parallel to $(10\bar{1})$ are formed. These planes 'sandwich' the TMP groups. Magnetic measurements will be carried out in due course as this compound is a possible candidate for a low-dimensional magnetic system.

A compound with similar composition, tetramethylammonium dicopper pentachloride, has been reported before (Weenk, 1976). The structure of this compound is unknown.

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References

Bacci, M. (1979). *Chem. Phys.* **40**, 237–244.
Crama, W. J. & Maaskant, W. J. A. (1983). *Physica*, **121B**, 219–231.
Graaff, R. A. G. de (1973). *Acta Cryst.* A**29**, 298–301.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Weenk, W. J. (1976). PhD Thesis. Utrecht State Univ.
Weenk, W. J. & Spek, A. L. (1976). *Cryst. Struct. Commun.* **5**, 805–810.

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Structure of Dipyridinebis(2,4,6-trichlorophenolato)copper(II)

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Abstract. $[Cu(C_6H_2Cl_3O)_2(C_5H_5N)_2]$, $M_r = 614{\cdot}6$, triclinic, $P\bar{1}$, $a = 8{\cdot}292\,(2)$, $b = 9{\cdot}002\,(2)$, $c = 9{\cdot}587\,(2)$ Å, $\alpha = 85{\cdot}91\,(2)$, $\beta = 72{\cdot}44\,(2)$, $\gamma = 63{\cdot}48\,(2)^\circ$, $V = 608{\cdot}9$ Å^3, $Z = 1$, $D_x = 1{\cdot}68$ g cm^{-3}, $F(000) = 306{\cdot}96$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 15{\cdot}9$ cm^{-1}, $T = 293$ K. 2158 unique reflections, of which 1819 had $I \geq 3\sigma(I)$, were refined to a final R of $0{\cdot}046$ ($R = 0{\cdot}036$ for the 3σ data set and $wR = 0{\cdot}032$). The structure consists of discrete centrosymmetric molecules with the stoichiometric formula indicated in the title. The CuO_2N_2 coordination sphere is *trans* planar [Cu—O = 1·909 (2), Cu—N = 2·036 (3) Å] with the fifth and sixth coordination sites blocked by chlorine atoms from the phenoxide ions [Cu—Cl = 2·912 (1) Å].

Introduction. The oxidation and polymerization of phenols is catalyzed by the presence of copper chloride and pyridine (Finkbeiner, Hay, Blanchard & Endres, 1966, and references therein). In methanol solution, the active species has been identified as $Cu_2Cl_2(OH)(OCH_3)(py)_2$ (Davies & El-Sayed, 1983). The crystal structure of the bis(methoxide) complex, $Cu_2Cl_2(OCH_3)_2(py)_2$, has been shown to contain dibridged methoxide dimers (Willett & Breneman, 1983). As part of a further study of this system, we have determined the structure of the copper(II) substrate complex in the presence of pyridine.

Experimental. Brown prismatic crystals separated out upon cooling of a saturated solution of the complex prepared as described by Blanchard, Finkbeiner & Russell (1962). A small crystal with maximum dimension 0·3 mm was selected for data collection. Data were collected on a Nicolet *R3m/E* diffractometer system with Mo $K\alpha$ radiation and a graphite monochromator (Campana, Shepherd & Litchman, 1980). Agreement between equivalent reflections: $R = 0{\cdot}019$. The triclinic unit cell and orientation matrix were defined by least-squares refinement of 25 accurately centered high-angle ($34^\circ < 2\theta < 39^\circ$) reflections. Empirical absorption corrections assuming an ellipsoidally shaped crystal (minimum transmission = 0·61, maximum transmission = 0·79). Data collected for all h and k, $l \geq 0$ (maximum values of h, k, l = 8, 10, 11). Three standards monitored every 50 reflections, variation within counting statistics. 2158 unique reflections ($2\theta \leq 50^\circ$); 1819 reflections with $I > 3\sigma(I)$. The Patterson function yielded positions of the Cu, O, N, and a Cl atom. Subsequent difference maps, starting with these positions, yielded all other atom positions. Final refinement on F of all positional parameters with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the H atoms gave a final value of $R = 0{\cdot}036$ and $wR = 0{\cdot}032$ with an average $\Delta/\sigma = 0{\cdot}034$ for all observed reflections

