

Tetraqua-1 κ O,2 κ^3 O-(μ -2,4-dinitrophenolato-1 κ^2 O¹,O²:2 κ O¹)(2,4-dinitrophenolato-1 κ^2 O¹,O²)dilithium(I): a dinuclear lithium(I) complex

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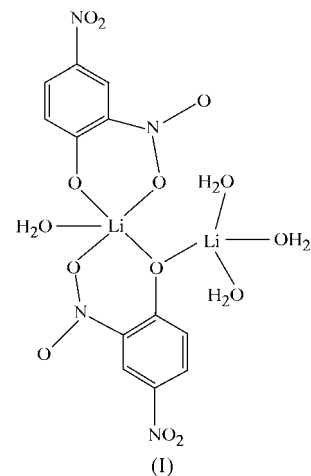
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The title complex, $[\text{Li}_2(\text{C}_6\text{H}_3\text{N}_2\text{O}_5)_2(\text{H}_2\text{O})_4]$, contains two kinds of Li atoms, *viz.* five-coordinated and four-coordinated. The five-coordinated Li ion has a tetragonal–pyramidal geometry, with a water molecule in the apical position and four O atoms from two 2,4-dinitrophenolate (2,4-DNP) ligands in the basal plane. The four-coordinated Li ion has a tetrahedral geometry, with three water molecules and one phenolate O atom of a 2,4-DNP ligand. The Li ions are bridged by a phenolate O atom, giving the complex a dinuclear structure. The crystal packing is stabilized by O–H \cdots O hydrogen-bonding interactions involving the water molecules and nitro O atoms.

Comment

Nitrophenols and their metal salts have been investigated extensively because they have useful properties as highly energetic materials. The thermal and combustion properties (Stammler, 1969; Brill *et al.*, 2000), and molecular structures and coordination behaviour (Harrowfield *et al.*, 1995*a,b*) of 2,4,6-trinitrophenol metal salts have been thoroughly studied. In our studies of the crystal structures and thermal properties of lithium 2,6-dinitrophenol (Yun *et al.*, 2004), yttrium 2,6-dinitrophenol (Suh *et al.*, 2002*a*), lanthanide 2,6-dinitrophenol (Suh *et al.*, 2002*b*; Yun *et al.*, 2006) and lanthanide 2,4,6-trinitrophenol (Yun *et al.*, 2005) salts, we have found that the coordination behaviour of the 2,6-dinitrophenol ligand is quite different from that of the 2,4,6-trinitrophenol ligand, in keeping with the electronic effect of the nitro substituent at the *para* position. As an extension of these studies, we have also employed the 2,4-dinitrophenol (2,4-DNP) ligand (Iwasaki & Kawano, 1977; Kagawa *et al.*, 1976). We report here the preparation and crystal structure of the title lithium(I) 2,4-DNP complex, (I).

As shown in Fig. 1, compound (I) is a unique dinuclear complex with two kinds of Li atoms and two kinds of 2,4-DNP



ligands. The geometries of the Li atoms are tetragonal–pyramidal (Li1) and tetrahedral (Li2), while the coordination modes of the 2,4-DNP ligands are chelation and chelation/bridging. The Li1 ion has a five-coordinate geometry, with a water molecule in the apical position and four O atoms from two 2,4-DNP ligands in the basal plane. As expected, the Li–O distances are slightly longer in the pyramid than in the tetrahedron (Table 1). Each of the 2,4-DNP ligands forms a six-membered chelate ring with Li1 through the O atoms of

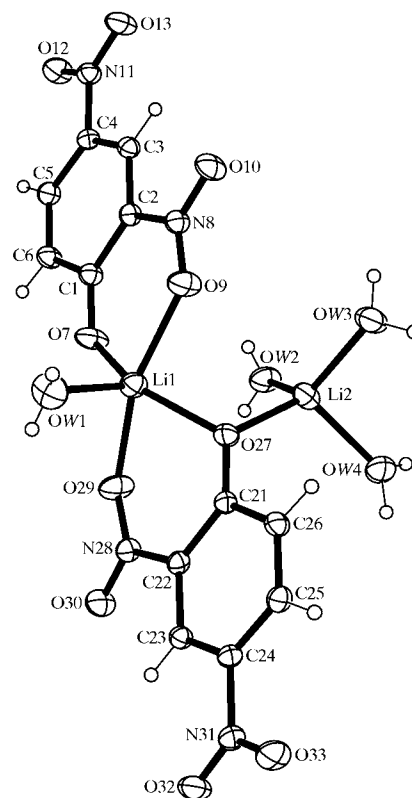


Figure 1
The molecular structure of complex (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

