

**Structure and Stability of Carboxylate Complexes. XV. The Crystal and Molecular Structures of Diaquobis-(*p*-methoxyphenoxyacetato)copper(II) Dihydrate and Diaquobis-(*p*-methoxyphenoxyacetato)copper(II) and Crystal Data for Diaquobis-(*p*-nitrophenoxyacetato)copper(II)**

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The crystal and molecular structures of diaquobis-(*p*-methoxyphenoxyacetato)copper(II) dihydrate (orthorhombic,  $a = 7.07$ ,  $b = 44.4$ ,  $c = 6.26$  Å,  $Ccm2_1$ , 1976 independent reflexions, linear diffractometer data,  $R = 0.074$ , full-matrix refinement) and diaquobis-(*p*-methoxyphenoxyacetato)copper(II) (triclinic,  $a = 14.90$ ,  $b = 6.56$ ,  $c = 5.31$  Å,  $\alpha = 104.4$ ,  $\beta = 75.4$ ,  $\gamma = 94.3^\circ$   $P\bar{1}$ , 3528 independent reflexions, four-circle diffractometer data,  $R = 0.044$ , full-matrix refinement) have been determined. In the former the Cu coordination is *trans* square planar [Cu–O(mean) 1.95 Å] with unidentate *p*-methoxyphenoxyacetate ligands coordinated through a carboxylate O atom. In the latter the Cu coordination is distorted octahedral and the *p*-methoxyphenoxyacetate ligands are bidentate with a short 1.955 Å contact to a carboxylate O atom and a long, 2.432 Å, contact to the phenoxy O atom: Cu–OH<sub>2</sub> is 1.945 Å. Crystal data are reported for diaquobis-(*p*-nitrophenoxyacetato)copper(II).

### Introduction

At least three unsubstituted phenoxyacetates of Cu(II) may be obtained from aqueous solution: an anhydrous bis(phenoxyacetato)copper(II), which is a hexamer of complex structure (Carruthers, Prout & Rossotti, 1975), a diaquobis(phenoxyacetato)copper(II), which is a *trans* distorted octahedral complex with bidentate phenoxyacetate ligands forming long Cu–O(phenoxy) and short Cu–O(carboxylate) contacts (Prout, Armstrong, Carruthers, Forrest, Murray-Rust & Rossotti, 1968) and triaquobis(phenoxyacetato)copper(II), in which the phenoxyacetates are unidentate and Cu five coordinate (Goebel & Doedens, 1971). Unidentate phenoxyacetates and five coordinate Cu(II) also occur in the mixed complex bis(phenoxyacetato)aquobis(pyridine)-copper(II) (Prout, Barrow & Rossotti, 1971). In the two last species, the five coordination of Cu appears to arise from crystal packing requirements, rather than from any intrinsic drive from the Cu(II) to achieve that coordination number. Of greater interest in the present context is the occurrence of both unidentate and bidentate phenoxyacetates in the solid state, since it is likely that in solution, also, there is a finely balanced acyclic  $\rightleftharpoons$  cyclic equilibrium involving the phenoxy O atom (Dillon & Rossotti, 1973).

In an investigation into the effect of phenyl-group substituents on the coordination of phenoxyacetates, Cu complexes of *p*-methoxyphenoxyacetate and *p*-nitrophenoxyacetate were examined in the hope that electrophilic and nucleophilic substituents might preferentially stabilize one or other type of complex. There are at least two *p*-methoxyphenoxyacetate com-

plexes, the structures of which are described below. The molecular structure of one is analogous to that of diaquobis(phenoxyacetato)copper(II); the other is a new type. It was at first thought that only one form of the *p*-nitrophenoxyacetate complex existed, diaquobis-(*p*-nitrophenoxyacetato)copper(II), containing complexes of the same type as the diaquophenoxyacetate and diaquo-*p*-methoxyphenoxyacetate. However, subsequent efforts to prepare the complex following the same method about a year after the original preparation gave other efflorescent crystal forms of indeterminate water content and different morphology.

