# Crystal and Molecular Structure of Aquabis(2,2′-bipyridine)di-μ-hydroxo-sulphatodicopper(II) Tetrahydrate

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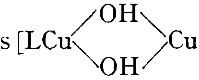
The structure of the title compound has been determined from single-crystal three-dimensional *X*-ray diffractometric data. The structure was solved by the heavy-atom method, and refined by least-squares techniques to *R* 0·078 for 1962 independent reflections. The copper atoms are bridged by two hydroxo-ligands to give a binuclear species with Cu ··· Cu 2·893(2) Å. Each copper atom has square pyramidal geometry with mean basal Cu–N 2·00 and Cu–O 1·94 Å; the apical $Cu-OH_2$ is 2·244(5) and $Cu-OSO_3$ 2·207(5) Å. The dihedral angle between the $CuO_2$ planes is 6·1°, and between the basal $CuN_2O_2$ planes 7·9°. The unco-ordinated water molecules provide a network for hydrogen bonding between the binuclear complexes. The unit cell is monoclinic with *Z* = 4, *a* = 9·683 ± 0·01, *b* = 34·52 ± 0·03, *c* = 7·822 ± 0·01 Å, β = 103·50 ± 0·05°, space group $P2_1/c$.

A SERIES of compounds, formulated as  $[\mathrm{LCu(OH)_2CuL}]\mathrm{X_2},n\mathrm{H_2O}$ [L = 1,10-phenanthroline or 2,2′-bipyridine (bipy), X = anion] has been reported.[1] Their room-temperature magnetic moments, per copper atom, were well above the spin-only value of 1·73 B.M. and of the order of 2·0 B.M. The compound thought to be di-μ-hydroxo-bis(bipyridine)dicopper(II) sulphate pentahydrate, $[(\mathrm{bipy})\mathrm{Cu(OH)_2Cu}(\mathrm{bipy})]\mathrm{SO_4},5\mathrm{H_2O}$, was found to obey the Curie–Weiss law ‡ over the temperature range from 83 to 293 K.[1] The magnetic moment, corrected for a Weiss constant of −13 K, was almost exactly uniform (1·90 B.M. per copper atom) over the temperature range.[1] Further measurements on this compound [2,3] have shown that the uncorrected magnetic moment rises from $1{\cdot}9_4$ B.M. at 298 K to $2{\cdot}0_4$ at 84 K and that the reciprocal susceptibility, $1/\chi_m$, follows Curie–Weiss behaviour with a Weiss constant of −11 K. Although this increase in magnetic moment is small it is believed to be significant and it probably indicates that the singlet level lies appreciably above the ground-state triplet level.[2,3] Magnetic measurements from 4 to 70 K on this compound tend to confirm the earlier conclusions; the iodide, bromide, and perchlorate salts all seem to have a triplet ground-state like the sulphate. [4a]

This kind of magnetic behaviour is surprising because antiferromagnetic interactions generally occur in binuclear complexes containing oxygen-bridged copper atoms.[1,4b,5] For example, in the di-μ-hydroxo-compounds with the ligands of *NNN′N′*-tetraethyldiaminoethane and *NN*-diethyl-*N′*-methyldiaminoethane ($X = ClO_4^-$, $n = 0$), the magnetic moments per copper atom fall from 1·63 and 1·89 B.M. respectively at 369 K to 1·38 and 1·69 B.M. at 298 K and almost to zero as the temperature is lowered to 77 K; [6] for the compound with the ligand *NNN′N′*-tetramethylethylenediamine (X = Br, $n = 0$) the room-temperature magnetic moment was 1·4 B.M.[7] Likewise, dipotassium di-μ-hydroxo-bis(biuretato)dicuprate(II) tetrahydrate (biuretato is the $\mathrm{NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH^{2-}}$ ligand) has a room-temperature magnetic moment of 1·10 B.M.[8] Subnormal magnetic moments at room temperature (1·49—1·51 B.M.) have been reported [9] for the $[(2\text{-ampy})_m\mathrm{Cu(OH)_2Cu}(2\text{-ampy})_m]\mathrm{X_2}$ compounds (2-ampy = 2-aminopyridine; $m = 2$, $X = NO_3^-$ or $ClO_4^-$, or $m = 3$, $X = ClO_4^-$).

An *X*-ray structure determination was undertaken on the bipyridyl compound because of its unusual magnetic properties.

## EXPERIMENTAL

*Crystal Data*.—$C_{20}H_{28}Cu_2N_4O_{11}S$, $M = 659$, Monoclinic, $a = 9{\cdot}683 \pm 0{\cdot}01$, $b = 34{\cdot}52 \pm 0{\cdot}03$, $c = 7{\cdot}822 \pm 0{\cdot}01$ Å, $\beta = 103{\cdot}50 \pm 0{\cdot}50°$, $U = 2542$ Å$^3$, $D_m = 1{\cdot}717 \pm 0{\cdot}01$,

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‡ $\chi_m(T + \theta_w)$ = constant, where $\theta_w$ is the Weiss constant. 1α B.M. ≈ $9{\cdot}27 \times 10^{-24}$ A m$^2$.

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$Z = 4$, $D_c = 1{\cdot}723$ g cm$^{-3}$, $F(000) = 4 \times 338$. Space group $P2_1/c$ ($C^5_{2h}$, No. 14). Cu-$K_\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, Siemens automatic diffractometer; $\mu = 34{\cdot}3$ cm$^{-1}$, absorption and empirical secondary extinction corrections were applied.

