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A Structure Containing Binuclear Cationic Cu^{II} Complexes of the 2-Methyl-1,3-di-2-pyridyl-2-propanol Monoanion as the Tetrachlorocuprate(II) Salt

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Abstract. Diaquabis-[μ-(2-methyl-1,3-di-2-pyridyl-2-propanolato)-μ-*O,N,N'*]-dicopper(II) bis-[μ-(2-methyl-1,3-di-2-pyridyl-2-propanolato)-μ-*O,N,N'*]-dicopper(II) tetrachlorocuprate(II), $[Cu_2(C_{14}H_{15}N_2O)_2(H_2O)_2]$-$[Cu_2(C_{14}H_{15}N_2O)_2][CuCl_4]_2$, $M_r = 1710$, triclinic, $P\bar{1}$, $a = 11{\cdot}277\,(3)$, $b = 11{\cdot}554\,(3)$, $c = 12{\cdot}275\,(3)$ Å, $\alpha = 89{\cdot}93\,(2)$, $\beta = 86{\cdot}09\,(2)$, $\gamma = 81{\cdot}51\,(2)°$, $V = 1578{\cdot}0\,(7)$ Å^3, $Z = 1$, $D_x = 1{\cdot}694\,(2)$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 23{\cdot}9$ cm^{-1}, $F(000) = 814$, $T = 295\,(1)$ K, final $R = 0{\cdot}033$ for 2597 observed reflections (θ–2θ scan) with $F_o{}^2 > 2\sigma(F_o{}^2)$. This crystal features Cu^{II} in three different coordination geometries: distorted tetrahedral, square planar and square pyramidal. The former is the $[CuCl_4]^{2-}$ ion. The latter two centrosymmetric, binuclear cations differ in the presence or lack of the loosely bound water molecules [Cu—O = 2·681 (4) Å]. These binuclear complexes are linked by bridging of the $[CuCl_4]^{2-}$ ion with long Cu—Cl interactions completing highly tetragonally distorted octahedral coordination of the positive ions [Cu—Cl 3·011 (1), 3·401 (1), 3·736 (1) Å]. Bond distances are normal: average Cu—O bridging = 1·910 (6) Å, Cu—N = 1·986 (5) Å and Cu—Cl = 2·250 (15) Å.

Introduction. In the course of syntheses of pyridine-based amine-oxime ligands, we prepared the present ligand, as a side product, by a new route. The ligand has been prepared previously by other methods (*e.g.* Goldberg, Barkley & Levine, 1951), but the structures of its metal complexes have not been characterized. Because of the potential bridging ability of the ligand we prepared the Cu^{II} complex and determined its structure.

Experimental. The ligand was obtained as one of the products of the reaction of α-picoline with $NaNH_2$ in liquid NH_3 on addition of ethyl acetate. It was isolated by fractional distillation, and its boiling point (421–424 K at 266 Pa) agreed with the literature (Goldberg *et al.*, 1951). Deep green crystals were obtained from a slightly basic aqueous solution of $CuCl_2$ with added tertiary alcohol ligand (Cu^{II} in excess).

The crystal chosen for X-ray study was about 0·2 × 0·2 × 0·3 mm. The crystal was placed in random orientation on an Enraf–Nonius CAD-4 diffractometer. After optical centering, 25 reflections ($2\theta = 18$–$36°$) were located by automatic search of reciprocal space and recentered twice. The setting angles of those reflections were used to determine the cell dimenions. Three standard reflections were measured after every 7200 s of X-ray exposure (no significant variation), three orientation standards after every 200 reflections with recentering of all 25 if any significant angular error, three ψ scans to obtain empirical absorption curve (less than 2% range, no correction). *hkl* range 0, −10, −11 to 10, 11, 11. 3833 reflections from $2\theta = 4$–$40°$, 2979 independent reflections (internal agreement factor on $F_o{}^2 = 0{\cdot}038$), 2597 reflections with $F_o{}^2 > 2\sigma(F_o{}^2)$ used in structure solution and refinement, structure solved by Patterson and difference Fourier methods, full-matrix least squares minimized $\sum w(|F_o| - |F_c|)^2$, H atoms from difference Fourier and calculation were not refined, all other atoms anisotropically, scattering factors including f' and f'' from *International Tables for X-ray Crystallography* (1974); computation on PDP11/34 and 11/24 computers using Enraf–Nonius (1984) *SDP* programs, 379 variables, $R = 0{\cdot}033$, $wR = 0{\cdot}045$, $S = 1{\cdot}66$, $w = 4F_o{}^2/[\sigma^2_{\rm counting} + (0{\cdot}040F_o{}^2)^2]$, max. shift/e.s.d. = 0·15, no extinction correction, max. and min. $\Delta\rho$ on final difference Fourier map 0·5 and −0·4 e Å^{-3}.

