X-Ray Crystal Structure of $\{\mathrm{Li{\cdot}[O{=}P(NMe_2)_3]_4}\}^+{\cdot}\{\mathrm{Li_5[N{=}CPh_2]_6{\cdot}[O{=}P{\cdot}(NMe_2)_3]}\}^-$: a Lithium 'Ate Complex, with a Pentanuclear $\mathrm{Li_5}$ Clustered-anion having Both μ_2 Edge and μ_3 Face Nitrogen to Lithium Bonding

Donald Barr,[a] William Clegg,*[b] Robert E. Mulvey,[a] and Ronald Snaith*[a]

[a] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.*

[b] *Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D3400 Göttingen, West Germany*

An *X*-ray crystallographic study of $\{\mathrm{Li{\cdot}[O{=}P(NMe_2)_3]_4}\}^+{\cdot}\{\mathrm{Li_5[N{=}CPh_2]_6{\cdot}[O{=}P(NMe_2)_3]}\}^-$, (**1**), has shown it to be a clustered lithium 'ate complex, with an unprecedented pentanuclear $\mathrm{Li_5}$ clustered-anion having both μ_2 edge and μ_3 face nitrogen to lithium bonding.

Despite their long-suspected existence, the first lithium 'ate complex, with a linear C–Li–C anion, was only very recently isolated and structurally characterised,[1] thus adding to the variety of structural types found in organolithium (*i.e.*, C–Li) chemistry.[2] The link between CLi and NLi structural chemistry has recently been strengthened by our report of the pseudo-cubane complexed tetramer $\mathrm{(Ph_2C{=}NLi.NC_5H_5)_4}$,[3] which, together with several imidolithium hexamers, $\mathrm{(LiN{=}CRR')_6}$, ($\mathrm{R{=}R'{=}Me_2N}$, $\mathrm{Bu^t}$;[4] R=Ph, $\mathrm{R'{=}Me_2N}$, $\mathrm{Bu^t}$[5]), form examples of electron-deficient cluster compounds with μ_3 N to Li face bonding, analogous to μ_3 C to Li links in familiar $\mathrm{(CLi)_4}$ and $\mathrm{(CLi)_6}$ species.[2] Structurally studied amidonitrogen–lithium compounds, however, have $\mathrm{(NLi)}_x$ rings with electron-precise μ_2 N to Li edge bonding, *e.g.*, dimers $\{\mathrm{[(LiNR_2)(L)]_2}$, $\mathrm{L{=}OEt_2}$; $\mathrm{R{=}PhCH_2}$,[5] $\mathrm{Me_3Si}$[6]$\}$, trimers $[\mathrm{(LiNR_2)_3}$, $\mathrm{R{=}PhCH_2}$,[5] $\mathrm{Me_3Si}$[7]$]$, and the tetramer $[\mathrm{Li\overline{NCMe_2(CH_2)_3C}Me_2}]_4$.[6] We now report the isolation and structure of a *clustered* lithium 'ate species $\{\mathrm{Li[O{=}P(NMe_2)_3]_4}\}^+{\cdot}\{\mathrm{Li_5[N{=}CPh_2]_6{\cdot}[O{=}P(NMe_2)_3]}\}^-$, (**1**).

Compound (**1**) was prepared by the reaction of the polymeric imidolithium $\mathrm{(LiN{=}CPh_2)}_n$ with HMPA $\mathrm{[O{=}P(NMe_2)_3]}$ in a warm diethyl ether–toluene solvent mixture; cooling at −78 °C afforded orange-red, extremely moisture-sensitive crystals (m.p. 149—151 °C; found C, 64.8; H, 7.3; N, 14.6; P, 7.7; Li, 2.1%). The analysis figures implied less than one HMPA molecule per imidolithium unit, and an *X*-ray crystallographic study has now revealed an empirical formula of $\mathrm{(Ph_2C{=}NLi{\cdot}5/6HMPA)}$.

$$\{\mathrm{Li[O{=}P(NMe_2)_3]_4}\}^+{\cdot}\{\mathrm{Li_5[N{=}CPh_2]_6{\cdot}[O{=}P(NMe_2)_3]}\}^-$$

(**1**)

The cation structure in (**1**) is not unusual, with lithium tetrahedrally co-ordinated by four oxygen atoms (mean Li–O, 1.84 Å) {as in the cation of $\mathrm{[Li(thf)_4]^+{\cdot}Li[C(SiMe_3)_3]_2^-}$(thf = tetrahydrofuran),[1] mean Li–O, 1.96(8) Å}. However, the structure of the anion (Figure 1)† is unique in lithium

