Insight into the mechanism of the protonation of cryptand 222 within a liquid clathrate medium: synthesis and X-ray crystal structure of $[H_3O][222–2H][(CoCl_3)_2(\mu\text{-}Cl)]$

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The reaction of $CoCl_2{\cdot}6H_2O$ with cryptand 222 in the presence of HCl(g) in toluene yields a two-phase liquid clathrate solution from which the complex $[H_3O][222–2H][(CoCl_3)_2(\mu\text{-}Cl)]$ is isolated; the crystal structure exhibits an oxonium ion which is situated to one side of the $[222–2H]^{2+}$ dication and interacts with two of its ethereal chains *via* $O^+–H{\cdots}O$ hydrogen bonds which lends a measure of support for the proposed mechanism of protonation of this flexible macrobicycle.

That the ionophoric behaviour exhibited by macro(poly)cyclic receptors (*e.g.* crown ethers, cryptands) is influenced by host conformation is now generally accepted.[1] Indeed, strong interactions between the host and guest are widely observed in preorganized supramolecular systems possessing both geometric and electronic complementarity. In many cases, the guest species may induce a conformational reorganization of the host to assist the recognition process.[2] In this context, we have recently demonstrated, through the interaction of oxonium ion species with crown ethers and cryptands,[3] the ability of hydrogen bonds to stabilize both low- and high-energy macro(poly)cyclic topologies in the solid state[3a–d] and solution.[3b]

Molecular dynamics simulations on cryptand 222 and its mono- and di-protonated forms have focused on the importance of ligand–solvent interactions in determining its ionophoric properties.[4] *Endo* protonation has been found to be favoured over *exo* protonation in aqueous media due to the formation of two *intra*ionic hydrogen bonds which we have shown[3b] to reorganize the ligand into an approximate chiral D_3 conformation in the solid state. Protonation of this form has been speculated to involve the delivery of a proton to a nitrogen atom lone pair by an oxonium ion (*i.e.* H_3O^+) located near the periphery of the ligand[4b] (Fig. 1). As part of our ongoing studies of liquid clathrate systems,[5] we now report the synthesis and X-ray crystal structure of a complex, $[H_3O][222–2H][(CoCl_3)_2(\mu\text{-}Cl)]$ **1**, which provides structural insight into the mechanism of cryptand 222 protonation. The complex exhibits an oxonium ion which is situated to one side of the $[222–2H]^{2+}$ dication and interacts with two of its ethereal chains *via* strong $O^+–H{\cdots}O$ hydrogen bonds.

Addition of anhydrous HCl(g) to a toluene solution of cryptand 222 in the presence of $CoCl_2{\cdot}6H_2O$ according to eqn. (1) immediately yielded a two-phase liquid clathrate solution and, subsequently, over a period of 10 min, light blue crystals suitable for X-ray analysis. The formulation of **1** was confirmed using single-crystal X-ray diffraction† and ^1H NMR spectroscopy.‡

$$\text{cryptand } 222 + HCl(g) + CoCl_2{\cdot}6H_2O \rightarrow [H_3O][222–2H][(CoCl_3)_2(\mu\text{-}Cl)] \qquad (1)$$

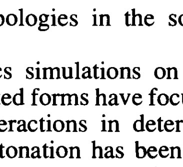

Fig. 1 Scheme proposed[4b] for protonation of the *endo* cryptand 222 conformer viewed along the N···N axis

An ORTEP perspective of the complex **1** is shown in Fig. 2. *Endo* protonation of the macrobicycle leads to the formation of two *intra*ionic $N^+–H{\cdots}O$ hydrogen bonds, and hence, an *in–in* conformation is adopted by the cryptate. Unlike $[H_3O]_2[222–2H][4Cl]{\cdot}4H_2O$ **2**,[3b] these hydrogen bonds are bifurcated rather than trifurcated[6] owing to an interaction between the $[222–2H]^{2+}$ dication and an oxonium ion which is situated to the side of the cryptate and hydrogen bonded to two of its ethereal chains *via* two strong $O^+–H{\cdots}O$ hydrogen bonds. The O-(oxonium)···O(cryptate) separations are 2.65(2) and 2.64(2) Å to O(1) and O(4), respectively. Moreover, as a consequence of this latter *inter*ionic interaction, the two chains containing O(1) and O(4) are pulled away from the third and the ligand exhibits a substantial deviation from approximate D_3 symmetry. This is illustrated by the O(1)···O(5) and O(4)···O(6) separations of each triangular face,§ 3.99(2) and 4.09(2) Å, respectively, which contrast with the remaining four distances which range from 3.64(2) to 3.75(2) Å. In comparison, the corresponding O···O separations in **2** range from 3.69 to 3.79 Å.[3b] In addition, the non-bonding N···N separation (6.44 Å), which is shorter than that of the empty cryptand (6.87 Å),[7] is substantially longer than in **2** (5.71 Å).

