Synthesis, Crystal Structure and Magnetic Properties of Di-μ-hydroxo-bis[(2,2′-bipyridine)(trifluoromethanesulfonato-*O*)-copper(II)]†

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The compound $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$ (bipy = 2,2′-bipyridine) has been synthesised and its crystal structure determined by X-ray crystallographic methods. Crystals are triclinic with $a = 8.165(2)$, $b = 14.265(2)$, $c = 18.748(5)$ Å, $\alpha = 93.10(1)$, $\beta = 100.58(2)$, $\gamma = 99.17(1)°$, space group $P\bar{1}$, and $Z = 3$. Least-squares refinement of 5872 reflections with $I \geqslant 3\sigma(I)$ and 679 parameters gave a final R = 0.042. The structure consists of discrete centrosymmetric and non-centrosymmetric di-μ-hydroxo-copper(II) dimers with 2,2′-bipyridine as outer ligand and semi-co-ordinated $CF_3SO_3^-$ anions. Intramolecular copper–copper distances are 2.920(1) and 2.8917(7) Å for the centrosymmetric and non-centrosymmetric dimers respectively. The co-ordination geometry around each copper ion is square pyramidal with the bridging hydroxo groups and two nitrogen atoms of the bipyridine ligand comprising the basal plane, and the apical site occupied by an oxygen atom of the $CF_3SO_3^-$ group. Coupled variable-temperature powder ESR spectral and magnetic susceptibility data demonstrate that the copper(II) ions within both dimeric molecules are ferromagnetically coupled ($J_c = 17$, $J_a = 158$ cm^{-1}, g 2.09 and 2.10, with J = singlet–triplet energy gap and subscripts c and a denoting the centrosymmetric and asymmetric dimers). The nature and strength of the exchange interaction is discussed on the basis of the structural features and correlated with previously reported magnetostructural data for other di-μ-hydroxo-bis[2,2′-bipyridine)copper(II)] complexes.

Bibridged copper(II) dimers, particularly the di-μ-hydroxo-copper(II) complexes,[1,2] represent one of the systems for which magnetostructural correlations have been established. It has been shown that the singlet–triplet energy gap (J) varies linearly with the angle at the bridging oxygen (Cu–O–Cu, θ) leading to singlet or triplet ground states for $\theta > 97.5$ or $< 97.5°$, respectively. This singlet–triplet splitting is accompanied by a zero-field splitting within the triplet state which is characterized by the axial (D) and rhombic (E) zero-field splitting parameters.[3] Dealing with the dependence of J *versus* θ, two semiquantitative interpretations have been proposed: one is based on an orthogonalized magnetic orbital approach of the interaction[4] and the other on non-orthogonalized magnetic orbitals and on the overlap density between them.[5] More recently, a topological approach aimed at interpreting the variation of the anisotropic interaction in this series of related complexes was developed.[6]

Although such geometric structure–magnetic properties correlations have led to a better understanding of the mechanism of the interaction, it seems extremely difficult to control the value of the structural parameters during the synthesis process. It has been pointed out that the value of θ is strongly influenced by the nature of the terminal ligands and the co-ordination of solvent molecules and counter ions.[1,2] It should be noted that the magnetic coupling in the di-μ-hydroxo-copper(II) complexes $[LCu(OH)_2CuL]^{2+}$ can be antiferromagnetic (L = diamine) or ferromagnetic (L = 2,2′-bipyridine) with N-donor ligands. Dealing with the role of the counter ion and restricting ourselves to the case for which 2,2′-bipyridine is used as outer ligand, a survey of the reported crystal structures reveals its ability to co-ordinate to copper(II) introducing unforeseeable structural modifications that affect the magnitude of J.[1,7–11]

In this work we focus on the subtle magnetostructural role of a given counter ion in the di-μ-hydroxo-bis[(bipyridine)-copper(II)] series. We report here the synthesis, the crystal and molecular structure and the magnetic properties of $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$. The coexistence in the unit cell of two dimeric complexes with identical composition and exhibiting a very different intradimer ferromagnetic coupling exemplifies the need for structural information when analysing magnetic properties and demonstrates that these magnetostructural correlations cannot be considered as actual foundations for molecular engineering.

Experimental

Materials and Measurements.—Sodium carbonate and 2,2′-bipyridine were Merck reagents whereas copper(II) trifluoromethanesulfonate (triflate) was prepared by a reported procedure.[12] The infrared spectrum was recorded with a Perkin-Elmer 1750 spectrophotometer as KBr pellets in the 4000–225 cm^{-1} region and X-band ESR spectra with a Bruker ER 200D spectrometer at 298–100 K. Magnetic susceptibility measurements were carried out at 300–15 K with a previously described pendulum-type apparatus[13a] equipped with a helium cryostat. The uncertainty in the data is lower than 0.1 K for temperature and 2×10^{-5} cm^3 mol^{-1} for susceptibilities. The apparatus was calibrated with $Hg[Co(NCS)_4]$. Experimental susceptibilities were corrected for both the diamagnetic contribution, estimated

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: G = 10^{-4} T.

