

Molecular Recognition of the Cyclic Water Trimer in the Solid State

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Noncovalent interactions (*e.g.* hydrogen bonding, cation- π , ion-pair) play a central role in determining the assembly of molecules and ions in solution,¹ the gas phase,² and the solid state,³ especially in aqueous systems of biological relevance.⁴ In this context, both experimental and theoretical studies have determined the attractive interaction between alkylammonium cations and water to be predominantly electrostatic and possess interaction energies of up to 10 kcal mol⁻¹.⁵

In its pure form, water, owing to the formation of intermolecular O—H \cdots O hydrogen bonds, has been shown to self-assemble into discrete higher oligomers [*i.e.* (H₂O)_{*n*} (*n* = 3–6)]⁶ in the gas phase with the hexamer⁷ representing the transition from two-dimensional cyclic to three-dimensional cagelike topologies. In particular, the water trimer has received considerable attention with both theoretical⁸ and experimental⁹ evidence establishing a six-membered minimum energy structure which is chiral and undergoes two types of degenerate structural rearrangements involving external and internal exchange among its hydrogen-bound protons. At the highest level of theory, the O \cdots O separations have been calculated to be 2.83 and 2.91 Å for the minimum and lowest transition state structures, respectively.^{8a}

As part of our ongoing studies of liquid clathrate systems,¹⁰ we now report the synthesis and X-ray crystal structure of a complex, [1-2H][CoCl₄] \cdot 1.5H₂O (**2**, where **1** = [2.2.2]cryptand), which provides insight into the nature of the alkylammonium–water interaction and evidence which confirms that the same cyclic geometry of the water trimer established for the isolated cluster also occurs in condensed phase environments. The complex exhibits a [1-2H]²⁺ dication involved in both an alkylammonium–water interaction with three water molecules and a charge–charge interaction with the [CoCl₄]²⁻ ion. As a consequence of these interactions, the ligand exhibits a structural reorganization from approximate D₃ symmetry to an elongated *in-in* conformation. To our knowledge, this represents the first case in which an alkylammonium–water interaction has been observed to contribute to the structural stability of an ionophore in the solid state and provides the first solid state evidence which supports the recently established cyclic geometry of the isolated water trimer.

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Addition of anhydrous HCl(g) to a mesitylene solution of **1** in the presence of an equimolar amount of CoCl₂ \cdot 6H₂O and a further 2–3 molar equiv of H₂O immediately yielded a two-phase liquid clathrate solution. After a period of 1 week, the upper layer was removed and blue crystals grew from the lower layer by allowing the solution to stand at room temperature for approximately 3 h. The formulation of **2** was confirmed by single-crystal X-ray diffraction,¹¹ analytical data,¹² IR spectroscopy,¹³ and thermogravimetric analysis.¹⁴

An ORTEP perspective of **2** is shown in Figure 1a. As in [H₃O]₂[1-2H][4Cl] \cdot 4H₂O (**3**)^{10c} and [1-2H][CoCl₄] \cdot 0.5C₆H₅CH₃ (**4**),^{10a} *endo* protonation of **1** leads to the formation of two intraionic trifurcated N⁺–H \cdots O hydrogen bonds,¹⁵ and hence, an *in-in* conformation is adopted by the ligand. Unlike **3**, but as in **4**, the two ends of the cryptate are distinct as revealed by their N⁺ \cdots O(cryptate) separations, 2.736(2) (N1) and 2.858(2) Å (N2), and the average distances between the edges of each triangular face, 3.621(3) (O1–O1–O1) and 3.923(2) Å (O2–O2–O2). Furthermore, the nonbonding N \cdots N separation (6.37 Å), which is shorter than that of the empty cryptand (6.87 Å),¹⁶ is substantially longer than that in **3** (5.71 Å), but equal to that in **4**, making the ligand cavities in **2** and **4** virtually identical.

