

## Dimeric Lithium *o*-Phenylenedioxydiacetate Trihydrate

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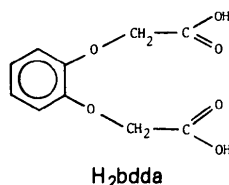
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(Received 3 January 1986; accepted 17 April 1986)

**Abstract.**  $(2\text{Li}^+\cdot\text{C}_{10}\text{H}_8\text{O}_6^{2-}\cdot 3\text{H}_2\text{O})_2$ ,  $M_r = 584.2$ , triclinic,  $P\bar{1}$ ,  $a = 5.296$  (1),  $b = 10.819$  (4),  $c = 11.508$  (5) Å,  $\alpha = 103.97$  (3),  $\beta = 97.45$  (3),  $\gamma = 91.96$  (3)°,  $V = 633.0$  (8) Å<sup>3</sup>,  $Z = 1$ ,  $D_m = 1.52$ ,  $D_x = 1.531$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.14$  mm<sup>-1</sup>,  $F(000) = 304$ ,  $T = 77$  K. Final  $R = 0.033$  for 1174 observed reflections. The title compound, prepared by reaction of *o*-phenylenedioxydiacetic acid ( $\text{H}_2\text{bdda}$ ) with excess  $\text{Li}_2\text{CO}_3$ , is a centrosymmetric dimer having two different Li centres. The first is five-coordinate, approximating a square pyramid, and involves four O atoms of the *bdda* ligand in the basal plane [mean Li–O, 2.054 (5) Å], with a water in the apical position [Li–O, 1.967 (5) Å]. The second Li centre is tetrahedral [mean Li–O, 1.946 (5) Å], with bonds to a second carboxy O of the *bdda* ligand, two to water O atoms and the fourth to an inversion-related coordinated *bdda* carboxylate O, completing a cyclic-dimer structure.

**Introduction.** *o*-Phenylenedioxydiacetic acid ( $\text{H}_2\text{bdda}$ ) is a compound related to the phenoxyalkanoic-acid herbicides and provides a potentially quadridentate ligand system for metal-ion coordination. Although it resembles *edta* in some respects as a sequestering reagent, complex-stability constants for divalent metal ions are considerably smaller compared to those of *edta* (Suzuki, Hattori & Yamasaki, 1968).



$\text{H}_2\text{bdda}$  is also analogous to  $\text{NaBPh}_4$  in forming a crystalline precipitate with  $\text{K}^+$  but not with  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$  or  $\text{NH}_4^+$ . The compound  $[\text{K}(\text{Hbdda})(\text{H}_2\text{bdda})]$  has pentagonal antiprismatic coordination about  $\text{K}^+$  with each of the *bdda* species planar (Green, Duax,

Smith & Wudl, 1975). The crystal structure of the complex  $\text{Na}[\text{La}(\text{bdda})_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$  (Kerfoot, Chopin & Kistenmacher, 1979) showed an *s*-capped square antiprismatic decacoordinate stereochemistry about  $\text{La}^{\text{III}}$  involving two essentially planar *bdda* ligands. In complexes with the divalent metal ions, the stereochemistry with one exception (Smith, O'Reilly, Kennard & Mak, 1986) involves the *bdda* ligand in pentagonal-bipyramidal coordination. The title compound was prepared as one of a series of Group Ia metal– $\text{H}_2\text{bdda}$  complexes and its structure determined to ascertain the nature of the association between the ligand and the metal ion.

**Experimental.** The title compound was prepared by a previously described method (Smith, O'Reilly, Kennard, Stadnicka & Oleksyn, 1981) by reacting *o*-phenylenedioxydiacetic acid (Sigma Chemicals) in 50% aqueous ethanol with excess lithium carbonate at *ca* 363 K. After removal of the unreacted excess by filtration, crystals grew from the solution as colourless needles after partial room-temperature evaporation. Cleaved specimen,  $0.40 \times 0.20 \times 0.18$  mm, used to collect data at liquid-nitrogen temperature (77 K) on a Nicolet R3m diffractometer using graphite-monochromatized Mo  $K\alpha$  radiation. Data-collection details:  $\omega$  scan;  $2\theta_{\text{max}} = 45^\circ$ ; range  $h$ , 0–3;  $k$ ,  $\pm 11$ ;  $l$ ,  $\pm 10$ ; 1248 reflections [1506 unique,  $R_{\text{int}} 0.028$ ; 332 unobserved; 1174 with  $I > 1\sigma(I)$  considered observed]; standards (variation),  $2\bar{2}\bar{1}$  (2.8%);  $3\bar{1}\bar{2}$  (4.1%);  $2\bar{3}\bar{3}$  (3.5%). Cell parameters (at 77 K) determined using 15 high-angle reflections. No corrections made for absorption or extinction.

