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# SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF DI-$\mu$-(2,6-DI-*TERT*-BUTYLPHENOXO)DI-LITHIUM BIS-DIMETHYLSULPHOXIDE SOLVATE, $C_{32}H_{54}Li_2O_4S_2$. COMPARISON OF THE STRUCTURE WITH OTHER DIMERIC LITHIUM ALKOXIDES

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**Abstract**—$\{Li(2,6\text{-}^tBu_2\text{-}OC_6H_3)(DMSO)\}_2$ was formed by the reaction of *n*-butyl lithium with 2,6-di-*tert*-butylphenol followed by recrystallization from toluene–DMSO solution. The single crystal X-ray diffraction data were collected at $-80°C$. The structural analysis showed that this phenoxide is a dimer and lithium metal is 3-coordinated. A special feature in this structure is the short O—Ar (Ar = $C_6H_3\text{-}2,6\text{-}^tBu_2$) bond length [1.315(13) Å] which is the shortest distance found in dimeric lithium phenoxides.

Organolithium compounds are a subject of interest from both synthetic and theoretical points of views. Lithium alkoxides have been used as alkoxo-transfer reagents for preparing the corresponding transition metal alkoxo complexes[1,2] and the structural characterization of Li-enolates has been an important factor in the elucidation of mechanisms in organic syntheses.[3-5]

Lithiated organic compounds tend to form aggregates both in the solid and liquid phases and lithium alkoxides even in the gas phase.[6] The size of aggregates depends on the alkyl group of the alkoxides and the solvate molecule varying from dimeric to polymeric. Different forms of alkoxo compounds have been detected in the solid state.[7] In the majority of these compounds lithium metal is 4-coordinated, while the coordination number 3 is still comparatively rare.[8-10] Steric hindrance has an important effect on the size of the aggregates. Sterically demanding ligands can stabilize the unusual structural form, e.g. when substituents are introduced to the ortho position on the phenoxo group a dimer is formed instead of a larger aggregate.[11-14]

In the present paper we report the synthesis and the crystal structure of $\{Li(2,6\text{-}^tBu_2\text{-}OC_6H_3)(DMSO)\}_2$ and compare the structure with those of some other dimeric lithium alkoxides.

## EXPERIMENTAL

Because the reagents used and the product were air and moisture sensitive all manipulations were carried out under argon using standard Schlenk techniques. DMSO (Merck) was dried with molecular sieves (4 Å) and toluene (R. P. Normapur, pro analysis grade) was purified by refluxing on $LiAlH_4$ followed by distillation under argon. The *n*-butyl lithium used was a 1.6 M solution in hexane (Merck). $^1H$ NMR data were recorded with a Varian Gemini-200 spectrometer (200 MHz).

### *Synthesis of* $\{Li(2,6\text{-}^tBu_2\text{-}OC_6H_3)(DMSO)\}_2$

2,6-Di-*tert*-butylphenol (1 g, 5 mmol) was dissolved in toluene (50 $cm^3$) and 3.6 $cm^3$ (6 mmol) BuLi (1.6 M solution in hexane) was added dropwise. The reaction mixture was then stirred overnight and the white solid formed was filtered and washed with pentane. The white solid was recrystallized from toluene–DMSO (10 : 1) solution. Suitable crystals for X-ray diffraction studies were obtained by cooling the refluxing solution to room

