy)_2(OH)(OH_2)(ClO_4)_3]$

Physical Measurements.—I.r. spectra were obtained on KBr pellets in the 4 000—250 cm^{-1} region using a Pye Unicam SP 2000 spectrophotometer. Diffuse reflectance electronic spectra were recorded on a Perkin-Elmer LAMBDA 9 UV/VIS/NIR spectrophotometer, e.s.r. spectra on a ER 200D Bruker spectrometer equipped with a nitrogen cryostat. Magnetic susceptibility measurements were performed in the temperature range 5—295 K using a pendulum-type apparatus equipped with a helium cryostat. The uncertainty in the data is lower than 0.1 K for temperatures and 2×10^{-5} cm^3 mol^{-1} for susceptibilities. Experimental susceptibilities were corrected for the diamagnetic contributions and for the temperature

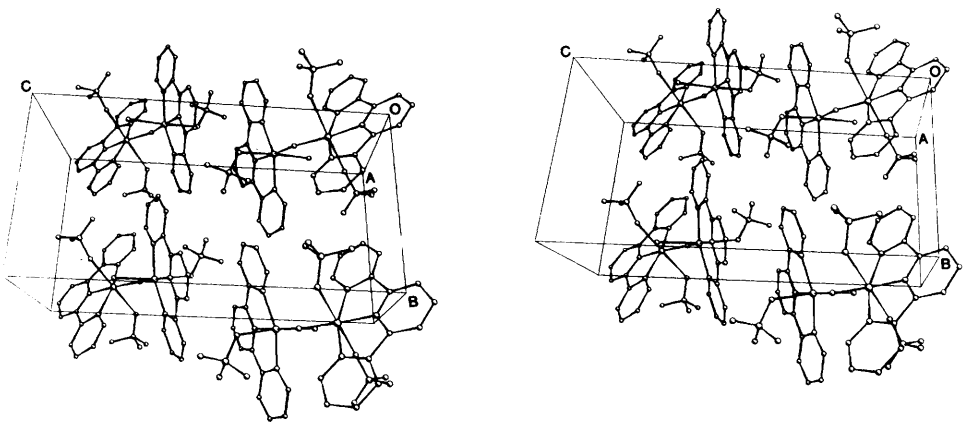

Figure 2. Stereoscopic view of the unit cell for $[Cu_2(terpy)_2(OH)(OH_2)(ClO_4)_3]$

Table 2. Selected bond distances (Å) and angles (°) in the complex $[Cu_2(terpy)_2(OH)(OH_2)(ClO_4)_3]$ with e.s.d.s in parentheses

Cu(1)–N(1)	2.040(5)	Cu(2)–N(4)	2.059(6)
Cu(1)–N(2)	1.923(5)	Cu(2)–N(5)	1.923(5)
Cu(1)–N(3)	2.051(5)	Cu(2)–N(6)	2.042(6)
Cu(1)–O(1)	1.902(4)	Cu(2)–O(1)	1.909(4)
Cu(1)–O(2)	2.424(7)	Cu(2)–O(7)	2.541(8)
Cu(1)–O(3)	2.564(7)	Cu(2)–O(11)	2.821(7)
Cu(1) · · · Cu(2)	3.642(1)		
N(1)–Cu(1)–N(2)	80.3(2)	N(4)–Cu(2)–N(5)	80.1(2)
N(2)–Cu(1)–N(3)	78.7(2)	N(5)–Cu(2)–N(6)	78.7(2)
N(1)–Cu(1)–N(3)	157.9(2)	N(4)–Cu(2)–N(6)	159.5(2)
N(2)–Cu(1)–O(1)	177.7(2)	N(5)–Cu(2)–O(1)	173.6(2)
O(2)–Cu(1)–O(3)	169.3(2)	O(7)–Cu(2)–O(11)	174.8(2)
O(3)–Cu(1)–O(1)	83.1(2)	O(11)–Cu(2)–N(4)	92.2(2)
O(3)–Cu(1)–N(1)	92.3(2)	O(11)–Cu(2)–N(5)	82.5(2)
O(3)–Cu(1)–N(2)	96.9(2)	O(11)–Cu(2)–N(6)	85.1(2)
O(3)–Cu(1)–N(3)	83.8(2)	O(11)–Cu(2)–O(1)	91.1(2)
O(1)–Cu(1)–N(3)	99.1(2)	O(1)–Cu(2)–N(4)	102.2(2)
O(1)–Cu(1)–N(1)	102.0(2)	O(1)–Cu(2)–N(6)	98.2(2)
O(2)–Cu(1)–N(1)	88.4(2)	O(1)–Cu(2)–O(7)	91.7(2)
O(2)–Cu(1)–N(1)	83.0(2)	O(7)–Cu(2)–N(4)	91.4(2)
O(2)–Cu(1)–N(3)	104.1(2)	O(7)–Cu(2)–N(5)	94.5(2)
O(2)–Cu(1)–N(2)	91.8(2)	O(7)–Cu(2)–N(6)	90.3(2)
Cu(1)–O(1)–Cu(2)	145.7(3)		
Hydrogen bonding			
O(2) · · · O(7)	2.870(5)	Cu(1)–O(2)–O(7)	100.2(5)
O(2) · · · O(11′)	3.083(6)	Cu(1)–O(2)–O(11)	112.9(6)
O(2) · · · O(13′)	3.071(6)	Cu(1)–O(2)–O(13)	93.0(5)

