Acta Cryst. (1983). C**39**, 52–54

Structure of a Binuclear Copper(II) Complex: μ-{2,6-Bis[(2-pyridyl)methyliminomethyl]-*p*-cresolato-*N,N′,N″,N‴*, μ-*O*}-μ-chloro-dichlorodicopper(II) Dihydrate, $C_{21}H_{19}Cl_3Cu_2N_4O.2H_2O$

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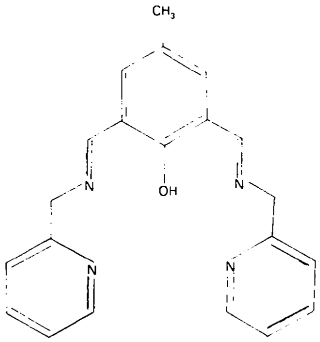
(*Received* 17 *May* 1982; *accepted* 28 *September* 1982)

Abstract. $M_r = 612{\cdot}5$, triclinic, $P\bar{1}$, $a = 11{\cdot}247\,(3)$, $b = 9{\cdot}300\,(3)$, $c = 12{\cdot}291\,(2)$ Å, $\alpha = 90{\cdot}19\,(2)$, $\beta = 104{\cdot}73\,(2)$, $\gamma = 103{\cdot}17\,(2)°$, $V = 1208{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}68$, $D_m = 1{\cdot}62$ g cm^{-3}, λ(Cu $K\alpha_1$) = 1·54051 Å, $\mu = 54{\cdot}44$ cm^{-1}, $T = 300$ K. Final $R = 0{\cdot}045$ for 2042 observed reflections. The title compound is a binuclear copper(II) complex linked to adjacent molecules by intermolecular hydrogen bonds resulting in parallel infinite chains of binuclear molecules.

Introduction. Binuclear copper(II) complexes display interesting and varied magnetic behavior. The magnetic properties of $Cu_2(C_{21}H_{19}N_4O)Cl_3.2H_2O$ are particularly unusual because, in addition to the expected strong magnetic coupling within the molecule, coupling through intermolecular hydrogen bonds forming infinite chains of binuclear molecules is also apparently significant (O'Conner & Eduok, 1982, unpublished results). The ligand, shown below, was designed to yield complexes which might model the active sites of binuclear copper proteins.



Experimental. Green rhombohedral-shaped crystal, longest dimension no greater than 0·32 mm, D_m measured by flotation in CH_3I/CCl_4, cell dimensions and lack of systematic absences indicated a triclinic space group with $Z = 2$, $P\bar{1}$ determined to be correct space group by successful determination of structure, lattice constants determined by least-squares fit of 86 carefully measured 2θ values (2° take-off angle and 0·05° slit) of Cu $K\alpha$ doublet for reflections with $2\theta > 60°$; three-dimensional intensity data collected on a General Electric XRD-490 fully automated diffractometer using balanced Ni and Co filters with Cu $K\alpha$ radiation, total of 3845 reflections measured, $2\theta_{\max} = 125°$, 2042 (53%) considered statistically significant by $[I_{\rm Ni} - 2\sigma(I_{\rm Ni})] - [I_{\rm Co} - 2\sigma(I_{\rm Co})] > 500$ with σ's based entirely on counting statistics, data corrected for polarization, absorption as a function of φ, background as a function of 2θ and reduced to structure amplitudes in the usual manner; three standard reflections measured after every 100 reflections showed no significant change in intensity.

The structure was determined by the usual heavy-atom techniques after the coordinates of the two Cu atoms were obtained from a Patterson map. The 31-atom structure was refined on F using *LINEX* 81, a full-matrix least-squares program (Becker & Coppens, 1974). All H atoms with the exception of one methyl H (found on a difference map) were calculated on the basis of sp^2 or sp^3 geometry and a C—H bond distance of 1·0 Å. The H-atom coordinates and isotropic temperature factors were allowed to refine resulting in C—H bond distances between 0·71 (5) and 1·07 (5) Å. Two additional peaks were located on a difference map and assumed to be water-molecule O atoms (the H atoms were not located). Continued refinement with anisotropic thermal parameters for all non-H atoms, isotropic thermal parameters for all H atoms, anomalous-scattering corrections for Cu and Cl scattering-factor curves and an isotropic secondary-extinction parameter [$g_{\rm iso} = 3{\cdot}1\,(4) \times 10^{-4}$] led to a final $R = 0{\cdot}045$, $R_w = 0{\cdot}057$ where $w = 1/\sigma^2(F)$ and $\sigma^2(I) = \sigma^2_{\rm CS} + (0{\cdot}02I)^2$ and $S = 2{\cdot}45$. The best fit to observed intensities was obtained using an isotropic type I extinction model with a Lorentzian mosaic distribution (Becker & Coppens, 1974). The ratio of the maximum

