Structure and Stability of Carboxylate Complexes.
XIV.* The Crystal and Molecular Structure of Anhydrous Copper(II) Phenoxyacetate

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The crystal structure of an anhydrous Cu(II) phenoxyacetate is described (rhombohedral-hexagonal cell, $a = 30\cdot23$, $c = 8\cdot96$ Å, twinned on (001), twin obliquity 60°, space group $R\bar{3}$, Cu $K\alpha$ radiation, Weissenberg visual data, 1432 reflexions, final R 0·115). The Cu atoms, in general positions, are linked by two types of crystallographically independent phenoxyacetate ligands, to form a complex hexamer with symmetry C_{3i} in which the carboxylate groups form both *syn–syn* and *syn–anti* bridges. Each Cu atom is chelated by only one phenoxyacetate ligand through the phenoxy O atom. The Cu atoms have an essentially tetragonally distorted octahedral coordination (Cu–O, 1·91, 1·96, 1·96, 1·98, 2·43, 2·47 Å).

Introduction

Several different crystalline Cu(II) phenoxyacetates have been found. Prout, Armstrong, Carruthers, Forrest, Murray-Rust & Rossotti (1968) reported a pale blue, monoclinic dihydrate to be a *trans* dichelate containing six-coordinate Cu. The crystals were prepared by the addition of a phenoxyacetate buffer solution ($pH < 5$) to a $Cu(ClO_4)_2$ solution containing $NaClO_4$. It was also noted that pale green, anhydrous crystals were formed in the absence of the $NaClO_4$. Goebel & Doedens (1971) found that three forms were obtained by the interaction of phenoxyacetic acid and $CuCO_3$ in aqueous ethanol. One was the dihydrate above and the second, described as a light-green polycrystalline material, may have been the anhydrous form, the structure of which we now report. Goebel & Doedens's (1971) third form was a blue, triclinic trihydrate containing unidentate carboxylate ligands and five-coordinate Cu(II).

Experimental and crystal data

Preparation

Spherical clusters of very fine pale green needles were obtained from a solution ($pH < 5$) of freshly prepared $CuCO_3$ in aqueous phenoxyacetic acid. The anhydrous crystals were grown to a suitable size for X-ray work by alternate warming and cooling over a

period of some months. (Found: Cu, 17·5; C, 52·6; H, 3·99; $(C_6H_5OCH_2COO)_2Cu$ requires Cu, 17·4; C, 52·5; H, 3·86.)

Crystal data

Copper(II) phenoxyacetate, $C_{16}H_{14}O_6Cu$. $M = 365\cdot8$. Rhombohedral. Space group $R\bar{3}$ (C_{3i}^2, No. 148 (hexagonal axes); no systematic extinctions). Twinned on (001). $a = 30\cdot23$ (3), $c = 8\cdot06$ (1) Å, $U = 7091\cdot4$ Å^3, $D_c = 1\cdot54$, $Z = 18$. Cu $K\alpha$ radiation, $\lambda = 1\cdot5418$ Å, $\mu = 22$ cm^{-1}. Crystal size $0\cdot05 \times 0\cdot05 \times 0\cdot2$ mm. 1432 independent reflexions.

Data collection

The initial photographs showed that the crystals were rhombohedral, twinned on (001) of the hexagonal super-cell with a twin obliquity of 60°. This requires that equivalent reflexions overlap in $hk0$, and non-equivalent reflexions in $hk3$ and $hk6$. For all other layers, the two components of the twin produce separate diffraction patterns.

The data were collected photographically on multiple-film equi-inclination Weissenberg photographs about c ($hk0-hk7$). A very fine-bore lead glass collimating system was devised to reduce background scatter so that exposure times from 7 to 28 days could be used. The diffraction pattern was initially indexed with orthohexagonal indices. The 2327 intensities estimated visually included more than one set of equivalent reflexions from each layer. In addition, on layers 1, 2, 4 and 5 the intensities of reflexions from both components of the twin were measured so that,

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in these layers, up to four independent observations of some reflexions were made.

