

CATENATED AND NON-CATENATED INCLUSION COMPLEXES OF TRIMESIC ACID

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ABSTRACT. Trimesic acid (benzene-1,3,5-tri-carboxylic acid; TMA) can in principle form two-dimensional hydrogen-bonded hexagonal networks in which central holes of the network have net diameters of 14 Å. Although such holes would be expected to be natural locations for guest molecules, non-catenated single networks have not been found in any of the crystals containing TMA studied in the last sixteen years. Instead, anhydrous α -TMA, TMA pentaiodide (TMA.I₅) and (so-called) γ -TMA have mutually triply-catenated structures in which triplets of networks are interlaced [3,4,5], while the hydrated complexes are based on non-catenated nets of composition TMA.H₂O [6]. We have now found conditions under which single networks are preserved without catenation, the cavities being occupied by guests such as n-tetradecane, n-heptanol, n-octanol, n-decanol, octene, cyclooctane and isooctane. The structures of 2TMA.n-tetradecane and 2TMA.isooctane have been solved and refined to R=13.0% and R=11.3%, respectively, disorder of the guest molecules having prevented further refinement of the room-temperature data. Determination of the crystal structures of the other complexes, which are isostructural with 2TMA.n-tetradecane, is now in progress. We are also investigating other potential guests.

Introduction

Trimesic acid (TMA; benzene-1,3,5-tricarboxylic acid) would be expected to be a favorable host for the formation of inclusion complexes since pair-wise hydrogen bonding between the carboxyl groups would lead to the formation of an infinite, two-dimensional "chicken-wire" network (Fig. 1). This network, based upon a hexagonal unit formed by six hydrogen-bonded TMA molecules, has a central hole having a net diameter (i.e. after taking into account the van der Waals radii of the TMA molecules) of 14 Å. A proper arrangement of these "chicken-wire" networks would lead to the formation of cylindrical channels characterized by a diameter of 14 Å. Such a situation should be contrasted with that found in urea channel inclusion complexes (net channel diameter ~ 4.5 Å) [1], those of thiourea (~ 5.5 Å) [1] and perhydrotriphenylene (~ 7 Å) [2]. Thus, TMA offers in potential much

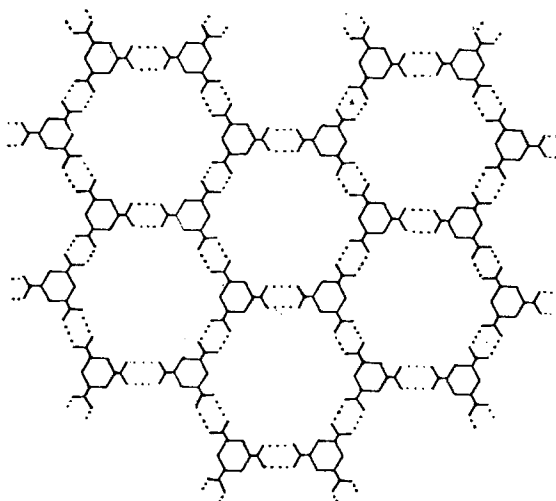


Figure 1: Idealised single "chicken-wire" network. The channels have net diameters of about 14 Å.

larger channels than those encountered in other channel inclusion complexes and may consequently act as host for guest molecules rather different from those forming complexes with urea or thiourea.

However, various attempts during the last 17 years to prepare crystals having empty "chicken-wire" networks and large guest molecules in the postulated cylindrical channels have failed. The various TMA polymorphs and complexes examined so far were found to be characterized by structures in which the channels formed by the TMA sheets are not available for accommodating guest molecules due to the remarkable phenomenon of mutual interlacing or triple catenation of the TMA networks [3,4,5].

Non-Catenated Complexes.

Recently we have succeeded in preparing TMA complexes in which the "chicken-wire" networks are preserved without catenation and so arranged as to form channels accommodating various guests. The guests used so far are: n-tetradecane, n-heptanol, n-octanol, n-decanol, octene, cyclooctane and isooctane. The crystals are colourless needles with pronounced cleavage normal to the needle axis and lose guest fairly easily to the atmosphere. Although complexes have been found with three different space groups, nevertheless comparison of cell dimensions suggests that the complexes are all isostructural.

