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The Crystal and Molecular Structure of *o*-Phthalatocopper(II) Dihydrate

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Crystals of the title compound are monoclinic, space group $P2_1$, with $Z = 2$ in a unit cell of dimensions: a = 10·263 (7), b = 6·540 (9), c = 6·795 (8) Å, β = 94·8 (1)°. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least squares to R = 0·031 for 1279 observed reflections. The Cu coordination polyhedron is a square pyramid whose base is formed by two water molecules [$Cu-O_w$ = 1·980 (5), 2·007 (5) Å] and by two O atoms [Cu–O = 1·950 (5), 1·965 (5) Å] from two *o*-phthalate groups. The *o*-phthalate anion bridges adjacent Cu atoms through two O atoms of both carboxylate groups in linear polymeric chains running along [001]. The apex of the pyramid is occupied by an O atom from an *o*-phthalate group of an adjacent chain [Cu–O = 2·154 (5) Å] so the anion behaves as a tridentate ligand bridging the chains along [010]. A sixth Cu–O = 2·861 (6) Å contact involving an O atom of a phthalate group makes coordination severely distorted octahedral. $O_w-H\cdots O$ hydrogen bonding completes the linkage of the polymeric chains in layers parallel to (100).

Introduction

Investigations on the behaviour of the *o*-phthalate (pht) anion as a ligand have been carried out in our laboratory [$Cu^{II}(NH_3)_2$pht (Cingi, Guastini, Musatti & Nardelli, 1970); $Li_2Cu^{II}pht_2.4H_2O$, $Rb_2Cu^{II}pht_2.2H_2O$ (Cingi, Lanfredi, Tiripicchio & Camellini, 1977); $Na_2Cu^{II}pht_2.2H_2O$, $K_2Cu^{II}pht_2.2H_2O$ (Cingi, Lanfredi, Tiripicchio & Camellini, 1978)] and others are in progress. In the above compounds the ligand always acts as a bridge when coordinating to Cu atoms giving rise to different kinds of polymeric chains. The compound described in the present paper was obtained from the mother liquid of the preparation of the Sr derivative, while the monohydrate form was prepared from a neutral aqueous solution containing only Cu^{II} and *o*-phthalate ions. The structure of this last compound was determined and the results agreed well with those found independently by Prout, Carruthers & Rossotti (1971).

Experimental

The compound gives blue crystals with the following crystallographic properties.

Crystal data

$C_8H_8CuO_6$, M_r = 263·7, monoclinic, a = 10·263 (7), b = 6·540 (9), c = 6·795 (8) Å, β = 94·8 (1)°, V = 454·5 (9) Å^3, D_c = 1·93 g cm^{-3}, Z = 2, F(000) = 266, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ(Mo $K\alpha$) = 24·11 cm^{-1}. Space group $P2_1$ from systematic absences and from structure determination. Unit-cell parameters were determined from rotation and Weissenberg photographs and refined from diffractometer data.

Intensity data

Intensity data were collected on a Siemens AED single-crystal diffractometer, by using Zr-filtered Mo $K\alpha$ radiation and the ω–2θ scan technique. A prismatic crystal of dimensions *ca* 0·30 × 0·39 × 0·46 mm was aligned with its [001] axis along the φ axis of the diffractometer and all the reflections with $2\theta < 58°$ were measured. Of the 1309 independent reflections measured, 1279 having $I > 2\sigma(I)$ were used in the analysis. Corrections for Lorentz and polarization factors were applied in the usual way, but no correction was considered for absorption effects. The first absolute scaling and the overall isotropic temperature factor were obtained by Wilson's (1942) method.

Table 1. *Fractional atomic coordinates* (×10^4 *for* Cu, O, C *atoms;* ×10^3 *for* H *atoms*) *with estimated standard deviations*

	x	y	z
Cu	4823 (1)	2500	1929 (1)
O(1)	6202 (4)	2821 (7)	4060 (6)
O(2)	6644 (5)	−476 (8)	3576 (7)
O(3)	5567 (4)	717 (7)	7773 (6)
O(4)	6177 (4)	3023 (7)	10111 (6)
O_w(1)	3380 (4)	2141 (8)	−165 (6)
O_w(2)	3583 (5)	1397 (8)	3800 (6)
C(1)	7958 (6)	1361 (10)	6030 (9)
C(2)	7746 (6)	1903 (10)	7984 (8)
C(3)	8802 (6)	2281 (16)	9352 (9)
C(4)	10073 (7)	2106 (15)	8829 (11)
C(5)	10281 (7)	1474 (15)	6880 (12)
C(6)	9229 (7)	1145 (13)	5501 (11)
C(7)	6856 (6)	1140 (10)	4475 (8)
C(8)	6394 (6)	1857 (10)	8636 (8)
H(1)	864 (6)	278 (11)	1067 (10)
H(2)	1085 (7)	301 (17)	969 (11)
H(3)	1115 (8)	131 (14)	637 (12)
H(4)	939 (8)	63 (14)	413 (11)
H(5)	342 (7)	267 (13)	−121 (10)
H(6)	333 (8)	77 (14)	−41 (11)
H(7)	378 (7)	27 (14)	436 (10)
H(8)	354 (7)	229 (21)	461 (10)

