Während die Temperaturparameter der β-Bernsteinsäure eine Beschreibung der thermischen Bewegung nach dem 'rigid body'-Modell zulassen (Broadley *et al.*, 1959), schlug beim Li-Succinat der Versuch einer entsprechenden Interpretation fehl. Bei einer Berechnung der Translations- und Librationstensoren mit Hilfe des Programms *TLS* von Schomaker & Trueblood (1968) fiel einer der Eigenwerte des Librationstensors negativ aus. Somit kann die Temperaturbewegung der Atome dieses Kristalls nicht durch 'rigid body'-Schwingungen des Succinat-Ions beschrieben werden. Als mögliche Ursache dafür dürften Torsionsschwingungen um die C–C-Bindungen anzunehmen sein.

Eine Korrektur der Bindungslängen durch Berücksichtigung der thermischen Bewegung wurde daher nur für die C–O-Bindungen nach dem 'riding'-Modell mit dem Programm *ORFFE* von Busing, Martin & Levy (1964) vorgenommen. Für die C–O-Bindungen ergab sich ein korrigierter Abstand von 1,263 bzw. 1,264 Å.

Unser herzlicher Dank gilt Herrn Professor Dr Th. Hahn (Aachen) für die Erlaubnis, diese Untersuchung an seinem Institut durchzuführen. Sein Rat sowie die zuvorkommende Unterstützung durch seine Mitarbeiter, Herrn Dr W. Gonschorek und Herrn Dr K. D. Reinartz, waren uns eine wertvolle Hilfe. Der Deutschen Forschungsgemeinschaft sei für die Bereitstellung des Diffraktometers gedankt.

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The Crystal Structure of Mellite[*]

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Mellite, $Al_2[C_6(COO)_6].16H_2O$, is tetragonal, space group $I4_1/acd$, with $Z=8$. The cell dimensions are: $a=15{\cdot}53\pm0{\cdot}01$, $c=23{\cdot}19\pm0{\cdot}01$ Å. The structure was solved by means of Patterson and direct methods. The Al atom is octahedrally surrounded by water oxygen atoms. One water molecule is not coordinated to the Al atom. The carbon framework, on the average parallel to (110), is not perfectly planar; the two independent carboxyl groups are tilted to the mean carbon plane by about 70 and 54° respectively. The connexions among the Al octahedra, the free water molecule and the mellitic radicals occur by means of strong hydrogen bonds. All bond distances and angles are within the limits given in the literature.

Introduction

Mellite is a hydrous salt of benzenehexacarboxylic acid; it occurs associated with brown coal and lignite.

On the basis of morphological studies, mellite was found to be tetragonal, with an axial ratio $c/a=0{\cdot}7463$. Barth & Ksanda (1933) studied the X-ray crystallography of mellite; their results are: $a=22{\cdot}0$, $c=23{\cdot}3$ Å, $c/a=1{\cdot}059$; $Z=16$, space group $P4_12$ or $P4_32$. According to these authors the agreement between the geometrical–physical properties of mellite and its symmetry as found by X-rays is not fully satisfactory.

Jobbins, Sergeant & Young (1965) published the X-ray powder pattern and a partial chemical analysis of mellite. According to the latter the water content is less than the 18 molecules quoted in the standard formula $Al_2C_{12}O_{12}.18H_2O$ (Palache, Berman & Frondel, 1951). The observed specific gravity, of 1·606 g cm^{-3}, determined on the Arten material, corresponds indeed to a water content of 15·7 H_2O.

The crystal structure of mellitic acid was determined by Darlow (1961); some quite large differences between

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the two crystallographically independent molecules as well as the non-coplanarity of the hydrogen bonded carboxyl groups are emphasized and discussed.

It seemed of some interest to determine the crystal structure of mellite in order to confirm or disprove the previous work on this mineral and to compare the results with those obtained for mellitic acid (Darlow, 1961).

