

Novel Group 1 Cation Cryptates: X-Ray and ^{23}Na NMR Studies

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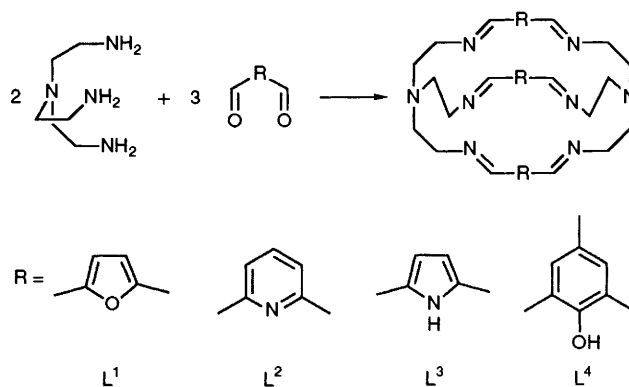
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Four new Schiff-base sodium cryptates are described and two structurally characterised; ^{23}Na NMR spectra imply that the phenolic cryptate $(\text{NaL}^4)^+$ has the highest stability constant.

Suitably modified calixarenes,¹ crown ethers² and their macrobicyclic analogues^{3,4} have been shown to mimic the ion transport of natural systems. The stability of these synthetic ligand complexes can be attributed to several factors including the goodness of fit of the cation in the ligand cavity and the nature of the donor set. In early studies emphasis was placed on ligands incorporating hard oxygen donors which were believed to be best suited for the coordination of group 1 ions. Recently however there have been a number of reports of group 1 metal complexes of ligands that provide an all N donor set.⁵⁻¹¹ Most of the examples include the harder sp^3 -N donors: only two of these examples have an all sp^2 -N donor set.^{5,8}

In this communication we report the synthesis of the sodium complexes of the four Schiff-base cryptands shown in Fig. 1. Ligands L^1 and L^2 were obtained by previously reported methods,¹² L^3 and L^4 by template synthesis on Ba^{2+} (Scheme 1). An X-ray crystallographic structure determination¹³ of the uncomplexed N_8O_3 ligand, L^1 , shows a divergent (uncoordinating) arrangement of the N donors and a tiny cavity *ca.* 10 Å long and 4 Å in diameter. This derives from a conformation with an all *trans* arrangement of imine functions with respect

to the C–O bonds of the furan ring. ^1H NMR evidence¹³ shows that this ligand has more than one available conformation suggesting that in the presence of suitable metal guests it may convert to a more convergent conformer; this is indeed



Scheme 1

Table 1 FAB MS and ^{23}Na NMR data

| Complex | FAB MS (m/z) ^a | | NMR ^b | | Solvent | T_c /(K) ^c | ΔG_c /kJ mol ^{-1d} | Ref. |
|----------------------|-------------------------------|-----------------|----------------------|---------------------|--|-------------------------|-------------------------------------|-----------|
| | NaL ⁺ | LH ⁺ | δ (Complexed) | δ (Solvated) | | | | |
| 1 | 559 (100) | 557 (12) | 1.5041 (260) | -6.3306 (260) | CD ₃ CN | 323 | 59.13 | This work |
| 2 | 613 (100) | | 6.7101 (294) | -6.4534 (294) | CD ₃ CN | 350 | 62.72 | This work |
| 3 | 576 (100) | 554 (26) | 0.0183 (233) | -6.1173 (233) | CD ₃ CN | 250 | 45.74 | This work |
| 4 | 669 (100) | | 0.935 (233) | -6.636 (233) | CD ₃ CN | — | — | |
| 5^e | | | | | Ethylene diamine | 323 | 62 | 16 |
| 6^f | | | | | CH ₃ OH-D ₂ O | 331 | 64 | 17 |
| | | | | | (CD ₃) ₂ SO- acetone | 310 | 59 | 18 |

^a Relative % intensity in parentheses. ^b Shifts given relative to 3 mol dm⁻³ aqueous solution of NaCl; T /K in parentheses. ^c Estimated value. ^d Calculated from the Eyring equation.¹⁹ ^e (Crypt-222) sodium perchlorate. ^f [NaL⁶]X.

confirmed by the isolation of both mono- and bi-nuclear complexes.¹⁴ For L²,¹⁵ ¹H NMR studies¹⁴ suggest a very different environment for the methylene protons in the complexed and metal-free forms.