* Atoms O(11′) and O(13′) are related to O(11) and O(13) by the symmetry operation $x - 1,y,z$.

independent paramagnetism estimated to be 60 × 10^{-6} cm^3 mol^{-1} per Cu^{II}.

Results and Discussion

Crystal Structure.—The atomic parameters are given in Table 1. Figure 1 shows a perspective view of the molecule with the atomic numbering scheme and Figure 2 a stereoscopic view of the unit cell. Selected bond distances and angles are listed in Table 2. The structure consists of asymmetric dimeric molecules which interact through hydrogen bonding between the water molecule and perchlorate anions as shown by the contact distances in Table 2.

The co-ordination geometry around each copper(II) ion is distorted elongated tetragonal octahedral [*i.e.* a copper(II) '4 + 1 + 1' co-ordination mode]. The equatorial positions are occupied by the three nitrogen atoms from the terpy ligand and the oxygen atom of the hydroxide anion, which bridges the two metallic centres. The Cu–N distances, ranging from 1.923(5) to 2.059(6) Å, are similar to those found in related N-heterocyclic copper(II) complexes.[1,2,5,10] The Cu(1,2)–O(1) bridging distances of 1.902(4) and 1.909(4) Å, respectively, are nearly symmetric and somewhat shorter than those reported by Hendrickson and co-workers[11] in the $[Cu_2(bipy)_4(OH)][ClO_4]_3$ (bipy = 2,2′-bipyridine) complex [1.930(5) Å]. The Cu(1)–O(1)–Cu(2) bridging angle (θ) is 145.7(3)°, and the resulting Cu(1) · · · Cu(2) distance is 3.642(1) Å. The four equatorial atoms are, in both copper(II) surroundings, practically coplanar with deviations from the least-squares planes lower than ±0.07 Å [N(1)N(2)N(3)O(1) plane] or ±0.05 Å [N(4)N(5)N(6)O(1) plane], and the copper atoms are 0.06 Å from these planes. In both metal environments the apical sites are occupied by oxygen atoms, belonging to the water molecule [O(2)] and one perchlorate anion [O(3)] for Cu(1), and to the other perchlorate anions [O(7) and O(11)] for Cu(2). The tetragonal distortion is greater for Cu(2) than for Cu(1) by virtue of the longer apical Cu–O distances (the calculated tetragonalities are 0.74 and 0.80, respectively).

The terpy ligands cannot be considered as totally planar since the deviations from the least-squares planes (non-hydrogen atoms) are 0.24 Å for terpy(2) and 0.14 Å for terpy(1). If we consider each terpy ligand as constructed of two symmetric halves separated along the N(2)–C(8) axis in one case and along the N(5)–C(23) axis in the other the deviations from planarity are no greater than 0.09 Å, except for N(2) which is 0.12 Å from one of the halves. The dihedral angles defined by these portions are 5.2° for terpy(1) and 9.8° for terpy(2). On the other hand, the mean least-squares planes defined by the full terpy ligands are twisted making an angle of 129.9°, whereas the planes defined by N(1)N(2)N(3)Cu(1)O(1) and N(4)N(5)N(6)Cu(2)O(1) make an angle of 127.3°. This twisting probably originates from the steric hindrances between the external pyridine rings of the terpy ligands.

As noted above, the perchlorate groups are undergoing considerable thermal motion, especially that corresponding to Cl(2) for which the calculated Cl–O bond lengths and O–Cl–O angles are in the range 1.329(8)—1.458(7) Å, and 100.5(4)—118.8(5)°, respectively.

