First structurally characterised lithium hexafluorophosphate complexes with acyclic Lewis bases: ion-separated $[Li_2(hmpa)_5]^{2+}\cdot 2(PF_6^-)$ and ion-contacted $[(pmdeta)LiPF_6]_2$ [hmpa = $(Me_2N)_3PO$; pmdeta = $MeN(CH_2CH_2NMe_2)_2$]

David R. Armstrong,[a] Amit H. Khandelwal,[b] Lesley C. Kerr,[c] Sonja Peasey,[c] Paul R. Raithby,[c] Gregory P. Shields,[c] Ronald Snaith*[c]† and Dominic S. Wright[c]

[a] *Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, UK G1 1XL*
[b] *Defence Evaluation and Research Agency, Structural Materials Centre, Farnborough, Hampshire, UK GU14 0LX*
[c] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*

Reactions of NH_4PF_6 with Bu^{n}Li in toluene containing hmpa or pmdeta afford the complexes $[Li_2(hmpa)_5]^{2+}\cdot 2(PF_6)^-$ 1, an ion-separated species containing an unusual dinuclear dication, and $[(pmdeta)LiPF_6]_2$ 2 in which PF_6^- anions bridge (pmdeta)Li$^+$ units *via* Li···F interactions, this being the first observation of a bridging mode for this anion; *ab initio* MO calculations help explain the very different structures of 1 and 2.

Lithium salts are favoured electrolytes in medium-sized rechargeable batteries[1] which have military use as well as use in laptops/personal computers and mobile phones. Anions stable at the voltages generated (typically, 4.2 V) are required for these applications. Hence, $LiPF_6$ dissolved in organic carbonates such as ethylene or dimethyl carbonate has attracted much interest. However, there are practical problems: commercially supplied $LiPF_6$ is expensive and often impure, it is difficult to handle owing to its sensitivity to air, moisture and light, and it releases toxic hydrogen fluoride upon hydrolysis. Further, and surprisingly, there are no published structural data on complexes of $LiPF_6$ with other than macrocyclic ligands (which lead to ion-separated species).[2] Given these deficiencies, we have investigated and now report a synthetic method for assembling $LiPF_6$ complexes *in situ* and the solid-state structures of two of them: $[Li_2(hmpa)_5]^{2+}\cdot 2(PF_6^-)$ **1** an ion-separated species containing a previously unknown dinuclear dication, and $[(pmdeta)LiPF_6]_2$ **2** an ion-contacted species in which PF_6^- anions bond in an unprecedented way, bridging metal centres *via* Li···F contacts. We report also the results of *ab initio* MO calculations on $LiPF_6$ and its complexes with selected acyclic Lewis bases.

Complexes **1** and **2** were synthesised by the 'ammonium salt' route whereby ammonium salts are reacted with metal sources in toluene containing stoichiometric amounts of a Lewis base.[3] Here, NH_4PF_6 suspended in toluene containing hmpa or pmdeta was treated with Bu^{n}Li solution, cooling of the resulting solutions affording high yields of crystalline materials, identified as **1** and **2**. The advantages of this *in situ* route are clear: $LiPF_6$ units are assembled from very pure precursors prior to being captured by Lewis bases present, and these steps occur quickly and under mild and anhydrous conditions. In contrast, the direct route to these complexes is ineffective: solid $(LiPF_6)_\infty$ dissolves in hmpa or pmdeta (neat or with non-polar solvents present also) to give oils, from which crystalline materials are unobtainable.

The solid-state structures of **1** and **2** have been determined by X-ray crystallography.‡ Complex **1** crystallises in the trigonal space group $P6_3/m$ and consists of dications $[Li_2(hmpa)_5]^{2+}$ and separate PF_6^- anions. The former (Fig. 1) are each made up of two terminal (hmpa)Li$^+$ units [Li(1)–O(1) 1.83(2) Å] linked by three μ-hmpa molecules [Li(1)–O(2) 1.992(12) Å]. Such triple μ-O bridges are extremely rare although they occur in the acetamide complex $(LiClO_4)_2\cdot(\mu\text{-}MeCONH_2)_3\cdot(MeCONHCOMe)_2$[4] and, in the closest analogy, in $[BrLi(\mu\text{-}hmpa)_3LiBr]$.[5]

