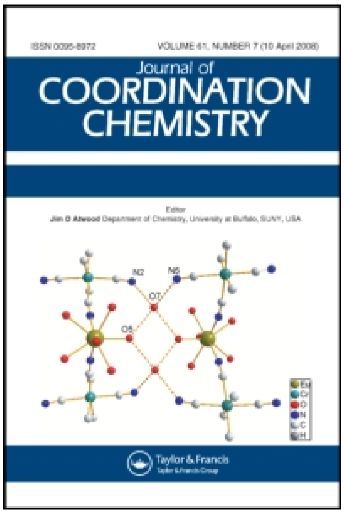

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# Crystal structure and thermal properties of a dimeric (2,6-dinitrophenolato)lithium(I) complex

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# CRYSTAL STRUCTURE AND THERMAL PROPERTIES OF A DIMERIC (2,6-DINITROPHENOLATO)LITHIUM(I) COMPLEX

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The crystal structure of a (2,6-dinitrophenolato)lithium complex has been determined by single-crystal X-ray diffraction methods. It is triclinic, space group $P\bar{1}$, with $a = 5.205(2)$, $b = 8.972(3)$, $c = 10.608(4)$ Å, $\beta = 77.99(6)°$, $V = 474.2(3)$ Å$^3$, $Z = 1$. The dimeric complex is centrosymmetric, excluding outer-sphere water molecules. The Li(I) ion is coordinated to five oxygen atoms to form square pyramidal geometry. There is a water molecule in the apical position, and four oxygen atoms from two 2,6-dinitrophenol (2,6-DNP) ligands form the basal plane. TG-DTG curves show that there are two steps for the mass loss during the thermal decomposition of the complex $[Li(2,6\text{-}DNP)(H_2O)]_2 \cdot 2H_2O$. The first, between 57 and 80°C, corresponds to dehydration, and the second, between 330 and 370°C, corresponds to decomposition of the complex with explosion.

*Keywords:* Lithium complex; 2,6-Dinitrophenol; Thermal analysis; Crystal structure

## INTRODUCTION

The nitrophenols and their metal salts as high energetic materials have been the subject of fairly extensive investigation involving thermal and combustion properties [1–3], molecular structures [4–8], solvent extraction [9,10] and coordination behavior [11–13]. The crystal structures of lanthanide complexes of picric acid (2,4,6-trinitrophenol) have been studied thoroughly [6]. In the picrate hydrates of earlier members of the lanthanide series (La to Tb), two picrate ligands are coordinated to the metal ion, one as a monodentate and the other being *quasi*-bidentate [6a]. On the other hand, only one picrate is coordinated as a monodentate in complexes of the later lanthanide metal ions (Dy to Lu) [6b].

With the expectation that the coordination behaviour of 2,6-dinitrophenol (2,6-DNP) would be very different to that of picric acid, we have studied the crystal structures of some lanthanide complexes of 2,6-DNP [7,8]. We found that 2,6-DNP acts as a bidentate forming neutral $ML_3$ complexes with lanthanide ions. We have

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now extended the investigation of the nitrophenols to the coordination chemistry of alkali metal ions, a subject that has received far less attention.

## EXPERIMENTAL

### Preparation of the Complex

The complex was prepared by the slow dropwise addition of an aqueous LiOH solution to a 2,6-DNP solution. The lithium metal solution was prepared by dissolving $LiOH{\cdot}H_2O$ (1 mmol, 0.042 g; Fisher Chemicals Scientific Co.) in distilled water ($20\,cm^3$) at room temperature. The ligand solution was prepared by dissolving 2,6-DNP (2 mmol, 0.368 g; 97% Aldrich) in distilled water ($30\,cm^3$) at 333 K with stirring. The pH of the ligand solution was adjusted to about 6 with 3 M LiOH solution. The reaction mixture was stirred for 3 h at 333 K after adjusting its pH to about 4 with 7 M $HNO_3$ solution and then cooled to room temperature. Orange crystals of the complex were obtained at room temperature over a few days.