Data processed using *SHELXTL* (Sheldrick, 1984). Structure solution by multisolution  $\sum_2$  sign-expansion direct methods of *SHELX76* (Sheldrick, 1976). Blocked-matrix least-squares refinement ( $F^2$ 's) with anisotropic thermal parameters on all non-H atoms gave  $R = 0.033$  and  $wR = 0.036$  with  $w = 2.1/(\sigma^2 F_o + 2.2 \times 10^{-4} F_o^2)$ . H atoms located in a difference-Fourier synthesis and included at fixed positions with isotropic  $U$  values set invariant at  $0.05$  Å<sup>2</sup>.  $(\Delta/\sigma)_{\text{max}} = 0.63$ ,

$(\Delta/\sigma)_{av} = 0.22$ . Max. and min. difference peaks,  $+0.20$  and  $-0.20 \text{ e } \text{\AA}^{-3}$  respectively. Scattering factors and  $f'$ ,  $f''$  terms for anomalous dispersion from *International Tables for X-ray Crystallography* (Ibers & Hamilton, 1974). Atomic positional and thermal parameters are listed in Table 1\* while bond distances and angles are given in Table 2.

**Discussion.** The structure of  $[\text{Li}_2(\text{bdda})(\text{H}_2\text{O})_3]_2$  comprises two stereochemically different lithium centres, one approximating square pyramidal, the other tetrahedral (Fig. 1). The first Li atom is bonded to the four 'inner' O atoms of the bdda ligand [mean Li—O,  $2.054(5) \text{ \AA}$ ], which provide an almost planar but distorted square configuration about the metal. The angle constraints imposed by the two phenoxy side-chains result in an enlargement of the angle opposite the phenyl ring  $[\text{O}(101)\text{—Li—O}(102)]$  to  $124.8(3)^\circ$ , relative to the inner three angles  $[72.1(2), 76.8(2), 77.0(2)^\circ]$ . It is within this outer angle that the bridging carboxylate O is accommodated in the polymeric complexes  $[\text{M}(\text{bdda})(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$  [ $\text{M} = \text{Ca}, \text{Mn}$ ] or the water molecule in the monomers  $[\text{M}(\text{bdda})(\text{H}_2\text{O})_3] \cdot 3.5\text{H}_2\text{O}$  [ $\text{M} = \text{Mg}, \text{Co}, \text{Zn}$ ] (Smith *et al.*, 1986). For this compound, there is a long interaction in this site [ $3.257(2) \text{ \AA}$ ] between Li(1) and one of the waters  $[\text{Ow}(3)]$  bonded to Li(2), but this is not considered as a bond.

Lithium carboxylates have a lesser tendency to expand their coordination polyhedra *via* water insertion than is the case with other Group Ia metals. They are either anhydrous (Mak, Yip, Kennard, Smith & O'Reilly, 1986) or have up to two coordinated waters as found about Li(2) in this example and in lithium acetate dihydrate (Galigné, Mouvet & Falgueirettes, 1970). Furthermore, regular tetrahedral coordination with short Li—O bonds is the most common stereochemistry. For the examples which are other than tetrahedral, *e.g.* ammonium lithium citrate monohydrate (Gabe, Glusker, Minkin & Patterson, 1967), the Li—O bonds become more elongated. In the present complex, the bond to the water molecule in the axial site of the square pyramid is more comparable with the normal tetrahedral values. Also, the Li atom lies slightly below the plane of the four bdda O atoms [ $0.31(1) \text{ \AA}$ ] and the fit of the metal into the ligand cavity is better than is the case with other complexes of bdda, with more equidimensional bonds to ether O atoms and carboxylate O atoms. As for the other complexes of bdda, the ligand is essentially planar and maintains

