

A Unique Octa-co-ordinated Environment for Sodium in a New Neutral Molecular Receptor: Synthesis and X-Ray Crystal Structure of [NaL]BPh₄ [L = 1,4,7,10-tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetra-azacyclododecane]

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The new pyrazole functionalised macrocyclic ligand 1,4,7,10-tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetra-azacyclododecane forms stable complexes with alkali metal cations; the crystal and molecular structure of the complex [NaL]BPh₄ has been determined; the cation is in a unique octa-co-ordinated environment formed by the nitrogen atoms of the macrocyclic ligand and the unsubstituted nitrogen atoms of the pendant pyrazole groups.

Although the co-ordination chemistry of the alkali metals is well developed in the presence of ethereal oxygens from cyclic and acyclic molecules¹ and oxygen donors are invariably present in new host molecules derived from calixarenes,² in recent years attention has been addressed to alkali metal complexes with nitrogen donor atoms. It is now apparent that polydentate host molecules containing amine³ or amine and imine⁴ nitrogen atoms form stable compounds with low atomic number alkali metals, particularly lithium. The preorganization of the binding sites prior to complexation appears to be the most important factor in determining the complexing ability of these ligands.

In this communication, we report lithium and sodium complexes with the lipophilic, potentially octa-dentate, new ligand 1,4,7,10-tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetra-azacyclododecane (L) which presents a flexible framework, with four nitrogen donor atoms on its pendant arms and the remaining N donors in a macrocyclic ring whose bonding cavity is too small to accommodate cations. The crystal and molecular structure of the sodium [NaL]BPh₄ complex is also reported.

1-(Hydroxymethyl)pyrazole⁵ (42 mmol) dissolved in dry acetonitrile (50 ml) was added to 1,4,7,10-tetra-azacyclododecane⁶ (10 mmol) in dry acetonitrile (80 ml); the resulting

solution was stirred at room temperature in a dry atmosphere for 48 h and finally evaporated to dryness *in vacuo*. The crude product, which is highly hygroscopic, was purified by dissolving a portion (1 g) in dichloromethane (20 ml) and passing it down a basic alumina column (15 × 2 cm); elution with dichloromethane-methanol (10:1, 150 ml) and evaporation to dryness gave pure L in 92% yield.† The complexes [ML]BPh₄ (M = Li, Na) were prepared by treating stoichiometric amounts of MBPh₄ in ethanol and the ligand L in acetone. Crystalline compounds which gave satisfactory elemental analyses for C, H, N, and Li or Na, were obtained by concentrating the solutions slowly. [NaL]BPh₄ exhibits† a single ²³Na resonance and sharp signals for the hydrogen atoms of the ligand, which are slightly highfield shifted with respect to those of the free ligand. The lithium derivative [LiL]BPh₄ yields† two sharp resonances for complexed Li. The ¹H spectrum shows intense signals (a) for the ethylene protons of the tetra-azacyclododecane, for those of the methylene chains and for the hydrogens of the pyrazole groups; moreover, each of the above resonances is accompanied by weaker signals. (b) The NMR data for the sodium derivative are consistent with the presence of a single species in solution, which may be assumed to be similar to that existing in the solid state (see below). The NMR data for the lithium derivative, on the other hand, are consistent with the presence of two predominant species in solution, which exchange slowly on the NMR time scale. One of these, yielding single resonances for the macrocycle, the CH₂ chains, and the pyrazole groups as found for [NaL]BPh₄, should contain the lithium ion in a similar environment to that proposed above for sodium. The other one, whose presence is implied by the numerous signals in the spectrum, in particular for the pyrazoles and the CH₂ chains, may have a lower co-ordination number and a different geometry about the metal atom.

Crystals of [NaL]BPh₄ suitable for X-ray diffraction were obtained by slow evaporation at room temperature of an acetone-ethanol solution. The crystal structure of