The lengthening of the cryptate in **2** may be attributed to attractive alkylammonium–water and charge–charge interactions which induce a structural reorganization upon the macrocycle causing it to elongate along its N \cdots N axis. As shown in Figure 1a, the three water molecules in **2**, each of which exhibits 2-fold disorder, lie around a crystallographic 3-fold axis and are sandwiched between two equivalent ends of two symmetry-related [1-2H]²⁺ ions in a way similar to the included aromatic in **4**. Moreover, they have self-assembled, *via* O–H \cdots O hydrogen bonds,¹⁷ to form a cyclic trimer [O3 \cdots O3 2.91(3) Å] (Figure 1b) which is statically disordered between two positions (N1 \cdots ring centroid 4.03 Å), each of which facilitates C–H δ^+ \cdots O [H1A \cdots O3 2.90(1) Å] interactions between three α -hydrogen atoms of each dication, each from a different methylene group, and an oxygen atom from each water molecule. Likewise, the [CoCl₄]²⁻ ion, located near N2 (N2 \cdots Co 4.43 Å), interacts with each cryptate *via* three C–H δ^+ \cdots Cl [H6B \cdots Cl2 3.049(4) Å] interactions resulting in the formation of a linear five-component supramolecular complex.^{10a}

(11) Crystal data for **2**: Crystal size 0.30 \times 0.35 \times 0.40 mm, trigonal, space group R3c, *a* = 11.146(2) Å, *c* = 76.47(2) Å, *U* = 8228(2) Å³, ρ_{calc} = 1.47 g cm⁻³, $2\theta_{\text{max}}$ = 46°, μ = 1.05 mm⁻¹, Mo K α radiation (λ = 0.71069 Å) for *Z* = 12. Intensity data were collected using the Siemens SMART system at 298 K. Final cell constants were calculated from a set of 5461 strong reflections from the actual data collection. The structure was solved using direct methods. Least-squares refinement based on 1249 reflections with $I_{\text{net}} > 2.0\sigma(I_{\text{net}})$ (out of 1330 unique reflections) and 103 parameters on convergence gave a final value of *R* = 0.0322. Structure solution was accomplished with the aid of SHELXS-86 (Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *A46*, 467) and refinement was conducted using SHELX93 (Sheldrick, G. M. *SHELX-76*, University of Cambridge, 1976) locally implemented on a pentium-based IBM compatible computer.

(12) Anal. Calcd: C, 35.67; H, 6.82; N, 4.62. Found: C, 35.90; H, 6.81; N, 4.48.

(13) IR (Nujol) cm⁻¹, O–H \cdots O 3455 (bs), O–H \cdots Cl–M 3144 (ss), N–H 3113 (ss).

(14) The TGA trace of **2** reveals a gradual, clean weight loss of 4.5% between 28 and 299 °C which corresponds to 1.5 H₂O molecules per cryptate (theoretical 4.5%). Inspection of single crystals of **2** upon heating reveals that the crystals become increasingly opaque within this temperature range. Immediately following this initial loss, an abrupt weight loss of 61.9% between 299 and 632 °C is observed which corresponds to the loss of **1** (theoretical 62.1%) leaving behind CoCl₂ \cdot 2HCl.

(15) Assignment of the N–H IR bands in **2** is based upon the N–H bands of **4** and the doubly protonated [1.1.1]cryptand (Brügge, H.-J.; Carboo, D.; von Deuten, K.; Knöchel, A.; Kopf, J.; Dreissig, W. *J. Am. Chem. Soc.* **1986**, *108*, 107).

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(17) Assignment of the broad O–H \cdots O IR band in **2** is based upon the O–H \cdots O IR band of the internally bound protons of (H₂O)₃ (Engdahl A.; Nelander, B. *J. Chem. Phys.* **1987**, *86*, 4831).

