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A Neutron Diffraction Study on Hydrogen Bonding in the Mineral Mellite ($Al_2[C_6(COO)_6] \cdot 16H_2O$) at 15 K*

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Lattice constants for tetragonal $Al_2[C_6(COO)_6] \cdot 16\,H_2O$ at 15 K are $a = 1555.3(5)$ and $c = 2311.0(8)$ pm, $Z = 8$, space group $I4_1/acd$. Anisotropic refinement on single-crystal neutron diffraction data led to $R_w = 0.039$. The crystal structure is made up by barely distorted $Al(H_2O)_6^{3+}$ octahedra linked by strong asymmetric hydrogen bonds to the $[C_6(COO)_6]^{6-}$ anions yielding a complicated three-dimensional framework. Additional water molecules not bound to Al^{3+} participate in hydrogen bonding as well. Hydrogen bonds involving water molecules bound to Al^{3+} as proton donors are markedly shorter ($O \cdots H_2O$ 257.6–266.4 pm) than those with noncoordinated water molecules (271.0 and 272.4 pm). O–H bond lengths corrected for thermal motion range from 99.5 up to 101.3 pm. The hexaanion has 222 symmetry with C–O bonds being equal (125.5–125.7 pm) within the limits of experimental error. The O–C–O angles are widened up considerably (124.96 and 126.30°). The C_6 ring of the anion deviates slightly, but significantly from an ideal hexagon. © 1991 Academic Press, Inc.

Introduction

Mellite ($Al_2[C_6(COO)_6] \cdot 16H_2O$) is a naturally occurring inorganic derivative of benzene hexacarboxylic acid (mellitic acid). Giacovazzo *et al.* furnished an X-ray structure analysis based on photographically determined intensity data (*1*). It revealed that mellite crystallizes in space group $I4_1/acd$ with approximate lattice dimensions $a = 1553$ pm and $c = 2319$ pm in contrast to standard textbooks of mineralogy which claim the space group $P4_12$ or $P4_32$ with $a = 2200$ pm and $c = 2330$ pm and 18 molecules of water per formula unit (*2, 3*). Giacovazzo's results are fully confirmed by our study.

Mellite attracted interest in the course of investigations on structure governing principles in polymeric coordination compounds of anions of various benzene carboxylic acids (*4–9*). These polydentate ligands are valuable components for the design of novel materials with tailor-made properties promising interesting applications in a wide field of solid state chemistry. New layer-like

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* Dedicated with best wishes to Prof. Dr. H. Jagodzinski on the occasion of his 75th birthday.

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structures capable of undergoing topotactical intercalation or ion exchange reactions are accessible in this way as well as compounds with zeolite-like or clathrate-like structures. The studies proved that in addition to the type of cations and anions employed a third component of equal importance has to be considered: the water of crystallization (*10–14*). Therefore the understanding of the hydrogen bonding systems is crucial for a successful design of these new solid state structures with predetermined structural properties and demands precise neutron diffraction data.

Furthermore, the crystal structure of $Al_2[C_6(COO)_6] \cdot 16H_2O$ which consists of $Al(H_2O)_6^{3+}$ octahedra linked to the $[C_6(COO)_6]^{6-}$ anions by strong intermolecular hydrogen bonds shows short water–oxygen contacts in a range hitherto scarcely studied by precise single crystal neutron diffractometry (*15*). This work is also part of a study focusing on influences on hydrogen bonding caused by strongly polarizing ions like Al^{3+}.

Experimental

A single crystal of naturally grown $Al_2[C_6(COO)_6] \cdot 16H_2O$ from Tatabanya (Hungary) with dimensions 1.4 × 1.8 × 4.0 mm was chosen for data collection on the D9 four-circle diffractometer at the Institute Laue-Langevin, Grenoble, France, under the following experimental conditions: measuring temperature 15 K chosen to reduce the effects of thermal motion and consequently to obtain a better definition of positional parameters, tetragonal cell with $a = 1555.3(5)$ pm and $c = 2311.0(8)$ pm (at 15 K), $V = 5590.2 \cdot 10^6$ pm^3, M_r 678.33, $Z = 8$, $D_{calc} = 1.61$ g · cm^{-3}, space group $I4_1/acd$ (No. 142). Data collection was carried out with thermal neutrons of wavelength 71.11 pm, Ge (220) monochromator, $\lambda/2$ contamination filtered by 0.25-mm iridium foil. A 32 × 32 pixel multidetector was employed and data processing made use of the program ADVANCE in order to increase the accuracy particularly on weak reflections (*16, 17*).

