Crystal and Molecular Structure of a Trinuclear Copper(II) Complex: μ_3-Hydroxo-tri-μ-(pyridine-2-carbaldehyde oximato)-μ_3-sulphato-tricopper(II)–16·3Water

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The crystal and molecular structure of the title complex has been determined by *X*-ray photographic methods. The unit cell is trigonal, with $a = b = 18{\cdot}05(1)$, $c = 7{\cdot}25(1)$ Å, space-group $P\bar{3}$, and $Z = 2$. The structure was solved by conventional Patterson and Fourier methods, and was refined by least-squares to R 0·15 for 2043 unique reflections. Only a few of the water molecules of crystallization could be located. The crystal is composed of trinuclear units of copper atoms each centred about a three-fold crystallographic axis so that the three copper atoms fall at the corners of an exact equilateral triangle of side 3·22 Å. The copper atoms are held together by three distinct bridging systems: (i) the oxygen atom of the hydroxy-group, situated on the three-fold axis, is bonded to all three copper atoms with Cu–O 1·98 Å, (ii) a sulphato-group, also on the three-fold axis, acts as a tripod bridge, bonding to all three copper atoms through three of its oxygen atoms, and (iii) three symmetry-related pyridine-2-carbaldehyde oximato-groups each functioning both as a bidentate chelate to one of the copper atoms (*via* both N atoms) and as a Cu–Cu bridging group (*via* oxime N and O). The trimer units are stacked in continuous columns parallel to the c axis and adjacent units are held together by hydrogen bonding. These columns are arranged such that a large almost cylindrically shaped hole (diameter *ca.* 10 Å) is formed, running along the length of the c axis, and containing the molecules of water of crystallization; these are not held in fixed positions but appear to be somewhat mobile. The structure of the complex confirms a prediction made on the basis of the observed temperature-independent magnetic moment of 1·0 B.M. per copper atom.

DURING an investigation of the reaction of pyridine-2-carbaldehyde oxime (HL) and copper(II) ions a series of compounds was isolated[1] of composition $Cu_3L_3(OH)X_2,xH_2O$ ($X = \frac{1}{2}SO_4^{2-}$, NO_3^-, ClO_4^-, and OH^-) all having anomalously low magnetic moments. A detailed study of the magnetic properties of the sulphate, hydroxide, and basic perchlorate has been made.[2] It was found that in the temperature range 100—400 K the magnetic data, when corrected for diamagnetism and temperature-independent paramagnetism, obey Curie's law with a magnetic moment μ_{eff} of *ca.* 1·0 B.M. per copper atom. This suggested[3] the presence of a trinuclear Cu_3 core in which strong metal–metal interaction has caused the pairing of two of the three unpaired electrons associated with the three copper atoms, as occurs in the somewhat analogous case of the $[Re_3Cl_{12}]^{3-}$ anion.[4] However, the magnetic data alone do not distinguish between the possible linear and triangular array of the metal atoms. This ambiguity has been resolved by the crystal-structure determination of $Cu_3L_3(OH)SO_4,16{\cdot}3H_2O$, which has shown that the molecular structure is based on a triangular Cu_3 core. We now report the results of this crystal-structure analysis.

EXPERIMENTAL

Preliminary Data.—The compound $Cu_3L_3(OH)SO_4$ was prepared by the method of ref. 1 and crystals suitable for *X*-ray analysis were obtained by slow cooling (*ca.* 10 days) of a saturated aqueous solution of the compound at pH 5·5. The crystals separated as light green, transparent, hexagonal prisms (with the crystallographic c axis coinciding with the prism axis) which on exposure to air effloresced, cracked, and became quite opaque. Chemical analysis showed that the freshly prepared crystals had the composition $Cu_3L_3(OH)SO_4,16{\cdot}3H_2O$.

X-Ray measurements were made on crystals sealed in Lindemann glass capillary tubes together with some of the mother liquor in order to prevent efflorescence. There were no systematic absences nor were there any equivalences between the various classes of reflections other than those required for the Laue symmetry group $\bar{3}$; the space-group was therefore $P3$ or $P\bar{3}$.[5] Cell dimensions were determined from calibrated Weissenberg photographs of the $hk0$ and $0kl$ layers.