### Thermal Analysis

The thermal decomposition of the complex was investigated on a TGA 50 instrument (Mettler-Toledo GmbH, Switzerland). Masses of about 0.67 mg were heated at a rate of $10^\circ C\,min^{-1}$ under a nitrogen atmosphere. DSC experiments were carried out with a model $821^e$ instrument (Mettler-Toledo GmbH) fitted with a standard aluminum sample pan, using a sample mass of about 0.44 mg and a heating rate of $10^\circ C\,min^{-1}$ under a nitrogen atmosphere. In the case of 2,6-DNP, a sample mass of 1.24 mg was used; indium was used as the reference. Analysis of Li was performed on a Jobin–Yvon Ultima-C inductively coupled plasma emission spectrometer.

### X-ray Crystallography

An orange crystal (dimensions $0.40 \times 0.26 \times 0.26$ mm) was selected for single-crystal analysis. Data were collected on an Enraf–Nonius CCD-4 diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. The standard direct method was used to position the atoms. Remaining nonhydrogen atoms were located from subsequent difference Fourier syntheses. Positional parameters for the H atoms on the 2,6-DNP rings were calculated geometrically and constrained to ride on their attached atoms with $U_{iso}(H) = 1.2\,U_{eq}(C)$. The water H atoms were located in a difference Fourier map and refined freely. The structure was refined using full-matrix least-squares methods on $F^2$ using the SHELX-97 program package [14]. Further details are given in Table I.

## RESULTS AND DISCUSSION

### Thermal Analyses

The lithium content of the complex was found to be 3.6% (calc. 3.1%). TG-DTG curves show two steps during the thermal decomposition of $[Li(2,6\text{-}DNP)(H_2O)]_2{\cdot}2H_2O$. At first, a weight loss of 16.6% (calc. 15.9%) was observed between 57 and

TABLE I Crystallographic data for the complex $[Li(2,6\text{-}DNP)(H_2O)]_2{\cdot}2H_2O$

| | |
|---|---|
| Empirical formula | $Li_2C_{12}H_{14}N_4O_{14}$ |
| Formula weight | 452.15 |
| Crystal size (mm) | 0.40 × 0.26 × 0.26 |
| $T$ (K) | 293(2) |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Radiation (Mo K$\alpha$) (λ/Å) | 0.71073 |
| $a$ (Å) | 5.2050(18) |
| $b$ (Å) | 8.972(3) |
| $c$ (Å) | 10.608(4) |
| $\alpha$ (°) | 78.15(5) |
| $\beta$ (°) | 77.99(6) |
| $\gamma$ (°) | 87.804(15) |
| $V$ (Å$^3$) | 474.2(3) |
| $Z$ | 1 |
| $d_{calc}$ (Mg m$^{-3}$) | 1.583 |
| Absorption coefficient, $\mu$ (mm$^{-1}$) | 0.144 |
| $F$(000) | 232 |
| $\theta$ range for data collection (°) | 2.00 to 25.49 |
| Index ranges | $-1 \le h \le 6$, $-10 \le k \le 10$, $-12 \le l \le 12$ |
| Reflections collected/unique | 2384/1768 [$R_{(int)} = 0.0295$] |
| Completeness to $\theta = 25.49$ | 100.0% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 1768/0/162 |
| Goodness-of-fit on $F^2$ | 1.042 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0564$[a], $wR_2 = 0.1089$[b] |
| Extinction coefficient | 0.051(7) |
| Largest diff. peak and hole (e A$^{-3}$) | 0.208 and −0.248 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

80°C, corresponding to the loss of four moles of water. Inner- and outer-sphere water was not distinguished but two endothermic peaks between 57 and 80°C were noted in the DSC curve (centered at 58.3 and 61.7°C). Dehydration enthalpies for outer- and inner-sphere water determined from DSC data are *ca* $\Delta H_{out} = 9.9\,\mathrm{kJ\,mol^{-1}}$ and *ca* $\Delta H_{inn} = 32.4\,\mathrm{kJ\,mol^{-1}}$.

A second weight loss was observed between 330 and 370°C on TG-DTG curves, corresponding to decomposition with explosion. The DSC curve shows a sharp exothermic peak for the explosive decomposition with a peak maximum temperature at 355.8°C. The enthalpy of decomposition was calculated from the peak area to be $\Delta H_{dec} = -654.2\,\mathrm{kJ\,mol^{-1}}$. 2,6-DNP, in contrast, shows only two endothermic peaks, one associated with melting at 64°C and the other with slow decomposition with a peak temperature of 255°C.