### Experimental and crystal data

#### Preparation

(i) *Diaquobis-(p-methoxyphenoxyacetato)copper(II) dihydrate*. A slight excess of CuCO<sub>3</sub> was added to a warm 0.1M solution of *p*-methoxyphenoxyacetic acid. The unreacted solid was filtered off and the mother liquor (pH ca 3.5) allowed to cool slowly. Thin blue plates were obtained after ca one day (Found: C, 43.5; H, 5.26. (CH<sub>3</sub>O.C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>COO)<sub>2</sub>Cu.4H<sub>2</sub>O requires C, 43.4; H, 5.27%.)

(ii) *Diaquo-(p-methoxyphenoxyacetato)copper(II)*. Over a period of several months the blue plates of the tetrahydrate redissolve in the mother liquor and paler blue, thin fragile plates are formed. The subsequent structure analysis confirmed that these were a dihydrate (Found: C, 46.7; H, 4.70. (H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>COO)<sub>2</sub>Cu(II) requires C, 46.8; H, 4.80%.)

(iii) *Diaquobis-(p-nitrophenoxyacetato)copper(II)*.

This was prepared by the same method as diaquobis-(*p*-methoxyphenoxyacetato)copper(II) dihydrate (Found: C, 38.9; H, 3.47; N, 5.87; Cu, 12.9.  $(\text{O}_2\text{NC}_6\text{H}_4\text{OCH}_2\text{COO})_2\text{Cu}\cdot 2\text{H}_2\text{O}$  requires C, 39.1; H, 3.28; N, 5.70; Cu, 12.9%.)

## X-ray structure analysis

(i) *Diaquobis-(p-methoxyphenoxyacetato)copper(II) dihydrate*

$(\text{CH}_3\text{OC}_6\text{H}_4\text{OCH}_2\text{COO})_2\text{Cu}\cdot 4\text{H}_2\text{O}$ ,  $M=497.7$ , orthorhombic,  $a=7.07$  (2),  $b=44.4$  (1),  $c=6.26$  (2) Å,  $U=2138$  Å<sup>3</sup>,  $d_m=1.60$  (1) g cm<sup>-3</sup> (by flotation),  $Z=4$ ,  $d_c=1.61$  g cm<sup>-3</sup>; space group  $Ccm2_1$  [No. 36, non-standard setting; general positions  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + (x, y, z; x, -y, z; -x, y, \frac{1}{2} + z; -x, -y, \frac{1}{2} + z)$ ] from the structure analysis; systematic extinctions,  $hkl$ ,  $h+k=2n+1$ ;  $0kl$ ,  $l=2n+1$ . Mo  $K\alpha$  radiation,  $\lambda=0.7107$  Å,  $\mu=11.7$  cm<sup>-1</sup>.

Preliminary cell dimensions and systematic extinctions were determined from Weissenberg and precession photographs. The refined cell dimensions and intensities were obtained from a Hilger and Watts linear diffractometer, layers  $hk0-hk7$  yielding 1976 independent reflexions with  $I > 3\sigma$ . These data were corrected for Lorentz and polarization effects but not absorption.

The systematic absences do not distinguish space groups  $Ccmm$  and  $Ccm2_1$ . However, with four molecules to the cell, the former requires the complex to possess  $C_{2v}$  or  $C_{2h}$  symmetry so that the non-centrosymmetric space group seemed the more probable. An unsharpened Patterson function placed the Cu atom at  $0.23, 0, \frac{1}{4}$  at a site of symmetry  $mm$  in space group  $Ccmm$ . Three independent neighbouring O atoms were also located. These atoms were used to phase an  $F_o$  synthesis which indicated positions for a further 11 atoms and confirmed  $Ccm2_1$ . The remaining two non-hydrogen atoms were located from the next  $F_o$  synthesis.  $R$  was then 0.29. The trial struc-

ture was refined first by the isotropic (six cycles) then anisotropic least-squares method. The anisotropic refinement converged at  $R=0.074$  after three cycles. The full normal matrix was used with the weighting scheme  $w=[1+(|F_o|/100)^2]^{-1}$ . The final difference map had no major features; H atoms could not be located.

