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# Synthesis and Magnetic Properties of Bis($\mu$-hydroxo)bis[(2,2'-bipyridyl)copper(II)] Squarate. Crystal Structure of Bis($\mu$-hydroxo)bis[(2,2'-bipyridyl)copper(II)] Squarate Tetrahydrate

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## Abstract

The compound $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot5.5H_2O$, where bipy and $C_4O_4{}^{2-}$ correspond to 2,2'-bipyridyl and squarate (dianion of 3,4-dihydroxy-3-cyclobutene-1,3-dione) respectively, has been synthesized. Its magnetic properties have been investigated in the 2–300 K temperature range. The ground state is a spin-triplet state, with a singlet–triplet separation of 145 cm$^{-1}$. The EPR powder spectrum confirms the nature of the ground state.

Well-formed single crystals of the tetrahydrate, $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot4H_2O$, were grown from aqueous solutions and characterized by X-ray diffraction. The system is triclinic, space group $P\bar{1}$, with $a = 9.022(2)$, $b = 9.040(2)$, $c = 8.409(2)$ Å, $\alpha = 103.51(2)$, $\beta = 103.42(3)$, $\gamma = 103.37(2)°$, $V = 642.9(3)$ Å$^3$, $Z = 1$, $D_x = 1.699$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 17.208 cm$^{-1}$, $F(000) = 336$ and $T = 295$ K. A total of 2251 data were collected over the range $1 \leqslant \theta \leqslant 25°$; of these, 1993 (independent and with $I \geqslant 3\sigma(I)$) were used in the structural analysis. The final $R$ and $R_w$ residuals were 0.034 and 0.038 respectively. The structure contains squarato-O$^1$,O$^3$-bridged bis($\mu$-hydroxo)bis[(2,2'-bipyridyl)copper(II)] units forming zigzag one-dimensional chains. Each copper atom is in a square-pyramidal environment with the two nitrogen atoms of 2,2'-bipyridyl and the two oxygen atoms of the hydroxo groups building the basal plane and another oxygen atom of the squarate lying in the apical position.

The magnetic properties are discussed in the light of spectral and structural data and compared with the reported ones for other bis($\mu$-hydroxo)bis[(2,2'-bipyridyl)copper(II)] complexes.

## Introduction

A clear correlation between structure and magnetic properties has been established in double bridged copper(II) complexes, particularly in the bis($\mu$-hydroxo) compounds [1]. In particular, Hatfield and Hodgson have shown that the singlet–triplet energy gap varies linearly with the angle $\theta$ = Cu–O–Cu, according to the relationship

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

when $\theta$ is not too far from 90°.

From this equation, singlet and triplet ground states are predicted for $\theta > 97.5°$ and $\theta < 97.5°$, respectively. This dependence of $J$ versus $\theta$ has received two semiquantitative interpretations, one based on an orthogonalized magnetic orbital approach [2] and the other based on non-orthogonalized magnetic orbitals and overlap density [3]. The experimental values of $\theta$ known so far vary in the narrow 95.6–104.1° range [4]. For the bis($\mu$-hydroxo)bis[(2,2'-bipyridyl)copper(II)] compounds only four systems have been prepared and characterized [5–8]. Binuclear ferromagnetic units antiferromagnetically coupled through molecular ligands are even rarer. Nevertheless, they could be model systems of $S = 1$ entities antiferromagnetically coupled, to check the Haldane conjecture about the presence of a quantum gap in $S = 1$, quasi-one-dimensional Heisenberg antiferromagnets [9, 10]. This work was undertaken precisely with this aim and provides an example of such a system of antiferromagnetically coupled $S = 1$ binuclear units.

The synthesis and the magnetic behaviour of the complex $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot5.5H_2O$ is reported and its magnetic properties are discussed in relation to similar systems. The crystallographic

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structure of a closely related tetrahydrate is also reported. A crystal suitable for X-ray analysis was obtained only once, unfortunately as a tiny crystal, which precluded the possibility of magnetic measurements on the crystallographically characterized species.

## Experimental

All reagents were commercial grade materials and were used without further purification. Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) was purchased from Aldrich. 3,4-Diamino-3-cyclobutene-1,2-dione was synthesized as reported in the literature [9]. Analyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Bioorganic Chemistry, C.S.I.C. (Barcelona). Copper content was estimated by atomic absorption spectrophotometry.

