Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

A Two Dimensional Clathrate Hydrate: Tetraethylammonium Terephthalate · 6 H_2O

W. Scott Furey[a]; C. V. Krishnamohan Sharma[a]; Michael J. Zaworotko[a]
[a] Department of Chemistry, Saint Mary's University, hali, Nova Scotia, Canada

To cite this Article Furey, W. Scott , Sharma, C. V. Krishnamohan and Zaworotko, Michael J.(1996) 'A Two Dimensional Clathrate Hydrate: Tetraethylammonium Terephthalate · 6 H_2O', Supramolecular Chemistry, 8: 1, 9 — 11
To link to this Article: DOI: 10.1080/10610279608233962
URL: http://dx.doi.org/10.1080/10610279608233962

SUPRAMOLECULAR CHEMISTRY, 1996, Vol. 8, pp. 9–11
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands under license by
Gordon and Breach Science Publishers
Printed in Malaysia

Communication

A Two Dimensional Clathrate Hydrate: Tetraethylammonium Terephthalate·6 H_2O

W. SCOTT FUREY, C. V. KRISHNAMOHAN SHARMA and MICHAEL J. ZAWOROTKO

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

(Received 10 April 1996)

The crystal structure of tetraethylammonium terephthalate·$6H_2O$, **1**·$6H_2O$, monoclinic, I2/a, a = 14.416(5), b = 12.913(2), c = 17.169(4)Å, β = 103.32(4)°, Vol = 3117.4(14), Z = 8, D_{calc} = 1.27, reveals a novel 2D clathrate hydrate anionic sheet that is sustained by a hexameric assembly of water molecules linking terephthalate anions through hydrogen bonds. The anionic layers are intercalated by layers of close packed cations and, *via* numerous inter layer C-H...O hydrogen bonds, form a stable crystalline architecture with high melting point (m.p. 160°C).

Hydrate compounds can be readily classified into two distinct categories, *simple hydrates* and *clathrate hydrates*. In the former, water molecules typically function as a double hydrogen bond donor and a single hydrogen bond acceptor and they tend to form low stoichiometry cocrystals with molecules that contain excess hydrogen bond acceptors.[1] Clathrate hydrates, which represent important early examples of host-guest complexes and the "template" effect, occur because water can also act as a double hydrogen bond donor and a double hydrogen bond acceptor. The 3D arrangement that results from tetrahedral self-assembly of water molecules generates cages which can enclathrate hydrophobic guest moieties such as gas molecules, alkylamines and quaternary ammonium cations.[1–3] Clathrate hydrates tend to have very high ratios of water to guest. Unfortunately, most clathrate hydrates are thermally unstable above ambient conditions and it would clearly be of interest to generate more stable clathrate host materials that have controllable physical features.[4–6] In this context we report herein the synthesis of an anion sustained 2D clathrate hydrate.[7]

It occurred to us that one should be able to control the dimensionality of hydrate networks by crystallizing multifunctional hydrogen bond acceptors from aqueous environments. Tetraethylammonium terephthalate, **1**, represents an ionic system that has no strong hydrogen bond donors but has multiple rigidly oriented strong hydrogen bond acceptors. Crystals of the hexahydrate of **1**, **1**·$6H_2O$, were prepared by refluxing terephthalic acid in tetraethylammonium hydroxide (40% aqueous solution) for one hour and slowly cooling to room temperature (m.p. 160° C). The crystal structure of **1**·$6H_2O$[8] reveals the presence of six equivalents of water molecules in a 2-D sheet with terephthalate anions which intercalates with layers of close-packed cations. A unique discrete hexameric unit of water molecules (O...O, 2.816(5), 2.816(3), 2.754(4)Å) links terephthalate anions (O...O, 2.768(2), 2.804(2)Å) through hydrogen bonds and affords an infinite 2D layer structure (Figure 1). The anionic layers contain cavities with an approximate 8Å internal diameter. **1**·$6H_2O$ therefore exhibits a unique 2D architecture.[9] The water molecules in the layer form two different four membered hydrogen bond rings: **i.** with two water molecules and two anion O atoms; **ii.** exclusively with four water molecules. Two of the water molecules in **ii** exhibit 2-fold disorder and are possibly hydrogen bonded through a *flip-flop* conformation. All water molecules donate two hydrogen bonds and accept only one hydrogen bond. The terephthalate anions in the layer are completely surrounded by water molecules and are additionally involved in C-H...O hydrogen bonds (C...O 3.48, 3.31Å, C-H...O 115.1, 118.9°).[10]