Experimental

The crystal used in this work came from Arten, Thuringia, D.D.R. An irregularly shaped crystal fragment was investigated by means of a Weissenberg apparatus. Oscillation and Weissenberg photographs showed mellite to be tetragonal with cell dimensions $a=15\cdot53\pm0\cdot01$, $c=23\cdot19\pm0\cdot01$ Å, $V=5593$ Å^3 and $c/a=1\cdot4932$, in good agreement with twice the axial ratio determined by morphological study ($0\cdot7463\times2=1\cdot4926$). The space group unequivocally determined is $I4_1/acd$, centrosymmetric with 32 general equivalent positions in the unit cell. With a molecular weight of 678·35 (16 H_2O) and $Z=8$ the calculated density is 1·611 g cm^{-3}, in good agreement with the experimental value of 1·606 g cm^{-3} (Jobbins *et al.*, 1965); whilst with 18 water molecules per formula unit the calculated density is 1·696 g cm^{-3}.

Table 1. *Observed and calculated structure factors*

Reflexions marked with (*) were unobservably weak and their F_o's were derived from $0\cdot5I_{\min}$.

Table 1 (*cont.*)

For intensity data collection the crystal was rotated about the *a* axis. Weissenberg equi-inclination photographs were recorded for the reciprocal levels with *h* from 0 to 13, using nickel-filtered Cu radiation and the multiple-film technique.

2412 reflexions (1355 observed) were collected and photometrically measured. The intensities were corrected for the Lorentz-polarization factor and α_1–α_2 splitting. No absorption correction was applied: this effect is almost negligible owing to the very low μ value and the small size of the crystal.

Auto-scaling was performed and 1312 independent reflexions (834 observed) were obtained.

Structure determination

A three-dimensional sharpened Patterson synthesis was carried out; Al, $O_w(1)$ and $O_w(4)$ positions were determined, but a subsequent Fourier synthesis did not show a reliable structure.

The intensity data were placed on an absolute scale by Wilson's method and normalized structure-factor magnitudes $|E|$ were derived. The structure was solved by application of the tangent formula of Karle & Karle (1966) to 121 independent reflexions with $|E|>1\cdot2$. A starting set comprising three reflexions, one origin-determining (at $\bar{1}$, at $0,-\frac{1}{4},\frac{1}{8}$ from $\bar{4}$), was selected.

The R_{Karle}, R_{Drew}, α and t criteria were employed (Kennard *et al.*, 1971); a phase was accepted as determined if $\alpha > 9·0$. The best solution ($R_{\text{Karle}} = 0·23$, $R_{\text{Drew}} = 0·185$) defined 118 phases; these were employed to refine 346 independent phases with $|E| > 0·80$ ($R_{\text{Karle}} = 0·29$).

To improve Fourier resolution, F values were employed in Fourier synthesis. The Al, $O_w(1)$ and $O_w(4)$ positions, as determined from a Patterson inspection, were confirmed; a subsequent inspection of the F map showed all non-hydrogen atoms (in agreement with Jobbins *et al.* (1965) 16 water molecules were located).

The parameters derived from Fourier synthesis were refined, first isotropically and then anisotropically using a modified full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962).

The H atoms were placed by inspection of interatomic distances, the isotropic temperature factors being fixed at 3 Å^2.

The final value of $R = \sum||F_o| - |F_c|| / \sum|F_o|$ is 0·047 (0·112 with non-observed reflexions). The observed and calculated structure factors are compared in Table 1.

Hydrogen atom locations

An inspection of O–O distances showed for each water oxygen atom two values consistent with hydrogen bonding; Table 2 gives these distances together with O–O_w–O angles. To confirm this hypothesis and in an attempt to locate the hydrogen atoms directly, a three-dimensional difference Fourier synthesis was computed at the end of the least-squares refinement. Some residual peaks were found to correspond satisfactorily to the positions expected for hydrogen atoms. Nevertheless these experimental indications were not considered conclusive owing to the low intensity of the maxima and the poor resolution of the maps. An indirect location of the hydrogen atom was chosen on the assumption that the H atom is located along the O–O vector at 1 Å from the oxygen to which it is bound. Postulated fractional coordinates are given in Table 3.