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least-squares shift-to-error was 0·02; $F(000) = 620$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Final fractional coordinates are given in Table 1.* The numbering system and bond lengths appear in Fig. 1 while bond angles may be found in Table 2.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

$U_{eq} = \frac{1}{3}\mathrm{tr}\,\mathbf{U}$.

	x	y	z	U_{eq}/U_{iso} (Å^2)
Cu(1)	−0·12731 (7)	0·11529 (9)	0·24645 (6)	0·03102
Cu(2)	0·13320 (7)	0·35549 (9)	0·30588 (6)	0·03175
Cl(1)	−0·2885 (1)	0·2708 (1)	0·2098 (1)	0·04866
Cl(2)	0·3160 (1)	0·2320 (1)	0·3598 (1)	0·05323
Cl(3)	0·0113 (1)	0·2205 (2)	0·1428 (1)	0·06178
O(1)	0·0030 (3)	0·2382 (4)	0·3733 (2)	0·03019
O(2)	0·5381 (5)	0·4704 (5)	0·2848 (4)	0·06963
O(3)	0·5524 (6)	0·0883 (6)	0·3774 (7)	0·10590
N(1)	−0·2309 (4)	−0·0484 (5)	0·1304 (3)	0·03107
N(2)	−0·1989 (4)	−0·0154 (5)	0·3477 (3)	0·02938
N(3)	0·1986 (4)	0·4945 (5)	0·4363 (3)	0·03109
N(4)	0·2238 (4)	0·5232 (5)	0·2313 (4)	0·03545
C(1)	−0·2339 (6)	−0·0546 (7)	0·0221 (5)	0·03969
C(2)	−0·3068 (6)	−0·1695 (8)	−0·0520 (5)	0·04901
C(3)	−0·3791 (7)	−0·2843 (8)	−0·0099 (6)	0·05593
C(4)	−0·3770 (6)	−0·2808 (7)	0·1000 (6)	0·04746
C(5)	−0·3025 (5)	−0·1593 (6)	0·1694 (4)	0·02989
C(6)	−0·2992 (6)	−0·1430 (8)	0·2920 (5)	0·03873
C(7)	−0·1753 (5)	0·0081 (7)	0·4542 (5)	0·03277
C(8)	−0·0849 (5)	0·1319 (6)	0·5220 (4)	0·02780
C(9)	−0·0814 (6)	0·1385 (7)	0·6375 (4)	0·03583
C(10)	−0·0025 (5)	0·2497 (7)	0·7129 (4)	0·03701
C(11)	0·0737 (6)	0·3600 (7)	0·6712 (4)	0·03526
C(12)	0·0788 (5)	0·3594 (6)	0·5582 (4)	0·02767
C(13)	−0·0007 (4)	0·2423 (6)	0·4804 (4)	0·02375
C(14)	0·1697 (5)	0·4832 (6)	0·5304 (4)	0·03086
C(15)	0·3007 (6)	0·6165 (7)	0·4241 (6)	0·04381
C(16)	0·2923 (5)	0·6380 (6)	0·3033 (5)	0·03529
C(17)	0·3549 (6)	0·7650 (8)	0·2648 (7)	0·04898
C(18)	0·3479 (7)	0·7719 (9)	0·1526 (7)	0·06012
C(19)	0·2804 (7)	0·6534 (9)	0·0790 (6)	0·05655
C(20)	0·2178 (6)	0·5303 (8)	0·1214 (5)	0·04520
C(21)	−0·0025 (8)	0·2556 (1)	0·8356 (5)	0·05204
H(1)	−0·190 (4)	0·012 (5)	0·003 (3)	−0·017 (11)
H(2)	−0·310 (5)	−0·169 (5)	−0·115 (4)	−0·004 (13)
H(3)	−0·420 (8)	−0·348 (9)	−0·044 (7)	0·065 (26)
H(4)	−0·427 (6)	−0·348 (7)	0·127 (5)	0·029 (19)
H(5)	−0·372 (6)	−0·135 (6)	0·287 (5)	0·012 (16)
H(6)	−0·295 (7)	−0·229 (8)	0·332 (6)	0·038 (21)
H(7)	−0·217 (6)	−0·049 (6)	0·490 (5)	0·015 (16)
H(8)	−0·136 (6)	0·066 (6)	0·649 (5)	0·015 (16)
H(9)	0·129 (6)	0·451 (7)	0·717 (5)	0·026 (18)
H(10)	0·206 (5)	0·560 (6)	0·603 (4)	0·006 (15)
H(11)	0·376 (6)	0·604 (6)	0·459 (5)	0·017 (18)
H(12)	0·296 (5)	0·681 (6)	0·452 (4)	0·003 (17)
H(13)	0·378 (5)	0·835 (6)	0·304 (4)	0·005 (17)
H(14)	0·388 (7)	0·845 (7)	0·138 (6)	0·041 (24)
H(15)	0·263 (7)	0·653 (7)	0·000 (6)	0·041 (23)
H(16)	0·176 (5)	0·458 (6)	0·077 (4)	0·007 (17)
H(17)	−0·090 (8)	0·255 (9)	0·850 (6)	0·062 (27)
H(18)	0·078 (9)	0·28 (1)	0·873 (8)	0·073 (31)
H(19)	−0·003 (6)	0·173 (6)	0·852 (4)	0·007 (18)

