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Investigation of some layered structures of cyanuric acid

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Abstract—Synthesis and molecular packing analysis of the crystal structures of three complexes of cyanuric acid with dimethylsulfoxide (DMSO), dimethylamine (DMA) and dimethylformamide (DMF) respectively, in a 2:2, 2:1 and 1:1 ratio has been reported. In all three molecular complexes, cyanuric acid molecules form molecular tapes through the formation of strong cyclic N–H···O hydrogen bonds between the adjacent molecules. These tapes are further arranged in two-dimensions yielding layered structures such that the guest molecules (DMSO, DMA and DMF) are being incorporated between the tapes. © 2002 Published by Elsevier Science Ltd.

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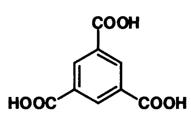
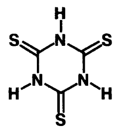
1. Introduction

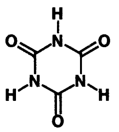
In the present era of studying chemistry 'beyond the molecule',[1] symmetrically substituted organic molecules are known to form exotic supramolecular assemblies in a variety of geometrical arrangements on their own or in combination with other molecules.[2–4] For instance, trimesic acid on its own forms an hexagonal network, which arranges in three-dimensions to form a catenated structure.[5] Also, it forms hexagonal, square and rectangular structures with many substrates such as methanol, water, several acyclic hydrocarbons, pyrene etc.[3] Similarly, trithiocyanuric acid, a cyclic thioamide is known to form a hexagonal assembly while crystallizing from acetone[6] and also yields different types of networks with other substrates.[6,7]



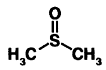
Trimesic acid



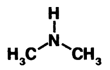
Trithiocyanuric acid



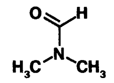
Cyanuric acid (CA)



Dimethylsulfoxide (DMSO)



Dimethylamine (DMA)

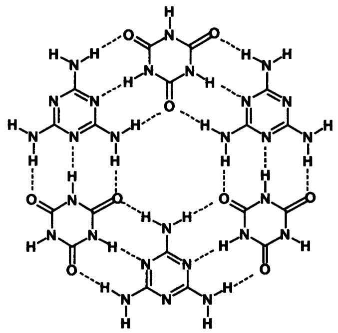


Dimethylformamide (DMF)

Surprisingly, cyanuric acid (CA), which is well known for the formation of a unique rosette structure[2c] with melamine, comprising 18 hydrogen bonds in each unit, as shown in Scheme 1, has no cyclic network structure either on its own or with any other substrates (except with melamine) in contrast to trimesic acid and trithiocyanuric acid. In addition, only a few cyanuric acid mediated supramolecular assemblies are known from the literature.[8] Among these, molecular complexes formed by CA with 4,4′-bipyridyl are noteworthy examples as different types of structures are formed depending upon the solvent used for the co-crystallization.[9] This has prompted us to investigate the effect of organic solvents on the crystallization of cyanuric acid with the hope that a cyclic network would result from one of the solvents. In this connection, crystallization of CA is attempted from polar solvents like DMSO, DMA and DMF. However, the anticipated cyclic structure was not obtained from any of these solvents, but the solvents were incorporated into the crystal lattice yielding interesting layered structures. We report a detailed analysis of three crystal structures **1**, **2** and **3** of cyanuric acid (CA) with dimethylsulfoxide (DMSO), dimethylamine (DMA) and dimethylformamide (DMF).

2. Results and discussion

CA forms adducts **1–3** with DMSO, DMA and DMF yielding



Scheme 1. Schematic representation of rosette structure in the cyanuric acid and melamine adduct.

Keywords: cyanuric acid; molecular tape; layered structure.