### *Preparation of* $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot 5.5H_2O$

A yellowish green solution was obtained when 0.104 g of $K_2C_4O_4\cdot H_2O$ (1 mmol) dissolved in a minimum amount of water was added to 50 cm$^3$ of a warm aqueous solution containing 0.483 g of $Cu(NO_3)_2\cdot 3H_2O$ (2 mmol) and 0.132 g of 2,2′-bipyridyl (2 mmol). Blue needle-like crystals appeared when dilute ammonia was added dropwise until the solution became colorless. The product was filtered off, washed thoroughly with water and dried in air. It turned green after several hours. *Anal.* Calc. for $C_{24}H_{29}Cu_2N_4O_{11.5}$: C, 42.12; H, 4.24; N, 8.18; Cu, 18.57. Found: C, 41.92; H, 3.64; N, 8.19; Cu, 19.16%. All attempts to grow single crystals failed because of the insolubility of this complex in common solvents. However, a few well-shaped crystals of a tetrahydrate were grown from aqueous solutions containing copper(II):2,2′-bipyridyl:3,4-diamino-3-cyclobutene-1,2-dione:lithium hydroxide in a 1:1:1:2 molar ratio. The slow hydrolysis reaction of the diamino species gave the squarate dianion [11] and single crystals of the tetrahydrate complex suitable for X-ray analysis. The yield was unfortunately very low and precluded physical measurements on the crystalline product.

### *Physical Measurements*

IR spectra were recorded with a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–225 cm$^{-1}$ spectral range. Magnetic measurements were carried out with a Faraday-type magnetometer equipped with a helium continuous-flow cryostat working in the 4.2–300 K temperature range and with a SQUID magnetometer, already described [12], in the 2–4.2 K temperature range. Independence of the magnetic susceptibility versus the magnetic field was checked at both room temperature

TABLE 1. Crystal and refinement data

| | |
|---|---|
| Molecular formula | $Cu_2C_{24}H_{26}N_4O_{10}$ |
| Molecular weight | 657.5 |
| $a$ (Å) | 9.022(2) |
| $b$ (Å) | 9.040(2) |
| $c$ (Å) | 8.409(2) |
| $\alpha$ (°) | 103.51(2) |
| $\beta$ (°) | 103.42(3) |
| $\gamma$ (°) | 103.37(2) |
| $V$ (Å$^3$) | 642.9(3) |
| $Z$ | 1 |
| Space group | $P\bar{1}$[a] |
| $D_{calc}$ (g cm$^{-3}$) | 1.699 |
| Radiation | graphite monochromated Mo K$\alpha$ ($\lambda$ = 0.71073 Å) |
| Temperature (K) | 295 |
| $\mu$ (cm$^{-1}$) | 17.208 |
| Scan technique | $\omega/2\theta$ |
| Scan speed (° m$^{-1}$) | 20–1.54 |
| Scan width (°) | 0.80 + 0.35 tg $\theta$ |
| Scan range (°) | $1 < \theta < 25$ |
| Total no. individual reflections | 2251 |
| Cutoff observed data | $3\sigma(I)$ |
| No. observed reflections | 1993 |
| No. refined parameters | 336 |
| $R$[b] | 0.034 |
| $R_w$[c] | 0.038 |

[a] Based on a centric distribution of $E$ values and later confirmed by the structural determination. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma(F_o)^2]^{1/2}$ (unit weights).

TABLE 2. Final atomic coordinates for non-hydrogen atoms[a] and equivalent temperature factors ($\times 10^4$)[b]

