

Self-assembly of $[H_4(\text{cyclam})]Cl_4$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) into a 3-D Polymeric Network with Microchannels that sustain a Symmetrical 1-D Polymer of Water Molecules

S. Subramanian and Michael J. Zaworotko*

Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, Canada B3H 3C3

The tetraprotonated form of cyclam self-assembles with chloride counter ions to generate a 3-D network that contains two types of microchannel, one of which sustains a symmetrical 1-D polymer of water molecules.

Crystal engineering of network solids *via* exploitation of directed noncovalent bonding,¹ even C-H \cdots O hydrogen bonds,² represents a relatively modern aspect of supramolecular chemistry. The potential significance of such a concept is illustrated by the relevance of network hydrogen bonding to

space group centrosymmetry and, therefore, the presence of second harmonic generation in solids.³ Superdiamondoid hydrogen bond networks formed from molecules or tectons⁴ with approximate S_4 symmetry have been of recent interest to ourselves⁵ and other groups^{4,6} and prompted us to investigate

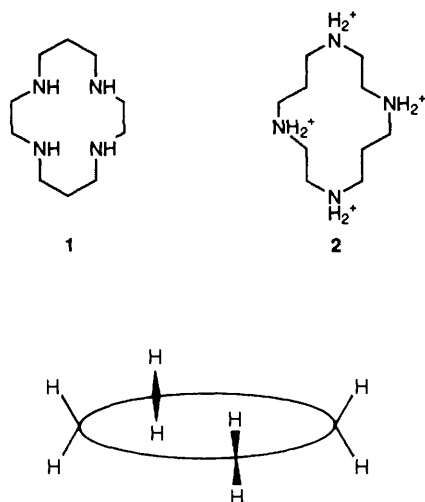


Fig. 1 Schematic representation of $[H_4(\text{cyclam})]^{4+}$ as it exists in **3**. The exodentate orientation of the NH_2^+ moieties facilitates network hydrogen bonding.

other potential tectons. Whereas 1,4,8,11-tetraazacyclotetradecane (cyclam) **1** readily adopts an endodentate conformation, and has therefore found widespread application as a macrocyclic ligand,⁷ the tetraprotonated amine derivative $[H_4(\text{cyclam})]^{4+}$ **2** remains largely uninvestigated.⁸ We recently demonstrated that **2** can simultaneously hydrogen bond to up to eight different hydrogen bond acceptors by virtue of its tendency to adopt an exodentate conformation (Fig. 1), thereby facilitating 1-D network hydrogen bonding with the following counter ions: $4\text{CF}_3\text{CO}_2^-$;⁹ *4p*-tosylate⁻;¹⁰ $[\text{FeCl}_5(\text{OH}_2)]^{2-}$; 2Cl^- .⁹ In this communication we demonstrate that crystallization of **2** with suitable counter ions can afford a 3-D hydrogen bond network that serendipitously contains microchannels with the requisite diameter and placement of hydrogen-bond acceptor sites to sustain a symmetrical polymer $(\text{H}_2\text{O})_n$.

The tetrachloride salt **3** of **2** readily crystallizes† from acidic aqueous solution to afford a network that is a manifestation of network $\text{N}-\text{H}\cdots\text{Cl}\cdots\text{H}-\text{N}^+$ hydrogen bonding between adjacent cations, $\text{N}\cdots\text{Cl}$ distances ranging from 3.065(3) to 3.242(3) Å.¹¹ The exodentate conformation of **2** and the ability of the chloride anions to bridge obtusely ($\text{N}\cdots\text{Cl}\cdots\text{N}$ angles average 137°) make the network 3-D instead of 1-D or 2-D.^{8,9} Fig. 2 reveals how the network sustains two types of microchannel parallel to the *a* axis. Both microchannels contain two water molecules per mole of cation. Those in microchannel *ii* are disordered (as either a polymer or oligomers) whereas microchannel *i* has the requisite size and placement of hydrogen bond acceptor sites to sustain what is to our knowledge an unprecedented symmetrical 1-D polymer of self-assembled water molecules, $(\text{H}_2\text{O})_n$. Water channels are well known in zeolites and zeolite-like solids but the water

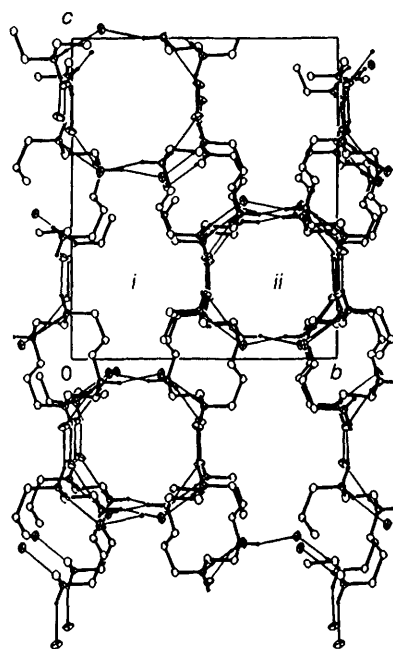


Fig. 2 View of the *bc* plane in **3**. Disordered water molecules lie in microchannel *ii* whereas the symmetrical water polymer lies in microchannel *i*.