Vibrational and Electronic Spectra.—Besides the bands due to terpy and perchlorate groups, the i.r. spectrum of this complex shows a relatively broad and medium-intensity band at 3 500 cm^{-1} with a shoulder at 3 600 cm^{-1}. These bands can be assigned

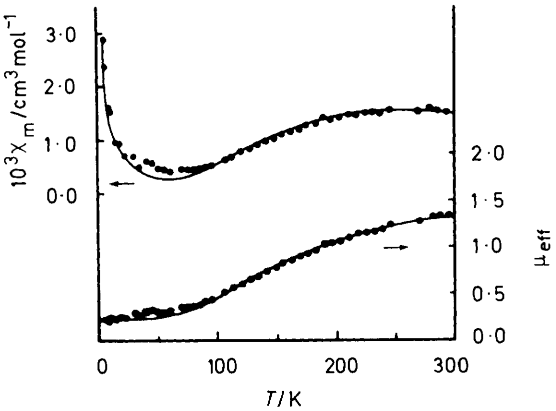

Figure 3. Corrected magnetic susceptibility per mol of copper dimer and effective magnetic moment of $[Cu_2(terpy)_2(OH)(OH_2)(ClO_4)_3]$ *vs.* temperature. The solid lines correspond to the best fit to the experimental data

Table 3. Magneto-structural data for copper(II) dimers with only a single hydroxo-bridge

Complex	$-2J$/ cm^{-1}	Cu–O–Cu/°	Geometry[a]	Ref.
$[Cu_2(bipy)_4(OH)][ClO_4]_3$	322	141.6	t.b.p.	11
$[Cu_2(phen)_4(OH)][ClO_4]_3$[b]	354		t.b.p.	11
$[Cu_2(tren)_2(OH)][ClO_4]_3$[b]	700		t.b.p.	12
$[Cu_2(tren)_2(OH)][PF_6]_3$[b]	760		t.b.p.	12
$[Cu_2(dien)_2(OH)(ClO_4)_3]$	400	128.0	d.o.	23
$[Cu_2(terpy)_2(OH)(OH_2)$-$(ClO_4)_3]$	303	145.7	d.o.	This work

[a] t.p.b. = Trigonal bipyramidal, d.o. = distorted octahedral. [b] *X*-Ray structural data have not been reported.

to the stretching O–H vibrations from the water molecule and hydroxide bridging group, respectively, in full accordance with the literature.[11,12] Furthermore, a weak band is observed at 570 cm^{-1}, which does not appear in the spectra of the related complexes $Cu(terpy)_2A_2$ and $Cu(terpy)X_2$ (A = PF_6 or ClO_4; X = Cl or Br).[19] This band is much too high in energy to be assigned to Cu–O vibrations, and it may be associated with the co-ordinated water wagging vibrations.[20]

The visible region of the electronic spectrum is dominated by a very broad band with an absorption maximum located near 15 000 cm^{-1}, including the non-resolved *d–d* transitions of the two $CuN_3OO'O''$ chromophores present in the complex.[21]

Magnetic Properties.—Variable-temperature magnetic susceptibility measurements have been performed from 295 down to 5 K and Figure 3 illustrates the data. Relatively strong antiferromagnetic interactions are present as evidenced by the fact that the effective magnetic moment per copper(II) ion is only 1.34 at 295 K, and falls to a value of 0.24 at 5 K. The data were fitted by equation (1). In this expression $2J$ is the singlet–triplet

$$\chi_m = (Ng^2\beta^2/2kT)\{[4(1-\rho)/3+\exp(-2J/kT)]+\rho\} \quad (1)$$

splitting, ρ is the proportion of uncoupled paramagnetic species assumed to have the molecular weight of the binuclear unit, and to follow a Curie law, and the other symbols have their usual meanings. The best fit was obtained with the parameters $2J = -303$ cm^{-1}, $g = 2.07$, and $\rho = 0.019$, and describes satisfactorily the experimental data (full line in Figure 3).

The presence in the samples of a small amount of monomeric impurity is also detected in the powder e.s.r. spectrum which shows a weak axial signal ($g_\parallel = 2.24$ and $g_\perp = 2.04$) with a four-component hyperfine structure on the parallel component ($A_\parallel = 170 \times 10^{-4}$ cm^{-1}). This signal is superimposed on a very broad weak signal centred near $g = 2.1$ which can be attributed to triplet transitions in the dimer.