After transformation of the indices to a hexagonal system, the ratio, k $(=I_2/I_1)$, of the intensities of the two components of the twin was determined by a least-squares procedure with the minimization function $M = \sum w(I_1 - I_2/k)$ with $w = 1/I_1$. The ratio was found to be $1:0\cdot218$. Equivalent reflexions were then merged, and Lorentz and polarization corrections applied. No correction was made for absorption. Initially the data were put on a common scale based on exposure times, and subsequently by refining the layer scales against $|F_c|$.

Structure determination

A Patterson function was computed with the raw data and no allowance for the overlap of reflexion on layers $hk3$ and $hk6$. The map was consistent with space group $R\bar{3}$, which was then assumed. The positions of all the non-hydrogen atoms, except C(13)–C(18) of one phenoxyacetate group, were determined. A Fourier map phased on these positions showed the missing atoms.

This structure was refined by four cycles of full-matrix least-squares method with isotropic temperature factors and unit weights. The structure-factor least-squares routine was specially modified to allow for overlapping of the reflexions hkl with $l = 3n$. The method used was essentially the same as that used for the refinement of the structure of copper maleate (Prout, Carruthers & Rossotti, 1971a). After refinement of the layer scale factors against $|F_c|$, two further cycles were computed. The weighting scheme on the $|F_c|$ scale was then determined to be: $w = [1 + (|F_o| - 11)^2/144]^{-1}$. The refinement converged after two

further cycles $(R = 0\cdot11)$. A difference map gave no indication of any H atoms, nor showed any abnormal features near C(17) or C(18) which, after the refinement, were too close $(1\cdot23$ Å$)$ for the C–C aromatic bond.

Scattering factors corrected for anomalous dispersion were taken from International Tables for X-ray Crystallography (1962). All calculations were carried out on the University of Rome Univac 1108 with a set of programs written by Carruthers, Domenicano & Spagna (1971).

The final atomic parameters are given in Table 1.* Standard deviations of interatomic distances and interbond angles, Table 2, were obtained from the leading diagonal terms of the variance-covariance matrix.

Discussion

The crystals are built up from the complex hexamers shown in Fig. 1. The hexamers, point symmetry C_{3i}, are centred on the threefold positions $(0,0,0; \frac{1}{3},\frac{2}{3},\frac{2}{3}; \frac{2}{3},\frac{1}{3},\frac{1}{3})$ and are therefore arranged in cubic close packing. There are no linkages between the hexamers other than van der Waals forces.

In the hexamers any one of the Cu atoms, which are at general positions in the unit cell, has exactly the same environment as the other five by the C_{3i} symmetry. The Cu atoms together form a compressed trigonal antiprism with six long edges (Cu–Cu 5·65 Å) bordering the equilateral triangular faces and six short edges
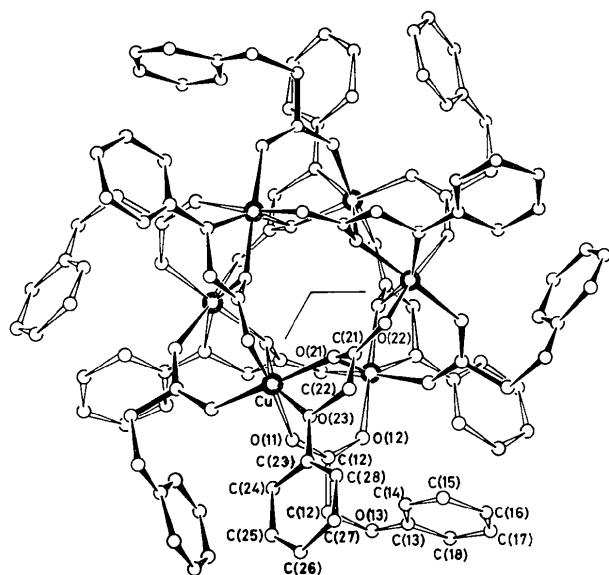

Fig. 1. Copper(II) phenoxyacetate; the hexamer seen in projection down z.