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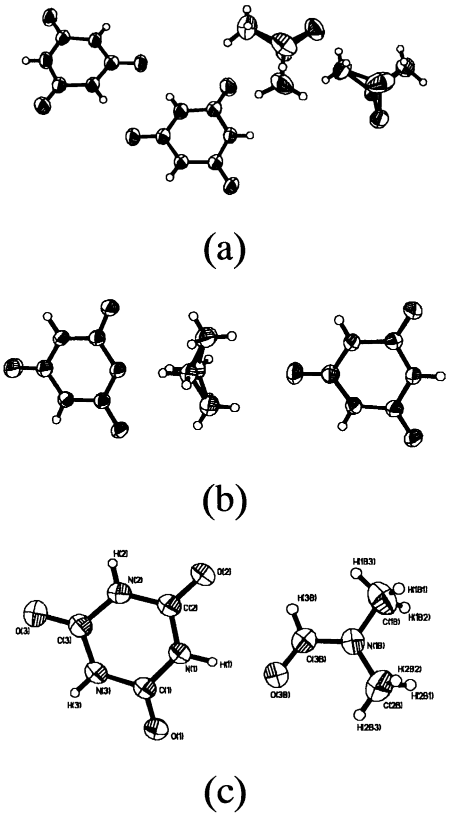


Figure 1. ORTEP drawings of the asymmetric unit in the crystal structures of (a) cyanuric acid–DMSO, **1**; (b) cyanuric acid–DMA, **2**; (c) cyanuric acid–DMF, **3**. A typical atom labelling scheme shown for structure **3** in (c).

Table 1. Bond lengths and angles of cyanuric acid moiety in the crystal structures of **1**–**3**

	1[a]	**2**[a,b]	**3**
Bond lengths (Å)			
C(1)–N(1)	1.370(4), 1.357(4)	1.353(2), 1.374(2)	1.363(2)
C(1)–N(3)	1.377(4), 1.371(4)	–	1.371(2)
C(2)–N(1)	1.369(4), 1.374(4)	1.381(2), 1.356(2)	1.363(2)
C(2)–N(2)	1.367(4), 1.364(4)	1.344(2), 1.364(2)	1.367(2)
C(3)–N(2)	1.363(4), 1.369(4)	–	1.372(2)
C(3)–N(3)	1.365(4), 1.374(4)	–	1.372(2)
C(1)–O(1)	1.213(4), 1.226(4)	1.221(3), 1.204(3)	1.224(2)
C(2)–O(2)	1.224(4), 1.221(4)	1.242(2), 1.204(3)	1.226(2)
C(3)–O(3)	1.224(4), 1.211(4)	–	1.209(2)
Bond angles (deg.)			
N(1)–C(1)–N(3)	114.1(3), 115.1(3)	–	115.4(1)
N(1)–C(2)–N(2)	115.4(3), 114.7(3)	119.0(1), 115.2(1)	115.8(2)
N(2)–C(3)–N(3)	115.4(3), 113.6(3)	–	113.9(1)
C(1)–N(1)–C(2)	125.2(3), 124.9(3)	123.6(1), 124.7(1)	124.3(2)
C(2)–N(2)–C(3)	124.5(3), 126.1(3)	–	125.2(2)
C(1)–N(3)–C(3)	125.3(3), 125.6(3)	–	125.4(2)
N(3)–C(1)–O(1)	122.3(3), 122.4(3)	–	122.7(2)
N(1)–C(1)–O(1)	123.7(3), 122.6(3)	122.7(1), 122.5(1)	122.0(2)
N(1)–C(2)–O(2)	122.6(3), 121.8(3)	118.0(1), 121.8(1)	121.7(2)
N(2)–C(2)–O(2)	122.0(3), 123.4(3)	123.0(1), 123.9(4)	122.5(2)
N(2)–C(3)–O(3)	121.9(3), 123.3(3)	–	123.0(2)
N(3)–C(3)–O(3)	122.7(3), 123.1(3)	–	123.2(2)

See Fig. 1(c) for the atom labels.

[a] Two molecules in the asymmetric unit.

[b] Symmetry related parameters are not quoted.

single crystals. Crystal structure determination reveals that **1**–**3** were formed in 2:2, 2:1and 1:1 ratios of CA and DMSO, DMA or DMF, respectively. The ORTEP drawings of the asymmetric unit are shown in Fig. 1(a)–(c). Details of the molecular geometry parameters (bond lengths and angles) of cyanuric acid in the three complexes are given in Table 1.