The X-RAY 70 series of programs (Stewart, Kundell & Baldwin, 1970) modified to run on an ICL 1906A computer were used for all calculations. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962) and were corrected for anomalous dispersion. The final atomic parameters are given in Table 1.\* The interatomic distances,

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30970 (24 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

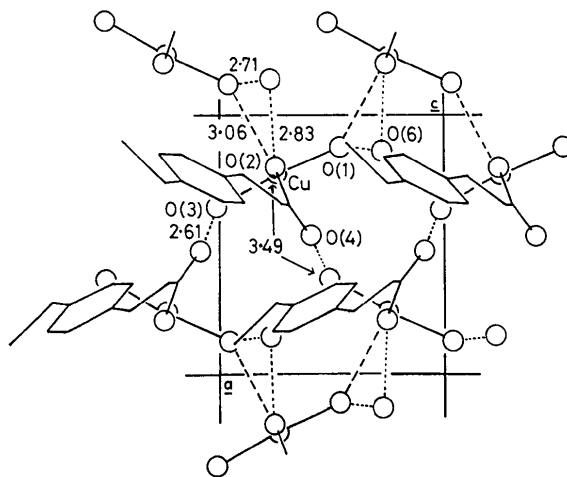


Fig. 1. The diaquobis-(*p*-methoxyphenoxyacetato)copper(II) dihydrate structure seen in projection down  $b$  onto the crystallographic mirror plane perpendicular to  $b$  at  $y=0$ . Hydrogen bonds and some non-bonded contacts are shown as broken lines. The contact distances are in Å.

Table 1. *Diaquobis-(p-methoxyphenoxyacetato)copper dihydrate*

Final atomic parameters ( $\times 10^3$  except  $y/b$  which are  $\times 10^4$ ) with standard deviations in parentheses.

	$x/a$	$y/b$	$z/c$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cu	230.5 (3)	0	$\frac{1}{4}$	29 (1)	14 (1)	44 (1)	0	3 (2)	0
O(1)	126 (2)	0	535 (3)	33 (7)	44 (8)	32 (9)	0	-1 (7)	0
O(2)	220 (1)	440 (1)	230 (2)	45 (5)	13 (3)	36 (7)	6 (4)	-2 (7)	2 (3)
O(3)	358 (2)	0	-16 (3)	52 (10)	44 (9)	52 (12)	0	24 (9)	0
O(4)	471 (1)	495 (2)	408 (2)	43 (7)	23 (4)	52 (7)	7 (4)	-14 (5)	2 (4)
O(5)	235 (1)	1000 (2)	97 (2)	44 (6)	11 (3)	49 (6)	6 (4)	-11 (6)	-6 (4)
O(6)	148 (1)	547 (2)	725 (3)	50 (6)	24 (4)	64 (9)	-12 (5)	-9 (8)	-4 (4)
O(7)	260 (1)	2152 (2)	-249 (4)	72 (7)	24 (3)	66 (7)	-6 (9)	-11 (10)	0 (4)
C(1)	349 (2)	595 (2)	307 (2)	26 (6)	9 (4)	43 (10)	3 (5)	3 (6)	2 (4)
C(2)	346 (2)	933 (2)	273 (3)	48 (7)	10 (4)	33 (8)	7 (5)	-3 (9)	0 (4)
C(3)	243 (2)	1289 (2)	14 (2)	30 (7)	19 (4)	35 (7)	3 (5)	4 (7)	6 (5)
C(4)	156 (2)	1339 (3)	-173 (3)	31 (8)	29 (6)	34 (8)	7 (5)	-4 (6)	2 (5)
C(5)	152 (2)	1626 (3)	-268 (3)	49 (8)	24 (5)	43 (10)	3 (7)	5 (11)	-6 (5)
C(6)	251 (2)	1863 (2)	-170 (2)	49 (8)	17 (4)	38 (7)	3 (4)	5 (7)	0 (6)
C(7)	340 (2)	1814 (3)	19 (3)	34 (8)	28 (6)	35 (9)	5 (6)	0 (7)	-2 (6)
C(8)	342 (2)	1525 (2)	112 (3)	40 (8)	7 (5)	57 (10)	-1 (5)	6 (8)	3 (5)
C(9)	160 (3)	2227 (4)	-435 (4)	115 (18)	41 (8)	78 (19)	29 (31)	26 (15)	-5 (10)

Table 2. *Diaquobis-(p-methoxyphenoxyacetato)-copper(II) dihydrate*

Interatomic distances (Å) and interbond angles (°) with standard deviations in parentheses.

