Acta Cryst. (1976). B**32**, 548

The Crystal Structure of Diaquobis(salicylato)copper(II), $Cu[C_6H_4(OH)COO]_2(H_2O)_2$

By Susan Jagner,* Rita Grønbæk Hazell and Karl Peder Larsen
Department of Inorganic Chemistry, Århus University, DK-8000 Århus C, Denmark

(*Received* 17 *June* 1975; *accepted* 20 *June* 1975)

$Cu[C_6H_4(OH)COO]_2(H_2O)_2$, DSC, crystallizes with a disordered (OD) structure. The two MDO structures have been determined from single-crystal X-ray diffractometer data. The MDO_1 structure, $a=7{\cdot}730$ (4), $b=11{\cdot}795$ (9), $c=31{\cdot}547$ (19) Å, space group $Pca2_1$ with $Z=8$, was refined to $R=0{\cdot}068$ for 1978 reflexions, while the MDO_2 structure, $a=7{\cdot}730$ (4), $b=11{\cdot}795$ (9), $c=31{\cdot}783$ (19) Å, $\beta=96{\cdot}98$ (1)°, space group $P2_1/a$ with $Z=8$, was refined to $R=0{\cdot}087$ for 3701 reflexions. DSC contains chains, parallel to **b**, in which one of the salicylate ligands acts as a bridge between two Cu atoms. Cu is square-pyramidally coordinated by O with $Cu\text{–}O_{eq}=1{\cdot}926$ (6)–2·010 (5), $Cu\text{–}O_{apic}=2{\cdot}266$ (5) Å.

Introduction

Although there would appear to be several crystalline forms of bis(salicylato)copper(II) (Inoue, Kishita & Kubo, 1964), only the structure of the tetrahydrate has been determined (Hanic & Michalov, 1960). This consists of discrete $\{Cu[C_6H_4(OH)COO]_2(H_2O)_2\}$ units, in which Cu is four-coordinated, linked together by hydrogen bonds involving the two remaining water molecules. Recently, the dioxane adduct of the monohydrate has been shown to contain $\{Cu_2[C_6H_4(OH)COO]_4(H_2O)_2\}$ dimers in which copper is octahedrally coordinated (Ablov, Kiosse, Dimitrova, Malinowski & Popovich, 1974). That the dihydrate crystallized with a disordered (OD) structure was first recognized by Dornberger-Schiff & Malinowski (1966). The present investigation was undertaken in order to determine the nature of the Cu coordination in this compound.

OD structure

Rotation photographs of crystals mounted along **a** showed discrete reflexions for $A=3{\cdot}865$ and diffuse streaks for $a=2A=7{\cdot}730$ Å. DSC thus crystallizes with a disordered structure of OD type (Dornberger-Schiff, 1966; Dornberger-Schiff & Malinowski, 1966), *i.e.* a structure which consists of ordered equivalent layers whose mode of stacking is disordered. Weissenberg photographs of diffuse layer lines showed that there were intensity maxima on the streaks, some of which had orthorhombic and some monoclinic symmetry. Both classes of maxima taken together required a doubling of c, the **c** direction being that of non-periodicity. The conditions limiting possible reflexion could thus be summarized:

(i) discrete reflexions, hkl, for $h=2H$; diffuse streaks, $hk\zeta$, for $h=2H+1$, where ζ can take any value;
(ii) $Hk0$: $H+k=2n$;
(iii) $0kl$: $l=2n$;
(iv) $h0\zeta$: $h=2n$;

where hkl refer to an orthogonal cell with dimensions $a=7{\cdot}730$, $b=11{\cdot}795$ and $c=31{\cdot}547$ Å.

From reflexion conditions (i), (ii) and (iii) it is apparent that the superposition structure, corresponding to the family reflexions, Hkl, has an a of half 7·730 Å and belongs to space group $Pcmn$ or $Pc2_1n$. Reflexion condition (iv) indicates that there is an a glide within the OD layer. Since $Pc2_1n$ is incompatible with such a glide, the space group of the superposition structure can be unequivocally determined to be $Pcmn$. It then follows that the layer symmetry is $P12_1/a(1)$ and that the partial symmetry operations converting one layer, L_p, into the next, L_{p+1}, are ${}_{p,p+1}[2_{-1/2}/c_21(2_2/n_{1/2,1})]$ or ${}_{p,p+1}[2_{1/2}/c_21(2_2/n_{-1/2,1})]$. These symmetry elements are illustrated in Fig. 1.

In accordance with the findings of Dornberger-Schiff & Malinowski (1966), DSC thus crystallizes as a family of structures characterized by the OD groupoid symbol: $P12_1/a(1)$ $\{2_{-1/2}/c_21(2_2/n_{1/2,1})\}$, this symbol giving the total symmetry of any pair of consecutive layers.

There are two ordered extreme structures, MDO (Dornberger-Schiff, 1966): an orthorhombic structure, MDO_1, obtained by a zigzag stacking of layers [Fig. 1(*a*)] and a monoclinic structure, MDO_2, obtained by an oblique stacking of layers [Fig. 1(*b*)]. The MDO_1 structure has $a=7{\cdot}730$, $b=11{\cdot}795$, $c=31{\cdot}547$ Å and belongs to space group $Pca2_1$, while the MDO_2 structure has $a=7{\cdot}730$, $b=11{\cdot}795$, $c=31{\cdot}783$ Å, $\beta=96{\cdot}98°$ and space group $P2_1/a$. The maxima on the streaks with monoclinic symmetry thus contain contributions from both MDO_2 'twins', *i.e.* that depicted in Fig. 1(*b*), in which consecutive layers are related by the partial symmetry operations ${}_{p,p+1}[2_{-1/2}/c_21(2_2/n_{1/2,1})]$ only, and that in which the stacking sequence is given by ${}_{p,p+1}[2_{1/2}/c_21(2_2/n_{-1/2,1})]$ only.

