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Novel Anionic Host Lattices Built of Squarate and Thiourea Molecules

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Abstract—The new inclusion complexes $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 4(NH_2)_2CS\cdot 2H_2O$ (**1**), $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 6(NH_2)_2CS$ (**2**) and $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 2(NH_2)_2CS\cdot 2H_2O$ (**3**) have been prepared and characterized by X-ray crystallography. In the crystal structure of (**1**), infinitely extended squarate–water chains inter-link adjacent puckered thiourea layers to generate a three dimensional host lattice with large uni-directional rectangular channels each containing a double column of well-ordered tetraethylammonium cations. In complex (**2**), well-ordered tetraethylammonium cations are stacked in single columns within the channel-type thiourea-squarate host lattice constructed by the cross-linkage of two types of layers. In complex (**3**), well-ordered teteraethylammonium cations are sandwiched between puckered layers generated by the cross-linkage between zigzag $(C_4O_4^{2-}\cdot 2H_2O)_\infty$ chains and singly hydrogen-bonded dimeric thiourea ribbons. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Crystal engineering requires a comprehensive understanding of intermolecular interactions.[1] It provides a key to answer why and how molecules pack themselves in specific ways and a systematic approach to design new crystals with desirable physical and chemical properties.[2] Hydrogen bonding is recognized as the most reliable directional interaction in supramolecular architecture. In the classical thiourea inclusion host lattice, a channel system is formed by the cross-linkage of three interpenetrating hydrogen-bonded thiourea ribbons. Neutral molecular guests such as medium-sized alicyclic or highly branched hydrocarbons, ketones, esters, halides, and even organometallics, can be accommodated within each channel.[3–5] In the presence of anions, the hydrogen bond is strengthened by two to three times (40–190 kJ mol^{-1}) compared with the bond strength involving uncharged molecular species (10–65 kJ mol^{-1}).[6] Using hydrophobic cationic guests, such as peralkylated ammonium cations, as templates and making use of conventional hydrogen bonds formed by urea, thiourea, or selenourea together with various anionic and other neutral molecular building blocks, a variety of novel host lattices with specific topochemical features have been generated in our laboratory.[7]

The chemistry of the monocyclic oxocarbon acids $H_2C_3O_3$ (deltic acid), $H_2C_4O_4$ (squaric acid), $H_2C_5O_5$ (croconic acid) and $H_2C_6O_6$ (rhodizonic acid) is well documented in several books and reviews.[8–12] Squaric acid, which is a strong acid ($pK_1=0.55$ and $pK_2=2.3$),[13] was first synthesized by Cohen et al. four decades ago.[14] Upon full deprotonation, the interesting 10π $C_4O_4^{2-}$ species is formed. Besides processing unique electronic and chemical properties in view of its high molecular symmetry,[15] the squarate dianion contains charged oxygen atoms that can function as strong hydrogen-bond acceptor sites.[16,17] We have now incorporated the squarate ion into the host lattices of three new inclusion complexes of thiourea, namely $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 4(NH_2)_2CS\cdot 2H_2O$ (**1**), $[(C_2H_5)_4N^+]_2$-$C_4O_4^{2-}\cdot 6(NH_2)_2CS$ (**2**) and $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 2(NH_2)_2CS\cdot 2H_2O$ (**3**), and determined their X-ray crystal structures. In the present paper, a common thiourea linkage pattern is used to correlate the structural characteristics of these inclusion complexes and the previously reported complex $(n\text{-}C_3H_7)_4N^+HCO_2^-\cdot 3(NH_2)_2CS\cdot H_2O$[18] in the context of solid-state supramolecular assembly.

Results and Discussion

Crystal structure of $[(C_2H_5)_4N^+]\,_2C_4O_4^{2-}\cdot 4(NH_2)_2CS\cdot 2H_2O$ (1)

The host lattice of (**1**) contains large one-dimensional rectangular channels extending parallel to the *a*-axial direction, as illustrated in Fig. 1. The channel framework is built of a parallel arrangement of puckered thiourea layers that are interlinked by straight chains made of squarate dianions and water molecules $(C_4O_4^{2-}\cdot H_2O)$ via N–H···O (squarate)

Keywords: oxocarbons; oxocarbon acid and derivatives; thiourea; inclusion complex; hydrogen bonding.

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† Dedicated to the memory of Dr Hson-Moa Chang (1923–2000).