Table 2. *Distances and angles between atoms involved in hydrogen bonding*

Estimated standard deviations for O–O distances are 0·006 Å and for O–O_w–O angles are 0·4°.

Bonds

$O_w(1)\cdots O(2^{vi})$	2·626 Å
$O_w(2)\cdots O(1^{v})$	2·582
$O_w(2)\cdots O_w(5^{vii})$	2·664
$O_w(3)\cdots O(3^{iv})$	2·567
$O_w(3)\cdots O_w(5^{viii})$	2·642
$O_w(4)\cdots O(2^{ix})$	2·677
$O_w(5)\cdots O(1^{v})$	2·724
$O_w(5)\cdots O(3^{iv})$	2·733

Angles

$O(2^{vi})\cdots O_w(1)\cdots O(2^{iii})$	83·3°
$O(1^{v})\cdots O_w(2)\cdots O_w(5^{vii})$	92·7
$O(3^{iv})\cdots O_w(3)\cdots O_w(5^{viii})$	111·8
$O(2^{ix})\cdots O_w(4)\cdots O(2^{iv})$	81·4
$O(1^{v})\cdots O_w(5)\cdots O(3^{iv})$	95·8

Table 3. *Postulated fractional hydrogen coordinates* (× 10^3)

Hydrogen atoms are given in the same order as the corresponding O–O distances in Table 2.

	x/a	y/b	z/c		x/a	y/b	z/c
H(1)	500	543	247	H(5)	375	536	356
H(2)	356	667	238	H(6)	159	458	247
H(3)	291	647	196	H(7)	320	781	315
H(4)	281	580	339	H(8)	251	740	350

Description of the structure

Table 4 gives the final coordinates together with the temperature factors, Table 5 the analysis of the anisotropic thermal parameters, and Tables 6 and 2 and Fig. 1 the angles and distances.

The structure of mellite, projected along the [010] axis, is shown in Fig. 2, the projection plane being at 45° from the plane of the benzene ring.

The Al atom, in a special position on a twofold axis, is octahedrally surrounded by six oxygen atoms, all of them belonging to water molecules; Al–O_w distances range from 1·860 to 1·903 Å, the average value being 1·872 Å. These Al octahedra, which are almost regular, are isolated in the structure, the connexions to the

Table 4. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (× 10^4)

E.s.d.'s are in parentheses.
The temperature factors refer to the expression $\exp[-(b_{11}h^2 + \ldots + 2b_{12}hk + \ldots)]$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	3310 (1)	5000	2500	9 (1)	7 (1)	8 (1)	0	0	−2 (1)
$O_w(1)$	4513 (3)	5000	2500	16 (2)	8 (2)	13 (1)	0	0	1 (1)
$O_w(2)$	3324 (3)	6128 (3)	2216 (2)	24 (2)	13 (2)	15 (1)	4 (1)	5 (1)	1 (1)
$O_w(3)$	3293 (3)	5420 (3)	3251 (2)	16 (2)	26 (2)	12 (1)	−9 (1)	3 (1)	−5 (1)
$O_w(4)$	2084 (3)	5000	2500	12 (2)	8 (2)	13 (1)	0	0	−2 (1)
$O_w(5)$	2765 (2)	7999 (3)	3453 (2)	14 (1)	23 (2)	12 (1)	−0 (1)	1 (1)	−3 (1)
O(1)	4982 (2)	1459 (2)	5155 (2)	14 (1)	30 (2)	10 (1)	−3 (1)	2 (1)	−4 (1)
O(2)	3620 (2)	1723 (2)	4934 (2)	11 (1)	19 (1)	16 (1)	−0 (1)	4 (1)	−3 (1)
O(3)	3899 (2)	440 (2)	3913 (2)	17 (2)	12 (1)	16 (1)	3 (1)	0 (1)	−4 (1)
C(1)	4361 (3)	1861	3750	8 (2)	8	9 (1)	−2 (2)	0 (1)	0
C(2)	4694 (3)	2171 (3)	4275 (2)	8 (2)	9 (2)	7 (1)	2 (1)	2 (1)	−0 (1)
C(3)	4410 (3)	1758 (3)	4831 (2)	9 (2)	9 (2)	10 (1)	2 (1)	0 (1)	0 (1)
C(4)	3678 (3)	1178	3750	10 (2)	10	7 (1)	−8 (2)	2 (1)	−2

remaining structural units, as well as the connexions to $O_w(5)$ which is not linked to the Al atom (see below), being provided by hydrogen bonds.

