

Fig. 1. Crystal structure of the title complex with displacement ellipsoids of 25% probability in arbitrary crystallographic orientation. The point symmetry of the complex is $\bar{1}$. The terminal C atoms of the methacrylate groups are twofold disordered. As a deviation from the point symmetry $\bar{1}$ of the complex each of the split positions of these atoms is displayed only once on one side of the molecule. Symmetry code: (i) $-x, -y, 1-z$.

final parameters of the non-H atoms are given in Table 1.*

Fig. 1 shows one molecule of the complex, main bond lengths are given in Table 2. The five-membered rings formed by each carboxyl group and the two Cu atoms are planar within 0.02 Å and approximately coplanar with the terminal 2-propenyl groups. Including the Cu—Cu distance of 2.655 (1) Å the coordination of the Cu atom is distorted octahedral with deviations from idealized angles up to 13°. The center of symmetry of the complex is located halfway between the two Cu

* Lists of anisotropic displacement parameters, calculated H-atom positions, bond angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52945 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) of the complex

The e.s.d.'s are 0.001–0.003 Å for distances including the Cu atom, 0.004–0.006 Å for other distances except 0.01–0.02 Å for split-atom participation.

Cu—Cu ⁱ	2.655	C9—C111	1.320	N—C1	1.328
Cu—O1	1.963	C9—C112	1.504	C1—C2	1.367
Cu—O2	1.971	O2—C8 ⁱ	1.249	C2—C3	1.370
Cu—O3	1.955	O3—C12 ⁱ	1.252	C3—C4	1.377
Cu—O4	1.971	O4—C12	1.259	C4—C5	1.370
Cu—N	2.170	C12—C13	1.486	N—C5	1.334
O1—C8	1.252	C13—C141	1.322	C3—C6	1.479
C8—C9	1.483	C13—C142	1.507	C6—C7	1.262
C9—C101	1.505	C13—C151	1.507		
C9—C102	1.321	C13—C152	1.321		

Symmetry operation: (i) $-x, -y, 1-z$.

atoms which are bridged by four methacrylate ligands.

Related literature. This skeleton has been characterized already in previous, less accurate X-ray studies of $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ (van Niekerk & Schoening, 1953) and of two modifications of $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ (Barclay & Kennard, 1961; Hanic, Stempelova & Hanicova, 1964). A comparable study of $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ by neutron diffraction has been reported by Brown & Chidambaram (1973).

References

- BARCLAY, G. A. & KENNARD, C. H. L. (1961). *J. Chem. Soc.* pp. 5244–5251.
 BROWN, G. M. & CHIDAMBARAM, R. (1973). *Acta Cryst.* B29, 2393–2402.
 HANIC, F., STEPELOVA, D. & HANICOVA, K. (1964). *Acta Cryst.* 17, 633–639.
International Tables for Crystallography (1983). Vol. A, pp. 35–37. Dordrecht: Kluwer Academic Publishers.
 KUCHEN, W. & SCHRAM, J. (1988). *Angew. Chem.* 100, 1757–1758; *Angew. Chem. Int. Ed. Engl.* 27, 1695–1697.
 NIEKERK, J. N. VAN & SCHOENING, F. R. L. (1953). *Acta Cryst.* 6, 227–232.
 SHELDRICK, G. M. (1983). *SHELXTL Users Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

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Triaquabis[dihydrogen-1,2,3-benzenetricarboxylato(1-)]copper(II) Trihydrate

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Abstract. $M_r = 589.94$, monoclinic, $C2/c$ (disordered), $a = 28.600$ (5), $b = 6.728$ (2), $c = 11.747$ (2) Å, $\beta =$

95.14 (2)°, $V = 2251.5$ Å³, $Z = 4$, $D_m = 1.85$, $D_x = 1.74$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 9.95$ cm⁻¹, $F(000) = 1212$, $T = 293$ K, $R = 0.065$, for 2335 reflexions with $|F_o| > 4\sigma(|F_o|)$. The coordination