molecules are typically disordered,¹² presumably a manifestation of wider microchannel dimensions. Perhaps the closest analogue of the polymer sustained by **3** is the water polymer seen in the sodium salt of adamantane-1,3,5,7-tetracarboxylate, a tetrahydrate in which the $\text{O}\cdots\text{O}$ separations are unsymmetrical at 2.679 and 3.010 Å.^{6c} The water molecules in **3** hydrogen bond to chloride anions [$\text{O}\cdots\text{Cl}(2)$ 3.215(4) Å] that are spaced at appropriate intervals along the walls of the microchannel (Fig. 3). Crystallographic symmetry means that the $\text{HO}-\text{H}\cdots\text{OH}_2$ hydrogen bonds are disordered, precluding location of half the hydrogen atoms. However, the hydrogen atom of the $\text{O}-\text{H}\cdots\text{Cl}$ interaction is locatable [$\text{O}-\text{H}\cdots\text{Cl}(2)$ 2.27 Å, 176°] and the $\text{O}\cdots\text{O}$ distances within $(\text{H}_2\text{O})_n$, 2.728(10) and 2.736(10) Å, compare well with 2.750–2.793 Å in ice¹³ and 2.805 Å in a host-guest complex of the water dimer.¹⁴ Strong, broad IR absorptions at below 3000 cm^{-1} are consistent with the observed $\text{O}\cdots\text{O}$ separations.¹⁵

It is hard to assess the degree of synergy between $(\text{H}_2\text{O})_n$ and microchannel *i*. Crystals of **3** do not appear to lose moisture prior to decomposition at *ca.* 287°C ; however, if allowed to stand in dry acetonitrile or methanol under ambient conditions they lose crystallinity within hours. The ability of $(\text{H}_2\text{O})_n$ to hydrogen bond to the chloride anions would therefore appear to be critically important in sustaining the stability of the open 3-D polymeric network. Indeed, given that $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds are recognized as being stronger than $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds one might even ask the question: does the spacing of hydrogen bond donor OH moieties in $(\text{H}_2\text{O})_n$ determine the chloride hydrogen bond acceptor spacing rather than *vice versa*? In this context it should be noted that the bromide analogue of **3**, $[H_4(\text{cyclam})]\text{Br}_4$ **4** also crystallizes‡ with four water molecules

† Large colourless crystals of **3** were afforded by slow evaporation of a solution of cyclam in 4 mol dm^{-3} HCl. *Crystal data*: orthorhombic, space group *Pnmb* (No. 52, nonstandard), $a = 7.7962(16)$, $b = 14.278(4)$, $c = 17.787(4)$ Å, $U = 1979.9(8)$ Å³, $Z = 4$, $D_c = 1.39\text{ Mg m}^{-3}$, $\mu = 5.9\text{ cm}^{-1}$, crystal dimensions $0.40 \times 0.60 \times 0.80$ mm. 1176 reflections with $I > 3\sigma(I)$ converged at $R = 0.051$ and $R_w = 0.069$. $[H_4(\text{cyclam})]^{4+}$ cations lie around crystallographic inversion centres and are linked to eight adjacent cations *via* $\text{N}-\text{H}\cdots\text{Cl}\cdots\text{H}-\text{N}$ hydrogen bonds. 3.75 molecules of water per cation were observed. Differential scanning calorimetry of the crystals shows only one phase change prior to irreversible decomposition at 287°C . The phase change occurs at *ca.* 100°C with no accompanying loss of crystallinity. 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.

‡ *Crystal data*: $M = 596.0$, triclinic, space group *P* $\bar{1}$, $a = 7.6860(8)$, $b = 7.8848(9)$, $c = 9.6385(11)$ Å, $\alpha = 105.111(16)$, $\beta = 95.495(18)$, $\gamma = 102.464(17)^\circ$, $U = 543.43(12)$ Å³, $Z = 1$, $D_c = 1.82\text{ Mg m}^{-3}$, $\mu = 73\text{ cm}^{-1}$, crystal dimensions $0.15 \times 0.25 \times 0.75$ mm. 1922 reflections with $I > 3\sigma(I)$ converged at $R = 0.034$ and $R_w = 0.041$. Br^- anions, water molecules and NH_2^+ moieties form channels that are separated by the hydrocarbon portion of the cations. The water molecules do not self-assemble, rather they bridge Br^- anions. Further details will be published elsewhere.