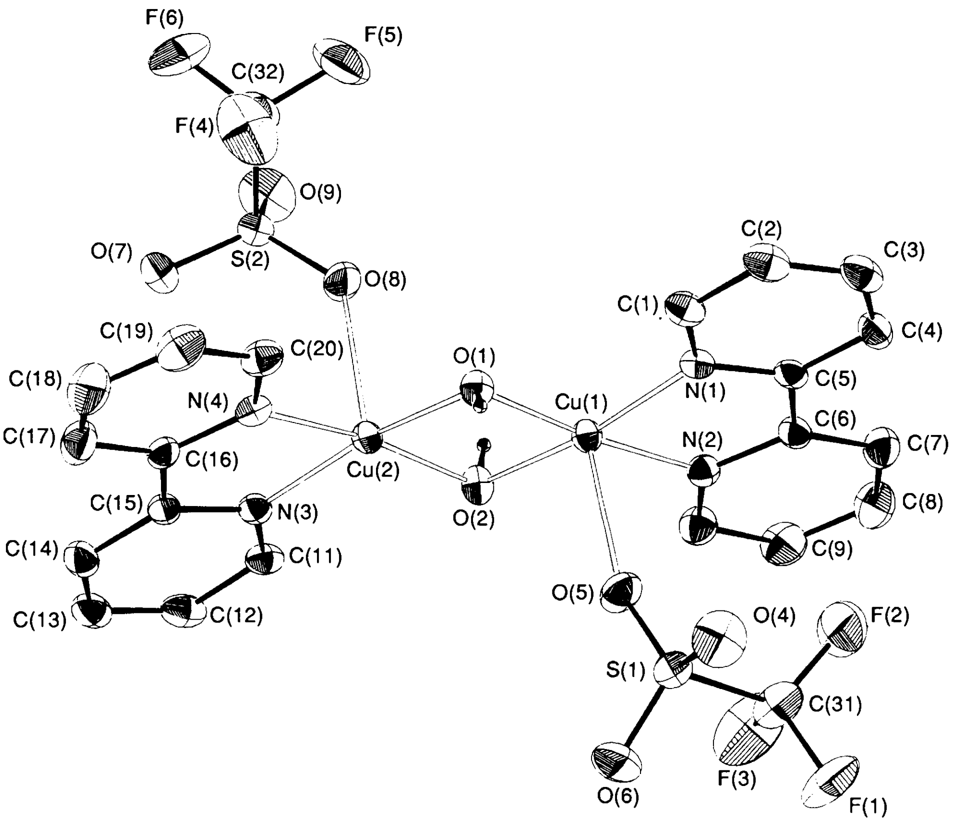

Fig. 1 An ORTEP drawing of $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$ showing the atom labelling. Thermal ellipsoids are drawn at the 30% probability level

from Pascal's constants[13b] to be -364×10^{-6} emu mol^{-1} (1 emu = SI $\times$ $10^{-6}/4\pi$) and the temperature-independent paramagnetism (60×10^{-6} cm^3 mol^{-1} per Cu^{II}).

Preparation of the Complex.—2,2′-Bipyridine (1 mmol) was added with stirring to a warm aqueous solution (80 cm^3) containing copper(II) triflate (1 mmol) yielding a blue-turquoise solution. Its colour became dark blue after addition of sodium carbonate (0.5 mmol) dissolved in the minimum amount of water. This colour change is due to hydroxo complex formation. Prismatic dark blue crystals of $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$ appeared upon slow evaporation at room temperature. They were filtered off, washed with cold water, ethanol and diethyl ether and stored over silica gel [Found: C, 33.15; H, 2.40; Cu, 16.25; N, 7.15. Calc. for $C_{22}H_{18}Cu_2F_6N_4O_8S_2$: C, 34.25; H, 2.35; Cu, 16.45; N, 7.25%).

Crystal Structure Determination and Refinement.—Diffraction data for $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$ were collected at 291 K with a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). The conditions for crystallographic data collection and structure refinement are summarized in Table 1. The unit-cell parameters were derived from least-squares refinement of 25 well centred reflections ($12 \leqslant \theta \leqslant 14°$). Examination of two standard reflections, monitored every 2 h, showed no significant intensity decay. The space group $P\bar{1}$ was assumed throughout the structure analysis and was confirmed by the successful refinement of the structure. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was performed by the use of DIFABS.[14]

The structure was solved by direct methods[15] followed by successive Fourier synthesis and least-squares refinements (CRYSTALS).[16] Least-squares refinements were carried out in seven blocks with anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms were found in a Fourier difference map and were included in the refinement with an overall isotropic thermal parameter. A secondary extinction coefficient was introduced in the final stage of the refinement. Atomic scattering factors and corrections for anomalous dispersion were taken from ref. 16. All calculations were performed by using a VAX 725 computer. The final Fourier difference maps showed residual maxima and minima of 0.60 and -0.48 e $Å^{-3}$. The goodness of the fit is 0.98. Fractional atomic coordinates and selected intramolecular bond lengths and angles are listed in Tables 2 and 3 respectively.