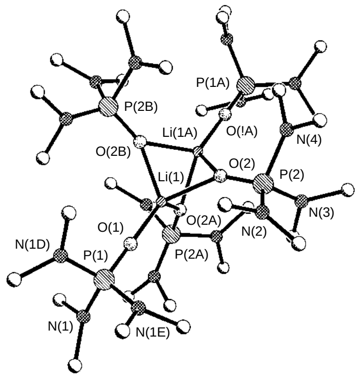

Fig. 1 Molecular structure of the cation of $[Li_2(hmpa)_5]^{2+}\cdot 2(PF_6^-)$ **1**; hydrogen atoms omitted for clarity

Rarity notwithstanding, the dication of **1** appears to represent something of a 'thermodynamic sink'. It forms irrespective of the stoichiometric amounts of hmpa provided during the synthesis of **1**. Further we have observed the same dication in the structures of $[Li_2(hmpa)_5]^{2+}\cdot(GeBr_3^-)_2$ and $[Li_2(hmpa)_5]^{2+}\cdot(SnPh_3^-)_2$.[6]

The solid-state structure of **2** also contains dinuclear units although here the ions are contacted (Fig. 2). Two (pmdeta)Li$^+$ units [Li–N 2.181(6), 2.189(6), 2.207(6) Å; mean 2.192 Å] are joined *via* two PF_6^- anions each of which provides two bridging fluorine atoms, one to each cation [Li(1)–F(1) 2.140(5), Li(1)–F(3A) 1.914(6) Å]. These bridges, which are almost linear (mean Li–F–P, 175.5°), result in formation of a central $(LiFPF)_2$ eight-membered ring. So far as we can ascertain, **2** is the first ion-contacted $LiPF_6$ complex. More widely, a bridging mode for the PF_6^- anion is seemingly unprecedented. Hitherto, whenever this anion has been found coordinating (in itself, a rare occurrence) it has done so to just one metal centre using one, two or three of its F atoms, *e.g.* η^1 in $(Me_3P)(NO)(CO)_3W(F)PF_5$,[7a] η^2 in $F_4P(F)_2Na\cdot$dibenzo-36-crown-