## Crystal Structure

Refined atomic parameters and selected bond lengths and angles for $[Li(2,6\text{-}DNP)(H_2O)]_2{\cdot}2H_2O$ are listed in Tables II and III, respectively. Table IV gives data for hydrogen bonds in the crystal. Figure 1 shows the coordination geometry of the Li(I) ion. It is coordinated to five oxygen atoms with square pyramidal geometry; a water molecule is in the apical position and four oxygen atoms from two 2,6-DNP ligands in basal positions with bond distances 1.926(6)–2.073(6) Å (these are shorter than the sum of the covalent radii of Li and O atoms, 2.180 Å). Each 2,6-DNP ligand provides two oxygen donors, a phenolato and a nitro oxygen atom.

TABLE II Atomic coordinates and equivalent isotropic thermal parameters for the nonhydrogen atoms in $[Li(2,6\text{-}DNP)(H_2O)]_2\cdot 2H_2O$

| | $x/a$ | $y/b$ | $z/c$ | $U_{(eq)}$ |
|---|---|---|---|---|
| Li | 1201(13) | 6302(7) | 157(5) | 58(2) |
| O(1) | 193(5) | 4295(2) | 1212(2) | 52(1) |
| N(1) | 3720(5) | 5465(3) | 2541(3) | 50(1) |
| O(2) | 3856(5) | 6128(3) | 1389(2) | 76(1) |
| O(3) | 5175(5) | 5855(3) | 3190(2) | 74(1) |
| N(2) | −3159(5) | 1711(3) | 2537(3) | 49(1) |
| O(4) | −3524(5) | 2279(3) | 1426(2) | 60(1) |
| O(5) | −4316(6) | 529(3) | 3164(2) | 79(1) |
| C(1) | 214(6) | 3694(3) | 2399(3) | 40(1) |
| C(2) | 1867(6) | 4221(3) | 3151(3) | 40(1) |
| C(3) | 1871(7) | 3576(4) | 4460(3) | 50(1) |
| C(4) | 225(8) | 2371(4) | 5118(3) | 59(1) |
| C(5) | −1404(7) | 1794(4) | 4458(3) | 52(1) |
| C(6) | −1404(6) | 2414(3) | 3154(3) | 40(1) |
| OW1 | −1017(7) | 7878(4) | 892(3) | 79(1) |
| OW2 | 1865(8) | 62(4) | 1425(4) | 96(1) |

TABLE III Selected bond lengths (Å) and angles (°) for $[Li(2,6\text{-}DNP)(H_2O)]_2\cdot 2H_2O$

