

1983; Dillen, Lenstra, Haasnoot & Reedijk, 1983). The Pd—N(3) distance of 2.014 (4) Å and the Pd—Br distance of 2.4196 (7) Å are normal by comparison with *trans*-Pd[2-(2'-thienyl)pyridine]<sub>2</sub>Br<sub>2</sub> (Giordano, Butler & Rasmussen, 1978). Two other related structures are *trans*-Pd(L)<sub>2</sub>Cl<sub>2</sub> (L = 1-methylimidazole and 2-methylimidazole), for which metal–nitrogen distances of 2.011 (4) and 2.005 (3) Å were found (Navarro-Ranninger, Martinez-Carrera & Garcia-Blanco, 1983*a,b*). The shortest Br—Br contact observed in the structure is 3.727 (1) Å. No hydrogen bonds between the methanol molecules and the bromine atoms were found. This agrees with the observed  $\nu_{\text{OH}}$  of MeOH of 3520 cm<sup>-1</sup>. The shortest intramolecular distance found is that between N(4) and H(11) with a distance of 2.61 (2) Å. Molecular packing is therefore dictated solely by van der Waals forces.

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## The Structure of Dilithium Dihydrogen 1,2,4,5-Benzenetetracarboxylate Tetrahydrate (Dilithium Dihydrogen Pyromellitate Tetrahydrate)

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**Abstract.** Li<sub>2</sub>C<sub>10</sub>H<sub>4</sub>O<sub>8</sub>·4H<sub>2</sub>O, *M<sub>r</sub>* = 338.1, triclinic, *P* $\bar{1}$ , *a* = 4.586 (1), *b* = 8.539 (4), *c* = 8.525 (3) Å,  $\alpha$  = 87.66 (5),  $\beta$  = 89.21 (3),  $\gamma$  = 89.80 (2)°, *V* = 333.5 (4) Å<sup>3</sup>, *Z* = 1, *D<sub>x</sub>* = 1.683 Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha)$  = 0.71069 Å,  $\mu$  = 0.15 mm<sup>-1</sup>, *F*(000) = 172, room temperature, *wR* = 0.034 for 1204 reflections [*I* > 2 $\sigma$ (*I*)]. The pyromellitate anions are located at centers of symmetry and are stacked along [100]. They form (11 $\bar{1}$ ) layers *via* two strong intermolecular hydrogen bonds (2.46 and 2.50 Å) which extend across centers of symmetry. These layers are connected by Li ions which have approximate tetrahedral coordination (two carboxylic O atoms and two H<sub>2</sub>O molecules).

**Introduction.** Recent IR spectroscopic investigations of several acid salts of pyromellitic acid (Luehrs, Cornilsen, Glover & Neils, 1988) suggested the presence of strong hydrogen bonds. Only a few of these salts have been characterized by crystal structure analysis so far. One of these, an acid Co-pyromellitate, has a very short intramolecular

hydrogen bond (Ward & Luehrs, 1983). Since several lithium salts of phthalic acid were found to have very short intramolecular hydrogen bonds (Gonschorek & Küppers, 1975; Adiwidjaja & Küppers, 1978; Küppers, Takusagawa & Koetzle, 1985), lithium was chosen as cation in the present study in order to find another example of a compound with a short intramolecular hydrogen bond.

**Experimental.** Single crystals were grown from an aqueous solution of a stoichiometric mixture of LiOH·H<sub>2</sub>O (Fluka, p.a.) and pyromellitic acid (Fluka, recrystallized) by slow evaporation. Optical microscopy indicated that two phases were present: (1) many poorly crystallized needles and (2) a few prismatic crystals of good quality. One of these (0.1 × 0.2 × 0.2 mm) was mounted on a Siemens–Stoe AED2 diffractometer and 2091 intensities were collected ( $\theta$  range 2–30°,  $\theta$ –2 $\theta$  mode, 153 reflections rejected as unobserved, 1627 unique, *R*<sub>int</sub> = 0.015). Index ranges were *h* – 6/6, *k* – 12/12, *l* 0/12. Three standard reflections monitored every 60 min

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^4$ )

$U_{eq}$  is one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$ or $U_{iso}^*$
C(1)	8310 (4)	318 (2)	8659 (2)	149 (5)
C(2)	8912 (4)	1507 (2)	9687 (2)	133 (4)
C(3)	569 (4)	1179 (2)	1015 (2)	159 (5)
C(4)	6422 (4)	653 (2)	7256 (2)	191 (5)
C(5)	7970 (4)	3187 (2)	9367 (2)	157 (5)
O(1)	4810 (3)	1801 (2)	7221 (2)	271 (4)
O(2)	3402 (4)	326 (2)	3852 (2)	363 (6)
O(3)	9235 (3)	4010 (2)	8361 (2)	228 (4)
O(4)	5869 (3)	3649 (2)	265 (2)	212 (4)
OW(1)	6004 (4)	4343 (2)	3394 (2)	270 (4)
OW(2)	847 (4)	3095 (2)	4820 (2)	304 (5)
Li	2294 (8)	3525 (4)	6881 (4)	271 (10)
H(2)	4333 (90)	170 (53)	4645 (49)	111 (113)*
H(3)	5205 (166)	4451 (61)	132 (92)	684 (239)*

