Formation in Solution, Preparation, Crystal Structure and Magnetic Characterization of Di-μ-hydroxo-bis[diaqua(2,2′-bipyrimidine)copper(II)] Diperchlorate Dihydrate†

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A new binuclear complex of formula $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2{\cdot}2H_2O$ (bipym = 2,2′-bipyrimidine) has been synthesised and its crystal structure determined by X-ray crystallographic methods. It crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.021(1)$, $b = 10.004(1)$, $c = 10.721(1)$ Å, $\alpha = 100.83(1)$, $\beta = 95.80(1)$, $\gamma = 99.05(1)^\circ$ and $Z = 1$. Least-squares refinement of 2888 reflections with $I > 3\sigma(I)$ and 256 parameters gave a final $R' = 0.0522$. The structure consists of discrete centrosymmetric di-μ-hydroxo-copper(II) dimers with 2,2′-bipyrimidine as outer ligand, weakly co-ordinated and crystallization water molecules, and unco-ordinated perchlorate anions. The co-ordination geometry around each copper(II) ion is approximately elongated tetragonal octahedral with the two bridging hydroxo groups and two nitrogen atoms of bipym building the equatorial plane and two water molecules occupying the axial positions. The Cu(1)–OH–Cu(1a) bridging angle and the intramolecular Cu(1)···Cu(1a) separation are 95.0(1)° and 2.870(1) Å, respectively. The temperature dependence of the magnetic susceptibility, studied in the range 300–4 K, shows a relatively strong intramolecular ferromagnetic coupling (+147 cm^{-1} for the singlet–triplet energy gap). Further evidence for the triplet ground state is provided by the variable-temperature ESR spectra. The strength of the exchange interaction is discussed on the basis of the structural features and correlated with reported magneto-structural data on parent double hydroxide-bridged copper(II) complexes. The formation of hydroxo complexes of $[Cu(bipym)(H_2O)]^{2+}$ has been investigated by potentiometry in aqueous solutions [equation (i); $\log K_1 = -10.350(1)$ (25 °C, 0.1 mol dm^{-3} $NaNO_3$)].

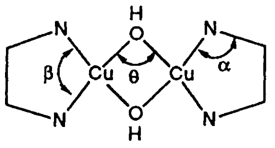
$$2[Cu(bipym)(H_2O)_2]^{2+} \overset{K_1}{\rightleftharpoons} [Cu_2(bipym)_2(OH)_2]^{2+} + 2H^+ + 2H_2O \qquad \text{(i)}$$

The value of this stability constant is compared to those reported for related $Cu^{II}L$ complexes where L are bidentate N-donor ligands.

A lot of work has been devoted to the magneto-structural characterization of di-μ-hydroxo-copper(II) complexes in the last fifteen years.[1] For this family of complexes, it has been found that the singlet–triplet energy gap (J) varies linearly with the Cu–OH–Cu bridging angle (θ) according to equation (1) for

$$J = -74.53\,\theta\,(cm^{-1}\,deg^{-1}) + 7270\,cm^{-1} \qquad (1)$$

θ values not far from 90°. From this equation, singlet and triplet ground states are predicted for θ > 97.5° and θ < 97.5°, respectively. These studies have revealed that the value of θ in the complexes $[LCu(OH)_2CuL]^{2+}$ is strongly influenced by the nature of the terminal ligands and the co-ordination of solvent molecules and counter ions. So, for instance the magnetic coupling in the di-μ-hydroxo-copper(II) complexes $[LCu(OH)_2CuL]^{2+}$ is found to be antiferromagnetic (L = diamine)[2–6] or ferromagnetic (L = 2,2′-bipyridine)[2,7–12] with bidentate N-donor groups as outer ligands. The co-ordination to copper(II) ion of sp^3-hybridized nitrogen atoms (see Scheme 1) for end-cap diamines and of sp^2 hybridization for 2,2′-bipyridine is at the heart of the different nature of the exchange coupling. The larger the angle C–N–Cu (α) the shorter is the angle N–Cu–N (β), and consequently θ is decreased favouring the ferromagnetic coupling. In this context it seems very interesting to use derivatives of 2,2′-bipyridine as outer ligands, to play on the value of θ and tune the magnitude of ferromagnetic coupling.



Scheme 1

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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, emu = SI × $10^6/4\pi$.

Table 1 Crystallographic data for $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2 \cdot 2H_2O$

Formula	$C_{16}H_{26}Cl_2Cu_2N_8O_{16}$
M	784.4
Space group	$P\bar{1}$
a/Å	7.021(1)
b/Å	10.004(1)
c/Å	10.721(1)
α/°	100.83(1)
β/°	95.80(1)
γ/°	99.05(1)
U/Å^3	723.8(2)
Z	1
D_c/g cm^{-3}	1.80
$F(000)$	398
Crystal size/mm	0.14 × 0.45 × 0.39
μ(Mo-Kα)/cm^{-1}	17.4
Scan method	ω–2θ
2θ range/°	3–54
No. of collected reflections	3488
No. of unique reflections	3172
No. of independent reflections[a]	2888
No. of refined parameters	256
$R\{=[\Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\Sigma\lvert F_o\rvert]\}$	0.0418
$R'\{=[\Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}\}$	0.0522
S[b]	1.37

[a] $I > 3\sigma(I)$. [b] Goodness of fit $= [\Sigma w(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)^2/(N_o - N_p)]^{\frac{1}{2}}$.