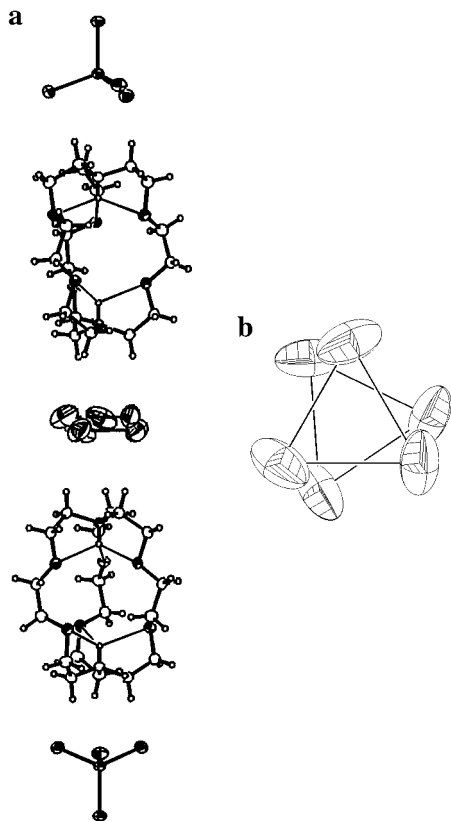


Figure 1. View of (a) the five-component supramolecular complex and (b) the water trimer along the 3-fold axis [$\text{O}\cdots\text{O}$ 2.91(3) Å]. The cluster exhibits 2-fold disorder across a crystallographic 32 site and is held into each position by $\text{C}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{Cl}-\text{M}$ interactions.

The topology of the water cluster reported herein is in agreement with both experimental⁹ and theoretical⁸ studies which establish a cyclic quasiplanar structure possessing oxygen atoms which are equidistant. Indeed, the $\text{O}\cdots\text{O}$ separations in **2** are comparable to those calculated for the internal rotation

transition state structure^{8a} which suggests that the assembly is an average of low-energy structures, the result of concerted hydrogen-bond tunneling motions. Interestingly, the $[\text{CoCl}_4]^{2-}$ ion is located in a position which facilitates three $\text{O}-\text{H}\cdots\text{Cl}-\text{M}$ interactions,¹⁸ between three chloride ligands of the anion and the externally bound protons of the trimer [$\text{O3}\cdots\text{Cl2}$ 3.37(1) Å], all of which extend on the same side of the $\text{O}-\text{O}-\text{O}$ plane.^{19,20} The observation that the trimer is capable of interacting with an ionophore in the solid state is novel and provides a measure of support for water being able to retain much of its intrinsic structure in the presence of solute ions and molecules.⁶

That attractive alkylammonium–water and charge–charge interactions may impart conformational stability to the flexible $[\text{1-2H}]^{2+}$ dication has been demonstrated. Indeed, the ability of three water molecules to form a cyclic trimer which recognizes the cationic region of diprotonated **1** has been illustrated. Such observations provide insight into questions concerning the nature of aqueous solvation, the structure and properties of bulk water, and molecular recognition processes involving macro(poly)cyclic receptors which are thought to play a role in determining their ionophoric properties.

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Supporting Information Available: Crystallographic report and tables of positional and thermal parameters, bond lengths, and angles, TGA trace, and IR spectra for **2** and **4** (9 pages). See any current masthead page for ordering and Internet access instructions.

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(18) Assignment of the $\text{O}-\text{H}\cdots\text{Cl}-\text{M}$ IR band in **2** is based upon $\text{O}-\text{H}\cdots\text{Cl}^-$ IR bands in crystalline hydrates of HCl (Gilbert, A. S.; Sheppard, N. *J. Chem. Soc., Faraday Trans.* **1973**, *69*, 1628).

(19) This topology is consistent with the calculated C_3 bowl structure in which all three external hydrogens are located on the same side of the $\text{O}-\text{O}-\text{O}$ plane (ref 8a).

(20) The disorder places the trimer in two positions each of which maximize its interaction with the ends of the cryptates and the $[\text{CoCl}_4]^{2-}$ ions.