

## Dilithiated salen Complexes: Chiral [(salen)Li<sub>2</sub>·hmpa]<sub>2</sub> and Deliberate Partial Hydrolysis to give [(salen)Li<sub>2</sub>]<sub>3</sub>·Li<sub>2</sub>O·2tmen·H<sub>2</sub>O [H<sub>2</sub>salen = *N,N'*-ethylenebis(salicylideneimine); hmpa = hexamethylphosphoramide; tmen = tetramethylethylenediamine]

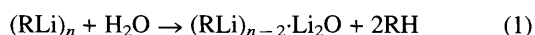
Sarah C. Ball,<sup>a</sup> Ian Cragg-Hine,<sup>a</sup> Matthew G. Davidson,<sup>a</sup> Robert P. Davies,<sup>a</sup> M. Isabel Lopez-Solera,<sup>a</sup> Paul R. Raithby,<sup>a</sup> David Reed,<sup>b</sup> Ronald Snaith<sup>\*a</sup> and Erasmus M. Vogl<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW

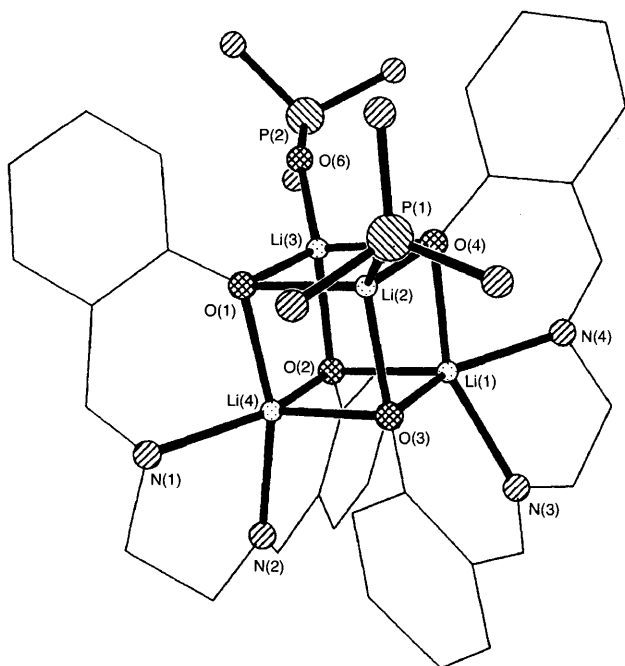
<sup>b</sup> Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ

Chiral [(salen)Li<sub>2</sub>·hmpa]<sub>2</sub> has a Li<sub>4</sub>O<sub>4</sub> cubane-type core in the solid but low-temperature NMR spectroscopy reveals a racemisation equilibrium in solution; deliberate addition of H<sub>2</sub>O to [(salen)Li<sub>2</sub>]<sub>n</sub> in the presence of tmen produces a species having two Li<sub>4</sub>O<sub>4</sub> cubes sharing a common oxygen and containing tmen ligands acting in a hitherto unobserved monofunctional mode.

Lithiated organic molecules, (RLi)<sub>n</sub> [R = alkyl, amido, enolato *etc.*] are key reagents for many organic syntheses.<sup>1</sup> They are commonly used under dry inert-atmosphere conditions to prevent their hydrolysis (to RH + LiOH). Despite such precautions, two chance products of partial hydrolysis have been reported. Here, just some of the (RLi)<sub>n</sub> aggregate is converted to LiOH or Li<sub>2</sub>O, which then co-aggregates with the residual (RLi)<sub>n</sub>. Thus, prolonged storage of *tert*-butoxylithium solution afforded a few crystals of (Bu<sup>t</sup>OLi)<sub>10</sub>·(LiOH)<sub>6</sub>.<sup>2</sup> A similarly low yield of [2,6-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li]<sub>6</sub>·Li<sub>2</sub>O ensued from the lithiation of 2,6-dimethoxybenzene.<sup>3</sup> The formation of such species was attributed to traces of moisture in the solvents and/or in admitted air but, irrespective of their unsought formation, both are clearly thermodynamically stable. Hence similar systems should be preparable by deliberate additions of water, and be so in repeatable and respectable yields. One strategy is expressed in eqn. (1), whereby two units of an (RLi)<sub>n</sub> aggregate are used to lithiate deliberately added water.