The blue crystals were parallelepipeds with well-developed $\pm(100)$, $\pm(02\bar{1})$, and $\pm(021)$ morphological faces; the longer diagonal of the $\pm(100)$ face, the most developed face, was found to be parallel to *b*. Poorly developed $\pm(010)$ faces were sometimes observed.

*Collection and Processing of Diffraction Data.*—Data were collected and processed as previously reported.[10] Complete data were recorded to a maximum Bragg angle $\theta$ of 45° from a crystal of dimensions $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}3$ mm to yield 1962 unique reflections. The half-scan range in $\theta$ was determined from $(0{\cdot}5 + 0{\cdot}1 \tan\theta)^\circ$ which was sufficient to allow for the largest observed profile of 0·8° for $\theta < 45°$. During data collection two check reflections, 702 and $\bar{3}06$, had random variations of up to 2·5% from their mean intensity sum and their intensity ratio varied from 0·58 to 0·66.

*Structure Determination and Refinement.*—The approximate co-ordinates of the two crystallographically-independent copper atoms were determined from a three-dimensional Patterson synthesis. A set of structure factors was calculated and used to phase a three-dimensional electron-density distribution from which the approximate positions of the donor atoms were located; further cycles of these calculations enabled all other non-hydrogen atoms to be located.

The co-ordinates and isotropic temperature factors of thirty-eight non-hydrogen atoms were refined by least-squares methods, yielding $R$ 0·12. When individual anisotropic temperature factors were introduced, $R$ was 0·087 and $R'$ 0·123 $[R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]$. The final refinements were carried out by use of the full-matrix least-squares programme ORFLS;[11] the expression $\Sigma w(|F_o| - |F_c|)^2$ was minimised where $w = [\sigma^2(|F_o|) + A|F_o|^2 + B\sum_j f_j^2]^{-1}$ where $\sum_j f_j^2$ is the sum over all atoms in the unit cell of the square of the scattering factor at $\theta$ of zero and where $|F_o|$ and $\sigma^2(|F_o|)$ are on the absolute scale.[12] Estimates of the empirical constants $A$ and $B$ were made by ensuring that $w(|F_o| - |F_c|)^2$ was approximately constant over zones of $|F_o|$ and $\sin\theta$; final values of 0·0033 and 0·0003 were chosen.† Because several low-angle, high-intensity reflections had $|F_o| \ll |F_c|$, corrections for secondary extinction were applied to the observed data by Zachariasen's method[13] where the constant, $c_z$,[10] was empirically determined as $4 \times 10^{-6}$ by comparison of observed and calculated data.

Convergence of all positional parameters was achieved; all positional parameters had shifts $<0{\cdot}05\sigma$. Final fractional co-ordinates of the non-hydrogen atoms are listed in Table 1. All shifts in the $b_{ij}$ parameters of the anisotropic thermal expression were $<0{\cdot}5\sigma$; a complete convergence was not attempted because, first, the data had only been collected up to $\theta$ 45° and, secondly, any slight change in the empirical constants of the weighting scheme ($A$ and $B$) or of the extinction correction [$c_z$] caused considerable shifts in the thermal parameters. For example, when the constant $c_z$ was increased from $2{\cdot}5 \times 10^{-6}$

TABLE 1

Final positional (fractional $\times 10^4$) co-ordinates, with estimated standard deviations in parentheses

| | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|
| Cu(1) | 680·7(11) | 899·6(3) | 1956·6(14) |
| Cu(2) | 1743·1(11) | 1644·1(3) | 1144·8(14) |
| O(1) | 106(5) | 1313(1) | 245(6) |
| O(2) | 2360(5) | 1208(1) | 2702(6) |
| N(1) | −922(6) | 542(2) | 943(8) |
| N(2) | 1429(7) | 417(2) | 3259(8) |
| N(3) | 819(6) | 2140(2) | 75(8) |
| N(4) | 3187(6) | 2027(2) | 2324(8) |
| C($1_1$) | −2148(9) | 643(2) | −171(11) |
| C($2_1$) | −3265(9) | 394(3) | −760(11) |
| C($3_1$) | −3084(9) | 5(3) | −166(12) |
| C($4_1$) | −1816(9) | −103(2) | 997(11) |
| C($5_1$) | −779(8) | 172(2) | 1535(10) |
| C($1_2$) | 2646(8) | 379(2) | 4449(10) |
| C($2_2$) | 3090(10) | 22(3) | 5288(11) |
| C($3_2$) | 2233(9) | −297(2) | 4865(11) |
| C($4_2$) | 951(10) | −264(2) | 3633(12) |
| C($5_2$) | 578(8) | 101(2) | 2833(10) |
| C($1_3$) | −430(9) | 2171(3) | −1078(11) |
| C($2_3$) | −1055(10) | 2533(3) | −1672(12) |
| C($3_3$) | −327(11) | 2859(3) | −1040(12) |
| C($4_3$) | 993(9) | 2835(2) | 212(12) |
| C($5_3$) | 1517(8) | 2466(2) | 714(10) |
| C($1_4$) | 4426(9) | 1928(3) | 3416(11) |
| C($2_4$) | 5427(10) | 2210(3) | 4164(12) |
| C($3_4$) | 5101(9) | 2604(3) | 3771(13) |
| C($4_4$) | 3810(9) | 2696(2) | 2682(12) |
| C($5_4$) | 2893(8) | 2403(2) | 1954(10) |
| S | 2758(2) | 1188(1) | −2167(2) |
| O(3) | 2953(6) | 1489(1) | −824(7) |
| O(4) | 3675(6) | 858(2) | −1544(8) |
| O(5) | 1267(6) | 1062(2) | −2608(7) |
| O(6) | 3130(6) | 1352(2) | −3721(7) |
| O(7) | −265(6) | 1153(2) | 4067(7) |
| O(8) | 6945(6) | 1260(2) | 3873(8) |
| O(9) | 4745(6) | 849(2) | 2079(8) |
| O(10) | −2522(8) | 1633(2) | 590(9) |
| O(11) | 6139(7) | 1448(2) | −2994(9) |