Reaction of L¹ or L² (Scheme 1) with NaClO₄·H₂O in CH₂Cl₂-MeCN solvent mixture gives crystalline products [NaL¹]ClO₄·H₂O·MeCN **1** and [NaL²]ClO₄·MeCN **2** respectively.† Both cations (Figs. 1 and 2) show approximate three-fold symmetry about the N(1)-Na-N(2) axis and an unsymmetrical placing of the sodium cation. The degree of asymmetry is different in the two structures. Neither the acetonitrile solvent nor the perchlorate anion have any significant interactions with the cations of **1** or **2**. The significant difference between the two structures is that in addition to the sodium ion there is an included water molecule within the cavity of the furan system. This inclusion of the water molecule has three effects. Firstly, the water molecule, which also approximately lies on the N(1)-Na-N(2) axis, shows strong hydrogen bonding interactions [O(12)···N(5) 2.854, O(12)···N(11) 2.979 Å] to two of the uncoordinated imine nitrogen atoms. This serves to reduce the cavity size as defined by the N(1)···N(2) distance. In **1** this distance is 8.58 Å compared to 10.4 Å in the uncomplexed structure and 9.08 Å

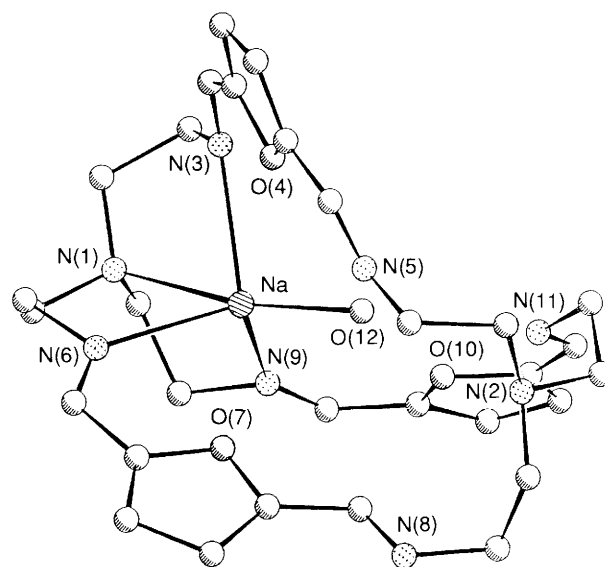


Fig. 1 View of [NaL¹·H₂O]⁺ cations. Selected bond distances (Å): Na-N(1) 2.646(5), Na-N(3) 2.540(6), Na-N(6) 2.520(6), Na-N(9) 2.636(6), Na-O(12) 2.241(6), Na-O(4) 3.420(5), Na-O(7) 3.144(5) and Na-O(10) 3.663(5). Atoms have been numbered to correspond with those in [NaL²]⁺.

† *Crystal data* for **1**: C₃₂H₄₁ClN₉NaO₈. $M = 738.2$, space group $P2_1/c$, monoclinic, $a = 11.117(3)$, $b = 25.852(6)$, $c = 13.396(3)$ Å, $\beta = 97.63(2)^\circ$, $U = 3816(1)$ Å³, $Z = 4$. Siemens P3/V2000 diffractometer, θ - 2θ scans, scan width 1.2° , scan range $3 < 2\theta < 55^\circ$, 8754 unique reflections, direct methods solution (SHELXS 86)²⁰ and least squares refinement (SHELX 76),²¹ non-hydrogen atoms anisotropic, all hydrogens located in ΔF map, but included at calculated positions (except the hydrogens of the water molecule, which were refined freely). $R = 0.074$ for 3487 data with $F > 4\sigma(F)$.

Crystal data for **2**: C₃₅H₄₂ClN₁₂NaO₄. $M = 753.2$, colourless, crystal dimensions $0.24 \times 0.3 \times 0.5$ mm, space group $P2_1/a$, monoclinic, $a = 12.993(7)$, $b = 24.260(9)$, $c = 13.730(5)$ Å, $\beta = 115.43(3)^\circ$, $U = 3909(3)$ Å³, $Z = 4$, $F(000) = 1584$. Data were collected on a Siemens R3v diffractometer using graphite-monochromated Mo-K α radiation. Using 1.7° ω -scans at a scan rate of $4.88^\circ \text{ min}^{-1}$ at room temperature, 5156 reflections were collected in the range $3 < 2\theta < 45^\circ$, of these, 4751 were unique and 1664 with $I > 3\sigma(I)$ were used in the structural analysis. Data were corrected for Lorentz and polarisation effects and the structure was solved by direct methods. The refinement converged with $R = 0.064$ and $R_w = 0.073$. All programs used for data reduction and structure solution are included in the SHELXS 86²⁰ and SHELXTL PC²² packages.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