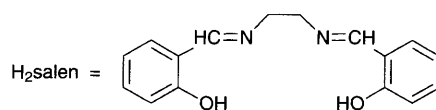
Here we describe the synthesis and structure of the first dilithiated salen complex. We show also how such a system can be deliberately partially hydrolysed by addition of water to give, in reasonable yield, an aggregate incorporating Li<sub>2</sub>O.



**Fig. 1** Molecular structure of [(salen)Li<sub>2</sub>·hmpa]<sub>2</sub> **1**. For clarity, the hydrocarbon units of the salen ligands are represented by line drawings, and all hydrogen atoms and the methyl groups of the hmpa ligands are omitted.

Treatment of H<sub>2</sub>salen in toluene at -20 °C with Bu<sup>n</sup>Li solution (2 equiv.) affords a white precipitate which dissolves on addition of hmpa and heating to 50 °C. Chilling of the solution gives cubic crystals of [(salen)Li<sub>2</sub>·hmpa]<sub>n</sub> **1**.<sup>†</sup> X-ray crystallography<sup>‡</sup> has revealed a dimer (*n* = 2) in the solid state, with an Li<sub>4</sub>O<sub>4</sub> cubane core (Fig. 1). Such an Li<sub>4</sub>X<sub>4</sub> (X = C, N, O) core is a common structural motif.<sup>1</sup> Specifically for the salen dianion, a cubane core is found also in [(salen)Na<sub>2</sub>·dme]<sub>2</sub> where dme is the bidentate Lewis base 1,2-dimethoxyethane.<sup>4</sup> However, there are several unusual features in the structure of **1**. Each Li<sup>+</sup> is bonded to three of the four oxygen centres provided by two salen dianions [mean Li–O, 2.002(6) Å]. Two of the cations [Li(2) and Li(3) in Fig. 1] are further complexed by one hmpa ligand each [mean Li–O, 1.872(6) Å] so making them four-coordinate. The remaining metal centres [Li(1) and Li(4)] are five-coordinate (distorted trigonal bipyramidal), each being chelated by the two N-centres of a particular salen ligand [mean Li–N, 2.071(6) Å]. The norm is that all metal centres in a cubane structure have equal coordination numbers: four in most complexed Li<sub>4</sub>X<sub>4</sub> species, *e.g.* five for Na<sup>+</sup> in [(salen)Na<sub>2</sub>·dme]<sub>2</sub> noted above. Furthermore, the particular unit of **1** depicted in Fig. 1 is chiral; the molecules enantiomeric to it are present in the crystal structure.