Analysis of the molecular arrangement of these structures (**1**–**3**) shows gross similarities in the overall packing of the molecules in three-dimensions with stacked layers being the common feature. However, the two-dimensional arrangement is of quite significant having both similarities and comparable differences. These features will be discussed in each case independently and then will be compared with each other.

The adduct **1**, comprising two symmetry independent molecules of CA (A and B) with each connected to a disordered DMSO (C and D) molecule through an N–H···O hydrogen bond constitute two-dimensional layers. A typical layer is shown in Fig. 2. In each layer, symmetry independent CA molecules are held together by cyclic N–H···O hydrogen bonds, forming infinite molecular tapes. The H···O distances in the cyclic motif are in the range 2.02–2.04 Å. In the two-dimensional arrangement, these molecular tapes are arranged in an *anti*-parallel manner at the distance of 11.602 and 11.883 Å from each other. Between these tapes, DMSO molecules are arranged in such a way that each symmetry independent DMSO molecule is located between the alternate tapes. In such an arrangement, each DMSO molecule interacts with both the CA molecules (A and B) by forming N–H···O (H···O, 1.84, 1.85 Å) and C–H···O (2.45, 2.53 Å) hydrogen bonds. An interesting feature is that the DMSO molecules exist as dimers being held together by a cyclic C–H···O hydrogen bond like acetone in its adducts with a resemblance to the well known O–H···O dimers formed by carboxylic acid groups. The H···O distance is 2.50 Å in the dimer constituted by molecules C, while the distance is 2.72 Å in the dimer formed by molecules D. To our knowledge, this is the

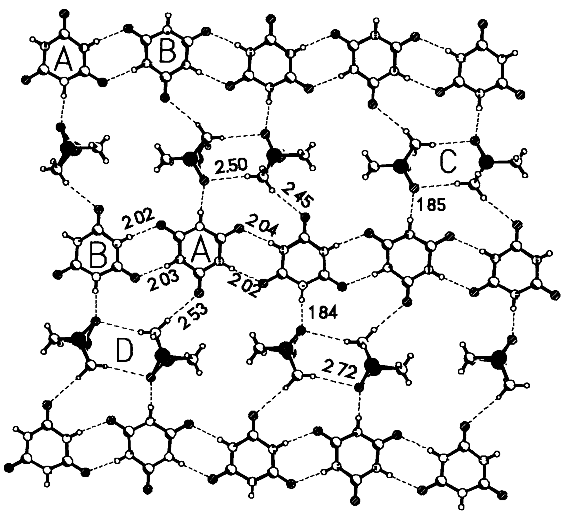


Figure 2. Arrangement of layers of cyanuric acid and DMSO molecules in the crystal structure of adduct **1**. Dashed lines represent hydrogen bonds. Notice the dimers formed by both the symmetry independent DMSO molecules.

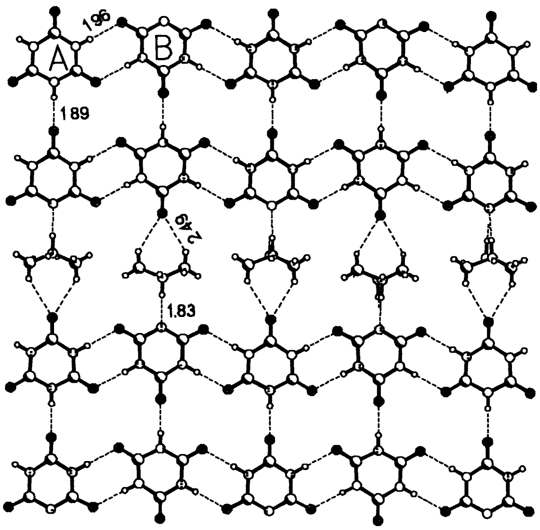


Figure 3. Incorporation of DMA molecules in between the bi-layers of cyanuric acid in the adduct **2**.

first example of an organic structure, where DMSO molecules crystallized in dimeric units.[10]