Intensity Measurements.—Intensity data were measured visually from equi-inclination Weissenberg photographs by the multiple-film technique, from the layers $hk0$—6, with Cu-K_α radiation. The crystal used for the preparation of the intensity photographs was a prism with an almost regular hexagonal cross-section. Its dimensions were 0·15 mm between parallel sides of the hexagonal face and 0·15 mm in length. Although preliminary data were recorded about the other axes photographs suitable for intensity measurements could only be obtained about the c axis. Corrections for Lorentz and polarization factors were applied but no allowance was made for either absorption or extinction. Because the intensity data available were about one axis only the exposure times were used to place the data for the different layers on approximately the same arbitrary common scale; 2043 non-zero unique reflections were obtained.

Crystal Data.—$Cu_3L_3(OH)SO_4,16{\cdot}3H_2O$, $M = 960{\cdot}6$, Trigonal, $a = b = 18{\cdot}05(1)$, $c = 7{\cdot}25(1)$ Å, $U = 2046$ Å^3; $D_m = 1{\cdot}57$, $Z = 2$, $D_c = 1{\cdot}56$, $F(000) = 968{\cdot}1$. Space-group $P\bar{3}$ (C^1_{3i}; No. 147); Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å. $\mu(\text{Cu-}K_\alpha) = 31{\cdot}5$ cm^{-1}. Single-crystal oscillation, Weissenberg, and precession photographs.

Structure Determination.—From the three-dimensional Patterson synthesis approximate co-ordinates of the copper and sulphur atoms were obtained in terms of the space.

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[1] R. W. Green and M. C. K. Svasti, *Austral. J. Chem.*, 1963, **16**, 356.

[2] B. F. Hoskins and D. G. Vince, unpublished results.

[3] R. Beckett, R. Colton, B. F. Hoskins, R. L. Martin, and D. G. Vince, *Austral. J. Chem.*, 1969, **22**, 2527.

[4] R. Colton and R. L. Martin, *Nature*, 1965, **205**, 239; 1965, **207**, 141.

[5] 'International Tables for *X*-Ray Crystallography,' vol. I, Kynoch Press, Birmingham, 1952.

group $P\bar{3}$. From these co-ordinates and an arbitrarily chosen overall isotropic temperature factor, with $B = 3{\cdot}5$ Å^2, a set of structure factors was calculated (R 0·44) and used to phase a three-dimensional electron-density distribution from which all the atoms of the asymmetric unit, except the oxygen atoms of the water molecules, were located. A further set of structure factors was calculated (R 0·36) and the scale factors were adjusted so that for each of the layers recorded $\Sigma|F_o| = \Sigma|F_c|$. At this stage no definite sites could be assigned to the oxygen atoms of the water molecules either from Fourier or difference syntheses. Refinement of the co-ordinates of the atoms so far located was commenced by means of a difference synthesis and then continued by a least-squares method in which the function $\Sigma w\Delta^2$ was minimized. Initially unit weights were used and the atomic co-ordinates, the overall temperature factor, and the individual scale factors were varied. This was followed by the introduction of individual isotropic temperature factors and refinement was continued until all the parameters of the atoms so far placed had converged; R was reduced to 0·25. A difference map indicated marked anisotropic thermal motion of the atoms included in the refinement but gave no information about the molecules of water of crystallization. A further round of three least-squares cycles was calculated in which the individual scale-factors were fixed and only the atomic co-ordinates and anisotropic thermal parameters were varied. For the first cycle unit weights were used (R 0·23) and for the other two cycles a weighting scheme of the form $w = 1/(0{\cdot}7|F_o|)$ was used; shifts in parameters were all $<0{\cdot}05\sigma$ and R was 0·19. With this weighting scheme and isotropic thermal parameters R was reduced to 0·21. A difference synthesis revealed no definite sites for any of the water molecules, the residual electron density over the region where they were expected to be found being diffuse and attenuated. It was concluded that most of the water molecules were randomly distributed. A number of possible sites were tested in least-squares calculations but mostly without success, even when occupancy factors were introduced to account for the possibility of partial occupation of the site. Five of these sites were included in the final structure-factor calculation because the values of their co-ordinates had converged satisfactorily (the final shifts being $<0{\cdot}05\sigma$) and their inclusion had reduced R to 0·15. However, the shifts in their occupation factors and their anisotropic thermal parameters were as much as 3σ and could not be reduced: the values quoted for these parameters (in Table 1) can at best only be regarded as estimates.

The final set of co-ordinates and thermal parameters together with their estimated standard deviations for each of the atoms is listed in Table 1.

