Crystal structure of disodium 1,2,4,5-tetrahydrogen-benzene-hexacarboxylate monohydrate, $Na_2(C_{12}H_4O_{12}) \cdot H_2O$

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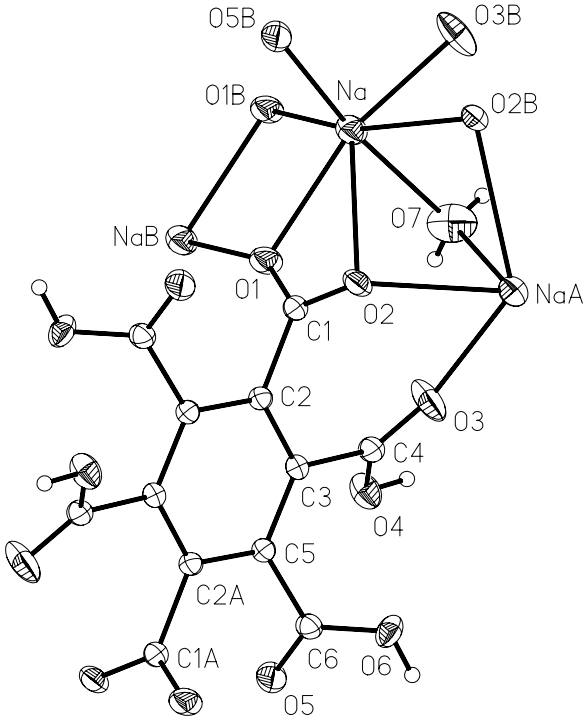

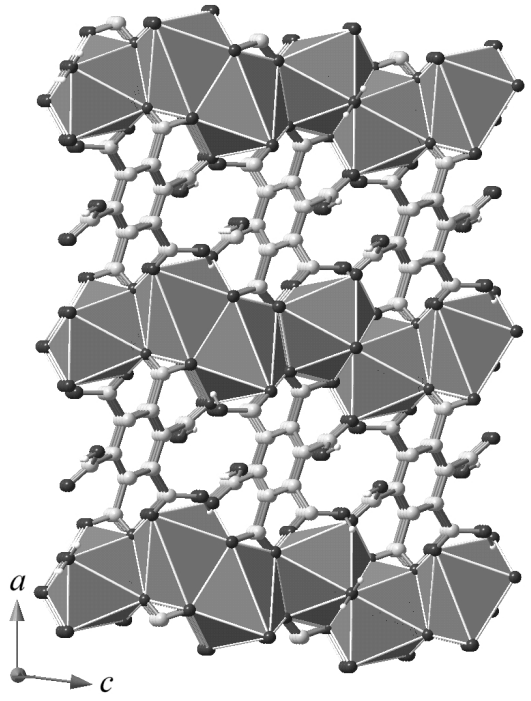

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Abstract

$C_{12}H_6Na_2O_{13}$, monoclinic, $C12/c1$ (no. 15), a = 19.313(5) Å, b = 6.660(2) Å, c = 11.199(3) Å, β = 97.072(4)°, V = 1429.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.032, $wR_{ref}(F^2)$ = 0.097, T = 293 K.

Source of material

The title compound was prepared by stirring mellitic acid (0.10 g, 0.29 mmol) and NaOH (0.03 g, 0.75 mmol) in 2 ml of water at 25 °C for 18 h under nitrogen. The solvent was then removed under reduced pressure leaving behind a white solid which was washed with 10 ml of hot methanol, filtered and dried under vacuum (yield 87 %). Crystals for X-ray diffraction studies were prepared by layering methanol over the aqueous solution in a 5 mm NMR tube.

Discussion

The title structure consists of a 3D framework of sodium ions coordinated to 3,6-dicarboxylato-benzene-1,2,4,5-tetracarboxylic acid anions (H_4dbt^{2-}) and water molecules (figure, top). The Na^+ ions possess a seven-coordinated distorted pentagonal bipyramidal environment defined by six O atoms from five H_4dbt^{2-} ligands and one water molecule with the Na—O bond distances averaged to 2.503 Å. In the axial position the bond angle of O7–Na–O5^{iv} is 170.17(5)°, showing a large deviation from linearity. The bond angles between atoms in the equatorial plane to the axial Na—O7 and Na—O5^{iv} vectors range from 70.91(4)° to 102.48(5)°. The water molecule O7 sits on a twofold axis (which pass through O7 and dissects the Na···Na^i bond).