Discussion. Final parameters for non-H atoms are in Table 1. The crystal structure is composed of three types of Cu^{II} complexes. The two centrosymmetric positive ions are dinuclear with bridging, deprotonated, tertiary alcohol O atoms. One of these is essentially four coordinate with near square planar geometry (Fig. 1) while the other has similar bonding of the organic ligand but also has a weakly coordinated water molecule on each Cu atom to produce near square pyramidal geometry (Fig. 2). A third geometry is observed for the $[CuCl_4]^{2-}$ counterion which has a flattened tetrahedral arrangement of the four chloride ions around the copper. From Fig. 3 weak interaction of three of the $[CuCl_4]^{2-}$ chloride ligands with the Cu atoms of the binuclear cations can be seen to result in highly distorted octahedral geometry for the Cu^{II} atoms of both of the binuclear cations; this produces an

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Table 1. *Positional parameters and their estimated standard deviations*

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\beta_{12}\cos\gamma + ac\beta_{13}\cos\beta + bc\beta_{23}\cos\alpha]$.

	x	y	z	B(Å^2)
Cu1	0·46284 (5)	−0·58628 (5)	0·42236 (5)	2·57 (1)
Cu2	0·09631 (5)	0·00693 (5)	0·07637 (5)	2·62 (1)
Cu3	−0·17305 (6)	−0·25864 (5)	0·23108 (5)	2·65 (1)
Cl1	−0·2275 (1)	−0·1408 (1)	0·0912 (1)	3·96 (3)
Cl2	−0·1610 (2)	−0·4299 (1)	0·1424 (1)	4·23 (4)
Cl3	−0·2744 (2)	−0·3048 (1)	0·3884 (1)	4·37 (4)
Cl4	−0·0386 (1)	−0·1615 (1)	0·3004 (1)	4·89 (4)
O1	0·4244 (3)	−0·4266 (3)	0·4697 (3)	2·19 (7)
O1′	0·0561 (3)	−0·0854 (3)	−0·0406 (3)	2·26 (7)
O2	0·5912 (4)	−0·4956 (4)	0·2605 (4)	5·4 (1)
N1′	0·0950 (4)	0·1073 (3)	0·2080 (3)	2·44 (9)
N1	0·5195 (4)	−0·7556 (3)	0·4007 (3)	2·30 (9)
N2′	0·2538 (4)	−0·0942 (4)	0·0896 (3)	2·46 (9)
N2	0·3396 (4)	−0·5671 (3)	0·3133 (3)	2·51 (9)
C1′	−0·1357 (5)	−0·0609 (5)	−0·3009 (4)	3·4 (1)
C1	0·5584 (5)	−0·1715 (5)	0·6192 (4)	3·1 (1)
C2	0·5232 (5)	−0·0534 (5)	0·6359 (5)	3·6 (1)
C2′	−0·1275 (5)	−0·1228 (5)	−0·3969 (4)	3·4 (1)
C3′	−0·0729 (5)	−0·2367 (5)	−0·3983 (4)	3·7 (1)
C3	0·4052 (6)	−0·0082 (5)	0·6318 (5)	3·7 (1)
C4′	−0·0274 (5)	−0·2844 (5)	−0·3054 (4)	3·0 (1)
C4	0·3253 (5)	−0·0813 (5)	0·6082 (4)	3·0 (1)
C5′	−0·0389 (4)	−0·2184 (4)	−0·2097 (4)	2·3 (1)
C5	0·3647 (5)	−0·1997 (4)	0·5917 (4)	2·2 (1)
C6	0·2803 (4)	−0·2828 (4)	0·5649 (4)	2·6 (1)
C6′	0·0123 (5)	−0·2658 (4)	−0·1072 (4)	2·5 (1)
C7	0·3158 (4)	−0·3500 (4)	0·4573 (4)	2·1 (1)
C7′	0·1109 (4)	−0·1994 (4)	−0·0702 (4)	2·0 (1)
C8′	0·2073 (5)	−0·1942 (5)	−0·1601 (4)	3·0 (1)
C8	0·3337 (5)	−0·2683 (5)	0·3630 (4)	3·3 (1)
C9	0·2180 (5)	−0·4253 (4)	0·4364 (4)	2·7 (1)
C9′	0·1621 (5)	−0·2588 (4)	0·0310 (4)	2·6 (1)
C10	0·2377 (4)	−0·4906 (4)	0·3302 (4)	2·5 (1)
C10′	0·2694 (5)	−0·2092 (4)	0·0656 (4)	2·4 (1)
C11′	0·3818 (5)	−0·2743 (5)	0·0674 (5)	3·6 (1)
C11	0·1564 (5)	−0·4707 (4)	0·2497 (5)	3·1 (1)
C12	0·1784 (5)	−0·5302 (5)	0·1532 (4)	3·5 (1)
C12′	0·4778 (5)	−0·2230 (5)	0·0926 (5)	4·0 (1)
C13	0·2822 (5)	−0·6068 (5)	0·1362 (4)	3·4 (1)
C13′	0·4625 (5)	−0·1063 (5)	0·1136 (5)	3·7 (1)
C14	0·3609 (5)	−0·6218 (5)	0·2162 (4)	3·3 (1)
C14′	0·3486 (5)	−0·0443 (5)	0·1114 (4)	3·3 (1)