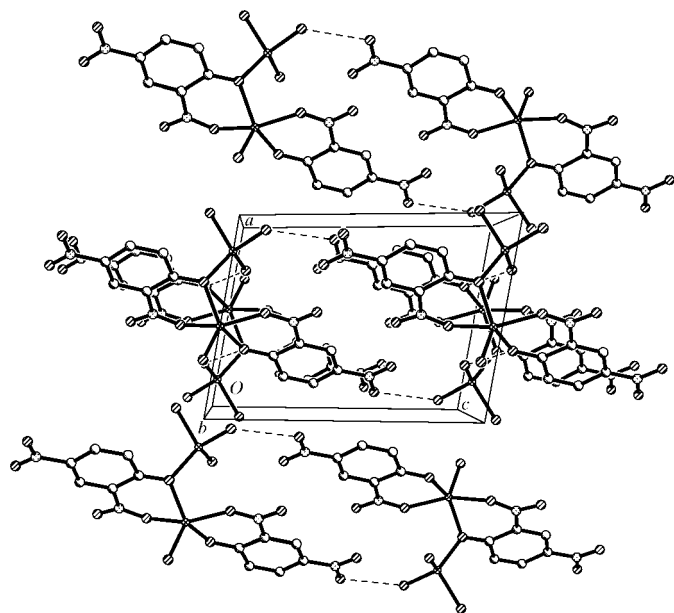


Figure 2
The crystal packing diagram of complex (I), viewed along the *b* axis. Hydrogen-bond interactions are shown as dashed lines.

the phenolate and nitro groups. Li2 has a four-coordinate geometry, formed by three water molecules and one phenolate O atom of a 2,4-DNP ligand. The phenolate O atom serves as the bridge between the Li1 and Li2 atoms. There is no metal-to-metal interaction; the Li1...Li2 distance is 3.172 (1) Å. The dinuclear complexes are linked in a three-dimensional manner by numerous intermolecular O_{water}—H...O_{2,4-DNP} and O_{water}—H...O_{water} hydrogen bonds (Fig. 2 and Table 2).

Although lithium is now known in at least 20 coordination geometries with coordination numbers ranging from 1 to 12 (Greenwood & Earnshaw, 1998), this dinuclear lithium 2,4-DNP complex with both four- and five-coordinate Li is unique. To our knowledge, only lithium *o*-phenylenedioxydiacetate trihydrate, [Li₂(C₁₀H₈O₆)(H₂O)₃]₂ (Smith *et al.*, 1986), has a similar geometry combination. However, this complex is dimeric, with four Li atoms bridged by the two *o*-phenylenedioxydiacetate ligands.

The structural features of (I) are very different from those of the dinuclear lithium 2,6-DNP complex, [Li(2,6-DNP)(H₂O)]₂·2H₂O, which we have studied recently (Yun *et al.*, 2004). Li1 and Li2 of the lithium 2,6-DNP complex are both coordinated to five O atoms in a square-pyramidal geometry, and there are both coordinated and free water molecules.

Experimental

The title lithium(I) 2,4-DNP complex, (I), was prepared in a manner similar to that used for the preparation of the lithium(I) 2,6-DNP complex (Yun *et al.*, 2004). Pale-yellow crystals of (I) suitable for single-crystal X-ray diffraction were obtained and characterized by energy dispersive X-ray spectroscopy, FT-IR and elemental analysis. Analysis calculated for C₁₂H₁₄Li₂N₄O₁₄: C 31.87, H 3.12, N 12.39, Li 3.07%; found: C 31.94, H 3.14, N 12.38, Li 3.05%. The 2,4-DNP ligand

was confirmed by assignment of the relevant FT-IR absorption bands (Nakamoto, 1997).