The ligand in this binuclear complex is pentadentate. Each Cu^{II} ion is coordinated to two N atoms and both Cu^{II} ions are coordinated to the phenolic O forming an O-atom bridge. Additionally, the Cu^{II} ions are bridged by a single Cl atom. Both Cu^{II} ions are

Table 2. *Pertinent angles* (°) *for the binuclear complex*

Cl(1)—Cu(1)—C(13)	103·37 (8)	Cu(2)—N(4)—C(20)	127·0 (5)
Cl(1)—Cu(1)—O(1)	99·6 (1)	C(16)—N(4)—C(20)	119·7 (6)
Cl(1)—Cu(1)—N(1)	95·4 (1)	N(1)—C(1)—C(2)	123·4 (7)
Cl(1)—Cu(1)—N(2)	97·3 (1)	C(1)—C(2)—C(3)	117·2 (7)
Cl(3)—Cu(1)—O(1)	83·2 (1)	C(2)—C(3)—C(4)	120·5 (6)
Cl(3)—Cu(1)—N(1)	96·2 (1)	C(3)—C(4)—C(5)	118·9 (7)
Cl(3)—Cu(1)—N(2)	159·3 (2)	N(1)—C(5)—C(4)	121·4 (6)
O(1)—Cu(1)—N(1)	164·7 (2)	N(1)—C(5)—C(6)	116·2 (5)
O(1)—Cu(1)—N(2)	92·4 (2)	C(4)—C(5)—C(6)	122·5 (6)
N(1)—Cu(1)—N(2)	82·8 (2)	N(2)—C(6)—C(5)	110·2 (5)
Cl(2)—Cu(2)—Cl(3)	101·95 (8)	N(2)—C(7)—C(8)	126·4 (6)
Cl(2)—Cu(2)—O(1)	104·6 (1)	C(7)—C(8)—C(9)	115·9 (5)
Cl(2)—Cu(2)—N(3)	93·3 (2)	C(7)—C(8)—C(13)	124·6 (5)
Cl(2)—Cu(2)—N(4)	95·3 (1)	C(9)—C(8)—C(13)	119·5 (5)
Cu(1)—Cl(1)—O(2)	154·2 (1)	C(8)—C(9)—C(10)	123·2 (6)
Cu(1)—Cl(1)—O(3)	93·3 (1)	C(9)—C(10)—C(11)	116·9 (5)
C(2)—Cl(1)—O(3)	70·0 (1)	C(9)—C(10)—C(21)	122·1 (7)
Cu(2)—Cl(2)—O(2)	101·5 (1)	C(11)—C(10)—C(21)	120·9 (6)
Cu(2)—Cl(2)—O(3)	168·4 (2)	C(10)—C(11)—C(12)	123·4 (6)
O(2)—Cl(2)—O(3)	71·1 (2)	C(11)—C(12)—C(13)	119·8 (5)
Cu(1)—Cl(3)—Cu(2)	86·87 (6)	C(11)—C(12)—C(14)	115·6 (5)
Cu(1)—O(1)—Cu(2)	105·8 (2)	C(13)—C(12)—C(14)	127·7 (5)
Cu(1)—O(1)—C(13)	126·0 (3)	O(1)—C(13)—C(8)	121·9 (5)
Cu(2)—O(1)—C(13)	128·0 (3)	O(1)—C(13)—C(12)	121·0 (5)