TABLE 2

Unique intermolecular contacts *

| | | | |
|---|---|---|---|
| Cu(1) ··· O(5) | 3·79 | Cu(1) ··· O(10) | 3·95 |
| Cu(1) ··· C($4_1^{III}$) | 3·91 | Cu(1) ··· O($6^{II}$) | 3·97 |
| Cu(1) ··· O(9) | 3·92 | Cu(1) ··· O(3) | 3·99 |
| Cu(2) ··· O(5) | 3·50 | Cu(2) ··· C($4_3^{IV}$) | 3·87 |
| Cu(2) ··· C($3_3^{IV}$) | 3·72 | Cu(2) ··· O(9) | 3·94 |
| Cu(2) ··· O(7) | 3·73 | | |
| O(8) ··· O(9) | 2·67 | O(6) ··· O(11) | 2·85 |
| O(7) ··· O($8^{I}$) | 2·70 | O(1) ··· O(5) | 2·86 |
| O(7) ··· O($5^{II}$) | 2·70 | O(10) ··· O($11^{I}$) | 2·87 |
| O(2) ··· O(9) | 2·76 | O(10) ··· O($8^{I}$) | 3·02 |
| O(2) ··· O($6^{II}$) | 2·77 | O(3) ··· O(9) | 3·35 |
| O(4) ··· O(9) | 2·78 | O(7) ··· O($6^{II}$) | 3·41 |
| O(8) ··· O($11^{II}$) | 2·82 | O(7) ··· O(10) | 3·48 |
| O(1) ··· O(10) | 2·84 | O(4) ··· O(11) | 3·52 |

Roman numeral superscripts refer to the following equivalent positions:

I $-1 + x, y, z$
II $x, y, 1 + z$
III $-x, -y, -z$
IV $x, \frac{1}{2} - y, \frac{1}{2} + z$

* All contacts <4 Å involving Cu atoms, and all oxygen–oxygen contacts <3·6 Å are listed.

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† The presence of the $B\sum_j f_j^2$ term was justified as it weighted those terms with low $|F_o|$ more satisfactorily; $R'$ was found to be dependent upon $B$ as it increased from 0·123 to 0·137 when, as a trial, $B$ was decreased from 0·0002 to zero.

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[12] D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Cryst.*, 1969, **B25**, 374; R. C. G. Killean, *ibid.*, p. 977.

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to $4{\cdot}0 \times 10^{-6}$ the $b_{11}$, $b_{13}$, and $b_{33}$ parameters for the copper atoms had shifts of *ca.* $3{\cdot}5\sigma$.

Scattering-factor curves chosen were those for the uncharged sulphur, carbon, and nitrogen atoms, and that for the divalent copper atom.[14a] Sulphate oxygen atoms were assigned a $\mathrm{O}^{-\frac{1}{2}}$ curve, obtained from O and $\mathrm{O}^{-1}$ curves.[14a] The curves for copper and sulphur were corrected for the effects of anomalous dispersion.[14a]

TABLE 3

Bond lengths and angles

(*a*) Distances (Å)

| | | | |
|---|---|---|---|
| Cu(1) · · · Cu(2) | 2·893(2) | C($1_2$)–C($2_2$) | 1·414(12) |
| O(1) · · · O(2) | 2·576(8) | C($1_3$)–C($2_3$) | 1·417(12) |
| Cu(1)–O(1) | 1·948(5) | C($1_4$)–C($2_4$) | 1·403(12) |
| Cu(1)–O(2) | 1·917(5) | C($2_1$)–C($3_1$) | 1·417(13) |
| Cu(2)–O(1) | 1·947(5) | C($2_2$)–C($3_2$) | 1·372(13) |
| Cu(2)–O(2) | 1·942(5) | C($2_3$)–C($3_3$) | 1·359(13) |
| Cu(1)–N(1) | 1·997(6) | C($2_4$)–C($3_4$) | 1·412(13) |
| Cu(1)–N(2) | 1·999(6) | C($3_1$)–C($4_1$) | 1·398(13) |
| Cu(2)–N(3) | 2·021(6) | C($3_2$)–C($4_2$) | 1·388(13) |
| Cu(2)–N(4) | 1·988(6) | C($3_3$)–C($4_3$) | 1·420(13) |
| Cu(1)–O(7) | 2·244(5) | C($3_4$)–C($4_4$) | 1·377(13) |
| Cu(2)–O(3) | 2·207(5) | C($4_1$)–C($5_1$) | 1·375(11) |
| S–O(3) | 1·461(6) | C($4_2$)–C($5_2$) | 1·414(11) |
| S–O(4) | 1·454(6) | C($4_3$)–C($5_3$) | 1·394(11) |
| S–O(5) | 1·469(6) | C($4_4$)–C($5_4$) | 1·378(11) |
| S–O(6) | 1·461(6) | N(1)–C($5_1$) | 1·354(10) |
| N(1)–C($1_1$) | 1·345(10) | N(2)–C($5_2$) | 1·362(10) |
| N(2)–C($1_2$) | 1·327(10) | N(3)–C($5_3$) | 1·349(10) |
| N(3)–C($1_3$) | 1·334(10) | N(4)–C($5_4$) | 1·345(10) |
| N(4)–C($1_4$) | 1·345(10) | C($5_1$)–C($5_2$) | 1·482(11) |
| C($1_1$)–C($2_1$) | 1·376(12) | C($5_3$)–C($5_4$) | 1·470(11) |