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and intraligand bond distances and angles and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43047 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2, \times 10^3$ )

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	$U_{eq}$
Li(1)	1079 (10)	2162 (4)	1743 (3)	24 (3)
Li(2)	613 (10)	6630 (4)	558 (3)	20 (3)
Ow(1)	2996 (4)	1027 (2)	619 (1)	21 (1)
Ow(2)	-2074 (4)	6813 (2)	1579 (1)	25 (1)
Ow(3)	2165 (4)	8396 (2)	957 (2)	24 (3)
C(1)	5372 (6)	3079 (2)	3846 (2)	15 (2)
C(2)	3932 (6)	2154 (2)	4196 (2)	14 (2)
C(3)	4652 (6)	1861 (2)	5292 (2)	17 (2)
C(4)	6855 (6)	2497 (2)	6025 (2)	17 (2)
C(5)	8315 (6)	3376 (2)	5668 (2)	20 (2)
C(6)	7553 (6)	3680 (2)	4559 (2)	20 (2)
O(71)	4348 (4)	3253 (2)	2738 (1)	22 (1)
C(81)	5053 (6)	4382 (2)	2380 (2)	17 (2)
C(91)	2858 (6)	4575 (2)	1460 (2)	14 (2)
O(101)	959 (4)	3772 (2)	1163 (1)	17 (1)
O(111)	3141 (4)	5545 (2)	1055 (1)	18 (1)
O(72)	1843 (4)	1645 (2)	3365 (1)	18 (1)
C(82)	223 (5)	653 (2)	3548 (2)	18 (2)
C(92)	-1902 (6)	315 (2)	2486 (2)	17 (2)
O(102)	-2031 (4)	989 (2)	1728 (1)	21 (1)
O(112)	-3394 (4)	-630 (2)	2446 (2)	24 (1)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ), associated with Li

Li(1)—Ow(1)	1.967 (5)	Li(2)—Ow(2)	1.945 (2)
Li(1)—O(71)	2.097 (5)	Li(2)—Ow(3)	1.977 (4)
Li(1)—O(72)	2.070 (5)	Li(2)—O(101)	1.984 (5)
Li(1)—O(101)	2.010 (5)	Li(2)—O(111)	1.931 (5)
Li(1)—O(102)	2.040 (5)		
Ow(1)—Li(1)—O(71)	94.1 (2)	Li(1)—O(71)—C(1)	120.9 (2)
Ow(1)—Li(1)—O(72)	105.4 (2)	Li(1)—O(71)—C(81)	116.6 (2)
Ow(1)—Li(1)—O(101)	104.3 (2)	Li(1)—O(72)—C(2)	122.0 (2)
Ow(1)—Li(1)—O(102)	101.4 (2)	Li(1)—O(72)—C(82)	117.4 (2)
O(71)—Li(1)—O(72)	72.1 (2)	Ow(2)—Li(2)—Ow(3)	101.5 (2)
O(71)—Li(1)—O(101)	77.0 (2)	Ow(2)—Li(2)—O(101)	109.1 (2)
O(71)—Li(1)—O(102)	147.9 (2)	Ow(2)—Li(2)—O(111)	110.7 (2)
O(72)—Li(1)—O(101)	138.1 (2)	Ow(3)—Li(2)—O(101)	106.8 (2)
O(72)—Li(1)—O(102)	76.8 (2)	Ow(3)—Li(2)—O(111)	108.5 (2)
O(101)—Li(1)—O(102)	124.8 (3)	O(101) <sup>b</sup> —Li(2)—O(111)	118.8 (2)
Li(1)—O(101)—C(91)	119.5 (2)	Li(2)—O(101) <sup>b</sup> —C(91)	116.2 (2)
Li(1)—O(102)—C(92)	118.1 (2)	Li(2)—O(111)—C(91)	129.5 (2)