It is the purpose of this paper to present our first contribution along this line. Herein we report the synthesis, crystal structure and magnetic properties of the first di-μ-hydroxo-bridged copper(II) complex of formula $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2 \cdot 2H_2O$ containing 2,2′-bipyrimidine (bipym) as outer ligand. The formation of hydroxo complexes of $[Cu(bipym)]^{2+}$ in aqueous solution is also reported.

Experimental

Materials.—All reagents were commercial grade materials and were used without further purification. 2,2′-Bipyrimidine (bipym) was purchased from Aldrich; 2,2′-bipyridylcopper(II) nitrate was prepared by a previously reported procedure.[13] Carbonate-free NaOH standardized against dried potassium hydrogenphthalate was used as titrant. In order to get a carbon dioxide-free system, presaturated argon was bubbled through the solutions during the course of the titrations. All potentiometric measurements were made at a temperature of 25.0 ± 0.1 °C and the ionic strength was maintained constant by using an electrolyte medium of 0.1 mol dm^{-3} $NaNO_3$.

Preparation of $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2 \cdot 2H_2O$.—2,2′-Bipyrimidine (1 mmol) dissolved in a minimum amount of ethanol was added to an aqueous solution (80 cm^3) containing copper(II) perchlorate hexahydrate (1 mmol) yielding a blue-turquoise solution. Its colour turned dark blue-greenish by slow addition of solid sodium carbonate (0.5 mmol) and a slight precipitate appeared. Nice dark blue rods of $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2 \cdot 2H_2O$ were grown by slow evaporation of the filtered solution at room temperature. They were filtered off, washed with cold water and ethanol and stored over calcium chloride (Found: C, 24.45; H, 3.05; N, 14.15. Calc. for $C_{16}H_{26}Cl_2Cu_2N_8O_{16}$: C, 24.50; H, 3.30; N, 14.30%).

Physical Techniques.—The infrared spectrum was taken on a Perkin-Elmer 1750 spectrophotometer as KBr pellets in the 4000–225 cm^{-1} region. Variable-temperature X-band ESR spectra were recorded on polycrystalline samples with a Brüker ER 200D spectrometer equipped with a nitrogen cryostat. Magnetic susceptibility measurements were carried out at 300–4.2 K with a previously described pendulum-type apparatus.[14] 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 from Pascal's constants[15] to be −398 × 10^{-6} emu mol^{-1} and the temperature independent paramagnetism (60 × 10^{-6} cm^3 mol^{-1} per Cu^{II}). Potentiometric titrations were performed using the equipment (burette, stirrer, electrode, pH meter, microcomputer, *etc.*) and following the experimental procedure which was described elsewhere.[16] A 70 cm^3 water-jacketed four-neck flask designed to accommodate a microburette delivery tube, argon inlet and outlet tubes, and a glass combined electrode was used as titration cell. The equilibrium constants for the reaction of $[Cu(bipym)(H_2O)_2]^{2+}$ and OH^- were determined by titrating aqueous solutions of $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2 \cdot 2H_2O$ (previously acidified with HNO_3 to pH 4). For the sake of comparison, the formation of hydroxo complexes of $[Cu(bipy)(H_2O)_2]^{2+}$ was reinvestigated by titrating aqueous solutions of (2,2′-bipyridyl)copper(II) nitrate with NaOH. The initial concentration of copper(II), c_M, was varied in the range (0.959–2.57) × 10^{-2} mol dm^{-3}. The sets of e.m.f. data from different experiments for each system, carried out in the pH range 4.0–8.0, were merged and treated simultaneously by the computer program SUPERQUAD[17] to determine the equilibrium constants involved in the hydroxo complex formation (see below). E.m.f. data from the pH ranges 5.4–7.2 and 5.9–7.0 for bipym and bipy systems respectively, were considered in the last refinement cycle.

Crystallography.—Diffraction data for $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2 \cdot 2H_2O$ were collected at 298 K with a Siemens R3m/V automatic diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Information concerning crystallographic data collection and structure refinement is summarized in Table 1. The unit-cell parameters were derived from least-squares refinement of the setting angles of 25 reflections in the 2θ range 14–30°. 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 every 100 reflections, showed no substantial intensity decay. A total of 3488 reflections were collected by the variable-speed ω–2θ scan method in the 2θ range 3–54° with index ranges $0 \leqslant h \leqslant 8$, $-12 \leqslant k \leqslant 12$, $-13 \leqslant l \leqslant 13$; 3172 of them were unique, and from these, 2888 were assumed as observed [$I > 3\sigma(I)$] and used for the structure refinement. Lorentz-polarization and ψ-scan absorption corrections,[18] but no extinction correction, were applied to the intensity data.