(*b*) Angles (°)

| | | | |
|---|---|---|---|
| O(1)–Cu(1)–O(2) | 83·6(2)° | C($1_4$)–N(4)–C($5_4$) | 119·7(6) |
| O(1)–Cu(2)–O(2) | 82·9(2) | N(1)–C($1_1$)–C($2_1$) | 124·1(8) |
| N(1)–Cu(1)–N(2) | 81·0(3) | N(2)–C($1_2$)–C($2_2$) | 122·4(8) |
| N(3)–Cu(2)–N(4) | 79·9(3) | N(3)–C($1_3$)–C($2_3$) | 122·9(8) |
| Cu(1)–O(1)–Cu(2) | 95·9(2) | N(4)–C($1_4$)–C($2_4$) | 121·0(8) |
| Cu(1)–O(2)–Cu(2) | 97·1(2) | C($1_1$)–C($2_1$)–C($3_1$) | 117·1(8) |
| O(1)–Cu(1)–N(1) | 96·3(2) | C($1_2$)–C($2_2$)–C($3_2$) | 119·1(8) |
| O(2)–Cu(1)–N(2) | 97·2(2) | C($1_3$)–C($2_3$)–C($3_3$) | 117·8(8) |
| O(1)–Cu(2)–N(3) | 95·9(2) | C($1_4$)–C($2_4$)–C($3_4$) | 118·7(8) |
| O(2)–Cu(2)–N(4) | 98·3(2) | C($2_1$)–C($3_1$)–C($4_1$) | 119·3(8) |
| O(7)–Cu(1)–O(1) | 96·9(2) | C($2_2$)–C($3_2$)–C($4_2$) | 119·6(8) |
| O(7)–Cu(1)–O(2) | 91·3(2) | C($2_3$)–C($3_3$)–C($4_3$) | 120·7(8) |
| O(7)–Cu(1)–N(1) | 96·9(2) | C($2_4$)–C($3_4$)–C($4_4$) | 118·8(8) |
| O(7)–Cu(1)–N(2) | 96·4(2) | C($3_1$)–C($4_1$)–C($5_1$) | 118·9(8) |
| O(3)–Cu(2)–O(1) | 97·2(2) | C($3_2$)–C($4_2$)–C)$5_2$) | 118·4(8) |
| O(3)–Cu(2)–O(2) | 96·6(2) | C($3_3$)–C($4_3$)–C($5_3$) | 117·2(8) |
| O(3)–Cu(2)–N(3) | 99·9(2) | C($3_4$)–C($4_4$)–C($5_4$) | 119·4(8) |
| O(3)–Cu(2)–N(4) | 93·1(2) | C($4_1$)–C($5_1$)–N(1) | 122·5(7) |
| O(1)–Cu(1)–N(2) | 166·6(2) | C($4_2$)–C($5_2$)–N(2) | 121·8(7) |
| O(2)–Cu(1)–N(1) | 171·7(2) | C($4_3$)–C($5_3$)–N(3) | 122·7(7) |
| O(1)–Cu(2)–N(4) | 169·4(2) | C($4_4$)–C($5_4$)–N(4) | 122·3(7) |
| O(2)–Cu(2)–N(3) | 163·5(2) | C($4_1$)–C($5_1$)–C($5_2$) | 124·2(7) |
| Cu(1)–N(1)–C($1_1$) | 125·7(5) | C($4_2$)–C($5_2$)–C($5_1$) | 123·1(7) |
| Cu(1)–N(2)–C($1_2$) | 126·6(5) | C($4_3$)–C($5_3$)–C($5_4$) | 122·5(7) |
| Cu(2)–N(3)–C($1_3$) | 126·3(5) | C($4_4$)–C($5_4$)–C($5_3$) | 124·1(7) |
| Cu(2)–N(4)–C($1_4$) | 123·5(5) | N(1)–C($5_1$)–C($5_2$) | 113·3(6) |
| Cu(1)–N(1)–C($5_1$) | 116·0(5) | N(2)–C($5_2$)–C($5_1$) | 115·0(6) |
| Cu(1)–N(2)–C($5_2$) | 114·6(5) | N(3)–C($5_3$)–C($5_4$) | 114·8(6) |
| Cu(2)–N(3)–C($5_3$) | 114·7(5) | N(4)–C($5_4$)–C($5_3$) | 113·5(6) |
| Cu(2)–N(4)–C($5_4$) | 116·8(5) | O(3)–S–O(4) | 110·5(3) |
| Cu(1)–N(1)–C($3_1$) | 174·5(4) | O(3)–S–O(5) | 109·5(3) |
| Cu(1)–N(2)–C($3_2$) | 174·1(4) | O(3)–S–O(6) | 107·8(3) |
| Cu(2)–N(3)–C($3_3$) | 173·7(4) | O(4)–S–O(5) | 109·7(3) |
| Cu(2)–N(4)–C($3_4$) | 175·5(4) | O(4)–S–O(6) | 109·5(3) |
| C($1_1$)–N(1)–C($5_1$) | 118·1(6) | O(5)–S–O(6) | 109·8(3) |
| C($1_2$)–N(2)–C($5_2$) | 118·7(6) | Cu(2)–O(3)–S | 132·4(3) |
| C($1_3$)–N(3)–C($5_8$) | 118·7(6) | | |