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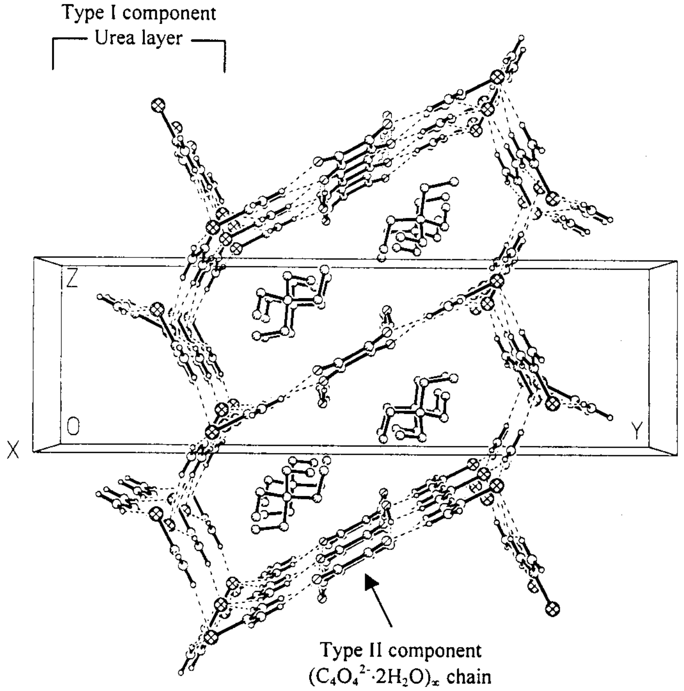

Figure 1. Channel-type crystal structure of $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 4(NH_2)_2CS\cdot 2H_2O$ (**1**). The origin of the unit cell lies at the lower left corner, with *a* pointing towards the reader, *b* from left to right and *c* upwards. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. Note that the nearly rectangular channels are viewed end-on.

hydrogen bonds. The host lattice of complex (**1**) can be considered as a combination of two major structural components (designated type I and type II) that are interlinked by N–H···O(squarate) hydrogen bonds. The type I component is built of two independent thiourea molecules **C**(**1**) [containing atoms C1, S1, N1 and N2, and hereafter referred to by naming the carbon atom for convenience] and **C**(**2**). They are alternately linked together by N–H···S hydrogen

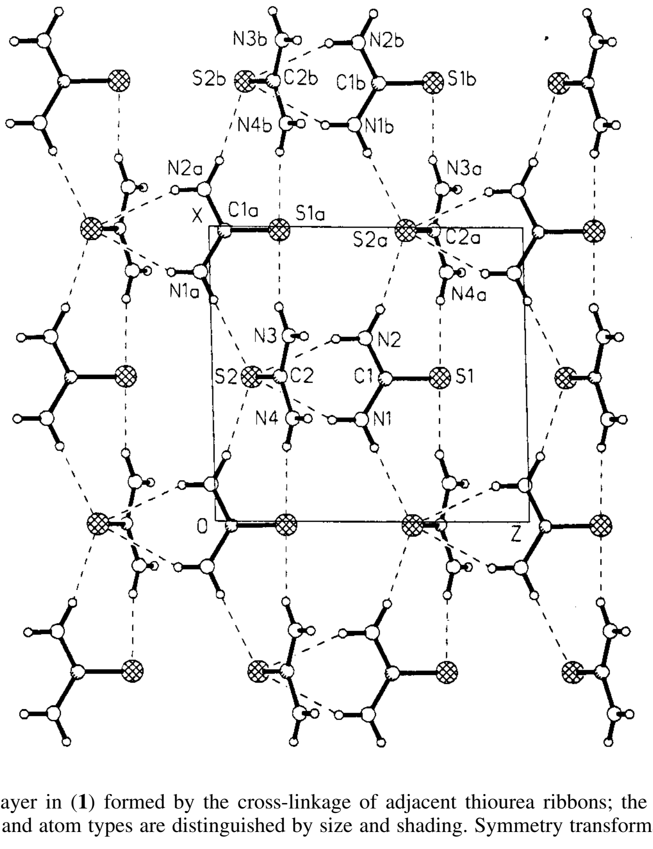

Figure 2. Hydrogen-bonded puckered layer in (**1**) formed by the cross-linkage of adjacent thiourea ribbons; the mean plane of this layer is at $y=1/4$. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. Symmetry transformations: (a) $(0.5+x, 0.5-y, 0.5+z)$; and (b) $(1+x, y, z)$.