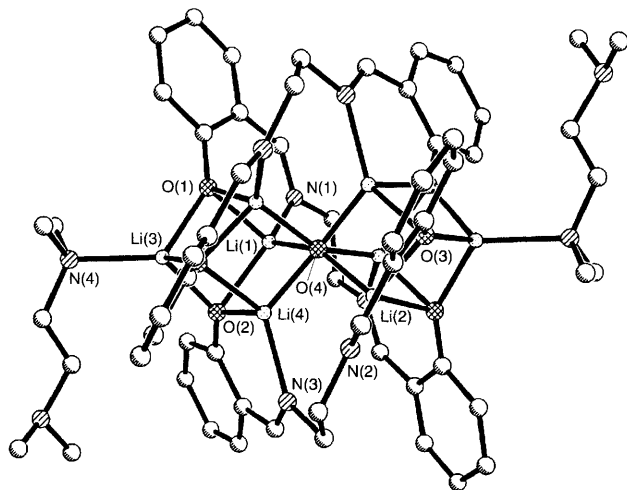
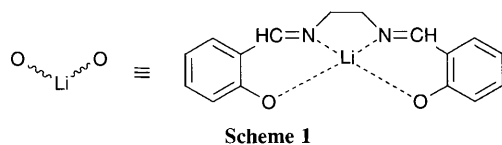
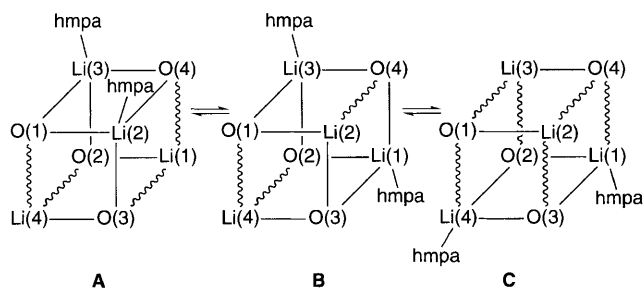
The solution behaviour of **1** has been probed by NMR experiments. In the static structure of the enantiomer shown in Fig. 1 the two halves of each salen ligand are inequivalent since, *e.g.* O(1) is attached to two four-coordinate Li centres and one five-coordinate one, while for, *e.g.* O(2) the opposite applies. This inequivalence is observed in the <sup>1</sup>H NMR spectrum of a toluene solution (0.06 g cm<sup>-3</sup>) of **1** at 203 K when each proton gives a separate signal: the =CH– ones are two singlets at δ 7.93 and 7.84, while the –CH<sub>2</sub>CH<sub>2</sub>– ones are broader yet distinct resonances at δ *ca.* 3.45, 3.25, 2.90 and 2.75. This shows that, at this temperature at least, the Li<sub>4</sub>O<sub>4</sub> dimers of **1** do not dissociate into Li<sub>2</sub>O<sub>2</sub> monomers since then the two halves of each salen dianion would be equivalent. Furthermore, at 203 K the hmpa ligands remain attached to two of the four lithium centres: the <sup>7</sup>Li NMR spectrum consists of two resonances of equal integrals, one a singlet and the other a doublet due to <sup>31</sup>P coupling [*J*(<sup>31</sup>P–<sup>7</sup>Li) = 9.1 Hz]. Returning to the <sup>1</sup>H NMR spectrum at 203 K, its features can be attributed to a relatively slow equilibrium between the enantiomers of **1**. As the temperature is raised, the methine and the methylene protons coalesce (at 300 and 305 K, respectively). The process responsible for this is illustrated in Scheme 1. Species **A** represents a molecule of **1** as shown in Fig. 1. The O(1) and O(4) halves of the salen ligands have the same environment. The O(2) and O(3) halves also have the same environment as each other, but one distinct from that of the O(1), O(4) halves. If one



salen ligand—say, that involving O(3) and O(4)—then flips so that its N-atoms attach to the neighbouring lithium [Li(2)] and if there is a concomitant move of one hmpa from Li(2) to Li(1), then enantiomer **B** results. The protons of the two halves of the shifted ligand have not changed their environment. However, those of the so-far static salen have. If this second salen now shifts, moving its N-centres from Li(4) to Li(3) at the same time that hmpa transfers from Li(3) to Li(4), then the result is species **C**. This is identical to **A**. However, all the protons have now changed environment: those along the O(1) and O(4) halves in **C** have the environment that those along the O(2) and O(3) halves had in **A**, and *vice versa*. The mean free energy of activation for this enantiomerisation equilibrium can be calculated<sup>5</sup> *via* coalescence phenomena as  $\Delta G^\ddagger = 62 \text{ kJ mol}^{-1}$ .

In a second synthesis, addition of tmen to a precipitate of  $[(\text{salen})\text{Li}_2]_n$  in toluene had no visible effect. However, subsequent addition of water gave a pale yellow solution which deposited colourless crystals, identified by NMR spectroscopy and elemental analysis,<sup>†</sup> and by X-ray crystallography,<sup>‡</sup> as  $[(\text{salen})\text{Li}_2]_3 \cdot \text{Li}_2\text{O} \cdot 2\text{tmen} \cdot \text{H}_2\text{O}$  **2**. The first-batch yield is around 30% and the synthesis is repeatable.

The structure of **2** (excluding  $\text{H}_2\text{O}$  molecules, which are severely disordered) is shown in Fig. 2. Its core consists of two distorted  $\text{Li}_4\text{O}_4$  cubes joined at a shared oxygen [O(4)]. Six Li atoms are attached to this central O [mean Li–O, 1.883(9) Å]. These atoms [Li(1), Li(2), Li(4) and their symmetry-related equivalents] are also each bonded to two O atoms provided by two different salen dianions [mean Li–O, 1.985(9) Å] and to one N atom of one of these dianions [mean Li–N, 2.020(9) Å]. Each