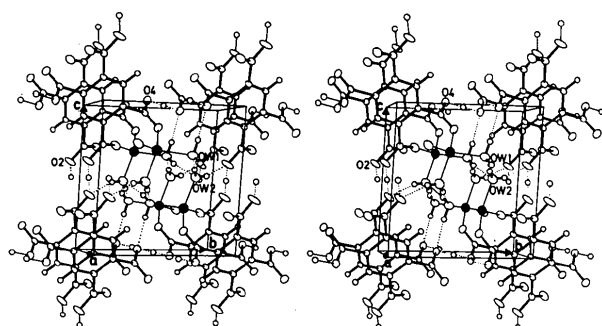


Fig. 1. Stereoscopic view of the crystal structure. Thermal ellipsoids are drawn at the 50% probability level. H(2) and H(3) are represented as not split. All H atoms have a fixed radius, Li<sup>+</sup> ions are given as full dots. Thin lines indicate Li...O bonds and dotted lines hydrogen bonds.

showed no systematic variation. The orientation matrix was checked every 6 h. No absorption correction was applied. Lattice parameters were determined by a least-squares fit to 30 diffractometer measured Bragg angles. The standard cell ( $a < b < c$ ) may be obtained by interchanging  $b$  and  $c$  and  $\beta$  with  $\gamma$ . The structure was solved by direct methods which located the positions of all but the H atoms which were found in a difference Fourier synthesis. If, according to the centrosymmetric space group, the two H atoms H(2) and H(3) were fixed at centers of symmetry,  $wR$  was 0.0341. Assuming statistical disorder and site occupation factor 0.5,  $wR$  improved to 0.0335 ( $R = 0.045$ ). Simultaneously, the displacement parameters of these two H atoms improved from 0.212 and 0.091 to 0.067 and 0.011, respectively. Weights  $w = 1/\sigma^2$ . Maximum  $\Delta/\sigma = 0.031$ . Anisotropic displacement parameters for non-H atoms and individual isotropic displacement parameters for H atoms were applied. Isotropic extinction parameter  $g = 3.1(2) \times 10^{-6}$  [ $F' = F(1 - gF^2/\sin\theta)$ ]. Residual electron density ranged

Table 2. Distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the [Li—O<sub>4</sub>] polyhedra

Li—O(1)	1.883 (4)	Li—OW(1 <sup>b</sup> )	1.988 (4)
Li—O(3 <sup>b</sup> )	1.929 (4)	Li—OW(2)	1.936 (4)
O(1)—Li—O(3 <sup>b</sup> )	121.8 (2)	O(3 <sup>b</sup> )—Li—OW(1 <sup>b</sup> )	98.0 (2)
O(1)—Li—OW(1 <sup>b</sup> )	118.9 (2)	O(3 <sup>b</sup> )—Li—OW(2)	113.1 (2)
O(1)—Li—OW(2)	100.5 (2)	OW(1 <sup>b</sup> )—Li—OW(2)	103.9 (2)

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

Table 3. Hydrogen bond distances ( $\text{\AA}$ )

O(2)—O(2 <sup>b</sup> )	2.505 (3)	OW(1)—OW(2)	2.835 (3)
O(4)—O(4 <sup>b</sup> )	2.464 (3)	OW(2 <sup>b</sup> )—OW(1)	2.738 (3)
OW(1)—O(4)	2.758 (3)	OW(2)—O(2)	2.785 (3)

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

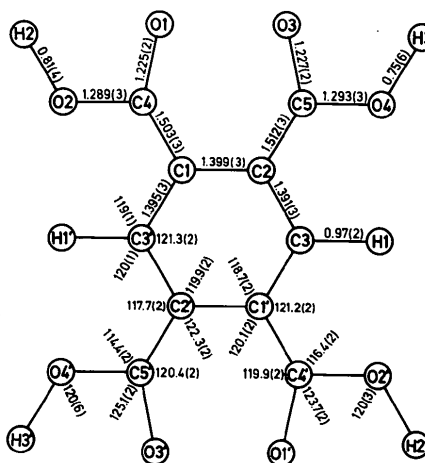


Fig. 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the pyromellitate anion.