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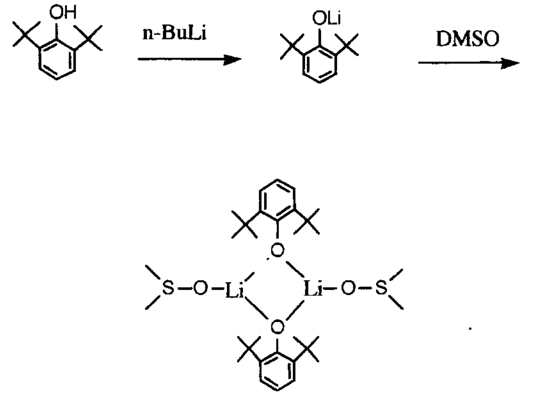
Table 1. Crystal data and structure refinement parameters

| | |
|---|---|
| Formula | $C_{32}H_{54}Li_2O_4S_2$ |
| $M_r$ | 580.76 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$ (Å) | 9.236(5) |
| $b$ (Å) | 14.328(4) |
| $c$ (Å) | 13.842(3) |
| $\beta$(°) | 109.17(3) |
| $V$(Å$^3$) | 1730.2(9) |
| $Z$ | 2 |
| $D_{calc}$ (g cm$^{-3}$) | 1.115 |
| $\mu$ (cm$^{-1}$) (Mo $K_\alpha$) | 1.85 |
| $F$(000) | 632 |
| $2\theta_{max}$ (°) | 53 |
| Unique refl. collected | 2651 |
| Observed refl. [$F > 6\sigma(F_0)$] | 938 |
| Parameters | 176 |
| $R$ | 0.074 |
| $S$ | 1.38 |
| Residual e-densities (e Å$^{-3}$) | 0.54, −0.27 |



Scheme 1. Preparation of lithium complex derived from 2,6-di-tert-butylphenol and *n*-BuLi.

temperature. Yield 1.2 g (80%). $^1$H-NMR shifts (in deuterated DMSO, TMS = 0): $\delta$ 6.63 (d), $\delta$ 5.70 (t), $\delta$ 2.43 (s), $\delta$ 1.24 (s).

### *X-Ray data collection and structure determination*

Details for crystal analysis, data collection and structure refinement are given in Table 1. Selected bond lengths and angles are listed in Table 2. A crystal was transferred from the mother liquid to the inert oil and cooled down to −80°C. The manipulation of the air sensitive crystal was made as described by Hope.[15] The $\omega$–$2\theta$ data collection was carried out with a Rigaku AFC-7S diffractometer[16,17] using Mo $K_\alpha$ ($\lambda = 0.71073$ Å) radiation. The data for structure determination were corrected for Lorentz and polarization, absorption ($T = 0.96$–$1.00$) and decay (−3.4%). The structure was solved and refined using SHELXTL[18] and SHELXL-93 programs. In the refinements hydrogen atoms were in the calculated positions.

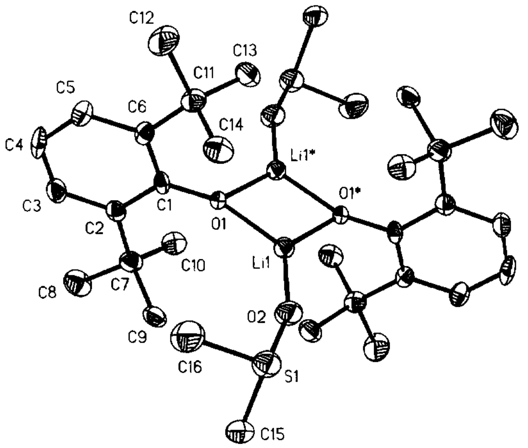


Fig. 1. Molecular structure of the lithium complex (hydrogen atoms omitted for clarity) and atomic numbering.

Table 2. Selected bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| Li(1)—O(2) | 1.853(17) | Li(1)—O(1) | 1.874(20) |
| Li(1)—Li(1$^{i}$) | 2.442(31) | O(1)—C(1) | 1.315(13) |
| S(1)—O(2) | 1.497(6) | S(1)—C(16) | 1.751(17) |
| S(1)—C(15) | 1.762(13) | | |
| O(2)—Li(1)—O(1) | 129.6(9) | O(2)—Li(1)—O(1$^{i}$) | 131.9(11) |
| O(1)—Li(1)—O(1$^{i}$) | 98.5(8) | C(1)—O(1)—Li(1) | 149.4(7) |
| C(1)—O(1)—Li(1$^{i}$) | 128.6(8) | Li(1)—O(1)—Li(1$^{i}$) | 81.5(8) |
| O(2)—S(1)—C(16) | 106.2(6) | O(2)—S(1)—C(15) | 105.5(5) |
| C(16)—S(1)—C(15) | 98.1(7) | S(1)—O(2)—Li(1) | 158.9(8) |

Symmetry code: ($^{i}$) = $1-x$, $2-y$, $-z$.

