The First Lithium Phenolate with a Trinuclear Structure and the Tetranuclear Product of 1:1 Addition of Lithium Iodide; X-Ray Structures of [LiOAr]₃ and [Li₂(OAr)I]₂ [OAr = OC₆H₂(CH₂NMe₂)₂-2,6-Me-4]

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Reaction of 2,6-bis[(dimethylamino)methyl]-4-methylphenol with n-butyllithium affords quantitatively [LiOAr]₃ [OAr = OC₆H₂(CH₂NMe₂)₂-2,6-Me-4] **1**, which has an unprecedented trinuclear structure both in solution (cryoscopy in C₆H₆) and in the solid state (X-ray); **1** reacts selectively with LiI to form the adduct [Li₂(OAr)I]₂ **2** which has a tetranuclear structure (X-ray).

Phenolate and alcoholate groups can be used as spectator ligands in organometallic chemistry in much the same way as phosphines or cyclopentadienyls, and their bulk can be selected to favour specific coordination numbers and geometries.[1] Our work involves the use of aryl ligands with tertiary amine substituents, which through intramolecular coordination can stabilize reaction intermediates or change the reactivity of a metal centre by blocking specific coordination sites.[2] In a related extension of this work we are now using the interesting properties of bulky phenolate ligands containing potentially coordinating substituents to develop a new, broad field of inorganic as well as organometallic chemistry. With the X-ray structure of the copper phenolate [Cu₂(μ-Br){μ-OC₆H₃(CH₂NMe₂)₂-2,6}{P(OMe)₃}₂] we have already demonstrated the interesting potential of a phenolate ligand with two ortho-chelating tertiary amine substituents.[3] Recently the structure of a tetranuclear barium complex, containing a related phenolate ligand, was published.[4] We now report the syntheses and structural aspects of both a lithium phenolate with an unprecedented trinuclear structure

in solution and in the solid state, and its tetranuclear 1:1 lithium iodide adduct.

The reaction of n-butyllithium with 2,6-bis[(dimethylamino)methyl]-4-methylphenol in hexane at 0 °C in a 1:1 molar ratio affords the lithium phenolate **1** quantitatively. Complex **1** was obtained as colourless crystals by cooling a saturated hexane solution to −30 °C. It is a moisture-sensitive solid which can be handled in air for short periods but which must be stored under an inert atmosphere for longer periods.

Elemental analysis and ¹H NMR data of **1**† are consistent with the formulation [LiOC₆H₂(CH₂NMe₂)₂-2,6-Me-4]ₙ.

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† Analytical data for **1**: ¹H NMR (C₆D₆, 300 MHz, 298 K): δ 6.93 (s, 2H, meta-H); 3.32 (br s, 4H, CH₂N); 2.34 (s, 3H, para-Me); 1.92 (s, 12H, NMe₂). Calc. for C₃₉H₆₃Li₃N₆O₃: C, 68.4; H, 9.3; N, 12.3. Found: C, 68.3; H, 9.1; N, 12.15%. Relative molecular mass determination by cryoscopy (0.50 g in 24.22 and 52.56 g of benzene): Calc. for monomer: 228.3 Found: 660 and 672 (degree of association: 2.9).

Cryoscopy measurements on **1** showed it to be a trimer in benzene in the concentration range of 0.037–0.080 mol dm^{-3}. To determine the stereochemistry of **1**, and its degree of association in the solid state, an X-ray structure determination was carried out.‡

The crystal structure consists of the packing of four discrete trimeric molecules in the unit cell, and each trimeric unit possesses a pseudo-threefold rotation axis. Two views of the molecular geometry of **1** are shown in Fig. 1.

Complex **1** is the first isolated and characterized lithium phenolate with a trinuclear stucture. Since **1** in solution also appears to have a trimeric structure this molecular arrangement must be particularly stable and the origins of this stability are reflected in various geometric parameters. Firstly, the Li–O bond lengths [average 1.865(9) Å] are comparable with the shortest ever reported in related complexes, e.g. dimeric lithium 2,6-di-*tert*-butyl-4-methylphenolate, **3**.[5] Secondly, the C$_{ipso}$–O distances are very short and range from 1.301(6) to 1.326(6) Å, while corresponding distances in **3** as well as in lithium enolates derived from ketones are close to 1.35 Å.[6] In **1** there is an almost perfectly planar Li$_3$O$_3$ six-membered ring, see view (*b*) in Fig. 1 (maximum least-squares deviation is 0.05 Å). In this ring the Li–O–Li and O–Li–O angles are in the ranges 126.5–129.7 and 110.1–112.4°, respectively, and Σ angles = 720.0°.