| Atom | $x/a$ | $y/a$ | $z/a$ | $U_{eq}$ (Å$^3$) |
|---|---|---|---|---|
| Cu | 0.46546(6) | 0.07112(6) | 0.15198(7) | 202(2) |
| O(1) | 0.60537(36) | 0.12600(34) | 0.01970(39) | 264(12) |
| N(1) | 0.34533(42) | 0.00953(41) | 0.31231(45) | 228(14) |
| C(1) | 0.23177(56) | −0.12321(53) | 0.27936(60) | 302(18) |
| C(2) | 0.14879(62) | −0.15209(59) | 0.39222(68) | 372(21) |
| C(3) | 0.18477(66) | −0.03985(66) | 0.54523(70) | 418(23) |
| C(4) | 0.30031(63) | 0.09692(61) | 0.58037(64) | 374(21) |
| C(5) | 0.37947(52) | 0.11910(51) | 0.46273(55) | 248(16) |
| C(6) | 0.50965(50) | 0.25996(51) | 0.48737(55) | 244(16) |
| C(7) | 0.57419(61) | 0.38095(58) | 0.63750(60) | 343(19) |
| C(8) | 0.69789(63) | 0.50380(59) | 0.64895(65) | 390(20) |
| C(9) | 0.75372(61) | 0.50413(58) | 0.50981(69) | 391(20) |
| C(10) | 0.68339(58) | 0.38137(55) | 0.36294(63) | 328(19) |
| N(2) | 0.56440(43) | 0.26031(41) | 0.35262(46) | 245(14) |
| O(2) | 0.24864(35) | 0.15494(35) | 0.03253(43) | 305(13) |
| C(11) | 0.11141(50) | 0.07121(47) | 0.01469(54) | 217(15) |
| C(12) | 0.02465(50) | −0.09245(48) | −0.07193(55) | 229(16) |
| O(3) | 0.05733(38) | −0.20160(36) | −0.15978(43) | 328(13) |
| O(4) | 0.34040(52) | 0.41307(43) | −0.07255(52) | 509(18) |
| O(5) | 0.07010(57) | −0.48813(49) | −0.12607(65) | 647(22) |

[a] e.s.d.s given in parentheses. [b] $U_{eq} = \frac{1}{3} \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$.

and 4.2 K. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Corrections for the diamagnetism were estimated from Pascal constants as $-370 \times 10^{-6}$ cm$^3$ mol$^{-1}$. X-band EPR spectra were recorded on polycrystalline samples with a Brüker ER 200D spectrometer at room and liquid nitrogen temperatures.

### *X-ray Structure Determination*

A greenish blue prismatic crystal of $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot 4H_2O$ of approximate dimensions $0.30 \times 0.30 \times 0.60$ mm was sealed in a capillary tube and mounted on an Enraf-Nonius CAD-4F automatic diffractometer. The crystallographic data are summarized in Table 1. Unit-cell constants were determined and refined from least-squares fitting of the setting angles of 25 reflections. The intensities of all 2251 unique reflections were measured at 295 K with graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) in the $\omega/2\theta$ scan mode with $1 < \theta < 25°$ ranging from $(\bar{1}\bar{0}, \bar{1}\bar{1}, 0)$ to (10, 11, 0). No appreciable change was observed in the periodically monitored standard reflections. Intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Cu were taken from ref. 13.

On the basis of the distribution of $E$ values, the $P\bar{1}$ space group was assumed and later confirmed by the successful refinement of the structure. The structure was solved by Patterson and Fourier methods. An empirical absorption correction [14] was applied at the end of the isotropic refinement. Anisotropic full matrix least-squares refinement with weight $w = w_1 w_2$, where $w_1 = 1/[A + B|F_o|]^2$ and $w_2 = 1/[C + D(\sin\theta)/\lambda]^2$ was applied. The coefficients $A$, $B$, $C$ and $D$ were calculated by the PESOS program [15]*. The hydrogen atoms of the 2,2′-bipyridyl were fixed at calculated positions whereas the ones of the water molecules and hydroxo groups were located on a difference synthesis and calculated with reflections having $(\sin\theta)/\lambda < 0.5$ Å$^{-1}$.

Final refinement with fixed isotropic temperature factors and coordinates for hydrogen atoms gave $R$ = 0.034 and $R_w$ = 0.038. Maximum and average shifts/error were 0.009 and 0.002 respectively. Table 2 reports the list of the final atomic coordinates for non-hydrogen atoms with estimated standard deviations obtained from the least-squares inverse matrix. Most of the calculations were carried out by using XRAY [16]. The molecular plots were drawn using the ORTEP program [17]. Bond distances and angles are given in Table 3.

## Results and Discussion

### *Description of the Structure*

The structure of $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot 4H_2O$ consists of centrosymmetric bis($\mu$-hydroxo)bis[(2,2′-

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*The calculated coefficients are as follows: $A$ = 1.29, 0.50 and 0.02 and $B$ = −0.15, −0.00 and 0.02 for $|F_o| < 5.5$, $5.5 < |F_o| < 18.2$ and $|F_o| > 18.2$, respectively; $C$ = 5.83 and 0.39 and $D$ = −14.44 and 0.70 for $(\sin\theta)/\lambda < 0.36$ and $>0.36$, respectively.