In the adduct **2**, the composition of CA and DMA molecules is 2:1 (See Fig. 1(b)). A two-dimensional arrangement of these molecules is shown in Fig. 3. The two CA molecules are connected to a disordered DMA molecule through a $N^{-}\cdots{}^{+}H–N$ (1.83 Å) hydrogen bond, resulting from the transfer of a proton from CA to DMA and a bifurcated C–H···O hydrogen bonds (H···O, 2.49 Å) formed between methyl hydrogen atoms and the carbonyl oxygen atom (See Fig. 3). Further, the two CA molecules are held together by cyclic N–H···O hydrogen bonds with H···O distances of 2.02 and 2.04 Å, yielding infinite molecular tapes. These tapes are further arranged in two-dimensional structure in a unique manner by forming bi-layers separated by a distance of 10.632 Å from each other, with DMA molecules inserted between the layers. Within each bi-layer, molecular tapes are held together by an N–H···O hydrogen bond with an H···O distance of 1.89 Å.

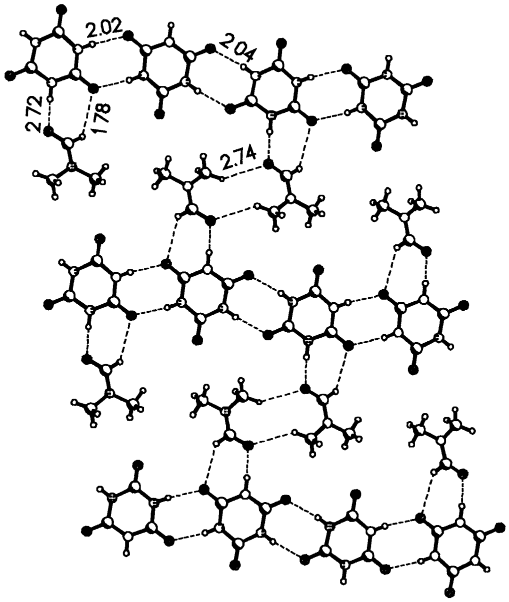
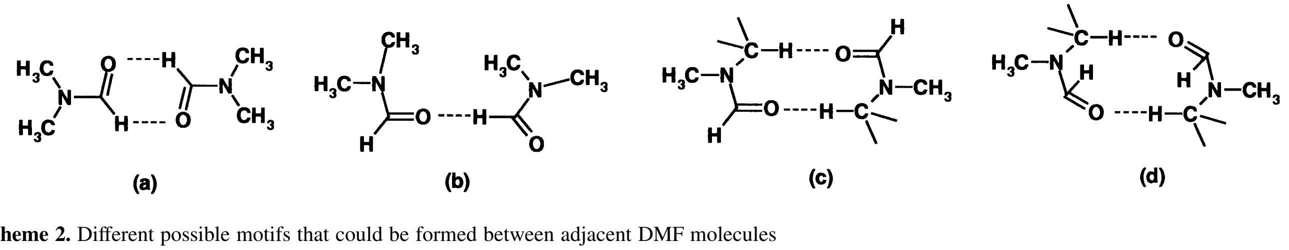


Figure 4. Arrangement of cyanuric acid and DMF molecules in a two-dimensional layer in the adduct **3**. Notice the arrangement of DMF molecules in pairs connected together by C–H···O hydrogen bonds.

