

Novel organic porous solids with channel and layered structures from 1,3,5-triazine-2,4,6-triaminehexaacetic acid and its calcium salt

S. N. Ghanashyam Acharya,^a R. Srinivasa Gopalan,^b G. U. Kulkarni,^b K. Venkatesan^a and Santanu Bhattacharya^{*a}

^a Department of Organic Chemistry, Indian Institute of Science, Bangalore, India 560 012.

E-mail: sb@orgchem.iisc.ernet.in; Fax: +91-80-360-0529

^b Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India 560 064

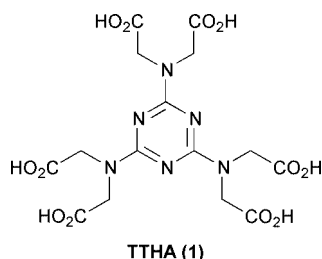
Received (in Cambridge, UK) 13th March 2000, Accepted 6th June 2000

Published on the Web 30th June 2000

Single crystals of a symmetrically substituted molecule, 1,3,5-triazine-2,4,6-triaminehexaacetic acid, (**TTHA**) and its Ca²⁺ salt have been synthesized, the analysis of which reveals the existence of novel channel type cavities and helical packing organizations in the crystals.

Nanoporous inorganic structures of widely varying three-dimensional arrangements are well known.¹ However, organic molecules are generally more amenable to chemical functionalization. Consequently there has been a steady rise in attempts to design organic molecules that can self-assemble *via* non-covalent interactions.² Indeed, intelligent use of the directional nature of the hydrogen bonding and other structure directing forces have generated solids with a whole variety of structural motifs from man-made organic templates.^{3,4}

Due to our continuing interest in the synthesis of organic solids⁵ with controllable crystalline packing, we considered the design of solids with framework structures, in which the building blocks within the individual infinite networks are linked either *via* H-bonds, or through metal-to-ligand bonds. One way to develop solids with predictable 3D organization requires design of a molecule with a symmetrical and well-defined spatial arrangement of subunits, that can associate through one or more non-covalent interactions. For this purpose we chose the aromatic triazine nucleus in melamine as a core which possesses -NH₂ substituents at the 2-, 4- and 6-positions. The ability of the melamine pendant residues to undergo H-bonding interactions with other molecules or ions has been exploited in both solution and the solid state.³ It occurred to us that the -NH₂ groups in melamine could be replaced by -N(CH₂CO₂H)₂ moieties, giving a core triazine nucleus with three symmetrically placed, strongly metal-complexing bidentate sites. The resulting ligand, 1,3,5-triazine-2,4,6-triaminehexaacetic acid (**TTHA**, **1**)[†] provides a symmetrical array of



three bidentate sites at which selected metal ions can be strongly bound, each site closely resembling those in the 'textbook' chelating agent EDTA and related derivatives. One important feature of the connecting ligands providing three bidentate residues on the triazine hub is that when a metal ion binds to three of them, the metal itself adopts the role of three nodal points from which further connections could be engineered. Therefore ligands like **TTHA** should be well poised to generate

a range of supramolecular framework structures in the solid state.

Crystallization of **TTHA** from its aqueous solution yields a solid which could be examined by single-crystal X-ray diffraction.[‡] In monoclinic crystals of **1** four molecules of **TTHA** were found to be packed in the unit cell in the space group *C2/c*, the molecular symmetry in the crystal lattice being *C₂(2)* which passes through the atoms N(11), C(12) and N(22) (not shown). The nature of the intramolecular bond lengths in the aromatic core is indicative of extensive π -electron delocalization, which results in the planarity of this molecular entity. From the values of the torsional angles it is clear that the conformations of each -N(CH₂CO₂H)₂ side-chain are slightly different. These conformations adjust according to the need to accommodate efficient intermolecular H-bonding interactions in the lattice and deviate out of the plane of the triazine rings.

TTHA forms H-bonded (O-H...O) dimers through the CO₂H residues. Other weak interactions such as C-H...O and C-H...N also exist. The supramolecular architecture produced upon non-covalent association of **TTHA**, results in a 'crinkled' molecular tape supported by O-H...O H-bonds, which extend in the direction of the *c*-axis (not shown). All six CO₂H groups in **TTHA** participate in such interactions and this association extends infinitely (Fig. 1). Such supramolecular sheets of **TTHA** are stacked along the *a*-axis giving exquisite channels of various sizes. While the polar CO₂H ends maintain the channels, the columns in the channels in such aggregates are made of triazine rings. The arrangement is reminiscent of pillared inorganic layered structures, the CO₂H residues