TABLE 3. Bond distances (Å) and angles (°)[a]

| | | | |
|---|---|---|---|
| Copper environment | | | |
| Cu–N(1) | 2.025(3) | Cu–O(2) | 2.380(2) |
| Cu–N(2) | 1.996(2) | Cu–Cu$^{i}$(intra) | 2.870(1) |
| Cu–O(1) | 1.930(2) | Cu–Cu$^{ii}$(intra) | 7.882(2) |
| Cu–O(1)$^{i}$ | 1.923(2) | Cu–Cu$^{iii}$(inter) | 6.227(2) |
| O(1)–Cu–O(2) | 100.38(9) | O(2)–Cu–N(1) | 87.42(10) |
| O(1)–Cu–O(1)$^{i}$ | 83.74(9) | O(2)–Cu–N(2) | 93.85(9) |
| O(1)–Cu–N(1) | 171.98(10) | O(1)$^{i}$–Cu–N(1) | 97.38(9) |
| O(1)–Cu–N(2) | 96.91(9) | O(1)$^{i}$–Cu–N(2) | 151.54(9) |
| O(2)–Cu–O(1)$^{i}$ | 95.73(8) | N(1)–Cu–N(2) | 80.62(10) |
| Cu–O(1)–Cu$^{i}$ | 96.4(2) | | |
| 2,2′-Bipyridyl | | | |
| N(1)–C(1) | 1.341(4) | C(6)–C(7) | 1.380(4) |
| N(1)–C(5) | 1.351(3) | C(7)–C(8) | 1.376(5) |
| C(1)–C(2) | 1.376(5) | C(8)–C(9) | 1.378(6) |
| C(2)–C(3) | 1.375(5) | C(9)–C(10) | 1.377(4) |
| C(3)–C(4) | 1.381(5) | C(10)–N(2) | 1.339(4) |
| C(4)–C(5) | 1.377(5) | N(2)–C(6) | 1.340(4) |
| C(5)–C(6) | 1.485(4) | | |
| Cu–N(1)–C(1) | 126.4(2) | C(4)–C(5)–C(6) | 124.6(2) |
| Cu–N(1)–C(5) | 114.5(2) | C(4)–C(5)–N(1) | 121.2(2) |
| C(1)–N(1)–C(5) | 118.9(3) | C(6)–C(5)–N(1) | 114.2(3) |
| Cu–N(2)–C(6) | 115.7(2) | C(5)–C(6)–N(2) | 114.8(2) |
| Cu–N(2)–C(10) | 124.8(2) | C(7)–C(6)–N(2) | 121.3(3) |
| C(10)–N(2)–C(6) | 119.4(2) | C(6)–C(7)–C(8) | 119.3(3) |
| N(1)–C(1)–C(2) | 122.4(3) | C(7)–C(8)–C(9) | 119.2(3) |
| C(1)–C(2)–C(3) | 118.8(3) | C(8)–C(9)–C(10) | 118.8(3) |
| C(2)–C(3)–C(4) | 119.2(4) | C(9)–C(10)–N(2) | 121.9(3) |
| C(3)–C(4)–C(5) | 119.5(3) | | |
| Squarate | | | |
| C(11)–O(2) | 1.252(3) | C(11)–C(12)$^{ii}$ | 1.460(4) |
| C(11)–C(12) | 1.471(3) | C(12)–O(3) | 1.248(4) |
| C(12)–C(11)–C(12)$^{ii}$ | 90.2(2) | C(11)–C(12)–C(11)$^{ii}$ | 89.8(2) |
| C(12)–C(11)–O(2) | 134.2(3) | C(11)–C(12)–O(3) | 134.0(3) |
| C(12)$^{ii}$–C(11)–O(2) | 135.6(2) | C(11)$^{ii}$–C(12)–O(3) | 136.2(2) |

[a] Symmetry code: (i) = $1 - x, -y, -z$; (ii) = $-x, -y, -z$; (iii) = $1 - x, -y, 1 - z$.

bipyridyl)copper(II)] binuclear units which are linked to each other by bis-monodentate squarate ligands. The four water molecules are non-coordinated, crystallization water molecules. A perspective view of the complex with the atom labelling scheme is shown in Fig. 1. It can be described as a one-dimensional alternating copper(II) chain in which the copper atoms are alternately bridged by two hydroxo groups and one squarate ligand. A crystallographic inversion center stands at the middle of the squarate group.

