

tion one would expect. In 2,3-tetramethylene-4-phenyl-6,6a-dithiafurophthene (Pinel, Mollier, Llaguno & Paul, 1971) the S(6)–S(6a) and S(6a)–O distances are 2·126 (4) and 2·255 (8) Å, respectively, and in 2,3-benzo-5-phenyl-6,6a-dithiafurophthene (Llaguno, Paul, Pinel & Mollier, 1972) they are 2·137 (3) and 2·184 (7) Å. The S(1)–S(6a) and S(6a)–O distances in 2-phenyl-4-benzoyl-5-aza-1,6a-dithiafurophthene, which Johnson, Reid & Paul (1971) reported to be 2·178 (2) and 2·034 (6) Å, respectively, show clearly that the sulphur–oxygen interaction in such molecules can affect the sulphur–sulphur bonding. The lengthening of the S–S bond seems to be detectable for S–O contacts shorter than 2·30 Å.

A stereoscopic view of the molecular packing is given in Fig. 2. There are no intermolecular contacts shorter than the corresponding van der Waals distances.

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The Crystal Structure of Lithium Hydrogen Maleate Dihydrate, $\text{LiC}_4\text{H}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$

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The crystal structure of lithium hydrogen maleate dihydrate has been determined by X-ray diffraction and refined by least-squares calculations to $R=0\cdot078$. The molecules are arranged in layers, hydrogen-bonded *via* the water molecules. There is also a short intramolecular hydrogen bond of 2·46 Å which may be 'statistically symmetrical'. The lithium ion has fourfold coordination.

The title compound was studied because of interest in the dimensions of the maleate ion. The hydrogen maleate ion (HM) has been found to have somewhat different dimensions in sodium hydrogen maleate (Gupta, Prasad & Yadav, 1972) and potassium hydrogen maleate (Darlow & Cochran, 1961). In sodium hydrogen maleate the HM ion has no symmetry, in potassium hydrogen maleate it has a crystallographic plane of symmetry perpendicular to the central C=C bond and

the plane of the molecule. The e.s.r. and n.m.r. spectra of the two compounds are also different (Toriyama & Iwasaki, 1971; Iwasaki & Itoh, 1964; Iwasaki & Toriyama, private communication).

Experimental

Crystals of lithium hydrogen maleate dihydrate (LiHM) grow as long rods and are hygroscopic, tending

to decompose rapidly in air. The length direction is [010]. For experimental work, the crystals were sealed in thin-walled Lindemann-glass capillary tubes and 694 independent reflexions were collected by Weissenberg photography around [010] and [100]. The cell dimensions were determined from high $\sin \theta$ reflexions on Weissenberg photographs with Ag lines as internal standards.

Crystallographic data

Monoclinic, $a=5.860$, $b=6.070$, $c=19.690$ Å, $\beta=106.3^\circ$, $d_o=1.54$, $d_c=1.56$ g cm $^{-3}$, $Z=4$. Space group $P2_1/c$, μ (Cu $K\alpha$) = 12.99 cm $^{-1}$.

Determination and refinement of the structure

The structure was solved from a sharpened Patterson projection down [010] and the Harker section at $Y=\frac{1}{2}$, which gave the orientation of the molecule and possible positions for the two water molecules. Fourier refinement down [010] and [100] gave a set of parameters for full-matrix least-squares refinement (Busing, Martin & Levy, 1962). R fell to 11.2%. The hydrogen atoms were located from a difference synthesis and their inclusion reduced R to 9.0%. Application of an extinction correction (Zachariasen, 1967) and weighting scheme ($\Delta F = a + bF_o$, a and b being for constants the group) reduced R finally to 0.078.

The numbering of atoms is given in Fig. 1. The positions and thermal parameters are given in Table 1. Observed and calculated structure factors are in Table 2.* Bond lengths and angles are in Table 3. The symmetry-related atoms are denoted by:

I	\bar{x} ,	\bar{y} ,	\bar{z}
II	x ,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
III	\bar{x} ,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
IV	\bar{x} ,	$1-y$,	$1-z$
V	x ,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
VI	$-1+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
VII	x ,	$-\frac{1}{2}-y$,	$\frac{1}{2}+z$

The equation for the least-squares plane through C(1), C(2), C(3) and C(4) is:

$$X - 25.2846Y - 0.4622Z + 43.6748 = 0. \quad (A)$$

The equations of the planes through the atoms of the two carboxyl groups are:

$$\begin{aligned} \text{O(1), C(1), O(2):} \\ X + 42.5341Y + 2.1850Z - 84.0555 = 0; \quad (B) \end{aligned}$$

$$\begin{aligned} \text{O(3), C(4), O(4):} \\ X - 104.8377Y + 3.2251Z + 120.8852 = 0. \quad (C) \end{aligned}$$

* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30601 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The deviations from plane A are given in Table 4. The direction cosines of the normal to the planes A , B , C referred to orthogonal axes a, b, c' (c' being normal to a and b) are:

Plane	l	m	n
A	0.0395	-0.9990	-0.0183
B	0.0235	0.9984	0.0513
C	0.0095	-0.9996	0.0308

Table 1. Atomic and thermal parameters

(a) Final atomic coordinates and their e.s.d.'s ($\times 10^4$, and for hydrogen atoms $\times 10^3$)

	x/a	y/b	z/c
C(1)	3504 (11)	2610 (14)	4086 (3)
C(2)	1673 (10)	2488 (14)	4499 (3)
C(3)	1929 (11)	2446 (13)	5198 (3)
C(4)	4113 (11)	2445 (14)	5810 (3)
O(1)	2804 (8)	2716 (11)	3438 (2)
O(2)	5719 (7)	2514 (10)	4416 (2)
O(3)	3850 (8)	2493 (11)	6412 (2)
O(4)	6191 (7)	2452 (10)	5698 (2)
W(1)	6876 (9)	2288 (14)	7796 (3)
W(2)	-12 (8)	2894 (10)	6913 (3)
Li	-52 (24)	3811 (27)	2789 (7)
H(C2)	1	232	422
H(C3)	41	229	535
H(W1)	583	250	732
H'(W1)	592	244	811
H(W2)	-150	243	670
H'(W2)	100	277	653

(b) Thermal parameters and their e.s.d.'s ($\times 10^4$ Å)

$$T = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	131 (18)	36 (34)	8 (2)	-3 (21)	12 (4)	-4 (6)
C(2)	61 (16)	92 (37)	12 (2)	-13 (21)	8 (4)	3 (6)
C(3)	99 (19)	92 (41)	12 (2)	-5 (21)	12 (5)	-9 (7)
C(4)	98 (18)	45 (35)	11 (2)	14 (21)	15 (4)	-4 (6)
O(1)	141 (15)	161 (36)	9 (1)	16 (16)	12 (3)	1 (5)
O(2)	79 (12)	142 (33)	9 (1)	10 (17)	8 (3)	-3 (5)
O(3)	154 (15)	208 (37)	10 (1)	-10 (17)	20 (3)	-4 (5)
O(4)	60 (13)	138 (32)	11 (1)	15 (16)	7 (3)	-5 (5)
W(1)	162 (18)	360 (42)	14 (2)	88 (20)	20 (4)	16 (6)
W(2)	84 (13)	180 (35)	10 (1)	-17 (14)	11 (3)	2 (4)
Li	173 (46)	185 (58)	17 (4)	8 (39)	18 (11)	10 (12)

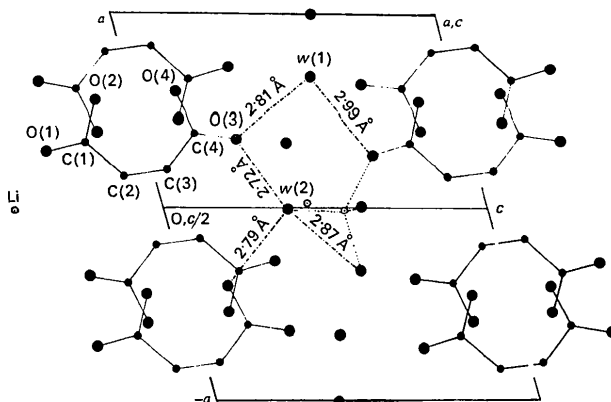


Fig. 1. The structure looking down the [010] axis.

Table 3. Bond lengths and bond angles

C(1)—O(1)	1.23 (1) Å	C(2)—H(C2)	0.98 Å
C(1)—O(2)	1.28 (1)	C(3)—H(C3)	1.02
C(4)—O(3)	1.24 (1)	W(1)—H(W1)	0.98
C(4)—O(4)	1.30 (1)	W(1)—H'(W1)	0.95
C(1)—C(2)	1.52 (1)	W(2)—H(W2)	0.90
C(2)—C(3)	1.34 (1)	W(2)—H'(W2)	1.09
C(3)—C(4)	1.49 (1)		
O(1)—C(1)—O(2)	121.7 (7)°	O(3)—C(4)—O(4)	122.5 (5)
O(1)—C(1)—C(2)	118.6 (5)	C(1)—C(2)—H(C2)	116.6
O(2)—C(1)—C(2)	119.6 (6)	C(3)—C(2)—H(C2)	112.1
C(1)—C(2)—C(3)	131.1 (5)	C(2)—C(3)—H(C3)	116.1
C(2)—C(3)—C(4)	130.7 (6)	C(4)—C(3)—H(C3)	113.0
C(3)—C(4)—O(3)	117.6 (6)	H(W1)—W(1)—H'(W1)	107.2
C(3)—C(4)—O(4)	119.8 (8)	H(W2)—W(2)—H'(W2)	107.4