Final calculated structure factors, observed structure amplitudes, and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21289 (10 pp., 1 microfiche).* Final values $R$ and $R'$ were 0·078 and 0·105 respectively. Relevant intermolecular contacts are listed in Table 2, covalent bond lengths and angles in Table 3, and an analysis of mean planes in Table 4.

TABLE 4

Equations of mean planes in the form $lX + mY + nZ + d = 0$, where $X$, $Y$, and $Z$ are co-ordinates in Å, such that $X = x + z \cos \beta$, $Y = y$, and $Z = z \sin \beta$. Deviations ($\text{Å} \times 10^{-3}$) of relevant atoms from the planes are given in square brackets

| | $l$ | $m$ | $n$ | $d$ |
|---|---|---|---|---|
| Plane (1): O(1), O(2), N(1), N(2) | 0·6258 | −0·3690 | −0·6871 | 1·7972 |
| [O(1) 33, O(2) −32, N(1) −53, N(2) 57, Cu(1) −182] | | | | |
| Plane (2): O(1), O(2), N(3), N(4) | 0·6652 | −0·2383 | −0·7077 | 1·2157 |
| [O(1) 42, O(2) −40, N(3) −67, N(4) 68, Cu(2) 231] | | | | |
| Plane (3): Cu(1), O(1), O(2) | 0·5914 | −0·4858 | −0·6436 | 2·2877 |
| Plane (4): Cu(2), O(1), O(2) | 0·6353 | −0·3912 | −0·6659 | 1·8606 |
| Plane (5): N(1), C($1_1$)—($5_1$) | 0·5844 | −0·2445 | −0·7737 | 1·6414 |
| [N(1) 6, C($1_1$) 1, C($2_1$) −11, C($3_1$) 7, C($4_1$) 8, C($5_1$) −12, Cu(1) −93] | | | | |
| Plane (6): N(2), C($1_2$)—($5_2$) | 0·6490 | −0·2324 | −0·7244 | 1·6171 |
| [N(2) −1, C($1_2$) −2, C($2_2$) 1, C($3_2$) 2, C($4_2$) −6, C($5_2$) 4, Cu(1) 13] | | | | |
| Plane (7): N(1), C($1_1$)—($5_1$), N(2), C($1_2$)—($5_2$) | 0·6224 | −0·2437 | −0·7438 | 1·7007 |
| [N(1) 48, C($1_1$) −20, C($2_1$) −82, C($3_1$) −50, C($4_1$) 16, C($5_1$) 43, N(2) −2, C($1_2$) −45, C($2_2$) −48, C($3_2$) −9, C($4_2$) 28, C($5_2$) 40, O(1) 494, O(2) 272] | | | | |
| Plane (8): N(3), C($1_3$)—($5_3$) | 0·6622 | −0·0106 | −0·7493 | −0·3915 |
| [N(3) 3, C($1_3$) −3, C($2_3$) −6, C($3_3$) 12, C($4_3$) −5, C($5_3$) −2, Cu(2) −125] | | | | |
| Plane (9): N(4), C($1_4$)—($5_4$) | 0·6203 | −0·0590 | −0·7822 | 0·1444 |
| [N(4) 0, C($1_4$) −9, C($2_4$) 6, C($3_4$) 8, C($4_4$) −16, C($5_4$) 9, Cu(2) 46] | | | | |
| Plane (10): N(3), C($1_3$)—($5_3$), N(4), C($1_4$)—($5_4$) | 0·6463 | −0·0382 | −0·7621 | −0·1512 |
| [N(3) 27, C($1_3$) 45, C($2_3$) 21, C($3_3$) −7, C($4_3$) −52, C($5_3$) −25, N(4) −45, C($1_4$) −19, C($2_4$) 49, C($3_4$) 67, C($4_4$) 6, C($5_4$) −21, O(1) −429, O(2) −718] | | | | |

Values of $\chi^2$: (1) 237, (2) 376, (5) 6·1, (6) 0·7, (7) 298, (8) 2·7, (9) 6·4, (10) 235

Dihedral angles (°): (1)—(2) 7·9, (3)—(4) 6·1, (5)—(6) 4·7, (8)—(9) 4·1

Peaks found in the final difference synthesis permitted the tentative identification of the hydrogen atoms bonding to oxygen atoms; details relevant to the probable hydrogen-bonding network are given in Table 5. As the observation-to-parameter ratio was already 5·7 : 1, no legitimate attempt could be made to refine these positions.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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## RESULTS AND DISCUSSION

*Intermolecular Structure.*—Although the binuclear $[(bipy)Cu(OH)_2Cu(bipy)]^{2+}$ complex ion probably exists in aqueous solutions, it is found to be bonding to both a sulphate ion and a water molecule in the solid state; the compound may thus be formulated as $[(H_2O)(bipy)Cu(OH)_2Cu(bipy)(OSO_3)],4H_2O$ (Figure 1).