The copper(II) ion is bonded to five donor atoms in a distorted square-pyramidal arrangement, $CuN_2O_3$: the basal plane is built by the N(1) and N(2) nitrogen atoms of the bipyridyl ligand and O(1) and O(1)$^{i}$ oxygen atoms of the two hydroxo bridging groups, whereas the apical position is occupied by the O(2) oxygen atom of the squarate ligand. The deviations of N(1), N(2), O(1) and O(1)$^{i}$ atoms from the mean basal plane are 0.018(4), −0.019(4), 0.014(4) and −0.014(4) Å respectively, and the copper(II) ion is displaced by 0.150(1) Å from this plane toward the apex. The four equatorial bonds to copper(II) ion occur in two sets: the copper to hydroxo-bridge oxygen (1.930(2) Å for Cu–O(1), 1.923(2) Å for Cu–O(1)$^{i}$) and the copper to bipyridyl nitrogen (2.025(3) Å for Cu–N(1) and 1.996(2) Å for Cu–N(2)). They are significantly shorter than the apical distance (2.380(2) Å for Cu–O(2)).

The bipyridyl rings show no significant deviation from planarity, but they display a small dihedral angle of 5.5(2)°. These features were already observed in other bis($\mu$-hydroxo)bis[(2,2′-bipyridyl)copper(II)]

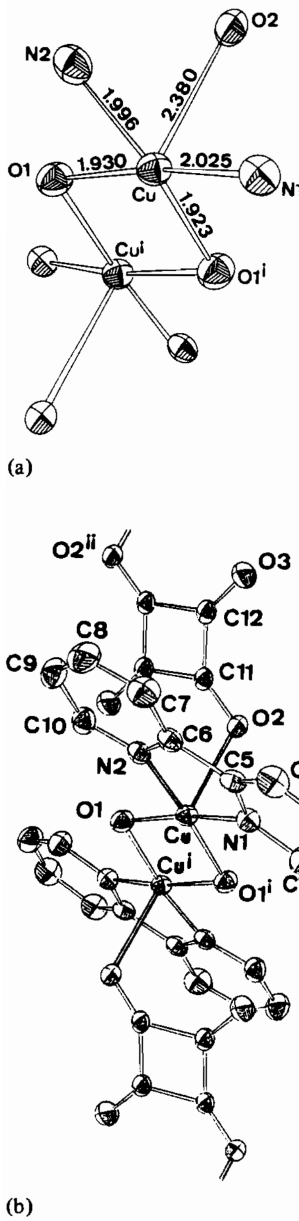

Fig. 1. (a) ORTEP drawing of the environment of the copper atom in the bis($\mu$-hydroxo binuclear unit. (b) ORTEP representation of $[Cu_2(bipy)_2(OH)_2](C_4O_4)$ with atomic numbering scheme. H atoms are omitted and thermal ellipsoids are at 50% probability level.

complexes [5–8]. The C–C and C–N bond lengths are in agreement with the reported ones for the non-coordinated 2,2′-bipyridyl [18]. The N(1)–Cu–N(2) angle of 80.62(10)° is significantly smaller than 90° because of the steric requirements of a bipyridyl ring system.

The squarate ligand is almost planar (the largest deviation from the mean plane is 0.008(4) Å for C(11)) and the values of C–C and C–O bond distances agree with the reported ones for other $\mu$-1,3-squaratocopper(II) complexes [19]. The dihedral angle between the CuO(1)O(1)$^i$Cu$^i$ plane – whose planarity is imposed by the inversion center – and the mean plane of the squarate is 30.2(1)°.

The Cu–O(1)–Cu$^i$ angle and the Cu···Cu$^i$ separation (96.4(2)° and 2.870(1) Å respectively) are close to the reported ones for related complexes [5–8]. The copper–copper distance through the squarato bridge is 7.882(2) Å, much longer than the copper–copper separation in the bis($\mu$-hydroxo)binuclear unit and even more longer than the shortest copper–copper interchain distance (6.227(2) Å). The two non-coordinated water molecules per copper(II) ion contribute to the packing via hydrogen bonding.