Structure determination and refinement

The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares, at first with isotropic, then with anisotropic thermal parameters. The H atoms were located directly from a ΔF synthesis after several cycles of least squares. Further least-squares cycles were computed with inclusion of the H atoms with isotropic thermal parameters. Unit weights were used in all the stages of the refinement as indicated by the $|\Delta F|$ *vs* $|F|$ plot. The final conventional R index was 0·031 (observed reflections only). Atomic scattering factors for the non-hydrogen atoms were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). Final atomic coordinates are given in Table 1.*

All the calculations were carried out on the CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna), with the programs written by Immirzi (1967).

Discussion

The crystal structure of *o*-phthalatocopper(II) dihydrate is represented in Fig. 1. Bond distances and angles are given in Table 2. The structure consists of polymeric chains running along [001] formed by five-coordinated Cu atoms bridged by pht anions coordinating through both their carboxylate groups. The coor-

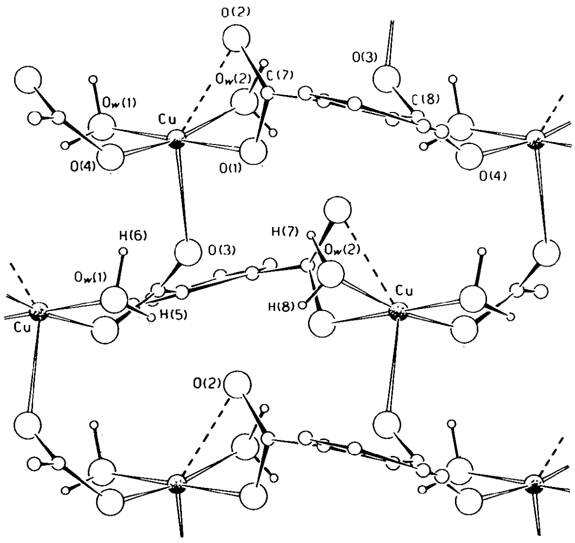

Fig. 1. Projection of the structure of Cu^{II}pht.2H_2O along [100].

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33001 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England, or from the authors.

dination polyhedron around Cu is a square pyramid, and also involves two water molecules which are arranged at the base of the pyramid, which shows a small tetrahedral distortion. Pentacoordination is reached because the pht anion behaves as a tridentate ligand, forming a Cu–O bond which bridges the chains along [010]. The Cu atom is displaced by 0·10 Å from the mean basal plane towards the apex of the pyramid (Table 3). The fourth O atom of the pht anion is involved in a long Cu–O(2) = 2·861 (6) Å contact, so the metal atom is six coordinated in a severely distorted octahedron. The distortion results mainly because O(2) is displaced by ~39° from the apical octahedral site because of the restricting geometry of the carboxylate group. The distance between two Cu atoms bridged by O(1) and O(4) from the pht anion is 6·795 Å, while that between two Cu atoms bridged by the O(4)–C(8)–O(3) group is 4·23 Å. The two C–O distances in each carboxyl group are not equal, the longer involving the O atom lying in the basal coordination plane. Both carboxylate groups are rotated on the same side with respect to the benzene plane by angles [C(1)–C(7)–O(1)–O(2) 63·7, C(2)–C(8)–O(3)–O(4) 28·6°] which are of the same order of magnitude as those found in the monohydrate derivative (50 and 33°) (Prout, Carruthers & Rossotti, 1971). The rotation of these groups is mainly due to the necessity of reducing the interaction between O(1) and O(3), O(1)···O(3) = 2·99 Å. In both compounds the carboxylate group which is less rotated is that which acts as a bridge. While in $\mathrm{Cu^{II}pht.H_2O}$ the two bridged Cu atoms are approximately in the same plane of the bridging carboxylate group, in the present compound the same atoms are not coplanar, the maximum and the mean displacements from the least-squares best plane being 0·49 and 0·20 Å respectively.