The scattering factors used were taken from ref. 6 and anomalous dispersion corrections for copper and sulphur from ref. 7. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20256 (9 pp., 1 microfiche).*

TABLE 1

Final atomic co-ordinates and thermal parameters (10^3 Å^2) with estimated standard deviations in parentheses

	Fractional co-ordinates				Anisotropic thermal parameters *					
Atom †	x/a	y/b	z/c	Occupation factor	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0·4193(1)	0·6384(1)	0·1999(3)		68	71	127	38	6	3
N(1)	0·4923(8)	0·5873(8)	0·2371(19)		85	91	154	50	15	24
N(2)	0·3275(7)	0·5170(7)	0·1869(20)		72	82	173	44	21	−3
C(1)	0·3563(11)	0·4620(8)	0·2118(27)		112	56	169	38	−6	9
C(2)	0·4444(9)	0·4973(9)	0·2364(19)		99	83	120	58	21	12
C(3)	0·4904(12)	0·4545(10)	0·2569(24)		129	105	154	83	6	2
C(4)	0·5775(11)	0·4974(11)	0·2774(26)		105	112	170	76	15	9
C(5)	0·6218(12)	0·5824(14)	0·2779(28)		123	140	175	99	14	5
C(6)	0·5973(11)	0·6274(10)	0·2517(25)		105	104	144	56	−10	2
O(1)	0·2460(6)	0·4876(6)	0·1662(19)		70	72	209	28	4	−14
O(2)	0·6667(0)	0·3333(0)	0·2218(25)		206	206	66	103	0	0
O(3)	0·2499(6)	0·5901(6)	0·4892(13)		91	86	109	36	6	8
O(4)	0·3333(0)	0·6667(0)	0·1032(21)		59	59	127	30	0	0
S	0·6667(0)	0·3333(0)	0·4256(10)		92	92	138	46	0	0
WO(1)	0·0000(0)	0·0000(0)	0·2366(70)	0·517	93	89	264	44	0	0
WO(2)	0·4314(30)	0·2383(30)	0·3252(70)	0·472	151	118	522	93	−208	−143
WO(3)	0·3513(30)	0·1831(30)	0·0688(70)	0·400	142	214	152	83	7	−11
WO(4)	0·2326(30)	0·2400(30)	0·0551(70)	0·393	209	190	274	138	−41	−26
WO(5)	0·1904(30)	0·0285(30)	0·1635(70)	0·295	224	465	85	225	51	85

* In the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^*, etc.)]$. † WO denotes the oxygen atom of a water molecule.

RESULTS AND DISCUSSION

Crystals of the compound $Cu_3L_3(OH)SO_4,16{\cdot}3H_2O$, are composed of trinuclear units of copper atoms. The units are centred around three-fold crystallographic axes of the type $\pm(1/3, 2/3, z)$ so that the three copper atoms fall at the corners of an exact equilateral triangle of side 3·220 Å. The general arrangement of the crystal structure is given in Figure 1 which shows a projection down the c axis. Bond lengths and bond angles are listed in Table 2 and Figures 2 and 3 give the numbering system used.

In each trimeric unit the copper atoms are held together by three distinct bridging systems (Figures 2 and 3). These are: (i) the oxygen atom of the hydroxy-group, situated on the three-fold axis about which the trinuclear unit is centred, so that its distance is 1·98(1) Å from each of the copper atoms and 0·697(15) Å above the

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[6] Ref. 5, vol. III, 1962, p. 201 *et seq.*

[7] Ref. 6, p. 214.

plane passing through the three metal atoms; (ii) the sulphato-group, also lying on the three-fold axis but below the plane containing the copper atoms, and acting as a tripod bridge bonding to all three copper atoms through three of its oxygen atoms (Figure 3), and (iii) the three symmetry-related pyridine-2-carbaldehyde oximato-groups each of which functions as a bidentate chelate to one of the copper atoms, through its two nitrogen atoms, and as a copper–copper bridging group through the nitrogen and oxygen atoms of the oximato-moiety (Figure 2).

