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Structure of Copper(II) Terephthalate Trihydrate

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Abstract. $\text{Cu}[\text{C}_6\text{H}_4(\text{COO})_2] \cdot 3\text{H}_2\text{O}$, $M_r = 281.71$, orthorhombic, *Pbcn*, $a = 6.869$ (3), $b = 22.985$ (11), $c = 6.298$ (3) Å, $V = 994.4$ (14) Å³, $Z = 4$, $D_x = 1.88$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.22$ mm⁻¹, $F(000) = 572$, room temperature, $R = 0.036$ for 812 unique reflections having $|F| > 4\sigma(|F|)$. The Cu atoms are coordinated by two carboxylate O atoms and four water-molecule O atoms in a significantly distorted octahedral arrangement. There are three different coordination Cu—O distances: two of 1.925 (2) Å with the two carboxylate O atoms, two of 1.981 (2) Å and the largest two of 2.479 (2) Å. The octahedra share common edges with octahedra of two neighbouring Cu atoms to form zigzag chains in the *c* direction. The chains are linked by hydrogen bonds and in addition the resulting layers are held together *via* hydrogen bridges building a three-dimensional network.

Introduction. In the search for new metal–aromatic compounds with a tetra- or hexacoordinated copper(II) atom, copper(II) terephthalate trihydrate (CuTT) was synthesized by polycondensation and obtained in single-crystalline form. The X-ray structure analysis revealed a regularly crystallized structure characterized by zigzag-like polymer chains described below. As expected, the compound is highly insulating in the range between room and liquid-nitrogen temperature, thus showing neither intrinsic conduction nor significant charge-carrier concentration. Previous reports on structures of copper carboxylates are known where Cu atoms are joined *via* four carboxylate groups forming dimers, like copper acetate tetrahydrate with a Cu—Cu distance of less than 3 Å (van Niekerk & Shoening, 1953), or copper arylcarboxylates forming polymer networks with Cu—Cu distances larger than 3 Å, like copper ben-

zoate trihydrate (Koizumi, Osaki & Watanabe, 1963), copper phthalate monohydrate (Prout, Carruthers & Rossotti, 1971) and copper 1,2,4,5-benzenetetracarboxylate decahydrate (Usuliev, Shnulin & Mamedov, 1982). Also, Tamura, Ogawa & Mori (1989) have reported a polymer structure with an intermediate type of copper configuration.

Experimental. CuTT was synthesized from solid sodium terephthalate and copper(II) sulfate pentahydrate at room temperature, in aqueous medium, by a diffusion-controlled reaction method (Date, Yamazaki, Motokawa & Tazawa 1970). By careful polycondensation, single crystals up to 3 mm in length and with a cross section of 1.2×0.5 mm were grown. The crystals were washed with water and dried under vacuum. The structural formula was worked out from microanalysis data: C 34.00, H 3.73%. These are in close agreement with the calculated values for $\text{Cu}[\text{C}_6\text{H}_4(\text{COO})_2]_2 \cdot 3\text{H}_2\text{O}$: C 34.10, H 3.57%.

A small crystal of about $0.1 \times 0.1 \times 0.1$ mm was chosen for a subsequent structure analysis. First it was examined by the precession method revealing the single-crystalline structure of the sample.

Intensity measurements were then carried out at room temperature with a Picker automated single-crystal diffractometer upgraded by Stoe, using monochromated $\text{Mo K}\alpha$ radiation. Unit-cell constants were calculated from 34 reflections with $20 < 2\theta < 30^\circ$. Intensity data were measured for 2155 reflections with $+h$, $+k$, $+l$ and $-h$, $+k$, $-l$ indices ($h_{\text{max}} = 8$; $k_{\text{max}} = 27$; $l_{\text{max}} = 7$), and 2θ values in the range $3 < 2\theta < 50^\circ$, using a θ/ω scan. Profile fitting was carried out by a learnt-profile method (Clegg, 1981). Three standard reflections (400, 0120 and 004) were measured at intervals of 90 min. No decay of intensities was observed. For the data reduction, software of Stoe (Stoe Corporation, 1987) was used. ψ scan measurements of selected reflections showed that an absorption correction could be omitted.