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

Results and Discussion

Description of the Structure.—The structure is made up of both centrosymmetric and asymmetric di-μ-hydroxo-bis[(2,2′-bipyridyl)copper(II)] dinuclear units with weakly co-ordinated trifluoromethanesulfonate anions. A perspective view of the asymmetric dimer with the atom-numbering scheme is depicted in Fig. 1. The unit cell contains three dinuclear complexes, one of them (the centrosymmetrical one) being crystallographically independent from the other two as shown by means of the corresponding stereoscopic view (see Fig. 2).

The co-ordination geometry around each copper(II) ion is best described as distorted square pyramidal, CuN_2O_3: two oxygen atoms of the bridging hydroxo groups and two nitrogen atoms of the bipyridyl ligand comprise the basal plane whereas an oxygen atom of the trifluoromethanesulfonate anion occupies the axial position. The four equatorial bonds to copper(II) ion occur in two sets as observed in other hydroxo-bridged (2,2′-bipyridine)copper(II) complexes:[7–11] the copper to hydroxo-bridge oxygen [1.917(3)–1.933(3) Å] and the

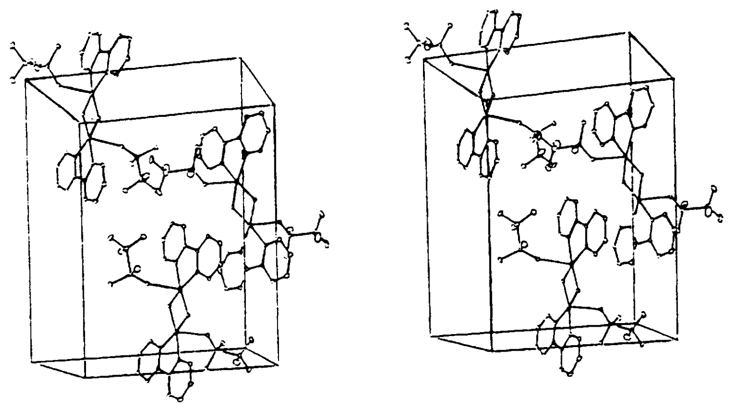

Fig. 2 Stereoscopic view of the unit cell of [$Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2$] down the *a* axis (the *c* axis is vertical)

Table 1 Summary of crystal data, intensity-data collection and structure refinement for [$Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2$]

Formula	$C_{22}H_{18}Cu_2F_6N_4O_8S_2$
M	771.6
Space group	$P\bar{1}$
a/Å	8.165(2)
b/Å	14.265(2)
c/Å	18.748(5)
α/°	93.10(1)
β/°	100.58(2)
γ/°	99.17(1)
U/Å^3	2111(2)
Z	3
D_c/g cm^{-3}	1.82
F(000)	1158
μ(Mo-Kα)/cm^{-1}	11.8
Range of transmission factors	0.73–1.00
Crystal size/mm	0.65 × 0.50 × 0.40
Scan type	ω–2θ
Scan width	1.2 + 0.34 tan θ
θ range/°	1–25
No. of measured reflections	7062
No. of unique reflections[a]	5872
No. of refined parameters	679
$R\{=[\Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|]\}$	0.041
$R'\{=[\Sigma(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}\}$[b]	0.042

[a] $I \geqslant 3\sigma(I)$. [b] Unit weights.

copper to bipyridine nitrogen [1.986(4)–2.006(4) Å]. They are shorter than the axial distances [2.418(3)–2.453(4) Å]. The four equatorial atoms at each copper atom are coplanar [O(1)O(2)N(3)N(4) plane] or practically coplanar with deviations from the least-squares planes lower than ±0.033 Å [O(1)O(2)N(1)N(2) and O(3)O(3^{I})N(5)N(6) planes]. In this latter case the dihedral angle between the mean basal planes is 2.1°. However, the copper atom is displaced by 0.161, 0.124 and 0.158 Å, respectively towards the apex. It is worthwhile noting that different values of the θ angle are exhibited by the two dimeric complexes: 97.7(1), 96.9(1) and 98.5(1)° for Cu(1)–O(1)–Cu(2), Cu(1)–O(2)–Cu(2) and Cu(3)–O(3)–Cu(3^{I}), respectively. These structural features are at the heart of the different magnitude of the exchange coupling observed for the two dinuclear entities (see below).