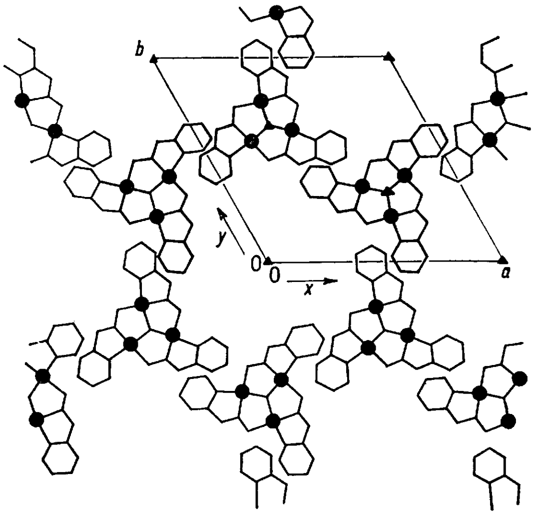

FIGURE 1 The general arrangement of the crystal structure viewed down the *c* axis; sulphato-groups omitted for clarity; filled circles denote copper atoms

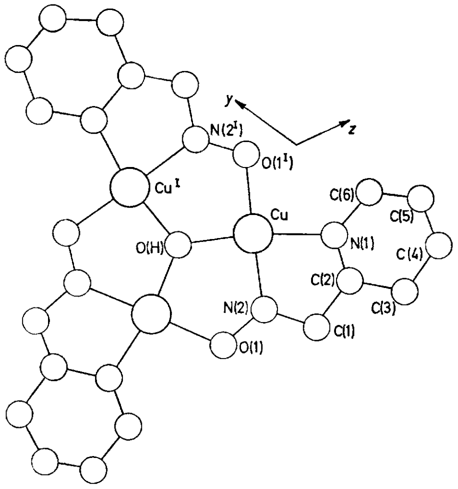

FIGURE 2 A projection of trimer unit down its three-fold axis; sulphato-group has been omitted for clarity. Transformations are defined in text

The three pyridine-2-carbaldehyde oximato-ligands of the trimer do not lie in the plane of the copper atoms but slope away slightly from the hydroxy-group so that this part of the structure resembles a shallow triangular pyramid with the hydroxy-oxygen atom situated at its imaginary apex.

TABLE 2

Intramolecular covalent bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses *

(*a*) Bond lengths

Cu–Cu$^{\mathrm{I}}$	3·220(3)	C(1)–C(2)	1·40(2)
Cu–N(1)	1·97(1)	C(2)–C(3)	1·40(2)
Cu–N(2)	1·98(1)	C(3)–C(4)	1·37(2)
Cu–O(3$^{\mathrm{I}}$)	2·15(1)	C(4)–C(5)	1·33(3)
Cu–O(1$^{\mathrm{I}}$)	1·98(1)	C(5)–C(6)	1·38(2)
Cu–O(H)	1·99(1)	C(6)–N(1)	1·37(2)
O(3$^{\mathrm{I}}$)–S$^{\mathrm{II}}$	1·57(1)	N(2)–O(1)	1·30(1)
S$^{\mathrm{II}}$–O(2$^{\mathrm{II}}$)	1·48(2)	N(2)–C(1)	1·34(2)
N(1)–C(2)	1·41(2)		

(*b*) Bond angles

N(1)–Cu–O(H)	163·7(5)	C(2)–C(3)–C(4)	122·1(16)
N(2)–Cu–O(1$^{\mathrm{I}}$)	170·1(5)	C(3)–C(4)–C(5)	120·6(15)
O(H)–Cu–O(1$^{\mathrm{I}}$)	91·2(3)	C(4)–C(5)–C(6)	119·2(18)
N(2)–Cu–O(H)	86·5(3)	C(5)–C(6)–N(1)	121·9(17)
N(1)–Cu–N(2)	82·7(5)	C(6)–N(1)–Cu	128·6(11)
N(1)–Cu–O(1$^{\mathrm{I}}$)	97·4(5)	C(6)–N(1)–C(2)	119·5(12)
O(H)–Cu–O(3$^{\mathrm{I}}$)	99·0(5)	C(1)–C(2)–N(1)	115·4(11)
N(1)–Cu–O(3$^{\mathrm{I}}$)	94·7(5)	N(1)–C(2)–C(3)	116·5(11)
N(2)–Cu–O(3)	98·5(5)	O(3$^{\mathrm{I}}$)–S$^{\mathrm{II}}$–O(2$^{\mathrm{II}}$)	92·4(10)
O(1$^{\mathrm{I}}$)–Cu–O(3)	91·4(5)	Cu–O(3$^{\mathrm{I}}$)–S$^{\mathrm{II}}$	123·1(5)
O(1)–N(2)–C(1)	119·5(12)	O(3$^{\mathrm{I}}$)–S$^{\mathrm{II}}$–O(3$^{\mathrm{II}}$)	105·6(11)
Cu–N(2)–C(1)	113·1(10)	Cu–O(H)–Cu$^{\mathrm{I}}$	108·2(4)
Cu–N(2)–O(1)	127·4(11)	Cu–O(H)–O(2$^{\mathrm{III}}$)	110·7(4)
N(2)–C(1)–C(2)	117·0(11)	Cu–O(1$^{\mathrm{I}}$)–N(2$^{\mathrm{I}}$)	110·3(5)
C(1)–C(2)–C(3)	128·1(10)	Cu–N(1)–C(2)	111·8(5)