The short Li–O and C$_{ipso}$–O bond lengths can be explained in terms of quasi-aromaticity of the Li$_3$O$_3$ ring;[7] the delocalized π-electrons, originating from the lone pairs of the oxygen atoms, slightly change the hybridization of the oxygen atoms from sp^3 to more sp^2 with a concomitant shortening of the bond lengths to oxygen.

Adjacent lithium atoms are *N*-coordinated by different CH$_2$NMe$_2$ substituents of their mutually *O*-bridging phenolate ligand, and the orientation of these ligands with respect to the Li$_3$O$_3$ ring provides a 'propeller-like' molecule with each trimer having screw-type chirality. (Both enantiomers are present in the crystal structure.) In these molecules each of the six equivalent CH$_2$NMe$_2$ substituents has inequivalent CH$_2$
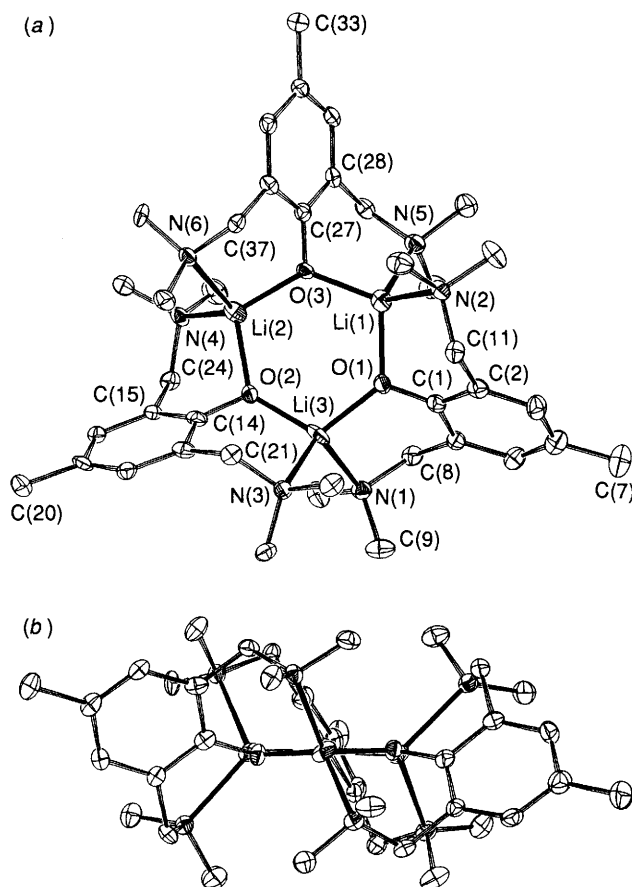

Fig. 1 Molecular structure of [LiOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4]$_3$, **1**; ORTEP drawings with 50% probability ellipsoids viewed (*a*) perpendicular to and (*b*) along the Li$_3$O$_3$ plane. Selected bond lengths (Å) and angles (°): Li(1)–O(1), 1.878(9); Li(1)–O(3), 1.869(9); Li(2)–O(3), 1.846(9); Li(2)–O(2), 1.887(9); Li(3)–O(2), 1.828(9); Li(3)–O(1), 1.881(9); Li(1)–N(2), 2.256(9); Li(1)–N(5), 2.223(9); Li(2)–N(4), 2.233(9); Li(2)–N(6), 2.325(9); Li(3)–N(1), 2.163(9); Li(3)–N(3), 2.227(9); O(1)–C(1), 1.301(6); O(2)–C(14), 1.326(6); O(3)–C(27), 1.324(6); O(1)–Li(1)–O(3), 112.0(4); Li(1)–O(1)–Li(3), 126.5(4); O(2)–Li(2)–O(3), 110.1(4); Li(2)–O(2)–Li(3), 129.7(4); O(1)–Li(3)–O(2), 112.1(4); Li(1)–O(3)–Li(2), 129.2(4).