The structure was solved by Patterson methods with the SHELXTL PLUS program[19] followed by successive Fourier syntheses and full-matrix least-squares refinements based on $|F_o|$. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms of the water molecules were located on a ΔF map and refined with constraints. All other hydrogen atoms were placed in calculated positions and refined as riding atoms. A common fixed isotropic thermal parameter was assigned to all hydrogen atoms. On the difference map several possible oxygen positions were localized due to different coexistent orientations of the perchlorate anion. This disorder was described by assigning population parameters of 0.7 and 0.3 to each pair of sites. The number of reflections/number of variable parameters was 11.3. The final values of the discrepancy indices R and R' were 0.0418 and 0.0522, respectively; $\Sigma w(||F_o| - |F_c||)^2$ was minimized where $w = 1/[\sigma^2(F_o) + 0.002\,421(F_o)^2]$ with $\sigma^2(F_o)$ from counting statistics. In the final difference map the residual maxima and minima were 0.99 and −0.58 e Å^{-3}, respectively. Atomic scattering factors and corrections for anomalous dispersion for Cu and Cl atoms were taken from ref. 20. All calculations were carried out on a micro-Vax II

Table 2 Final atomic coordinates for $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2 \cdot 2H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.0867(1)	0.3838(1)	1.0202(1)
O(1)	0.0411(3)	0.4812(2)	0.8817(2)
O(2)	0.3959(4)	0.5274(3)	1.0972(3)
O(3)	−0.2601(5)	0.2343(3)	0.9456(4)
O(4)	0.3675(6)	0.6327(7)	0.7879(4)
N(1)	0.1913(3)	0.2276(2)	0.9171(2)
C(1)	0.2227(5)	0.2108(3)	0.7938(3)
C(2)	0.2784(5)	0.0914(4)	0.7345(3)
C(3)	0.2969(5)	−0.0073(3)	0.8039(3)
N(3)	0.2691(4)	0.0085(2)	0.9273(3)
C(4)	0.2197(3)	0.1266(3)	0.9784(3)
C(5)	0.1937(4)	0.1566(3)	1.1163(3)
N(4)	0.2329(4)	0.0653(3)	1.1863(3)
C(6)	0.2186(6)	0.1009(4)	1.3095(4)
C(7)	0.1645(6)	0.2247(4)	1.3634(3)
C(8)	0.1196(5)	0.3095(3)	1.2834(3)
N(2)	0.1353(3)	0.2741(2)	1.1568(2)
Cl(1)	−0.2844(2)	0.2757(1)	0.5585(1)
O(5)[a]	−0.4473(11)	0.3386(10)	0.6125(8)
O(6)[a]	−0.3745(14)	0.1486(7)	0.4919(8)
O(7)[a]	−0.2183(20)	0.3648(13)	0.4860(12)
O(8)[a]	−0.1512(21)	0.2821(13)	0.6568(10)
O(5′)[b]	−0.1523(40)	0.1537(23)	0.5323(23)
O(6′)[b]	−0.3354(69)	0.2731(37)	0.6638(27)
O(7′)[b]	−0.0905(27)	0.3718(16)	0.5939(24)
O(8′)[b]	−0.3465(40)	0.2560(27)	0.4383(17)

[a] Atom with a population parameter of 0.7. [b] Atom with a population parameter of 0.3.

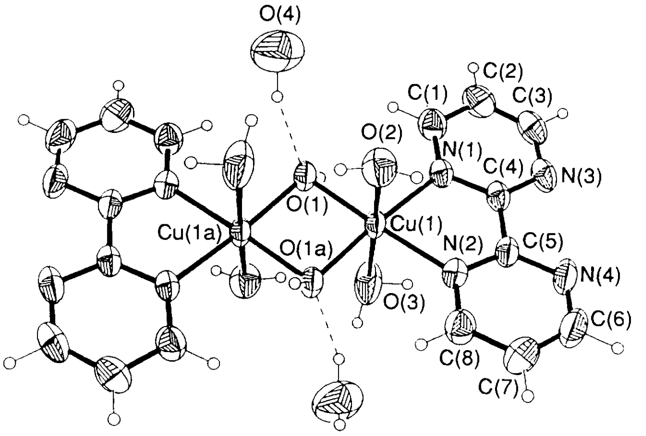

Fig. 1 ORTEP drawing of the cationic unit $[Cu_2(bipym)_2(H_2O)_4(OH)_2]^{2+}$ showing the atom labelling. Thermal ellipsoids are drawn at 30% probability level

computer, using the SHELXTL and PARST[21] program package. The molecular plot was drawn with the SHELXTL PLUS program. The final atomic coordinates for non-hydrogen atoms and selected bond lengths and angles are listed in Tables 2 and 3.

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

Results and Discussion

Description of the Structure.—The structure is made up of cationic centrosymmetric di-μ-hydroxo-bis[diaqua(2,2′-bipyrimidine)copper(II)] dinuclear units, crystallization water molecules and unco-ordinated perchlorate anions. A perspective view of the dinuclear entity with the atom-numbering scheme is depicted in Fig. 1.