**Fig. 2** Molecular structure of  $[(\text{salen})\text{Li}_2]_3 \cdot \text{Li}_2\text{O} \cdot 2\text{tmen} \cdot \text{H}_2\text{O}$  **2**. Hydrogen atoms are omitted, as are the severely disordered  $\text{H}_2\text{O}$  molecules which lie between the tmen ligands of successive units of **2**.

salen ligand threads its way over the central O(4) such that one of its oxygen centres is at the front of one cube and the second is at the back of the other. The unique Li atoms [Li(3), Li(3')] at the extremities of the cubes are coordinated by three oxygens of three different salen dianions [mean Li–O, 1.954(9) Å] and by one N of a tmen ligand [Li–N, 2.080(9) Å]. In fact, to our knowledge this represents a new mode for tmen coordination, certainly to lithium. Hitherto, this ligand has been found chelating, often in dimers of type  $(\text{RLi-tmen})_2$  or acting as a bifunctional bridge linking Li centres in neighbouring aggregates, often cubane tetramers of type  $(\text{RLi})_4 \cdot (\text{tmen})_n$  ( $n = 1$  or  $2$ ).<sup>1</sup> Recent related examples include  $(\text{Bu}^n\text{Li-tmen})_2$  and  $[(\text{Bu}^n\text{Li})_4 \cdot \text{tmen}]_\infty$ .<sup>6</sup> In **2**, however, the tmen ligands are monofunctional. The N-centres uninvolved with Li centres in one  $\text{Li}_8\text{O}_7$  unit do not link to other units. Instead, they appear to interact with the one  $\text{H}_2\text{O}$  found in each molecule of **2**, although disorder prevents details being studied. Such interactions certainly link molecules of **2** in the lattice.

In effect, the formation of **2** involves the dilithiation of  $\text{H}_2\text{O}$  by one  $(\text{salen})\text{Li}_2$  unit of every two  $[(\text{salen})\text{Li}_2]_2$  aggregates, so producing  $\text{Li}_2\text{O}$  (and 1 equiv. of regenerated  $\text{H}_2\text{salen}$ ) which becomes incorporated in the  $(\text{salen})_3\text{Li}_6$  residue. The precise nature of uncomplexed dilithiated salen is unknown, but its insolubility and the isolation of complexes **1** and **2** suggest that it is a polymer composed of linked  $[(\text{salen})\text{Li}_2]_2$  cubanes. Numerous lithiations of organic compounds afford seemingly polymeric materials, many of which are thought to be long stacks or ladders of  $(\text{RLi})_n$ ,  $n = 2$  or  $3$ , rings.<sup>1</sup> Given the synthesis of the soluble oligomeric complex **2**, we are investigating the action of  $\text{H}_2\text{O}$  on a selection of these polymers.

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## Footnotes

<sup>†</sup> *Experimental data for 1*:  $\text{Bu}^n\text{Li}$  (5.0 mmol, in hexane) was added to a solution of  $\text{H}_2\text{salen}$  (0.67 g, 2.5 mmol) in toluene (10 ml) at  $-20^\circ\text{C}$ . The white precipitate formed at room temperature dissolved on addition of hmpa (0.90 g, 5.0 mmol) and heating to  $50^\circ\text{C}$ . Chilling of the solution afforded colourless cubic crystals of **1**: yield 90%, mp  $247\text{--}248^\circ\text{C}$ . X-Ray crystallographic analysis of **1** found one lattice toluene solvent molecule per four asymmetric units. Found: C 59.2, H 7.3, N 14.5, P 6.5.  $\text{C}_{95}\text{H}_{136}\text{Li}_8\text{N}_{20}\text{O}_{12}\text{P}_4$  requires C 59.1, H 7.1, N 14.5, P 6.4%.  $^1\text{H}$  NMR (360 MHz,  $[\text{D}_8]\text{toluene}$ , 303 K):  $\delta$  7.95 (br, 2 H,  $-\text{CH}=\text{}$ ), 7.35–6.55 (m, 8 H, aryl), 3.40 (br, 2 H,  $-\text{CH}_2-$ ), 2.90 (br, 2 H,  $-\text{CH}_2-$ ), 2.12 (d, 18 H, hmpa).