The tetraethylammonium cations form a hydrophobic layer that intercalates the anion-water layer (Figure 2), cavities in the anionic layer being covered by the cations. Furthermore, they form interlayer C-H...O hydrogen bonds with neighbouring hydrophilic layers. There are as

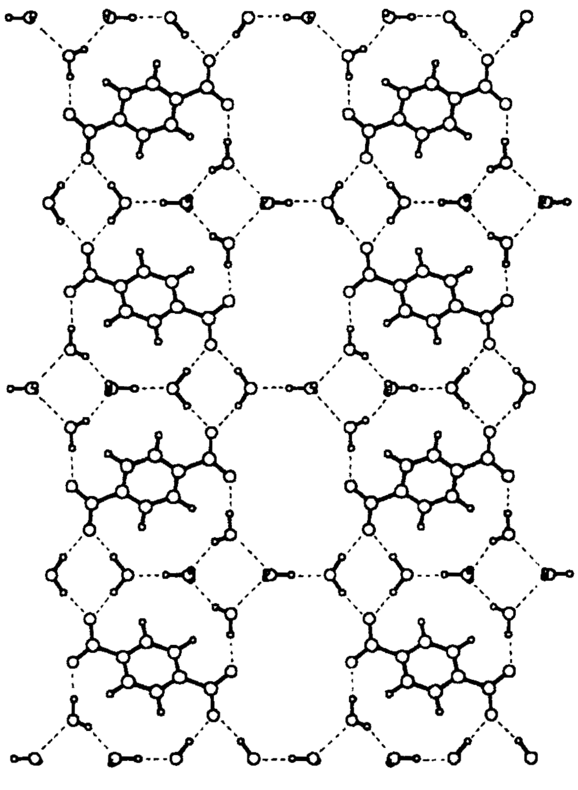

FIGURE 1 PLUTO diagram of the 2D clathrate hydrate, **1**·$6H_2O$, formed through hydrogen bonding (shown as dotted lines) between terephthalate anions and water molecules. Note the presence of discrete hexameric assemblies of water molecules and cavities.