Table 3 Selected interatomic distances (Å) and bond angles (°) for $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2 \cdot 2H_2O$ with e.s.d.s in parentheses[a]

Copper environment			
Cu(1)–O(1)	1.950(2)	Cu(1)–O(1a)	1.943(2)
Cu(1)–N(2)	2.022(3)	Cu(1)–N(1)	2.020(2)
Cu(1)–O(2)	2.381(2)	Cu(1)–O(3)	2.611(3)
O(1)–Cu(1)–O(1a)	85.0(1)	O(1)–Cu(1)–N(2)	177.0(1)
O(1)–Cu(1)–N(1)	96.8(1)	O(1)–Cu(1)–O(2)	92.2(1)
O(1)–Cu(1)–O(3)	88.4(1)	O(1a)–Cu(1)–N(1)	173.4(1)
O(1a)–Cu(1)–N(2)	97.8(1)	O(1a)–Cu(1)–O(2)	90.6(1)
O(1a)–Cu(1)–O(3)	86.4(1)	N(2)–Cu(1)–N(1)	80.3(1)
N(2)–Cu(1)–O(2)	88.8(1)	N(2)–Cu(1)–O(3)	90.7(1)
N(1)–Cu(1)–O(2)	95.6(1)	N(1)–Cu(1)–O(3)	87.3(1)
Cu(1)–O(1)–Cu(1a)	95.0(1)		
2,2′Bipyrimidine			
N(1)–C(1)	1.345(4)	C(1)–C(2)	1.377(5)
C(2)–C(3)	1.357(6)	C(3)–N(3)	1.341(5)
N(3)–C(4)	1.319(4)	N(1)–C(4)	1.334(4)
C(4)–C(5)	1.487(4)	C(5)–N(4)	1.329(4)
N(4)–C(6)	1.320(5)	C(6)–C(7)	1.391(6)
C(7)–C(8)	1.363(6)	C(8)–N(2)	1.357(4)
C(5)–N(2)	1.317(4)		
Cu(1)–N(1)–C(1)	127.6(2)	Cu(1)–N(1)–C(4)	114.6(2)
C(1)–N(1)–C(4)	117.7(2)	N(1)–C(1)–C(2)	120.1(3)
C(1)–C(2)–C(3)	117.8(3)	C(2)–C(3)–N(3)	122.9(3)
C(3)–N(3)–C(4)	115.9(3)	N(1)–C(4)–N(3)	125.6(3)
N(1)–C(4)–C(5)	114.4(2)	N(3)–C(4)–C(5)	120.0(3)
C(4)–C(5)–N(4)	118.1(2)	C(4)–C(5)–N(2)	115.4(3)
N(4)–C(5)–N(2)	126.5(3)	C(5)–N(4)–C(6)	115.6(3)
N(4)–C(6)–C(7)	122.7(4)	C(6)–C(7)–C(8)	117.7(3)
C(7)–C(8)–N(2)	119.9(3)	Cu(1)–N(2)–C(5)	114.8(2)
Cu(1)–N(2)–C(8)	127.6(2)	C(5)–N(2)–C(8)	117.6(3)

Hydrogen bond[b]

A	D	H	A···D	A···H–D
O(1)	O(4)	H(6w)	2.92(1)	147(3)

[a] Atoms Cu(1a) and O(1a) are related to Cu(1) and O(1) atoms by the symmetry operation −*x*, 1 − *y*, 2 − *z*. [b] A = acceptor, D = donor atom.

The co-ordination geometry around each copper(II) ion is distorted elongated tetragonal octahedral, CuN_2O_4: the equatorial positions are occupied by the two nitrogen atoms of 2,2′-bipyrimidine and the two oxygen atoms of the bridging hydroxo groups, whereas the apical sites are filled by oxygen atoms of water molecules. The Cu–N distances, 2.020(2) and 2.022(3) Å for Cu(1)–N(1) and Cu(1)–N(2) respectively, are similar to those found in other 2,2′-bipyrimidine-containing copper(II) complexes.[22–25] The Cu–O(hydroxo bridge) distances, 1.950(2) and 1.943(2) Å for Cu(1)–O(1) and Cu(1)–O(1a) respectively, are slightly shorter but very close to those observed in parent di-μ-hydroxo-bis[(2,2′-bipyridyl)-copper(II)] complexes.[7–12] The four equatorial atoms are practically coplanar with deviations from the least-squares plane lower than 0.055 Å, the copper atom being displaced 0.064(1) Å towards the axial O(2) oxygen atom. The two Cu–O(water) axial distances, 2.381(2) and 2.611(3) Å, are much longer than the equatorial bonds. The calculated tetragonality[26] is 0.79.

