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The 'Broken Cube' Polymer Structure of $(LiBr{\cdot}thf)_\infty$ (thf = tetrahydrofuran)

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The reaction of $GeBr_4$ with 2 equivalents of $Li_2[C_{10}H_7N]$ ($C_{10}H_7N$ = 1-naphthylamido dianion) in tetrahydrofuran (thf)–diethyl ether produces $(LiBr{\cdot}thf)_\infty$ as a product, which has an infinite 'corrugated' ladder structure in the solid state and can be regarded as arising from the association of cubes of $(LiBr{\cdot}thf)_4$.

As a generic family, alkali-metal organometallic compounds (containing C–M, N–M, O–M, *etc.*, bonds) have been studied extensively in the solid state and in solution in the past twenty years, particularly those of lithium.[1–4] Although diverse, their oligomeric complexes have in many cases been broadly described as molecular (rings or 'stacks') or as polymeric (chains or 'ladders').[2,3] The structures of the inorganic alkali-metal complexes, of which the halide and pseudohalide salt complexes with Lewis-base donor molecules have been most well studied, are often related structurally to the organometallic derivatives. Thus the cubane-like structures of the organometallic complex $(PhLi{\cdot}OEt_2)_4$[5] and of the inorganic salt complex $(LiCl{\cdot}hmpa)_4$[6] (hmpa = hexamethylphosphoramide) arise through similar ionic and steric factors.[2,3] Alternatively, the salt complexes can be regarded as fragments of the well known ionic lattices and the extents of oligomerisation of these often molecular species can be viewed simplistically in terms of the thermodynamic balance between the lattice energy of the parent salt on one hand and the strength of Lewis-base solvation on the other.[7]

We report the fortuitous synthesis and the solid-state structure of the unusual polymeric ('corrugated' ladder) complex $(LiBr{\cdot}thf)_\infty$ **1** (thf = tetrahydrofuran) which can be regarded as being constructed from the polymerisation of thf-solvated cubanes, $(LiBr{\cdot}thf)_4$. The formation of a polymeric structure for **1**, as opposed to separate $(LiBr{\cdot}thf)_4$ cubanes, may result from a reduction in $Br^- \cdots Br^-$ repulsion and more favourable packing of the thf ligands.

In an attempt to synthesise a germanium–amide cage compound $[Ge(NR)_2]_n$, $GeBr_4$ was treated with 2 equivalents of $Li_2[C_{10}H_7N]$ ($C_{10}H_7N$ = 1-naphthylamido dianion) in Et_2O–thf. Cooling of the filtered toluene solution of the residue however produced crystals of **1** as the only solid product.†

A low-temperature X-ray crystallographic study ‡ shows **1** to have a polymeric structure in the solid state constructed from 'folded' ladder segments (Fig. 1). These segments further associate so as to produce a 'corrugated' ladder in which all the Li centres are pseudo-tetrahedral [Fig. 2(*a*)]. The planar $(LiBr)_2$ units of the polymeric core are, within the estimated standard deviations, identical and have a regular rhombic shape [Li–Br–Li (av.) 78.1 and Br–Li–Br 101.8°]. These units build together with a regular pattern of alternating angles at Li and Br down the line of the polymer [Li–Br–Li 119.4(4), Br–Li–Br 121.9(4)°]. There are no significant differences in the Li–Br distances involved either within or connecting these units [2.518(10)–2.530(11)]. The regularity of the polymeric chain is seen most dramatically in a view down the centre of the core of **1** [Fig. 2(*b*)], in which the rhombic $(LiBr)_2$ units stagger alternately in order to accommodate thf donor solvation of the Li^+ cations. The co-ordination of these thf ligands to Li^+ [Li–O(1) 1.904(11) Å] is typical.[9]

Overall, the structure of **1** can be regarded as being constructed from the polymerisation of identical thf-solvated cubanes, $(LiBr{\cdot}thf)_4$, in which two opposite edges of one face have been broken. Although a similar 'corrugated' ladder arrangement to **1** has been observed in the structure of $[PhCH_2SLi{\cdot}py]_\infty$ (py = pyridine)[10] which has the same stoichiometry as **1**, and discrete ladder the structures are well known for lithium metalloorganic complexes,[11] to our knowledge there are no examples of infinite ladder structures for any inorganic salt complexes. However, it should be pointed out here that mono-thf-solvated complexes such as $LiBF_4{\cdot}thf$ have been basically characterised previously which may have structures similar to **1**.[12] For lithium halide complexes, the closest structurally characterised analogue to **1** is that of $[(LiBr)_4{\cdot}6dmpy]$ (dmpy = 2,6-dimethylpyridine) which has a

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† Synthesis of **1**: Tetrabromogermanium (0.3 cm^3, 2.5 mmol) was added to a solution of $Li_2[C_9H_7N]$ (5 mmol) dissolved in diethyl ether (8 cm^3) and thf (10 cm^3) at 20 °C. A red-orange solution was produced which was reduced under vacuum to *ca.* 2 cm^3, giving a red oil. This was dissolved in toluene (20 cm^3) and a faint precipitate was filtered off. Cooling of the resulting orange solution (−35 °C, 1 week) gave a crop of large needles of **1** in low yield. Complex **1** is extremely soluble in toluene and is isolated with great difficulty; once isolated, it rapidly desolvates giving LiBr. Complex **1** could finally only be characterised by low-temperature X-ray crystallography. The crystals were mounted directly from solution at low temperature (−40 °C).