TABLE 5

Hydrogen atoms (H) bonded to oxygen atoms (O) with a near oxygen contact (O′); distances in Å, angles in °

| Electron density | Fract. co-ords. | Atom O | O–H | Atom O′ | O′ · · · H | O · · · O′ | $\widehat{OHO'}$ | H from O ⟶ O′ |
|---|---|---|---|---|---|---|---|---|
| 0·49 | 0·01, 0·12, −0·09 | O(1) | 0·93 | O(5) | 2·05 | 2·86 | 145 | 0·38 |
| 0·48 | 0·27, 0·12, 0·40 | O(2) | 1·00 | O(6$^{II}$) | 1·77 | 2·77 | 180 | 0·00 |
| 0·81 | 0·03, 0·11, 0·53 | O(7) | 0·99 | O(5$^{II}$) | 1·71 | 2·70 | 180 | 0·00 |
| 0·37 | −0·10, 0·12, 0·33 | O(7) | 0·83 | O(8$^{I}$) | 2·12 | 2·70 | 127 | 0·53 |
| 0·46 | 0·62, 0·10, 0·32 | O(8) | 1·22 | O(9) | 1·58 | 2·67 | 145 | 0·42 |
| 0·68 | 0·67, 0·13, 0·50 | O(8) | 1·09 | O(11$^{II}$) | 1·76 | 2·82 | 161 | 0·23 |
| 0·53 | 0·46, 0·08, 0·09 | O(9) | 0·89 | O(4) | 1·93 | 2·78 | 160 | 0·21 |
| 0·30 | 0·41, 0·09, 0·23 | O(9) | 0·75 | O(2) | 2·02 | 2·76 | 180 | 0·00 |
| 0·42 | −0·15, 0·17, 0·17 | O(10) | 1·17 | O(11$^{I}$) | 1·93 | 2·87 | 134 | 0·56 |
| 0·37 | −0·31, 0·15, 0·14 | O(10) | 1·00 | O(8$^{I}$) | 2·11 | 3·02 | 150 | 0·35 |
| 0·44 | 0·52, 0·15, −0·35 | O(11) | 0·86 | O(6) | 2·05 | 2·85 | 155 | 0·26 |
| 0·60 | 0·66, 0·15, −0·17 | O(11) | 1·03 * | † | | | | |

* Mean 0·98. † No short contact.

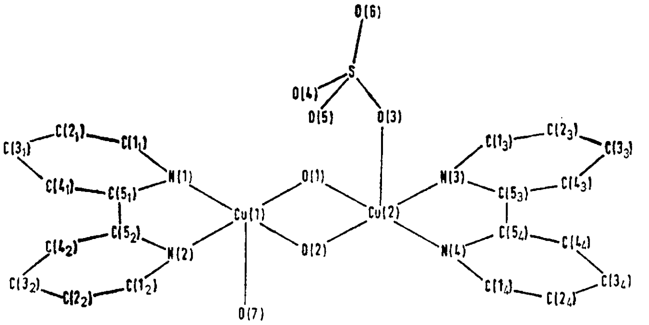

FIGURE 1 The binuclear complex, showing the labelling of the atoms

Twelve unique oxygen–oxygen contacts (Tables 2 and 5) are found within the range of 2·49—3·15 Å (mean 2·74 Å) quoted [14b] for OH · · · O type hydrogen bonds in hydrated inorganic salts. These contacts (Figure 2) appear to provide a network of hydrogen bonding which explains the positioning of both the $-SO_3$ segment of the sulphato-ligand and the water molecules of crystallization. Each water molecule has from two [O(7)] to four [O(8)] oxygen–oxygen contacts in the range 2·67—3·02 Å.

The hydrogen atom assumed to be attached to a bridging oxygen atom [O(1)] is positioned [angle O(2)···O(1)–H *ca.* 120°] where it appears to form an intramolecular hydrogen bond with a sulphato-oxygen atom [O(5)], giving an O(1)–H · · · O(5) angle of *ca.* 145° (Table 5). The hydrogen atom assumed to be attached to the other bridging oxygen atom [O(2)] is directed [O(1) · · · O(2)–H *ca.* 140°] at a sulphato-oxygen atom [O(6$^{II}$)] of the adjacent binuclear complex; this O(2) · · · O(6$^{II}$) contact and one other [O(7) · · · O(5$^{II}$)] contact are the only direct contacts between neighbouring complexes (Figure 2), and the data in Table 5 suggest they involve 180° hydrogen bonds.