A numerical absorption correction (*18*) (calculated $\mu = 1.3$ cm^{-1}) and an isotropic extinction correction (*19*) were applied. A total of 4038 reflections up to $\Theta_{max} = 36°$ were recorded and merged to 3331 unique reflections (merging $R = 0.020$). There were 2337 reflections having $I > 2\sigma_I$ considered observed and employed for structure refinement. Scattering lengths were taken from Ref. (*20*). Refinement on $|F|$ was carried out using the program system Prometheus (*21*), minimizing $\Sigma w(|F_o| - |F_c|)^2$ and assigning weights $1/\sigma^2_{|F|}$ derived from counting statistics. Starting parameters were obtained from the results of the X-ray structure determination (*1*). No significant anharmonic motion could be detected on the hydrogen atoms. Full-matrix least-squares refinement with harmonically anisotropic displacement parameters for all atoms converged at $R = 0.048$ and $R_w = 0.039$, GOF $= 1.30$ (171 parameters). Final atomic parameters are given in Table I. Supplementary material has been deposited.[1]

Results and Discussion

Al^{3+} is situated on a twofold axis of space group $I4_1/acd$ (Wyckoff notation 16*e*). It is coordinated by water molecules (O(w1), O(w2), O(w3), and O(w4)) in a slightly distorted octahedral fashion (Fig. 1). A further crystallographically independent water molecule (O(w5)) has no coordinative contact with Al^{3+}, but is involved in hydrogen bonds with water molecules (O(w2), O(w3)) of the

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[1] Further details of the structure determination have been deposited as Supplementary Publication No. CSD 55079. Copies may be obtained through Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany.

TABLE I

PARAMETERS FOR $Al_2[C_6(COO)_6] \cdot 16H_2O$

Atom	x	y	z	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Al	0.33164(15)	0.5	0.25	0.00293(84)	0.00417(84)	0.00359(81)	0	0	−0.00101(72)
O(w1)	0.45281(9)	0.5	0.25	0.00489(54)	0.00691(55)	0.00902(53)	0	0	−0.00039(48)
O(w2)	0.33309(7)	0.61346(7)	0.22181(4)	0.00867(42)	0.00495(40)	0.00862(39)	−0.00054(34)	−0.00191(33)	0.00074(33)
O(w3)	0.32959(7)	0.54165(7)	0.32600(4)	0.00773(42)	0.00912(43)	0.00547(38)	0.00214(34)	−0.00106(33)	−0.00167(33)
O(w4)	0.20829(9)	0.5	0.25	0.00456(54)	0.00602(53)	0.00904(55)	0	0	−0.00045(48)
O(w5)	0.27570(7)	0.79943(7)	0.34470(5)	0.00878(42)	0.00674(42)	0.00839(39)	0.00016(33)	0.00096(34)	−0.00100(33)
O(1)	0.49829(7)	0.14651(7)	0.51657(4)	0.00579(39)	0.01008(41)	0.00561(33)	0.00172(36)	−0.00007(32)	0.00240(32)
O(2)	0.36139(6)	0.17144(7)	0.49361(4)	0.00452(38)	0.00733(40)	0.00881(39)	−0.00019(33)	0.00119(32)	0.00126(33)
O(3)	0.39024(7)	0.04421(7)	0.39113(4)	0.00572(40)	0.00551(40)	0.00991(39)	−0.00112(32)	−0.00076(33)	0.00130(33)
C(1)	0.43663(6)	0.18663	0.375	0.00430(29)	0.00430	0.00441(41)	−0.00060(36)	−0.00022(26)	0.00022
C(2)	0.46949(6)	0.21710(6)	0.42767(4)	0.00492(34)	0.00568(35)	0.00381(28)	−0.00062(25)	0.00008(26)	0.00049(27)
C(3)	0.44078(6)	0.17582(6)	0.48392(4)	0.00508(34)	0.00563(35)	0.00491(30)	−0.00037(27)	0.00012(25)	0.00089(26)
C(4)	0.36800(6)	0.11800	0.375	0.00486(28)	0.00486	0.00549(44)	.00009(38)	−0.00060(28)	0.00060
H(1)	0.49183(14)	0.54919(14)	0.24417(10)	0.01702(91)	0.01599(84)	0.02988(98)	−.00137(74)	0.00049(81)	0.00298(79)
H(2)	0.36115(14)	0.66293(13)	0.24199(9)	0.02100(93)	0.01455(84)	0.01999(88)	−.00209(71)	−0.00548(74)	−0.00109(69)
H(3)	0.29190(15)	0.63948(14)	0.19414(9)	0.02147(97)	0.01950(92)	0.02076(88)	−.00025(76)	−0.00650(77)	0.00247(75)
H(4)	0.28093(14)	0.57589(14)	0.34200(9)	0.01643(88)	0.02014(95)	0.01826(86)	0.00417(71)	0.00123(70)	−0.00183(73)
H(5)	0.37829(13)	0.53853(15)	0.35337(9)	0.01448(86)	0.02537(103)	0.01759(83)	0.00329(74)	−0.00476(68)	−0.00209(75)
H(6)	0.16989(14)	0.45036(14)	0.24910(11)	0.01707(89)	0.01676(88)	0.03138(106)	−0.00294(73)	−0.00069(83)	−0.00111(86)
H(7)	0.32578(14)	0.78559(14)	0.32024(9)	0.01890(94)	0.02063(97)	0.02225(95)	0.00050(77)	0.00646(74)	−0.00195(77)
H(8)	0.24795(15)	0.74404(15)	0.35346(9)	0.02240(90)	0.01735(89)	0.02398(90)	−0.00473(80)	0.00348(83)	0.00098(77)