* Roman numerals as superscripts refer to atoms in the following equivalent positions.

I $1 - y, 1 + (x - y), z$

II $x - y, x, 1 - z$

III $x - y, x, -z$

In the crystal there are continuous columns of the trinuclear units stacked parallel to the *c* axis so that the centres of each adjacent pair are separated by *c*. The units are held together by hydrogen bonding, along the

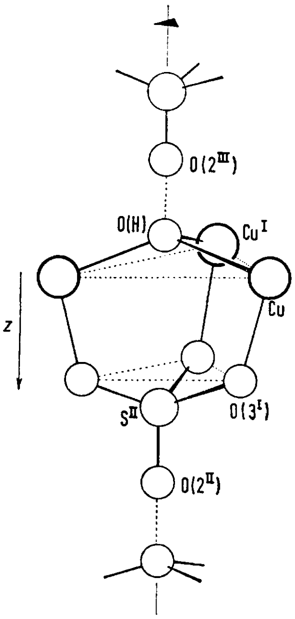

FIGURE 3 A schematic view perpendicular to the three-fold axis showing the relationship of the Cu_3 core, the hydroxy-group, and the sulphato-group

axis of symmetry about which the units are centred, and between the unco-ordinated sulphato-oxygen atom of one unit and the hydroxy-group of the neighbouring cluster (Figure 3). The distance between the two hydrogen-bonded oxygen atoms is 2·36(2) Å which is unusually short. Lengths of O–H · · · O hydrogen bonds are usually [8] in the range 2·36—3·20 Å and this short distance strongly suggests the possibility of a symmetrical hydrogen bond in which the hydrogen atom is centrally situated between the two oxygen atoms.[9]

The closest distance of approach between atoms of neighbouring trimeric units is 3·55 Å and this is between two carbon atoms. Other intermolecular distances <4·0 Å are listed in Table 3, and are consistent with previously observed non-bonded contacts for comparable systems.