Cu—O(1)	1.96 (2)	O(2)—Cu—O(3)	88.1 (4)
Cu—O(2)	1.96 (1)	O(1)—Cu—O(2)	92.3 (4)
Cu—O(3)	1.93 (2)	O(1)—Cu—O(3)	173.7 (7)
O(2)—C(1)	1.30 (2)	Cu—O(2)—C(1)	118.1 (8)
O(4)—C(1)	1.22 (2)		
C(1)—C(2)	1.52 (1)	O(2)—C(1)—O(4)	126 (1)
C(2)—O(5)	1.42 (2)	O(2)—C(1)—C(2)	117 (1)
O(5)—C(3)	1.39 (1)	O(4)—C(1)—C(2)	117 (1)
C(3)—C(4)	1.37 (2)	C(1)—C(2)—O(5)	109 (1)
C(4)—C(5)	1.41 (2)	O(5)—C(3)—C(4)	117 (1)
C(5)—C(6)	1.44 (2)	O(5)—C(3)—C(8)	123 (1)
C(6)—C(7)	1.38 (2)	C(4)—C(3)—C(8)	121 (1)
C(7)—C(8)	1.41 (2)	C(3)—C(4)—C(5)	121 (1)
C(8)—C(3)	1.43 (2)	C(4)—C(5)—C(6)	118 (2)
C(6)—O(7)	1.37 (2)	C(5)—C(6)—C(7)	121 (1)
O(7)—C(9)	1.44 (3)	C(5)—C(6)—O(7)	123 (1)
O(4)···O(3) <sup>I</sup>	2.61 (1)	C(7)—C(6)—O(7)	116 (1)
O(1)···O(6)	2.71 (1)	C(6)—C(7)—C(8)	120 (1)
O(6)···O(2) <sup>II</sup>	2.83 (1)	C(7)—C(8)—C(3)	119 (1)
Cu···O(1) <sup>II</sup>	3.06 (2)	C(6)—O(7)—C(9)	119 (1)
Cu···O(3) <sup>I</sup>	3.49 (2)		

(I)  $1-x, -y, \frac{1}{2}+z$ ; (II)  $-x, y, \frac{1}{2}+z$ .

interbond angles, and dihedral angles are in Tables 2 and 5.

(ii) *Diaquobis-(p-methoxyphenoxyacetato)copper(II)*

$(\text{CH}_3\text{OC}_6\text{H}_4\text{OCH}_2\text{CO}_2)_2\text{Cu}(\text{H}_2\text{O})_2$ ,  $M=461.7$ , triclinic,  $a=14.90$  (2),  $b=6.56$  (1),  $c=5.31$  (1) Å;  $\alpha=104.4$  (2),  $\beta=75.4$  (2),  $\gamma=94.3$  (2)°,  $U=486.3$  Å<sup>3</sup>;  $d_m=1.66$  (1) g cm<sup>-3</sup> (by flotation),  $Z=1$ ,  $d_c=1.684$  g cm<sup>-3</sup>. Space group  $P\bar{1}$  (No. 2,  $C_1^1$ ) from the structure analysis; no systematic extinctions. Mo  $K\alpha$  radiation, graphite crystal monochromator,  $\lambda=0.7107$  Å,  $\mu=13.0$  cm<sup>-1</sup>.

