# The Novel Magnetism and Crystal Structure of the Complex Di-μ-hydroxybis(bipyridyl)dicopper(II) Sulphate Pentahydrate

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*Summary* For the complex di-$\mu$-hydroxybis(bipyridyl)-dicopper(II) sulphate pentahydrate the effective magnetic moment per copper atom rises from 1·94 B.M. to 2·04 B.M. as the temperature is lowered from 298 to 84 K; the binuclear nature of the complex has been confirmed by a crystal structure determination.

RECENTLY Harris, Sinn, Walker, and Woolliams[1] reported a series of compounds which were formulated as [chelate $Cu(OH)_2Cu$ chelate]$X_2,nH_2O$, where chelate = 1,10-phenanthroline or 2,2′-bipyridyl (bipy) and X = a variety of mono- and bi-valent anions. For all the compounds prepared, the room-temperature magnetic moments per copper atom were observed to be well above the spin-only value and of the order of 1·9—2·0 B.M. The compound [bipy $Cu(OH)_2Cu$ bipy]$SO_4,5H_2O$, di-$\mu$-hydroxybis(bipyridyl)dicopper(II) sulphate pentahydrate, was found to obey a Curie–Weiss law over the liquid-nitrogen temperature range, and the effective magnetic moment was recorded as a constant 1·91 B.M. per copper atom over the whole range.

*Magnetic behaviour of* [bipy $Cu(OH)_2Cu$ bipy]$SO_4,5H_2O$

| Temp. K | $10^6\chi_M$ | $\mu_{eff}$/Cu atom |
|---|---|---|
| 298·5 | 1584 | 1·94 |
| 280·0 | 1708 | 1·96 |
| 265·0 | 1812 | 1·96 |
| 245·5 | 1955 | 1·96 |
| 228·5 | 2121 | 1·97 |
| 211·0 | 2279 | 1·96 |
| 190·5 | 2528 | 1·96 |
| 171·5 | 2850 | 1·98 |
| 154·0 | 3201 | 1·99 |
| 138·5 | 3594 | 2·00 |
| 124·0 | 4152 | 2·03 |
| 111·0 | 4643 | 2·03 |
| 99·3 | 5160 | 2·03 |
| 91·2 | 5681 | 2·04 |
| 84·0 | 6211 | 2·04 |

$10^6\ \chi_M$ has been corrected for the diamagnetism of the ligands and also for a T.I.P. of $60 \times 10^{-6}$ cgs units per copper atom.

However, it is more instructive to consider the variation of the magnetic moment with temperature without including $\theta$. Our data (Table) show that the effective magnetic moment per copper atom rises from 1·94 B.M. at 298 K to 2·04 B.M. at 84 K, the lowest temperature of our apparatus. The reciprocal susceptibility follows Curie–Weiss behaviour with $\theta = -11$ K. This increase in magnetic moment is small but, we believe, significant and it probably indicates that the singlet level lies appreciably above the ground state. This kind of magnetic behaviour is most surprising because antiferromagnetic interactions generally occur in complexes containing oxygen bridged copper atoms. For example, in the analogous compounds where the donor nitrogen atoms are provided by *NN*-diethylethylenediamine or *NNN′N′*-tetraethylethylenediamine the magnetic moment per copper atom falls almost to zero as the temperature is lowered to 85K.[2]

A crystal structure determination of [bipy $Cu(OH)_2Cu$ bipy]$SO_4,5H_2O$, using *X*-ray diffraction techniques, has confirmed the binuclear nature of the complex cation. Each copper atom of the dimeric unit is bonded to five donor atoms in a distorted square-pyramidal configuration as is shown in the Figure. For each copper atom the basal atoms are the two bridging oxygen atoms and the two nitrogen atoms of one of the bipyridyl molecules. One of

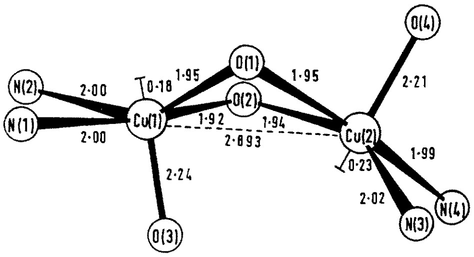

FIGURE. *The environments of the copper atoms of the dimeric cation of* [bipy $Cu(OH)_2Cu$ bipy]$SO_4,5H_2O$. *Important bond lengths are shown. Relevant bond angles are as follows:*

| | | | |
|---|---|---|---|
| Cu(1)–O(1)–Cu(2) | 97°, | O(1)–Cu(1)–N(2) | 167°, |
| O(3)–Cu(1)–O(2) | 91°, | O(4)–Cu(2)–O(2) | 97°, |
| O(1)–Cu(1)–N(1) | 96°, | O(1)–Cu(2)–N(3) | 96°, |
| N(1)–Cu(1)–N(2) | 81°, | N(3)–Cu(2)–N(4) | 80°, |
| O(4)–Cu(2)–O(1) | 97°, | O(3)–Cu(1)–O(1) | 97°, |
| O(4)–Cu(2)–N(4) | 93°, | O(3)–Cu(1)–N(2) | 96°, |
| O(1)–Cu(2)–O(2) | 83°, | O(1)–Cu(1)–O(2) | 84°, |
| O(2)–Cu(2)–N(3) | 164°, | O(2)–Cu(1)–N(1) | 172°, |
| Cu(1)–O(2)–Cu(2) | 97°, | O(4)–Cu(2)–N(3) | 100°, |
| O(3)–Cu(1)–N(1) | 97°, | O(2)–Cu(2)–N(4) | 98°, |
| O(2)–Cu(1)–N(2) | 97° | O(1)–Cu(2)–O(4) | 169°. |

the apical atoms [O(4)] is the oxygen atom of the sulphate anion while the other [O(3)] is the oxygen atom of one of the water molecules. Each copper atom is displaced about 0·20 Å towards the apical atom from the mean plane through its basal atoms. The dihedral angle between the two basal planes is 7·9(3)° and that between the two OCuO planes is 6·1(3)°. Important dimensions of the complex cation are given in the Figure. These agree well with previously reported values. The average estimated standard deviation of the copper to donor atom bond lengths is of the order of 0·006 Å and that for the copper to copper distance is 0·002 Å.

Crystal data: $C_{20}H_{28}O_{11}N_4SCu_2$, $M = 659$, monoclinic, $a = 9{\cdot}683(3)$, $b = 34{\cdot}52(1)$, $c = 7{\cdot}822(3)$ Å, $\beta = 103{\cdot}50(2)°$, $U = 2542$ Å$^3$, $D_m = 1{\cdot}72$, $Z = 4$, $D_c = 1{\cdot}72$ g cm$^{-3}$, space group $P2_1/c$ ($C^5_{2h}$, No. 14), Cu-$K_\alpha$ radiation, Siemens automatic diffractometer, $\mu = 34{\cdot}3$ cm$^{-1}$; absorption corrections were applied. All reflections up to a maximum Bragg angle of 45° were recorded. This gave 1962 unique significant observations. The atomic co-ordinates were obtained in the usual way and the structure is being refined by a full-matrix least-squares procedure where individual anisotropic temperature factors are being applied. At present the value of $R$ is 0·09.

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[1] C. M. Harris, E. Sinn, W. R. Walker, and P. R. Woolliams, *Austral. J. Chem.*, 1968, **21**, **631**.
[2] W. E. Hatfield, T. S. Piper, and U. Klabunde, *Inorg. Chem.*, **1964**, **2**, **629**.