

**Alkali Metal Complexes of Planar Pentadentate Macrocycles;
a Unique Environment for Lithium in the Crystal and Molecular Structure of
(LiL¹)[PF₆]{L¹ = 1,6-dimethyl-1,2,5,6-tetra-aza-[6.0.0](2,6)pyridinophane-2,4-diene}**

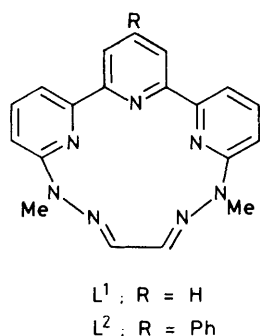
Edwin C. Constable,* Michael J. Doyle, John Healy, and Paul R. Raithby

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

Multinuclear n.m.r. and chemical studies indicate that the planar pentadentate macrocyclic ligands 1,6-dimethyl-1,2,5,6-tetra-aza-[6.0.0]pyridinophane-2,4-diene (L¹) and L² (L² = 17-phenyl-L¹) form complexes with remarkably high stability to aquation with alkali metal cations; the crystal and molecular structure of the complex [LiL¹][PF₆] has been determined, and the metal shown to be in a unique planar pentadentate environment.

Although the co-ordination chemistry of alkali metals with cyclic and acyclic ethers is well-developed, it is only in recent years that attention has been given to complexes with nitrogen donor species.¹ The majority of studies to date have been concerned with the interaction with saturated amine donors.¹

Compounds with imine donors have been reported,² but other donor atoms are commonly present and structural characterisation is sparse.³ We recently reported the structure of a six-co-ordinate lithium complex in which a planar pentadentate macrocycle occupied the basal plane of a pentagonal-



based pyramidal complex, with the axial site occupied by a methanol molecule.⁴ In this communication we report a series of alkali metal complexes with the planar pentadentate macrocyclic ligand 1,6-dimethyl-1,2,5,6-tetra-aza-[6.0.0]-(2,6)pyridinophane-2,4-diene (L^1), and describe the crystal and molecular structure of the planar pentagonal lithium complex, in which the metal ion is bonded to nitrogen donors only.

The salts $[H_2L^1][PF_6]_2$ and $[H_2L^2][PF_6]_2$ ($L^2 = 17$ -phenyl- L^1) are readily prepared by transient template condensations involving dimethyltin(IV).⁵ Treatment of orange solutions containing $[H_2L][PF_6]_2$ ($L = L^1$ or L^2) with excess MOH or MOR ($M = Li, Na, K, Rb, \text{ or } Cs; R = Me \text{ or } Et$) results in a colour change to yellow; this change is reversible upon the addition of acid. Treatment of the solutions with $[Bu^4N][PF_6]$ led to the precipitation of yellow microcrystalline solids. Fast atom bombardment (f.a.b.) mass spectroscopy and elemental analysis suggest that these complexes are of stoichiometry $[ML][PF_6]$. The 1H n.m.r. spectra of these solids in CD_3CN solution differed from that of $[H_2L][PF_6]_2$ and from each other. The spectrum of the lithium complex was sharp and well-resolved whereas the spectra of the other complexes were broadened and temperature dependent. All resonances experienced an upfield shift with respect to $[H_2L][PF_6]_2$. The 7Li n.m.r. spectrum of a solution containing both $[LiL][PF_6]$ and $LiCl$ exhibited two sharp signals, indicating that no exchange occurs between free and co-ordinated lithium ion. The i.r. spectra of the complexes show systematic changes with metal ion; the combined C=N modes occur at 1636 and 1612 cm^{-1} in $[H_2L^1][PF_6]_2$, 1587 and 1575 cm^{-1} in $[LiL^1][PF_6]$, 1580 cm^{-1} in $[NaL^1][PF_6]$, 1577 cm^{-1} in $[KL^1][PF_6]$ and $[RbL^1][PF_6]$ and 1572 cm^{-1} in $[CsL^1][PF_6]$. The complex $[LiL^1][PF_6]$ could be recovered unchanged after treatment with boiling water.