---

† Atomic co-ordinates are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

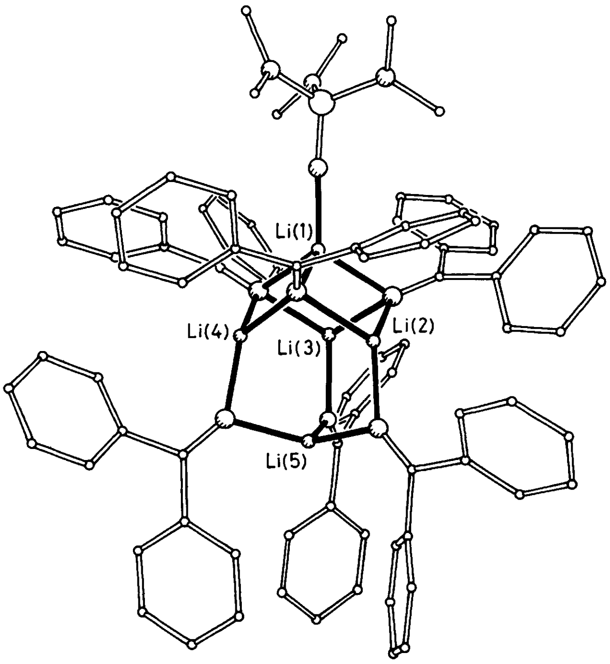

Figure 1. Structure of the $[Li_5(N{=}CPh_2)_6(HMPA)]^-$ anion. Bonds to lithium filled, others open. *Crystal data:* $C_{84}H_{78}Li_5N_9OP$, monoclinic, space group $P2_1$, $a = 15.965(2)$, $b = 25.883(3)$, $c = 16.532(2)$ Å, $\beta = 118.34(1)°$, $Z = 2$. Current $R = 0.15$ for 4936 reflections with $F > 3\sigma(F)$, isotropic thermal parameters, phenyl groups as regular hexagons, no H atoms.

chemistry; no other Li_5 cluster is known, or has been postulated to exist, in either neutral or charged species with Li–X bonds (*e.g.*, X = C, O, N, Cl). The five lithium atoms are arranged in a distorted trigonal bipyramid. Thus, four Li atoms [Li(2)—Li(5) inclusive] form a tetrahedron with a mean Li···Li edge 3.02 Å, while the fifth, top Li atom 'caps' the face at the base of this tetrahedron but with significantly shorter Li···Li contacts (mean 2.60 Å). This unique Li is bonded to the single HMPA ligand (Li–O, 1.83 Å). Three imido N atoms bridge the Li_3 triangular faces involving Li(1) (mean Li···N, 2.05 Å), while the remaining three bridge the Li_2 edges (mean Li···N, 2.02 Å) involving Li(5).

Assuming that Li···Li bonding is negligible, this anionic structure could be rationalised in terms of electron-precise (*i.e.*, of bond order 1) μ_2 edge and electron-deficient (of bond order 0.66) μ_3 triangular face nitrogen to lithium bonds. Thus, the cluster has a total of 12 electron pairs ($6 \times 3e^-$ from the six imido N ligands, $5 \times 1e^-$ from the 5 Li atoms, and $1\,e^-$ due to its anionic character), allowing a total of 6 pairs to be allocated to the 3 μ_2 units and 6 to the 3 μ_3 units. The shortness of the Li···Li distances involving the capping Li atom [Li(1)] reflects the electron-deficiency of the μ_3 N···Li bonding in this part of the cluster, a view reinforced by the presence of the HMPA ligand attached to this metal atom.

Interestingly, the anion in (**1**) may be regarded as being derived from the (unknown) tetrahedral anion $[Li_4(N{=}CR_2)_6]^{2-}$, with exclusively μ_2 imido ligands, by capping the open face with the $(HMPA)Li^+$ unit. Such face capping would convert three μ_2-imido ligands into μ_3 ligands, reducing the bond order with which they interact with the three Li atoms of the capped face, and thereby introducing an element of Li···Li bonding that is possibly reflected in the short Li···Li distances to the capping metal atom [Li(1)].

We thank the S.E.R.C. (D. B., R. E. M.) and the Verband der Chemischen Industrie (W. C.) for support.

Received, 8th November 1983; Com. 1460

References

1 C. Eaborn, P. B. Hitchcock, J. D. Smith, and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1983, 827.

2 M. E. O'Neill and K. Wade, 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, 1982, vol. 1, p. 1; J. L. Wardell, p. 43.

3 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 79.

4 W. Clegg, R. Snaith, H. M. M. Shearer, K. Wade, and G. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1983, 1309.

5 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, unpublished observations.

6 M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers, and R. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302.

7 R. D. Rogers, J. L. Atwood, and R. Grüning, *J. Organomet. Chem.*, 1978, **157**, 229.