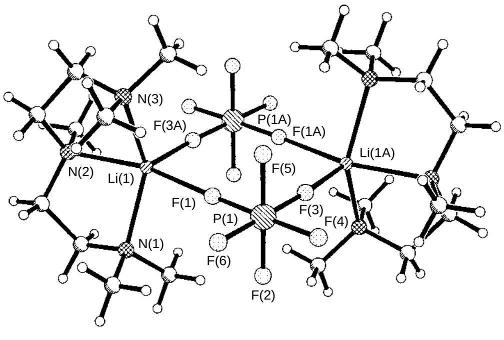

Fig. 2 Molecular structure of $[(pmdeta)LiPF_6]_2$ **2**

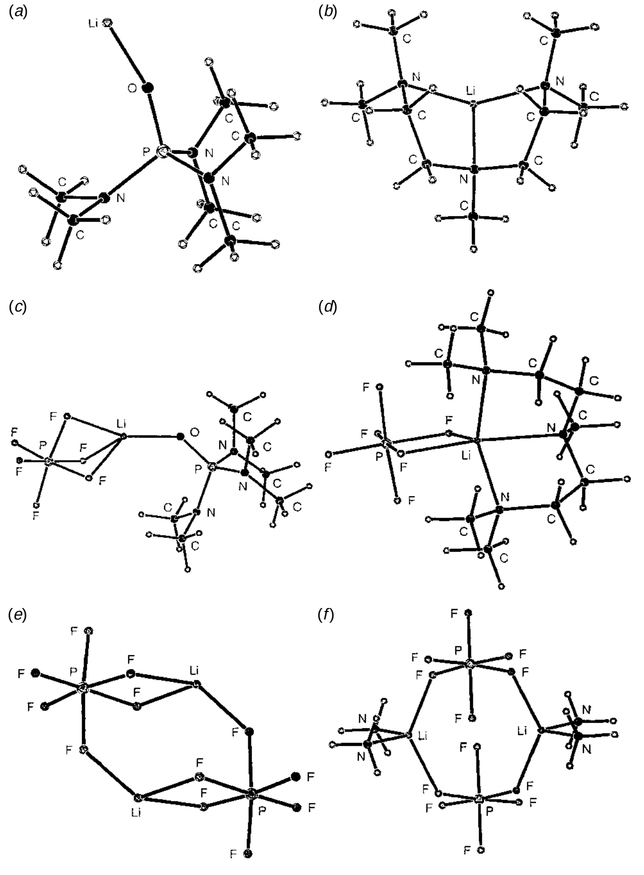

Fig. 3 Optimised structures (6-31G** basis set) of (*a*) Li$^+$·hmpa, (*b*) Li$^+$·pmdeta, (*c*) LiPF$_6$·hmpa, (*d*) LiPF$_6$·pmdeta, (*e*) (LiPF$_6$)$_2$, (*f*) (LiPF$_6$·2NH$_3$)$_2$

12·Na(F)$_2$PF$_4$,[7b] and η^3 in F$_3$P(F)$_3$Na·ferrocene benzo-15-crown-5.[7c]

Finally, we have employed *ab initio* MO calculations (6-31G** basis set[8] and using the program GAMESS[9]) to probe the reasons behind the very different molecular structures of **1** and **2** and to examine the energetics of LiPF$_6$ complexation. Species were optimised without constraint and confirmed as true minima by positive frequency tests. Monomeric, uncomplexed LiPF$_6$ itself favours an η^3-structure F$_3$P(F)$_3$Li; an η^2 arrangement is almost as stable (relative energy, +0.7 kcal mol^{-1}) but an η^1 one is of much higher energy (+13.2 kcal mol^{-1}). Calculations on pmdeta and hmpa show that the charges on the N centres of the former are −0.59 (two NMe$_2$) and −0.62 (NMe), and that the charge on the O centre of the latter is −0.75. In purely electrostatic terms, both of these molecules are more attractive to Li$^+$ than is anionic PF$_6^-$, for which the charge on each F centre is −0.49. This is especially so for hmpa, a point borne out by the complexation energy of Li$^+$ by a single hmpa ligand [Fig. 3(*a*)] being a massive −69.3 kcal mol^{-1}; the enthalpy of formation of Li$^+$·pmdeta, with all three N atoms coordinated [Fig. 3(*b*)] is −94.5 kcal mol^{-1}. From such data one can see why highly polar hmpa ligands will likely exclude PF$_6^-$ anions from Li$^+$ coordination spheres, especially so since it is feasible stereochemically to place four hmpa ligands around each Li$^+$, in a Li(hmpa)$_4^+$ cation or in a dinuclear species [Li$_2$(hmpa)$_5$]$^{2+}$, as found in **1**. In contrast, the optimised structure of Li$^+$·pmdeta shows clearly that it would not be possible to place even two (less polar) pmdeta ligands around a Li$^+$ cation; hence the appearance of Li–F contacts in **2**.

The monomeric complexes LiPF$_6$·hmpa and LiPF$_6$·pmdeta were also calculated. The lowest energy structure of the former [Fig. 3(*c*)] shows the PF$_6^-$ anion η^3-bonded to Li$^+$ [Li–F distances, 1.983 Å (twice) and 1.938 Å] and the complexation energy of LiPF$_6$ by hmpa is −39.7 kcal mol^{-1}. For the latter [Fig. 3(*d*)], the asymmetry imposed by the pmdeta ligand (and seen in the structure of **2**) is reflected in two different Li–F bond lengths (1.917, 1.988 Å) and in three different Li–N bond lengths (2.142, 2.194, 2.251 Å); the complexation energy is −49.0 kcal mol^{-1}. Finally, we optimised the structures of some dimeric species. For (LiPF$_6$)$_2$ itself [Fig. 3(*e*)], each Li$^+$ has three Li–F contacts, two provided by one PF$_6^-$ anion (Li–F 1.877 Å) and one by the other (1.663 Å). This basic structure is retained when each Li$^+$ is complexed by a single monodentate Lewis base, as in the structure found for (LiPF$_6$·NH$_3$)$_2$. However, bis(complexation), as in (LiPF$_6$·2NH$_3$)$_2$ [Fig. 3(*f*)], reproduces the key structural features found in **2**, each Li$^+$ centre now contacting two F atoms (Li–F, 1.972, 1.973 Å) provided by two PF$_6^-$ anions.