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(Sheldrick, 1984); max. $\Delta/\sigma = 0{\cdot}003$; $w = \sigma^2(F_o) + g|F_o|^2$, $g = 0{\cdot}0020$. The goodness of fit was equal to 1·24. The largest residual on the final difference map was approximately 0·2 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction. Refinements performed with *SHELXTL* (Sheldrick, 1984). Final positional parameters are given in Table 1 with selected bond distances and angles reported in Table 2.*

Table 1. *Atomic coordinates* (×10^4) *and isotropic thermal parameters* (Å^2 × 10^3)

U_{eq} = equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu	0	0	0	32 (1)
Cl(1)	6476 (1)	−281 (1)	1154 (1)	47 (1)
Cl(2)	3743 (1)	2377 (1)	4616 (1)	55 (1)
Cl(3)	1547 (1)	3335 (1)	6156 (1)	55 (1)
O	9252 (3)	426 (2)	2075 (2)	35 (1)
C(1)	6025 (4)	871 (3)	2737 (3)	33 (1)
C(2)	4212 (4)	1536 (4)	3698 (3)	36 (1)
C(3)	3819 (4)	2478 (4)	4927 (3)	38 (1)
C(4)	5210 (4)	2736 (4)	5217 (3)	39 (1)
C(5)	7008 (4)	2041 (4)	4243 (3)	35 (1)
C(6)	7523 (4)	1068 (3)	2954 (3)	30 (1)
N	8564 (3)	2470 (3)	−243 (2)	34 (1)
C(11)	7875 (4)	2988 (4)	−1383 (3)	37 (1)
C(12)	7050 (5)	4646 (4)	−1642 (4)	46 (2)
C(13)	6930 (5)	5803 (4)	−718 (4)	50 (2)
C(14)	7629 (5)	5290 (4)	453 (4)	45 (2)
C(15)	8432 (4)	3615 (4)	653 (3)	39 (1)

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

Cu—O	1·909 (2)	N—C(11)	1·343 (4)
Cu—N	2·036 (2)	C(11)—C(12)	1·376 (4)
C(6)—C(1)	1·406 (6)	C(12)—C(13)	1·366 (4)
C(1)—C(2)	1·381 (4)	C(13)—C(14)	1·374 (6)
C(2)—C(3)	1·370 (5)	C(14)—C(15)	1·376 (4)
C(3)—C(4)	1·380 (6)	C(15)—N	1·334 (5)
C(4)—C(5)	1·378 (4)		
C(5)—C(6)	1·407 (4)		
C(6)—O	1·304 (3)		
C(1)—Cl(1)	1·748 (3)		
C(3)—Cl(3)	1·739 (3)		

O—Cu—N	90·8 (1)	C(1)—C(6)—O	124·9 (3)
Cu—O—C(6)	126·2 (2)	C(5)—C(6)—O	121·2 (3)
C(1)—C(6)—C(5)	113·8 (2)	C(6)—C(1)—Cl(1)	118·2 (2)
C(2)—C(1)—C(6)	124·0 (3)	C(2)—C(1)—Cl(1)	117·8 (3)
C(3)—C(2)—C(1)	118·7 (4)	C(2)—C(3)—Cl(3)	119·7 (3)
C(4)—C(3)—C(2)	120·9 (3)	C(4)—C(3)—Cl(3)	119·4 (2)
C(5)—C(4)—C(3)	118·9 (3)	C(4)—C(5)—Cl(2)	118·6 (3)
C(6)—C(5)—C(4)	123·7 (4)	C(6)—C(5)—Cl(2)	117·8 (2)
C(15)—N—C(11)	118·1 (3)	C(15)—N—Cu	120·6 (2)
N—C(11)—C(12)	122·0 (3)	C(11)—N—Cu	121·0 (2)
C(11)—C(12)—C(13)	119·2 (3)		
C(12)—C(13)—C(14)	119·4 (3)		
C(13)—C(14)—C(15)	118·5 (4)		
C(14)—C(15)—N	122·8 (3)		