in **2**. Secondly, in order to include the water molecule the sodium ion is pushed towards the bridgehead nitrogen N(1) resulting in bond formation. Thirdly, the inclusion of water results in a significant overall difference in ligand conformation in L¹ and L². For **1** five of the six imine nitrogen atoms lie in a convergent arrangement with only N(8) having its lone pair directed away from the cavity (Fig. 2). In **2** three of the imine nitrogen atoms are directed inwards and three outwards. Thus the overall coordination sphere of each sodium ion is different in **1** and **2**. The former system is five coordinate with the sodium ion being coordinated to three imine nitrogens, one bridgehead nitrogen and the oxygen of the water molecule; there are also three weaker interactions with the furan oxygens. The asymmetrical position of the sodium ion in **2** is presumably adopted in order to make best use of six of the available sp²-N donors, with the sodium ion forming bonds with the three pyridine nitrogen atoms and three stronger bonds to three imine nitrogen atoms. These sodium-N(imine) bonds in **2** are significantly shorter than the three imine-sodium bonds in the furan system.

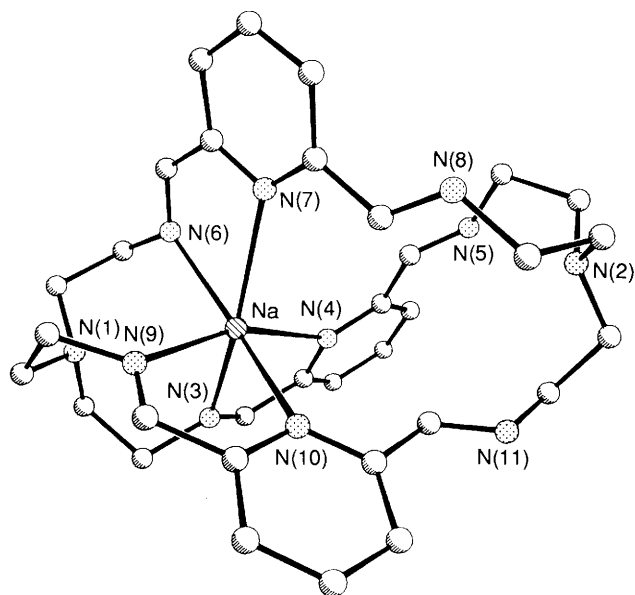
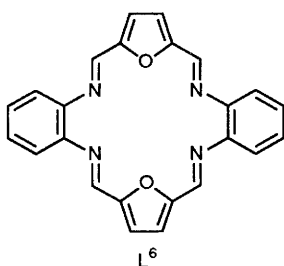


Fig. 2 View of the $[\text{NaL}_2]^+$ cation. Selected bond distances (\AA): Na–N(3) 2.428(10), Na–N(4) 2.610(9), Na–N(6) 2.434(7), Na–N(7) 2.675(10), Na–N(9) 2.405(10) and Na–N(10) 2.694(7).



Crystal structures of $[\text{NaL}^3]\text{BPh}_4$ **3** and $[\text{NaL}^4]\text{X}$ **4** are not at present available; however fast atom bombardment mass spectrometry (FAB MS) has been used to characterise these complexes (Table 1). The FAB MS of **3**‡ was interesting because in addition to the base-ion peak at $m/z = 576$ corresponding to **3** there is a peak at $m/z = 554$ (26%) which corresponds to metal-free L^3 . This may suggest that the sodium ion is less strongly held than in **1** or **2** where no signal due to uncomplexed ligand is observed. For **4** the only important peak occurs at 699 which confirms the formation of mononuclear sodium cryptate.

The ^{23}Na NMR spectra run in CD_3CN (Table 1) shows for **1** [Fig. 3(a)] and to a greater extent **2**, slow exchange of the sodium cations between the two sites: complexed and solvated. ^{23}Na NMR studies in methanol were attempted with **1** and **2** but it was not possible to obtain two clearly resolved signals although increased broadening and asymmetry of the single broad peak as the temperature was decreased suggest a slow exchange of the sodium ion between the complexed and uncomplexed sites on the NMR time-scale in this solvent.

