Crystal and Molecular Structure of Di-μ-hydroxo-bis[bipyridylcopper(II)] Diperchlorate

By **Mahmood Toofan, A. Boushehri, and Mazhar-Ul-Haque,***† Department of Chemistry, Pahlavi University, Shiraz, Iran

The crystal structure of the title compound has been determined from three-dimensional X-ray diffractometer data. Crystals are monoclinic with unit-cell dimensions, $a = 13.614(3)$, $b = 15.244(3)$, $c = 6.279(1)$ Å, $\beta = 113.64(2)°$, space group $C2/m$, $Z = 2$. The structure was solved by the heavy-atom techniques, and refined by block-diagonal least-squares methods to R 0.054 for 1 916 independent reflections. The compound is binuclear. The geometry of the copper atom is square planar with two more distant Cu $\cdots$ O (perchlorate) contacts at 2.797 Å completing an octahedron. Cu $\cdots$ Cu is 2.871, Cu–O 1.918, and Cu–N 1.990 Å.

THERE has been considerable interest in the use of 2,2′-bipyridyl as a ligand in metal complexes. Recently many copper(II) complexes have been studied by X-ray diffraction techniques,[1-6] including bisbipyridyl-di-μ-hydroxo-dicopper(II) nitrate.[5] The magnetic moment of the title compound is 1.89 B.M., and an X-ray study of it was undertaken in order to determine the reason for this large value, to substantiate the presence of the dimer in the crystalline state, and to investigate the effect of hydroxo-bridges on the copper–copper separation.

EXPERIMENTAL

Crystal Preparation.[7]—Hydrated copper(II) perchlorate (0.001 mol) and 2,2′-bipyridyl (0.001 mol) were added to hot water (40 ml). The precipitate was dissolved by addition of a further 50 ml of water. After heating, pH was adjusted to 6.0 by addition of NaOH solution, and flocculent crystals appeared. When these were dissolved in water (2 l), the pH was 7.5. The solution was concentrated to 100 ml by evaporating slowly on a steam-bath for 24 h; it was then allowed to cool to room temperature, and dark blue needle-like crystals appeared.

Crystal Data.—$C_{20}H_{18}Cl_2Cu_2N_4O_{10}$, $M = 672.37$, Monoclinic, $a = 13.614(3)$, $b = 15.244(3)$, $c = 6.279(1)$ Å, $\beta = 113.64(2)°$, $U = 1\,193.7(4)$ Å^3, $D_m = 1.86$, $Z = 2$, $D_c = 1.87$, $F(000) = 676$. Space group $C2/m$. Mo-K_α radiation, $\lambda = 0.710\,73$ Å, $\mu(\text{Mo-}K_\alpha) = 21.41$ cm^{-1}.

Preliminary Weissenberg and precession photographs showed the systematic absences to be: hkl, $h + k = 2n + 1$, consistent with space groups $C2$, Cm, or $C2/m$; the last-named was shown to be correct from subsequent solution and refinement of the structure. The site-symmetry of the dimer is C_{2h}; the two-fold axis passes through the two copper atoms, while the perpendicular mirror plane contains the bridging oxygens. A dark blue crystal of dimensions *ca.* 0.13 × 0.19 × 0.25 mm was used for intensity data collection on a Syntex $P\bar{1}$ diffractometer,‡ with graphite-monochromated Mo-K_α radiation at a take-off angle of 3°. Accurate unit-cell dimensions were obtained by computer-centring of reflections, followed by least-squares refinement of the setting angles. The intensities of 2 131 independent reflections were measured [to $2\theta(\text{Mo-}K_\alpha) \leqslant 65°$] by the θ—2θ scan technique, with a variable scan rate of 4—24° min^{-1}, background counts being taken at each end of the scan range. 1 916 Reflections were considered observed, having $I > 3\sigma(I)$. Three standard reflections, measured periodically, showed no significant change in intensity during data collection. Lorentz and polarization corrections were applied.

Structure Determination and Refinement.—N.R.C. crystallographic programs [8] were used for the solution and refinement of the structure. Calculations were carried out on the Pahlavi University IBM 370/135 computer.

The positions of the copper and chlorine ions were determined from a three-dimensional Patterson map. A three-dimensional Fourier map phased by these atoms revealed all the non-hydrogen atom positions. Scattering factors for non-hydrogen atoms were taken from ref. 9, and for hydrogen from ref. 10; for copper and chlorine, corrections for anomalous dispersion ($\Delta f'$ and $\Delta f''$) were taken from ref. 11. Four cycles of block-diagonal least-squares reduced R to 0.10. Five more cycles of least squares, refining the atomic positions and individual anisotropic temperature factors, reduced R to 0.065. At this stage a three-dimensional difference-Fourier map revealed all the hydrogen atom positions. Non-hydrogen atoms were then refined anisotropically and the hydrogen atoms isotropically to a final R of 0.054. A Hughes-type weighting scheme [12] was used $\sqrt{w} = 1$ for $|F_o| < P$, $\sqrt{w} = P/|F_o|$ for $|F_o| \geqslant P$, with $P = 20$. No absorption corrections were included.