Comparing the crystal structure of the dihydrate

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

(*a*) In the coordination polyhedron

Cu–O(1)	1·950 (5)	Cu–O(4^{i})	1·965 (5)
Cu–O_w(1)	1·980 (5)	Cu–O(3^{ii})	2·154 (5)
Cu–O_w(2)	2·007 (5)	Cu–O(2)	2·861 (6)
O_w(2)–Cu–O(1)	91·6 (2)	O(3^{ii})–Cu–O(4^{i})	92·1 (2)
O_w(2)–Cu–O(2)	86·3 (2)	O(1)–Cu–O(2)	51·2 (2)
O_w(2)–Cu–O_w(1)	86·4 (2)	O(1)–Cu–O(3^{ii})	87·4 (2)
O_w(2)–Cu–O(3^{ii})	99·1 (2)	O_w(1)–Cu–O(3^{ii})	92·9 (2)
O_w(2)–Cu–O(4^{i})	168·6 (2)	O_w(1)–Cu–O(2)	128·7 (2)
O(1)–Cu–O(4^{i})	86·6 (2)	O(1)–Cu–O_w(1)	178·0 (2)
O(2)–Cu–O(4^{i})	83·8 (2)	O(2)–Cu–O(3^{ii})	138·4 (2)
O_w(1)–Cu–O(4^{i})	95·4 (2)		

(*b*) In the phthalate anion

C(1)–C(2)	1·409 (8)	C(1)–C(7)	1·489 (9)
C(2)–C(3)	1·390 (9)	C(7)–O(1)	1·307 (8)
C(3)–C(4)	1·385 (10)	C(7)–O(2)	1·231 (8)
C(4)–C(5)	1·420 (11)	C(2)–C(8)	1·492 (9)
C(5)–C(6)	1·386 (11)	C(8)–O(4)	1·293 (7)
C(1)–C(6)	1·389 (10)	C(8)–O(3)	1·240 (8)
C(3)–H(1)	0·98 (7)	C(5)–H(3)	0·99 (8)
C(4)–H(2)	1·12 (9)	C(6)–H(4)	1·02 (8)
C(6)–C(1)–C(2)	119·5 (6)	C(4)–C(5)–C(6)	120·4 (7)
C(6)–C(1)–C(7)	118·7 (6)	C(1)–C(6)–C(5)	120·3 (7)
C(2)–C(1)–C(7)	121·7 (5)	C(1)–C(7)–O(1)	114·7 (5)
C(1)–C(2)–C(3)	120·1 (6)	C(1)–C(7)–O(2)	121·9 (6)
C(1)–C(2)–C(8)	119·7 (5)	O(1)–C(7)–O(2)	123·3 (6)
C(3)–C(2)–C(8)	119·8 (5)	C(2)–C(8)–O(4)	116·3 (5)
C(2)–C(3)–C(4)	120·8 (6)	C(2)–C(8)–O(3)	119·3 (5)
C(3)–C(4)–C(5)	118·8 (7)	O(4)–C(8)–O(3)	124·5 (6)
C(2)–C(3)–H(1)	119 (4)	C(4)–C(5)–H(3)	125 (5)
C(4)–C(3)–H(1)	120 (4)	C(6)–C(5)–H(3)	115 (5)
C(3)–C(4)–H(2)	118 (4)	C(5)–C(6)–H(4)	120 (5)
C(5)–C(4)–H(2)	119 (4)	C(1)–C(6)–H(4)	120 (5)

(*c*) In the water molecules

O_w(1)–H(5)	0·79 (7)	O_w(2)–H(7)	0·85 (9)
O_w(1)–H(6)	0·91 (9)	O_w(2)–H(8)	0·81 (11)
H(5)–O_w(1)–H(6)	106 (8)	H(7)–O_w(2)–H(8)	110 (9)

(*d*) Hydrogen bonds

O_w(1)–H(5)···O(2^{iii})	2·791 (7)	H(5)–O_w(1)···O(2^{iii})	9 (6)
H(5)···O(2^{iii})	2·01 (7)	O_w(1)–H(5)···O(2^{iii})	168 (8)
O_w(1)–H(6)···O(4^{iv})	2·731 (8)	H(6)–O_w(1)···O(4^{iv})	16 (5)
H(6)···O(4^{iv})	1·87 (9)	O_w(1)–H(6)···O(4^{iv})	156 (7)
O_w(2)–H(7)···O(1^{iv})	2·753 (7)	H(7)–O_w(2)···O(1^{iv})	11 (5)
H(7)···O(1^{iv})	1·93 (9)	O_w(2)–H(7)···O(1^{iv})	165 (7)
O_w(2)–H(8)···O(2^{ii})	2·736 (7)	H(8)–O_w(2)···O(2^{ii})	3 (6)
H(8)···O(2^{ii})	1·93 (11)	O_w(2)–H(8)···O(2^{ii})	176 (9)