Interatomic distances and angles of the H_4dbt^{2-}anion are within the ranges of values of previously determined by mellitic acid [1]. The center of mass of the mellitate anion coincides with a crystallographic inversion center, the two oxygen atoms (O1 and O2) of carboxylato group chelate one Na atom and each O atom bridges another Na atom with a Na···Na separation of 3.607(1) Å (Na···Na^i, symmetry code i: 1–x,–y,1–z), 3.629(2) Å (Na···Na^{ii}, symmetry code ii: 1–x,y,1/2–z), respectively. The remaining carboxylic groups (O3 and O6) only act as a unidentate ligand to bind one metal ion. Through these coordination modes each H_4dbt^{2-} ligand bridges eight Na atoms to form a three-dimensional framework (figure, bottom). The Na and Na^i atoms are bridged by two symmetry-related O1 atoms at x,y,z and 1–x,–y,1–z, however, the Na and Na^{ii} atoms are bridged by one water molecule (O7) and two O2 atoms at x,y,z and 1–x,y,1/2–z, the [NaO_7] polyhedra are alternately edge-shared and face-shared to generate metal-oxygen chains extending infinitely along the [001] directions. The carboxyl O6 atoms act as hydrogen donors to carboxylato O2 atom to form strong intermolecular hydrogen bond with d(O···O) = 2.436 Å. The O6 atom also acts as hydrogen acceptor to carboxyl group O4–H4 to form hydrogen bond with d(O···O) = 2.578 Å, which makes a significant contribution to stabilization of the crystal structure.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.18 × 0.20 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.23 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX II CCD, φ/ω
$2\theta_{max}$:	55.46°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4038, 1558
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1311
$N(param)_{refined}$:	124
Programs:	SHELXS-97 [2], SHELXL-97 [3]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(4)	8*f*	0.7064	–0.3203	0.3080	0.044
H(6)	8*f*	0.8695	–0.0754	0.2531	0.040
H(7)	8*f*	0.5289	–0.2364	0.2805	0.081

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	8*f*	0.44681(4)	0.1090(1)	0.37276(5)	0.0234(4)	0.0354(4)	0.0269(3)	0.0033(3)	–0.0005(3)	0.0051(2)
C(1)	8*f*	0.60064(8)	0.2254(2)	0.4211(1)	0.0169(8)	0.0207(7)	0.0183(6)	–0.0014(6)	0.0015(5)	–0.0025(5)
C(2)	8*f*	0.67849(8)	0.2413(2)	0.4598(1)	0.0151(8)	0.0203(7)	0.0159(6)	–0.0003(5)	0.0022(5)	0.0012(5)
C(3)	8*f*	0.72458(8)	0.1065(2)	0.4163(1)	0.0168(8)	0.0206(7)	0.0159(5)	–0.0007(6)	0.0005(5)	–0.0018(5)
C(4)	8*f*	0.69537(8)	–0.0562(2)	0.3311(1)	0.0179(9)	0.0245(7)	0.0217(6)	–0.0015(6)	0.0020(6)	–0.0051(6)
C(5)	8*f*	0.79615(8)	0.1160(2)	0.4546(1)	0.0160(8)	0.0202(7)	0.0158(6)	0.0014(5)	0.0017(5)	0.0008(5)
C(6)	8*f*	0.84704(8)	–0.0146(2)	0.3972(1)	0.0174(8)	0.0206(7)	0.0220(6)	–0.0008(6)	0.0006(6)	–0.0037(5)
O(1)	8*f*	0.56410(6)	0.1254(2)	0.47908(9)	0.0190(7)	0.0381(7)	0.0282(5)	–0.0062(5)	0.0035(5)	0.0090(5)
O(2)	8*f*	0.57446(6)	0.3203(2)	0.32485(9)	0.0175(6)	0.0336(6)	0.0227(5)	–0.0018(5)	–0.0028(4)	0.0056(4)
O(3)	8*f*	0.64870(8)	–0.0256(2)	0.2516(1)	0.0419(9)	0.0376(7)	0.0432(7)	0.0087(6)	–0.0238(6)	–0.0151(6)
O(4)	8*f*	0.72455(6)	–0.2298(2)	0.3549(1)	0.0335(8)	0.0199(5)	0.0321(6)	–0.0012(5)	–0.0055(5)	–0.0052(4)
O(5)	8*f*	0.89030(7)	–0.1174(2)	0.4574(1)	0.0289(7)	0.0405(7)	0.0260(5)	0.0158(5)	–0.0017(5)	–0.0022(5)
O(6)	8*f*	0.84000(7)	0.0002(2)	0.28139(9)	0.0340(7)	0.0278(6)	0.0200(5)	0.0119(5)	0.0077(4)	–0.0004(4)
O(7)	4*e*	½	–0.1497(3)	¼	0.043(1)	0.049(1)	0.072(1)	0	0.011(1)	0

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