The crystal system and preliminary values for the cell dimensions were obtained from Weissenberg and precession photographs. A Hilger and Watts four-circle diffractometer was used to refine the cell dimensions by a least-squares procedure (Watson, Shotton,

Cox & Muirhead, 1970) and the intensities of 3500 independent X-ray reflexions with  $I>3\sigma$  were measured by a step-counting technique with ordinate analysis. Lorentz, polarization and empirical absorption (North, Phillips & Mathews, 1968) corrections were applied.

With one molecule in the cell the Cu atom may be placed at the origin. The Cu phased  $F_o$  map revealed 14 independent atoms of a centrosymmetric complex. Two cycles of full-matrix least-squares refinement with unit weights and isotropic temperature factors followed by one cycle with anisotropic temperature factors reduced  $R$  to 0.06. The 11 H atoms were located from two successive difference syntheses. Two further cycles of anisotropic refinement for all atoms, excluding H, reduced  $R$  to 0.044. The final weighting scheme was  $w=[20+|F_o|+0.5|F_o|^2]^{-1}$ .

These calculations were carried out with a set of programs provided by Dr G. M. Sheldrick and modified for the Oxford ICL 1906A by Dr R. A. Forder. Scattering factors were taken from Cromer & Waber (1965) and corrected for anomalous dispersion. Observed structure amplitudes and structure factors calculated from the final atomic parameters in Table 3 are available.\* The interatomic distances and interbond angles are in Table 4 and some dihedral angles in Table 5.

(iii) *Diaquobis-(p-nitrophenoxyacetato)copper(II)*

$(\text{NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{CO}_2)_2\text{Cu}(\text{H}_2\text{O})_2$ ,  $M=491.6$ , monoclinic,  $a=14.02$  (5),  $b=7.26$  (4),  $c=9.55$  (5) Å,  $\gamma=91.8$  (3)°, space group  $P2_1/b$  (No. 14, first setting) systematic extinctions  $hk0$ ,  $k=2n+1$ ,  $00l$ ,  $l=2n+1$ . The crystal structure was determined from limited visually estimated intensities and refined by least-squares calculations with isotropic temperature factors to  $R=0.15$ . The structure of the complex is closely similar to that of diaquobis(phenoxyacetato)copper(II) and diaquobis-(p-methoxyphenoxyacetato)copper(II). Further work on this crystal is not contemplated.

\* See previous footnote.

Table 3. *Diaquobis-(p-methoxyphenoxyacetato)copper(II)*Final atomic parameters ( $\times 10^3$  except space parameters at C and O which are  $\times 10^4$ ) with standard deviations in parentheses.

	$x/a$	$y/b$	$z/c$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cu	0	0	0	35.4 (4)	27.1 (3)	19.0 (3)	14.0 (2)	-4.7 (2)	1.4 (2)
O(1)	360 (2)	-1893 (4)	1886 (5)	45 (2)	44 (2)	28 (1)	22 (1)	-4 (1)	3 (1)
O(2)	-106 (3)	-2452 (5)	-2855 (7)	71 (2)	41 (2)	27 (2)	15 (1)	-9 (1)	-11 (2)
O(3)	1664 (2)	-435 (4)	-1793 (5)	43 (2)	38 (1)	38 (1)	25 (1)	1 (1)	5 (1)
O(4)	4175 (2)	2553 (5)	-9738 (6)	50 (2)	58 (2)	49 (2)	35 (2)	3 (1)	2 (1)
O(5)	1275 (2)	-4458 (5)	1719 (7)	55 (2)	45 (2)	62 (2)	37 (2)	-6 (1)	4 (1)
C(1)	1110 (3)	-2900 (6)	997 (7)	46 (2)	33 (2)	29 (2)	16 (2)	-8 (2)	1 (2)
C(2)	1903 (3)	-2221 (6)	-1047 (9)	44 (2)	32 (2)	40 (2)	23 (2)	-2 (2)	3 (2)
C(3)	2322 (3)	241 (6)	-3808 (7)	35 (2)	33 (2)	29 (2)	17 (1)	-3 (1)	-3 (1)
C(4)	2038 (3)	1841 (6)	-4706 (8)	33 (2)	40 (2)	38 (2)	20 (2)	-5 (2)	3 (2)
C(5)	2641 (3)	2643 (6)	-6707 (8)	46 (2)	40 (2)	36 (2)	23 (2)	-6 (2)	1 (2)
C(6)	3518 (3)	1870 (6)	-7762 (8)	40 (2)	39 (2)	32 (2)	18 (2)	-3 (2)	-5 (2)
C(7)	3808 (3)	267 (7)	-6859 (9)	39 (2)	45 (2)	45 (2)	23 (2)	2 (2)	7 (2)
C(8)	3199 (3)	-577 (6)	-4858 (8)	49 (2)	38 (2)	40 (2)	23 (2)	-2 (2)	5 (2)
C(9)	3907 (4)	4195 (8)	-10726 (10)	63 (3)	52 (2)	46 (3)	31 (2)	-8 (2)	-7 (2)