infinite chain of $[CuCl_4]^{2-}$ bridged binuclear cations. The resulting Cu—Cl distances [Cu2—Cl1 3·011 (1) Å, Cu1—Cl3 3·407 (1) Å and Cu2—Cl4 3·736 (1) Å] are much longer than 'normal' Cu—Cl distances such as in the $[CuCl_4]^{2-}$ ion [average 2·250 (15) Å].

Table 2 gives the important bond distances and angles for the copper coordination. One interesting feature is the change in the organic-ligand-to-copper bonds on addition of a water in the fifth position. The bridging alkoxide-oxygen-to-copper distances increase by about 0·10 Å while the Cu—N(pyridine) distances decrease by about the same amount. We cannot identify a reason for this effect. In both of the dinuclear complexes the ligand square plane has significant tetrahedral distortion as observed in the least-squares planes* and the bond angles where *trans* angles range from 166–169° (Table 2). The O1—Cu1—O1 and O1′—Cu2—O1′ angles [76·7 (1)°] are considerably smaller than the 'ideal' 90° value. This may be because of Cu—Cu repulsive interaction [Cu1—Cu1 = 3·005 (1) Å and Cu2—Cu2 = 2·986 (1) Å]. There is flattening of the $[CuCl_4]^{2-}$ ion with angles from 97·64 (5) to 134·00 (6)°. This $[CuCl_4]^{2-}$ geometry is intermediate between the slightly flattened ion in

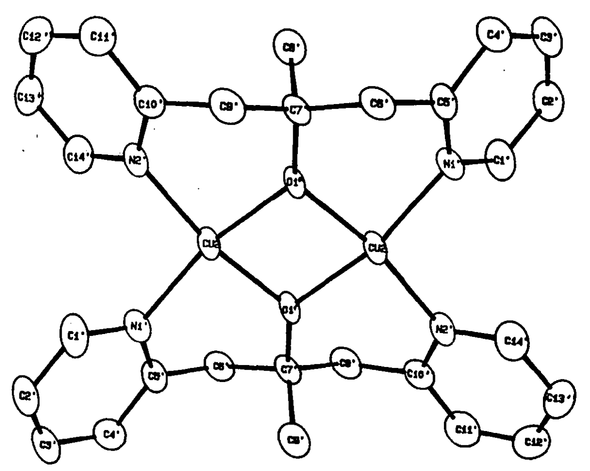

Fig. 1. Perspective view of $[Cu_2(C_{14}H_{15}N_2O)_2]^{2+}$ showing atom labeling and thermal ellipsoids.

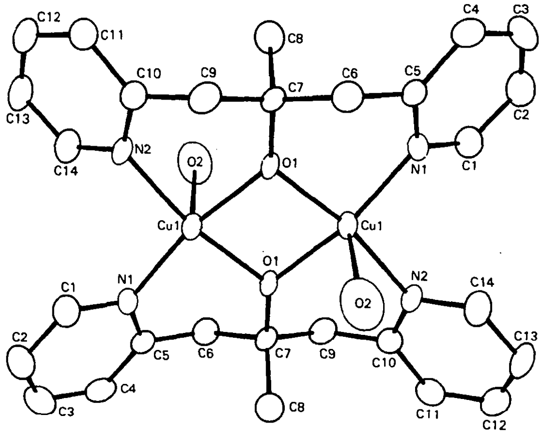

Fig. 2. Perspective view of $[Cu_2(C_{14}H_{15}N_2O)_2(H_2O)_2]^{2+}$ showing atom labeling and thermal ellipsoids.

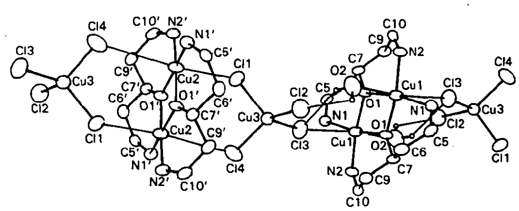

Fig. 3. Perspective view showing the bridging of $[CuCl_4]^{2-}$ ions between binuclear cations and the hydrogen bonding to the coordinated water molecule (O2). Some of the ligand C atoms have been eliminated to improve clarity.