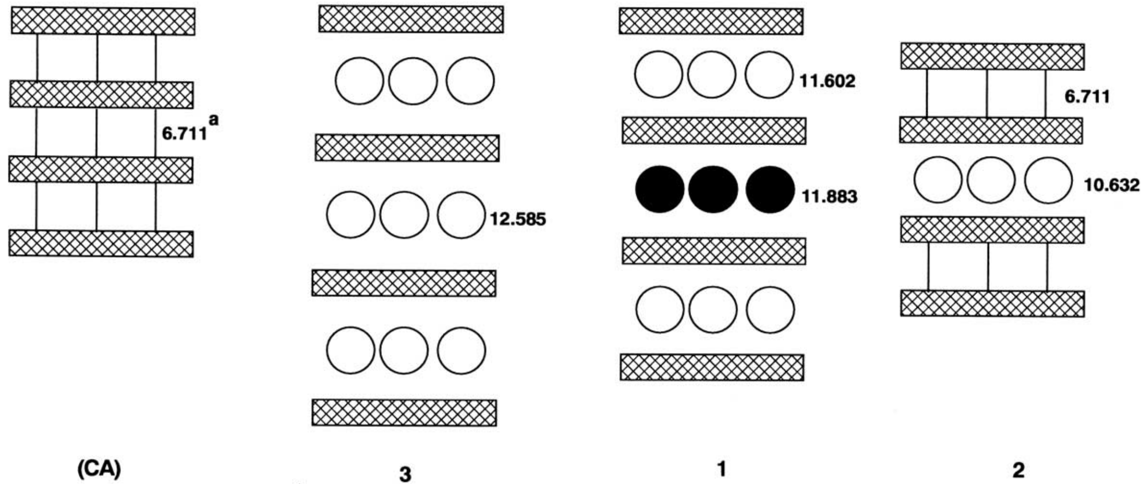
In the adduct **3**, (Fig. 4) the packing arrangement of a 1:1 composition of CA and DMF molecules is straight-forward without any major deviation from the features already observed in the adducts **1** and **2**. The CA molecules are held together by centrosymmetric cyclic N–H···O hydrogen bonds with H···O distances of 2.02 and 2.04 Å. These tapes are arranged in a two-dimensional structure separated from each other by a distance of 12.585 Å. In between these tapes, the DMF molecules are arranged by connecting them with CA molecules by a pair-wise cyclic coupling comprising N–H···O and C–H···O hydrogen bonds. The corresponding H···O distances are 1.78 and 2.72 Å, respectively. Further, DMF molecules also exist as dimers by forming centrosymmetric cyclic C–H···O hydrogen bonds between the methyl hydrogen atoms and the carbonyl group with an H···O distance of 2.74 Å.

In the adduct **3**, the arrangement of DMF molecules is of quite interesting, belonging to a second major category (motif (c) in Scheme 2), of the known motifs of DMF.[10] In principle, DMF can form at least four types of hydrogen-bonded motifs as shown in Scheme 2. Among these while, (a) and (b) are due to the interaction between the aldehyde proton and carbonyl oxygen atom, (c) and (d) are due to the interaction between the methyl hydrogen atoms and carbonyl oxygen atom. The motifs (c) and (d) are similar in their topological arrangement except for the difference in the position of aldehyde proton—*cis* or *trans* to the methyl group participated in the formation of hydrogen bond. Except for motif (a), three other motifs are known to exist in the literature with (d) being present in a majority of the structures.[10]

In comparison, all the three structures have molecular tapes formed by cyclic N–H···O hydrogen bonds, which apparently seems to be a robust structure directing unit as it is also noted in many metal–cyanurate complexes.[11] However, the two-dimensional arrangement of these tapes



Scheme 2. Different possible motifs that could be formed between adjacent DMF molecules



[a] distance between the tapes in Å.

Scheme 3. Schematic representation of arrangement of molecular tapes in the crystal structures of CA and adducts **1**–**3**.

is unique in each structure with the insertion of solvent molecules between the tapes in different modes. A comparison of these different layer structures with the layer structure existing in the pure crystal structure of cyanuric acid, as shown schematically in Scheme 3 is very interesting. It is evident from Scheme 3 that the adducts **1**–**3** are the result of replacement of hydrogen bonds existing between the molecular tapes, present in the crystal structure of CA, by the solvent guest molecules. In this process, the molecular tapes are being separated in a systematic manner with a gradation of 1 Å from **3**→**1**→**2**. This correlation between CA and adducts **1**–**3** shows a close resemblance to the incorporation of guest molecules between the layers of inorganic clays like montmorillonite, with CA being a clay type material.[15]

In conclusion, the three structures reported here demonstrate that the cyclic hydrogen bonds being stronger than the single hydrogen bonds, the guest molecules (DMSO, DMA and DMF) incorporated between the molecular tapes, breaking the single hydrogen bonds only, in the crystal structure of CA, in all the cases. In addition, this study suggests that organic compounds of this type could be useful for the synthesis of a new class of intercalated compounds, since the distance between the layers is being varied with the nature of the guest molecule(s).