Table 3 (cont.)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>iso</sub>
H(1)	202 (3)	-336 (7)	-260 (9)	14 (9)
H(2)	248 (3)	-195 (7)	-49 (9)	19 (10)
H(3)	146 (3)	231 (6)	-402 (7)	8 (8)
H(4)	241 (3)	377 (6)	-733 (8)	16 (9)
H(5)	440 (4)	-20 (7)	-756 (9)	21 (11)
H(6)	342 (3)	-178 (6)	425 (8)	18 (9)
H(7)	386 (4)	544 (11)	-944 (13)	40 (17)
H(8)	333 (4)	390 (9)	-1136 (12)	36 (14)
H(9)	441 (5)	455 (10)	-1208 (14)	46 (17)
H(10)	-49 (4)	-335 (10)	-261 (12)	27 (15)
H(11)	-2 (4)	257 (10)	-420 (15)	36 (19)

Table 4. *Diaquobis-(p-methoxyphenoxyacetato)-copper(II)*

Interatomic distances and interbond angles.

Cu—O(1)	1.955 (2)	O(1)—Cu—O(2)	92.0 (1)
Cu—O(2)	1.945 (3)	O(1)—Cu—O(3)	74.8 (1)
Cu—O(3)	2.432 (3)	O(2)—Cu—O(3)	95.0 (1)
O(1)—C(1)	1.264 (5)	Cu—O(1)—C(1)	122.2 (2)
C(1)—O(5)	1.237 (5)	Cu—O(3)—C(2)	106.5 (2)
C(1)—C(2)	1.512 (5)	Cu—O(3)—C(3)	134.7 (2)
C(2)—O(3)	1.421 (4)	O(1)—C(1)—O(5)	124.6 (3)
O(3)—C(3)	1.394 (4)	O(1)—C(1)—C(2)	121.1 (3)
C(3)—C(4)	1.387 (5)	O(5)—C(1)—C(2)	114.3 (3)
C(4)—C(5)	1.391 (5)	C(1)—C(2)—O(3)	111.2 (3)
C(5)—C(6)	1.367 (6)	C(2)—O(3)—C(3)	116.1 (3)
C(6)—O(4)	1.382 (5)	O(3)—C(3)—C(4)	115.3 (3)
O(4)—C(9)	1.430 (5)	O(3)—C(3)—C(8)	124.5 (3)
C(6)—C(7)	1.395 (6)	C(4)—C(3)—C(8)	120.2 (3)
C(7)—C(8)	1.397 (6)	C(3)—C(4)—C(5)	120.2 (3)
C(8)—C(3)	1.368 (6)	C(4)—C(5)—C(6)	119.9 (4)
O(1)···O(2)	2.805 (4)	C(5)—C(6)—C(7)	120.2 (3)
O(2)···O(5)	2.655 (4)	C(6)—C(7)—C(8)	119.6 (4)
		C(7)—C(8)—C(3)	120.0 (4)
		C(5)—C(6)—O(4)	124.9 (4)
		C(7)—C(6)—O(4)	114.8 (4)
		C(6)—O(4)—C(9)	116.8 (4)