The six-membered rings of the outer bipyridine ligand are planar as expected with deviations from the mean planes not greater than ±0.010 Å. Nevertheless, they form a small dihedral angle ranging from 6.0 to 1.7°. These features have also been observed in other bipyridine-containing copper(II) complexes.[7–11] Average carbon–carbon and -nitrogen bond lengths are close to those reported for unco-ordinated 2,2′-bipyridine.[17] The significant deviation of the N–Cu–N angle [80.9(2)–81.5(2)°] from the ideal value (90°) is due to steric requirements of a bipyridine ring ligand.

The structure contains unidentate trifluoromethanesulfonate anions. They are semi-co-ordinated as expected from its poor co-ordination ability.[18] The bonding parameters for the $CF_3SO_3^-$ ligand are very close to those found for previously reported unidentate co-ordinated triflate groups.[19–21] In the present case these anions exhibit a staggered-ethane conformation about the S–C bond. The values of the O–S–O angles are greater than the C–S–O ones as predicted on the basis of bond-pair repulsions dealing with S–O and S–C regions. The mean value of the S–O bond length involving the oxygen atom bound to copper (1.435 Å) is somewhat longer than the average value of those concerning the terminally bound oxygen atoms (1.424 Å).

Hydrogen bonding occurs between hydroxo groups and oxygen atoms of the triflate anions as shown by the contact distances at the end of Table 3. The intramolecular copper–copper distances [2.8917(7) and 2.920(1) Å for Cu(1) ··· Cu(2) and Cu(3) ··· Cu(3^{I}), respectively] are much smaller than the shortest intermolecular distance [5.978(1) Å for Cu(2) ··· Cu(2^{V}). V being the symmetry operation −*x*, 1 − *y*, 2 − *z*].

Infrared and ESR Spectra.—The high-frequency side of the IR spectrum of the [$Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2$] complex consists of a sharp medium-intensity peak centred at 3530 cm^{-1} which can be unambiguously assigned to the OH stretch of the bridging hydroxo groups.[22] This feature together with the occurrence of the OH bending vibration which appears at 970 cm^{-1} as a weak absorption support the presence of the $Cu(OH)_2Cu$ unit[23] as evidenced by X-ray diffraction data. The ring C–C and C–N vibrations of co-ordinated 2,2′-bipyridine[24] are observed at *ca.* 1600, 1500, 1475 and 1450 cm^{-1} as sharp medium-intensity peaks. This chelating situation is also inferred from the splitting of the out-of-plane C–H bending vibrations at *ca.* 750 cm^{-1}.[25] As far as the triflate group is concerned, the number of its IR bands indicates lowering of symmetry from C_{3v} to C_s as expected for unidentate sulfonate co-ordination. In C_{3v} symmetry six infrared-active bands (3E and $3A_1$) are expected for this group, while in C_s the E modes are split and nine peaks would occur.[18,19] In fact, ν_4 (E) is clearly split by 40 cm^{-1} (two SO_3 stretching modes at 1290 and 1250 cm^{-1} as strong absorptions) and ν_5 (E) is only slightly split (two SO_3 deformation modes at 530 and 520 cm^{-1} as a shoulder and a strong peak, respectively), whereas no splitting is observed for ν_1 (A_1) 1035s, ν_2 (A_1) 760w and ν_3 (A_1) 635s cm^{-1}.

The powder ESR spectrum of the compound up to 12 000 G and at 105 K is shown in Fig. 3. It exhibits eight features at 1690, 3213, 5300, 5900, 6760, 8531, 10 700 and 11 500 G. The second one is most likely due to a diluted copper(II) impurity. Unfortunately, we are unable to offer conclusive evidence to support this assignment, but the temperature dependence agrees