The fictitious superposition structure $\hat{\varrho}(xyz)$, which is related to the real structure $\varrho(x,y,z)$ by

$$\hat{\varrho}(x,y,z)=\tfrac{1}{2}[\varrho(x,y,z)+\varrho(x+\tfrac{1}{2},y,z)]$$

---

* On leave from: Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, Fack, S-402 20 Göteborg 5, Sweden.

has $A=3{\cdot}865$, $b=11{\cdot}795$ and $c=31{\cdot}547$ Å and belongs to space group *Pcmn* [Fig. 1(*c*)].

Crystal data

$[Cu(C_6H_5(OH)COO)_2(H_2O)_2]$. $M=373{\cdot}7$, $D_m=1{\cdot}723$, $D_c=1{\cdot}725$ g cm^{-3}. MDO$_1$: orthorhombic, $a=7{\cdot}730$ (4), $b=11{\cdot}795$ (9), $c=31{\cdot}547$ (19) Å, $U=2876$ Å^3, $Z=8$, $Pca2_1$. MDO$_2$: monoclinic, $a=7{\cdot}730$ (4), $b=11{\cdot}795$ (9), $c=31{\cdot}783$ (19) Å, $\beta=96{\cdot}98$ (1)°, $U=2876$ Å^3, $Z=8$, $P2_1/a$. Superposition structure: orthorhombic, $A=3{\cdot}865$ (2), $b=11{\cdot}795$ (9), $c=31{\cdot}547$ (19) Å, $U=1438$ Å^3, $Z=4$, *Pcmn*. Cu $K\alpha$ radiation, $\lambda=1{\cdot}5418$ Å, $\mu=25{\cdot}9$ cm^{-1}.

Experimental

Crystals were prepared by adding 25 ml 0·2 *M* $CuSO_4$ solution to 50 ml of a solution 0·2 *M* in salicylic acid and 0·2 *M* in NaOH. The solution was allowed to evaporate slowly over a period of a few days, after which green needle-shaped crystals of DSC were deposited.

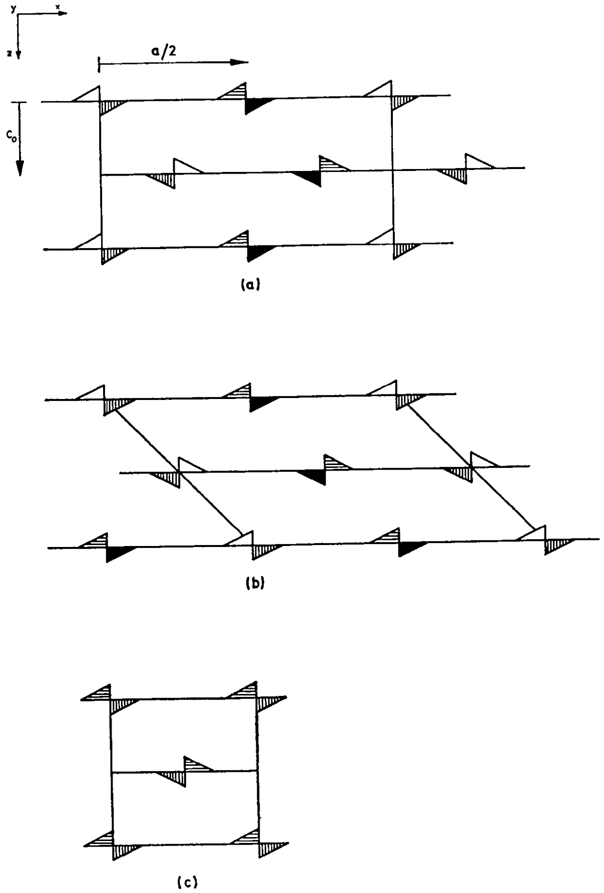

Fig. 1. Schematic representation of the stacking of layers in (*a*) the MDO$_1$ structure, (*b*) the MDO$_2$ structure and (*c*) the superposition structure. Notation: (*a*) and (*b*): empty triangles: y; filled triangles: $-y$; vertically shaded triangles: $\frac{1}{2}+y$; horizontally shaded triangles: $\frac{1}{2}-y$. (*c*): vertically shaded triangles: $-y$ and $\frac{1}{2}+y$; horizontally shaded triangles: y and $\frac{1}{2}-y$.

A crystal, 0·1 × 0·015 × 0·005 cm, was mounted along **a** and the intensities of the family reflexions ($h=2H$) and of the streaks ($hk\zeta$, $h=2H+1$) at the reciprocal lattice points corresponding to the MDO$_1$ and MDO$_2$ structures were measured with a computer-steered Supper diffractometer (Kryger, 1975). Graphite-monochromatized Cu $K\alpha$ radiation was used and data were collected for $\sin\theta<0{\cdot}875$. The background–peak–background method was used for the family reflexions, whereas a function of background *v*. $\sin\theta$ was used in the processing of the non-family reflexions. For the MDO$_1$ structure 1978 independent reflexions for which $F_o^2>3{\cdot}0\sigma(F_o^2)$, according to counting statistics, *i.e.* 1020 family reflexions and 958 non-family reflexions, were used in the subsequent calculations. The same criterion yielded 3701 reflexions for the MDO$_2$ structure, *i.e.* 2040 family reflexions and 1661 non-family reflexions. No correction was applied for absorption.

