

Hexaaquacobalt(II) Dihydrogen 1,2,4,5-Benzenetetracarboxylate, $[\text{Co}(\text{H}_2\text{O})_6][\text{C}_{10}\text{H}_4\text{O}_8]$

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Abstract. $M_r = 419.16$, monoclinic, $P2/m$, $a = 6.530(4)$, $b = 9.930(4)$, $c = 6.508(3)$ Å, $\beta = 115.48(3)^\circ$, $V = 381.0(4)$ Å³, $Z = 1$, $D_m = 1.83(2)$, $D_x = 1.827(3)$ g cm⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, $\mu = 11.259$ cm⁻¹, $F(000) = 215$, $T = 295$ K. Final $R = 0.034$ for 2158 observed unique reflections. The structure consists of a three-dimensional hydrogen-bonded network linking octahedral hexaaquacobalt(II) cations with dihydrogen 1,2,4,5-benzenetetracarboxylate anions. There are intramolecular hydrogen bonds between adjacent carboxyl groups.

Introduction. The report by Wroblewski & Brown (1979) that mixed-valence complexes of tetradentate ligands with delocalized electrons were electrically conducting suggested that the limited number of compounds known to be one-dimensional conductors could be substantially increased. One-dimensional conductors are of considerable theoretical and practical interest (Miller & Epstein, 1976). In an attempt to prepare new one-dimensional conductors, a number of salts of 1,2,4,5-benzenetetracarboxylic acid were prepared in this laboratory. This study reports the first determination of the crystal structure of a salt of this acid. Other results will be reported later. Salts of this acid are also of interest as potential detergent builders (Ruppert, 1975), catalysts (Ota & Imamura, 1971), in gravimetric analysis (Mukherji, 1964), as heat stabilizers (Grinblat *et al.*, 1973), and in applying dyes (Ichikawa, Yanagi, Hosoi, Nishikawa, Masuda & Ito, 1970).

Experimental. D_m measured by flotation in aqueous lead perchlorate. Pink rods (from water) (calc: C 28.65, H 3.85, Co 14.06%; found: C 28.70, H 3.72, Co 13.37%), $0.4 \times 0.4 \times 0.3$ mm. Picker FACS-I automatic diffractometer, graphite-monochromatized Mo $K\alpha_1$. 14 reflections used for measuring lattice parameters, $35 < 2\theta < 45^\circ$. Absorption corrections on I (Templeton & Templeton, 1973) 1.354 to 1.680. $2\theta < 80^\circ$. $0 \leq h \leq 11$, $0 \leq k \leq 17$, $-11 \leq l \leq 10$. Three

standard reflections (204, 090, 60 $\bar{3}$), variations 0.992 to 1.012. 2622 measured, 2477 unique, $R_{\text{int}} = 0.0121$, 319 unobserved [$I < 3\sigma(I)$]. Structure solved by Patterson map and MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). F used in LS refinement. H atoms located in difference map. Non-H anisotropic, H isotropic fixing only those parameters constrained by symmetry. $R = 0.034$, $R_w = 0.046$, $S = 2.27$; $w = 1/\sigma^2(F)$. $\Delta/\sigma_{\text{max}} = 0.13$ (non-H), 0.55 (H). $\Delta\rho = -1.03-0.55$ e Å⁻³. Extinction[†] parameter 0.71×10^{-7} mm⁻¹. Atomic scattering factors, f' and f'' from *International Tables for X-ray Crystallography* (1974). Details of computer programs used have been deposited.

Discussion. Final atomic parameters are listed in Table 1.† The crystal structure (Fig. 1) consists of octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions and planar $\text{C}_{10}\text{H}_4\text{O}_8^{2-}$ ions (Fig. 2) linked together by a three-dimensional hydrogen-bonding network involving all H atoms of the water molecules. An additional symmetrical intramolecular hydrogen bond exists between adjacent carboxyl groups in the anion. Bond distances, bond angles, and the hydrogen bonding are reported in Table 2.

The octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions are situated with Co^{II} at the inversion center (0,0,0), one pair of O atoms on the twofold axis (0,y,0), and the other two pairs of O atoms in the mirror plane (x,0,z); the two O atoms in a pair are related to each other by the inversion center. The orthogonality of the octahedral coordination is perfect except for the 90.16(11)° angle between O atoms lying in the mirror plane. The Co...O distances are 2.048(2), 2.063(2) and 2.115(1) Å; the longest distance is to the O atoms on the twofold axis.

† Lists of structure factors, anisotropic thermal parameters, least-squares planes (Table 3), computer programs used and a comparison of intramolecular hydrogen bonding between adjacent carboxyl groups of several substituted benzene compounds (Table 4) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38641 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates and isotropic thermal parameters with calculated standard deviations in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}/B_{iso}(\text{\AA}^2)$
Co	0	0	0	1.50 (1)
O(1)	0	0.2129 (1)	0	2.99 (5)
O(2)	0.2526 (3)	0	0.3250 (2)	3.25 (5)
O(3)	0.2396 (4)	0	-0.1277 (4)	3.77 (8)
O(4)	0.1990 (2)	0.38013 (9)	0.3853 (1)	2.86 (3)
O(5)	0.3072 (2)	0.21106 (9)	0.6244 (1)	3.10 (3)
C(1)	0.500	0.3637 (1)	1.0	1.63 (4)
C(2)	0.3928 (2)	0.42881 (8)	0.7906 (1)	1.45 (2)
C(3)	0.2927 (2)	0.33299 (9)	0.5890 (2)	1.83 (3)
H(1)	0.077 (4)	0.249 (3)	0.106 (4)	4.3 (5)
H(2)	0.276 (4)	0.076 (3)	0.400 (4)	3.9 (5)
H(3)	0.234 (5)	0.080 (3)	-0.198 (5)	5.5 (7)
H(4)	0.217 (7)	0.500	0.423 (7)	4.4 (8)
H(5)	0.500	0.265 (6)	1.000	6.5 (11)

Table 2. Bond distances (Å) and angles (°) in the title compound and hydrogen-bond geometry of the anion

(A) Distances and angles

Co—O(1)	2.115 (1)	C(1)—C(2)	1.394 (1)
Co—O(2)	2.048 (2)	C(2)—C(2 ^{iv})	1.414 (2)
Co—O(3)	2.063 (2)	C(2)—C(3)	1.522 (1)
		C(3)—O(4)	1.286 (1)
		C(3)—O(5)	1.299 (1)
O(1)—Co—O(1 ⁱ)	180.00	C(2)—C(1)—C(2 ⁱⁱⁱ)	124.72 (6)
O(1)—Co—O(2)	90.00 (3)	C(1)—C(2)—C(2 ^{iv})	117.64 (7)
O(1)—Co—O(3)	90.00 (3)	C(1)—C(2)—C(3)	113.66 (10)
O(2)—Co—O(2 ^{iv})	180.00	C(2 ^{iv})—C(2)—C(3)	128.69 (5)
O(2)—Co—O(3)	90.16 (11)	C(2)—C(3)—O(4)	119.92 (9)
O(3)—Co—O(3 ^{iv})	180.0	C(2)—C(3)—O(5)	118.97 (9)
		O(4)—C(3)—O(5)	121.09 (8)

(B) Hydrogen-bond geometry

	H...O	O...O	O—H...O
O(1)—H(1)...O(4)	2.098 (26) Å	2.816 (2) Å	162.1 (21)°
O(2)—H(2)...O(5)	1.932 (27)	2.778 (2)	163.3 (16)
O(3)—H(3)...O(5 ^v)	1.930 (31)	2.793 (2)	157.2 (18)
O(4)...H(4)...O(4 ^{iv})	1.211 (7)	2.381 (2)	159.0 (18)

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

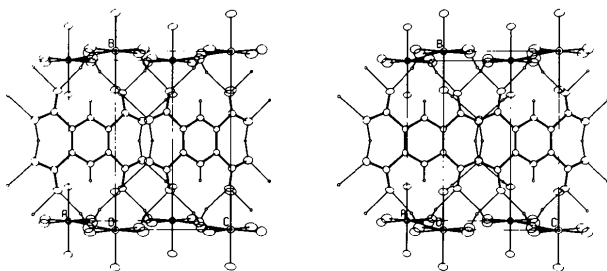


Fig. 1. Stereoview of the crystal structure of the title compound, drawn with ORTEP (Johnson, 1965), with 50% probability ellipsoids. Hydrogen bonds are indicated by fine lines.