Table 2 Final atomic coordinates for $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$ with standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.049 45(7)	0.716 25(4)	0.783 83(3)	C(1)	0.301 2(6)	0.892 1(4)	0.780 5(3)
Cu(2)	−0.029 62(7)	0.677 69(4)	0.924 67(3)	C(2)	0.389 4(7)	0.960 6(4)	0.746 3(4)
Cu(3)	−0.022 55(7)	1.024 55(4)	0.573 78(3)	C(3)	0.364 4(7)	0.955 3(4)	0.672 6(4)
S(1)	0.388 4(2)	0.567 82(9)	0.754 30(7)	C(4)	0.247 3(7)	0.881 6(4)	0.632 3(3)
S(2)	−0.344 0(1)	0.803 03(9)	0.973 35(7)	C(5)	0.159 2(6)	0.815 2(3)	0.668 7(3)
S(3)	−0.353 7(1)	1.161 12(9)	0.581 72(7)	C(6)	0.026 6(6)	0.736 1(3)	0.632 0(3)
F(1)	0.410 3(6)	0.482 7(3)	0.630 5(2)	C(7)	−0.027 4(8)	0.720 1(4)	0.557 7(3)
F(2)	0.292 3(8)	0.605 4(4)	0.621 2(2)	C(8)	−0.152 4(9)	0.642 9(5)	0.530 4(3)
F(3)	0.159 7(6)	0.477 1(4)	0.647 5(3)	C(9)	−0.221 5(8)	0.584 7(5)	0.576 2(3)
F(4)	−0.106 8(6)	0.939 4(3)	1.039 4(3)	C(10)	−0.165 0(7)	0.603 4(4)	0.650 4(3)
F(5)	−0.276 2(6)	0.981 7(3)	0.949 7(2)	C(11)	−0.285 7(6)	0.505 2(3)	0.931 0(3)
F(6)	−0.354 1(8)	0.957 2(3)	1.051 0(3)	C(12)	−0.367 4(7)	0.433 6(4)	0.965 3(4)
F(7)	−0.310(1)	1.319 1(4)	0.520 8(4)	C(13)	−0.322 2(7)	0.433 1(4)	1.039 0(4)
F(8)	−0.149(1)	1.319 8(4)	0.619 9(5)	C(14)	−0.197 2(7)	0.503 5(4)	1.077 4(3)
F(9)	−0.403(1)	1.330 7(3)	0.617 3(4)	C(15)	−0.120 3(6)	0.573 2(3)	1.041 0(3)
O(1)	0.127 4(4)	0.763 9(2)	0.883 9(2)	C(16)	0.016 5(6)	0.651 3(3)	1.076 2(2)
O(2)	−0.109 3(4)	0.629 3(2)	0.823 8(2)	C(17)	0.083 6(8)	0.665 4(5)	1.150 3(3)
O(3)	−0.117 1(4)	0.929 4(2)	0.494 0(2)	C(18)	0.213(1)	0.740 2(6)	1.175 9(4)
O(4)	0.542 1(5)	0.630 1(4)	0.755 4(3)	C(19)	0.272 9(9)	0.799 0(5)	1.128 5(4)
O(5)	0.257 7(5)	0.611 3(3)	0.777 1(2)	C(20)	0.202 3(7)	0.784 5(4)	1.055 8(3)
O(6)	0.410 3(7)	0.479 5(3)	0.785 5(3)	C(21)	−0.247 4(7)	0.881 9(4)	0.638 6(3)
O(7)	−0.326 8(5)	0.755 6(3)	1.038 6(2)	C(22)	−0.302 2(8)	0.836 5(4)	0.695 5(4)
O(8)	−0.233 0(5)	0.783 6(3)	0.925 7(2)	C(23)	−0.234 4(9)	0.875 7(5)	0.765 8(4)
O(9)	−0.513 2(5)	0.804 4(3)	0.937 2(3)	C(24)	−0.119 7(8)	0.958 2(5)	0.777 2(3)
O(10)	−0.337 9(5)	1.143 2(3)	0.656 5(2)	C(25)	−0.067 4(6)	1.001 8(4)	0.718 6(3)
O(11)	−0.227 2(4)	1.131 0(3)	0.545 8(2)	C(26)	0.056 2(6)	1.089 6(4)	0.723 8(3)
O(12)	−0.520 6(5)	1.138 3(4)	0.540 5(3)	C(27)	0.130 4(9)	1.146 4(5)	0.787 7(3)
N(1)	0.187 5(5)	0.820 5(3)	0.742 0(2)	C(28)	0.244 2(9)	1.227 1(5)	0.785 7(4)
N(2)	−0.042 7(5)	0.678 1(3)	0.678 0(2)	C(29)	0.287 9(8)	1.249 9(5)	0.720 7(4)
N(3)	−0.164 2(4)	0.574 3(3)	0.968 0(2)	C(30)	0.210 9(7)	1.191 6(4)	0.658 7(3)
N(4)	0.077 0(5)	0.711 2(3)	1.029 7(2)	C(31)	0.307 8(8)	0.530 5(5)	0.659 1(3)
N(5)	−0.133 4(5)	0.961 1(3)	0.649 9(2)	C(32)	−0.266 8(9)	0.927 1(4)	1.004 8(4)
N(6)	0.097 9(5)	1.112 5(3)	0.659 8(2)	C(33)	−0.305(1)	1.290 0(6)	0.584 5(6)