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Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters

$$B_{eq} = \frac{1}{3}(\sum B_{ii} + 2B_{12}\cos\beta).$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Cu	0.0000	0.0832 (1)	0.2500	1.67
O(1W)*	0.0075 (4)	-0.2392 (13)	0.3033 (10)	5.78
O(2W)*	0.0153 (3)	0.1755 (14)	0.4134 (6)	2.23
O(3W)*	-0.0164 (3)	0.0551 (18)	0.0858 (8)	3.70
O(4W)	0.1182 (1)	-0.2535 (6)	0.2164 (3)	2.22
O(5W)*	-0.0047 (8)	0.4563 (15)	0.5305 (18)	9.10
O(1)	0.1637 (1)	0.2621 (7)	-0.0722 (3)	2.89
O(2)	0.0966 (1)	0.1716 (7)	-0.0041 (3)	3.37
O(3)	0.0656 (1)	0.4137 (6)	0.1974 (3)	2.68
O(4)	0.0668 (1)	0.0862 (5)	0.2312 (3)	1.93
O(5)	0.1012 (1)	0.3254 (7)	0.4395 (3)	2.94
O(6)	0.1694 (1)	0.2397 (7)	0.5325 (3)	2.94
C(1)	0.1638 (2)	0.2359 (7)	0.1264 (4)	1.67
C(2)	0.1399 (2)	0.2483 (7)	0.2253 (4)	1.62
C(3)	0.1664 (2)	0.2567 (8)	0.3323 (4)	1.91
C(4)	0.2151 (2)	0.2484 (10)	0.3389 (4)	2.79
C(5)	0.2382 (2)	0.2357 (11)	0.2395 (5)	3.34
C(6)	0.2129 (2)	0.2289 (10)	0.1346 (5)	2.86
C(7)	0.1373 (2)	0.2205 (8)	0.0104 (4)	2.21
C(8)	0.0868 (2)	0.2542 (7)	0.2173 (3)	1.57
C(9)	0.1417 (2)	0.2759 (8)	0.4387 (4)	1.92

* Atoms marked have been treated as disordered (s.o.f. = 0.5)

Table 2. Bond lengths (Å) and angles (°)

Cu—O(4)	194.4 (3)	C(1)—C(2)	140.1 (6)
Cu—O(1W)	226.3 (9)	C(1)—C(6)	139.9 (7)
Cu—O(2W)	202.8 (8)	C(1)—C(7)	150.4 (6)
Cu—O(3W)	195.4 (8)	C(2)—C(3)	140.9 (6)
O(1)—C(7)	131.2 (6)	O(2)—C(8)	151.5 (7)
O(2)—C(7)	120.5 (7)	C(3)—C(4)	139.2 (7)
O(3)—C(8)	124.4 (6)	C(3)—C(9)	149.3 (7)
O(4)—C(8)	128.3 (6)	C(4)—C(5)	139.3 (8)
O(5)—C(9)	120.7 (6)	C(5)—C(6)	137.4 (8)
O(6)—C(9)	132.1 (6)		
O(4)—Cu—O(1W)	88.4 (3)	C(3)—C(2)—C(8)	120.6 (4)
O(4)—Cu—O(2W)	88.4 (2)	C(2)—C(3)—C(4)	120.2 (5)
O(4)—Cu—O(3W)	92.4 (3)	C(2)—C(3)—C(9)	119.6 (4)
O(4)—Cu—O(4)	178.8 (2)	C(4)—C(3)—C(9)	120.1 (4)
O(4)—Cu—O(1W)	92.7 (3)	C(3)—C(4)—C(5)	120.1 (5)
O(4)—Cu—O(2W)	91.1 (3)	C(4)—C(5)—C(6)	120.3 (5)
O(4)—Cu—O(3W)	87.9 (3)	C(1)—C(6)—C(5)	120.4 (5)
O(2W)—Cu—O(1W)	91.4 (4)	O(1)—C(7)—C(1)	112.1 (4)
O(3W)—Cu—O(1W)	100.9 (5)	O(2)—C(7)—O(1)	124.4 (5)
O(3W)—Cu—O(2W)	167.7 (5)	O(2)—C(7)—C(1)	123.4 (5)
O(8)—O(4)—Cu	118.5 (3)	O(3)—C(8)—C(2)	120.2 (4)
C(2)—C(1)—C(6)	120.3 (4)	O(4)—C(8)—O(3)	124.7 (4)
C(2)—C(1)—C(7)	120.7 (4)	O(4)—C(8)—C(2)	115.1 (4)
C(6)—C(1)—C(7)	118.9 (4)	O(5)—C(9)—C(3)	123.7 (4)
C(1)—C(2)—C(3)	118.7 (4)	O(6)—C(9)—O(5)	123.3 (5)
C(1)—C(2)—C(8)	120.7 (4)	O(6)—C(9)—C(3)	113.0 (4)