For the structure solution, 881 unique reflections were used, of which 812 were observed [$|F| > 4\sigma(|F|)$]; $R_{\text{int}} = 0.02$. Neutral complex scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 71) were used. The crystal structure was solved using the *SHELXTL-Plus* software (Sheldrick, 1988). The structure could be easily solved with Patterson and direct methods (however it may be noted that the direct-method trials with default values were successful only with a non-centrosymmetric space group). The first difference density map revealed the position of the O atoms of the water molecules. After isotropic refinement all H atoms could be located in a subsequent difference density map. Final refinement based on $|F|$ (881

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

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_{eq}/U
Cu	0.5000	0.5000	0.5000	17 (1)
O(1)	0.5224 (2)	0.5810 (1)	0.4268 (3)	23 (1)
C(1)	0.5000	0.6054 (1)	0.2500	17 (1)
C(2)	0.5000	0.6711 (1)	0.2500	18 (1)
C(3)	0.4349 (3)	0.7015 (1)	0.0707 (3)	21 (1)
C(4)	0.4300 (3)	0.7615 (1)	0.0737 (3)	22 (1)
C(5)	0.5000	0.7915 (1)	0.2500	18 (1)
C(6)	0.5000	0.8579 (1)	0.2500	23 (1)
O(2)	0.4021 (3)	0.8828 (1)	0.1088 (3)	33 (1)
O(3)	0.7177 (3)	0.4808 (1)	0.3060 (3)	20 (1)
O(4)	0.5000	0.9397 (1)	0.7500	30 (1)
H(1)	0.381 (3)	0.685 (1)	-0.045 (4)	21 (6)
H(2)	0.380 (4)	0.778 (1)	-0.044 (5)	34 (7)
H(3)	0.781 (9)	0.505 (2)	0.267 (5)	21 (13)
H(4)	0.772 (4)	0.450 (2)	0.332 (5)	56 (10)
H(5)	0.513 (3)	0.926 (2)	0.642 (5)	24 (8)

reflections, 97 parameters) resulted in $R = 0.036$, $wR = 0.083$, $S = 0.97$, with isotropic atomic displacement parameters for H atoms and anisotropic atomic displacement parameters for non-H atoms. Weights were assigned as $w = 1/[\sigma^2(|F|) + 0.007|F|^2]$, $(\Delta/\sigma)_{\text{max}} = 0.049$, $(\Delta\rho)_{\text{max}} = 0.35$, $(\Delta\rho)_{\text{min}} = -1.19 \text{ e \AA}^{-3}$.

The final values of the atomic coordinates, isotropic and anisotropic displacement parameters and their e.s.d.'s are given in Table 1.*

Discussion. The polymeric structure consists of sheets parallel to the yz plane of terephthalate ions which are joined along the y axis through Cu atoms on one side, and hydrogen-bonded water molecules on the other (*cf.* Fig. 1). Two consecutive sheets along the x axis are shifted with respect to each other in such a way that the copper-bonded carboxylate groups lie between the hydrogen-bonded carboxylate groups immediately above and below. Only one of the two carboxylates of each terephthalate group is bound to the metal atoms (see Fig. 2). Each terephthalate group is bound to two adjacent Cu atoms, whereas each Cu atom binds two terephthalate groups thus yielding a zigzag chain lying in the yz plane and having its chain axis parallel to the z axis. The other carboxylate group is joined *via* hydrogen bridging of intermediate water molecules with the two carboxylate oxygens of two neighbouring terephthalate groups located in the same yz plane, as shown in Fig. 1. All the O atoms except O(1) are involved in

* Lists of observed and calculated structure factors, anisotropic displacement parameters of the non-H atoms and atomic and isotropic displacement parameters of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53261 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

hydrogen bonding. There are two types of water molecules in the cell: type *A* with O(3) – which is coordinated with Cu atoms – and type *B* with O(4) – which is not coordinated with Cu (see Fig. 1). Both types of water molecules are involved in hydrogen