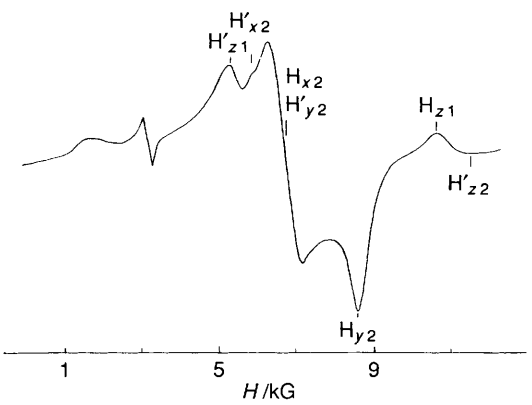

Fig. 3 X-Band powder ESR spectrum of $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$ at 105 K. Primed transitions belong to one triplet state

with it. The absolute intensities of the other seven features quickly diminish when the sample is heated confirming the triplet nature of the ground state. Any band below the impurity peak at 3213 G results from either the $\Delta M_s = \pm 2$ or the low-field parallel transitions. As we have not observed with our spectrometer any peak except the one at 1690 G at low field, we assumed that this feature corresponds to the $\Delta M_s = \pm 2$ transitions. The occurrence of other peaks at high field indicates that the axial zero-field splitting parameter D is larger than the incident quantum (*ca.* 0.3 cm^{-1}) as previously observed for other copper triplet states with $|D| > h\nu$.[1,26–30] To interpret the spectrum quantitatively, we made two assumptions. First, it was assumed that Wasserman's equations[31] were valid, *i.e.* that the D and g tensor axes were coincident. Secondly, we assumed that the observed ESR spectrum corresponds to the overlapping of two triplet spectra arising from the asymmetric and centrosymmetric dinuclear copper(II) complexes which coexist in the unit cell. In the present case only one attribution leads to reasonable values for the principal g tensors with $g_x = 2.09$, $g_y = 2.01, g_z = 2.20, |D| = 1.41$ cm^{-1}, and $E = 0.028$ cm^{-1} for a first block of transitions (6760, 8531 and 10 700 G corresponding to H_{x2}, H_{y2} and H_{z1}, respectively) and $g_x = 2.07, g_y = 2.01$, $g_z = 2.20$, $|D| = 0.87$ cm^{-1}, and $E = 0.015$ cm^{-1} for a second group (5300, 5900, 6760 and 11 500 G corresponding to H_{z1}, H_{x2}, H_{y2} and H_{z2}, respectively). The agreement between experimental and calculated fields is then excellent as shown in Table 4. The zero-field splitting within the triplet state has two origins, namely the magnetic dipole interaction and the anisotropic exchange interaction.[32] In both cases the $|D|$ value is much larger than it would be if only the dipolar interaction were operative. A trend to a decrease of $|D|$ on increasing the copper–copper intramolecular separation has been observed for hydroxo, alkoxo and N-oxo bridges.[6,33] In our case, the small difference between the intramolecular copper–copper separation (0.03 Å) of the dimeric units does not allow us to establish a unambiguous correspondence between $|D|$ (1.41 and 0.87 cm^{-1}) and g values (2.10 and 2.09).

Magnetic Properties.—The magnetic behaviour of the compound is shown in Fig. 4 in the form of a $\chi_M T$ *vs.* T plot, χ_M being the magnetic susceptibility per two copper(II) ions and T the temperature. At room temperature $\chi_M T = 0.93$ cm^3 K mol^{-1}, a value somewhat higher than expected for two uncoupled copper(II) ions; $\chi_M T$ increases upon cooling, reaching a value of 1.10 cm^3 K mol^{-1}. This behaviour is characteristic of a ferromagnetic interaction with a high-spin ground state. Keeping in mind that the unit cell contains three dinuclear entities, two of them asymmetrical and identical and the other centrosymmetrical, we interpret the magnetic behaviour in terms of a simple Bleaney–Bowers equation (1) where N, β, k, g

Table 3 Selected interatomic distances (Å) and bond angles (°) for $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$ with e.s.d.s in parentheses

Asymmetric dimer		Centrosymmetric dimer	
Cu(1)–O(1)	1.917(3)	Cu(3)–O(3)	1.922(3)
Cu(1)–O(2)	1.931(3)	Cu(3)–O(3^I)[a]	1.932(3)
Cu(1)–N(1)	2.002(4)	Cu(3)–N(5)	2.006(4)
Cu(1)–N(2)	2.001(4)	Cu(3)–N(6)	1.986(4)
Cu(1)–O(5)	2.453(4)	Cu(3)–O(11)	2.438(3)
Cu(2)–O(1)	1.923(3)		
Cu(2)–O(2)	1.933(3)		
Cu(2)–N(3)	1.996(4)		
Cu(2)–N(4)	2.001(4)		
Cu(2)–O(8)	2.418(3)		
O(1)–Cu(1)–O(5)	97.6(1)	O(3)–Cu(3)–N(5)	97.9(1)
O(1)–Cu(1)–O(2)	82.8(1)	O(3)–Cu(3)–O(3^I)	81.5(1)
O(1)–Cu(1)–N(1)	96.5(1)	O(3)–Cu(3)–O(11)	97.5(1)
O(1)–Cu(1)–N(2)	174.3(2)	O(3)–Cu(3)–N(6)	172.6(2)
O(2)–Cu(1)–O(5)	97.6(1)	O(3^I)–Cu(3)–N(6)	97.7(2)
O(2)–Cu(1)–N(2)	98.6(1)	O(3^I)–Cu(3)–O(11)	96.1(1)
O(2)–Cu(1)–N(1)	170.9(2)	O(3^I)–Cu(3)–N(5)	168.9(1)
N(1)–Cu(1)–N(2)	81.2(2)	N(5)–Cu(3)–O(11)	95.0(1)
Cu(1)–O(1)–Cu(2)	97.7(1)	N(5)–Cu(3)–N(6)	81.5(2)
Cu(1)–O(2)–Cu(2)	96.9(1)	N(6)–Cu(3)–O(11)	90.0(1)
O(1)–Cu(2)–O(8)	95.5(1)	Cu(3)–O(3)–Cu(3^I)	98.5(1)
O(1)–Cu(2)–O(2)	82.6(1)		
O(1)–Cu(2)–N(4)	97.8(1)		
O(1)–Cu(2)–N(3)	170.6(1)		
O(2)–Cu(2)–O(8)	95.4(1)		
O(2)–Cu(2)–N(3)	97.2(1)		
O(2)–Cu(2)–N(4)	170.5(2)		
N(3)–Cu(2)–N(4)	80.9(2)		