Table 4. Deviations of atoms from plane (Å)

C(1)	-0.006 (8)	O(1)	-0.050 (7)
C(2)	0.002 (8)	O(2)	0.084 (6)
C(3)	-0.006 (8)	O(3)	-0.059 (7)
C(4)	0.011 (8)	O(4)	0.061 (6)

The angles between planes *A* and *B* and *A* and *C* are 4.1 and 3.2° respectively.

The crystal and molecular structure

In the crystal the HM ions are arranged in layers at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. The lithium ion is sandwiched between the layers of HM ions and has fourfold coordination with an average Li—O distance of 1.99 Å. Li—O distances and angles are given in Table 5.

Table 5. Li—O distances and angles around Li

Li—O(1)	1.92 (1) Å	W(1 ^{VI})—Li—W(2 ^{VII})	93.6 (6)°
Li—W(1 ^{VI})	1.92 (1)	W(2 ^{VII})—Li—W(1 ^{VI})	105.9 (8)
Li—W(2 ^V)	2.02 (2)	O(1)—Li—W(2 ^{IV})	101.6 (7)
Li—W(2 ^{IV})	2.08 (2)	O(1)—Li—W(2 ^{II})	100.1 (6)

Hydrogen bonds

The HM ions in the same layer are linked by hydrogen bonds *via* the two water molecules (Fig. 1), water molecule *W*(1) providing the linkage between adjacent HM ions along *c*, the hydrogen bonds being 2.81 and 2.99 Å. Water molecule *W*(2) provides the linkage to adjacent HM ions again in the same layer along *a*, the hydrogen bonds being 2.72 and 2.79 Å. There is another hydrogen bond of 2.87 Å between *W*(1) and *W*(2) and this is part of a bifurcated system (2.79, 2.87 Å), H(*W*2) being shared by acceptors O(4) and water *W*(1) (Parthasarathy, 1969; Ferraris & Franchini-Angela, 1972).

The dimensions of the HM and maleate ions in different structures are given in Table 6. It would appear that the HM ion in this crystal is similar to that found in KHM and although there is no symmetry found in the HM ion in this work, it is nearly symmetrical and also strained, as in KHM.

Table 6. Dimensions of HM and maleate ions in various structures

	LiHM (This work)	KHM (Darlow & Cochran, 1961)	NaHM (Gupta, Prasad & Yadav, 1972)	Li ₂ C ₄ H ₂ O ₄ (Town & Small, 1973)
C(1)—O(1)	1.23 Å	1.24 Å	1.26 Å	1.25 Å
C(1)—O(2)	1.28	1.28	1.27	1.28
C(4)—O(3)	1.24	1.24	1.25	1.25
C(4)—O(4)	1.30	1.28	1.24	1.27
C(1)—C(2)	1.50	1.52	1.48	1.50
C(2)—C(3)	1.34	1.35	1.33	1.33
C(3)—C(4)	1.49	1.50	1.51	1.51
C(2)—H(C2)	0.98	0.98	0.99	1.09
C(3)—H(C3)	1.02	0.98	0.97	0.88
O(1)—C(1)—O(2)	121.7°	122.7°	120.2°	123.5°
O(2)—C(1)—C(2)	118.6	117.0	116.1	117.3
O(2)—C(1)—C(2)	119.6	120.3	123.7	119.2
C(1)—C(2)—C(3)	131.1	130.4	129.3	125.1
C(2)—C(3)—C(4)	130.7	130.4	129.0	127.4
C(3)—C(4)—O(4)	119.8	120.3	121.7	119.1
C(3)—C(4)—O(3)	117.7	117.0	114.9	116.8
O(3)—C(4)—O(4)	122.5	122.7	123.2	124.1
C(1)—C(2)—H(C2)	116.6	113.8	104.8	116.0
C(3)—C(2)—H(C2)	112.1	115.8	125.4	118.0
C(2)—C(3)—H(C3)	116.1	115.8	112.9	120.0
C(4)—C(3)—H(C3)	113.0	113.8	118.0	113.0

Unambiguous location of the hydrogen atom involved in the intramolecular hydrogen bond of 2.46 Å has not been possible as we find two comparable peaks not far from the mid-point of the O(2)—O(4) line at 1.12 Å from O(2), 1.14 Å from O(4). The mid-point of the O(2)—O(4) line also has comparable electron density. This may be due to a 'statistical distribution' (Darlow & Cochran, 1961).