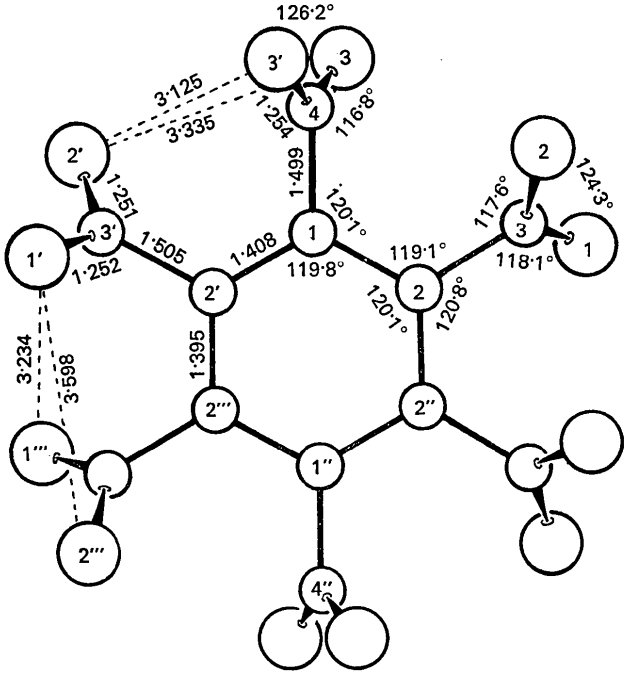

Fig. 1. Bond lengths (Å) on the left and angles on the right, in $C_6(COO)_6$ projected along [110]. All oxygen–oxygen contacts ≤3·6 Å between different carboxyl groups are shown as dashed lines. Estimated standard deviations for C–C and C–O bond lengths are 0·006 Å and for C–C–C, C–C–O and O–C–O angles, 0·5°.

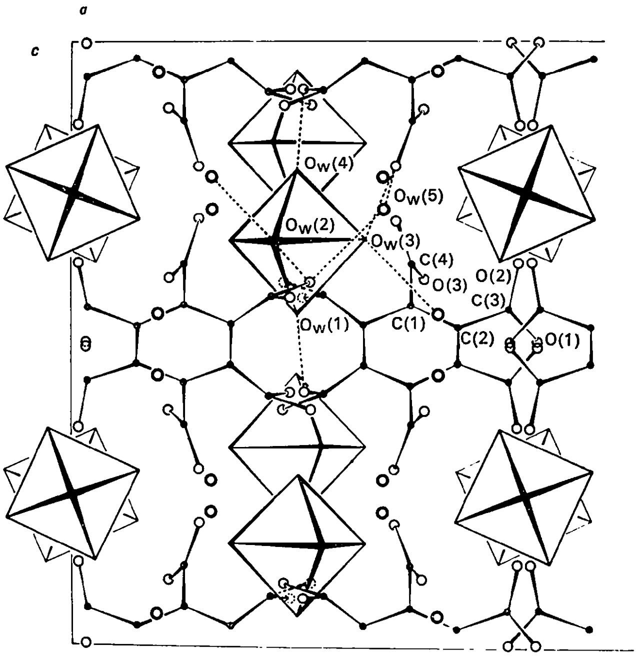

Fig. 2. The structure of mellite projected along the [010] axis. Dashed lines represent the hydrogen bonds.

Table 5. *Analysis of anisotropic thermal parameters*

α, β and γ are the angles of the principal axes of the thermal ellipsoids with respect to the crystallographic axes.