Crystal data

[Li₂(C₆H₃N₂O₅)₂(H₂O)₄]
M_r = 452.15
 Triclinic, *P* $\bar{1}$
a = 8.3038 (2) Å
b = 10.1267 (3) Å
c = 11.2984 (3) Å
 α = 76.733 (2)°
 β = 79.565 (2)°

γ = 86.276 (2)°
V = 909.16 (4) Å³
Z = 2
 Mo *K*α radiation
 μ = 0.15 mm⁻¹
T = 296 (2) K
 0.39 × 0.23 × 0.14 mm

Data collection

Bruker SMART APEXII CCD
 area-detector diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2000)
*T*_{min} = 0.944, *T*_{max} = 0.979

18045 measured reflections
 4473 independent reflections
 3497 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.024

Refinement

R[*F*² > 2σ(*F*²)] = 0.037
wR(*F*²) = 0.115
S = 1.04
 4473 reflections
 314 parameters
 5 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}}$ = 0.22 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.29 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Li1—O7	1.923 (2)	Li2—OW4	1.936 (2)
Li1—OW1	2.001 (3)	Li2—OW3	1.944 (2)
Li1—O27	2.004 (2)	Li2—OW2	1.967 (2)
Li1—O9	2.053 (2)	Li2—O27	1.978 (2)
Li1—O29	2.068 (2)		
O7—Li1—OW1	105.87 (11)	O27—Li1—O29	82.37 (8)
O7—Li1—O27	144.96 (13)	O9—Li1—O29	158.14 (13)
OW1—Li1—O27	109.11 (10)	OW4—Li2—OW3	97.58 (10)
O7—Li1—O9	84.53 (8)	OW4—Li2—OW2	103.81 (11)
OW1—Li1—O9	105.18 (11)	OW3—Li2—OW2	118.93 (11)
O27—Li1—O9	88.33 (9)	OW4—Li2—O27	111.11 (10)
O7—Li1—O29	91.78 (9)	OW3—Li2—O27	115.48 (11)
OW1—Li1—O29	96.56 (10)	OW2—Li2—O27	108.59 (10)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
OW1—HW1A...O32 ⁱ	0.79 (2)	2.53 (2)	3.3083 (15)	171 (2)
OW1—HW1B...O27 ⁱⁱ	0.82 (2)	2.41 (2)	3.1461 (15)	151 (2)
OW1—HW1B...O9 ⁱⁱ	0.82 (2)	2.59 (2)	3.1821 (15)	130 (2)
OW2—HW2A...O29 ⁱⁱⁱ	0.76 (2)	2.58 (2)	2.9592 (12)	113 (2)
OW2—HW2A...O13 ^{iv}	0.76 (2)	2.59 (2)	3.1262 (13)	129 (2)
OW2—HW2B...O7 ⁱⁱⁱ	0.83 (2)	1.96 (2)	2.7936 (13)	174 (2)
OW3—HW3A...O12 ^{iv}	0.84 (2)	2.04 (2)	2.8725 (14)	173 (2)
OW3—HW3B...OW1 ^v	0.80 (2)	2.50 (2)	3.2655 (17)	159 (2)
OW4—HW4A...OW2 ^{vi}	0.80 (2)	2.16 (2)	2.9560 (16)	178 (2)
OW4—HW4B...O33 ^{vii}	0.82 (2)	2.02 (2)	2.8381 (13)	174 (2)

Symmetry codes: (i) $-x + 1, -y, -z + 3$; (ii) $-x + 1, -y, -z + 2$; (iii) $-x + 1, -y + 1, -z + 2$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x - 1, y, z$; (vi) $-x, -y + 1, -z + 2$; (vii) $-x, -y, -z + 3$.

The H atoms on the 2,4-DNP ligand were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The water H atoms were located in a difference electron-density map and refined with *U*_{iso}(H) = 1.5*U*_{eq}(O) and with O—H distances restrained to 0.82 (2) Å.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3089). Services for accessing these data are described at the back of the journal.

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