TABLE 3

Intermolecular distances (Å) *

$\mathrm{N}(1) \cdots \mathrm{C}(3^{\mathrm{IV}})$	3·79	$\mathrm{C}(1) \cdots \mathrm{C}(4^{\mathrm{V}})$	3·70
$\mathrm{N}(1) \cdots \mathrm{C}(4^{\mathrm{IV}})$	3·79	$\mathrm{C}(1) \cdots \mathrm{C}(5^{\mathrm{V}})$	3·70
$\mathrm{C}(1) \cdots \mathrm{C}(4^{\mathrm{IV}})$	3·84	$\mathrm{C}(2) \cdots \mathrm{C}(2^{\mathrm{V}})$	3·95
$\mathrm{C}(1) \cdots \mathrm{C}(5^{\mathrm{IV}})$	3·85	$\mathrm{C}(2) \cdots \mathrm{C}(3^{\mathrm{V}})$	3·73
$\mathrm{C}(2) \cdots \mathrm{C}(3^{\mathrm{IV}})$	3·82	$\mathrm{C}(2) \cdots \mathrm{C}(4^{\mathrm{V}})$	3·75
$\mathrm{C}(2) \cdots \mathrm{C}(4^{\mathrm{IV}})$	3·55	$\mathrm{C}(2) \cdots \mathrm{C}(5^{\mathrm{V}})$	3·96
$\mathrm{C}(2) \cdots \mathrm{C}(5^{\mathrm{IV}})$	3·76	$\mathrm{C}(3) \cdots \mathrm{C}(6^{\mathrm{V}})$	3·93
$\mathrm{C}(3) \cdots \mathrm{C}(3^{\mathrm{IV}})$	3·83	$\mathrm{C}(3) \cdots \mathrm{N}(2^{\mathrm{V}})$	3·73
$\mathrm{C}(3) \cdots \mathrm{C}(4^{\mathrm{IV}})$	3·84	$\mathrm{C}(5) \cdots \mathrm{WO}(4^{\mathrm{V}})$	3·82
$\mathrm{C}(3) \cdots \mathrm{C}(5^{\mathrm{IV}})$	3·82	$\mathrm{C}(6) \cdots \mathrm{WO}(3^{\mathrm{V}})$	3·79
$\mathrm{C}(3) \cdots \mathrm{C}(6^{\mathrm{IV}})$	3·82	$\mathrm{C}(6) \cdots \mathrm{WO}(4^{\mathrm{V}})$	3·75
$\mathrm{C}(6) \cdots \mathrm{WO}(2^{\mathrm{IV}})$	3·97	$\mathrm{WO}(2) \cdots \mathrm{C}(4^{\mathrm{VI}})$	3·68
$\mathrm{N}(1) \cdots \mathrm{C}(3^{\mathrm{V}})$	3·70	$\mathrm{WO}(2) \cdots \mathrm{C}(5^{\mathrm{VI}})$	3·50
$\mathrm{N}(1) \cdots \mathrm{C}(4^{\mathrm{V}})$	3·99	$\mathrm{WO}(2) \cdots \mathrm{O}(2^{\mathrm{VI}})$	3·78
$\mathrm{N}(2) \cdots \mathrm{C}(4^{\mathrm{V}})$	3·84	$\mathrm{WO}(2) \cdots \mathrm{S}^{\mathrm{VI}}$	3·77
$\mathrm{N}(2) \cdots \mathrm{O}(2^{\mathrm{V}})$	3·98	$\mathrm{WO}(3) \cdots \mathrm{C}(5^{\mathrm{VI}})$	3·68

* Roman numerals as superscripts refer to atoms in the following equivalent positions:

IV $1 - x, 1 - y, 1 - z$ VI $1 - y, x - y, z$
V $1 - x, 1 - y, -z$

In the crystals the trimeric units are arranged so as to leave large almost cylindrically shaped holes, each of diameter *ca.* 10 Å, and running the length of the *c* axis (Figure 1). The molecules of water of crystallization seem to be contained within this volume but because only a small fraction of those present could be located it appears that most of the water of crystallization is liquid in nature, moving randomly throughout the containing volume. Even though the water molecules are not rigidly held in the lattice, they seem essential to the structure of the crystal for a loss of water leads to a collapse of the crystals which crack, become opaque, and partially amorphous in character. This randomness is very similar to part of the water structure observed for wet crystals of vitamin B_{12}.[10]

The Copper Environment.—Each copper atom is bonded to five atoms which are situated at the corners of an approximate tetragonal pyramid (Figure 4).

The four atoms constituting the basal plane are the two nitrogen atoms of one pyridine-2-carbaldehyde oximato-group [N(1) and N(2)], the oxygen atom from the oximato-moiety of the adjacent ligand [$\mathrm{O}(1^{\mathrm{I}})$], and the oxygen atom of the central hydroxy-group [O(H)]. Within experimental limits these four atoms are co-planar, their mean deviation from the least-squares plane taken through their positions being 0·029 Å [average estimated standard deviation is 0·014 Å; Table 4, plane (1)]. The copper atom does not lie in the basal plane but slightly above it [0·197(2) Å] towards the apical atom. The four basal atoms appear to be at normal covalent distances from the copper atom. These bond lengths are: Cu–N(1) 1·969(12), Cu–N(2) 1·982(12), Cu–$\mathrm{O}(1^{\mathrm{I}})$ 1·987(5), and Cu–O(H) 1·987(5) Å.