Table 1. Final atomic coordinates
with standard deviations in parentheses

	x/a	y/b	z/c	$B_{(\mathrm{Iso})}$
Cu	0·1015 (7)	0·0117 (7)	0·1118 (2)	2·53 (5)
O(11)	0·163 (3)	0·062 (4)	0·007 (1)	4·0 (2)
O(12)	0·162 (3)	0·129 (3)	−0·094 (1)	3·9 (2)
O(13)	0·264 (4)	0·189 (4)	−0·080 (1)	4·8 (2)
C(11)	0·184 (5)	0·106 (5)	−0·040 (2)	3·5 (2)
C(12)	0·243 (6)	0·136 (6)	−0·034 (2)	4·7 (3)
C(13)	0·256 (6)	0·220 (7)	0·015 (2)	5·0 (3)
C(14)	0·235 (7)	0·207 (7)	0·154 (2)	5·7 (4)
C(15)	0·228 (8)	0·240 (8)	0·247 (3)	6·7 (4)
C(16)	0·244 (10)	0·290 (10)	0·185 (3)	8·8 (6)
C(17)	0·266 (10)	0·304 (11)	0·063 (3)	9·1 (6)
C(18)	0·273 (10)	0·269 (9)	−0·036 (3)	8·3 (6)
O(21)	0·072 (3)	0·057 (3)	0·125 (1)	3·7 (2)
O(22)	0·035 (3)	0·088 (3)	0·265 (1)	3·9 (2)
O(23)	0·136 (3)	0·065 (3)	0·337 (1)	3·9 (2)
C(21)	0·068 (5)	0·075 (5)	0·241 (2)	3·1 (2)
C(22)	0·107 (5)	0·090 (5)	0·365 (2)	3·6 (2)
C(23)	0·186 (5)	0·088 (5)	0·400 (2)	3·6 (2)
C(24)	0·216 (7)	0·069 (6)	0·337 (2)	5·2 (3)
C(25)	0·267 (7)	0·093 (7)	0·388 (2)	5·8 (4)
C(26)	0·286 (8)	0·131 (8)	0·497 (3)	6·7 (4)
C(27)	0·253 (7)	0·145 (7)	0·560 (2)	5·9 (4)
C(28)	0·203 (6)	0·124 (6)	0·510 (2)	4·8 (3)

Table 2. *Interatomic distances* (Å) *and interbond angles* (°) *with standard deviations*

Cu——Cu[I]	3·531 (3)		O(21)···O(22)	2·20 (2)
Cu——O(11)	1·96 (1)		O(21)——C(21)	1·21 (2)
Cu——O(12)[I]	1·91 (1)		O(22)——C(21)	1·27 (2)
Cu——O(21)	1·96 (1)		O(21)···O(23)	2·63 (1)
Cu——O(21)[I]	2·43 (1)		C(21)——C(22)	1·51 (2)
Cu——O(22)[II]	1·98 (1)		C(22)——O(23)	1·43 (2)
Cu——O(23)	2·47 (1)		O(23)——C(23)	1·43 (2)
			C(23)——C(24)	1·41 (3)
O(11)···O(12)	2·25 (2)		C(23)——C(28)	1·36 (2)
O(11)——C(11)	1·24 (2)		C(24)——C(25)	1·43 (3)
O(12)——C(11)	1·27 (2)		C(25)——C(26)	1·39 (3)
O(12)···O(13)	2·70 (1)		C(26)——C(27)	1·41 (4)
C(11)——C(12)	1·54 (2)		C(27)——C(28)	1·39 (3)
C(12)——O(13)	1·46 (2)			
O(13)——C(13)	1·37 (2)		O(11)——Cu-O(12)[I]	85·3 (5)
C(13)——C(14)	1·37 (2)		O(11)——Cu-O(21)	94·4 (5)
C(13)——C(18)	1·39 (3)		O(11)——Cu-O(21)[I]	89·7 (4)
C(14)——C(15)	1·40 (4)		O(11)——Cu-O(22)[II]	163·4 (5)
C(15)——C(16)	1·43 (4)		O(11)——Cu-O(23)	87·5 (3)
C(16)——C(17)	1·23 (4)			
C(17)——C(18)	1·48 (5)			