Table 3 summarizes the available magneto-structural data for copper(II) dimers with only a single hydroxo bridge. Examples of copper(II) dimers containing a single hydroxo bridge and other additional bridging groups are also known.[22] They have not been considered in Table 3 since it has been pointed out that these bridges strongly contribute to the total superexchange interaction.[22] The only compound which is structurally related to that reported in this paper is the dien (diethylenetriamine) derivative[23] since in both complexes the copper(II) co-ordination geometry is distorted tetragonal octahedral. In the other compounds listed in Table 3, the co-ordination geometry is trigonal bipyramidal.[11,12] In these cases, the higher *J* values found for the tren [tris(2-aminoethyl)amine] derivatives, when compared to those of bipy and phen (1,10-phenanthroline), are understood on the basis of the actual geometry of the CuN_4O chromophores, and the way they are bridged. In the tren dimers the hydroxo-bridge occupies an apical position in each copper(II) co-ordination polyhedron allowing a direct overlapping between the σ orbitals of the bridge and the main lobe of the copper(II) d_{z^2} magnetic orbitals. However, in the bipy and phen dimers, the OH group is situated in equatorial positions and the overlapping involves only the doughnut lobe of the copper(II) d_{z^2} orbitals. On the other hand, the Cu–O–Cu bridging angle in the tren complexes is expected to be close to 180°, whereas in phen and bipy dimers this angle may be significantly lower (141.6° in the bipy complex).[11,12]

Let us now compare the *J* values found for dien and terpy dimers. In both cases the copper(II) ground state is basically $d_{x^2-y^2}$, with a small z^2-type contribution which decreases as the tetragonal elongation increases. The hydroxide group occupies an equatorial position. For this type of geometry a stronger antiferromagnetic interaction is expected as the bridging angle (θ) approaches 180°, since the copper(II) $d_{x^2-y^2}$ orbitals are then more favourably positioned to overlap in a σ fashion with the bridging moiety.[24] However, we observe the opposite trend: the terpy dimer with a larger bridging angle (θ = 145.7°) exhibits an exchange coupling weaker than that of the dien dimer (θ = 128.0°). This unexpected result can be understood by taking into account the differences observed in the co-ordination geometries around the copper(II) ions of both dimers. Thus, the Cu–O axial bond distances of both environments are greater in the dien dimer which results in a larger tetragonal distortion. The calculated tetragonalities for this dimer are 0.77 and 0.71. On the other hand, the N–Cu–N angles are closer to 90° in the dien derivative (mean 84°) than in the terpy dimer (mean 79°), by virtue of the rigidity imposed by the terpy ligand. From such differences a larger d_{z^2} contribution to the copper(II) ground state is expected in the terpy case, decreasing the $d_{x^2-y^2}$ character, and hence the antiferromagnetic exchange interaction.

Finally, it is interesting to compare the *J* values found for the μ-hydroxo-copper(II) complexes with those expected from the correlation established for planar di-μ-hydroxo-copper(II) complexes.[25] Using this correlation, *J* values much larger than the experimental ones result. For example, in the case of terpy and dien dimers, the expected *J* values would be, respectively, −897 and −567 cm^{-1} for the bridging angles found. In the case of the phen, bipy, and tren complexes in Table 3, this discrepancy has been attributed to the different electronic ground states of the copper(II) ions (d_{z^2} in these complexes, and $d_{x^2-y^2}$ in the di-μ-hydroxo cases).[11] The fact that this disagreement also occurs in the case of μ-hydroxo dimers with $d_{x^2-y^2}$ copper(II) ground states (terpy and dien complexes) rules out the above explanation and further emphasizes that the correlation found for the di-μ-hydroxo-copper(II) dimers cannot be extended to this series.

Conclusions

Despite the very few examples of known copper(II) dimers with only a single hydroxo bridge, the above discussion allows us to anticipate that a simple correlation of *J* with the bridging angle, such as that reported for di-μ-hydroxo-copper(II) dimers, is unexpected in this series. This is due to the large variety of geometries assumed either by the dimer or by the environments around copper(II), which can lead to a wide array of superexchange pathways. Thus, any attempt to correlate the *J* value with the bridging angle will often be complicated by other structural features, such as the distortions of the metal environments, which in some cases (dien and terpy dimers) seems to be the dominant factor controlling the superexchange.

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