Atom	R.m.s.	α	β	γ
Al	0·086	90°	166°	104°
	0·106	0	90	90
	0·151	90	76	166
$O_w(1)$	0·098	90	177	87
	0·138	0	90	90
	0·188	90	93	177
$O_w(2)$	0·119	72	161	93
	0·156	37	73	122
	0·215	121	97	148
$O_w(3)$	0·114	149	121	90
	0·153	108	59	37
	0·214	114	47	127
$O_w(4)$	0·096	90	173	97
	0·122	0	90	90
	0·193	90	83	173
$O_w(5)$	0·130	167	85	78
	0·154	79	35	57
	0·194	97	55	144
O(1)	0·127	168	99	81
	0·152	87	59	31
	0·207	78	147	60
O(2)	0·108	166	85	77
	0·148	83	12	80
	0·215	102	79	163
O(3)	0·109	67	154	101
	0·149	23	68	84
	0·213	89	78	167
C(1)	0·090	135	135	90
	0·108	45	135	93
	0·158	92	88	177
C(2)	0·083	144	57	77
	0·115	59	33	99
	0·140	106	91	164
C(3)	0·092	46	136	90
	0·115	44	46	92
	0·167	92	91	178
C(4)	0·052	135	135	90
	0·130	117	63	39
	0·159	123	57	129

There is only one crystallographically independent $C_6(COO)_6$ radical, whereas in mellitic acid (Darlow, 1961) the $C_6(COOH)_6$ molecules are in two independent sets with quite large differences, particularly in the tilts of the carboxyl group to the benzene ring. In mellite the planes of the carbon atom framework are, on the whole, parallel to (110) and symmetry-related planes. The deviations of the various atoms from this mean plane are represented in Fig. 3. The displacements of the benzene atoms are slight but significant with respect to the estimated standard deviations, whereas the carboxyl carbon atoms [except C(4) and C(4'')] are significantly out of the mean plane, alternately above and below it. A similar situation (but with smaller displacements) can also be found in other structures: *e.g.*

Table 6. *Interatomic distances and angles in the* Al *octahedron*

Estimated standard deviations for Al–O distances are 0·005 Å and for O–Al–O angles are 0·3°.

Distances

Al–O_w(1)	1·868 Å
Al–O_w(2)	1·871 (×2)
Al–O_w(3)	1·860 (×2)
Al–O_w(4)	1·903

Angles

O_w(1)–Al–O_w(2)	89·3°
O_w(1)–Al–O_w(3)	90·8
O_w(1)–Al–O_w(4)	180
O_w(2)–Al–O_w(3)	90·1
O_w(2)–Al–O_w(2^x)	178·6
O_w(2)–Al–O_w(3^x)	89·9
O_w(3)–Al–O_w(4)	89·2
O_w(3)–Al–O_w(3^x)	178·4
O_w(4)–Al–O_w(2^x)	90·7

The atoms of the different asymmetric units are related to the atoms of the fundamental unit as follows:

Superscript	Coordinates		
none	x	y	z
i	$\frac{1}{4}+y$	$x-\frac{1}{4}$	$\frac{3}{4}-z$
ii	$1-x$	$\frac{1}{2}-y$	z
iii	$\frac{3}{4}-y$	$\frac{3}{4}-x$	$\frac{3}{4}-z$
iv	$\frac{1}{4}-y$	$\frac{1}{4}+x$	$\frac{3}{4}-z$
v	$\frac{1}{4}+y$	$\frac{1}{4}+x$	$z-\frac{1}{4}$
vi	$\frac{3}{4}-y$	$\frac{1}{4}+x$	$z-\frac{1}{4}$
vii	$\frac{1}{2}-y$	$\frac{3}{2}-y$	$\frac{1}{2}-z$
viii	$y-\frac{1}{4}$	$\frac{1}{4}+x$	$\frac{3}{4}-z$
ix	$\frac{1}{4}-y$	$\frac{3}{4}-x$	$z-\frac{1}{4}$
x	x	$1-y$	$\frac{1}{2}-z$
xi	$\frac{1}{2}-x$	y	$1-z$

This also applies to Table 2 and Figs. 1 and 2.

potassium acid phthalate, $KC_6H_4COOH.COO$ (Okaya, 1965) and trimesic acid, $C_6H_3(COOH)_3$ (Duchamp & Marsh, 1969). In mellitic acid (Darlow, 1961) all the carbon atoms are accurately coplanar, but in this compound the coordinates of the carbon atoms were refined on the assumption (from Fourier maps) of a perfect planarity.

