Structure of Copper(II) Chloranilate Trihydrate

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Abstract. Copper(II) 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone trihydrate, $Cu(C_6Cl_2O_4).3H_2O$, $M_r = 324.56$, triclinic, $P\bar{1}$, $a = 7.040\,(4)$, $b = 7.962\,(4)$, $c = 9.364\,(5)$ Å, $\alpha = 84.58\,(3)$, $\beta = 89.25\,(3)$, $\gamma = 76.53\,(3)°$, $V = 508.1\,(5)$ Å^3, $Z = 2$, $D_x = 2.12$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 2.7$ mm^{-1}, $F(000) = 322$, room temperature, $R = 0.048$ for 1465 unique reflections having $|F| > 3\sigma(|F|)$. The Cu atoms are coordinated in a moderately distorted octahedral arrangement by four ligand atoms and two water molecules. There are three significantly different Cu—O distances: 1.966 (4) and 1.965 (5) Å to the two 'phenolic' O atoms, 2.252 (4) and 2.265 (4) Å to the two quinoid O atoms and to the two water-molecule O atoms 1.996 (4) and 2.015 (5) Å. There are layers of linear coplanar chains of Cu atoms bridged by chloranilate dianions. Between the chains there is one 'free' water molecule per Cu atom.

Introduction. In the search for new metal-aromatic compounds with a tetra- or hexa-coordinated Cu^{II} atom, after the structure analysis of copper terephthalate trihydrate in our group (Cueto, Gramlich, Petter, Rys & Rys, 1991), copper(II) chloranilate trihydrate (chloranilate is the dianion of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone) was synthesized by polychelation and obtained in single crystalline form. The X-ray structure analysis gave evidence of a crystallized structure characterized by coplanar linear polymer chains as described below. The compound in its microcrystalline form is highly insulating between room and liquid nitrogen temperatures, and shows neither an intrinsic conductivity nor a significant charge-carrier concentration. The compound shows antiferromagnetic behaviour with $T_N = 20 \pm 1$ K. Previous reports on structures of binuclear quinoid Cu^{II} complexes are known

(Tinti, Verdaguer, Kahn & Savariault, 1987; Pierpont, Francesconi & Hendrickson, 1977), but no single-crystal data of infinite linear polychelate chains have been published. According to Verdaguer, Michalowicz, Girerd, Alberding & Kahn (1980), a Japanese research team (Kanda, 1963) claimed to have grown a single crystal of $Cu(C_6Cl_2O_4)$. A planar-chain structure was considered to be consistent with the antiferromagnetic behaviour of this compound (Kobayashi, Haseda, Kanda & Kanda, 1963) and with *EXAFS* data (Verdaguer, Michalowicz, Girerd, Alberding & Kahn, 1980). In contrast, a number of polycomplexes of 3,6-disubstituted 2,5-dihydroxy-*p*-benzoquinones with other cations have been investigated in detail, *i.e.* with Ca^{2+} (Robl & Sheldrick, 1988), Ca^{2+} and Sr^{2+} (Robl, 1987*a*), Y^{3+} (Robl, 1987*b*), Zn^{2+} (Robl & Weiss, 1986*a*), Mn^{2+} and Cd^{2+} (Weiss, Riegler & Robl, 1986).

Experimental. Copper(II) chloranilate trihydrate was crystallized at room temperature from aqueous solutions of cupric nitrate trihydrate and disodium chloranilate. The concentration of both reactants was 2.5×10^{-4} *M*. Crystals, approximately 0.4 mm in length, were collected after 20 days, washed with water and dried in air. A crystal approximately $0.2 \times 0.1 \times 0.07$ mm was chosen for the structure analysis. The precession method was used to determine the crystal system and the space group. Intensity measurements were then carried out at room temperature with a Picker automated single-crystal diffractometer upgraded by Stoe Corporation (1987), using monochromated Mo $K\alpha$ radiation. Unit-cell constants were calculated from 26 reflections with $20 < 2\theta < 25°$. Intensity data were measured for 1790 unique reflections with hkl, $\bar{h}kl$, $h\bar{k}l$ and $\bar{h}\bar{k}l$ indices ($-8 \le h \le 8$, $-9 \le k \le 9$, $-11 \le l \le 11$), and 2θ values in the range $4 < 2\theta < 50°$, using a θ/ω scan. The profile