Notes and References

† E-mail: rs10003@cus.cam.ac.uk

‡ *Crystal structure determinations*: **1**: C$_{30}$H$_{90}$F$_{12}$Li$_2$N$_{15}$O$_5$P$_7$, M_r = 1199.4, trigonal, space group $P6_3/m$, a = 12.931(7), c = 20.62(2) Å, U = 2986(4) Å^3, T = 150(2) K, Z = 2, D_c = 1.335 g cm^{-3}, μ(Mo-Kα) = 2.91 cm^{-1}, F(000) = 1268, λ = 0.71073 Å, 4253 reflections, 1338 unique. Final $R(F)$ = 0.0798 for 712 reflections with [$I > 2\sigma(I)$] and $wR(F^2)$ = 0.203 on all data, 138 parameters, GOF = 1.059. **2**: C$_9$H$_{23}$F$_6$LiN$_3$P, M_r = 325.21, monoclinic, space group $P2_1/c$, a = 9.025(6), b = 9.829(9), c = 18.199(6) Å, β = 103.92(4)°, U = 1567(2) Å^3, T = 150(2) K, Z = 4, D_c = 1.379 g cm^{-3}, μ(Mo-Kα) = 2.29 cm^{-1}, F(000) = 680, λ = 0.71069 Å, 2941 reflections, 2757 unique. Final $R(F)$ = 0.0466 for 1769 reflections with [$I > 2\sigma(I)$] and $wR(F^2)$ = 0.258 on all data, 186 parameters, GOF = 1.056; CCDC 182/791.

1 G. Pistoia, *Lithium batteries: new materials, developments and perspectives*, Industrial Chemistry Library, Elsevier, Amsterdam, 1994, vol. 5; A. G. Ritchie, *Philos. Trans. R. Soc. London A*, 1996, **354**, 1643.

2 Four solid-state structures of LiPF$_6$ complexes are known, all containing cyclic ligands and all being ion-separated: R. Schwesinger, K. Piontek, W. Littke and H. Prinzbach, *Tetrahedron Lett.*, 1985, **26**, 1201; E. C. Constable, L.-Y. Chung, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1986, 1719; E. C. Constable, M. J. Doyle, J. Healy and P. R. Raithby, *ibid.*, 1988, 1262; C. G. Choo, S. D. Rychnovsky and M. C. Etter, *Chem. Mater.*, 1994, **6**, 1200.

3 R. Snaith and D. S. Wright, in *Lithium Chemistry: A Theoretical and Experimental Overview*, eds. A.-M. Sapse and P. v. R. Schleyer, Wiley, New York, 1995, ch. 8.

4 P. S. Gentile, J. G. White and D. D. Cavalluzzo, *Inorg. Chim. Acta*, 1976, **20**, 37.

5 D. Barr, M. J. Doyle, R. E. Mulvey, P. R. Raithby, D. Reed, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1989, 318.

6 D. Stalke and D. S. Wright, unpublished work.

7 (*a*) R. V. Honeychuck and W. W. Hersh, *Inorg. Chem.*, 1989, **28**, 2869; (*b*) J. M. Maud, J. F. Stoddart, H. M. Colquhoun and D. J. Williams, *Polyhedron*, 1984, **3**, 675; (*c*) P. D. Beer, H. Sikanyika, C. Blackburn, J. F. McAleer and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1990, 3295.

8 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213; J. D. Dill and J. A. Pople, *J. Chem. Phys.*, 1975, **62**, 2921.

9 M. Dupuis, D. Spangler and J. J. Wendoloski, GAMESS NRCC Software Catalogue, Program No. 2 GOI, vol. 1, 1980; M. F. Guest, J. Kendrick and S. A. Pope, GAMESS Documentation, Daresbury Laboratory, Warrington, UK, 1983; M. F. Guest, P. Fantucci, R. J. Harrison, J. Kendrick, J. H. van Lenthe, K. Schoeffel and P. Sherwood, GAMESS-UK Daresbury (CFS Ltd., 1993).

Received in Cambridge, UK, 19th December 1997; revised manuscript received 13th February 1998; 8/01280F