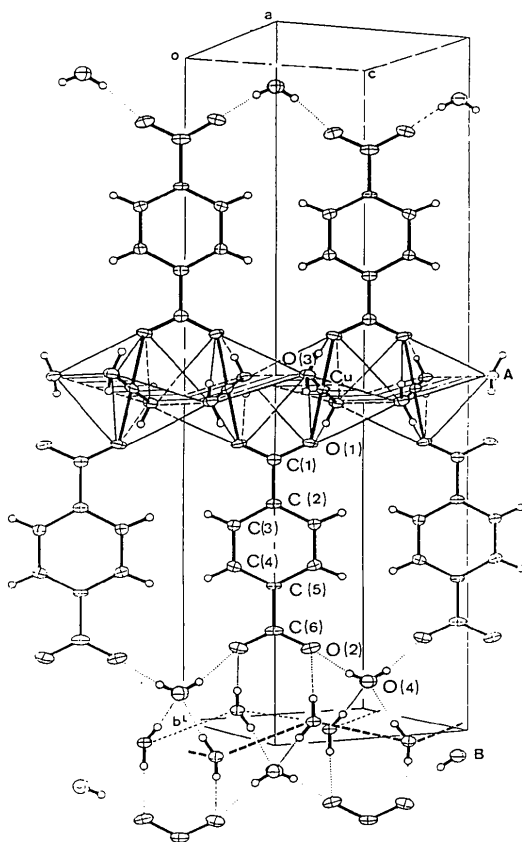


Fig. 1. *yz* section of the copper(II) terephthalate trihydrate structure. The chains of edge-sharing CuO_6 octahedra are shown and the hydrogen-bond network is indicated at the lower end. Hydrogen bonds are dotted and the dashed lines indicate the edges of the neighbouring octahedral CuO_6 chains.

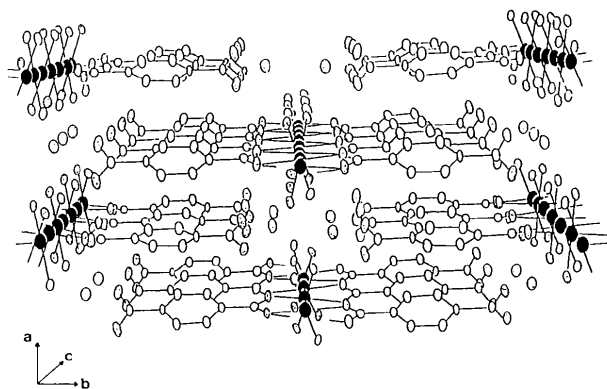


Fig. 2. Perspective view of the structure along CuO_6 octahedral chains.

Table 2. Selected bond lengths (Å) and angles (°) for Cu^{II} terephthalate trihydrate

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

Cu—O(1)	1.925 (2)	O(1)—Cu—O(3)	90.4 (1)
Cu—O(3)	1.981 (2)	O(1)—Cu—O(1')	180.0
Cu—O(1')	1.925 (2)	O(3)—Cu—O(1')	89.6 (1)
Cu—O(3')	1.981 (2)	O(3)—Cu—O(3')	180.0
Cu—O(3 ⁱⁱ)	2.479 (2)	O(1')—Cu—O(3')	90.4 (1)
Cu—O(3 ⁱⁱⁱ)	2.479 (2)	O(1)—Cu—O(3 ⁱⁱ)	89.6 (1)
		O(3 ⁱⁱ)—Cu—O(3 ⁱⁱⁱ)	180.0

Symmetry code: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 1 - y, z + \frac{1}{2}$; (iii) $1 - x, y, \frac{1}{2} - z$.

Table 3. Hydrogen-bond parameters (Å and °) for Cu^{II} terephthalate trihydrate

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

Donor oxygen—acceptor oxygen		Proton—acceptor O	
O(4)—O(2)	2.697 (1)	H(5 ^v)—O(2')	1.96 (3)
O(4)—O(2 ⁱⁱ)	2.697 (1)	H(5)—O(2 ⁱⁱ)	1.96 (3)
O(3)—O(4 ⁱⁱⁱ)	2.688 (3)	H(3)—O(4 ⁱⁱⁱ)	1.97 (5)
O(3)—O(2 ^v)	2.640 (3)	H(4)—O(2 ^v)	1.82 (3)
Proton—donor O		O—H—O	
H(5 ^v)—O(4)	0.75 (3)	167 (3)	
H(5)—O(4)	0.75 (3)	167 (3)	
H(3)—O(3)	0.75 (4)	160 (5)	
H(4)—O(3)	0.81 (4)	178 (4)	

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

bridging as follows: molecules of type *B* are donors due to their bridging with the carboxylate O atoms [O(2)] and are acceptors due to their bridging with the water molecules of type *A* located in the *yz* planes below and above the plane outlined in Fig. 1; the water molecules of type *A* are donors by bridging type *B* water molecules and carboxylate groups located in the upper or lower *yz* planes. The parameters for the hydrogen bonds and associated protons are given in Table 3.