<sup>‡</sup> *For 2*: The dilithiation of  $\text{H}_2\text{salen}$  was repeated as above. Addition of excess tmen (1.16 g, 10 mmol) had no apparent effect on the white precipitate formed. However, addition of  $\text{H}_2\text{O}$  (*ca.* 0.03 g, *ca.* 1.6 mmol) resulted in the initial formation of a yellow oil which dispersed on stirring. On standing at room temperature the clear, pale yellow solution deposited colourless crystals of **2**: yield 31%, mp  $> 320^\circ\text{C}$ . Found: C 64.4, H 6.9, N 12.6.  $\text{C}_{60}\text{H}_{76}\text{Li}_8\text{N}_{10}\text{O}_8$  requires C 64.3, H 6.8, N 12.5%.  $^1\text{H}$  NMR (250 MHz,  $\text{CD}_3\text{SOCD}_3$ , 298 K):  $\delta$  8.19 (s, 3 H,  $-\text{CH}=\text{}$ ), 7.01, 6.46, 6.26 (m, 12 H, aryl), 3.58 (br s, 6 H, salen  $-\text{CH}_2-$ ), 3.36 (s, 1 H,  $\text{H}_2\text{O}$ ), 2.29 (s, 4 H, tmen  $-\text{CH}_2-$ ), 2.18 (s, 12 H, tmen  $\text{CH}_3$ ).

<sup>‡</sup> *Crystal data for 1*:  $[(\text{salen})\text{Li}_2 \cdot \text{hmpa}]_2 \cdot 0.5\text{C}_7\text{H}_8$ :  $\text{C}_{47.5}\text{H}_{68}\text{Li}_4\text{N}_{10}\text{O}_6\text{P}_2$ ,  $M = 964.82$ , triclinic, space group  $P\bar{1}$ ,  $a = 12.867(3)$ ,  $b = 14.017(3)$ ,  $c = 15.532(3)$  Å,  $\alpha = 94.67(3)$ ,  $\beta = 96.34(3)$ ,  $\gamma = 108.10(3)^\circ$ ,  $V = 2626.5(10)$  Å<sup>3</sup>,  $F(000) = 1026$ ,  $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å,  $\mu(\text{Mo-K}\alpha) = 0.138 \text{ mm}^{-1}$ ,  $T = 153(2)$  K,  $Z = 2$ ,  $D_c = 1.220 \text{ Mg m}^{-3}$ . Data were collected on a Stoe-Siemens diffractometer in the range  $3.5^\circ \leq \theta \leq 22.5^\circ$  (6871 reflections collected, 6837 independent reflections). The structure was solved by direct methods<sup>7</sup> and refinement, based on  $F^2$ , was by full-matrix least-squares techniques<sup>8</sup> (all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions; no hydrogen atoms were added to the disordered toluene) to  $R_1$  (on  $F$ ) = 0.0561 for 5706 unique reflections [ $I > 2\sigma(I)$ ] and  $wR_2 = 0.1439$  for all reflections.

For 2:  $\{[(\text{salen})\text{Li}_2]_3 \cdot \text{Li}_2\text{O} \cdot 2\text{tmen} \cdot \text{H}_2\text{O}\}_{0.5} \cdot \text{C}_{30}\text{H}_{38}\text{Li}_4\text{N}_5\text{O}_4$ ,  $M = 560.41$ , monoclinic, space group  $C2/c$ ,  $a = 14.092(3)$ ,  $b = 33.004(7)$ ,  $c = 14.359(3)$  Å,  $\beta = 107.00(3)^\circ$ ,  $V = 6387(2)$  Å<sup>3</sup>,  $F(000) = 2376$ ,  $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å,  $\mu(\text{Mo-K}\alpha) = 0.076$  mm<sup>-1</sup>,  $T = 153(2)$  K,  $Z = 8$ ,  $D_c = 1.166$  Mg m<sup>-3</sup>. Data were collected on a Stoe-Siemens diffractometer in the range  $3.56 \leq \theta \leq 22.52^\circ$  (10728 reflections collected, 4178 independent reflections). The structure was solved by direct methods<sup>7</sup> and refinement, based on  $F^2$ , was by full-matrix least-squares techniques<sup>8</sup> (all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions; no hydrogen atoms were added to the disordered water) to  $R_1$  (on  $F$ ) = 0.0840, for 2720 unique reflections [ $I > 2\sigma(I)$ ] and  $wR_2 = 0.1955$  for all reflections.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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