Table 3. Selected bond lengths (Å) of some dimeric lithium alkoxides

| Formula | M—O<br>(alkoxo) | O—C<br>(alkoxo) | M—O<br>(solvate) | Ref. |
|---|---|---|---|---|
| $[LiOC{}^tBu_3]_2$ | 1.75(8) | 1.387(13) | — | 9 |
| $[Li(2,6\text{-}{}^tBu_2\text{-}4\text{-}Me\text{-}OC_6H_2)(Et_2O)]_2$ | 1.849(11)<br>1.867(10) | 1.345(6) | 1.961(11) | 12 |
| $[Li(2,6\text{-}{}^tBu_2\text{-}OC_6H_3)(Et_2O)]_2$ | 1.830(7)<br>1.880(7) | 1.342(5) | 1.904(7) | 13 |
| $[Li(OC{}^tBu_3)(THF)]_2$ | 1.835(10)<br>1.852(9)<br>1.846(11)<br>1.830(12) | 1.393(7) | 1.963(10)<br>2.009(11) | 14 |
| $[Li(2,6\text{-}{}^tBu_2\text{-}OC_6H_3)(DMSO)]_2$ | 1.874(20) | 1.315(13) | 1.853(17) | This work |

## RESULTS AND DISCUSSION

$\{Li(2,6\text{-}{}^tBu_2\text{-}OC_6H_3)(DMSO)\}_2$ was synthesized by the reaction of *n*-butyl lithium and 2,6-di-*tert*-butylphenol followed by recrystallization from toluene–DMSO solution (Scheme 1).

$\{Li(2,6\text{-}{}^tBu_2\text{-}OC_6H_3)(DMSO)\}_2$ appears as a centrosymmetric dimer with one solvate molecule (DMSO) coordinated to the lithium atom (Fig. 1). The 2,6-di-*tert*-butylphenoxo ligands are equivalent and form bridges between two lithium atoms. The lithium atoms in this molecule have 3 coordination. The $Li_2(\mu\text{-}O)_2$ unit is exactly planar owing to the symmetry and the plane of the phenoxo ligand is almost perpendicular (89.5°) to this plane. The bond between Li(1) and O(2) (DMSO oxygen) is shorter than the one between Li(1) and O(1) (Li—OAr). The short Li—O(2) (DMSO) bond indicates a certain degree of double bonding between the metal and the solvate oxygen. Also the Li—OAr bond exhibits some double bond nature. Table 3 compares some dimeric lithium alkoxo compounds found in the literature. When the double bond character increases between Li—O(solvate) [shorter Li—O(solvate) bond] the double bond character between Li—OAr decreases [longer Li—OAr bond]. This reflects the C—O bond in the phenoxo group. When there is less double bond character between Li and OAr the C—O bond is shorter.

It is noteworthy that the Li(1)—O(2) is the shortest distance found between Li and an oxygen atom of a coordinated solvent. Also the O—Ar bond is the shortest found in dimeric lithium phenoxides. The bond lengths in the DMSO molecule are quite normal. The Li—Li$^i$ distance is short 2.442(31) Å, which indicates that there is some interaction between the Li atoms. The Li—O—Li$^i$ angle [81.5(8)°] is also smaller than O(1)—Li—O(1$^i$) [98.5(8)°]. This geometry of the $Li_2(\mu\text{-}O)_2$ cycle can be taken as indicative of Li—Li$^i$ bonding.

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