It is interesting to note that in Li₂C₄H₂O₄ also the two carboxyl groups have nearly the same shape and dimensions and there is a significant difference between the two C—O distances in the same carboxyl group.

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Strukturen von Kobalt(II)-Komplexen der Stöchiometrie $\text{Co}(\text{CNR})_4\text{J}_2$ mit $\text{R} = \text{Phenyl}$ bzw. $2,6\text{-Diäthylphenyl}$

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The structures of the two compounds $\text{Co}(\text{CNC}_6\text{H}_5)_4\text{I}_2$ (*A*) and $\text{Co}(\text{CNC}_6\text{H}_3(\text{C}_2\text{H}_5)_2)_4\text{I}_2$ (*B*) have been determined from three-dimensional diffractometer data with $\text{Mo K}\alpha$ radiation, and refined by least-squares methods to $R=0.089$ (*A*) and $R=0.106$ (*B*). The crystals of *A* are triclinic with $a=11.058$ (3), $b=11.878$ (3), $c=12.462$ (3) Å, $\alpha=93.19$ (2), $\beta=107.69$ (2), $\gamma=104.64^\circ$ (2), $Z=2$. The crystals of *B* are monoclinic with $a=19.780$ (8), $b=10.885$ (6), $c=23.668$ (9) Å, $\beta=118.8^\circ$ (3), $Z=4$. While the paramagnetic crystals of *B* consist of monomeric $\text{Co}(\text{CNR})_4\text{I}_2$ units, the crystals of *A* are formed by binuclear $[\text{I}-\text{Co}(\text{CNR})_4-\text{I}-\text{Co}(\text{CNR})_4-\text{I}]^+$ cations with iodide counterions. The diamagnetism of this structure can be explained by a spin-exchange in the central $\text{Co}-\text{I}-\text{Co}$ moiety of the cation.

Einleitung

Die Festkörpereigenschaften von einigen – erstmals von Malatesta & Sacco (1953) beschriebenen – Verbindungen der Stöchiometrie $\text{Co}(\text{CNR})_4\text{J}_2$ deuten auf starke Wechselwirkungen zwischen den Zentralmetallionen hin.

Wie früher gezeigt werden konnte, fallen Komplexe mit $\text{R} = p\text{-Methylphenyl}$, $p\text{-Methoxyphenyl}$ und $p\text{-Dimethylaminophenyl}$ unter bestimmten experimentellen Bedingungen zunächst in einer diamagnetischen, metallisch glänzenden sog. α -Modifikation an, wobei die metallische Reflexion linear polarisiert ist. Durch Erwärmen dieser Kristalle entsteht eine paramagnetische, sog. β -Form, deren Magnetismus auf einen 'low-spin' Kobalt(II)-Komplex hinweist. Die Kristall- und Molekülstruktur der letztgenannten paramagnetischen Form von Dijodotetrakis-(p -methylphenylisonitril)kobalt(II) wurde kürzlich veröffentlicht (Gilmore, Watkins & Woodward, 1969). Im Kristall findet man isolierte sechsfach koordinierte Kobalt(II) Ionen mit angenäherter D_{4h} -Symmetrie.

Über die Struktur einer diamagnetischen Form von $\text{Co}(\text{CNR})_4\text{J}_2$ mit $\text{R} = \text{Phenyl}$ haben wir kurz berichtet (Baumann, Endres, Keller & Weiss, 1973).

Die physikalischen Eigenschaften von Komplexen dieses Typs lassen strukturelle Besonderheiten vermuten. Wir haben deshalb als weiteren Vertreter dieser Reihe den paramagnetischen Komplex mit den sterisch anspruchsvollen Liganden 2,6-Diäthylphenylisonitril röntgenographisch untersucht. Über die Ergebnisse dieser Untersuchung sowie über die abschliessende Verfeinerung der obengenannten Struktur wird im folgenden berichtet.

Experimentelles

Die Verbindungen $\text{Co}(\text{CNC}_6\text{H}_5)_4\text{J}_2$ (*A*) und $\text{Co}(\text{CNC}_{10}\text{H}_{13})_4\text{J}_2$ (*B*) wurden nach der Methode von Malatesta & Sacco (1953) hergestellt. Weissenberg-Aufnahmen mit $\text{Cu K}\alpha$ -Strahlung ergaben die Symmetrie, die Auslöschungsbedingungen und die ungefähren Gitterdimensionen der genannten Verbindungen. Die genauen Gitterkonstanten wurden aus diffraktometrisch exakt bestimmten Glanzwinkeln θ von 41