Cu(1)—N(1)—C(5)	114·8 (4)	C(8)—C(13)—C(12)	117·1 (5)
Cu(1)—N(1)—C(1)	126·6 (4)	C(12)—C(14)—N(3)	125·1 (5)
C(1)—N(1)—C(5)	118·6 (5)	N(3)—C(15)—C(16)	110·3 (5)
Cu(1)—N(2)—C(6)	114·8 (4)	N(4)—C(16)—C(15)	116·0 (5)
Cu(1)—N(2)—C(7)	126·0 (4)	N(4)—C(16)—C(17)	120·5 (6)
C(6)—N(2)—C(7)	118·8 (5)	C(15)—C(16)—C(17)	123·4 (6)
Cu(2)—N(3)—C(14)	127·6 (4)	C(16)—C(17)—C(18)	119·4 (7)
Cu(2)—N(3)—C(15)	112·9 (4)	C(17)—C(18)—C(19	120·3 (7)
C(14)—N(3)—C(15)	119·3 (5)	C(18)—C(19)—C(20)	118·0 (7)
Cu(2)—N(4)—C(16)	113·3 (4)	N(4)—C(20)—C(19)	122·0 (7)

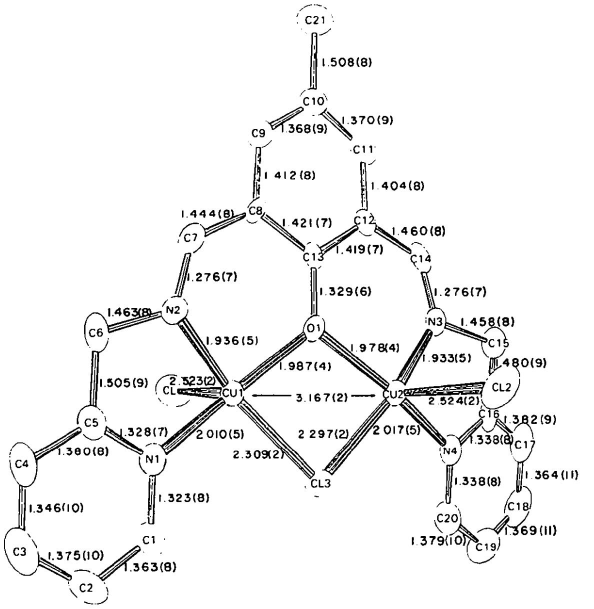

Fig. 1. Bond distances (Å) and labeling scheme in $Cu_2(C_{21}H_{19}N_4O)Cl_3$. H atoms have been omitted.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38147 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

pentacoordinate resulting in coordination spheres with distorted square-pyramid geometries with non-bridging Cl atoms at the apex of the pyramid. The distortion is a result of the constraints imposed by the formation of a five-membered ring on one side due to the coordination of the metal ion by two N atoms. The axial bond distances of 2·523 (2) Å for Cu—Cl(1) and 2·524 (2) Å for Cu(2)—Cl(2) are significantly longer than the range of 2·27 to 2·35 Å found for non-axial Cu—Cl distances (Klein, Trefonas, O'Connor & Majeste, 1981; Swank, Needham & Willett, 1979; Roundhill, Roundhill, Bloomquist, Landee, Willett, Dooley & Gray, 1979) but significantly shorter than the Cu—Cl bridging bonds of 2·70 to 3·19 Å found in Cu—Cl—Cu bridging systems (Willett & Rundle, 1964; Hodgson, Hale & Hatfield, 1971).