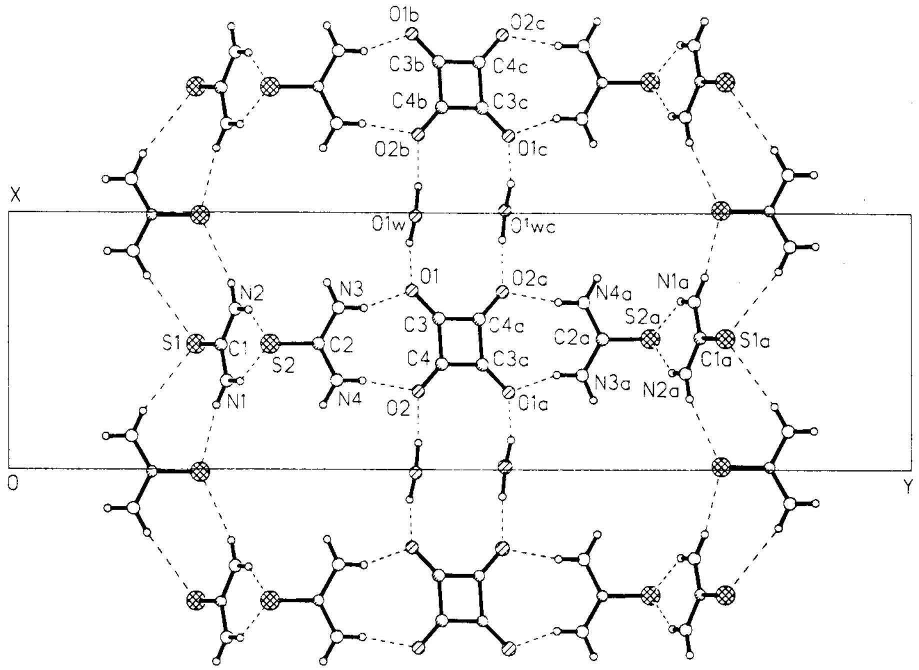

Figure 3. Projection diagram of the hydrogen-bonded squarate–water chains in the crystal structure of $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 4(NH_2)_2CS\cdot 2H_2O$ (**1**). Each squarate ion cross-links two adjacent thiourea molecules to form a wide platform matching the $(02\bar{1})$ family of planes. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. Symmetry transformations: (a) $(1-x, 1-y, 1-z)$; (b) $(1+x, y, z)$; (c) $(2-x, 1-y, 1-z)$.

bonds in a shoulder-to-shoulder fashion to form a zigzag and puckered thiourea ribbon extending along the *a*-axial direction, as shown in Fig. 2. The relevant torsion angles in each thiourea ribbon are: C1–S1···N4a–C2a=48.0°, C1–N2···S2a–C2a=23.7° and C1b–N1b···S2a–C2a=−44.9°, C2a–N3a···S1b–C1b=−52.4°, respectively. With these zigzag and puckered thiourea ribbons arranged side by side, the sulphur atom of each **C**(**2**) molecule forms two additional acceptor hydrogen bonds with an adjacent thiourea ribbon through N1 and N2 of molecule **C**(**1**) in a

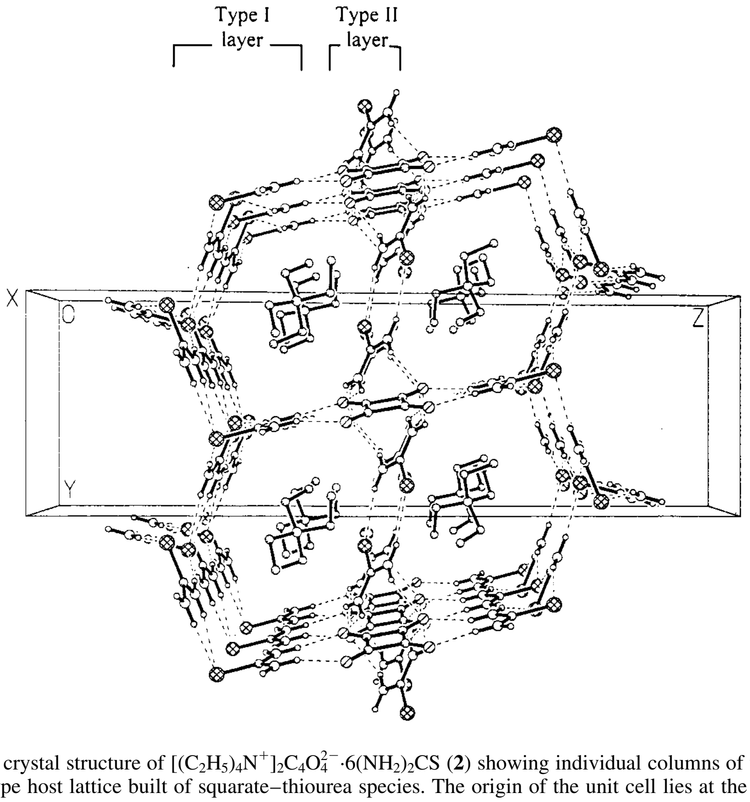

Figure 4. Perspective view of the crystal structure of $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 6(NH_2)_2CS$ (**2**) showing individual columns of well-ordered tetraethylammonium cations enclosed in the channel-type host lattice built of squarate–thiourea species. The origin of the unit cell lies at the upper left corner, with *a* pointing towards the reader, *b* downward and *c* from left to right. Broken lines represent hydrogen bonds and atom types are distinguished by size and shading.