Note. w, water oxygen atom; anisotropic temperature factors in the form $\exp(-2\pi^2(U^{11}h^2a^{*2} + \cdots + 2U^{12}hka^*b^* + \cdots))$.

$Al(H_2O)_6^{3+}$ octahedron and with oxygen atoms of the $[C_6(COO)_6]^{6-}$ anion (Fig. 6).

The Al–H_2O distances (Table II) cover the lower range known for sixfold Al–O coordination (*22*). This points to water oxygen atoms which are negatively polarized to a considerable extent. Thus the bonding order calculated employing the method of Brown (*23*) exceeds the expected value of 3.0 markedly. Since Al, O(w1), and O(w4) lie on the same twofold axis, both H_2O molecules are

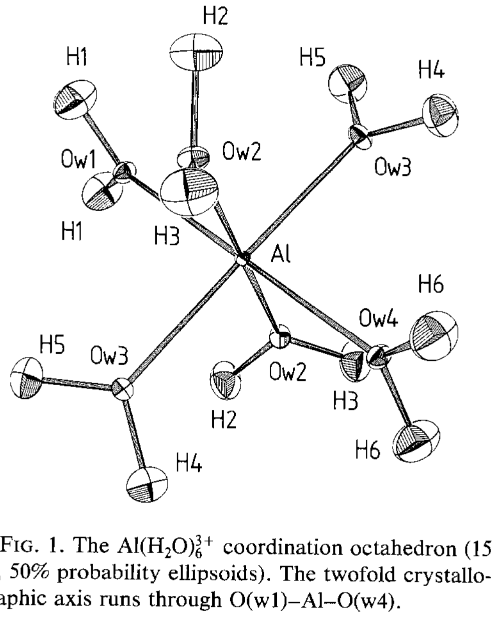

FIG. 1. The $Al(H_2O)_6^{3+}$ coordination octahedron (15 K, 50% probability ellipsoids). The twofold crystallographic axis runs through O(w1)–Al–O(w4).

TABLE II

THE COORDINATION SPHERE OF Al

			Bonding order
Al–O(w3)	187.2(1) pm	2×	0.541
Al–O(w2)	188.1(1)	2×	0.530
Al–O(w1)	188.5(3)		0.525
Al–O(w4)	191.8(3)		0.487
			Σ = 3.154

Angles A–Al–B (°)

A/B			A–B (pm)
O(w3)/O(w3)′	178.05(15)		374.4
O(w3)/O(w2)	89.99(4)	2×	265.4
O(w3)/O(w2)′	90.03(4)	2×	265.5
O(w3)/O(w1)	90.98(8)	2×	267.9
O(w3)/O(w4)	89.02(8)	2×	265.8
O(w2)/O(w2)′	178.63(15)		376.2
O(w2)/O(w1)	89.31(8)	2×	264.7
O(w2)/O(w4)	90.69(8)	2×	270.3
O(w1)/O(w4)	180.0		380.3

Note. w, water oxygen atom.