*Bipyridyl Ligands.*—The aromatic C–C and C–N bond lengths are in agreement with those reported [15] for unco-ordinated 2,2′-bipyridine. The ligands have maximum displacements from planarity of 0·082 [plane (7)] to 0·067 Å [plane (10), Table 4], agreeing closely with a displacement of 0·084 Å for the bipyridine ligand in the analogous nitrate compound [(I) in Table 6]; these distortions are all considerably more than in unco-ordinated 2,2′-bipyridine which has a maximum displacement of 0·014 Å. Each ligand is buckled so that its outer carbon atoms are displaced towards the apical atom [O(7) and O(3) respectively] of the square-

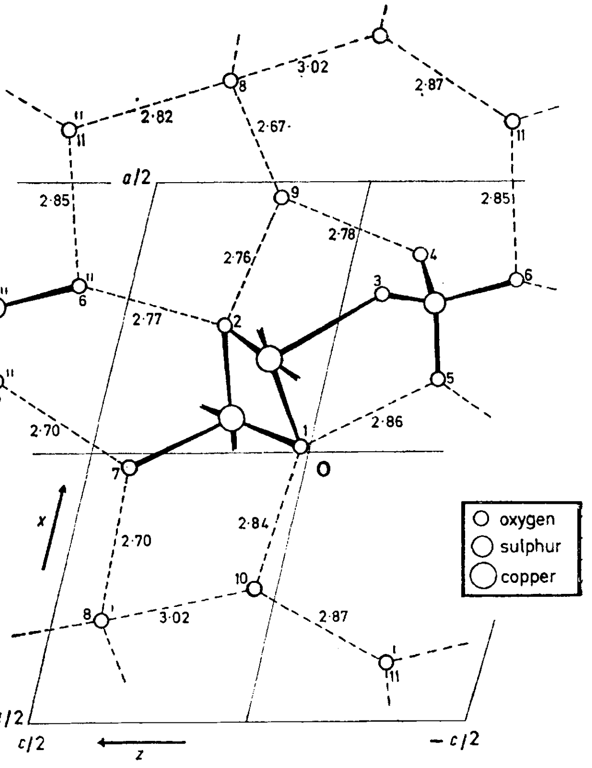

FIGURE 2 The network of probable hydrogen bonding viewed along the *b* axis. For clarity, the bipyridyl ligands are not included

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[15] L. L. Merritt, jun., and E. D. Schroeder, *Acta Cryst.*, 1956, **9**, 801.

pyramidal arrangement about the copper atom; the dihedral angles between the planar pyridyl rings of each bipyridine ligand are 4·7 and 4·1° respectively (Table 4). The in-plane distortion of each bipyridine ligand can be seen by a comparison of the mean ' outer ' (125·5°, range 3·1°) with the mean ' inner ' Cu–N–C angle (115·5°, range 2·2°; Table 3).

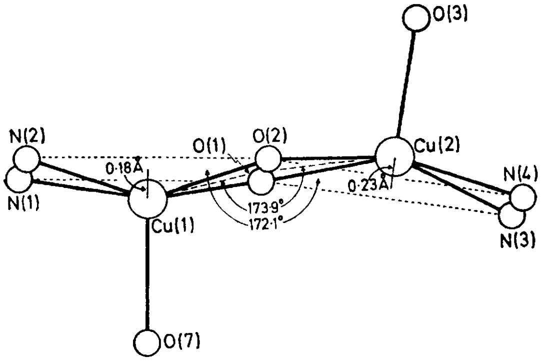

FIGURE 3 The environments of the copper atoms

TABLE 6

Comparison of structures of some di-μ-hydroxo-copper(II) compounds; distances in Å, angles in °

| Compound | (I) | (II) | (III) | (IV) | (V) | (VI) | (VII) | (VIII) | (IX) | (X) |
|---|---|---|---|---|---|---|---|---|---|---|
| Stereochemistry | Sq. pyramid | Sq. pyramid | Sq. plane | Sq. pyramid | Sq. pyramid | Octahedral | Octahedral | Sq. pyramid | Octahedral | Sq. planar |
| Unit | Binuclear | Binuclear | Binuclear | Tetranuclear | Tetranuclear | Planar chains | Planar chains | Binuclear | Binuclear | Binuclear |
| Cu–Cu | 2·847 | 2·893(2) | 3·000(4) | 2·782 | 2·995 | 2·95 | 2·825 | 2·917(5) | 2·938(1) | 2·978(2) |
| OR ··· OR | *ca.* 2·58 (R = H) | 2·576(8) (R = H) | *ca.* 2·34 (R = H) | 2·497 (R = H) | 2·37 (R = $CH_2Ph$) | 2·51 (R = H) | 2·64 (R = H) | (R = H) [a] | (R = H) [a] | (R = H) [a] |
| Dihedral angle between | | | | | | | | | | |
| (i) the basal planes | *a* | 7·9 | 0 | 50·8 | *a* | 0 | 0 | 1·4 | 0 | 0 |
| (ii) O, Cu, O planes | 0 | 6·1 | 0 | *a* | *ca.* 1 | 0 | 0 | 0 | 0 | 0 |
| Cu–OH–Cu | 95·6 | 95·9, 97·1 | 104·1 | *a* | 100·9, 105·8 | *ca.* 99 | 95 | 99·2 | 98·4 | 103·0 |
| OH–Cu–OH | 84·4 | 82·9, 83·6 | 75·9 | 78·6—79·1 | 76·7 | *ca.* 81 | 85 | 80·8 | 81·6 | 77·0 |
| Cu–OH (basal) | 2(1·920),<br>2(1·923) | 1·917—<br>1·948 | 1·902 | 2(1·94),<br>2(1·99) | 1·87—1·95 | 1·93—1·94 | 2(1·93),<br>2(1·98) | 1·895—<br>1·930 | 1·936,<br>1·947 | 1·899,<br>1·907 |
| Cu–O(apical) | 2·379 [b] | 2·207(5), [c]<br>2·244(5) [d] | | 2·40, [e]<br>2·37 [d] | 2·42, [f]<br>2·71 [g] | 2·63 [h] | 2·53 [i] | 2·562, [j]<br>2·618 [j] | 2·716, [k]<br>2·782 [k] | |

[a] Not reported. [b] Two $NO_3$. [c] One $SO_4$. [d] One $H_2O$. [e] One OH. [f] One $OCH_2Ph_2$. [g] One acac. [h] Four OH. [i] Four $SO_4$. [j] One $ClO_4$. [k] Two $ClO_4$.