Asymmetric units

(i)	$x, y, z-1$	(iii)	$1-x, \frac{1}{2}+y, -z$
(ii)	$1-x, \frac{1}{2}+y, 1-z$	(iv)	$1-x, -\frac{1}{2}+y, 1-z$

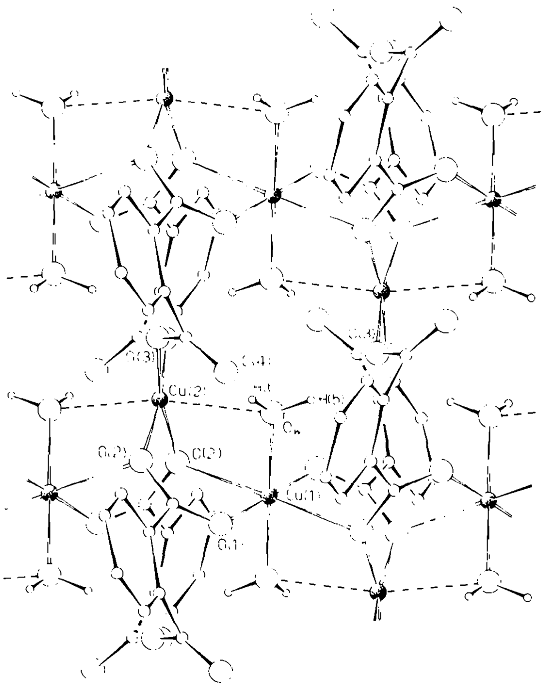

Fig. 2. Projection of the structure of $\mathrm{Cu^{II}pht.H_2O}$ along [100] (*cf.* Prout, Carruthers & Rossotti, 1971).

Table 3. *Least-squares planes*

Equations of least-squares planes are in the form: $AX + BY + CZ = D$, where X, Y and Z are coordinates in Å referred to orthogonal axes and obtained from fractional coordinates by applying the matrix: (a,0,c cos β/0,b,0/0,0,c sin β). Deviations (Å) of relevant atoms from the planes are in square brackets.

	A	*B*	*C*	*D*
Plane (I): O(1), O(4), O_w(1), O_w(2)	0·2663	−0·9595	−0·0916	−0·3008
[O(1) −0·088 (5), O(4) 0·084 (5), O_w(1) −0·106 (5), O_w(2) 0·110 (5), Cu −0·099 (1), O(3'') −2·247]				
Plane (II): C(1), C(2), C(3), C(4), C(5), C(6)	0·0228	0·9633	−0·2674	−0·0659
[C(1) 0·010 (7), C(2) −0·010 (7), C(3) 0·003 (10), C(4) 0·018 (10), C(5) −0·020 (10), C(6) −0·001 (8), C(7) 0·128 (7), C(8) −0·190 (7), O(1) 1·248 (5), O(2) −0·731 (5), O(3) −0·770 (5), O(4) 0·271 (5)]				
Plane (III): C(1), C(7), O(1), O(2)	0·6854	0·2552	−0·6820	2·7949
[C(1) 0·010 (6), C(7) −0·023 (6), O(1) 0·005 (4), O(2) 0·008 (5)]				
Plane (IV): C(2), C(8), O(3), O(4)	−0·2174	0·7397	−0·6369	−4·1499
[C(2) −0·002 (6), C(8) 0·004 (6), O(3) −0·001 (4), O(4) −0·001 (4)]				

with that of the monohydrate (Fig. 2) it appears that the main differences concern both metal coordination and bridging of the pht anion. In the dihydrate, coordination is essentially pyramidal with a distorted octahedral Cu—O extra contact, the pht anion forming a single bridge. In the monohydrate there are two kinds of Cu complexes, both elongated bipyramids, one on a twofold axis the other on a symmetry centre. The Cu atoms on the twofold axis are joined together by double pht bridges forming chains similar to those found in the K, Rb, Cs *o*-phthalatocuprates(II) (Cingi, Lanfredi, Tiripicchio & Camellini, 1977, 1978). But, while in these alkali compounds the chains are held together by the interactions the O atoms exert on the alkali metal atoms, in copper(II) *o*-phthalate monohydrate the joining of the chains is due to the interactions the carboxylate groups exert on the Cu atoms at the centres of symmetry.

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