hydrogen atoms and NMe groups. However, the solution ^{1}H NMR spectrum of **1** at 20 °C shows equivalent NMe groups and equivalent methylene hydrogens, i.e. there is a fast fluxionality which causes an inversion of absolute configuration of the nitrogen atoms.† We believe this fluxionality is based on lithium–nitrogen dissociation–association processes such as those reported in, for example, 2,6-bis[(dimethyl-amino)methyl]phenyllithium.[8]
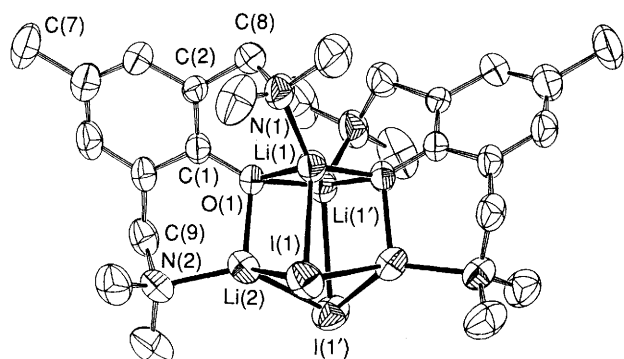
When three equivalents of LiI are added to a benzene solution of **1**, at 20 °C, a lithium iodide adduct **2** is obtained in a clean reaction. Complex **2** was obtained after crystallization from a pentane-layered benzene solution as colourless, moisture-sensitive crystals, and preliminary microanalytical data suggested it to be the 1 : 1 Li(OAr) : LiI species. With ^{1}H NMR spectroscopy one can discern two inequivalent but coordinated (dimethylamino)methyl groups, i.e. **2** is at least a dinuclear species with two inequivalent lithium atoms.§ To elucidate the degree of association of **2** and to have proof for the tertiary amine coordination, we have carried out an X-ray structure determination.‡ The crystal structure of **2** involves

Fig. 2 Molecular structure of $[Li_2\{OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-Me-}4\}I]_2$, **2**; ORTEP drawing with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Li(1)–O(1), 1.917(9); Li(1')–O(1), 1.903(7); Li(2)–O(1), 1.934(9); Li(1)–N(1), 1.999(9); Li(2)–N(2), 1.983(10); Li(1)–I(1), 2.814(8); Li(2)–I(1), 2.738(9); Li(2)–I(1'), 2.829(9); O(1)–C(1), 1.355(5); Li(1)–O(1)–Li(2), 95.2(4); Li(1')–O(1)–Li(2), 95.8(4); Li(1)–O(1)–Li(1'), 83.4 (3).

the packing of four discrete $Li_4(OAr)_2I_2$ clusters in the unit cell. The molecular structure of **2**, which possesses a twofold rotation axis, is shown in Fig. 2.

Complex **2** is a tetranuclear species, which is most easily described as a distorted Li_4 tetrahedron with the two iodide atoms and the two oxygen atoms of the phenolate ligands coordinating above the four Li_3 faces. The four tertiary amine substituents are all coordinated to different lithium atoms which thereby acquire a tetrahedral coordination sphere, two with an I,O_2,N environment and two with an I_2,O,N environment [Li(1) and Li(2), respectively]. Chemically the structure can be seen as a dimer of two lithium phenolate units each of which contains one molecule of LiI caught by a coordinating amine group.

The Li–O and C_{ipso}–O distances of 1.918(9) (average) and 1.355(5) Å, respectively, are significantly longer than those in **1**, but are comparable with those reported earlier for lithium

phenolates and enolates.[5,6] These results emphasize the unusual nature, *i.e.* 'quasi-aromaticity' of trimeric **1**.

The molecular structures of **1** and **2** nicely demonstrate the potential of phenolate ligands with tertiary amine substituents to coordinate to more than one metal centre, and to stabilize unusual aggregates. The application of this type of bis-*ortho*-chelating phenolate as a ligand for early transition and lanthanide metals is currently being studied.

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