| | | | |
|---|---|---|---|
| Li–O(1)#1 | 1.926(6) | O(4)–Li#1 | 2.073(6) |
| Li–O(1) | 1.941(6) | C(1)–C(2) | 1.439(4) |
| Li–OW1 | 1.973(8) | C(1)–C(6) | 1.444(4) |
| Li–O(2) | 2.072(6) | C(2)–C(3) | 1.391(4) |
| Li–O(4)#1 | 2.073(6) | C(3)–C(4) | 1.379(5) |
| Li–Li#1 | 2.801(11) | C(3)–H(3) | 0.9300 |
| O(1)–C(1) | 1.267(3) | C(4)–C(5) | 1.380(5) |
| O(1)–Li#1 | 1.926(6) | C(4)–H(4) | 0.9300 |
| N(1)–O(3) | 1.228(3) | C(5)–C(6) | 1.381(4) |
| N(1)–O(2) | 1.233(3) | C(5)–H(5) | 0.9300 |
| N(1)–C(2) | 1.456(4) | OW1–HW1 | 0.76(6) |
| N(2)–O(5) | 1.233(3) | OW1–HW2 | 0.94(7) |
| N(2)–O(4) | 1.235(3) | OW2–HW3 | 0.89(6) |
| N(2)–C(6) | 1.457(4) | OW2–HW4 | 0.93(5) |
| O(1)#1–Li–O(1) | 87.2(2) | O(4)–N(2)–C(6) | 121.6(2) |
| O(1)#1–Li–OW1 | 110.7(3) | N(2)–O(4)–Li#1 | 131.6(2) |
| O(1)–Li–OW1 | 110.4(3) | O(1)–C(1)–C(2) | 123.4(3) |
| O(1)#1–Li–O(2) | 152.9(4) | O(1)–C(1)–C(6) | 124.3(3) |
| O(1)–Li–O(2) | 81.6(2) | C(2)–C(1)–C(6) | 112.3(2) |
| OW1–Li–O(2) | 96.3(3) | C(3)–C(2)–C(1) | 123.5(3) |
| O(1)#1–Li–O(4)#1 | 82.6(2) | C(3)–C(2)–N(1) | 116.1(3) |
| O(1)–Li–O(4)#1 | 151.5(4) | C(1)–C(2)–N(1) | 120.4(2) |
| OW1–Li–O(4)#1 | 98.1(3) | C(4)–C(3)–C(2) | 120.5(3) |
| O(2)–Li–O(4)#1 | 95.6(3) | C(4)–C(3)–H(3) | 119.7 |
| O(1)#1–Li–Li#1 | 43.81(16) | C(2)–C(3)–H(3) | 119.7 |
| O(1)–Li–Li#1 | 43.37(17) | C(3)–C(4)–C(5) | 119.3(3) |
| OW1–Li–Li#1 | 119.0(4) | C(3)–C(4)–H(4) | 120.3 |
| O(2)–Li–Li#1 | 120.8(4) | C(5)–C(4)–H(4) | 120.3 |
| O(4)#1–Li–Li#1 | 121.4(3) | C(4)–C(5)–C(6) | 120.7(3) |
| C(1)–O(1)–Li#1 | 134.4(3) | C(4)–C(5)–H(5) | 119.6 |
| C(1)–O(1)–Li | 132.4(3) | C(6)–C(5)–H(5) | 119.6 |
| Li#1–O(1)–Li | 92.8(2) | C(5)–C(6)–C(1) | 123.6(3) |
| O(3)–N(1)–O(2) | 119.6(3) | C(5)–C(6)–N(2) | 116.6(3) |
| O(3)–N(1)–C(2) | 119.0(3) | C(1)–C(6)–N(2) | 119.8(2) |
| O(2)–N(1)–C(2) | 121.4(3) | Li–OW1–HW1 | 113(4) |
| N(1)–O(2)–Li | 131.5(3) | Li–OW1–HW2 | 114(4) |
| O(5)–N(2)–O(4) | 120.2(3) | HW1–OW1–HW2 | 114(5) |
| O(5)–N(2)–C(6) | 118.2(3) | HW3–OW2–HW4 | 107(5) |

Symmetry transformation used to generate equivalent atoms: $\#1 = -x, -y+1, -z$.

TABLE IV Hydrogen bonds in $[Li(2,6\text{-}DNP)(H_2O)]_2{\cdot}2H_2O$ [lengths (Å) and angles (°)]

| $D–H \cdots A$ | $d(D–H)$ | $d(H \cdots A)$ | $d(D \cdots A)$ | $\angle(DHA)$ |
|---|---|---|---|---|
| OW1–HW1 ··· O(2)#2 | 0.76(6) | 2.43(6) | 3.043(4) | 140(5) |
| OW1–HW1 ··· O(3)#2 | 0.76(6) | 2.39(6) | 3.101(5) | 156(6) |
| OW1–HW2 ··· OW2#3 | 0.94(7) | 1.80(7) | 2.728(5) | 167(6) |
| OW2–HW3 ··· O(4)#4 | 0.89(6) | 2.57(6) | 3.176(4) | 126(5) |
| OW2–HW3 ··· O(5)#4 | 0.89(6) | 2.22(7) | 3.072(5) | 160(6) |
| OW2–HW4 ··· OW1#1 | 0.93(5) | 2.03(6) | 2.860(6) | 147(5) |

Symmetry transformations used to generate equivalent atoms: #1 = $-x$, $-y+1$, $-z$; #2 = $x-1$, $y$, $z$; #3 = $x$, $y+1$, $z$; #4 = $x+1$, $y$, $z$.