Final atomic co-ordinates and their estimated standard deviations are given in Table 1, bond distances and bond angles in Tables 2 and 3. Thermal parameters for non-hydrogen atoms, details of least-squares planes, intermolecular contacts $\leqslant$3.5 Å, and final observed and

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† *Present address:* Department of Chemistry, University of Petroleum and Minerals, Dhahrain, Saudi Arabia.

‡ Intensity data were collected on a Syntex $P\bar{1}$ diffractometer by Molecular Structure Corporation, P.O. Box DF, College Station, Texas 77840, U.S.A.

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calculated structure factors are listed in Supplementary Publication No. SUP 21548 (8 pp., 1 microfiche).*

TABLE 1

Fractional co-ordinates {for copper and chlorine ($\times 10^5$), others $\times 10^4$, hydrogen $\times 10^3$} and isotropic temperature factors, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
Cu	0	9 417(3)	0	
Cl	25 119(9)	0	−6 421(18)	
N	539(2)	1 930(2)	2 240(4)	
O(1)	458(3)	0	2 207(6)	
O(2)	3 632(3)	0	913(8)	
O(3)	2 418(4)	0	−3 013(7)	
O(4)	2 002(3)	775(2)	−226(6)	
C(1)	1 102(3)	1 858(3)	4 534(6)	
C(2)	1 474(3)	2 596(3)	5 947(6)	
C(3)	1 273(3)	3 419(3)	4 966(6)	
C(4)	685(3)	3 489(2)	2 580(6)	
C(5)	316(2)	2 734(2)	1 273(5)	
H(1)	120(4)	128(3)	534(8)	3.9(10)
H(2)	179(3)	253(3)	750(7)	2.7(8)
H(3)	147(3)	393(3)	580(7)	2.2(7)
H(4)	46(3)	411(3)	185(7)	2.6(8)
H(5)	104(7)	0	283(9)	6.6(12)

TABLE 2

Interatomic distances (Å), with estimated standard deviations in parentheses

Cu–N	1.990(3)	C(4)–C(5)	1.385(4)
Cu–O(1)	1.918(2)	C(5)–C(5′$^{\mathrm{I}}$)	1.481(4)
Cu–O(4)	2.797(4)	O(1)–H(5)	0.73(11)
Cl–O(2)	1.443(5)	C(1)–H(1)	1.00(5)
Cl–O(3)	1.442(4)	C(2)–H(2)	0.90(4)
Cl–O(4)	1.446(4)	C(3)–H(3)	0.92(4)
N–C(1)	1.337(4)	C(4)–H(4)	1.05(4)
N–C(5)	1.348(4)		
C(1)–C(2)	1.396(6)	Cu · · · Cu$^{\mathrm{II}}$	2.871(1)
C(2)–C(3)	1.375(6)	O(1) · · · O(1′$^{\mathrm{I}}$)	2.543(5)
C(3)–C(4)	1.391(5)	O(1)–H(5) · · · O(3)	3.115(6)

Roman numerals denote the following equivalent positions:

I $-x, y, -z$
II $x, -y, z$

TABLE 3

Valence angles (°), with estimated standard deviations in parentheses

O(1)–Cu–O(1′$^{\mathrm{I}}$)	83.06(14)	C(2)–C(3)–H(3)	124.1(27)
O(1)–Cu–O(4)	85.86(12)	H(3)–C(3)–C(4)	117.3(27)
N–Cu–O(4)	90.80(11)	C(3)–C(4)–C(5)	119.30(34)
O(1)–Cu–N	97.75(13)	C(3)–C(4)–H(4)	118.7(26)
O(1)–Cu–N′$^{\mathrm{I}}$	176.98(13)	H(4)–C(4)–C(5)	121.6(27)
N–Cu–N′$^{\mathrm{I}}$	81.58(11)	C(4)–C(5)–N	121.76(29)
Cu–O(1)–Cu′$^{\mathrm{II}}$	96.94(15)	C(4)–C(5)–C(5′$^{\mathrm{I}}$)	123.72(29)
Cu–N–C(1)	126.10(24)	C(5′)–C(5)–N	114.49(26)
Cu–N–C(5)	114.70(21)	O(2)–Cl–O(3)	109.33(22)
C(1)–N–C(5)	119.19(29)	O(2)–Cl–O(4)	109.32(22)
N–C(1)–C(2)	121.58(34)	O(3)–Cl–O(4)	109.63(22)
N–C(1)–H(1)	121.3(29)	O(4)–Cl–O(4′$^{\mathrm{II}}$)	109.60(21)
H(1)–C(1)–C(2)	116.7(29)		
C(1)–C(2)–C(3)	119.59(37)	O(1)–Cu–O(4″$^{\mathrm{I}}$)	86.35(12)
C(1)–C(2)–H(2)	119.3(28)	N–Cu–O(4″$^{\mathrm{I}}$)	97.09(11)
H(2)–C(2)–C(3)	120.8(27)	O(4)–Cu–O(4″$^{\mathrm{I}}$)	169.59(10)
C(2)–C(3)–C(4)	118.55(37)		