### *Infrared Spectra*

The IR spectra of complexes $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot 4H_2O$ and $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot 5.5H_2O$ are nearly identical, the only difference occurring in the 3500 cm$^{-1}$ region, where the water bands are stronger and broader for the second compound. A shoulder at 3610 cm$^{-1}$ can be assigned to the OH stretch in the bridging hydroxo groups, and a weak absorption at 970 cm$^{-1}$ may originate in the OH bending vibration. They support the presence of the $Cu(OH)_2Cu$ unit [20]. Sharp bands of medium intensity, centered at 1605, 1480 and 1450 cm$^{-1}$, correspond to the C–C and C–N ring vibrations of the coordinated 2,2′-bipyridyl [21], observed at lower frequencies than in the uncomplexed 2,2′-bipyridyl. Such a coordination is also indicated by the splitting of the singlet at 1000 cm$^{-1}$ (pyridine breathing mode in free 2,2′-bipyridyl) into a doublet at 1025 and 1035 cm$^{-1}$ and by the presence of two out-of-plane CH bending vibrations at 735 and 775 cm$^{-1}$ [20]. A medium absorption band at 510 cm$^{-1}$ and a weak one at 265 cm$^{-1}$ are assigned to asymmetric Cu–O and Cu–N stretching vibrations [20, 22]. The strong and broad absorption at 1500 cm$^{-1}$ is assigned to the $\nu$(C–C) + $\nu$(C–O) stretching vibration of the coordinated squarate [23] which appears at 1530 cm$^{-1}$ in the IR spectra of the free squaric acid.

### *Magnetic Properties and EPR Spectra*

The magnetic behaviour of the complex $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot 5.5H_2O$ is shown in Fig. 2 in the form of a $\chi_M T$ versus $T$ plot, $\chi_M$ 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, a value which is somewhat higher than what is expected for two uncoupled copper(II) ions. $\chi_M T$ increases upon cooling down, reaches a plateau in the 85–45 K range with $\chi_M T$ = 1.13 cm$^3$ mol$^{-1}$ K and then decreases when cooling to pumped liquid helium temperature. The behaviour in the 45–300 K region is characteristic of a ferromagnetic interaction with a ground spin-triplet state

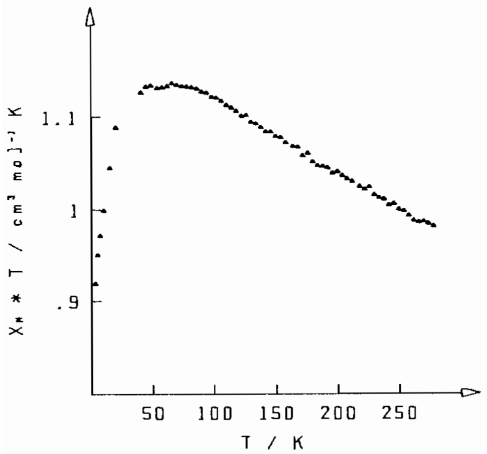

Fig. 2. Temperature dependence of $\chi_M T$ for $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot 5.5H_2O$.

much lower in energy than the spin-singlet state. Only the ground triplet state is significantly populated in the temperature range where $\chi_M T$ is constant. The magnetic susceptibility per two copper(II) ions can be expressed by the equation

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

where $J$ is the singlet–triplet gap defined by the phenomenological Hamiltonian with quantum spin operators $\hat{S}_1$ and $\hat{S}_2$

$$\hat{\mathcal{H}} = -J\hat{S}_1\cdot\hat{S}_2$$

and $N$, $g$, $\beta$ and $T$ have their usual meaning. $\theta$ is the Weiss correction which accounts for both intermolecular effects and zero-field splitting in the triplet. $J$, $g$ and $\theta$ values of 145 cm$^{-1}$, 2.16 and $-1.41$ K were obtained by a least-squares fit of the experimental data. The agreement factor $R$ defined as $\Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\Sigma(\chi_M T)^2_{obs}$ was then equal to $1.21 \times 10^{-4}$.