3. Experimental

3.1. Synthesis of 1–3

All the chemicals were obtained from commercial suppliers and used as such without further purification. HPLC grade solvents were used for the crystallization experiments for the preparation of the adducts **1**–**3**. The adducts were obtained by dissolving 645 mg (5 mmol) of cyanuric acid (CA) in 5 ml of DMSO, DMA and DMF, as the case may be, and allowing them to slowly evaporate at room temperature (25°C). Single crystals of good quality were obtained from all the flasks within 3 days. The crystals showed instability over a period of one week at laboratory ambient conditions after separated out from the mother liquor.

3.2. X-Ray crystallography

Good quality single crystals of **1**–**3** were selected by carefully observing under a polarizing microscope. The crystals were glued to a glass fiber with the aid of adhesive (cyanoacrylate). All the crystals were coated with a layer of an adhesive to avoid deterioration during the data collection process. X-Ray intensity data were collected for **1** and **2** on a Siemens diffractometer equipped with SMART CCD area detector, while data for **3** were collected on a Bruker diffractometer equipped with APEX CCD area detector. The data collection process was smooth in all the cases and no significant deterioration of the crystal was noted. Intensity data were processed using Bruker suite of data processing programs (SAINT)[12] and no absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL[13] suite of programs (XS, XL, XP, XCIF) and all the structures converged to good *R*-factors. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were obtained from the Fourier maps and refined isotropically. All the refinements were smooth except that in **1** and **2**, the solvent molecules are disordered. Other crystallographic details pertaining to individual structures are as given below. All the hydrogen bond distances and angles were computed using PLATON[14] software. Full details of crystallographic information are deposited at Crystallographic Data Centre as supplementary publication (**1**, CCDC 178515; **2**, CCDC 178516; **3**, CCDC 178517). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB12 1EZ, UK [fax: +44(0)-1223-336033 or email: deposit@ccdc.cam.ac.uk].

3.2.1. Crystal data for 1. $C_{10}H_{18}N_6O_8S_2$, fw=414.2, triclinic, space group $P\bar{1}$, a=9.750(1), b=9.785(1), c=11.241(1) Å, α=69.26(1), β=66.75(1), γ=82.22(1)°, V=921.5(2) Å^3, Z=2, D_c=1.494 Mg m^{-3}, $F(000)$=432, μ(Mo-K$_\alpha$)=0.340 mm^{-1}, λ=0.71073 Å, crystal dimensions=0.35 mm×0.25 mm×0.30 mm, 3606 reflections collected, 2563 independent, $R1=0.051$, $wR2=0.011$ for $I>2\sigma(I)$.

3.2.2. Crystal data for 2. $C_8H_{13}N_7O_6$, fw=303.3, monoclinic, space group $C2/c$, $a=8.690(1)$, $b=17.014(3)$, $c=8.379(1)$ Å, $\beta=92.56(1)°$, $V=1237.6(3)$ Å^3, $Z=4$, $D_c=1.628$ Mg m^{-3}, $F(000)=632$, $\mu(\text{Mo-K}_\alpha)=0.140$ mm^{-1}, $\lambda=0.71073$ Å, crystal dimensions=0.35 mm×0.25 mm×0.25 mm, 2618 reflections collected, 893 independent, $R1=0.048$, $wR2=0.117$ for $I>2\sigma(I)$.

3.2.3. Crystal data for 3. $C_6H_{10}N_4O_4$, fw=202.2, triclinic, space group $P\bar{1}$, $a=6.320(1)$, $b=7.923(1)$, $c=10.587(2)$ Å, $\alpha=74.94(1)$, $\beta=87.28(1)$, $\gamma=67.22(1)°$, $V=471.2(1)$ Å^3, $Z=2$, $D_c=1.425$ Mg m^{-3}, $F(000)=212$, $\mu(\text{Mo-K}_\alpha)=0.120$ mm^{-1}, $\lambda=0.71073$ Å, crystal dimensions=0.30 mm×0.20 mm×0.20 mm, 1855 reflections collected, 1316 independent, $R1=0.034$, $wR2=0.094$ for $I>2\sigma(I)$.

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