A[b]	D[c]	H	A···D	A···H–D
O(1)	O(9^{II})	H(100)	2.874(5)	172(8)
O(2)	O(4^{III})	H(200)	2.902(6)	169(6)
O(3)	O(12^{IV})	H(300)	2.902(6)	164(6)

[a] Symmetry translations: I $-x, 2-y, 1-z$; II $1+x, y, z$; III $x-1, y, z$; IV $-x-1, -y+2, -z+1$. [b] Acceptor atom. [c] Donor atom.

Table 4 Observed and calculated magnetic fields for the two triplets of the ESR spectrum of $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$

	Magnetic field/G			Magnetic field/G	
Resonance	Exptl.	Calc.	Resonance	Exptl.	Calc.
H_{x2}	6 760	6 751	H_{z1}	5 300	5 387
H_{y2}	8 531	8 532	H_{x2}	5 900	5 924
H_{z1}	10 700	10 672	H_{y2}	6 760	6 791
H_{z2}	—	16 728	H_{z2}	11 500	11 450

$$\chi_M T = \frac{4N\beta^2 g_a^2}{3k}[3 + \exp(-J_a/kT)]^{-1} + \frac{2N\beta^2 g_c^2}{3k}[3 + \exp(-J_c/kT)]^{-1} \quad (1)$$

and T have their usual meanings and J is the singlet–triplet energy gap. Subscripts a and c refer to the asymmetrical and centrosymmetrical dinuclear complexes, respectively. The J_a and J_c values were determined by minimizing the reliability factor $R = \Sigma_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\Sigma_i[(\chi_M T)_{obs}(i)]^2$ and found to be 158 and 17 cm^{-1}, respectively; R is then equal to 4.69×10^{-5} showing that a good fit is obtained. The values of the g factors from the ESR spectrum (2.10 and 2.09) were used as fixed parameters in the fitting. Nearly identical J_a, J_c and R values were obtained when the g_a and g_c values were exchanged in the fitting.

Both techniques, magnetic susceptibility measurements and ESR spectroscopy, reveal that the nature of the exchange coupling in $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$ is ferromagnetic. In Table 5 we have gathered the reported structural and magnetic data for dihydroxo-bridged (2,2 -bipyridine)copper(II) complexes. All the cases cited exhibit a triplet groupd state and are examples of the so-called accidental orthogonality[5] of the magnetic orbitals φ_A and φ_B from each copper(II) ion within the binuclear units: (*i*) the overall overlap integral $S = \langle\varphi_A|\varphi_B\rangle$ is ≈ 0 for the given Cu_A–O–Cu_B angles; (*ii*) the short Cu–O(bridge) distance favours large spin delocalization on the oxygen bridges, leading to a large density overlap $\varphi_A\varphi_B$ in the bridge surroundings. Consequently, the singlet–triplet energy gap which is given by expression (2) [where j is the two-electron

$$J = 2j + 4\beta S \quad (2)$$

exchange integral $\langle\varphi_A(1)\varphi_B(2)|e^2/r_{12}|\varphi_A(2)\varphi_B(1)\rangle$ and β is the one-electron resonance integral $\langle\varphi_A(1)|h|\varphi_B(1)\rangle$ in which h is the one-electron Hamiltonian of electron 1] tends to $2j$ which is always positive.