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fitting was carried out by a learnt-profile method (Clegg, 1981). Three standard reflections (003, 041, 301) were measured after every 69 reflections. No decay of intensities was observed. For the data reduction, Stoe software (Stoe Corporation, 1987) was used. ψ-scan measurements of selected reflections showed that an absorption correction could be omitted. For the structure solution, 1790 unique reflections were used, of which 1465 were observed [$|F| > 3\sigma(|F|)$]; $R_{int} = 0.027$. Neutral complex scattering factors from Cromer & Mann (1968) were used. The crystal structure was solved using *XTAL* 2.6 software (Hall & Stewart, 1989). The structure could be easily solved with the Patterson method after anisotropic refinement. Final refinement based on $|F|$ (1465 reflections, 146 parameters) resulted in $R = 0.048$, $wR = 0.050$, $S = 2.8$, with anisotropic atomic displacement parameters. Unfortunately, the H atoms could not be located properly and were not included in the structure analysis. Weights were assigned as $w = 1/\sigma$, $(\Delta/\sigma)_{max} = 0.073$; $(\Delta\rho)_{max} = 0.930$, $(\Delta\rho)_{min} = -0.934$ e Å^{-3}. The final values of the atomic coordinates and equivalent isotropic displacement parameters and their e.s.d.'s are given in Table 1.*

Discussion. The polymeric structure consists of almost coplanar, linear polychelate chains along the y axis (*cf.* Figs. 1 and 2). The coplanar chains form layers parallel to the yz plane, at a distance of approximately 3.43 (14) Å. The chains have a lateral distance of 9.322 (5) Å and they are shifted by 0.885 (1) Å against each other. The Cu atom is coordinated by six O atoms in a moderately distorted octahedron with remarkably small chelating bond angles O(1)—Cu—O(2) and O(3)—Cu—O(4) (*cf.* Table 2). There are three pairs of different Cu—O distances. Thus, the Cu ion shows the (2 + 2 + 2) type of coordination which is consistent with a Jahn–Teller distortion. Note that the apically coordinated water molecules O(5) and O(6) are closer to the Cu atom than the chelating O(2) and O(3) atoms in the basal plane. Exact values are given in Table 2. An analogous phenomenon has already been observed in copper squarate dihydrate (Robl & Weiss, 1986*b*) and was suggested for microcrystalline Cu(C$_6$O$_4$X$_2$).2NH$_3$, X = Cl, Br, based on magnetic data (Verdaguer, Michalowicz, Girerd, Alberding & Kahn, 1980). The difference between the lengths of the phenolic C—O and the quinoid C=O bonds is rather small, 0.04 (2) Å, despite the O atoms not

Table 1. *Atomic coordinates and equivalent isotropic displacement parameters* ($\text{Å}^2 \times 10^3$)

E.s.d.'s are given in parentheses. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

|	x	y	z	U
Cu	0.2480 (1)	0.47500 (9)	0.18565 (8)	19.7 (4)
Cl(1)	0.2502 (2)	0.0348 (2)	−0.1534 (1)	25 (1)
Cl(2)	0.2611 (3)	−0.0910 (2)	0.5264 (2)	33 (1)
O(1)	0.2600 (6)	0.2925 (5)	0.0560 (4)	24 (3)
O(2)	0.2462 (6)	0.2405 (5)	0.3423 (4)	27 (3)
O(3)	0.2401 (6)	0.6563 (5)	0.3157 (4)	26 (3)
O(4)	0.2429 (6)	0.7100 (5)	0.0305 (4)	26 (3)
O(5)	0.5388 (6)	0.4234 (7)	0.2003 (5)	38 (4)
O(6)	−0.0456 (6)	0.5196 (5)	0.1799 (5)	29 (3)
C(1)	0.2528 (8)	0.1413 (7)	0.1122 (6)	19 (4)
C(2)	0.2506 (8)	0.1118 (8)	0.2761 (6)	20 (4)
C(3)	0.2539 (9)	−0.0571 (8)	0.3409 (6)	22 (4)
C(4)	0.2473 (8)	0.8095 (7)	0.2619 (6)	19 (4)
C(5)	0.2443 (8)	0.8385 (7)	0.0981 (7)	21 (4)
C(6)	0.2486 (9)	0.0034 (8)	0.0323 (6)	20 (4)
O(7)	0.2672 (7)	0.4498 (6)	−0.4197 (5)	41 (4)
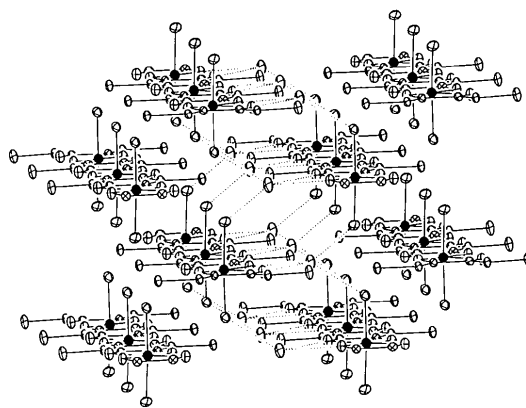
Fig. 1. Perspective view of the structure along the polychelate chains. Dotted lines indicate possible hydrogen bonds. The Cu sites are shown as black dots.
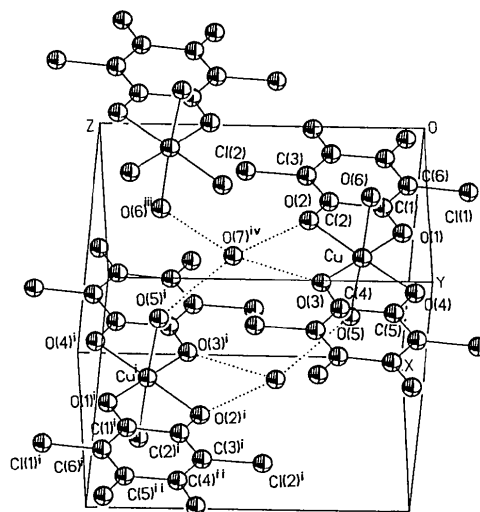