Determination and refinement of the MDO$_1$ structure

The main features of the superposition structure were determined from a Patterson function and successive electron density calculations based on the family reflexions (hkl, $h=2H$). From a Patterson function based on the orthorhombic non-family reflexions, which yields (Dornberger-Schiff, 1966) vectors only between atoms within a single OD layer, in conjunction with the coordinates of the superposition structure, it was possible to determine the positions of the Cu atoms in the MDO$_1$ structure. The positions of the O atoms were then derived from the superposition structure and those of the remaining atoms obtained from successive electron-density calculations.

In the initial stages of refinement, the partial symmetry operations of the OD groupoid symbol were preserved by introducing the extra* equipoints: $\frac{1}{4}-x,\frac{1}{2}+y,\bar{z}$; $\frac{3}{4}-x,\frac{1}{2}-y,\bar{z}$; $\frac{3}{4}+x,\frac{1}{2}-y,\frac{1}{2}-z$; $\frac{1}{4}+x,\frac{1}{2}+y,\frac{1}{2}-z$, it being sufficient to preserve the partial twofold screw of the layer for all the partial symmetry operations to be preserved. Three cycles of full-matrix least-squares refinement, with isotropic temperature factors for all atoms and separate scale factors for the family and non-family reflexions, gave $R=0{\cdot}111$. Release of the extra symmetry constraints resulted in $R=0{\cdot}092$. Since continued refinement yielded unrealistic coordinates for some of the atoms in the phenyl rings, these rings were constrained (Pawley, 1972) to be planar with *mmm* symmetry. The inclusion of anisotropic temperature factors for the non-group atoms yielded $R=0{\cdot}078$ and removal of the mirror plane perpendicular to the line joining the phenyl ring C atom bonded to the carboxyl group with that diametrically opposite gave $R=$

---

* Equipoints of No. 29, $Pca2_1$: x,y,z; $\frac{1}{2}+x,\bar{y},z$; $\bar{x},\bar{y},\frac{1}{2}+z$; $\frac{1}{2}-x,y,\frac{1}{2}+z$.

Table 1. *Fractional coordinates* (× 10⁴) *and thermal parameters for the non-group* (Å² × 10⁻⁴) *and group* (Å²) *atoms in the MDO*₁ *structure*

The anisotropic temperature coefficient is $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$, while the isotropic temperature coefficient is $\exp[-B(\sin^2\theta/\lambda^2)]$. Estimated standard deviations are given in parentheses. The occupation numbers for O(7), O(15) and O(17) are given in the text.

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	1858 (3)	3579 (2)	532	197 (9)	273 (10)	254 (9)	21 (8)	−12 (9)	−33 (9)
O(1)	−660 (13)	3867 (10)	522 (5)	262 (62)	479 (71)	394 (66)	239 (54)	−80 (75)	101 (67)
O(2)	848 (14)	−1538 (10)	76 (4)	262 (64)	227 (67)	260 (70)	−57 (49)	22 (47)	14 (53)
O(3)	1773 (18)	3824 (13)	1139 (5)	478 (96)	472 (84)	237 (77)	0 (67)	−105 (57)	−25 (64)
O(4)	1441 (16)	1680 (9)	560 (6)	476 (71)	294 (60)	479 (75)	−87 (56)	−99 (85)	6 (68)
O(5)	4326 (13)	3336 (11)	519 (5)	213 (64)	547 (78)	572 (82)	−5 (55)	81 (81)	−225 (78)
O(6)	1758 (18)	5724 (12)	1067 (5)	369 (81)	448 (86)	428 (90)	−80 (63)	−50 (60)	114 (70)
O(8)	397 (19)	331 (11)	23 (5)	457 (83)	332 (76)	458 (86)	36 (68)	−124 (73)	27 (64)
C(7)	1488 (22)	4885 (13)	1289 (5)	129 (66)	196 (80)	88 (73)	−28 (64)	33 (63)	−15 (65)
C(14)	919 (22)	−561 (17)	235 (6)	215 (79)	431 (113)	149 (89)	22 (77)	33 (67)	−15 (81)
Cu(2)	700 (3)	8581 (2)	−553 (1)	206 (11)	251 (11)	245 (12)	−52 (9)	−18 (10)	7 (11)
O(9)	3177 (13)	8846 (11)	−547 (5)	171 (63)	615 (79)	436 (73)	19 (54)	87 (76)	−35 (72)
O(10)	1700 (15)	3452 (11)	−104 (5)	388 (75)	307 (74)	311 (79)	73 (56)	−52 (52)	121 (56)
O(11)	678 (17)	−1127 (12)	−1155 (5)	476 (95)	268 (66)	350 (85)	−284 (60)	−38 (56)	157 (65)
O(12)	1128 (17)	6686 (8)	−589 (5)	569 (76)	135 (51)	416 (71)	−2 (52)	−150 (79)	−54 (61)
O(13)	−1828 (12)	8333 (9)	−548 (5)	153 (61)	317 (62)	647 (84)	−42 (47)	−130 (79)	123 (69)
O(14)	732 (17)	747 (12)	−1081 (5)	299 (81)	457 (88)	542 (94)	−161 (62)	173 (62)	−253 (72)
O(16)	2114 (18)	5271 (10)	−37 (4)	479 (77)	273 (69)	141 (57)	82 (63)	−107 (58)	−66 (51)
C(21)	986 (27)	−229 (22)	−1283 (7)	195 (90)	870 (174)	311 (123)	82 (105)	−134 (91)	−59 (106)
C(28)	1621 (21)	4441 (17)	−244 (6)	121 (73)	441 (114)	294 (101)	50 (75)	−15 (72)	−19 (93)