between  $-0.36$  and  $+0.40 e \text{\AA}^{-3}$ . Programs used: *SHELX76* (Sheldrick, 1976); *SHELXS86* (Sheldrick, 1986); *ORFFE* (Busing, Martin & Levy, 1964) and *ORTEPII* (Johnson, 1976). Atomic coordinates and equivalent isotropic thermal parameters  $U_{eq}$  for all atoms are listed in Table 1.\*

**Discussion.** The packing is shown by a stereoscopic *ORTEP* plot in Fig. 1. There is one pyromellitate anion per unit cell located at an inversion center. The anions are stacked along [100]. The two carboxylic O atoms O(2) and O(4) form strong intermolecular hydrogen bonds *via* centers of symmetry in  $\frac{1}{2}, \frac{1}{2}, 0$  and  $\frac{1}{2}, 0, \frac{1}{2}$ , building chains parallel to [110] and [101],

\* Lists of structure factors, anisotropic thermal parameters and full H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53203 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

respectively, and layers parallel to (11 $\bar{1}$ ). These layers are linked by Li ions which are coordinated by the carboxylic O atoms O(1) and O(3) of two different

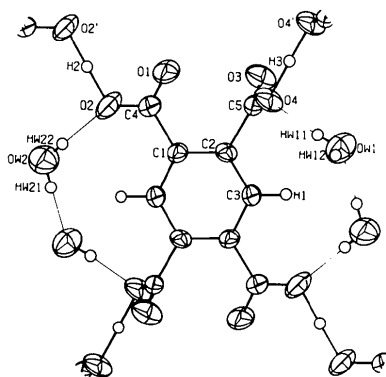


Fig. 3. Thermal ellipsoid plot of the pyromellitate anion and the interconnecting hydrogen bonds (probability level = 90%).

anions and by the two water molecules (see Table 2). The water molecules themselves form hydrogen bonded zigzag chains parallel to [100] and are (as well as the Li ions) located in a channel parallel to [100]. Distances and angles inside the pyromellitate anion are within expected ranges (Fig. 2). The tilt angles between the carboxylic groups and the mean plane through the benzene ring are as follows: O(1)—C(4)—O(2) 19.7°, O(3)—C(5)—O(4) 74.7°. The hydrogen bond distances are listed in Table 3. The shape of the molecule and the hydrogen bonds are shown in Fig. 3.

According to Speakman's classification the present short intermolecular hydrogen bonds [O—O distances 2.505 (3) and 2.464 (3) Å] are of 'Type A' (Speakman, 1972), since the O atoms of each bond are equivalent by symmetry. If the H atoms were actually centered, a relatively long O—H distance would result. The slightly improved *R* value favors a splitting of the positions although care has to be