Recrystallisation from MeCN–MeOH yielded X-ray quality yellow crystals of $[LiL^1][PF_6]$. The crystal and molecular structure of the cation in the complex $[LiL^1][PF_6]$, together with the numbering scheme adopted, is shown in Figure 1.[†]

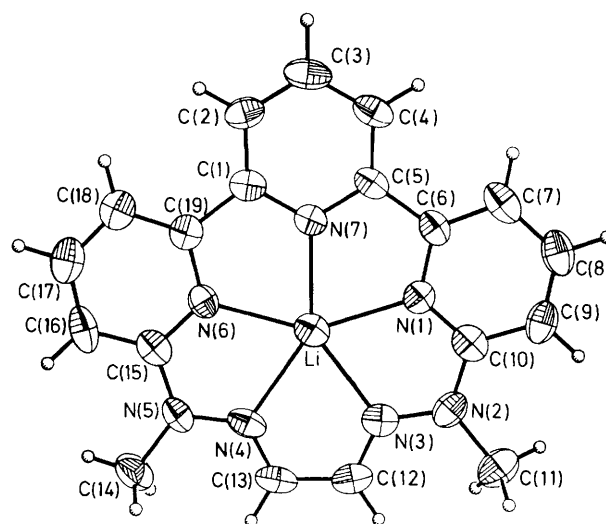


Figure 1. The crystal and molecular structure of the $[LiL^1]^+$ cation in $[LiL^1][PF_6]$ showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are depicted at a 50% probability level. Selected bond lengths (\AA): Li–N(1) 2.15(2), Li–N(3) 2.21(2), Li–N(4) 2.23(2), Li–N(6) 2.15(2), Li–N(7) 2.11(2). Selected bond angles ($^\circ$): N(1)–Li–N(3) 70.6(5), N(3)–Li–N(4) 71.4(5), N(3)–Li–N(6) 142.0(7), N(1)–Li–N(7) 73.3(5), N(4)–Li–N(7) 144.7(8), N(1)–Li–N(4) 142.0(8), N(1)–Li–N(6) 147.2(7), N(4)–Li–N(6) 70.7(5), N(3)–Li–N(7) 143.8(8), N(6)–Li–N(7) 74.0(5).

The lithium ion is in a unique environment, within the pentagonal plane of the macrocyclic ligand. The metal is exactly within the plane described by the five donor nitrogen atoms N(1), N(3), N(4), N(6), and N(7) (sum of N–Li–N angles 360.0°), with all N–Li–N angles within the range 70.6 – 74.0° . The Li–N distances are all in the range 2.11 – 2.23 \AA , and do not differ significantly from those observed in the pentagonal-based pyramidal complex reported earlier.⁴ All molecular dimensions within the macrocyclic ligand are closely similar to those previously reported for the other derivatives of L^1 and L^2 .⁵ and the macrocyclic bonding cavity ('hole-size') may be ascribed a radius of 2.17 \AA . The metal ion is significantly displaced towards the 'terpyridyl' portion of the molecule, with long Li– N_{imine} bonds of $2.21(2)$ and $2.23(2)$ \AA and shorter Li– N_{py} bonds of $2.11(2)$, $2.15(2)$, $2.15(2)$ \AA . This phenomenon had previously been noted in nickel(II) complexes of related macrocyclic ligands, and assigned to a preferential π -bonding interaction with the terpyridine; such an explanation is clearly not viable in the case of the π -neutral lithium ion. There are no short contacts between the cation and adjacent cations or the anions.

The structure of the complex is unique in alkali metal chemistry, with a metal cation in a planar pentagonal environment. All previous complexes of transition metal cations with planar pentadentate macrocyclic ligands have possessed one or two axial interactions. The stability of the complexes with respect to the formation of $[M(H_2O)_n]^+$ is remarkable, and indicates a very strong interaction between the planar pentadentate donor set and the metal ions. Conventional explanations for the bonding in alkali metal co-ordination compounds involve ionic and dipolar interactions; such interactions cannot be the sole factor responsible for the very strong M–N bonding in these complexes. The structural characterisation of the complex cation $[LiL^1]^+$ provides further evidence for strong interactions between planar polydentate nitrogen donors and alkali metals.⁶

[†] Crystal data: $C_{19}H_{17}F_6LiN_7P$, yellow tablets, $M = 495.34$, monoclinic, space group $P2_1/c$, $a = 7.249(1)$, $b = 19.645(3)$, $c = 14.711(2)$ \AA , $\beta = 103.18(1)^\circ$, $U = 2039.8(6)$ \AA^3 , $Z = 4$, $F(000) = 1008$, $D_c = 1.612$ $g\ cm^{-3}$, Cu– $K\alpha$ radiation ($\lambda = 1.5418$ \AA), $\mu(Cu-K\alpha) = 19.16$ cm^{-1} . 3320 Reflections collected on a Nicolet R3m μ four-circle diffractometer in the range $5.0 \leq 2\theta \leq 116.0^\circ$. The data was averaged and 1957 unique reflections with $F > 3\sigma(F)$ were used in structure solution and refinement. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked cascade least-squares to $R = 0.114$, $R_w = 0.131$. The hexafluorophosphate ion was disordered and was treated as three interlocking octahedra with partial occupancies. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No 1.

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