## Results and discussion

(i) *Diaquobis-(p-methoxyphenoxyacetato)copper(II) dihydrate*

The crystal structure is built up from diaquobis-(*p*-methoxyphenoxyacetato)copper(II) units, the Cu atom

and water molecules of which lie in the mirror plane at  $y=0$  of space group  $Ccm2_1$  (Fig. 1). The two *p*-methoxyphenoxyacetato ligands are related by the mirror plane (Fig. 2). The Cu atom is four coordinate with *trans* aquo ligands at *ca* 1.95 Å and unidentate *p*-methoxyphenoxyacetato groups linked to Cu by carboxylate O atoms [Cu—O(2) 1.96 Å]. The second carboxylate O atom, O(4), is 3.04 Å away from the Cu atom, a similar distance to that found in aquobis-(phenoxyacetato)bis(pyridine)copper(II) (Prout *et al.*, 1971), but longer than that in triaquophenoxyacetato-copper(II) (Goebel & Doedens, 1971) (both complexes with similar Cu-carboxylate group arrangements). The long Cu···O contact in the methoxyphenoxyacetato system is regarded as non-bonding. The bond lengths and angles in the *p*-methoxyphenoxyacetato ligand do not differ from expected values and the ligand is almost planar (relevant dihedral angles are given in Table 5).

Each square planar complex is linked to two neighbouring complexes to form a chain parallel to *c* by hydrogen bonds 2.61 Å long from the water molecules O(3) to the two mirror-plane related carboxylate atoms O(4) and O(4'), Fig. 1. The intermolecular Cu···O(3) contact of 3.49 Å is not only too long for a bonding contact, but is also directed between the two water H

Table 5. *Dihedral angles* (°)

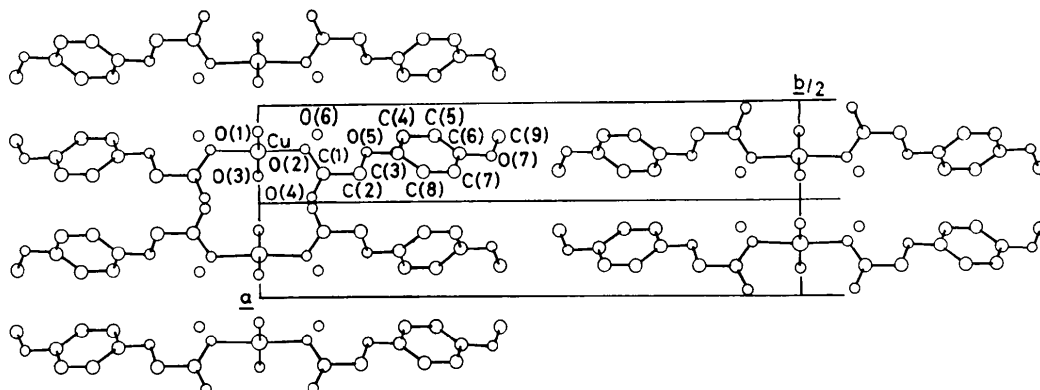
The dihedral angle about the bond *J*—*K* is the angle the bond *K*—*L* is rotated from the *IJK* plane. It is positive when, looking from *IJ* to *KL*, the rotation is clockwise.

(a) *Diaquobis-(p-methoxyphenoxyacetato)copper(II) dihydrate*

<i>I</i>	<i>J</i>	<i>K</i>	<i>L</i>	
O(1)	C(1)	C(2)	O(3)	21
C(1)	C(2)	O(3)	C(3)	-168
C(2)	O(3)	C(3)	C <sub>6</sub> H <sub>5</sub> plane C(8)	-8
C <sub>6</sub> H <sub>5</sub> plane C(5)	C(6)	O(7)	C(9)	4

(b) *Diaquobis-(p-methoxyphenoxyacetato)copper(II)*

<i>I</i>	<i>J</i>	<i>K</i>	<i>L</i>	
O(1)	C(1)	C(2)	O(3)	1
C(1)	C(2)	O(3)	C(3)	176
C(2)	O(3)	C(3)	C <sub>6</sub> H <sub>5</sub> plane C(8)	7
C <sub>6</sub> H <sub>5</sub> plane C(5)	C(6)	O(4)	C(9)	0

Fig. 2. The diaquobis-(*p*-methoxyphenoxyacetato)copper(II) dihydrate structure seen in projection down *c*.