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

polyhedron is a square pyramid formed by two monodentate carboxylic groups of different acid molecules and three water molecules. The molecule shows idealized symmetry C_{2v} . This symmetry is not exactly given, because the water molecule [O(1W)] is displaced from the twofold axis and the water molecules in the base [O(2W), O(3W)] are not projected on each other. The base of the pyramid is slightly distorted towards a tetrahedron.

Experimental. Blue square pyramidal crystals by diffusion of aqueous solution of $\text{Cu}(\text{ClO}_4)_2$ into 1,2,3-benzenetricarboxylic acid in ethanol. D_m by flotation in an aqueous solution of thallium(I) formate/malonate. Enraf-Nonius CAD-4 diffractometer, Mo $K\alpha$, graphite monochromator. Crystal of about 0.35×0.40 mm (base), 0.50 mm (base-apex). Lattice parameters from 20 reflexions in the range $18.2 < \theta < 27.9^\circ$, intensity measurement $2 < \theta < 28^\circ$ ($-30 \leq h \leq 30$; $0 \leq k \leq 8$; $0 \leq l \leq 14$), three intensity control reflexions every hour of data collection, two reflexions for orientation every 200 reflexions, no significant decay. 2674 reflexions measured, Lp correction, no correction for absorption. 2335 reflexions with $|F_o| > 4\sigma(|F_o|)$ were used for structure refinement. Systematic extinctions $hkl: h+k=2n, h0l: h,l=2n$ indicated space groups $C2/c$ or Cc . According to $Z=4$ the Cu atom was located on the twofold axis in $C2/c$, y coordinate from a Patterson synthesis. O and C positions were obtained from subsequent Fourier syntheses. One water O atom [O(1W)] was located on the twofold axis representing the apex of the coordination polyhedron, another [O(5W)], belonging to a crystal water molecule on a centre of symmetry.

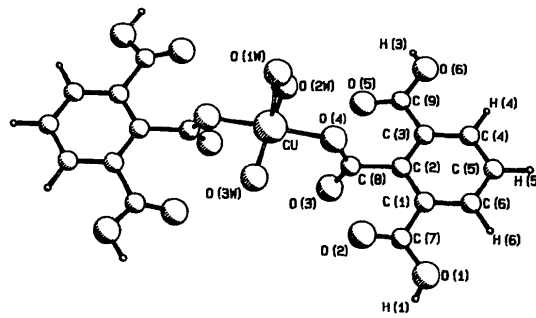


Fig. 1. View of the molecule and numbering scheme.

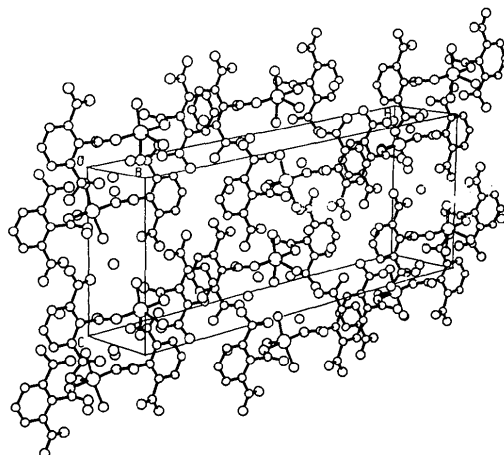


Fig. 2. Perspective view of the unit cell.