Table 1 (*cont.*)

	x	*y*	*z*	*B*
O(7)	544 (29)	3127 (19)	1853 (8)	3·35 (60)
O(17)	667 (38)	6850 (24)	1764 (9)	2·85 (97)
O(15)	2010 (28)	−1923 (18)	−1869 (7)	5·03 (61)
O(18)	1937 (100)	2071 (60)	−1745 (23)	5·14 (179)
C(1)	−457	4022	2345	4·80 (44)
C(2)	316	3957	1936	2·76 (31)
C(3)	−768	5088	2504	4·69 (35)
C(4)	732	4943	1710	1·26 (27)
C(5)	−391	6087	2299	4·81 (44)
C(6)	380	6003	1891	3·31 (34)
C(8)	3020	−1073	1307	4·12 (41)
C(9)	2233	−1261	905	2·79 (32)
C(10)	3235	35	1432	3·01 (40)
C(11)	1709	−349	652	1·20 (24)
C(12)	2749	968	1199	2·56 (31)
C(13)	1965	761	798	1·79 (28)
C(15)	2851	1458	−2243	3·73 (33)
C(16)	2087	1194	−1844	5·67 (54)
C(17)	3273	561	−2502	3·54 (32)
C(18)	1788	67	−1726	4·24 (49)
C(19)	3013	−563	−2404	2·29 (25)
C(20)	2248	−808	−2004	4·60 (43)
C(22)	−229	5988	−1216	2·72 (32)
C(23)	588	5777	−819	1·95 (29)
C(24)	−743	5058	−1447	3·40 (43)
C(25)	848	4667	−675	1·74 (28)
C(26)	−527	3949	−1324	3·66 (38)
C(27)	293	3757	−926	2·85 (32)

0·076. A difference map at this stage showed peaks ~2 e Å^{-3} in the vicinity of C(6) and C(16). It was thus apparent that the hydroxyl O atoms, O(7) and O(15), of the salicylate ligands bonded to only one Cu atom were involved in statistical disorder. Occupation numbers were therefore refined for O(7) and O(17) [bonded to C(6)] and for O(15) and O(18) [bonded to C(16)]. This yielded an occupation number of 0·52 (3) for O(7) and of 0·83 (4) for O(15), and a final *R* of 0·068 (R_w=0·069) for 253 parameters. It would thus seem likely that O(15) is not actually involved in statistical disorder but that O(18) with an occupation number of 0·17 is in fact an H atom. That the additional disorder associated with O(7) was not solely a result of the mirror plane inherent in the family reflexions was confirmed by refinement based on the non-family reflexions only, which yielded a comparable drop in *R* and an identical occupation factor for O(7).

A final difference map showed a maximum electron density of 1·1 e Å^{-3} in probable H atom positions. No attempt was, however, made to insert the H atoms of the phenyl groups or to locate those of the water molecules or hydroxyl groups.

Re-introduction of the constraints with respect to the partial twofold screw of the OD layer yielded R= 0·083 (R_w=0·080) for 131 parameters. Since $R_{w,\text{constr.}}/R_{w,\text{unconstr.}}$= 1·1618 and $\mathscr{R}_{122,1725,0\cdot001}$= 1·0506 (Pawley, 1970), the model based only on the space group symmetry of the MDO₁ structure must be regarded as the most appropriate.

The final atomic and thermal parameters for the MDO₁ structure are listed in Table 1, the atomic numbering being in accordance with Fig. 4. Centres and Euler angles (Pawley, 1972) for the four phenyl groups are given in Table 2, and inertial coordinates for the ring C atoms in Table 3. The ring coordinates refer to orthogonal molecular axes defined with the origin at the centre of the ring, *z* perpendicular to the plane of the ring and *x* joining the C atom bonded to the carboxyl group with that diametrically opposite. The positive direction of *x* is away from the carboxyl group.

Table 2. *Euler angles* (rad) *and centres for the benzene rings in the* MDO_1 *and* MDO_2 *structures*

	Ring	φ	θ	ψ	x_0	y_0	z_0
MDO_1							
	1	1·6355 (75)	1·1379 (74)	1·5642 (99)	−0·0009 (11)	0·5014 (7)	0·2102 (3)
	2	1·7274 (61)	2·0202 (76)	1·5527 (80)	0·2462 (11)	−0·0159 (6)	0·1037 (3)
	3	4·4807 (73)	1·1419 (87)	−4·6670 (90)	0·2521 (13)	0·0311 (7)	−0·2109 (3)
	4	4·5551 (63)	2·0418 (80)	−4·6890 (84)	0·0062 (10)	0·4860 (6)	−0·1056 (3)
MDO_2							
	1	1·7223 (36)	1·1425 (31)	1·5463 (52)	0·2294 (6)	0·2699 (4)	0·2105 (2)
	2	1·7199 (31)	2·0326 (26)	1·5449 (42)	0·4226 (5)	−0·2660 (3)	0·1046 (2)

Table 3. *Inertial coordinates for the ring* C *atoms in the* MDO_1 *and* MDO_2 *structures*

	x	y	z
MDO_1			
C(1)	0·7654 (75)	1·2209 (46)	0·0000
C(2)	−0·6580 (71)	1·2095 (46)	0·0000
C(3)	−1·3655 (74)	0·0000	0·0000
C(4)	1·4000	0·0000	0·0000
MDO_2			
C(1)	0·7710 (69)	1·2147 (42)	0·0000
C(2)	−0·6548 (65)	1·2126 (42)	0·0000
C(3)	−1·3605 (67)	0·0000	0·0000
C(4)	1·4000	0·0000	0·0000