The pyrimidyl rings of the outer bipyrimidine ligand are planar as expected with deviations from the mean planes not greater than 0.020 Å. However, they are not coplanar: each bypyrimidine ligand is buckled so that its outer carbon and nitrogen atoms are displaced towards the axial atoms [O(2) and O(3) respectively] of the distorted octahedral arrangement about the copper atom; the dihedral angle between

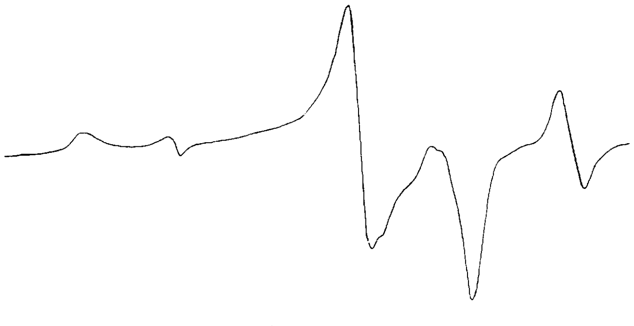

Fig. 2 X-band powder ESR spectrum of $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2{\cdot}2H_2O$ at 100 K

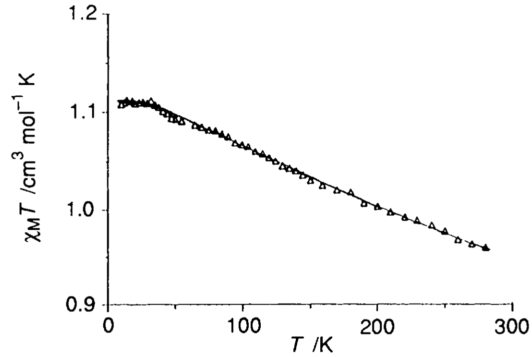

Fig. 3 Temperature dependence of $\chi_M T$ for $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2{\cdot}2H_2O$: (Δ) experimental data and (——) theoretical curve

Table 4 Observed and calculated magnetic fields for the triplet of the ESR spectrum of $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2{\cdot}2H_2O$

	Magnetic field/G	
Resonance	Exptl.	Calc.
H_{x_2}	6 586	6 583
H_{y_2}	8 616	8 606
H_{z_1}	10 565	10 506
H_{z_2}	—	16 552

the planar six-membered pyrimidyl rings is 7.1°. The bond distances and angles within the bipyrimidine ligand are in agreement with those previously reported for unco-ordinated,[27] chelating[24–25] and bis-chelating[22,23,25] 2,2′-bipyrimidine. The N(1)–Cu(1)–N(2) angle of 80.3(1)° is significantly smaller than the ideal value of 90° because of the geometrical constraints of a bipyrimidyl ring system.

Hydrogen bonding occurs between hydroxo groups and oxygen atoms of unco-ordinated water molecules as shown by the contact distances at the end of Table 3. The intramolecular copper–copper separation [2.870(1) Å for Cu(1)···Cu(1a)] is much smaller than the shortest intermolecular distance of the copper from its equivalent position $1 - x, 1 - y, 2 - z$, which is 5.993(1) Å.

Infrared and ESR Spectra.—The most relevant features of the IR spectrum of the $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2{\cdot}2H_2O$ complex are those concerning the presence of hydroxo bridges and 2,2′-bipyrimidine as outer ligand. The presence of the $Cu(OH)_2Cu$ unit is supported by the occurrence of a weak and sharp peak at 3530 cm^{-1} (bridging OH stretching) and a weak absorption at 940 cm^{-1} (OH bending vibration).[28,29] The coexistence of crystallization and co-ordinated water molecules is consistent with the occurrence of a strong and broad absorption centred at 3400 cm^{-1} (antisymmetric and symmetric OH stretching) and medium intensity peaks at 1640 cm^{-1} (HOH bending), 670 and 510 cm^{-1} (rocking and wagging frequencies of co-ordinated water). The pattern of CH stretching vibration in bipym (3210m, 3060s, 3025m and 2980m cm^{-1}) appears as three weak peaks at 3060, 3040 and 2980 cm^{-1} in the present complex. The strong ring-stretching modes of bipym (1560, 1550 cm^{-1}) are observed as two intense and sharp bands of nearly equal intensity located at somewhat higher frequencies, *ca.* 1580 and 1560 cm^{-1}. Another ring-stretching mode which appears as a strong band at 1400 cm^{-1} in bipym is also observed as a single and strong band at 1445 cm^{-1}. This shift towards higher frequencies is common to other 2,2′-bipyrimidine-containing copper(II) complexes in which the bipym acts either as a chelating[24,25] or bis-chelating[22,23,25] ligand. However, the higher frequency doublet is very asymmetric (sharp and strong absorption at 1580 cm^{-1} and weak at 1560 cm^{-1}) for bipyrimidine-bridged copper(II) complexes revealing that the quasi-symmetrical or asymmetrical doublet in this region can be used as diagnostic of chelating or bis-chelating bipym. The β-CH vibration of bipym (1140 cm^{-1}) is obscured by the Cl–O perchlorate stretching vibrations in our complex. Finally, the antisymmetric γ-CH vibration of bipym (830, 820 cm^{-1}) appears as a single medium intensity feature at 825 cm^{-1} for the present complex.

