vergleichbar mit denen in $[Co(pyridin)_4]Cl_2$ (2,18 Å) (Long & Clarke, 1978) und $[Co(1\text{-vinylimidazol})_4]Cl_2$ (DeVaal, Hulsbergen & DeGraaff, 1983). Die Geometrie der ClO_4^--Anionen entspricht den Erwartungswerten; die beobachteten Werte der Temperaturparameter lassen auf eine geringe Fehlordnung schliessen.

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Structure of *catena*-Aqua(1,10-phenanthroline)-μ-phthalato-copper(II) Hemihydrate, $[Cu(C_8H_4O_4)(H_2O)(1,10\text{-}C_{12}H_8N_2)].0{\cdot}5H_2O$

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Abstract. $M_r = 434{\cdot}9$, orthorhombic, $Pbcm$, $a = 11{\cdot}670\,(3)$, $b = 11{\cdot}175\,(3)$, $c = 14{\cdot}073\,(3)$ Å, $V = 1835{\cdot}3\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}57$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 1{\cdot}23$ mm^{-1}, $F(000) = 888$, room temperature, $R = 0{\cdot}055$ for 1708 independent reflections. The structure consists of square-pyramidal $[Cu(C_8H_4O_4)(H_2O)(1,10\text{-}C_{12}H_8N_2)]$ complexes linked in polymeric chains by bridging phthalate anions. Pentacoordination of Cu involves two O atoms from different phthalate anions, two N atoms from a phenanthroline ligand, and the apical O atom of a water molecule. Another water molecule, occupying only one half of the available sites, is bonded to phenanthroline through two $C—H\cdots OH_2$ interactions. The chains are joined in layers parallel to (100) by hydrogen bonds between H_2O ligands and phthalate ions.

Introduction. Phthalate anions within mixed Cu^{II} complexes have been shown to act as bridging ligands through two, three or four O atoms from both their carboxylate groups (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1981; Krstanović, Karanović, Stojaković & Golič, 1982; Prout, Carruthers & Rossotti, 1971). The polymeric chains so obtained can be held together in the lattice in various ways. In $[Cu(pht)(C_5H_5N)_2]$ (pht = phthalate anion) there are only van der Waals interchain contacts (Biagini Cingi *et al.*, 1981), whereas in the $[Cu(pht)(NH_3)_2]$ (Biagini Cingi, Guastini, Musatti & Nardelli, 1970) and $[Cu(pht)(C_2H_8N_2)]$ (Krstanović *et al.*, 1982) complexes the carboxylate O atom belonging to one chain forms the apex of the Cu coordination polyhedron in the adjacent chain. In the present compound, $[Cu(pht)(H_2O)(1,10\text{-}C_{12}H_8N_2)].0{\cdot}5H_2O$, pht behaves as a bridging ligand using only two O atoms, and the interchain contacts are realized through hydrogen bonds between carboxylate groups in one chain and the coordinated H_2O molecule in the next chain.