Because of symmetry restraints on the benzene atoms, there are only two independent C(ring)–C(ring) distances (see Fig. 1), which are almost equivalent. The average value is 1·403 Å, not very different from 1·395 Å given in *International Tables for X-ray Crystallography* (1962) and 1·387 Å found in mellitic acid. The C–C–C ring angles are 120°, within the standard deviations. The average C(ring)–C(carboxyl) distance is 1·503 Å compared with 1·521 Å in mellitic acid and 1·489 Å in trimesic acid.

Of the two independent $\mathrm{C{-}C}{<}^{\mathrm{O}}_{\mathrm{O}}$ groups the one containing C(1) lies on a twofold axis, the other one has no symmetry restraints. Both are planar; the maximum perpendicular displacements are 0·006 Å in $\mathrm{C(2){-}C(3)}{<}^{\mathrm{O(2)}}_{\mathrm{O(1)}}$ and 0·0000 Å, because of symmetry, in $\mathrm{C(1){-}C(4)}{<}^{\mathrm{O(3)}}_{\mathrm{O(3')}}$. The average C–O bond length is 1·253 and none of the three independent values differs significantly from the average.

Owing to steric hindrance of the six carboxyl groups attached to the benzene ring, the carboxyl oxygens can no longer remain in the plane of the benzene ring. Indeed each of the carboxyl groups is twisted about the C(ring)–C(carboxyl) bond; twist angles are 70·3° for the C(4) group and 54·3° for the C(3) group (see Fig. 3 for the displacements from the mean carbon plane). Similar situations were found in mellitic acid (Darlow, 1961), in potassium acid phthalate (Okaya, 1965), in *o*-phthalic acid (Nowacki & Jaggi, 1957) *etc.* The effect of steric hindrance can also be seen in the displacements of the carboxyl groups, as a result of a slight but significant bending of the C(ring)–C(carboxyl) bonds out of the plane of the benzene ring. This bending also contributes to a larger separation between carboxyl oxygens and water oxygens, the latter being coordinated to the Al atoms.

Unlike the arrangement in mellitic acid, there are no layers of $C_6(COO)_6$ radicals; the arrangement of mellitic radicals and $Al(H_2O)_6$ octahedra is schematically illustrated in Fig. 2. All contacts ≤3·6 Å between oxygens in different carboxyl groups, whithin the same $C_6(COO)_6$ radical are shown in Fig. 1; the shortest length is 3·125 Å. The closest approach between carboxyl oxygens in different $C_6(COO)_6$ radicals, namely O(2)–O(2)^{xi}, is 3·492 Å.

Among the five independent water oxygens (two are in special positions on twofold axes) only O_w(5), the 'free' water molecule, acts as proton donor [to O(3) and O(1)] and proton acceptor [from O_w(2) and O_w(3)], the remaining water oxygens behaving only as proton donors (see Table 2). As in mellitic acid the O–O