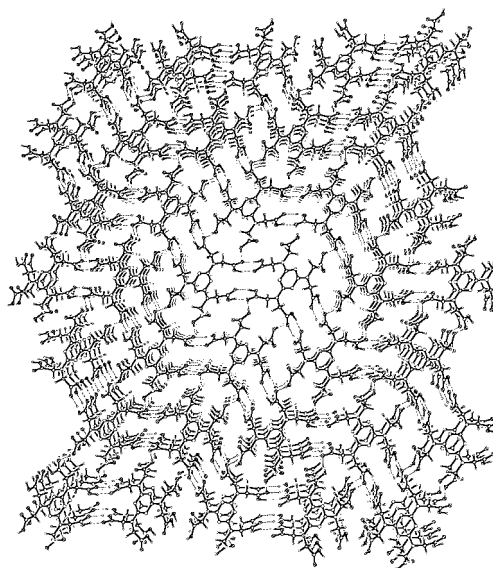


Fig. 1 Crystal packing of layers of **TTHA** in 3D showing the superposition of eight layers of **TTHA** molecules leading to the formation of channels.

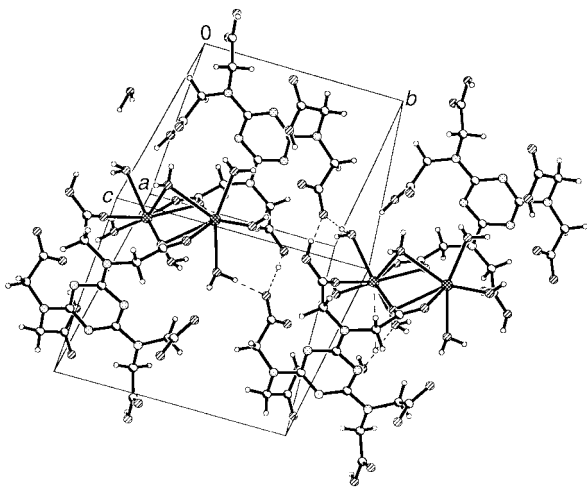


Fig. 2 Ca^{2+} ion induced supramolecular motif of **TTHA** showing the helical organization.

forming pillars between the layers formed by **TTHA** in **TTHA**.

This observation prompted us to explore the possibilities of generating an open-framework metal-coordination polymer of **TTHA**, using an oxophilic metal such as the Ca^{2+} ion. Indeed, crystals of a suitable quality for single-crystal X-ray diffraction of the Ca^{2+} salt of **TTHA**† were obtained upon prolonged incubation in water. The structure of the Ca^{2+} salt of **TTHA** consists of two molecules of **TTHA**, bound to two Ca^{2+} ions in the asymmetric unit (not shown). The two crystallographically independent **TTHA** molecules are related by an approximate non-crystallographic centre of symmetry. However, the side-arm $-\text{N}(\text{CH}_2\text{CO}_2^-)_2$ anions projecting from the same triazine hub show appreciable differences in their conformations.

From the crystal structure it is also evident that the two Ca^{2+} ions, Ca1 and Ca2 are octa-coordinated and are bridged by two carboxy groups maintaining a distance of 4.84 Å. As many as eight water molecules in the asymmetric unit are also found to be involved in the formation of a 3D network of $\text{O}-\text{H}\cdots\text{O}$ H-bonds. The most predominant feature of the solid state organization is that Ca^{2+} and the water molecules are confined to the crystal space between the two independent **TTHA** molecules. This feature is shown in Fig. 2, which omits the intermolecular H-bond connectivities for clarity. This also shows that the supramolecular architecture of the molecules along the *b*-axis is stabilized by $\text{O}-\text{H}\cdots\text{O}$ H-bonds. The planar triazine part of the **TTHA** moieties is essentially perpendicular to the *c*-axis of the unit cell. In this situation, the side-arms of **TTHA** project out in such a manner that its terminal carboxy groups not only participate in the intermolecular $\text{O}-\text{H}\cdots\text{O}$ H-bonds but are also able to ligate with the Ca^{2+} ions. The planar rings of the crystallographically independent triazines are parallel to one another, separated by ~ 3.5 Å. However, the triazine rings do not overlap completely and are partially displaced from one another. Further inspection shows that a helical organization exists in this polymeric network where multiple, short triazine–triazine π or $\text{C}-\text{H}\cdots\pi$ triazine contacts probably assist in stabilizing such helical organizations.

In summary, we were able to design a new supramolecular scaffold utilizing **TTHA** as a central tecton which can form self-organized entities in the solid state. The results presented herein augur well for the future generation of a whole variety of crystalline coordination polymers based on templates bearing

aminodiacetic acid (EDTA and related ligands) with a wide choice of metal centers, in some cases with channel-like organizations. In view of the increasing demand for the synthesis of planar molecular templates with trigonal and hexagonal symmetry for materials design,⁶ **TTHA** should provide convenient routes to prepare a new family of solids, the packing organizations of which could be controlled by crystal engineering. Other metal substitution may allow the generation of porous solids with redox or charged subsites and these might offer new matrices with altered physical properties for specific catalytic and separation science applications. Synthesis and investigation of the properties of these novel solid materials are underway.