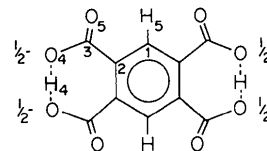


Fig. 2. The dihydrogen 1,2,4,5-benzenetetracarboxylate ion, $[\text{C}_{10}\text{H}_4\text{O}_8]^{2-}$

The $[\text{C}_{10}\text{H}_4\text{O}_8]^{2-}$ ion lies with the non-substituted ring atoms on the twofold axis ($\frac{1}{2}, y, 1$) and the ring bisected by the mirror plane ($x, \frac{1}{2}, z$). The anion is quite planar, as the least-squares planes (Table 3, deposited) will attest. The central six-atom aromatic ring is constrained by the $2/m$ symmetry to be absolutely planar. If the anion is viewed as a three-ring molecule (the outer rings closed by the symmetrical intramolecular hydrogen bonds), it shows a slight 'chair' shape as the planes of the outer rings are tilted $2.3(2)^\circ$ with respect to the plane of the central ring. The carboxyl group [C(2), C(3), O(4), and O(5)] is planar to within $\pm 0.007(1)$ Å and is rotated slightly about the C(2)—C(3) bond in addition to being displaced from the plane of the central ring; the torsion angles C(1)—C(2)—C(3)—O(5) of $2.01(15)^\circ$ and C(1)—C(2)—C(3)—O(4) of $-176.56(10)^\circ$ reflect this slight rotation about the C(2)—C(3) bond. The anion is quite long, in relation to the unit-cell parameters, extending from hydrogen bonds from O(1) at (0, y , 0) to bonds from O(1) at (1, y , 2).

The very short intramolecular hydrogen bond has occasionally been observed in other 1,2-benzenedicarboxylic acid derivatives. Table 4 (deposited) compares the short, nearly symmetrical hydrogen bonds in four compounds (some with both X-ray and neutron structure determinations) with that in the present structure. The interatomic distances are very similar among all the listed compounds; the O(4)...O(4^v) distance of 2.381(2) Å in the present structure is among the shortest reported to date. The differences to note are that the H atom in the present structure is constrained by symmetry to be equidistant from the two O atoms and that the H atom is displaced inwards (towards the aromatic ring) from the line joining the two O atoms involved in the hydrogen bond.

The structure of the dihydrogen 1,2,4,5-benzenetetracarboxylate anion differs from that of the parent acid (Takusagawa, Hirotsu & Shimada, 1971) (reported as the dihydrate) primarily in the presence of the intramolecular hydrogen bond and in the related rotations of the carboxyl groups from the plane of the benzene ring; these rotations are 18 and 74° for the parent acid and about $\pm 2^\circ$ for the present structure.

There appears to be considerable distortion of the bond angles in the present structure at C(2) where the carboxyl group is attached to the benzene ring. While in the parent acid the maximum (averaged) deviation from 120° is only 1.0° , the present structure exhibits an $8.69(5)^\circ$ deviation as the carboxyl groups are forced apart. In contrast, while the parent acid exhibits (averaged) deviations from 120° of up to 6.4° at the carboxyl C, the angles in the present structure are within $1.09(8)^\circ$ of 120° around C(3). The enlarged ring angle at C(1) in the present structure [$124.72(6)$ vs 120.6° in the parent acid] appears to be associated with the distortions at C(2). The remaining significant differences in bond lengths appear to be the results of the rotations of the carboxyl groups, the formation of the intramolecular hydrogen bonds, and of the loss of two protons from the parent acid. The effects of intermolecular hydrogen bonds on the dihydrogen 1,2,4,5-benzenetetracarboxylate anion have not been considered.

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