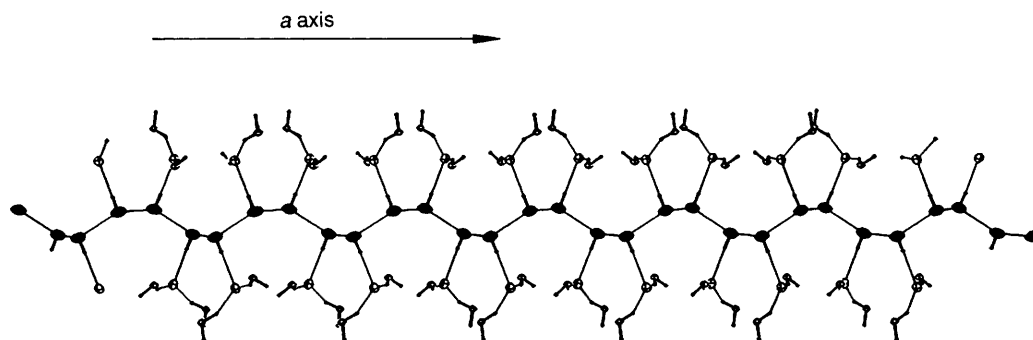


Fig. 3 Perspective view of the ordered water polymer in **3** and its environment. Oxygen atoms are represented by filled ellipsoids. The hydrogen bonded groups illustrated are either chloride anions or NH_2^+ moieties. The $\text{O}\cdots\text{O}$ distances within the polymer are statistically identical, 2.728(10) and 2.736(10) Å.

but the structure is markedly different from that of **3**. In summary, this work further illustrates the ability of directed noncovalent bonds to sustain open 3-D structures, in this instance generating a host framework for $(\text{H}_2\text{O})_n$.

We thank NSERC, Canada, for financial support and Saint Mary's University for provision of the X-ray diffractometer.

Received, 1st February 1993; Com. 3/00616F

References

- 1 G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647; G. R. Desiraju, in *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304.
- 2 G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290.
- 3 G. M. Frankenbach and M. C. Etter, *Chem. Mater.*, 1992, **4**, 272; M. C. Etter and K.-S. Huang, *Chem. Mater.*, 1992, **4**, 824; C. B. Aakeroy, P. B. Hitchcock, B. D. Moyle and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1989, 1856; C. B. Aakeroy, P. B. Hitchcock and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1992, 553; C. B. Aakeroy, G. S. Bahra, P. B. Hitchcock, Y. Patell and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1993, 152.
- 4 M. Simard, D. Su and J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696.
- 5 S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1992, **114**, 8719.
- 6 (a) O. Ermer, *J. Am. Chem. Soc.*, 1988, **110**, 3747; (b) O. Ermer and A. Eling, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 829; (c) O. Ermer and L. Lindenberg, *Chem. Ber.*, 1990, **123**, 1111; (d) O. Ermer and L. Lindenberg, *Helv. Chim. Acta*, 1991, **74**, 825.
- 7 L. F. Lindoy, in *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1989.
- 8 C. Nave and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, 1974, 2351.
- 9 S. Subramanian and M. J. Zaworotko, *Can. J. Chem.*, in the press.
- 10 S. Subramanian and M. J. Zaworotko, unpublished results.
- 11 M. N. Joesten and L. J. Schadd, in *Hydrogen Bonding*, Marcel Dekker, New York, 1974; M. V. Gaudet, M. J. Zaworotko and P. S. White, *Inorg. Chem.*, 1989, **28**, 1191; R. H. Dubois, M. J. Zaworotko and P. S. White, *Inorg. Chem.*, 1989, **28**, 2019; J. M. Martell and M. J. Zaworotko, *J. Chem. Soc., Dalton Trans.*, 1991, 1495.
- 12 R. C. Haushalter and L. A. Mundi, *Chem. Mater.*, 1992, **4**, 31.
- 13 S. J. La Placa, W. C. Hamilton, B. Kamb and A. Prakash, *J. Chem. Phys.*, 1977, **66**, 498; A. H. Narten, C. G. Venkatesh and S. A. Rice, *J. Chem. Phys.*, 1976, **64**, 1106.
- 14 P. J. Dutton, F. R. Fronczek, T. M. Fyles and R. D. Gandour, *J. Am. Chem. Soc.*, 1990, **112**, 8984.
- 15 R. C. Lord and R. E. Merrifield, *J. Chem. Phys.*, 1953, **21**, 166.