We thank Professor C. N. R. Rao for helpful discussions. This work was supported by the Swarnajayanti Fellowship Grant of the Department of Science and Technology, Govt. of India.

Notes and references

† **TTHA** and its precursors have been characterized spectroscopically and also by elemental analysis and the corresponding data were consistent with their proposed structures.

‡ Single crystal X-ray diffraction studies. X-Ray diffraction intensities were measured at room temperature by ω scans using a Siemens three-circle diffractometer attached to a CCD area detector and a graphite monochromator for the $\text{Mo-K}\alpha$ radiation (50 kV, 40 mA). The crystal structures were solved by direct methods using the SHELXTL program⁷ and refined by full matrix least squares on F^2 . All the non-hydrogen atoms were refined anisotropically. H atoms were located by the difference Fourier method and were refined isotropically. CCDC 182/1677.

Crystal data: $\text{C}_{15}\text{H}_{18}\text{O}_{12}\text{N}_6$ (**TTHA**), $M = 474.3$, monoclinic, space group $C2/c$, $a = 5.057(1)$, $b = 21.607(2)$, $c = 17.406(2)$ Å, $\beta = 91.69(1)^\circ$, $V = 1900.0(0)$ Å³, $Z = 4$, $D_{\text{calcd.}} = 1.797$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.07$ mm⁻¹, $F(000) = 492$. Crystal dimensions $0.35 \times 0.35 \times 0.20$ mm. The final R -values were $R_1 = 0.0464$, $R_w = 0.1267$ and GOF = 1.162 for 1386 reflections.

$\text{C}_{30}\text{H}_{32}\text{O}_{24}\text{N}_{12}\text{Ca}_2 \cdot 8\text{H}_2\text{O}$ (Ca^{2+} salt of **TTHA**), $M = 1168.9$, triclinic, space group $P1$, $a = 10.407(1)$, $b = 10.990(2)$, $c = 20.543(8)$ Å, $\alpha = 92.82(2)$, $\beta = 98.82(2)$, $\gamma = 95.43(2)^\circ$, $V = 2306.5(8)$ Å³, $Z = 4$, $D_{\text{calcd.}} = 1.68$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.37$ mm⁻¹, $F(000) = 1212.0$. Crystal dimensions $0.63 \times 0.60 \times 0.43$ mm. The final R -values were $R_1 = 0.0403$, $R_w = 0.1334$ and GOF = 1.148 for 4911 reflections.

- 1 S. Oliver, A. Kuperman and G. A. Ozin, *Angew. Chem., Int. Ed.*, 1998, **37**, 46; J. M. Thomas, *Chem. Eur. J.*, 1997, **3**, 1557; M. E. Davies, *Chem. Eur. J.*, 1997, **3**, 1745; W. M. Meier, D. H. Olson and Ch. Baerlocher, *Atlas of Zeolite Structure Types*, Elsevier, Boston, 1996.
- 2 J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; J. R. Fredericks and A. D. Hamilton, *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vogtle, Pergamon, Oxford, 1996, pp. 565.
- 3 G. M. Whitesides, E. E. Simanek, J. P. Mathies, C. T. Seto, D. N. Chin, M. Mammen and D. M. Gordon, *Acc. Chem. Res.*, 1995, **28**, 37; V. R. Pedireddi, S. Chatterjee, A. Ranganathan and C. N. R. Rao, *J. Am. Chem. Soc.*, 1997, **119**, 10 867; A. Ranganathan, V. R. Pedireddi and C. N. R. Rao, *J. Am. Chem. Soc.*, 1999, **121**, 1752.
- 4 S. S.-Y. Chin, S. M. F. Lo, J. P. H. Charemant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; K. Biradha, C. Seward, M. J. Zaworotko and B. F. Abrahams, *Angew. Chem., Int. Ed.*, 1999, **38**, 492; G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
- 5 S. S. Mandal, R. Kadirvelraj, T. N. Guru Row and S. Bhattacharya, *Chem. Commun.*, 1996, 2725; S. Bhattacharya, P. Dastidar and T. N. Guru Row, *Chem. Mater.*, 1994, **5**, 531.
- 6 F. Cherioux, P. Audebest and P. Hapiot, *Chem. Mater.*, 1998, **10**, 1984; D. C. Talmassebi and T. Sasaki, *J. Org. Chem.*, 1998, **63**, 728; P. V. Bernhardt and E. J. Hays, *J. Chem. Soc., Dalton Trans.*, 1998, 3539; G. A. Downing, C. S. Franapton, J. H. Gall and D. D. MacNicol, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1547.
- 7 SHELXTL (SGI version) Siemens Analytical X-ray Instruments Inc. 1995, Madison, Wisconsin, USA.