The non-bridging Cl atoms are coordinated on opposite sides of the molecule. Each Cu^{II} ion is displaced from the plane in the direction of the non-bridging Cl atom which is coordinated to it [Cu(1) −0·411 (5) Å out of plane and Cu(2) +0·332 (5) Å out of plane], as can be seen from the packing diagram in Fig. 2. The ligand is near planar except for slight rotations of the pyridine ring planes [N(1)C(1)C(2)-C(3)C(4)C(5) and N(4)C(16)C(17)C(18)C(19)C(20)] about the C(5)—C(6) bond and the C(15)—C(16) bond. The resulting dihedral angles between pyridine ring planes and the rest of the ligand are 173·5 (7) and 166·3 (7)° respectively.

An intermolecular hydrogen-bond network results from the two water molecules of hydration found in the unit cell. Both are hydrogen-bonded to Cl(2) and also to a Cl(1) translated by one unit cell along the *a* axis. The hydrogen bonds linking two adjacent binuclear complexes result in an infinite linear chain of binuclear molecules. The water O—Cl distances are somewhat longer [Cl(1)—O(2) 3·265 (6), Cl(1)—O(3) 3·293 (8) Å and Cl(2)—O(2) 3·266 (6), Cl(2)—O(3) 3·199 (6) Å] than the Cl—O hydrogen-bond distances reported in the literature [2·99–3·05 (6) Å] (*International Tables for X-ray Crystallography*, 1968).

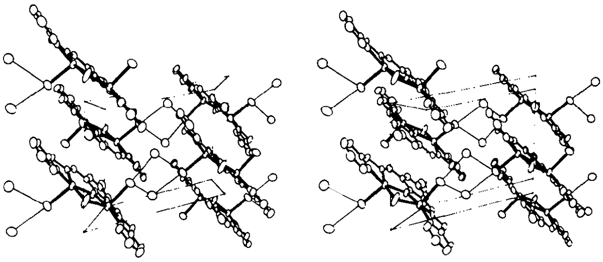

Fig. 2. Stereoview of the molecular-packing diagram showing the intermolecular hydrogen-bond network.

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Acta Cryst. (1983). C**39**, 54–56

1,3-Diethoxy-1,2;1,4;2,3,4:2,3;3,4;1,2,4-bis-μ_4-{[2-hydroxymethyl-2-methyl-1,3-propanediolato(3−)]-μ-*O*,μ-*O*′,μ-*O*″}-tetrakis[*cis*-dioxomolybdenum(VI)], $C_{14}H_{28}Mo_4O_{16}$

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(*Received* 19 *May* 1982; *accepted* 1 *October* 1982)

Abstract. $M_r = 836\cdot1$, triclinic, $P\bar{1}$, $a = 8\cdot500\,(1)$, $b = 9\cdot581\,(1)$, $c = 7\cdot903\,(1)$ Å, $\alpha = 103\cdot16\,(1)$, $\beta = 103\cdot07\,(1)$, $\gamma = 100\cdot41\,(2)°$, $V = 591\cdot90$ Å^3, $D_o = 2\cdot34$, $D_x = 2\cdot35$ Mg m^{-3}, $Z = 1$, $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot5418$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 18\cdot548$ mm^{-1}, $R = 0\cdot031$ for 1438 observed reflections. In this complex the four Mo coordination centres are of two kinds within one crystallographically centrosymmetric molecule. They are linked by a system of double and triple bridges formed by the O atoms of the triply deprotonated 2-hydroxymethyl-2-methyl-1,3-propanediol ligands. For one pair of Mo atoms this bridging itself provides six-coordination, but each Mo atom of the other pair carries an ethoxy group to complete the coordination.

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