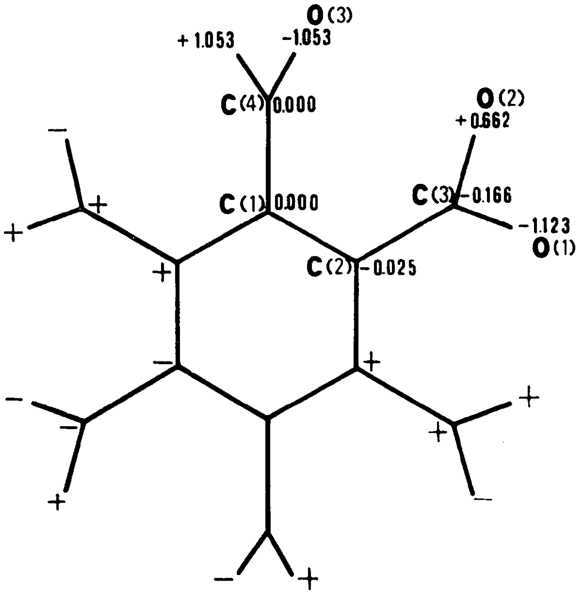

Fig. 3. Displacements (Å) of C and O atoms from the mean carbon plane; + and − signs indicate whether the atoms are above or below the plane.

distances referred to as hydrogen bonds are fairly short (between 2·567 and 2·733 Å in mellite, between 2·64 and 2·68 Å in mellitic acid); accordingly the H-bonds are strong enough to justify the cohesion of mellite. All the oxygen atoms excepting $O_w(5)$ have three neighbouring atoms: 1 Al and 2 H for water oxygens, 1 C and 2 H for carboxyl oxygens. $O_w(5)$ is approximately tetrahedrally surrounded by four hydrogen atoms.

It is not unlikely that the observed tilts of the carboxyl groups with respect to the benzene ring are related, partly at least, to the hydrogen bonding system. If, for instance, the plane of the carboxyl groups were perpendicular to the benzene ring, the $O_w(4)$–$O(2^{ix})$ distance would be too long for a hydrogen bond; on the other side the $O_w(5)$–$O(1^v)$ distance would be too short.

In conclusion, the structure of mellite can be regarded as composed of discrete $Al(H_2O)_6$ octahedra and $C_6(COO)_6$ radicals with strong hydrogen bonds between octahedra and metallic radicals, with the additional contribution of the 'free' water molecule.

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The Crystal and Molecular Structure of Adenosine Hydrochloride

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The crystal structure of adenosine hydrochloride ($C_{10}H_{13}N_5O_4.HCl$) has been determined using three-dimensional intensity data collected on a four-circle diffractometer. The crystal is monoclinic, space group $P2_1$. There are two molecules in the unit cell of dimensions $a = 6·647 \pm 0·003$, $b = 16·739 \pm 0·005$, $c = 6·397 \pm 0·002$ Å and $\beta = 114°54' \pm 4'$. The structure was solved by the heavy-atom method and refined by the method of block-diagonal least squares. The final R value is 0·037 for 1895 observed reflexions including those of zero intensity. Adenosine is protonated at N(1) in the crystal. The purine ring is almost exactly planar. In comparison with the structure of the non-protonated adenosine molecule reported by Lai & Marsh [*Acta Cryst.* (1972). B**28**, 1982–1989] significant differences have been found in four bond lengths and three bond angles in the purine ring. The dihedral angle between the least-squares planes of the base and the ribose is 107·9° and the glycosidic torsional angle, φ_{CN}, is $-43°$. The ribose ring is in the C(2′)-*endo*-C(3′)-*exo* conformation, and the C(2′) atom is displaced by 0·60 Å from the least-squares plane of the remaining four ring atoms. The orientation of the C(5′)–O(5′) bond is *gauche* with respect to the bonds C(4′)–O(1′) and C(4′)–C(3′).

Introduction

Accurate information is desired on the structure of the adenosine molecule because of its importance in bioenergetics and genetics. In this connexion a considerable number of studies have been carried out on the non-protonated adenosine compounds, *viz.*, deoxyadenosine (Watson, Sutor & Tollin, 1965), 3′-*O*-acetyladenosine (Rao & Sundaralingam, 1970), 2′-amino-2′-deoxyadenosine (Rohrer & Sundaralingam, 1970) and adenosine (Lai & Marsh, 1972), and on protonated adenosine compounds, *viz.*, adenosine 5′-phosphate (Kraut & Jensen, 1963) and adenosine 3′-phosphate (Sundaralingam, 1966). The present paper provides accurate information on the structure of protonated adenosine molecule in the crystal of adenosine hydrochloride.

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