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Experimental. Crystals suitable for X-ray determination were obtained by allowing a dilute aqueous solution of sodium diaquadiphthalatocuprate(II) to diffuse slowly into a dilute solution of bis(1,10-phenanthroline)-copper(II) nitrate in water–ethanol. Blue plate, 0·05 × 0·21 × 0·63 mm. Syntex $P\bar{1}$ diffractometer, ω scan with variable scan rate, Mo $K\alpha$, graphite monochromator. Lattice parameters from 15 strong hkl with $7 < \theta < 14°$. No absorption correction. $2\theta_{\max} = 60°$, $h = 0$–16, $k = 0$–15, $l = 0$–19. 3 standard reflections, intensity variation <3%. 1941 independent reflections measured (= total number of reflections measured, because only 100 equivalent reflections were measured to check the symmetry of the crystal and stability of the measurements), 1708 observed with $I \geq 3\sigma(I)$. Position of the Cu atom obtained from the Patterson function; remaining non-hydrogen atoms located from subsequent Fourier maps; H-atom positions from difference maps, except for those belonging to water molecules, and included in the structure factor calculations at fixed positions with isotropic temperature factors; anisotropic thermal parameters for non-hydrogen atoms. Based on the height of the peak on Fourier and difference Fourier maps, and the behaviour of the temperature factors during the refinement, an occupancy factor of 0·5 was assigned to O*W*(2). 142 variables, 1708 observations, $R = 0·055$, $wR = 0·067$, S not calculated; $\sum w|\Delta F|^2$ minimized; unit weights; in final cycle $(\Delta/\sigma)_{\max} = 0·248$ (mean = 0·044); max. $\Delta\rho$ in final difference Fourier map 1·13, min. −0·52 e Å^{-3}. Scattering factors from Cromer & Mann (1968), f' and f'' values from Cromer & Liberman (1970). Structure solution and refinement calculation carried out with *SHELX* (Sheldrick, 1975) and geometry calculations with *CRYSTAN* (Burzlaff, Böhme & Gomm, 1977).

Discussion. The atomic coordinates are listed in Table 1.* The crystal structure consists of [Cu(pht)(H_2O)-(1,10-$C_{12}H_8N_2$)] complexes linked in polymeric chains, running along **c**, by bridging pht anions (Fig. 1). Bond distances and angles are given in Table 2. Each pht anion behaves as a bidentate ligand bridging two adjacent Cu atoms through O(1) atoms from both carboxylate groups. The coordination polyhedron around the Cu atom can be described as a square pyramid (Fig. 2). The Cu is at a mirror plane and the atoms forming the base of the pyramid are two O atoms from different phthalate anions and two N atoms from a phenanthroline ligand. The apex of the pyramid is occupied by the O*W*(1) atom from a water molecule. The Cu—O(1) and Cu—N distances in the basal plane as well as the corresponding angles are in good agreement with those found in related Cu complexes (Biagini Cingi *et al.*, 1970, 1981; Krstanović *et al.*, 1982). Also in good agreement with the related complexes is the fact that, owing to the Jahn–Teller effect in Cu$^{\text{II}}$ compounds, the apical Cu—O*W*(1) distance [2·411 (6) Å] is significantly longer than the basal Cu—O(1) distances [1·930 (4) Å]. At the same time, the apical Cu—O*W*(1) distance in the present complex is slightly greater than the corresponding ones in [Cu(pht)(NH_3)$_2$] [2·313 (5) Å (Biagini Cingi *et al.*, 1970)], in [Cu(pht)($C_2H_8N_2$)] [2·35 (4) Å (Krstanović

Table 1. *Atomic positional* (×10^4) *and thermal* (Å^2 ×10^3) *parameters for non-hydrogen atoms, with e.s.d.'s in parentheses*

$$U = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	*y*	*z*	*U*
Cu	4766 (1)	1134 (1)	2500	27 (1)
O(1)	3582 (3)	1355 (4)	1559 (3)	37 (2)
O(2)	4177 (3)	3133 (3)	1013 (3)	38 (2)
O*W*(1)	4488 (5)	−1004 (5)	2500	36 (3)
O*W*(2)	1961 (9)	−661 (12)	2500	54 (8)
N	6058 (4)	960 (4)	1561 (3)	31 (2)
C(1)	3474 (4)	2307 (5)	1052 (4)	29 (3)
C(2)	2382 (4)	2373 (4)	484 (3)	25 (2)
C(3)	1346 (5)	2270 (5)	959 (4)	36 (3)
C(4)	308 (5)	2399 (6)	487 (4)	41 (3)
C(5)	6025 (5)	982 (5)	607 (4)	36 (3)
C(6)	6997 (6)	733 (6)	54 (5)	45 (3)
C(7)	8006 (5)	422 (5)	488 (5)	43 (3)
C(8)	8063 (5)	393 (5)	1495 (5)	38 (3)
C(9)	7076 (5)	680 (5)	1995 (4)	32 (3)
C(10)	9070 (5)	100 (6)	2012 (5)	48 (3)