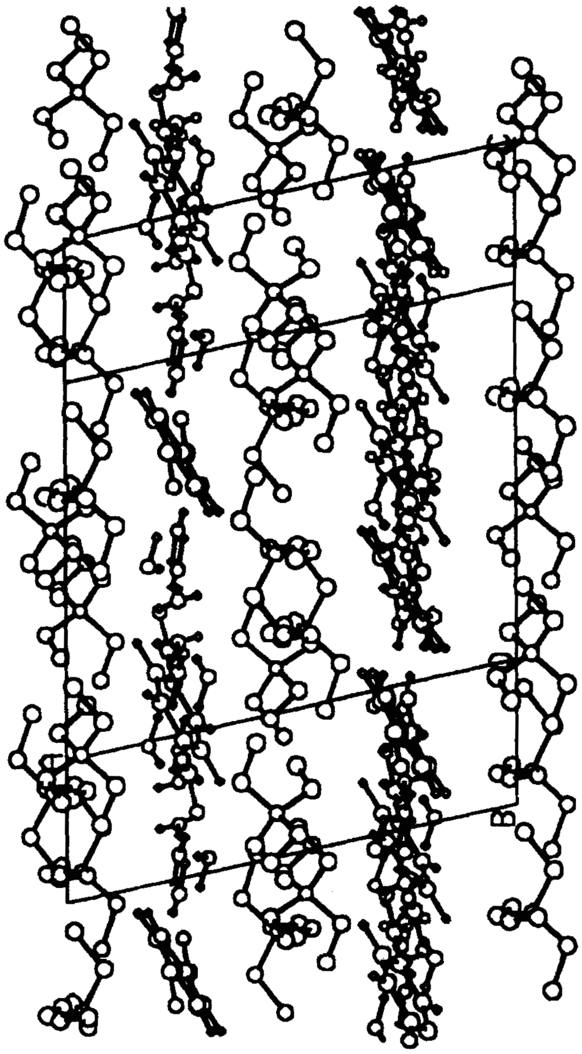

FIGURE 2 PLUTO cell packing diagram of the ac plane in the crystal structure of **1**·$6H_2O$. The intercalation of the anionic and cationic layers is illustrated.

many as sixteen independent C-H...O hydrogen bonds between the two layers with C...O distances and C-H...O angles ranging between 3.3–3.75Å and 108–174°, respectively. It is likely that these interactions play a significant role in promoting the 2D clathrate hydrate architecture.

In summary, **1**·$6H_2O$ is a 2-D clathrate hydrate system that represents a class of compound, layered hydrates, that is intermediate between simple hydrates and 3D clathrate hydrates. **1**·$6H_2O$ is stable above the boiling point of water and exhibits a unique hydrogen bonding architecture with cavities. We feel that the structures of **1**·$6H_2O$ and tetraethylammonium acetate·$4H_2O$, which also forms a 2D grid,[11] suggest that one can influence the water content and self-organisation in hydrates by simply varying cation size and anion geometry and functionality. We are presently investigating the nature of related networks sustained by other multifunctional anions.

Acknowledgements

We gratefully acknowledge the financial support of the NSERC and Saint Mary's University.

References

[1] Jeffrey, G.A.; Saenger, W. *Hydrogen Bonding in Biological Structures*, Springer, Berlin, **1991**.

[2] Vögtle, F.; Weber, E. (eds), '*Host-Guest Complex Chemistry, Macrocycles*', Springer, Berlin, **1985**.

[3] Muller, A.; Reuter, H.; Dillinger, S. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328.

[4] Desiraju, G.R. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311.

[5] Zaworotko, M.J. *Chem. Soc. Rev.* **1994**, 283.

[6] Aakeroy, C.B.; Seddon, K.R. *Chem. Soc. Rev.* **1993**, *22*, 397.

[7] Biradha, K.; Edwards, R.E.; Foulds, G.J.; Robinson, W.T.; Desiraju, G.R. *J. Chem. Soc., Chem. Commun.* **1995**, 1705.

[8] Crystal Data for **1**: Tetraethylammonium terepthalate·$6H_2O$, M = 298.4, monoclinic, I2/a, a = 14.416(5), b = 12.943(2), c = 17.169(4)Å, β = 103.32(4)°, Vol = 3117.4(14)$Å^3$, Z = 8, D_{calc} = 1.27 $Mg.m^{-3}$, λ = 0.70930Å, F(000) = 1176. 1553 absorption corrected reflections with $I_{net} > 3\sigma (I_{net})$ out of 2030 unique reflections measured at 290K for a crystal of dimensions 0.4 × 0.6 × 0.6 mm on an Enraf-Nonius CAD4 diffractometer using the ω scan mode ($4 < 2\theta < 45°$) afforded on convergence final values of R_f = 0.045 and R_w = 0.050. All non-hydrogen atoms were anisotropically refined. H atoms were located via difference Fourier map inspection and fixed with temperature parameters based upon the carbon atom to which they are bonded. All crystallographic calculations were carried out with the PC version of the NRCVAX programme package locally implemented on an 80486 based IBM compatible computer.

[9] Anions can also be part of the infinite framework in clathrate hydrates as exemplified by $[NBu_4]$[benzoate]·39.5 H_2O: Bonamico, M. Geffrey, G.A.; McMullan, R.K. *J. Chem. Phys.* **1962**, *37*, 2219.

[10] Desiraju, G.R. *Acc. Chem. Res.* **1991**, *24*, 290.

[11] Mak, T.C.W. *J. Inc. Phen.* **1985**, *4*, 273.