

The First Stable Lithium Complex of a Pentadentate Macrocyclic Incorporating sp^2 -Nitrogen Donor Atoms only; the X-Ray Crystal Structure of $[\text{Li}(\text{L}^2)(\text{MeOH})][\text{PF}_6]$ $\{\text{L}^2 = 6,13\text{-}(\text{Bis-2-hydroxyethyl})\text{-}6H,13H\text{-}tripyrido[cd,fg,lm] [1,2,4,7,9,10,13]\text{hepta-azapentadecine}\}$

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The preparation and structural characterisation of a lithium complex of a pentadentate macrocycle incorporating only pyridine and imine donors is described; the metal is in a very unusual pentagonal-based pyramidal environment, in which the sixth axial site is occupied by a solvent methanol molecule.

Until recently, the co-ordination chemistry of group 1A metals was predominantly limited to that with polydentate oxygen donor ligands.^{1,2} It is now apparent that the smaller members of the group, particularly lithium, form complexes with polydentate amines and a variety of anionic amido, alkoxide, or carbon-donor ligands.^{3–5} There have been intriguing reports over the last fifty years of adducts of alkali metal cations with polydentate imine donor ligands, such as 2,2'-bipyridine or 1,10-phenanthroline.^{6,7} Our interest was stimulated by reports of stable lithium complexes with 2,2':6',2'':6'',2''':6''',2''''-quinquepyridine⁸ and sodium complexes with *cyclo-sexi*-pyridines,⁹ and our own observations of the formation of alkali metal complexes with 2,2':6',2'':6'',2''':6''',2''''-quinquepyridine.¹⁰ The pentadentate macrocyclic ligand $[\text{H}_2\text{L}^2][\text{PF}_6]_2$ was prepared by the reaction of the hydroxyethyl derivative $[\text{H}_2\text{L}^1][\text{PF}_6]_2$ with an

excess of thionyl chloride, followed by treatment with $[\text{NH}_4][\text{PF}_6]$. The chloroethyl derivative exhibits ¹H n.m.r., i.r., and mass spectroscopic and analytical properties in accord with the proposed formulation. Treatment of a solution of $[\text{H}_2\text{L}^2][\text{PF}_6]_2$ (0.3 mmol) in boiling methanol (100 ml) with lithium hydroxide (1.4 mmol) led to a colour change from red to yellow. Upon slow evaporation, yellow crystals of the complex $[\text{LiL}^2(\text{MeOH})][\text{PF}_6]$ were deposited.

An X-ray crystallographic analysis revealed the presence of two independent, but structurally similar, $[\text{Li}(\text{L}^2)(\text{MeOH})][\text{PF}_6]$ species in the asymmetric unit.† The structure of a cation is shown in Figure 1, together with selected bond parameters. The N₅ donor set of the macrocycle is planar [max. deviation for N(5) of 0.005 Å], and the whole of the macrocyclic ring system shows only minor deviations from planarity. The Li atom is displaced by 0.305 Å from the plane of the N₅ donor set towards the methanolic oxygen atom. The geometry about the Li atom is best described as a flattened pentagonal-based pyramid. The lithium–imine nitrogen distances are similar to those observed for the lithium–pyridine (py) nitrogen distances in $\{[\text{Ph}_2\text{C}=\text{N}(\text{py})]_4\}$.⁴

The macrocyclic 'hole-size,' as defined by the radius of the best-fit circle circumscribed through the N-donor atoms is 2.1 Å. This is similar to the value found in the solid state structures of complexes of related pentadentate nitrogen-donor macrocycles.¹² The bond parameters within the macrocycle itself are not significantly different from those found in the related chromium cation $[\text{Cr}(\text{L}^1)(\text{H}_2\text{O})_2]^{3+}$.¹³

This is the first example of a structurally characterised complex of a lithium complex with a neutral ligand containing only sp^2 hybrid nitrogen donor atoms. The isolation of such a complex from an oxygen donor medium, combined with the structural characterisation as a 'true' co-ordination compound rather than a less well-defined adduct, suggest the possibility of a rich co-ordination chemistry for alkali metals with oligopyridine and related ligands.

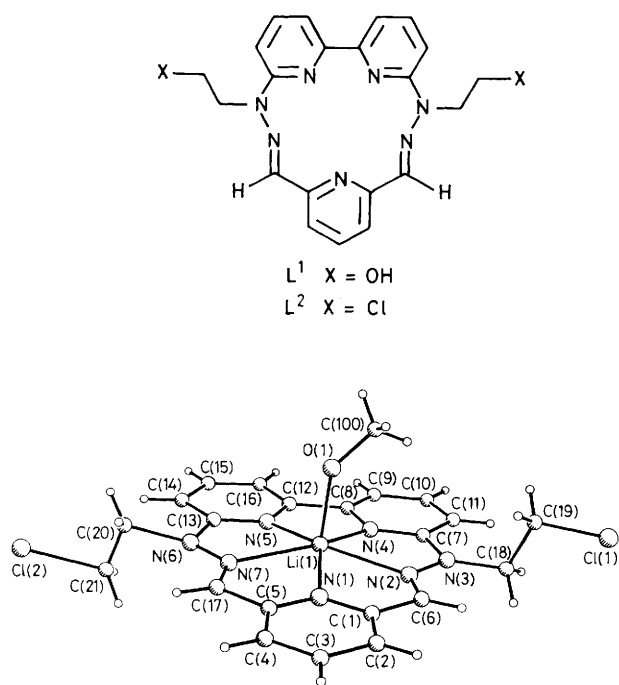


Figure 1. The molecular structure of the cation $[\text{Li}(\text{L}^2)(\text{MeOH})]^+$, showing the atom numbering scheme. Bond lengths (values for second molecule in square brackets): Li(1)–N(1), 2.160(14) [2.168(13)]; Li(1)–N(2), 2.257(14) [2.276(13)]; Li(1)–N(4), 2.152(14) [2.136(13)]; Li(1)–N(5), 2.148(14) [2.142(13)]; Li(1)–N(7), 2.271(14) [2.283(14)]; Li(1)–O(1), 2.041(15) [2.017(14)] Å. Bond angles: Li(1)–O(1)–C(100), 132.3(7) [128.6(7)]°.

† *Crystal Data:* $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{F}_6\text{LiN}_7\text{OP}$, $M = 625.29$, monoclinic, space group $P2_1/c$ (No. 14), $a = 16.801(1)$, $b = 13.680(2)$, $c = 23.366(3)$ Å, $\beta = 90.63(1)^\circ$, $U = 5370.1$ Å³, $D_c = 1.546$ g cm⁻³, $Z = 8$, $F(000) = 2464$, Cu-K α radiation, $\lambda = 1.5418$ Å, $\mu = 34.4$ cm⁻¹. Nicolet R3m diffractometer, 9023 measured reflections, 2θ range 5–120°, empirical absorption correction, 5583 unique observed reflections, $F > 3\sigma(F)$. Structure solved by random start tangent refinement and Fourier difference techniques. Refinement by blocked-cascade least-squares, P, Cl, O, N, and C anisotropic, PF_6^- treated as two intersecting F octahedra with partial occupancies, hydrogens AFIXed; converged $R = 0.112$, $R_w = 0.124$. 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, 1986.

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