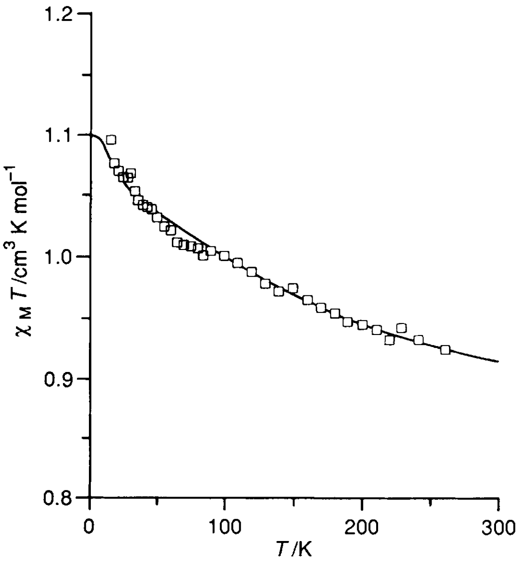

Fig. 4 Temperature dependence of $\chi_M T$ for $[Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2]$: (□) experimental data; (—) calculated curve per two copper(II) ions (see text)

The copper(II) ions of the asymmetric dimer as well as those of the centrosymmetric ones are ferromagnetically coupled. However, the values of the interaction are markedly different: relatively strong for the former and weak for the latter. This lowering of the value of J is as expected according to the increasing value of θ when going from asymmetric to the centrosymmetric complex. The most striking feature is the fact that a ferromagnetic coupling is observed for θ > 97.5°. Table 5 provides other cases of deviation of the J values from the predicted ones by applying Hatfield's linear correlation.[1,2] The deviations from planarity of the $Cu(OH)_2Cu$ network, small variances in the Cu–O(bridge) distances and spin-density changes induced by the bonding of the counter ion are the origin of them.

We conclude with a brief comment on the determinant role of the counter ion from a magnetostructural point of view. Two aspects are very important: (*i*) the great variety of counter ions facilitates the isolation of charged polynuclear compounds both as polycrystalline powdered samples and single crystals, and (*ii*) the counter ion is used to separate the polynuclear entities in order to minimize the intermolecular interactions. However, the counter ion can act as a ligand in spite of its poor coordinating ability, and cause unexpected structural modifications which can affect dramatically the magnetic properties. The series of dihydroxo complexes in Table 5 exemplifies this non-innocent role: the perchlorate and sulfate complexes are

Table 5 Structural data and isotropic exchange parameters for hydroxo-bridged (2,2′-bipyridine)copper(II) complexes[a]

Compound	Cu–O/Å	Cu · · · Cu/Å	Cu–O–Cu/°	OCuO/OCuO/°	J/cm^{-1}	Ref.
$Cu_2(bipy)_2(OH)_2(NO_3)_2$	1.922	2.847	95.6	0.0	+172	1, 7
$Cu_2(bipy)_2(OH)_2(C_4O_4)\cdot 4H_2O$	1.927	2.870	96.4	0.0	+145	10
$Cu_2(bipy)_2(OH)_2(ClO_4)_2$	1.918	2.871	96.9	0.0	+93	1, 9
$Cu_2(bipy)_2(OH)_2(CF_3SO_3)_2$	1.927	2.920	98.5	0.01	+17	This work
	(1.926)[b]	(2.8917)	(97.3)	(0.13)	(+158)	This work
$Cu_2(bipy)_2(OH)_2(SO_4)\cdot 5H_2O$	1.939	2.893	96.5	6.1	+49	1, 8
$Cu_2(bipy)_2(OH)_2(PF_6)_2$	1.953	2.914	96.5	16.5	+12	11

[a] Average bond distances and angles are given for each structure. [b] Values in parentheses refer to the asymmetric dimer.

made up of isolated $[Cu_2(bipy)_2(OH)_2]^{2+}$ entities together with 1,2-bisunidentate perchlorate and unidentate sulfate respectively; the nitrate and squarate (3,4-dihydroxycyclobut-3-en-1,2-dionate) complexes consist of one-dimensional arrangements of $[Cu_2(bipy)_2(OH)_2]^{2+}$ entities, the squarate acting as a 1,3-bis(unidentate) ligand and the nitrate linking a copper atom of a dinuclear unit with a hydroxo group of another unit through two of its oxygen atoms. A tetranuclear hydroxo-bridged copper(II) cluster of the cubane type is obtained when using hexafluorophosphate as counter ion. Finally, the structure reported herein provides a more exotic example: the same counter ion (triflate anion) acting as a unidentate ligand is able to yield two complexes with the same formula which coexist in the same single crystal and exhibit very different ferromagnetic couplings.

Prior to this work and in the light of the available data in Table 5, one might think that the θ value and the planarity of the $Cu(OH)_2Cu$ network were determined by the nature of the counter ion. However, the results reported herein rule out this, because even with a given counter ion different θ values can be achieved in complexes with identical composition.

Related rare situations caused by the counter ion have been observed by some of us in oxalato[34] and oxamidato[35] copper(II) complexes.

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