The powder ESR spectrum of the compound up to 12 000 G and at 100 K is shown in Fig. 2. It exhibits five features at 1620, 3250, 6586, 8616 and 10 564 G. The spectrum is qualitatively similar to that observed for other copper-pair triplet states with $|D| > h\nu$.[2,12,30–34] The second feature is most likely due to a diluted copper(II) impurity. Unfortunately, we are unable to offer conclusive evidence to support this assignment, but its temperature dependence agrees with it. The absolute intensities of the other four features quickly diminish when the sample is heated confirming the triplet nature for the ground state. Any band below the 3250 G impurity peak 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 1620 G in such low-field range, we assumed that this feature corresponds to the $\Delta M_S = \pm 2$ transition. In fact, its low intensity does not conflict with this assignment. The occurrence of other peaks at high field values indicates that the axial zero-field splitting parameter D is larger than the incident quantum (*ca.* 0.3 cm^{-1}). To interpret the spectrum quantitatively, it was assumed that Wasserman's equations[35] were valid, *i.e.* that the D and g tensor axes were coincident. In the present case only one attribution leads to reasonable values for the principal g tensors with $g_x = 2.08$, $g_y = 2.02$, $g_z = 2.21$, $|D| = 1.40$ cm^{-1}, and $E = 0.033$ cm^{-1}, the bands at 6586, 8616 and 10 565 G corresponding to H_{x_2}, H_{y_2} and H_{z_1}, respectively. The agreement between experimental and calculated fields is then excellent as shown in Table 4. However, if the g and D tensors were not coincident, Wasserman's equations could not be used and the previous fit would be fortuitous.[32] The splitting of the lines at higher field in Fig. 2 would point towards this possibility.

Magnetic Properties.—The magnetic behaviour of the title compound is shown in Fig. 3 under the form of the $\chi_M T$ *vs.* T plot, $\chi_M T$ being the magnetic susceptibility per two copper(II) ions and T the temperature. At room temperature $\chi_M T$ is equal to 0.96 cm^3 mol^{-1} K, which is a value already higher than what is expected for two uncoupled copper(II) ions. The value of $\chi_M T$ increases upon cooling and reaches a plateau around 38 K with $\chi_M T = 1.11$ cm^3 mol^{-1} K, which remains practically constant until 4.2 K. This magnetic behaviour is characteristic of a ferromagnetic interaction with a triplet ground state. In order to determine the singlet-triplet energy gap (J), the simple theoretical Bleaney–Bowers expression [equation (2)] was used

$$\chi_M T = 2N\beta^2 g^2/kT{\cdot}[3 + \exp(-J/kT)]^{-1} \qquad (2)$$

Table 5 Structural data and isotropic exchange parameters for $[Cu_2L_2(OH)_2]^{2+}$ complexes (L = bipy or bipym)[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	2, 8
$[Cu_2(bipy)_2(OH)_2]C_4O_4{\cdot}4H_2O$	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	2, 7
$[Cu_2(bipy)_2(OH)_2][CF_3SO_3]_2$	1.927	2.920	98.5	0.01	+17	12
	(1.926)[b]	(2.8917)	(97.3)	(0.13)	(+158)	12
$[Cu_2(bipy)_2(OH)_2]SO_4{\cdot}5H_2O$	1.939	2.893	96.5	6.1	+49	2, 9
$[Cu_2(bipy)_2(OH)_2][PF_6]_2$	1.953	2.914	96.5	16.5	+12	11
$[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2{\cdot}2H_2O$	1.950	2.870	95.0	0.0	+147	This work

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

where N, β, k, g and T have their usual meanings. The average value of the g factor for the triplet state can be deduced from the value of the plateau ($\chi_MT = 2N\beta^2g^2/2k$). This gives $g = 2.107$, which is practically identical to the deduced one from the ESR spectrum ($g_{av} = 2.10$). We determined J by a least-squares-fitting procedure (g was kept constant and equal to 2.107 in the fitting process) and found $J = 147$ cm^{-1}. The agreement factor defined as $\Sigma_i[(\chi_MT)_{obs}(i) - (\chi_MT)_{calc}(i)]^2/\Sigma_i[(\chi_MT)_{obs}(i)]^2$ is then equal to 2.39×10^{-4}.

Both techniques, magnetic susceptibility measurements and ESR spectroscopy, reveal that the nature of the exchange coupling in $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2{\cdot}2H_2O$ is ferromagnetic. For the sake of comparison, we have gathered in Table 5 the reported structural and magnetic data dealing with dihydroxo-bridged (2,2′-bipyridine)copper(II) complexes and the present complex. All the cases cited therein exhibit a triplet ground state and are examples of the so-called accidental orthogonality[36] of the magnetic orbitals φ_A and φ_B from each copper(II) ion within the binuclear units.