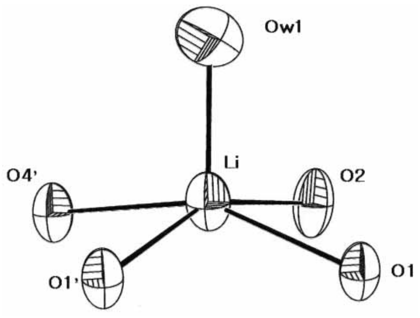

FIGURE 1 Square pyramidal geometry around the Li atom.

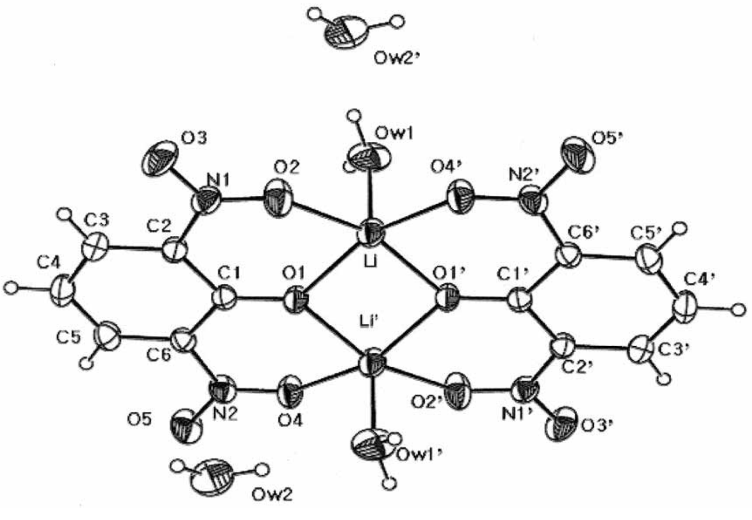

FIGURE 2 ORTEP3 diagram of $[Li(2,6\text{-}DNP)(H_2O)]_2{\cdot}2H_2O$ showing the atom-numbering scheme and 30% probability ellipsoids.

Figure 2 provides the view of the dimeric structure of the centrosymmetric complex. The complex consists of two $Li(2,6\text{-}DNP)(H_2O)$ fragments with two water molecules in the outer sphere. The two Li atoms are bridged through the enolato oxygen atoms and bind to the oxygen atoms of the nitro groups of two ligands.

Dihedral angles between the benzene ring and the nitro groups in 2,6-DNP provide good evidence for the interaction between O and Li atoms and are in the range 2.6(3)–7.8(3)°. Usually the dihedral angle is larger than 40° for uncoordinated nitro groups in DNP metal complexes [7,8]. As found in organometallic lithium compounds with phenyl derivatives [15], the benzene ring is distorted in this complex. In the planar benzene ring, the $C_1$–$C_2$ and $C_1$–$C_6$ bonds [1.439(4) and 1.444(4) Å] are significantly longer than the other carbon–carbon bonds (average 1.383 Å). The $C_2$–$C_1$–$C_6$ angle of 112.3° is rather small compared to the angles of neighboring carbon atoms (average 121.5°). In 2,6-DNP itself [4], $C_1$–$C_2$ and $C_1$–$C_6$ bonds (1.400 and 1.399 Å) are a little longer than the average distance (1.387 Å) and the $C_2$–$C_1$–$C_6$ angle (116.0°) is small, although the bonds are significantly elongated and the angle more acute in the complex.

Li–O interatomic distances (1.941–1.926 Å) in the Li–phenolato bonds and Li–O–Li (92.8°) and O–Li–O (87.2°) bond angles of the dimeric core make it almost perfectly square planar. The Li–O interatomic distances for the nitro and coordinated water molecules are 2.072(6) and 1.973(8) Å, respectively. There is no Li–Li interaction, with a rather long distance of 2.801(11) Å. In the unit cell, molecules are connected through intermolecular hydrogen bonds between $-NO_2$ groups and outer- and inner-sphere $H_2O$, as well as outer-sphere $H_2O$ and inner-sphere $H_2O$. Details are given in Table IV.

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## *Supplementary material*

Complete lists of atomic coordinates, anisotropic displacement parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre, 912 Union Road, Cambridge CB2 1EZ, UK [CCDC No. 226027].

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