The crystal structures of 2TMA.n-tetradecane (trigonal, space group $P3_1$ or $P3_2$, $a=b=16.500(6)$, $c=10.071(4)$ Å, $Z=3$, $D_m=1.290$ g cm $^{-3}$, $D_{calc}=1.297$ g cm $^{-3}$) and of 2TMA.isooctane (monoclinic, space group $C2/c$, $a=28.599(9)$, $b=16.596$, $c=6.927(4)$ Å, $\beta=102.55(2)^\circ$, $Z=4$, $D_{calc}=1.107$ g cm $^{-3}$) have been determined in outline. In both cases data collection was performed on a Philips PW 1100/20 four circle diffractometer (graphite-monochromated MoK α), structures solved by MULTAN [7] and refined using SHELX 77 [8]. Refinement converged to agreement factors of $R_F=0.130$ and $R_F=0.113$ for the n-tetradecane and isooctane

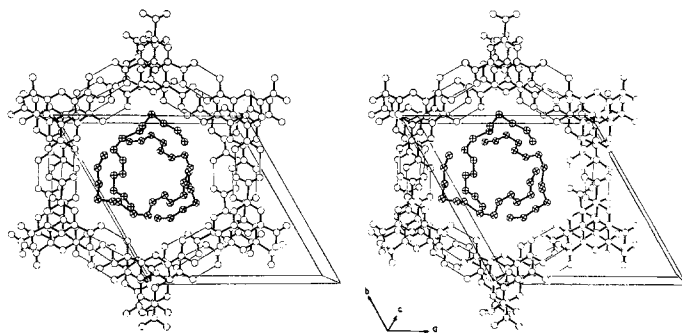


Figure 2: ORTEP [9] stereodiagram of the 2TMA.n-tetradecane complex viewed down the c axis.

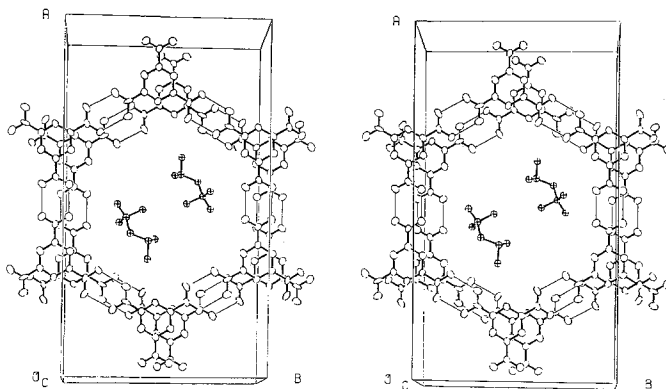


Figure 3: Stereodiagram of the $C2/c$ polymorph of 2TMA.isooctane viewed down the c axis; guest molecule representations in both diagrams are schematic.

complexes, respectively, the disorder of the guest molecules having prevented further refinement of the room temperature data. The structure of 2TMA.n-tetradecane is shown in Fig.2. The guest molecules are disordered and their representation in the channels is schematic only. There are three TMA networks along the channel axis.

2TMA.isooctane has been found in two polymorphic forms; one is isomorphous with the tetradecane complex while the second is shown in Fig. 3. There are two networks in one period along the channel axis. The networks are somewhat non-planar in both crystals.

The 2TMA.n-octanol complex, whose structure has not yet been determined, should have, considering the length of the c axis, five TMA networks in one period along the channel axis.

In the future we plan to prepare and solve the structures of a variety of non-catenated TMA inclusion complexes with different types of guest molecules to test the chemical and steric limits to the formation of these complexes. It is our hope that the 14 Å diameter channels will provide a means for separating between large molecules of different shapes and sizes, some of which will be accommodated in the channels while others will not fit.

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