TABLE III

WATER AND HYDROGEN BONDS

	Uncorrected	Riding Model bond length correction		
O(w1)–H(1)	98.6(2)	100.3	H(1)–O(w1)–H(1)′	104.00(22)
H(1)–O(2)	166.0(2)		O(w1)–H(1)–O(2)	162.48(21)
O(w1)–O(2)	261.7(2)			
O(w2)–H(2)	100.0(2)	101.3	H(2)–O(w2)–H(3)	105.59(20)
O(w2)–H(3)	99.2(2)	100.8	O(w2)–H(2)–O(1)	170.08(21)
H(2)–O(1)	159.1(2)		O(w2)–H(3)–O(w5)	168.89(21)
H(3)–O(w5)	167.7(3)			
O(w2)–O(1)	258.2(2)			
O(w2)–O(w5)	265.7(2)			
O(w3)–H(4)	99.7(2)	101.0	H(4)–O(w3)–H(5)	111.77(20)
O(w3)–H(5)	98.8(2)	100.3	O(w3)–H(4)–O(3)	170.84(21)
H(4)–O(3)	158.7(2)		O(w3)–H(5)–O(w5)	171.90(21)
H(5)–O(w5)	165.6(2)			
O(w3)–O(3)	257.6(2)			
O(w3)–O(w5)	263.8(2)			
O(w4)–H(6)	97.6(2)	99.5	H(6)–O(w4)–H(6)′	104.57(22)
H(6)–O(2)	171.9(2)		O(w4)–H(6)–O(2)	161.56(21)
O(w4)–O(2)	266.4(2)			
O(w5)–H(7)	98.6(2)	100.2	H(7)–O(w5)–H(8)	105.85(21)
O(w5)–H(8)	98.5(3)	100.2	O(w5)–H(7)–O(1)	166.97(21)
H(7)–O(1)	174.0(2)		O(w5)–H(8)–O(3)	171.05(21)
H(8)–O(3)	174.7(3)			
O(w5)–O(1)	271.0(2)			
O(w5)–O(3)	272.4(2)			

Note. Distances in pm, angles in (°).

in common planes with Al. The same is true in good approximation for O(w2) and O(w3) and their H atoms. Only small deviations from least-squares planes fitted to these H_2O molecules and Al occur with O(w2) (9 pm) and O(w3) (3 pm). Hence the bonding between Al^{3+} and H_2O may be considered as mainly dominated by electrostatic interactions.

There are eight unique hydrogen bonds. O(w1) and O(w4) occupying a twofold axis (Wyckoff position 16*e*) form hydrogen bonds (O(w1)–H(1)···O(2), O(w4)–H(6)···O(2)) having exclusively oxygen atoms of the carboxylate groups of the mellitate hexaanion as proton acceptors. The fifth unique water molecule (O(w5)), which is not bound to Al^{3+}, acts as proton acceptor for O(w2) and O(w3) besides carboxylate oxygen atoms in the hydrogen bonds O(w2)–H(3)···O(w5)–H(7)···O(1) and O(w3)–H(5)···O(w5)–H(8)···O(3). Table III gives bond distances and angles of the hydrogen bonds. A riding model bond length correction was applied to all O–H bonds yielding distances between 99.5 and 101.3 pm corresponding well to the high hydrogen bonding strength. It clearly shows up that the strength of the hydrogen bonds is associated to the polarizing effects of Al^{3+} with very little influence of the proton accepting oxygen atoms—water or carboxylate groups. The Al–O(w3) bond is the shortest Al–O distance and accordingly the hydrogen bonds involving O(w3) have the shortest mean $O \cdots H_2O$ contact (260.7 pm) while the hydrogen bonds with O(w4), which shows the weakest $Al–H_2O$ bond, has an $O \cdots H_2O$ contact of 266.4 pm. The hydrogen bonds with O(w1) and O(w2) are between these margins (mean $O \cdots H_2O$ 262.0 pm for O(w2), $O \cdots H_2O$ 261.7 pm for O(w1)). All hydrogen bonds involving water molecules coordinated to Al^{3+} are considerably shorter (257.6–266.4 pm) than those with O(w5) acting as proton donator (271.0 and 272.4 pm). The H–O–H angles are mainly similar to that known from free water molecules (104.00–105.85°). Only the angle H(4)–O(w3)–H(5) (111.77°) is even markedly greater than tetrahedral and resembles the H–O–H angle in the crystal structure of $BeSO_4 \cdot 4H_2O$ (112.7°), which contains $Be(H_2O)_4^{2+}$ tetrahedra linked to the SO_4^{2-} anions by intermolecular hydrogen bonds (*24*). It was assumed (*25*) that wide H–O–H angles occur if the bisector of the lone pairs of the water molecule points toward a polyvalent metal ion. Obviously this represents too simple a model since this coordination mode is realized with O(w1), O(w2), and O(w4) as well which have quite usual H–O–H angles between 104.00 and 105.59°.