Determination and refinement of the MDO_2 structure

The atomic coordinates of the MDO_2 structure were calculated from those of the MDO_1 structure according to $x_{\text{mon}} = x_{\text{orth}} + z_{\text{orth}}/2 + 0{\cdot}125$, $y_{\text{mon}} = y_{\text{orth}} - 0{\cdot}25$ and $z_{\text{mon}} = z_{\text{orth}}$. All atoms occupy general positions* in space group $P2_1/a$. The partial symmetry operations of the OD groupoid symbol were preserved by constraining the partial c_2 glide planes between the layers, *i.e.* by introducing the extra equipoints $\pm(1+z-x, y, \frac{1}{2}+z;\ \frac{1}{2}+z-x, \frac{1}{2}-y, \frac{1}{2}+z)$. Since the non-family reflexions with monoclinic symmetry contain contributions from both MDO_2 'twins', those from the smaller 'twin' were accounted for by introducing the 'twin' equipoints $\pm(z-x, y, z;\ z-\frac{1}{2}-x, \frac{1}{2}-y, z;\ x-\frac{1}{2}, y, \frac{1}{2}+z;\ x, \frac{1}{2}-y, \frac{1}{2}+z)$ and calculating structure factors according to $|F_c| = k(F_c'^2 + s^2F_c''^2)^{1/2}$ where k is the appropriate scale factor (*i.e.* for the family or the non-family reflexions) and s the 'twin' scale factor scaling the contributions from the smaller MDO_2 'twin'. Least-squares refinement in which the benzene rings were constrained as in the refinement of the MDO_1 structure and with anisotropic temperature factors for the non-group atoms and isotropic temperature coefficients for the group atoms, both s and k being refined, yielded $R = 0{\cdot}087$ ($R_w = 0{\cdot}081$) for 132 parameters. As in the refinement of the MDO_1 structure an occupation factor was refined for O(7), a final value of 0·64 (19) being obtained. An identical refinement based on the larger MDO_2 'twin' only yielded $R = 0{\cdot}146$. The final value of s, 0·431 (6), indicated that the intensity of the smaller MDO_2 'twin' was 18% of that of the larger. Together the MDO_2 'twins' provided 37% of the total intensity while the MDO_1 form was responsible for 61% of the total intensity.

Release of the c_2 constraint yielded $R = 0{\cdot}086$ ($R_w = 0{\cdot}080$) for 255 parameters. Since $R_{w,\text{constr.}}/R_{w,\text{unconstr.}} = 1{\cdot}0098$ and $\mathscr{R}_{123,3446,0{\cdot}25} = 1{\cdot}0192$ (Pawley, 1970), the model in which all the partial symmetry elements of the OD groupoid symbol are preserved must be regarded as being the most appropriate for the MDO_2 structure. In the above calculations the family reflexions were averaged as for orthorhombic symmetry, each reflexion being included twice. Attempts were made to refine the MDO_2 structure based on the non-

Table 4. *Fractional coordinates* ($\times 10^4$) *and thermal parameters for the non-group* ($\text{Å}^2 \times 10^{-4}$) *and group* ($\text{Å}^2$) *atoms in the* MDO_2 *structure*

The anisotropic temperature coefficient is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$, and the isotropic temperature coefficient is $\exp[-B(\sin^2\theta/\lambda^2)]$. Estimated standard deviations are given in parentheses. The occupation numbers for O(7) and O(17) are given in the text.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	3351 (1)	1080 (1)	543 (0)	199 (5)	251 (5)	249 (5)	30 (4)	7 (5)	−19 (4)
O(1)	851 (7)	1358 (5)	535 (2)	236 (29)	511 (40)	441 (34)	143 (27)	25 (27)	111 (34)
O(2)	2118 (6)	−4044 (4)	92 (1)	308 (27)	244 (27)	281 (25)	−42 (23)	1 (23)	−50 (20)
O(3)	3624 (9)	1355 (5)	1145 (2)	430 (34)	372 (35)	293 (28)	138 (31)	−11 (29)	−100 (25)
O(4)	2942 (7)	−818 (4)	573 (2)	469 (33)	193 (26)	498 (31)	−27 (24)	−114 (29)	43 (23)
O(5)	5845 (7)	830 (5)	532 (2)	164 (27)	461 (38)	605 (39)	−9 (25)	35 (27)	−154 (36)
O(6)	3538 (9)	3240 (5)	1074 (2)	345 (34)	457 (38)	513 (38)	50 (33)	109 (33)	204 (31)
O(8)	1649 (7)	−2196 (4)	28 (1)	397 (30)	358 (39)	267 (25)	−25 (24)	−91 (24)	53 (22)
C(7)	3382 (8)	2356 (9)	1286 (2)	156 (28)	422 (52)	209 (29)	−6 (40)	−26 (24)	68 (41)
C(14)	2264 (9)	−3065 (6)	241 (2)	200 (36)	348 (40)	206 (35)	−52 (33)	39 (32)	19 (33)

---

* Equipoints of general position of $P2_1/a$ (conventional setting, No. 14, $P2_1/c$): $\pm(x, y, z;\ \frac{1}{2}+x, \frac{1}{2}-y, z)$.

Table 4 (*cont.*)

	x	y	z	B
O(7)	2688 (14)	604 (8)	1869 (3)	3·70 (21)
O(17)	2773 (27)	4427 (16)	1752 (6)	4·07 (39)
C(1)	1957	1772	2378	3·65 (17)
C(2)	2518	1604	1971	3·60 (17)
C(3)	1743	2866	2504	4·70 (22)
C(4)	2830	2537	1717	2·42 (10)
C(5)	2025	3810	2272	4·47 (19)
C(6)	2586	3638	1865	4·26 (19)
C(8)	4940	−3571	1314	4·37 (20)
C(9)	3933	−3762	914	2·79 (14)
C(10)	5214	−2470	1439	3·21 (12)
C(11)	3266	−2844	664	1·37 (11)
C(12)	4600	−1539	1211	2·61 (14)
C(13)	3594	−1734	811	1·80 (12)

averaged family reflexions. This yielded $R=0·091$ and $R_w=0·087$ when all the partial symmetry operations of the OD groupoid symbol were preserved and $R=0·096$ ($R_w=0·094$) when the c_2 constraint was released.