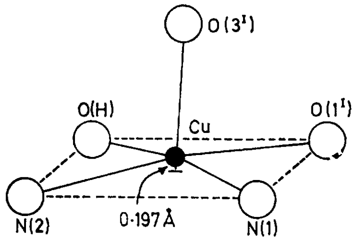

FIGURE 4 The stereochemical environment of the copper atom

TABLE 4

Equations of planes in the form ($lX + mY + nZ - p = 0$) * with distances (Å) of atoms from the planes in square brackets

	l	*m*	*n*	*p*
Plane (1): N(1), N(2), $\mathrm{O}(1^{\mathrm{I}})$, O(H)	0·2321	−0·1040	−0·9671	−1·8226
[N(1) 0·038(14), N(2) 0·040(15), $0(1^{\mathrm{I}})$ 0·025(14), O(H) 0·016(15) ,Cu 0·197(2)]				
Plane (2): N(1), N(2), O(1), C(1)–C(6)	0·1381	−0·0085	−0·9904	−1·2560
[N(1) 0·029(14), N(2) 0·017(15), O(1) 0·003(14), C(1) 0·014(19), C(2) 0·020(14), C(3) 0·007(18), C(4) 0·018(19), C(5) 0·007(21), C(6) 0·027(18), Cu 0·015(2)]				

* Planes are referred to a set of orthogonal axes such that *X* is along the ***a*** axis, *Y* is in the *a,b* plane, and *Z* is along the *c** axis.

The apical position of the distorted tetragonal pyramid is occupied by the sulphato-oxygen atom with Cu–O 2·154(9) Å. This is somewhat less than values frequently observed for copper–apical oxygen distances which, for comparable systems, are usually >2·3 Å although values as low as 2·20 Å have been observed.[11,12]

Distortion of the metal environment is also evident from the somewhat depressed value of 82·7(5)° found for the angle N(1)–Cu–N(2). The angle N(1)–Cu–$\mathrm{O}(1^{\mathrm{I}})$, where the co-ordinating atoms are from different groups, is 97·4(5)°.

The Pyridine-2-carbaldehyde Oximato-ligand.—The

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[8] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, New York, 1968, p. 203.

[9] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968, p. 52.

[10] C. Brink-Shoemaker, D. W. J. Cruickshank, D. Crowfoot-Hodgkin, M. J. Kamper, and D. Pilling, *Proc. Roy. Soc.*, 1964, *A*, **278**, 1.

[11] A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Comm.*, 1970, 904.

[12] F. D. Whillans, Ph.D. Thesis, University of Melbourne, 1971.

pyridine-2-carbaldehyde oximato-ligand is planar and the copper atom is also contained in this plane [Table 4, plane (2)]; the mean deviation from the calculated mean plane through the atoms is 0·017 Å (mean estimated standard deviation of atomic positions 0·017 Å). The mean C–N and C–C bond lengths for the pyridyl ring are 1·39(2) and 1·37(2) Å, which are in agreement with previously reported values for comparable systems.[12] The C–C [1·40(2) Å], C–N [1·34(2) Å], and N–O [1·30(2) Å] distances in the oximato-group compare well with those found in conjugated systems containing these atoms.[13] The bond angles in the pyridine-2-carbaldehyde oximato-ligand fall in the range 115—128° (mean σ 1·4°). This together with the bond lengths and the planarity of the ligand indicates that each of its atoms is sp^2 hybridized and that the π electrons of the pyridyl ring and the oximato-moiety are delocalized to form a conjugated system.

The Sulphato-group.—Each of the sulphato-oxygen atoms is bonded to another atom. Three are co-ordinated to the three copper atoms of one trinuclear unit and the other is hydrogen bonded to the hydroxy-group of a neighbouring trimer. This tripod arrangement of the sulphato-ligand with the three copper atoms is a unique example of this type of bonding for this or a similar ligand. The S–O distances for the two types of oxygen atoms are significantly different: S^{II}–$O(3^{I})$ 1·574(10), and S^{II}–$O(2^{II})$ 1·477(18) Å. These distances compare well with previously observed values for sulphate ions co-ordinated to metal atoms and involved in hydrogen bonding.[13,14] The longer S–O distance is associated with that oxygen atom co-ordinated to the copper atom. This may reflect the strength of the co-ordinate relative to the hydrogen bond.

The Hydroxy-group.—The hydroxy-group is bonded to all three copper atoms of the trimer and is also involved in hydrogen bonding with an un-co-ordinated sulphato-oxygen atom. The Cu–O(H)–Cu^{I} angle [108·2(4)°] strongly suggests sp^3 hybridization of the hydroxy-oxygen atom, supporting the prediction that the hydrogen atom lies along the line between the atoms O(H) and O(3). This triple bridging role of the hydroxy-group, although not unknown, is unusual. It has been observed for the hexanuclear nickel(II) complex di-μ-aquo-di-μ_3-hydroxo-deca(1,1,1-trifluoropentane-2,4-dionato)hexanickel(II).[15]

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