‡ Crystal data: C_4H_8BrLiO, $M = 158.95$, orthorhombic, space grou *Pbcn*, $a = 14.872(3)$, $b = 11.348(2)$, $c = 7.759(2)$ Å, $U = 1309.5(5)$ Å^3, $Z = 8$, $D_c = 1.613$ Mg m^{-3}, $\lambda = 0.710\,73$ Å, $T = 153(2)$ K, μ(Mo-Kα) = 6.162 mm^{-1}. Data were collected on a Stoe AED diffractometer using an oil-coated rapidly cooled crystal of dimensions 0.24 × 0.22 × 0.19 mm by the 2θ–ω method ($7.2 \leqslant 2\theta \leqslant 45°$). Of a total of 1703 reflections collected, 855 were independent. The structure was solved by direct methods and refined by full-matrix least squares on F^2 with final R [$F > 4\sigma(F)$] and $wR2$ (all data) values of 0.039 and 0.095 respectively $\{R = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}\}$.[8] Largest peak and hole in the final difference map 0.556 and −0.795 e Å^{-3}. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

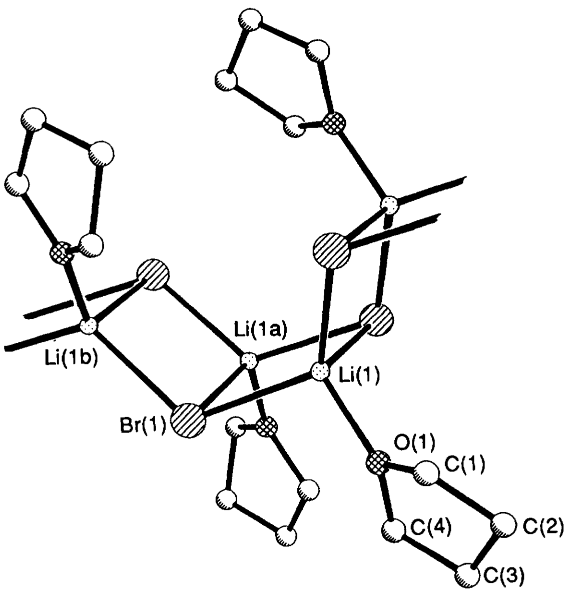

Fig. 1 The basic units of the corrugated ladder structure of complex **1**. Hydrogen atoms have been omitted for clarity. Key bond lengths (Å): Li(1)–Br(1) 2.523(10), Li(1a)–Br(1) 2.518(10), Li(1b)–Br(1) 2.530(11), Li(1)–O(1) 1.904(11), Li–Br–Li 119.4(3), Br–Li–Br 121.9(4). Average chain angles (°): Li–Br–Li 119.4(3), Br–Li–Br 121.9(4). Average internal angles (°): Li–Br–Li 78.1, Br–Li–Br 101.8

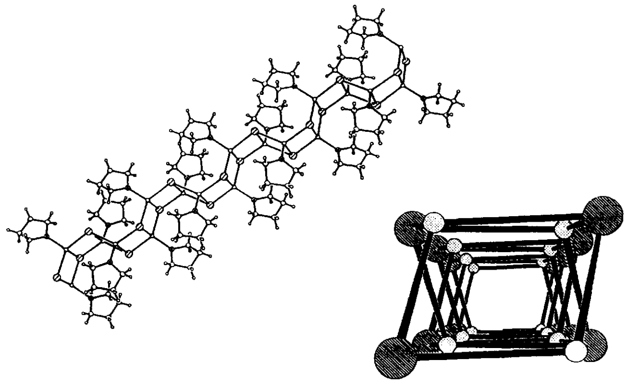

Fig. 2 (*a*) The polymeric structure of complex **1** and (*b*) a view of the core of **1** down the centre of the polymer chain

'staggered' (rather than folded) discrete ladder arrangement and a very different stoichiometry to **1**.[13]

On the basis of the observed 1 : 1 stoichiometry of LiBr to thf in **1**, a cubane structure similar to those observed in a range of lithium complexes in which a variety of heteroatomic groups and Lewis-base donor ligands are present could be expected, *e.g.*, such as in the solid-state structures of $(PhLi{\cdot}OEt_2)_4$,[5] $(LiCl{\cdot}hmpa)_4$,[6a] $(Ph_2C{=}NLi{\cdot}py)_4$,[6] $[CH_2{=}C(Bu^t)OLi{\cdot}thf]_4$.[14] However, although LiBr units have been observed in a number of mixed-aggregate cubanes, *e.g.*, one in $[(PhLi{\cdot}OEt_2)_3{\cdot}LiBr]$,[5] two in $[(C_3H_5Li{\cdot}OEt_2)_2{\cdot}(LiBr{\cdot}OEt_2)_2]$ (C_3H_5 = cyclopropyl)[15] and three in $[(Me_3Si)_3CCd{\cdot}(LiBr{\cdot}OEt_2)_3{\cdot}OSiMe_3]$,[16] there are no structurally characterised examples of 'pure' donor-solvated $(LiBr)_4$ cubane fragments.

The observation of a polymeric structure for **1** may suggest that, where large electron-rich anions are involved, anion ••• anion core repulsion can play a role in influencing the structures of such complexes, at least where weak sterically undemanding Lewis-base donors are present. Thus polymerisation of cubane-like $(LiBr{\cdot}thf)_4$ units into **1** (a polymer of 'broken cubanes') is likely to give a net reduction in Br^- ••• Br^- repulsion, as well as possibly giving more effective ligand ••• ligand packing, while still maintaining a four-co-ordinate geometry for Li^+. A similar model can also be used to rationalise the polymeric corrugated ladder arrangement of $(PhCH_2SLi{\cdot}py)_\infty$ in which an electron rich thiolate anion is present and where the relatively sterically undemanding benzyl groups and pyridine ligands can pack effectively into a continuous ladder arrangement similar to **1**.[10]

Acknowledgements

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