A thorough inspection shows that the hydrogen bonds link the $Al(H_2O)_6^{3+}$ octahedra to the anions yielding an intricate three-dimensional framework. O(w1) and O(w4) connect in the [001] direction and parallel to (001) neighboring anions, which are oriented perpendicular to each other (Fig. 2). A simi-

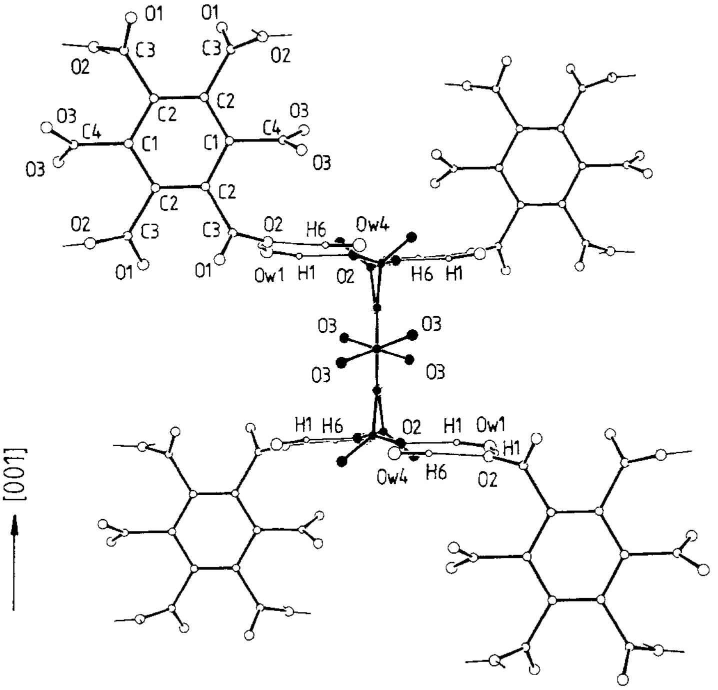

FIG. 2. Hydrogen bonding between O(w1), O(w4), and oxygen atoms (O(2)) of the carboxylate groups of the mellitate hexaanion viewed in the [110] direction, which is the direction of a twofold crystallographic axis running through the anion along the C(1)–C(4) bond. O(w1) and O(w4) lie on another twofold axis (see Fig. 1). These hydrogen bonds establish an infinite three-dimensional connection between the anions. The central anion, the atoms of which are represented as black balls, is orientated perpendicular to the paper plane and is the common reference point of Figs. 2–6 (arbitrary atomic radii in Figs. 2–6).

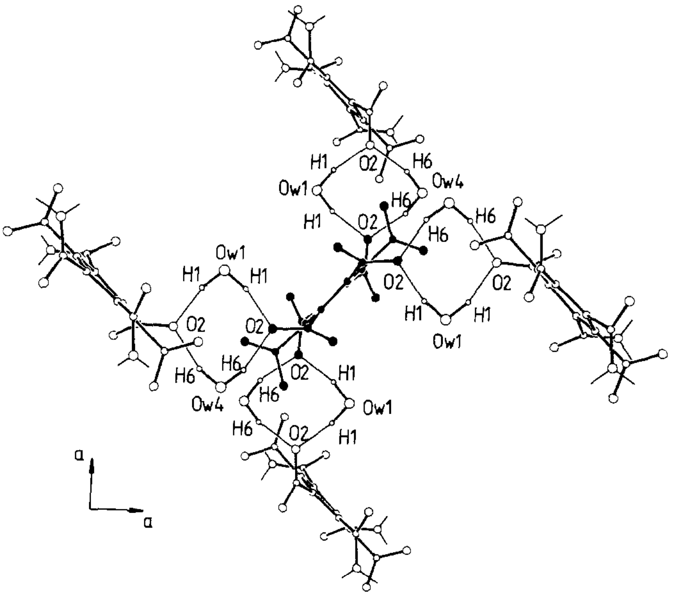

FIG. 3. The same arrangement as shown in Fig. 2 viewed in the [001] direction. It clearly comes out that the C_6 ring plane of the central anion (black balls) is perpendicular to the planes of the other anions.