(I) $[(O_2NO)(bipy)Cu(OH)_2Cu(bipy)(ONO_2)]$, ref. 27; (II) $[(H_2O)(bipy)Cu(OH)_2Cu(bipy)(OSO_3)],4H_2O$, present work; (III) $[LCu(OH)_2CuL]Br_2$, L = $Me_2N\cdot[CH_2]_2\cdot NMe_2$, ref. 24; (IV) $[\{H_2O(MeNH_2)_2Cu(OH)_2Cu(MeNH_2)_2\}_2](SO_4)_2$, ref. 23; (V) $[(acac)Cu(OCH_2Ph)_2Cu(acac)]$, acac = acetylacetonato, ref. 25; (VI) $[Cu(OH)_2]_n$, ref. 26; (VII) Linarite, $Pb_n[Cu(OH)_2]_n(SO_4)_n$, ref. 19; (VIII) $[L(O_3ClO)Cu(OH)_2Cu(OClO_3)L]$, L = 2-(2′-ethylaminoethyl)pyridine, ref. 28(*a*); (IX) $[LCu(OClO_2O)_2(OH)_2CuL]$, L = 2-(2′-dimethylaminoethyl)pyridine, ref. 28(*b*); (X) $[LCu(OH)_2CuL](ClO_4)_2$, L = $Et_2N\cdot[CH_2]_2\cdot NEt_2$, ref. 29.

An analysis[16] of the bipyridine bond lengths and angles suggests that σ for all positional parameters have been underestimated by *ca.* 25%.

*Environments of the Copper Atoms.*—Each copper atom of the binuclear complex is bonded to five donor atoms in a distorted square-pyramidal arrangement (Figure 3). Carbon atoms from neighbouring binuclear complexes are positioned in the sixth co-ordinating site of each copper atom: Cu(2) ··· C($3_3^{IV}$) 3·72, and Cu(1) ··· C($4_1^{III}$) 3·91 Å. For each copper atom the basal atoms are the two bridging oxygen atoms and the two nitrogen atoms of one of the bipyridine ligands. One of the apical atoms [O(3)] is an oxygen atom of the sulphate anion while the other [O(7)] is that of a water molecule. Each copper atom is displaced towards the apical atom *ca.* 0·2 Å from the mean plane through its basal atoms; this is in agreement with the displacements reported for other square-pyramidal copper(II) compounds.[17] The dihedral angle between the two basal planes is 7·9(3)° and that between the two O,Cu,O planes is 6·1(3)° (Figure 3 and Table 4).

One of the four copper-bridging-oxygen distances [Cu(1)–O(2)] has a deviation of 0·021 Å (4·5$\sigma_i$) from the mean (1·938 Å) for these distances. Likewise, one of the four copper–nitrogen distances [Cu(2)–N(3)] has a deviation of 0·020 Å (3·4$\sigma_i$) from their mean (2·001 Å). Although these deviations may be significant, it is possible that they result from systematic error.

The shortness of the copper–apical-oxygen bonds is surprising. First, while the copper–apical-sulphate oxygen distance [Cu(2)–O(3) 2·207(5) Å] is longer than that (2·15 Å)[18] in the trinuclear cluster $[(OSO_3)Cu_3L_3(OH)],nH_2O$ (L = pyridine-2-aldoximate), it is significantly shorter than the copper–axial-sulphate oxygen distances usually found (2·35—2·56 Å) in distorted octahedral copper(II) complexes.[19,20] Secondly, while the copper–apical-water oxygen distance [Cu(1)–O(7) 2·244(5) Å] is in good agreement with the apical distance (2·23 Å)[21] in $Cu_8Mg_8(CO_3)_4(OH)_{24},8H_2O$

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(callaghanite), it is much shorter than those usually observed[22,23] (2·37—2·76 Å) in other square-pyramidal complexes.

A comparison of the structural features of some di-μ-hydroxo-dicopper(II) compounds (Table 6)[19,23-29] is interesting in view of the dissimilarity between the compounds; while the present Cu(1)–Cu(2) distance [2·893(2) Å] is in good agreement with those [2·78—3·00 Å] observed in these other compounds, it is much shorter than the range (3·10—3·44 Å) for other ferromagnetic copper(II) compounds.[30-32] A qualitative 90° superexchange mechanism by which the ferromagnetic coupling in this compound occurs has been discussed tentatively elsewhere.[3,4a,16] Further, a linear correlation has been found[28,29] between $2J$, the singlet–triplet splitting, and an angle Cu–OH–Cu in four compounds [(II), (III), (VIII), and (X)]; it has been hypothesised that as the $p$ character of the oxygen bonding orbitals increase, *i.e.* as the Cu–OH–Cu angle decreases, the less pronounced is the antiferromagnetic effect.[28,29]

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