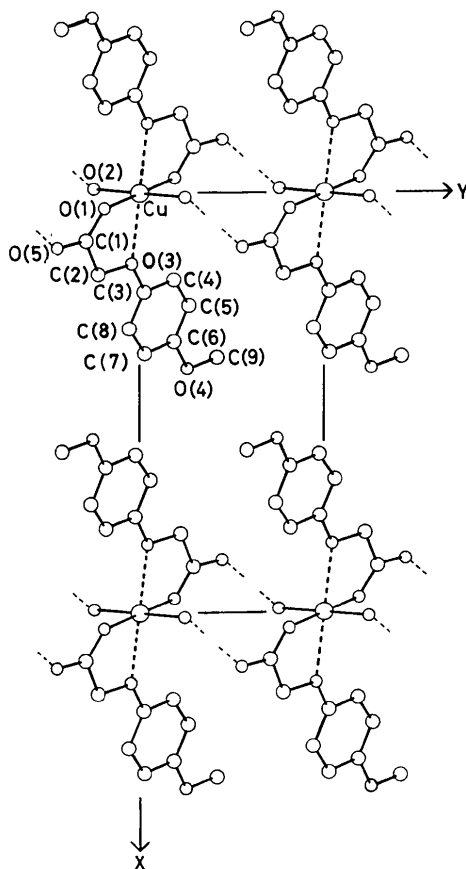


Fig. 3. The crystal structure of diaquobis-(*p*-methoxyphenoxyacetato)copper(II) projected down *c*.

atoms. The hydrogen-bond system effectively blocks the fifth coordinating position of the Cu atom. The arrangement again closely parallels that in the aquobis-(phenoxyacetato)bis(pyridine) complex.

The chains are linked by the lattice water O(6), which forms hydrogen bonds to a carboxylate O(2) of one chain and the coordinating water O(1) of a complex in a neighbouring chain (Fig. 1) to give sheets in the *ac* plane. The hydrogen bonding brings the water O(1) of one complex to 3.06 Å from a neighbouring Cu atom, a very long contact when compared with the 2.24 Å and 2.27 Cu–OH<sub>2</sub> contacts in the five-coordinate aquobis(phenoxyacetato)bis(pyridine)copper(II) (Prout *et al.*, 1971) and triaquobis(phenoxyacetato)copper(II) (Goebel & Doedens, 1971) respectively.

Again the long 3.06 Å contact is thought to be non-bonding.

The two-dimensional hydrogen-bonded sheets pack together to form the crystal using the translations of the C-centring.

#### (ii) *Diaquobis-(p-methoxyphenoxyacetato)copper(II)*

The crystals are built up from *trans* dichelate diaquobis-(*p*-methoxyphenoxyacetato)copper(II) units about symmetry centres, Fig. 3. The Cu coordination is that of a distorted octahedron with four short and two long contacts. The long contacts to the phenoxy atoms O(3) (2.432 Å) of a bidentate *p*-methoxyphenoxyacetato ligand are shorter than that found in the diaquobis(phenoxyacetato) complex but probably not significantly so. The Cu–water, Cu–O(2) 1.945 Å and Cu–O(carboxylate) contacts, Cu–O(1) 1.955 Å, are the same within experimental error as those found in the diaquobis(phenoxyacetato)copper(II) complex (Prout *et al.*, 1968) and diaquobis-(*p*-methoxyphenoxyacetato)copper(II) dihydrate. The *p*-methoxyphenoxyacetato ligand is near planar (pertinent dihedral angles are given in Table 5) and its dimensions are unexceptional.

In the crystal the diaquo-(*p*-methoxyphenoxyacetato)copper(II) complexes are linked by hydrogen bonding, O(2)–H(10)···O(5), 2.648 Å, parallel to *b*.

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