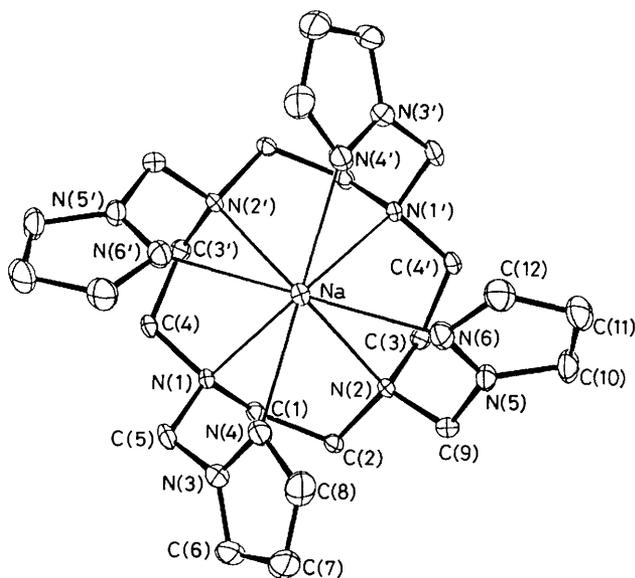


Figure 1. Selected bond lengths (Å) and angles (°) for [NaL]BPh₄: Na-N(1) 2.703(4), Na-N(2) 2.701(4), Na-N(4) 2.585(5), Na-N(6) 2.580(5); N1-Na-N(2) 68.9(1), N(1)-Na-N(2') 68.6(1), N(4)-Na-N(6) 81.0(2), N(4)-Na-N(6') 80.8(2), N(1)-Na-N(4) 67.4(1), N(2)-Na-N(6) 67.2(1). Primed atoms are related to the corresponding unprimed ones by a two-fold axis passing through the Na atom position.

† All NMR spectra were recorded in CD₂Cl₂ (ca. 10⁻² M) at room temperature. δ ¹H with respect to Me₄Si; δ ⁷Li and ²³Na downfield with respect to LiBPh₄ (0.026 M) in CD₂Cl₂⁷ and to NaCl (0.25 M) in D₂O,⁷ respectively. Coupling constants (*J*) in Hz. Ligand, L: ¹H, δ 2.71 (s, 16H, CH₂), 4.87 (s, 8H, CH₂), 6.21 (t, 4H, C₄H, *J* 2.0), 7.42 (d, 4H, CH, *J* 1.9), 7.70 (d, 4H, CH, *J* 2.0). [NaL]BPh₄: ²³Na, δ 9.69 p.p.m., ν_{1/2} 105 Hz; ¹H, δ 2.41 (s, 16H, CH₂), 4.21 (s, 8H, CH₂), 6.22 (t, 4H, C₄H, *J* 2.0), 7.32 (d, 4H, CH, *J* 2.0), 7.43 (d, 4H, CH, *J* 2.0). [LiL]BPh₄: ⁷Li, δ 3.26, 3.14 p.p.m.; ¹H, (a) δ 2.50 (s, 16H, CH₂), 4.18 (s, 8H, CH₂), 6.25 (t, 4H, C₄H, *J* 2.0), 7.33 (d, 4H, CH, *J* 2.0), 7.57 (d, 4H, CH, *J* 2.0); (b) δ 2.40 (s), 2.61 (s), 3.89 (s), 3.95 (s), 4.43 (s), 4.50 (s), 6.19 (t), 6.34 (t), 7.13 (d), 7.47 (d), 7.69 (d). The coupling constants for the multiplets are invariably 2.0.

[NaL]BPh₄‡ reveals that the Na⁺ ion, lying on a two-fold axis, is in an approximately prismatic arrangement of eight nitrogen atoms, with the basal faces of the prism, parallel to each other by symmetry, defined by the aminic and, respectively, the pyrazole N atoms (Figure 1). The two faces are rotated by *ca.* 31.4° about the two-fold axis with respect to each other, from the ideal prismatic orientation. The Na⁺ ion lies at 1.627(3) and 1.029(3) Å from the basal planes, in the above order. The Na–N(pyrazole) distances are 0.12 Å shorter than the Na–N(macrocyclic) ones. To the best of our knowledge, the present cation provides the first example of an eight-coordinate Na complex with a donor set formed by nitrogen atoms.

The high lipophilicity of the neutral ligand permits a rapid extraction of Li⁺ and Na⁺ from aqueous phases; 10^{−3} M solutions of the ligand in CH₂Cl₂ extract quantitatively 10^{−3} M LiBPh₄ or NaBPh₄ from the aqueous phase in less than 5 min

‡ *Crystal data:* C₄₈H₅₆BNa₁₂, *M* = 834.86, monoclinic, space group *P2₁/n* (No. 13), *a* = 12.959(2), *b* = 13.461(2), *c* = 12.962(2) Å, β = 90.03(1)°, *U* = 2 261.0(6) Å³, *Z* = 2, *T* = 295 K, *D_c* = 1.226 g cm^{−3}, *F*(000) = 888, μ(Cu-Kα) = 6.42 cm^{−1}. 2094 reflections with *I* > 3σ(*I*) using a CAD4 diffractometer and Cu-Kα radiation, 2θ_{max.} = 60°; no absorption correction applied. Structure solved by direct methods, SIR,⁸ and refined with 257 parameters using the SHELX76 program.⁹ All nonhydrogen atoms refined anisotropically with rigid phenyl groups. Final *R* = 0.085 and *R_w* = 0.096. 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.

(no metal tetraphenylborate extraction results without receptor in CH₂Cl₂).

Received, 30th November, 1989; Com. 9/051301

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