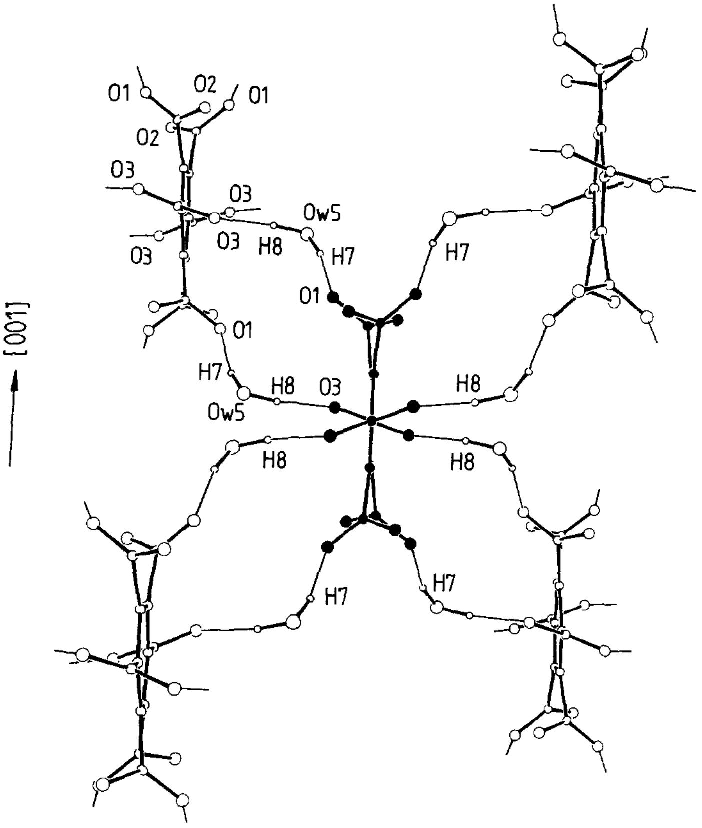

FIG. 4. Viewed in the [110] direction: It is shown how O(w5) connects neighboring anions by hydrogen bonds taking O(1) and O(3) as proton acceptors. These hydrogen bonds establish a three-dimensional framework as those shown in Figs. 2 and 3.

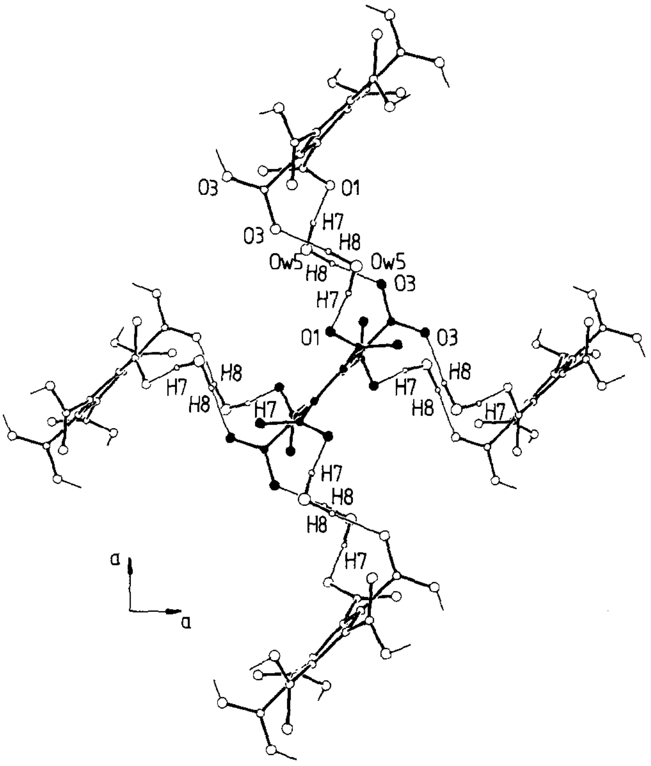

FIG. 5. The arrangement of Fig. 4 viewed in the [001] direction. These hydrogen bonds involve anions aligned parallel to each other.

lar connection is established by O(w5) taking O(1) and O(3) as proton acceptors stemming, however, from anions with C_6 rings aligned parallel to a common plane (Fig. 4 and 5). O(w2) does not link adjacent anions as it is solely participating in a quasiintramolecular ring of hydrogen bonds together with O(w5) (Fig. 6). O(w3) connects anions lying perpendicular to each other taking O(w5) as a proton acceptor for H(5) (Fig. 6).