The structure of the compound with 5.5 water molecules is probably very close to the one of the herein reported tetrahydrate complex. Water molecules are not coordinated to the metal ion and are easily lost at low temperatures in both cases. Consequently, it is most probable that $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot 5.5H_2O$ is an alternating chain similar to the tetrahydrate derivative. In this hypothesis, magnetic properties can be understood as follows. The unpaired electron of the copper(II) ion can be described by a magnetic orbital of $d_{x^2-y^2}$ symmetry with a large spin delocalization on the N(1) and N(2) nitrogen and on the O(1) and O(1)$^i$ oxygen nearest neighbours. The presence of an axial oxygen atom of squarate at a further distance would lead only to a small admixture of $d_{z^2}$ in the magnetic orbital.

Two orbital interactions can be expected: within the binuclear bis-hydroxo unit and through the squarato bridge. At high temperature, the predominant interaction appears to be within the binuclear unit: the $Cu_A$–O–$Cu_B$ angle is in the range where ferromagnetic coupling is expected following Hatfield correlations. We are in a case where the so-called accidental orthogonality of the magnetic orbitals $\phi_A$ and $\phi_B$, proposed by Kahn and Charlot [3] is operating: (i) the overall overlap integral $S = \langle\phi_A|\phi_B\rangle$ is $\approx 0$ for the given Cu–O–Cu angle; (ii) the short Cu–O (bridge) distance favors large spin delocalization on the oxygen bridges, hence a large density overlap $\phi_A\phi_B$ in the bridge surroundings. Therefore, the singlet–triplet gap, approximated by the expression: $J = 2j + 4\beta S$, (where $j$ is the bielectronic exchange integral $\langle\phi_A(1)\phi_B(2)|e^2/r_{12}|\phi_A(2)\phi_B(1)\rangle$ and $\beta$ is the monoelectronic resonance integral $\langle\phi_A(1)|h|\phi_B(1)\rangle$) tends to $2j$ which is always positive. The triplet is the ground state, stabilized by 145 cm$^{-1}$ compared to the first singlet state. The singlet state is practically depopulated between 85 and 45 K and the system behaves as an insulated spin $S = 1$ ($\chi_M T = 1.2$). Below this temperature, the decrease of the $\chi_M T$ product can be interpreted by an antiferromagnetic interaction between the spins, either within the chain through the 1,3-squarato ligand (which is known to be weak [19b]) or between the chains. The experimental points were recorded down to 2 K, but no maximum of the $\chi_M$ versus $T$ curve was observed, hence no conclusion about the Haldane behavior of the compound can be reached.

The powder EPR spectrum at room temperature is shown in Fig. 3. It exhibits four features at 1630, 6310, 8110 and 9900 G belonging to the actual compound and a sharp feature with a hyperfine structure around 3100 G, probably due to a non-coupled dilute copper(II) impurity. The absolute intensities of the four features quickly increase when cooling down to liquid nitrogen temperature but their relative intensities remain unchanged. Both the form of the spectrum and its temperature dependence confirm that the ground state is a triplet state. The spectrum is qualitatively similar to that observed for other copper-pair triplet states with $|D| < h\nu$ [24–29].

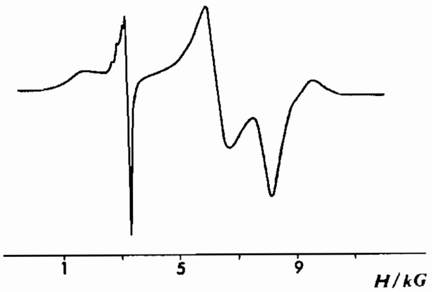

Fig. 3. X-band powder EPR spectrum of $[Cu_2(bipy)_2(OH)_2](C_4O_4)\cdot 5.5H_2O$ at room temperature.

Nevertheless, in our case it was not possible to analyze the spectrum in terms of the axial spin Hamiltonian using the equations of Wasserman *et al.* [30]; no reasonable assignment of the transitions led to reasonable $g$ values. Further work on single crystals is needed in order to overcome the difficulties associated to the probable occurrence of non-parallel $g$ and $D$ tensors in the compound.

## Supplementary Material

Tables of thermal parameters, calculated positions of hydrogen atoms and mean planes (4 pages) as well as a listing of observed and calculated structure factors (16 pages) are available from the authors on request.

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