Table 2. *Bond distances* (Å) *and angles* (°) *for non-hydrogen atoms, with e.s.d.'s in parentheses*

Cu—O(1)	1·930 (4)	C(3)—C(4)	1·389 (8)
Cu—O*W*(1)	2·411 (6)	C(4)—C(4$^{\text{vi}}$)	1·389 (8)
Cu—N	2·014 (5)	C(5)—C(6)	1·403 (9)
O(1)—C(1)	1·287 (7)	C(6)—C(7)	1·371 (9)
O(2)—C(1)	1·236 (6)	C(7)—C(8)	1·419 (10)
N—C(5)	1·343 (7)	C(8)—C(9)	1·387 (8)
N—C(9)	1·372 (7)	C(8)—C(10)	1·420 (9)
C(1)—C(2)	1·506 (7)	C(9)—C(9$^{\text{vii}}$)	1·421 (8)
C(2)—C(2$^{\text{vi}}$)	1·392 (6)	C(10)—C(10$^{\text{vii}}$)	1·374 (10)
C(2)—C(3)	1·386 (7)		
O(1)—Cu—O(1$^{\text{vii}}$)	86·7 (2)	C(3)—C(2)—C(2$^{\text{vi}}$)	119·3 (5)
O(1)—Cu—O*W*(1)	91·7 (2)	C(2)—C(3)—C(4)	121·4 (4)
O(1)—Cu—N	95·6 (2)	C(3)—C(4)—C(4$^{\text{vi}}$)	119·3 (5)
N—Cu—N$^{\text{vii}}$	82·0 (2)	N—C(5)—C(6)	121·8 (5)
N—Cu—O*W*(1)	90·3 (2)	C(5)—C(6)—C(7)	119·8 (5)
Cu—O(1)—C(1)	123·8 (3)	C(6)—C(7)—C(8)	119·4 (5)
Cu—N—C(5)	129·2 (4)	C(7)—C(8)—C(9)	117·6 (5)
Cu—N—C(9)	112·2 (3)	C(7)—C(8)—C(10)	123·8 (5)
C(5)—N—C(9)	118·3 (5)	C(9)—C(8)—C(10)	118·7 (5)
O(1)—C(1)—O(2)	125·2 (4)	N—C(9)—C(8)	123·1 (5)
O(1)—C(1)—C(2)	114·7 (4)	N—C(9)—C(9$^{\text{vii}}$)	116·4 (4)
O(2)—C(1)—C(2)	120·1 (4)	C(8)—C(9)—C(9$^{\text{vii}}$)	120·5 (5)
C(1)—C(2)—C(2$^{\text{vi}}$)	122·0 (4)	C(8)—C(10)—C(10$^{\text{vii}}$)	120·8 (5)
C(1)—C(2)—C(3)	118·6 (4)		

Equivalent positions

(i) $x, 0·5 - y, -z$
(ii) $-x, 0·5 + y, 0·5 - z$
(iii) $-x, -y, z$
(iv) $-x, -y, -z$
(v) $-x, 0·5 + y, z$
(vi) $x, 0·5 - y, 0·5 + z$
(vii) $x, y, -z$

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* Lists of structure factors, anisotropic thermal parameters, ring torsion angles, mean-planes data and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39775 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

et al., 1982)] or in $\mathrm{Ba[Cu(pht)_2(H_2O)_2]}$ [2·289 (9) Å (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1978*a*)]. The four basal atoms are coplanar by symmetry requirements, and the Cu atom is slightly displaced [0·035 (2) Å] from the corresponding plane toward the apex of the pyramid. The Cu—O*W*(1) bond is almost strictly perpendicular to that plane, the angle between them being 89·1 (2)°. Thus the square pyramid around Cu is less distorted than that in the related complex $\mathrm{[Cu(pht)(C_5H_5N)_2]}$ (Biagini Cingi *et al.*, 1981).