Discussion. The structure consists simply of discrete centrosymmetric $Cu(C_6H_2Cl_3O)_2(C_5H_5N)_2$ molecules (Fig. 1). A stereoscopic view of the molecule is given in Fig. 2. The Cu ion has a planar coordination geometry with Cu—O distances of 1·909 (2) Å and Cu—N distances of 2·036 (2) Å. The pyridine rings are twisted 30·8° out of the CuO_2N_2 plane, presumably to reduce repulsions between the α H atoms and the oxygens on the phenoxide. However, the phenoxide rings are twisted nearly perpendicular to the coordination plane (dihedral angle = 97·4°). In addition, the ring is tipped so that the Cu—O—C(6) bond angle (126·2°) is consistent with an oxygen lone-pair interaction with the Cu^{II} ion. This forces one of the chlorine atoms, Cl(1), into a position so as to block an axial coordination site of the Cu^{II} ion. The Cu—Cl(1) distance obtained, 2·914 (1) Å, is comparable to that observed for semi-coordinated chloride ions in $(RNH_3)_2CuCl_4$ structures (Willett, Jardine, Rouse, Wong, Landee & Numata, 1981), but clearly in this case cannot constitute a bonding interaction. The length of the C—Cl bond (1·740 Å, average) clearly plays a role in the effectiveness of the phenoxide ion in blocking these two extra coordination sites. The enhanced catalytic activity exhibited by the 2,4,6-trichlorophenolate complex, as compared with other phenolates, may be due to

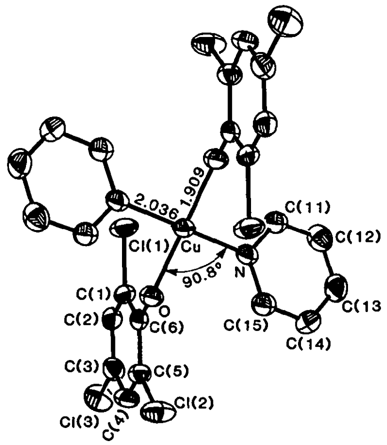

Fig. 1. Illustration of the molecular geometry in $[Cu(C_6H_2Cl_3O)_2(C_5H_5N)_2]$.

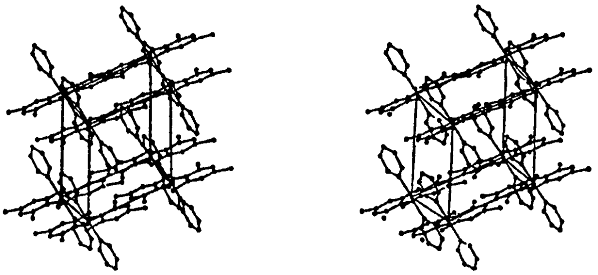

Fig. 2. Stereoscopic view of the structure of $[Cu(C_6H_2Cl_3O)_2(C_5H_5N)_2]$. The *a* axis is vertical, and the *c* axis nearly horizontal.

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* Anisotropic thermal parameters, hydrogen-atom positions, and a list of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 42959 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

this steric factor preventing coordination of solvent ligands which, if coordinated, would prevent the formation of polymeric species.

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References

Blanchard, H. S., Finkbeiner, H. C. & Russell, G. A. (1962). *J. Polym. Sci.* **58**, 469–490.

Campana, C. F., Shepherd, D. F. & Litchman, W. N. (1980). *Inorg. Chem.* **20**, 4039–4044.

Davies, G. & El-Sayed, M. A. (1983). *Inorg. Chem.* **22**, 1257–1267.

Finkbeiner, H., Hay, A. S., Blanchard, H. S. & Endres, G. F. (1966). *J. Org. Chem.* **31**, 549–563.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Sheldrick, G. M. (1984). *SHELXTL Users Manual.* Nicolet XRD Corporation, Madison, Wisconsin.