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

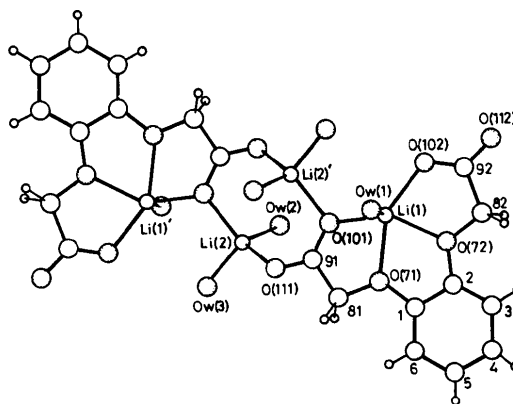


Fig. 1. Molecular configuration and atom-naming scheme for  $[\text{Li}_2(\text{bdda})_2(\text{H}_2\text{O})_6]$ .

regular O...O separations within the molecular cavity [O(71)...O(101), 2.557 (3); O(72)...O(102), 2.553 (3); O(71)...O(72), 2.450 (3) Å].

The second Li has regular tetrahedral coordination [mean Li—O, 1.946 (5) Å] with the carboxylate O [O(111)], two water molecules and a carboxylate O [O(101')(-x, -y, -z)] forming a dimer across an inversion centre in the cell. This gives an Li(2)...Li(2') separation of 3.457 (8) Å while Li(1)...Li(2) is 3.265 (8) Å. The only other known lithium phenoxy-alkanoate structure, anhydrous lithium 2-(carbamoyl-phenoxy)acetate (Mak *et al.*, 1986), is tetrahedral but forms polymeric bridges *via* both the amide and carboxyl groups.

The dimeric molecules of the title compound appear to be stabilized by the presence of intramolecular hydrogen-bonding interactions involving O(111) and its inversion-related water [Ow(2')] [2.763 (3) Å]. Packing of the molecules in the unit cell involves only two interdimer hydrogen bonds, Ow(1)...Ow(3) [2.989 (3) Å (1 - x, -y, -z)] and O(112)...O(72) [2.913 (3) Å (1 + x, y, z)].

The authors acknowledge financial assistance from the Queensland Institute of Technology and the University

of Queensland. Professor Bruce Penfold and Dr Ward Robinson of the Department of Chemistry, University of Canterbury, Christchurch, New Zealand, are thanked for the use of data-collection facilities.

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*Acta Cryst.* (1986). **C42**, 1331–1333

## Structure of Methyltriphenylphosphonium Tetrachloroferrate(III)

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(Received 1 July 1985; accepted 8 May 1986)

**Abstract.** [P(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>][FeCl<sub>4</sub>], *M<sub>r</sub>* = 474.99, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 10.976 (3), *b* = 13.554 (4), *c* = 14.818 (4) Å, *V* = 2204.5 (9) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.43 (1), *D<sub>x</sub>* = 1.431 Mg m<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 1.25 mm<sup>-1</sup>, *F*(000) = 964, room temperature, *R* = 0.039 for 2032 reflections. The structure consists of CH<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub><sup>+</sup> cations and FeCl<sub>4</sub><sup>-</sup> anions; the iron(III) atom is tetrahedrally coordinated by four Cl ligands with Fe—Cl distances in the range 2.171 (2)–2.182 (2) Å and Cl—Fe—Cl angles 107.8 (1)–112.4 (1)°. The planes of the phenyl groups

in the cation form dihedral angles of 113.7 (1), 75.2 (1) and 104.9 (2)°.

**Introduction.** In studies of the oxidation of triphenylphosphine (PPh<sub>3</sub>) to triphenylphosphine oxide (OPPh<sub>3</sub>) with O<sub>2</sub> catalysed by the [FeCl<sub>2</sub>(OPPh<sub>3</sub>)<sub>4</sub>][FeCl<sub>4</sub>] complex considerable influence of various solvents on the course of the reaction was observed: in the reaction between FeCl<sub>3</sub> and PPh<sub>3</sub> in the presence of O<sub>2</sub> in acetonitrile the [FeCl<sub>2</sub>(OPPh<sub>3</sub>)<sub>4</sub>][FeCl<sub>4</sub>] complex was formed (Vančová, Ondrejkořičová & Ondrejovič, 1984); in ether the FeCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> complex was prepared; and from methanol the title compound was

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