The charge separation within a molecular group may be described by two positive charge units at the Cu atom (counted half) and one negative charge unit in the region of the mentioned hydrogen bridges. This charge polarization is consistent with the observed stacking of the neighbouring layers.

The coordination polyhedron of copper is a distorted octahedron. In the basal plane two water-molecule O atoms and two carboxylate O atoms are coordinated with copper; the two apical positions are occupied by two other water-molecule O atoms. There are three different pairs of Cu—O distances. Thus the copper ions display the (2 + 2 + 2) type of coordination, which is consistent with a Jahn–Teller distortion; this type of coordination has been observed and reported for other examples, by Gallucci & Gerkin (1989) and in references cited therein. The Cu—Cu separation is 3.149 (2) Å within the chains of the edge-sharing CuO_6 octahedra. Similar chains

of Cu atoms have also been observed in (2,5-DM-DCNQ)₂Cu (Aumüller, Erk, Klebe, Hünig, von Schütz, & Werner, 1986), but with a larger distance between the copper centres (3.88 Å) and tetrahedral CuO₄ arrangement.

Selected interatomic distances and angles in the coordination polyhedra around copper are given in Table 2.

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Structures of Neodymium(III) Complexes with Amino Acids: (I) *catena*-Poly{[triaquatrichloroneodymium(III)]- μ -(β -alanine-*O, O'*)}; (II) Pentaqua-chloro- μ -(L-proline-*O, O'*)-neodymium(III) Hexaqua- μ -(L-proline-*O, O'*)-neodymium(III) Pentachloride

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Abstract. (I) [NdCl₃(H₂O)₃(C₃H₇NO₂)], *M_r* = 393.7, monoclinic, *P*2₁/*c*, *a* = 6.018 (2), *b* = 16.562 (6), *c* = 12.518 (4) Å, β = 116.18 (4)°, *V* = 1119.7 Å³, *Z* = 4, *D_m* = 2.33, *D_x* = 2.34 Mg m⁻³. Mo *K*α, λ = 0.71069 Å, μ = 5.36 mm⁻¹, *F*(000) = 756, *T* = 298 (2) K. Final *R* = 0.035 for 2363 reflections with *F* > 6σ(*F*). (II) [NdCl(H₂O)₅(C₅H₉NO₂)]Cl₂·[Nd(H₂O)₆(C₅H₉NO₂)]Cl₃, *M_r* = 929.6, monoclinic, *C*2, *a* = 25.076 (5), *b* = 8.132 (2), *c* = 18.361 (4) Å, β = 120.68 (5)°, *V* = 3220.1 Å³, *Z* = 4, *D_m* = 1.93, *D_x* = 1.92 Mg m⁻³, Mo *K*α, λ = 0.71069 Å, μ = 3.76 mm⁻¹, *F*(000) = 1824, *T* = 298 (3) K. Final *R* = 0.040 for 3540 reflections with *F* > 7σ(*F*). These are the first known cases of lanthanide carboxylate complexes where the inner sphere contains Cl ions

attached to the metal. In both structures the Nd ions are eight coordinate. There are three Cl ions bonded to the Nd^{III} centre in (I) while in (II) one Cl ion is attached to Nd(1) and Nd(2) is coordinated exclusively by O atoms. The structure of (I) is that of a linear polymer while that of (II) consists of dinuclear species of two distinct types. The carboxylate group acts as a bridging ligand in both structures.

Introduction. Our investigation of lanthanide complexes with L-α-alanine (Dao, Głowiak, Huskowska & Legendziewicz, 1988, and references therein) revealed that when the stoichiometric ratio Ln^{III}:amino acid is 1:2 the structures consist of pseudosymmetric dinuclear units. However, when