The final atomic and thermal parameters for the MDO_2 structure are listed in Table 4, while centres, Euler angles (Pawley, 1972) and ring coordinates for the two phenyl groups are given in Tables 2 and 3.*

Computational details

Calculations were carried out on a CDC6400 computer, with the following programs: data averaging, *DSORTH*, State University of New York at Buffalo; Patterson and Fourier syntheses, *FORDAP* and *JIMDAP*, A. Zalkin; constrained least-squares refinement, G. S. Pawley, modified by R. G. Hazell; distances and angles, *ORFFE* (Busing, Martin & Levy, 1964); stereoscopic drawings, *ORTEP* (Johnson, 1965).

The quantity minimized was $r=\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2$ with unit weights. The scattering factors were those of Cromer & Mann (1968). An anomalous dispersion correction (Cromer & Liberman, 1970) was included for Cu. R and R_w are defined as $R=\sum||F_o-F_c||/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, respectively.

Discussion

Stereoscopic projections, down **a**, of the MDO_1 and MDO_2 structures are shown in Figs. 2 and 3, respectively. Bond lengths are given in Table 5 and angles within the Cu coordination polyhedron in Table 6.

Table 5. *Bond distances* (Å)

Estimated standard deviations (× 10^3) for bonds between non-group atoms are given in parentheses.

MDO_1

Cu(1)–O(1)	1·976 (10)	Cu(2)–O(9)	1·940 (11)
Cu(1)–O(10)	2·016 (14)	Cu(2)–O(2)	1·995 (13)
Cu(1)–O(3)	1·938 (16)	Cu(2)–O(11)	1·929 (15)
Cu(1)–O(5)	1·930 (10)	Cu(2)–O(13)	1·976 (10)
Cu(1)–O(4)	2·265 (11)	Cu(2)–O(12)	2·263 (10)
C(7)—O(3)	1·356 (22)	C(21)–O(11)	1·158 (28)
C(7)—O(6)	1·231 (22)	C(21)–O(14)	1·332 (28)
C(28)–O(10)	1·248 (23)	C(14)–O(2)	1·258 (22)
C(28)–O(16)	1·236 (23)	C(14)–O(8)	1·311 (24)
C(7)—C(4)	1·453	C(21)–C(18)	1·567
C(28)–C(25)	1·511	C(14)–C(11)	1·472
C(13)–O(4)	1·379	C(23)–O(12)	1·360
C(2)—O(7)	1·028	C(20)–O(15)	1·400
C(6)—O(17)	1·099	C(16)–O(18)	1·086
C(1)—C(2)	1·424	C(2)—C(4)	1·401
C(1)—C(3)	1·376		

MDO_2 [(′) atom in $\frac{1}{2}-x,\frac{1}{2}+y,-z$]

Cu——O(1)	1·957 (5)	C(7)—C(4)	1·499
Cu——O(2′)	2·010 (5)	C(14)–C(11)	1·491
Cu——O(3)	1·929 (6)	C(13)–O(4)	1·379
Cu——O(5)	1·955 (5)	C(2)—O(7)	1·235
Cu——O(4)	2·266 (5)	C(6)—O(17)	1·015
C(7)—O(3)	1·284 (11)	C(1)—C(2)	1·426
C(7)—O(6)	1·255 (11)	C(1)—C(3)	1·367
C(14)–O(2)	1·249 (8)	C(2)—C(4)	1·403
C(14)–O(8)	1·288 (8)		

Table 6. *Angles* (°) *within the* Cu *coordination polyhedron*

Estimated standard deviations (× 10) are given in parentheses.

MDO_1

O(1)–Cu(1)–O(5)	177·5 (7)	O(9)—Cu(2)–O(13)	178·6 (7)
O(3)–Cu(1)–O(10)	173·1 (5)	O(11)–Cu(2)–O(2)	173·2 (5)
O(1)–Cu(1)–O(10)	86·4 (6)	O(9)—Cu(2)–O(2)	86·8 (6)
O(1)–Cu(1)–O(3)	87·5 (6)	O(9)—Cu(2)–O(11)	89·5 (6)
O(5)–Cu(1)–O(10)	91·6 (6)	O(13)–Cu(2)–O(2)	92·1 (6)
O(5)–Cu(1)–O(3)	94·4 (6)	O(13)–Cu(2)–O(11)	91·5 (6)
O(4)–Cu(1)–O(1)	91·7 (5)	O(12)–Cu(2)–O(9)	90·9 (5)
O(4)–Cu(1)–O(10)	87·5 (6)	O(12)–Cu(2)–O(2)	88·4 (5)
O(4)–Cu(1)–O(3)	96·0 (6)	O(12)–Cu(2)–O(11)	97·4 (6)
O(4)–Cu(1)–O(5)	89·7 (5)	O(12)–Cu(2)–O(13)	89·9 (4)

MDO_2 [(′) atom in $\frac{1}{2}-x,\frac{1}{2}+y,-z$]

O(1)–Cu–O(5)	178·0 (2)	O(5)–Cu–O(3)	93·1 (3)
O(3)–Cu–O(2′)	173·2 (2)	O(4)–Cu–O(1)	91·3 (2)
O(1)–Cu–O(2′)	86·7 (3)	O(4)–Cu–O(2′)	87·8 (2)
O(1)–Cu–O(3)	88·4 (3)	O(4)–Cu–O(3)	97·0 (2)
O(5)–Cu–O(2′)	91·7 (3)	O(4)–Cu–O(5)	89·7 (2)