Willett, R. D. & Breneman, G. L. (1983). *Inorg. Chem.* **22**, 326–329.

Willett, R. D., Jardine, F. H., Rouse, I., Wong, R. J., Landee, C. P. & Numata, M. (1981). *Phys. Rev. B*, **24**, 5372–5381.

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Structure of Tetrakis[μ-(3,3′-dimethylacrylato)]-bis(ethanol)dicopper(II)

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Abstract. $[\mathrm{Cu_2(C_5H_7O_2)_4(C_2H_6O)_2}]$, $M_r = 615\cdot7$, triclinic, $P\bar{1}$, $a = 10\cdot484\,(2)$, $b = 12\cdot296\,(2)$, $c = 14\cdot303\,(3)$ Å, $\alpha = 65\cdot97\,(1)$, $\beta = 71\cdot69\,(1)$, $\gamma = 68\cdot93\,(1)^\circ$, $V = 1540\cdot7$ Å^3, $Z = 2$, $D_x = 1\cdot327$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0\cdot71073$ Å, $\mu = 1\cdot43$ mm^{-1}, $F(000) = 644$, $T = 293$ K, $R = 0\cdot042$ for 3398 observed reflections. Centrosymmetric binuclear molecules with four carboxylate bridges spanning a Cu···Cu separation of 2·594 (2) Å are linked to form chains by hydrogen bonding between axial ethanol ligands and the carboxylates. The C=C double bonds of the carboxylate ligands are not involved in coordination of the Cu atoms.

Introduction. A polarographic and potentiometric investigation into the copper(II) complexes formed with a variety of unsaturated carboxylic acids (Resnik & Douglas, 1963) concluded that there was some indication of interaction between copper(II) and the C=C double bond. Edmondson & Lever (1965) presented spectroscopic data for α,β-unsaturated copper(II) carboxylates and tentatively assigned a band at approximately 1500 cm^{-1} in their infrared spectra as a coordinated C=C double-bond stretching mode. Subsequently, several authors have used ESR spectroscopy (Newton & Tabner, 1979), magnetic susceptibility measurements (Zelentsov & Aminov, 1969; Kumar & Suri, 1981) or both techniques (Newton, Oldham & Tabner, 1980; Mrozinski & Heyduk, 1983, 1984; Bukowska-Strzyzewska, Skoweranda, Heyduk & Mrozinski, 1983) to ascertain the exact nature of the bonding in α,β-unsaturated copper(II) carboxylates and their adducts, but no conclusive evidence for the presence of a copper(II)–double-bond interaction has been found. Our work is the first crystallographic investigation into this problem and is also part of a wider study of oligonuclear α,β-unsaturated metal carboxylate complexes.

Experimental. Compound prepared from basic copper carbonate and 3,3′-dimethylacrylic acid in refluxing ethanol, crystals obtained by concentration and cooling. Exposure to air leads to crystal degradation by loss of ethanol. Crystal 0·25 × 0·4 × 0·6 mm mounted in Lindemann capillary, Siemens AED2 diffractometer, cell parameters from 2θ values of 32 reflections measured at $\pm\omega$ ($20 < 2\theta < 22^\circ$). Intensities measured in ω/θ-scan mode, scan width = 1·12° + α-doublet splitting, scan time = 11·6 s, $2\theta_{\max} = 45^\circ$, h −11→0, k −13→13, l −15→15, no significant variation of three standard reflections, no absorption correction. 4016 data (all unique), 3398 with $F > 4\sigma(F)$ for structure determination by Patterson and difference syntheses and blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0\cdot0002F^2$. Anisotropic thermal parameters for non-H atoms, H atoms constrained [C—H = 0·96 Å, olefinic H on C—C—C external bisectors, rigid methyl groups, H—C—H = 109·5°, $U(\mathrm{H}) = 1\cdot2U_{\mathrm{eq}}(\mathrm{C})$; O-H atoms freely refined], isotropic extinction parameter $x = 1\cdot5\,(2) \times 10^{-6}$ $[F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}]$. 364

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