The $[C_6(COO)_6]^{6-}$ anion has crystallographic 222 symmetry with its center of

TABLE IV

THE $[C_6(COO)_6]^{6-}$ ANION

C(1)–C(2)	140.3(1)	C(1)–C(4)	151.0(1)
C(2)–C(2)′	139.6(1)	C(2)–C(3)	151.7(1)
C(3)–O(1)	125.6(1)	C(3)–O(2)	125.7(1)
C(4)–O(3)	125.5(1)		
C(2)–C(1)–C(2)′	120.46(7)	C(2)–C(1)–C(4)	119.77(5)
C(1)–C(2)–C(2)′	119.70(8)	C(1)–C(2)–C(3)	119.56(8)
C(3)–C(2)–C(2)′	120.69(8)	O(1)–C(3)–O(2)	124.96(10)
O(1)–C(3)–C(2)	117.31(9)	O(2)–C(3)–C(2)	117.70(9)
O(3)–C(4)–O(3)′	126.30(9)	O(3)–C(4)–C(1)	116.85(8)

Note. Distances in pm, angles in (°).

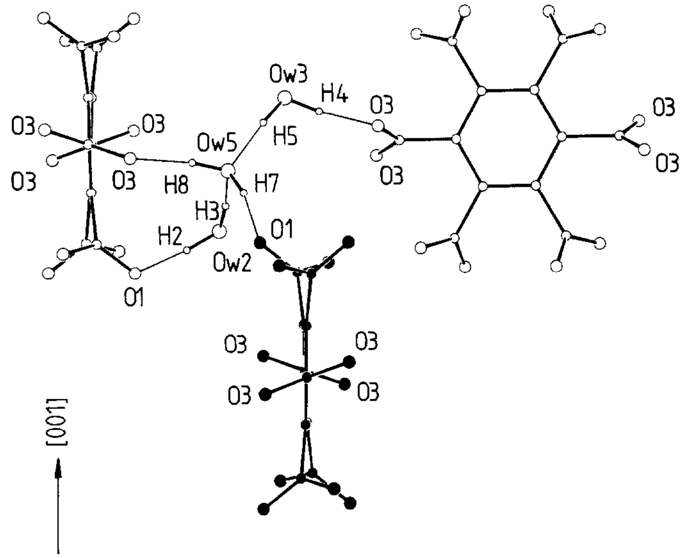

FIG. 6. A view in the [110] direction shows hydrogen bonding of O(w2) and O(w3) with O(w5) acting as proton acceptor. O(w2) is involved in a quasi-intramolecular ring of hydrogen bonds, thus not contributing topologically to the three-dimensional connection between the anions.

gravity at 0, 0.25, 0.125 (Wyckoff position 8*b*). The C_6 ring is in good approximation planar (maximum deviation from least-squares plane, 2.6 pm). The carboxylate group with C(3) (C(3), O(1), and O(2)) is tilted against the C_6 ring plane by 54° and suffers from a higher steric repulsion than the carboxylate group with C(4) (C(4), $2 \times$ O(3)), which is approximately perpendicular to the C_6 ring with a dihedral angle of 71°. Thus C(3) deviates by 16.5 pm from the mean plane fitted to the C_6 ring, whereas C(4) lies ideally in that plane. The C–O bond lengths are identical within the limits of experimental error (125.5–125.7 pm, Table IV). The C–C single bond with C(3) is slightly longer (C(2)–C(3), 151.7 pm) than that with C(4) (C(1)–C(4), 151.0 pm) obviously due to steric reasons (vide supra). The O–C–O angles of both unique carboxylate groups are widened up considerably (124.96 and 126.30°). Bond distances and angles of the C_6 ring deviate slightly, but significantly from an ideal hexagon. A TLS analysis (*26*) did not yield any evidence for significant rigid body motion.

Acknowledgments

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