After anisotropic refinement of this model all H atoms except those belonging to water molecules in the coordination sphere and to O(5W) were located in a difference Fourier map and added to the model for final calculation with fixed isotropic thermal parameters of 0.08 Å², benzene H left riding on the C atoms with C—H bond lengths fixed to 1.08 Å, and constraints of O—H bond lengths being not shorter than 0.85 Å and angles H—O—H in the water molecule not smaller than 104°. Full-matrix refinement converged at $R = 0.074$. Unusually high thermal parameters resulted for water O atoms in the coordination sphere [O(1W): $B_{\text{eq}} = 21.45$, O(2W): $B_{\text{eq}} = 10.09$ Å²] and the crystal water on the centre of symmetry [O(5W): $B_{\text{eq}} = 17.71$ Å²]. Therefore a full-matrix refinement in *Cc* was tried, which resulted in R values of $R = 0.037$, $wR = 0.033$ [$w = 1/\sigma^2(F_o)$] and thermal parameters of $B_{\text{eq}} = 5.38$ [O(1W)], 2.95 [O(2W)], 4.57 [O(3W)], 8.84 Å² [O(5W)]. On the other hand, severe distortions in the geometry of the anions were observed, e.g. bond lengths in the benzene rings ranging from 1.352 to 1.448 Å. This was taken as a strong indication for *Cc* not being the correct space group. Thus refinement in *C2/c* was performed treating part of the atoms as disordered (s.o.f. = 0.5) by untying the coordination water O atoms from the twofold axis, and the crystal water O(5W) from the centre of symmetry. This refinement converged at $R = 0.065$, $wR = 0.061$ [$w = 1/\sigma^2(F_o)$]. Max. Δ/σ on final cycle = 0.007, $\Delta\rho$ fluctuations within +0.60 and -0.61 e Å⁻³. All calculations

were performed with *SHELX76* (Sheldrick, 1976) using scattering factors of Cromer & Mann (1968); drawings by *PLUTO* (Motherwell & Clegg, 1976).

Atomic positions and equivalent isotropic thermal parameters are given in Table 1,* bond lengths and angles in Table 2. Fig. 1 shows the surrounding of the Cu atom, Fig. 2 a perspective view of the unit cell.

Related literature. An analogous coordination sphere was observed in copper(II) 1,2,4,5-benzenetetracarboxylate decahydrate (Usabaliyev, Shnulin & Mamedov, 1982) and in *catena-triaqua-μ*-[1,3,5-benzenetricarboxylato(2-)]-copper(II) (Pech & Pickardt, 1988).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53015 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 MOTHERWELL, W. D. S. & CLEGG, W. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
 PECH, R. & PICKARDT, J. (1988). *Acta Cryst.* **C44**, 992–994.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 USABALIEV, B. T., SHNULIN, A. N. & MAMEDOV, K. H. S. (1982). *Koord. Khim.* **8**(11), 1532–1538.

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Structure of an Iron(II) Bromide Complex of 15-Crown-5 at 163 K

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Abstract. (1,4,7,10,13-Pentaoxacyclopentadecane)-iron(II) bromide dichloromethane solvate (I), [Fe(C₁₀H₂₀O₅)]²⁺·2Br⁻·CH₂Cl₂, $M_r = 520.87$, orthorhombic, $P2_12_12_1$, $a = 12.088$ (9), $b = 13.425$ (7), $c = 11.235$ (6) Å, $V = 1823$ (3) Å³, $Z = 4$, $D_x = 1.897$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 54.791$ cm⁻¹, $F(000) = 1032$, $T = 163$ K, $R = 0.0436$ for 1875 reflections ($F \geq 4\sigma_F$). The Fe²⁺ ion is coor-

minated to the five oxygens of the crown and to the two Br⁻ ions. The range of Fe···O distances is 2.175 (6)–2.265 (6) Å. The average C—O and C—C bond lengths in the crown are 1.437 (8) and 1.502 (11) Å. The O atoms are nearly planar [r.m.s. deviation: 0.0947 (3) Å], with the cation only -0.0122 (12) Å from the mean plane. The average O—Fe—O angle for adjacent O atoms is 72.1 (16)°. All C—O and C—C torsion angles in the crown are *anti* and *gauche*, respectively. The Fe—Br distances are 2.6228 (15) and 2.6281 (14) Å. The CH₂Cl₂ molecule is well behaved.

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