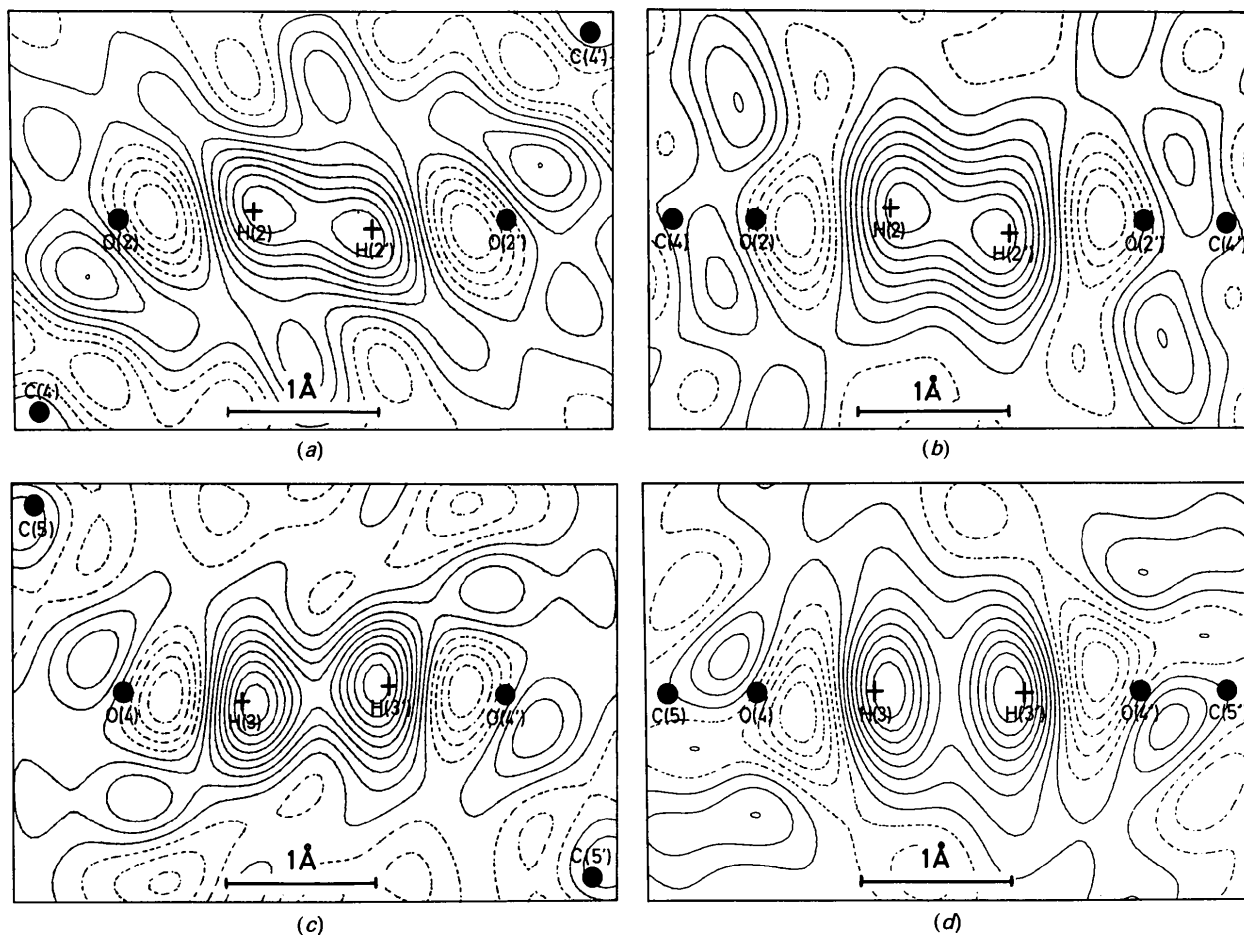


Fig. 4. Difference Fourier sections of the short intermolecular hydrogen bonds. The lines indicate electron density in steps of  $0.03 \text{ e } \text{Å}^{-3}$ . Dashed lines indicate negative electron densities. The crosses mark the hydrogen positions found in the refinement. (a) Section along plane C(4)—O(2)···O(2')—C(4'). (b) Section (a) rotated 90° around the line O(2)···O(2'). (c) Section along plane C(5)—O(4)···O(4')—C(5'). (d) Section (c) rotated 90° around the line O(4)···O(4').

taken with regard to the KKM effect (Kroon, Kanters, Peerdeman & Vos, 1971). In addition, therefore, difference Fourier syntheses [Figs. 4(a-d)] were calculated (program *GENFOR*; Craven, Weber & Ruble, 1979). The splitting is evident in all these maps. The positions of the maxima are in good agreement with the positions obtained in the refinement. All calculations were carried out on a MicroVAX and on the PDP10 of the Rechenzentrum der Universität Kiel.

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## Structure of (Ethylenediamine)(tetramethylenediamine)(trimethylenediamine)-cobalt(III) Hexacyanocobaltate(III) Monohydrate, $\Delta-(+)$ <sub>589</sub>[Co(en)(tn)(tmd)]-[Co(CN)<sub>6</sub>].H<sub>2</sub>O

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**Abstract.** [Co(C<sub>2</sub>H<sub>4</sub>N<sub>2</sub>)(C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>)(C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>)]-[Co(CN)<sub>6</sub>].H<sub>2</sub>O, *M<sub>r</sub>* = 514.5, triclinic, *P*1, *a* = 9.599 (2), *b* = 15.344 (3), *c* = 8.944 (2) Å,  $\alpha$  = 100.47 (2),  $\beta$  = 113.93 (2),  $\gamma$  = 81.37 (2)° *V* = 1179.9 (4) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.45 Mg m<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71073 Å,  $\mu$  = 1.43 mm<sup>-1</sup>, *F*(000) = 513.4, *T* = 120 (2) K, final *R* = 0.069 for 3935 reflections. The five-, six- and seven-membered chelate rings of the complex cation take *lel*, *lel*(skew-boat), *lel* configuration. The complex cations take two possible orientations around the approximate twofold axis

through the Co atom and the center of the C—C bond of the five-membered chelate ring with interchanging six- and seven-membered chelate rings. The disorder was analyzed by a split atom model. A conformational analysis has been performed to show that the *lel*<sub>3</sub> conformation observed in the crystal has the second lowest strain energy with a difference of only 2.2 kJ mol<sup>-1</sup> owing to the relatively small non-bonded interactions.

**Introduction.** Conformations of the five-, six- and seven-membered chelate rings in several tris-bidentate Co<sup>III</sup> complexes have been investigated

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