Comparison of ^1H NMR-derived exchange rates for **1** and **2** are consistent with structural data which indicate shorter imine bonds and a higher coordination number for **2** than **1**. Complex **3** shows similar behaviour to **1** and **2** in that there is slow exchange of the sodium ion: however the very much lower coalescence temperature for the exchange process in this instance supports the inference from FAB mass spec-

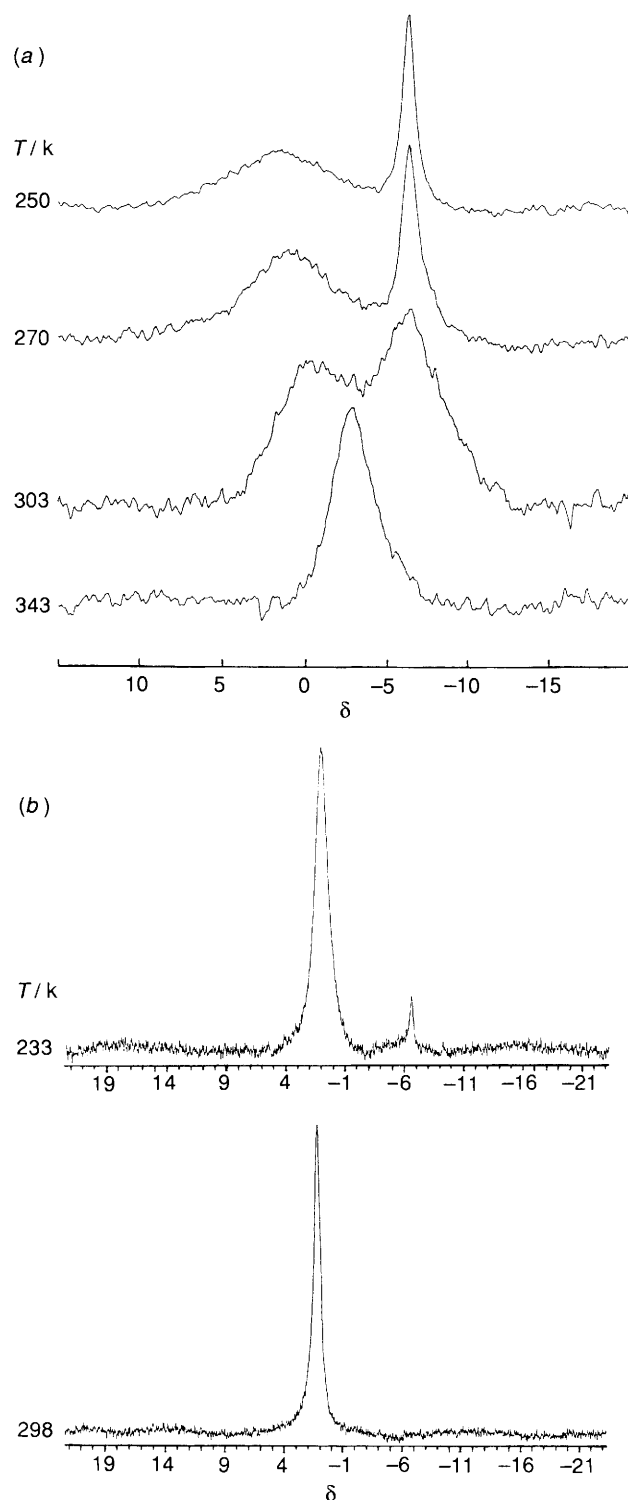


Fig. 3 ^{23}Na NMR spectra of (a) **1** and (b) **4** run in CD_3CN (400 MHz) variable-temperature

troscopy that the stability of **3** is lower than that of **1** or **2**. With **4** it was very difficult to identify a coalescence temperature because of the very small (< 4%) fraction of solvated Na^+ present at equilibrium [Fig. 3(b)] which indicates enhanced thermodynamic stability of $[\text{NaL}^4]^+$ relative to the other cryptates. This result suggests that L^4 is capable of adopting a conformation which permits interaction of one or more of the relatively 'hard' phenolic donors with the cationic guests.

‡ Complex **3** was generated accidentally on treatment of $[\text{BaL}^3]^{2+}$ with NaBPh_4 .

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