Fig. 2. Unit cell of the structure. Dotted lines indicate possible hydrogen bonds. Some atoms are omitted for better clarity.

Table 2. *Selected bond lengths (Å) and angles (°) for copper*(II) *chloranilate trihydrate*

E.s.d.'s are given in parentheses.

Cu—O(1)	1.966 (4)	O(1)—Cu—O(2)	78.1 (2)
Cu—O(2)	2.265 (4)	O(1)—Cu—O(3)	179.2 (2)
Cu—O(3)	1.965 (5)	O(1)—Cu—O(4)	102.1 (2)
Cu—O(4)	2.252 (4)	O(1)—Cu—O(5)	91.5 (2)
Cu—O(5)	1.996 (4)	O(1)—Cu—O(6)	88.8 (2)
Cu—O(6)	2.015 (5)	O(2)—Cu—O(3)	101.7 (2)
O(1)—C(1)	1.280 (7)	O(2)—Cu—O(4)	178.9 (2)
O(2)—C(2)	1.241 (8)	O(2)—Cu—O(5)	89.9 (2)
O(3)—C(4)	1.287 (7)	O(2)—Cu—O(6)	87.5 (2)
O(4)—C(5)	1.254 (8)	O(3)—Cu—O(4)	78.1 (2)
O(7^{iv})—O(2)	2.931 (7)	O(3)—Cu—O(5)	87.7 (2)
O(7^{iv})—O(3)	2.824 (6)	O(3)—Cu—O(6)	92.0 (2)
O(7^{iv})—O(5^i)	2.866 (8)	O(4)—Cu—O(5)	91.4 (2)
O(7^{iv})—O(6^{iii})	2.931 (7)	O(4)—Cu—O(6)	91.2 (2)
		O(5)—Cu—O(6)	177.2 (2)

Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $1 - x$, $2 - y$, $1 - z$; (iii) $-x$, $1 - y$, $1 - z$; (iv) x, y, $1 + z$.

being equal in respect to their affinity to the Cu atom (*cf.* Table 2).

The shortest Cu—Cu distance along the polychelate chains is equal to the unit-cell constant *b*. A shorter distance, 4.991 (2) Å, is found between Cu^i and Cu^{iv} across the centre of the *xy* plane. The structure contains one non-coordinated water molecule per Cu atom, O(7), which deviates no more than 0.17 (6) Å from the polychelate layer. O(7^{iv}) is almost centred between O(2), O(3), O(5^i) and O(6^{iii}) (*cf.* Table 2). Moreover, there is a slight inclination of O(5) and O(6) towards the next positioned free water molecule. This indicates a possible network of interchain hydrogen bonds (dotted lines in Figs. 1 and 2), similar to the structure of copper squarate dihydrate cited above. Since the crystal structure collapses when the crystals are dried under vacuum

at room temperature the presence of non-coordinated water is essential for its stability.

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Structure of the Sodium Salt of 1,4,5,8-Naphthalenetetracarboxylic Acid 4,5-Anhydride Hydrate

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Abstract. Sodium hydrogen 1,3-dioxo-1H,3H-naphtho[1,8-*cd*]pyran-6,7-dicarboxylate hydrate, Na[C$_{14}$H$_5$O$_7$].H$_2$O, $M_r = 326.2$, triclinic, $P\bar{1}$, $a = 9.520$ (2), $b = 9.549$ (3), $c = 7.860$ (1) Å, $\alpha = 105.88$ (2), $\beta = 110.29$ (1), $\gamma = 100.89$ (2)°, $V = 611.9$ (3) Å^3, $Z = 2$, $D_x = 1.77$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71073 Å, $\mu = 1.67$ cm^{-1}, $F(000) = 332$, $T = 295$ K, $R = 0.042$ for 1665 unique reflections having $I > 3\sigma_I$. The organic portion of this structure demonstrates near-*C2* symmetry with a pseudo-twofold axis coincident with the central C—C naphthalene ring bond. The atoms of the naphthopyran three-ring

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