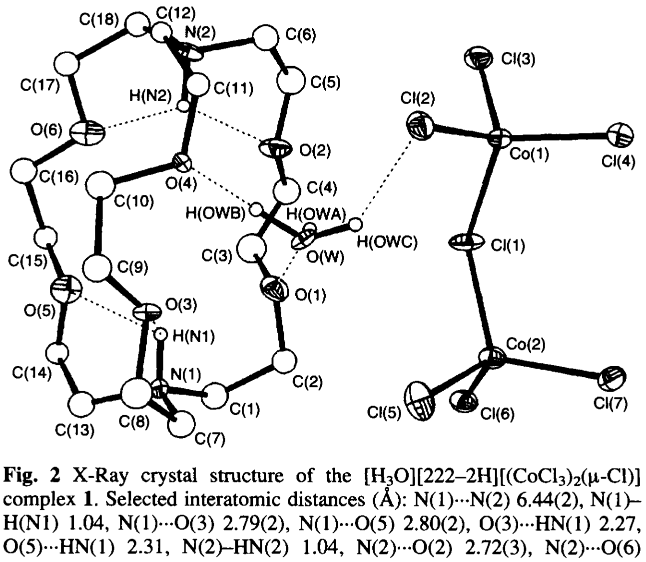

Fig. 2 X-Ray crystal structure of the $[H_3O][222–2H][(CoCl_3)_2(\mu\text{-}Cl)]$ complex **1**. Selected interatomic distances (Å): N(1)···N(2) 6.44(2), N(1)–H(N1) 1.04, N(1)···O(3) 2.79(2), N(1)···O(5) 2.80(2), O(3)···HN(1) 2.27, O(5)···HN(1) 2.31, N(2)–HN(2) 1.04, N(2)···O(2) 2.72(3), N(2)···O(6) 2.85(2), O(2)···H(N2) 2.18, O(6)···H(N2) 2.31, O(W)–H(OWA) 1.08, O(W)–H(OWB) 1.01, O(W)–H(OWC) 1.03, O(W)···O(1) 2.65(2), O(W)···O(4) 2.64(2), O(W)···Cl(2) 3.01(2), O(1)···H(OWA) 1.90, O(4)···H(OWB) 1.68, Cl(2)···H(OWC) 2.15.

These observations support the proposed mechanism of the protonation of the *endo* conformer of cryptand 222 in which it is suggested that a bridging oxonium ion transfers a proton to a nitrogen atom lone pair at a position near the periphery of the ligand between two of its ethereal chains.[4b] In **1**, the oxonium ion is approximately equidistant from each nitrogen atom, O(W)···N(1) 4.25(2) and O(W)···N(2) 4.38(2) Å, presumably since the ligand is diprotonated.¶

This study also reveals the first X-ray structure of the $[(CoCl_3)_2(\mu\text{-}Cl)]^{3-}$ anion. Fig. 2 shows that an $M–Cl\cdots H–O^+$ hydrogen bond[8] [Cl(2)···O(W) 3.01(2) Å] is formed between the anion and the oxonium ion. The cobalt(II) centres are separated at a distance of 4.205(4) Å and display distorted tetrahedral coordination geometries with average terminal Co–Cl bond lengths of 2.310(7) Å which fall at the upper limit of those found in the $[CoCl_4]^{2-}$ anion.[9] The terminal Cl–Co–Cl angles range from 95.4(2) to 117.4(3)° while the bridging chloride ligand exhibits Co–Cl distances of 2.336(6) and 2.388(6) Å to Co(1) and Co(2), respectively, and a Co(1)–Cl(1)–Co(2) angle of 125.8(3)°. This latter value compares favourably to that of the Zn–Cl–Zn linkage (139.8°) reported by Graf and Stoeckli-Evans[10] in which a single chloride ligand bridges two zinc(II) chloride tetrahedra. Values of 125.1 and 129.5° have also been found in the pentanuclear $[Cu_5Cl_{14}]^{4-}$ anion in which a chloride bridge is found between a tetrahedral and a square-pyramidal copper(II) centre.[11] Interestingly, the length of the anion in **1** complements that of the cryptate as illustrated by the non-bonding Cl(3)···Cl(6) [7.00(1) Å] and C(13)···C(18) [7.43(3) Å] separations of the anion and cryptate, respectively.

The fact that cryptand 222 is suitable for the generation of proton-rich macrocycle-based liquid clathrate systems has been demonstrated. Moreover, we have shown that structural information, especially in the context of ligand–solvent interactions, may be gained from these systems since assemblies not typically accessible by conventional methods (*i.e.* common solvents) of preparation may be achieved.

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Footnotes

† *Crystal data* for $[H_3O][222–2H][(CoCl_3)_2(\mu\text{-}Cl)]$; monoclinic, space group $P2_1/n$, a = 8.788(2), b = 19.968(2), c = 18.726(5) Å, β = 92.80(1)°, U = 3282(1) Å^3, D_c = 1.54 g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å) for Z = 4. Least-squares refinement based on 1692 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 4014 unique reflections) collected on an Enraf Nonius CAD-4 diffractometer and 235 parameters on convergence gave final values of R = 0.090, R_w = 0.082. Methylene hydrogen atoms were placed in calculated positions ($d_{C–H}$ = 1.08 Å) with their positional and thermal parameters fixed, temperature factors being based upon the carbon atoms to which they are bonded. All hydrogen atoms involved in hydrogen bonding were located *via* inspection of a difference Fourier map and their positional and thermal parameters were fixed, temperature factors being based upon the atoms to which they are bonded. Owing to high thermal motion all carbon atoms were refined isotropically. Crystallographic calculations were conducted using the NRCVAX program package locally implemented on a pentium-based IBM compatible computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been desposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Despite extensive line broadening owing to the paramagnetic nature of the Co^{II} species, the ^1H NMR spectrum exhibits resonances typical of the $[222–2H]^{2+}$ dication [see reference 3(*b*)].

§ The triangular faces are defined by the planar arrangement of oxygen atoms O(1)O(3)O(5) and O(2)O(4)O(6).

¶ From an electrostatic viewpoint, the oxonium ion is at a location which minimizes repulsive forces (*i.e.* between positive charges) and maintains attractive hydrogen-bonding interactions.

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