Roman numerals are defined in footnote to Table 2.

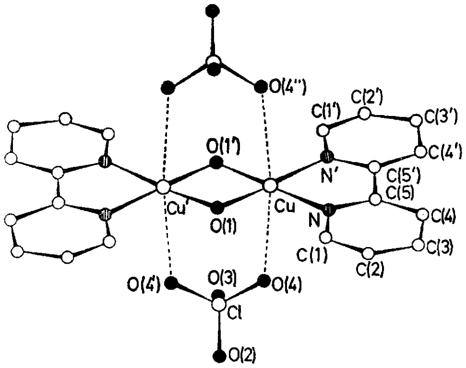
DISCUSSION

The *X*-ray study of the title compound has established that it possesses the binuclear structure shown in the Figure. The geometry at copper is best described as square planar, with two oxygen atoms of the bridging hydroxo-groups and two nitrogen atoms of the bipyridyl ligand forming the basal plane. The axial sites however are occupied by two more distant oxygen atoms at 2.797 Å, completing a distorted octahedron.

The six-membered ring of the bipyridyl group is planar, no atom being >0.012 Å from a least-squares plane. The atoms of the copper–bipyridyl system are also nearly coplanar, the largest deviations from the least-squares plane being 0.053 Å.

The only short contact between the bridging hydroxo-groups and the oxygen atoms of the perchlorate anions is O(1)–H(5) · · · O(3) 3.12 Å, and hydrogen bonding at this distance is unlikely. The O–H distance (0.73 Å) is significantly shorter than that (0.858 Å) found in a similar structure.[5]

The Cu · · · Cu separation (2.871 Å) is in the range (2.78—3.21 Å) found in chain or layer structures[3,5,13-22] having copper bridged to copper by hydroxo-groups but significantly longer than the Cu · · · Cu separations (2.63—2.65 Å) found in binuclear copper complexes.[20-22]



The structure of di-μ-hydroxo-bis[bipyridylcopper(II)] diperchlorate showing the numbering scheme used

The Cu–O distance (1.918 Å) agrees well with values found in similar structures.[3,5,18,19] The Cu–N distance (1.990 Å) is comparable with the 1.988 and 2.000 Å found in bis-bipyridyl-di-μ-hydroxo-dicopper(II) nitrate.[5] The present OH · · · OH separation (2.543 Å) is much shorter than the sum of the van der Waals radii given by Pauling[23] (2.80 Å), but agrees well with the value (2.58 Å) found in the nitrate.[5]

The O–Cu–O, Cu–O–Cu, N–Cu–O, and N–Cu–N angles

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(Table 3) agree well with the values found in the nitrate.[5] The N–Cu–N angle (81.58°) is significantly less than 90°, and this may be due to the steric requirement of a bipyridyl ring system. The bond distances and angles in the ring system are as expected.

The perchlorate anion is very nearly tetrahedral with O–Cl–O angles varying from 109.32 to 109.63° The Cl–O distances (Table 2) agree very well with one another and are as expected.

The most significant intramolecular distance is a Cu ··· Cu separation of 2.871 Å, greater than the interatomic distance in metallic copper (2.56 Å). Although it is postulated [24] that the magnetic moment of complexes having anionic bridges will be small, and will decrease with increasing metal–metal ion distance, the observed magnetic moment is 1.89 B.M. This large value is therefore probably due to bipyridyl which delocalizes electron density such that the separation of electronic ground- and excited-states is decreased. This would give some orbital contribution to the magnetic moment, and would account for the increase of the spin-only value from 1.73 to 1.89 B.M.

There are six intermolecular contacts $\leqslant 3.5$ Å. All are quite normal, and none are less than the sum of van der Waals radii.[23]

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