In contrast to $[Cu(C_6H_4(OH)COO)_2(H_2O)_2].2H_2O$ (Hanic & Michalov, 1960) and $[Cu(C_6H_4(OH)COO)_4(H_2O)_2].C_4H_8O_2$ (Ablov *et al.*, 1974), DSC contains infinite chains, parallel to **b**, in which one of the salicylate ligands acts as a bridge between two Cu atoms. Part of such a chain in the MDO_1 structure is illustrated in Fig. 4. There are no significant differences between the molecular structures obtained in the MDO_2 and MDO_1 structures, despite the fact that all the partial symmetry operations of the OD groupoid symbol are preserved in the former but not in the latter. The MDO_1 and MDO_2 structures thus differ solely in the mode of stacking of the OD layers (*cf.* Figs. 2 and 3 with Fig. 1). All interatomic distances and angles quoted in the following refer to the MDO_2 structure.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31213 (24 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

As is evident from Fig. 4 and Tables 5 and 6, Cu is square-pyramidally coordinated by O. The Cu atom lies in the best plane through the four equatorial O atoms, the deviations from this plane of all five atoms being approximately 0·04 Å. The Cu–O_{eq} distances range from 1·93–2·01 Å, whereas the apical bond length is significantly longer. The distance between Cu and the carboxyl O of the non-bridging salicylate ligand, 1·929 (6) Å, is slightly shorter than that between Cu and the carboxyl O of the bridging salicylate ligand, 2·010 (5) Å. The Cu–O(H_2O) lengths are intermediate between these values, 1·956 (2) Å (mean value). Opposite the apical coordination site there are Cu···O contacts of 2·724 (5) to O(8) and 3·050 (7) Å to O(6), O(4)–Cu···O(8) and O(4)–Cu···O(6) being 141·0 (2) and 143·1 (2)°, respectively. The configuration of ligands about Cu is thus very similar to that found in bis(phenoxyacetato)triaquocopper(II) (Goebel & Doedens, 1971). The closest distance of approach of the Cu atoms, 5·114 (3) Å, is considerably longer than that in $\{Cu[C_6H_4(OH)COO]_2(H_2O)_2\}.2H_2O$, 3·728 Å (Hanic & Michalov, 1960), and in $\{Cu[C_6H_4(OH)COO]_4(H_2O)_2\}.C_4H_8O_2$, 2·64 Å (Ablov *et al.*, 1974).

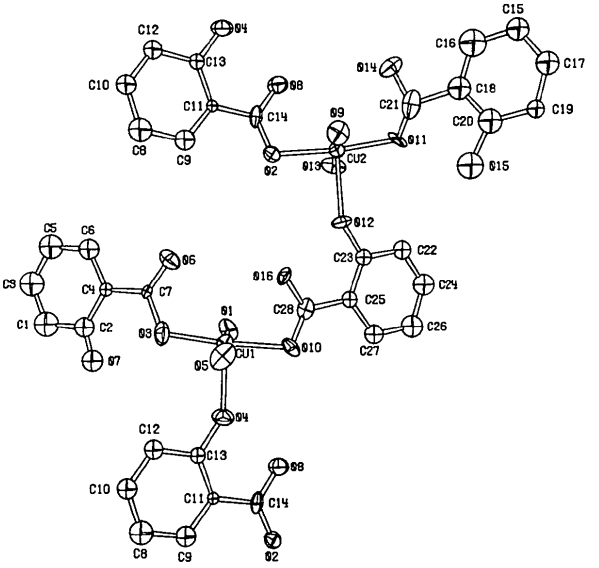

Fig. 4. Part of an infinite Cu–salicylate chain in the MDO_1 structure.

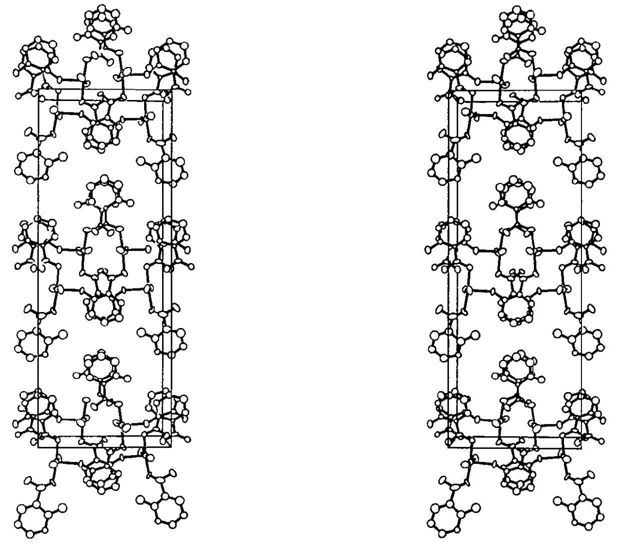

Fig. 2. Stereoscopic projection of the MDO_1 structure down **a**; **b** is horizontal.

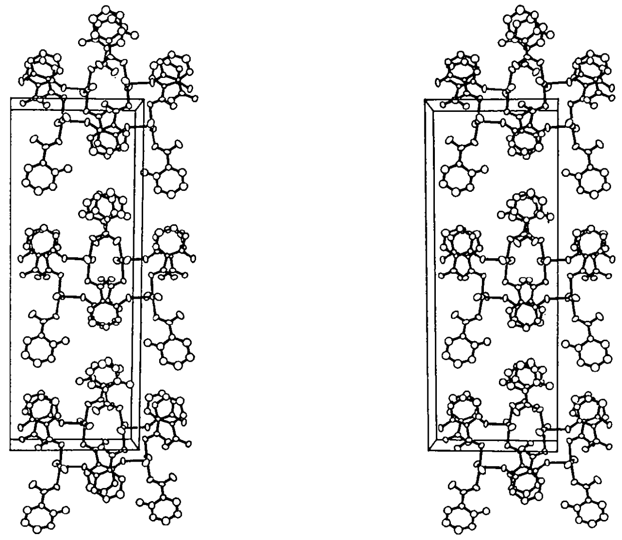

Fig. 3. Stereoscopic projection of the MDO_2 structure down **a**; **b** is horizontal.