The value of $\theta = 95.0(1)$ (<97.5°) for $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2{\cdot}2H_2O$ is in agreement with the ferromagnetic interaction observed for this complex. The use of bipym as outer ligand allowed us to achieve the smallest θ angle of the series of complexes of Table 5. However, the corresponding J value is not the greatest. This is due to the fact that the Cu–O(hydroxo bridge) distance is one of the largest, leading to smaller density overlap $\varphi_A\varphi_B$ in the bridge surroundings. Therefore, although the value θ angle can be tuned, the Cu–O(bridge) distance varies in an unforseeable fashion making difficult the control of the resulting J value.

The ferromagnetic coupling observed in $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2{\cdot}2H_2O$ demonstrates that this species has a triplet ground state. This complex is very interesting as a precursor of polymetallic compounds $[Cu_2M]$ (alternation of spins $S_{Cu_2} = 1$ and S_M) because of the bis-chelating character of 2,2′-bipyrimidine. Although we have isolated and characterized the $[Cu_2(bipym)_2(OH)_2]^{2+}$ complex as a perchlorate salt, a study of the existence of $[Cu_2(bipym)_2(OH)_2]^{2+}$ in aqueous solution as a function of pH is very appropriate in order to design further synthetic work.

Solution Study.—Series of aqueous solutions of the complex $[Cu_2(bipym)_2(H_2O)_4(OH)_2][ClO_4]_2{\cdot}2H_2O$ (previously acidified with nitric acid to pH 4) were titrated with sodium hydroxide to investigate the formation of hydroxo complexes of $[Cu_2(bipym)_2(H_2O)_2]^{2+}$. The data analysis by means of the program SUPERQUAD allowed us to determine the equilibrium constant of equation (3): $\log K_1 = -10.350(1)$. Since equilibrium (4) may be written in terms of equilibrium (3)

$$2[Cu(bipym)(H_2O)_2]^{2+} \overset{K_1}{\rightleftharpoons} [Cu_2(bipym)_2(OH)_2]^{2+} + 2H^+ + 2H_2O \quad (3)$$

$$2[Cu(bipym)(H_2O)_2]^{2+} + 2OH^- \overset{K_2}{\rightleftharpoons} [Cu_2(bipym)_2(OH)_2]^{2+} + 2H_2O \quad (4)$$

and K_w for water, K_2 may be expressed as K_1/K_w, from which a value of $\log K_2 = 17.06$ was calculated. The corresponding distribution diagram of the existing species as a function of pH (Cu^{II}:bipym in a 1:1 molar ratio) shows that $[Cu_2(bipym)_2(OH)_2]^{2+}$ is the predominant species at pH > 6.3, being the only one existing at pH > 7.5. We have not found any evidence of the formation of other hydroxo complexes under our experimental conditions.

The similarity between bipym and bipy led us to reinvestigate the formation of hydroxo complexes of $[Cu(bipy)(H_2O)_2]^{2+}$ in aqueous solution. As for the bipym system, the $[Cu_2(bipy)_2(OH)_2]^{2+}$ binuclear complex is the only hydroxo species whose formation has been observed under our experimental conditions, the values of $\log K_3$ and $\log K_4$ [equations (5) and (6)]

$$2[Cu(bipy)(H_2O)_2]^{2+} \overset{K_3}{\rightleftharpoons} [Cu_2(bipy)_2(OH)_2]^{2+} + 2H^+ + 2H_2O \quad (5)$$

$$2[Cu(bipy)(H_2O)_2]^{2+} + 2OH^- \overset{K_4}{\rightleftharpoons} [Cu_2(bipy)_2(OH)_2]^{2+} + 2H_2O \quad (6)$$

being −10.774(1) and 16.73, respectively. These values are very close to those reported previously under the same experimental conditions (25 °C and $I = 0.1$ mol dm^{-3}).[37] Although the presence of monohydroxo $\{[Cu(bipy)(OH)(H_2O)]^+\}$ and dihydroxo $\{[Cu(bipy)(OH)_2]\}$ species was observed in aqueous solution,[37,38] we have not detected them. In a more recent work[39] it was reported that the $[Cu_2(bipy)_2(OH)_2]^{2+}$ complex is the predominant hydroxo species in aqueous solutions containing Cu^{II} and bipy in a 1:1 molar ratio. The same situation was found for related systems containing 1,10-phenanthroline or histamine as chelating ligands.

A comparison of the values of $\log K_1$ and $\log K_3$ [equations (3) and (5)] shows that $[Cu(bipym)(H_2O)_2]^{2+}$ is somewhat more acidic than $[Cu(bipy)(H_2O)_2]^{2+}$. The overall charge, chromophore and chelating ring are identical for both complexes. However, the greater π-acceptor character of bipym with respect to bipy[40] enhances the Lewis acid character of the metal ion and makes the co-ordinated water more acidic in the bipyrimidyl-containing copper(II) complex.

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References

1 W. E. Hatfield, in *Magneto-Structural Correlations in Exchange Coupled Systems*, eds. R. D. Willett, D. Gatteschi and O. Kahn, NATO-ASI Series, Reidel, Dordrecht, 1985, p. 555 and refs. therein.