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* Lists of structure factors, H-atom parameters, other bond distances and angles, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51419 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°)

Cu1–O1	1·914 (2)	Cu2–N1′	1·988 (3)
Cu1–O1	1·919 (2)	Cu2–N2′	1·994 (3)
Cu1–O2	2·681 (4)	Cu3–Cl1	2·252 (1)
Cu1–N1	1·979 (3)	Cu3–Cl2	2·242 (1)
Cu1–N2	1·984 (3)	Cu3–Cl3	2·279 (1)
Cu2–O1′	1·908 (2)	Cu3–Cl4	2·228 (1)
Cu2–O1′	1·900 (3)		

O1–Cu1–O1	76·7 (1)	O1′–Cu2–N1′	165·9 (1)
O1–Cu1–O2	83·4 (1)	O1′–Cu2–N2′	92·6 (1)
O1–Cu1–N1	168·5 (1)	O1′–Cu2–N1′	91·8 (1)
O1–Cu1–N2	92·7 (1)	O1′–Cu2–N2′	169·2 (1)
O1–Cu1–O2	95·0 (1)	N1′–Cu2–N2′	99·0 (1)
O1–Cu1–N1	92·3 (1)	Cl1–Cu3–Cl2	97·64 (5)
O1–Cu1–N2	169·2 (1)	Cl1–Cu3–Cl3	132·43 (5)
O2–Cu1–N1	101·1 (1)	Cl1–Cu3–Cl4	100·05 (5)
O2–Cu1–N2	81·7 (1)	Cl2–Cu3–Cl3	98·77 (5)
N1–Cu1–N2	98·4 (1)	Cl2–Cu3–Cl4	134·00 (6)
O1′–Cu2–O1′	76·7 (1)	Cl3–Cu3–Cl4	99·78 (5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Cs_2CuCl_4 (Morosin & Lingafelter, 1961), Cl—Cu—Cl range from 102·5 to 124·9°, and the planar conformation in the 2-aminobenzothiazolium salt (Antolini, Benedetti, Fabretti & Giusti, 1988). A nearly identical 'flattening' angle (Smith, 1976) was recently reported (Koman, Siroklin, Andrejovic, Corradi & Battaglia, 1988) for $[\textit{iso}\text{-}Bu_2NH_2]_2[CuCl_4]$ where the Cl—Cu—Cl angles range from 97·2–138·6°, and the average Cu—Cl distance of 2·249 (7) Å is identical with the present value of 2·250 (15) Å. Longer distances are associated with greater flattening (Smith, 1976). There is also considerable variation in the Cu3—Cl distances [2·228 (1) to 2·279 (1) Å]. This variation can be correlated with the extent of the interaction of the chloride ligands with the Cu^{II} atoms in the binuclear complexes (see above) and with the water molecule through hydrogen bonding (see below).

Other than the chloride bridges between copper ions, there are no unusually short intramolecular contacts. Water hydrogens are involved in relatively weak hydrogen bonds with Cl2 and Cl3 of the $[CuCl_4]^{2-}$ ion [O2···Cl3, 3·308 (1) Å; O2—H1O2···Cl3, 143°; O2···Cl2, 3·250 (1) Å; O2—H2O2···Cl2, 122°] (see Fig. 3).

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Structure of a Dipotassium Tetrathiocyanatomercurate(II) Salt with Dibenzo-18-crown-6

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Abstract. Bis[(dibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadeca-2,11-diene)potassium] tetrathiocyanatomercurate(II) ethanolate, $[K(C_{20}H_{24}O_6)]_2[Hg(SCN)_4]$.$C_2H_5OH$, $M_r = 1278{\cdot}0$, monoclinic, $C2/c$, $a = 29{\cdot}763\ (5)$, $b = 14{\cdot}690\ (3)$, $c = 25{\cdot}314\ (5)$ Å, $\beta = 99{\cdot}06\ (1)$°, $U = 10930\ (3)$ Å^3, $Z = 8$, $D_m = 1{\cdot}55\ (3)$, $D_x = 1{\cdot}55$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 31{\cdot}69$ cm^{-1}, $F(000) = 5095$, at 153 K, final $R = 0{\cdot}042$ for 4599 $[I > 3\sigma(I)]$ independent observed reflections. The molecule consists of two dibenzo-18-crown-6 potassium cations linked through three out of the four end N atoms of the tetrathiocyanatomercurate(II) anion. In addition to the six O atoms in the crown ether one potassium is coordinated to a thiocyanate N atom with K···N distance of 2·727 (11) Å, while the other potassium is coordinated to two other N atoms with K···N distances 2·961 (11) and 2·924 (11) Å respectively. The longer distances observed in the latter case

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