The non-bridging salicylate ligand is essentially planar, while the bridging group is planar apart from the carboxyl O atom bonded to Cu which is displaced approximately 0·2 Å from the ligand plane towards the O(1) [MDO_1, O(1) and O(9)] water molecule. The salicylate ligands *trans* to one another are bent towards this water molecule, the dihedral angle between them being approximately 51°. O(3)–Cu–O(2) differs, moreover, significantly from 180°. There are no significant differences between the C–O lengths involving the coordinated and the non-coordinated carboxyl O atoms, the mean C–O length being 1·269 (4) Å. The low accuracy associated with the determination of the C(2)–O(7) and C(6)–O(17) lengths can be ascribed to the additional disorder involving O(7) and O(17).

There are several short O···O contacts between the water molecules and carboxyl O atoms in adjacent chains (*cf.* Table 7). The Cu–salicylate chains are thus linked together to form layers by means of hydrogen bonds. A detailed description of the hydrogen-bonding network is not, however, feasible without knowledge of the positions of the H atoms. As is seen in Table 7, the O atoms of both the coordinated and the non-coordinated hydroxyl groups are involved in intramolecular O···O contacts of approximately the same magnitude as found in $\{Cu[C_6H_4(OH)COO]_2(H_2O)_2\}.2H_2O$ (Hanic & Michalov, 1960).

Table 7. *Short* O···O *contacts* (Å)

Estimated standard deviations (× 10^3) are given in parentheses.

MDO_1 Notation: (′) atom in $x-\frac{1}{2}, 1-y, z$
(″) atom in $\frac{1}{2}+x, 1-y, z$
(‴) atom in $\frac{1}{2}+x, -y, z$

O(1)····O(16′)	2·666 (17)	O(9)····O(14″)	2·640 (18)
O(1)····O(6′)	2·677 (20)	O(9)····O(8″)	2·666 (20)
O(4)····O(8)	2·461 (21)	O(12)···O(16)	2·530 (18)
O(5)····O(6″)	2·784 (19)	O(13)···O(14′)	2·749 (18)
O(5)····O(2‴)	2·797 (16)	O(13)···O(10′)	2·773 (17)
O(7)····O(3)	2·578 (28)	O(15)···O(11)	2·651 (26)
O(17)···O(6)	2·705 (33)		

MDO_2 Notation: (′) atom in $\bar{x}, \bar{y}, \bar{z}$
(″) atom in $x-\frac{1}{2}, \frac{1}{2}-y, z$
(‴) atom in $\frac{1}{2}+x, \frac{1}{2}-y, z$
(iv) atom in $\frac{1}{2}+x, -\frac{1}{2}-y, z$

O(1)···O(8′)	2·660 (8)	O(5)····O(2^{iv})	2·774 (8)
O(1)···O(6″)	2·664 (9)	O(7)····O(3)	2·646 (12)
O(4)···O(8)	2·494 (7)	O(17)···O(6)	2·695 (20)
O(5)···O(6‴)	2·763 (9)		

There are no forces other than van der Waals between the OD layers, the closest distance of approach of salicylate ligands in adjacent layers being 3·55 Å. Within a layer the shortest such distance is 3·43 Å.

The partial symmetry operations of the OD groupoid symbol would appear to be exact in the MDO_2 structure but approximate in the MDO_1 structure. Refinement of four MDO structures of different compounds, with and without extra symmetry constraints, has shown (Hazell & Jagner, 1975) that in three of the four cases models based only on the space-group symmetry of the MDO structure are to be preferred. For none of these structures did the data permit refinement of more than one MDO from the same crystal. Ďurovič (1974) has suggested that the more ordered the crystal, the less it complies with the ideal OD model. This suggestion is, however, somewhat difficult to reconcile with the present and previous (Hazell & Jagner, 1975) results. There were no indications for the crystal used in this investigation that the maxima on the streaks corresponding to the MDO_2 structure were more diffuse or differed in any way from those corresponding to the MDO_1 structure.

References

Ablov, A. V., Kiosse, G. A., Dimitrova, G. I., Malinowski, T. I. & Popovich, G. A. (1974). *Kristallografiya*, **19**, 168–169.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Dornberger-Schiff, K. (1966). *Lehrgang über OD-Strukturen*. Berlin: Akademie-Verlag.

Dornberger-Schiff, K. & Malinowski, T. I. (1966). *Acta Cryst.* **21**, A171–A172.

Ďurovič, S. (1974). *Acta Cryst.* **B30**, 2214–2217.

Goebel, C. V. & Doedens, R. J. (1971). *Inorg. Chem.* **10**, 2607–2613.

Hanic, F. & Michalov, J. (1960). *Acta Cryst.* **13**, 299–302.

Hazell, R. G. & Jagner, S. (1975). *Acta Cryst.* **B31**, 1412–1416.

Inoue, M., Kishita, M. & Kubo, M. (1964). *Inorg. Chem.* **3**, 239–242.

Johnson, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

Kryger, L. (1975). Thesis, Univ. of Århus, Denmark.

Pawley, G. S. (1970). *Acta Cryst.* **A26**, 691–692.

Pawley, G. S. (1972) *Advanc. Struct. Res. Diffr. Meth.* **4**, 1–64.