(Cu–Cu 3·53 Å). Even the short contacts are far longer than might be expected for Cu–Cu bonds.

The Cu coordination is distorted octahedral with four short and two long Cu–O contacts. The short contacts (1·91–1·98 Å) which are coplanar, are to carboxylate O atoms of two symmetry-related pairs of phenoxyacetate ligands and lie in the planes of their respective carboxylate groups. The long contacts are to an ether O atom (2·47 Å) of one of these and a carboxylate O atom (2·43 Å) of a fifth ligand, but the latter contact is not coplanar with the carboxylate group.

There are two chemically and crystallographically distinct phenoxyacetate ligands in the hexamer. In one of these the carboxylate group containing O(11) and O(12) has the *syn–syn* conformation with respect to Cu coordination and bridges pairs of Cu atoms forming the shorter sides of the trigonal antiprism. Both the Cu–O contacts are short [Cu–O(11) 1·96, Cu–O(12) 1·91 Å] and this ligand forms no other coordinate linkages to Cu. Similar carboxylate bridges were found in copper phthalate monohydrate (Prout, Carruthers & Rossotti, 1971*b*), but in that complex, which is a chain polymer, the Cu–Cu contact is only 3·22 Å. In the other phenoxyacetate ligand the carboxylate group containing O(21) and O(22) has the *syn–anti* conformation with respect to Cu coordination and bridges pairs of Cu atoms forming the longer sides of the trigonal antiprism. Both these Cu–O contacts are short [Cu–O(21) 1·96, Cu–O(22) 1·98 Å]. Similar *syn–anti* bridges were observed in the sheet polymers in copper maleate monohydrate (Prout,

Carruthers & Rossotti, 1971*a*). The short contacts to Cu by symmetry-related phenoxyacetates are *cis*. In addition the second type of phenoxyacetate ligand forms two long contacts to Cu atoms. The phenoxy O(23) completes a five-membered chelate ring including O(21). In addition O(21) itself forms a second long, out-of-plane, contact to the Cu atom which together with the two Cu atoms linked by the *syn–anti* bridge, form one of the isosceles triangular faces of the trigonal antiprism.

The configurations of the two phenoxyacetate groups are different as is demonstrated by the torsional angles in Table 3. The phenoxyacetate that forms a *syn–syn* bridge has almost exactly the same configuration as the bent phenoxyacetate ligand in aquobis(phenoxyacetato)bis(pyridine)copper(II) (Prout, Barrow & Rossotti, 1971) whereas the second phenoxyacetate that forms *syn–anti* bridges closely resembles the extended chelating ligands in the di-aquobis(phenoxyacetato)copper(II) (Prout *et al.*, 1968).

Table 3. *Dihedral angles* (°)

The dihedral angle about the bond *J–K* is the angle the bond *K–L* is rotated from the *IJK* plane. It is positive when, on looking from *IJ* to *KL*, the rotation is clockwise.

I	J	K	L	
O(11)	C(11)	C(12)	O(13)	5
C(11)	C(12)	O(13)	C(13)	115
C(12)	O(13)	C(13)	C₆H₅ plane C(14)	−7
O(21)	C(21)	C(22)	O(23)	−13
C(21)	C(22)	O(23)	C(23)	155
C(22)	O(23)	C(23)	C₆H₅ plane C(24)	15

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