In addition to the water molecule at the apex of the pyramid, O*W*(1), there is another H_2O in the lattice that is hydrogen-bonded to the H(C10) and H(C10$^{\rm vii}$)-(x, y, $0{\cdot}5 - z$) atoms of the phenanthroline ligand. Its position is only half occupied. The H(C10)···O*W*(2) and H(C10$^{\rm vii}$)···O*W*(2) distances (2·655 Å) are considerably longer than the H···O interactions usually found for aromatic H atoms (2·20–2·30 Å) and are close to the van der Waals H(C)···O distances (2·60 Å, Hamilton & Ibers, 1968).

The polymeric chains are joined in layers almost parallel to (100), this being achieved by hydrogen bonds between the apical O*W*(1) belonging to one chain and the two O(2) atoms of a pht anion in the adjacent chain. The O*W*(1)···O(2) and O*W*(1)···O(2$^{\rm vii}$) distances [2·781 (5) Å] are very close to the O(water)···O(pht) distances for similar cases of hydrogen-bonded interactions, *e.g.* in $\mathrm{Cu(pht).2H_2O}$ (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1978*b*), in hydrated $M_2\mathrm{[Cu(pht)_2]}$ complexes [M = Li,Na,K,Rb (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1977, 1978*c*)], and in hydrated $M\mathrm{[Cu(pht)_2]}$ complexes [M = Mg,Sr,Ba (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1978*a*,*d*)].

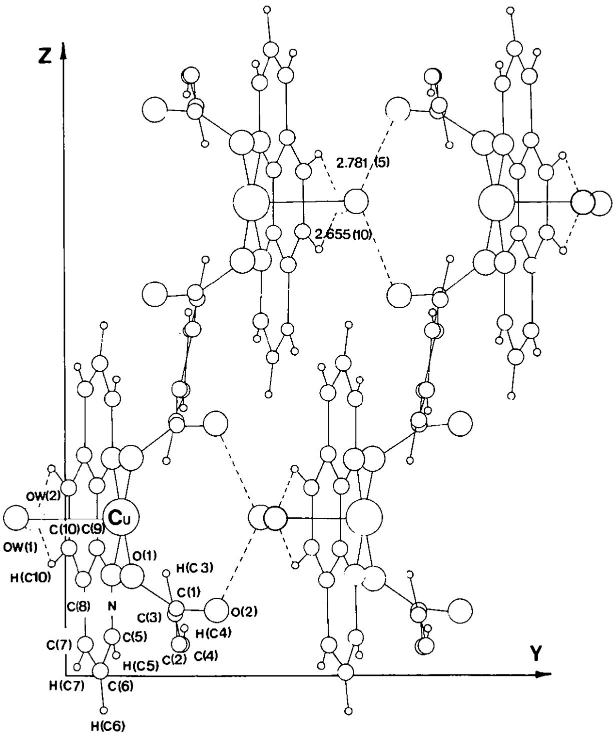

Fig. 1. Projection of the crystal structure along **a**, with numbering of atoms. Hydrogen bonds are shown as dotted lines with distances in Å.

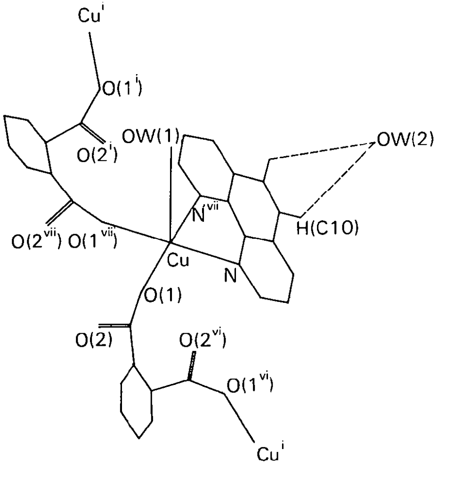

Fig. 2. Schematic drawing showing the environment of the Cu atom. Symmetry-equivalent positions are given in Table 2.

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