2 Van H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107.
3 C. Arcus, K. P. Fivizzani and S. F. Pavkovic, *J. Inorg. Nucl. Chem.*, 1977, **39**, 285.
4 M. Näsäkkälä, *Ann. Acad. Sci. Fenn, Ser. A2*, 1977, 15–25 and 54–58.
5 J. R. Wasson, T. P. Mitchell and W. H. Bernard, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2865; T. P. Mitchell, W. H. Bernard and J. R. Wasson, *Acta Crystallogr., Sect. B*, 1970, **26**, 2096; B. J. Cole and W. H. Brumage, *J. Chem. Phys.*, 1970, **53**, 4718.
6 W. E. Hatfield, T. S. Piper and U. Klabunde, *Inorg. Chem.*, 1963, **2**, 629; E. D. Estes, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1974, **13**, 1654.
7 M. Toofan, A. Boushehri and M. Ul-Haque, *J. Chem. Soc., Dalton Trans.*, 1976, 217.
8 R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, 1970, **74**, 3497; K. T. McGregor, N. T. Watkins, D. L. Lewis, R. F. Drake, D. J. Hodgson and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 423.
9 A. T. Casey, B. F. Hoskins and F. D. Whillans, *Chem. Commun.*, 1970, 904; B. F. Hoskins and F. D. Whillans, *J. Chem. Soc., Dalton Trans.*, 1975, 1267; J. A. Barnes, W. E. Hatfield and D. J. Hodgson, *J. Chem. Soc., Chem. Commun.*, 1970, 1593; K. T. McGregor, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1973, **12**, 731; J. A. Barnes, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1972, **11**, 144.
10 I. Castro, J. Faus, M. Julve, M. Verdaguer, A. Monge and E. Gutiérrez-Puebla, *Inorg. Chim. Acta*, 1990, **170**, 251.
11 J. Sletten, A. Sørensen, M. Julve and Y. Journaux, *Inorg. Chem.*, 1990, **29**, 5054.
12 I. Castro, J. Faus, M. Julve, J. A. Real, F. Lloret and C. Bois, *J. Chem. Soc., Dalton Trans.*, 1992, 47.
13 I. Castro, J. Faus, M. Julve, M. C. Muñoz, W. Díaz and X. Solans, *Inorg. Chim. Acta*, 1991, **179**, 59.
14 J. C. Bernier and P. Poix, *Actual. Chim.*, 1978, **2**, 7.
15 A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, London and New York, 1968.
16 F. Lloret, M. Julve, M. Mollar, I. Castro, J. Latorre, J. Faus, X. Solans and I. Morgenstern-Badarau, *J. Chem. Soc., Dalton Trans.*, 1989, 729.
17 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.
18 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
19 SHELX PLUS, Version 3.4, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, 1989.
20 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 72–99.
21 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
22 G. De Munno and G. Bruno, *Acta Crystallogr., Sect. C*, 1984, **40**, 2030.
23 M. Julve, G. De Munno, G. Bruno and M. Verdaguer, *Inorg. Chem.*, 1988, **27**, 3160.
24 G. De Munno, G. Bruno, M. Julve and M. Romeo, *Acta Crystallogr., Sect. C*, 1990, **46**, 1828.
25 M. Julve, G. De Munno, J. A. Real and M. Verdaguer, unpublished work.
26 I. M. Procter, B. J. Hathaway and P. Nicholls, *J. Chem. Soc. A*, 1968, 1678.
27 L. Fernholt, C. Rømming and S. Samdal, *Acta Chem. Scand., Ser. A*, 1981, **35**, 707.
28 J. R. Ferraro and W. R. Walker, *Inorg. Chem.*, 1965, **4**, 1382.
29 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986, p. 230 and refs. therein.
30 D. V. Jeter, D. L. Lewis, J. C. Hempel, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1972, **11**, 1958.
31 J. A. Barnes, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1972, **11**, 144.
32 L. Banci, A. Bencini, D. Gatteschi and C. Zanchini, *J. Magn. Reson.*, 1982, **48**, 9.
33 L. Banci, A. Bencini and D. Gatteschi, *J. Am. Chem. Soc.*, 1983, **105**, 761.
34 S. Sikorav, I. Bkouche-Waksman and O. Kahn, *Inorg. Chem.*, 1984, **23**, 492.
35 E. Wasserman, L. C. Snyder and W. A. Yager, *J. Chem. Phys.*, 1964, **41**, 1763.
36 O. Kahn and M. F. Charlot, *Nouv. J. Chim.*, 1980, **4**, 567.
37 R. L. Gustafson and A. E. Martell, *J. Am. Chem. Soc.*, 1959, **81**, 525.
38 A. E. Martell, S. Chebereck, jun., R. C. Courtney, S. Westerback and H. Hyytiainen, *J. Am. Chem. Soc.*, 1957, **79**, 3036.
39 D. D. Perrin and V. S. Sharma, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1271.
40 R. R. Ruminsky and J. D. Petersen, *Inorg. Chim. Acta*, 1985, **97**, 129.

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