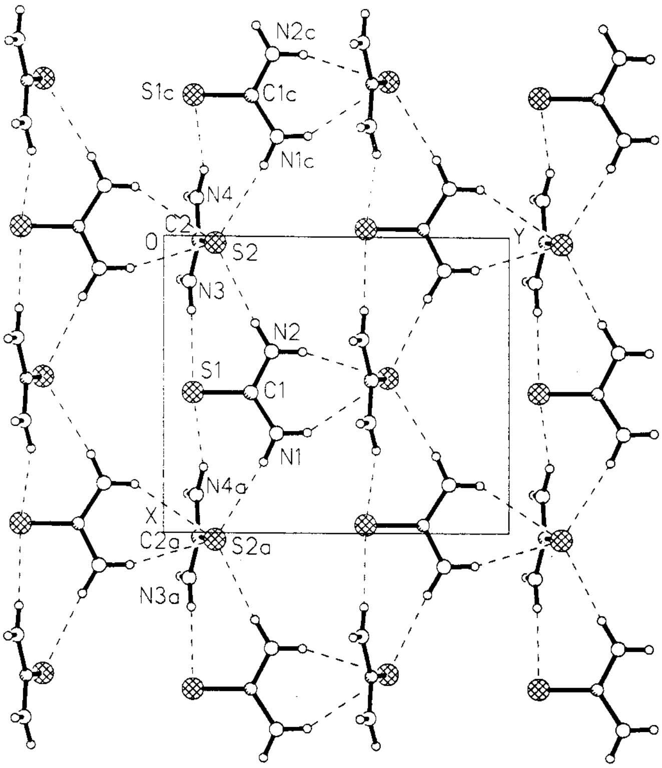

Figure 5. Projection diagram of the type I layer in (**2**) composed of two independent thiourea molecules **C**(**1**) and **C**(**2**). Hydrogen-bonded thiourea ribbons running along the *a*-axis cross-link with each other to yield a puckered layer with its mean plane at $z=1/4$. Symmetry transformations: (a) (x, y, z); (b) $(x, 1+y, z)$; and (c) $(-1+x, y, z)$.

folded head-to-tail fashion, such that this type of cross-linkage gives a puckered layer which is normal to the *b*-axis. The dihedral angles between adjacent ribbons in complex (**1**) are quite large, as can be seen from the relevant torsion angles: C1–N1···S2–C2=−83.8° and C1–N2···S2–C2=98.8°. These puckered thiourea layers constitute pairs of opposite walls of the large channels.

The type II component is of great interest from the structural point of view. Adjacent squarate dianions, each occupying an inversion centre, are bridged by a pair of centrosymmetrically related water molecules with a pair of hydrogen bonds, O1W–H···O1 (squarate)=2.823 Å and O1Wc–H···O2 (squarate)=2.751 Å, to yield a seat-belt-like chain running parallel to the *a*-axis (Fig. 3). Each linear $(C_4O_4^{2-}\cdot 2H_2O)_\infty$ chain contains 14-membered rings each constituted by two pairs of distinct types of hydrogen bonds related by an inversion centre. The pattern can be either described as $\boldsymbol{R_4^4}$**(14)** to emphasize the ring or $\boldsymbol{C_2^2}$**(7)** to emphasize the chain, and the 'chain of rings' notation is $\boldsymbol{C_2^2}$**(7)**[$\boldsymbol{R_4^4}$**(14)**] according to the graph set topological terminology[19] for the analysis of hydrogen-bonded network patterns.[20,21] Note that the water molecules do not partake in acceptor hydrogen bonding with other structural units, and the thiourea molecules of type **C**(**2**) reach out from both sides of each thiourea layer to facilitate their linkage to the squarate–water chains. This squarate–water chain links two adjacent puckered thiourea layers together by forming two pairs of N–H···O (squarate) hydrogen bonds (N3–H···O1=2.879 Å and N4–H···O2=2.822 Å) from two **C**(**2**) thiourea molecules to generate two side walls of a large channel, with their mean planes matches the $(02\bar{1})$ family of planes. Combination of the type I and type II structural components gives channels of nearly rectangular cross-section of 16.96 Å×7.73 Å running parallel to the *a*-axis. Well-ordered tetraethylammonium cations are accommodated as a double column within each channel, as illustrated in Fig. 1.

Crystal structure of $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 6(NH_2)_2CS$ (2)

As illustrated in Fig. 4, the host lattice of (**2**) can be considered as a combination of two different kinds of layers, designated as type I and type II for discussion. The type I layer is built of two independent thiourea molecules in the asymmetric unit while the type II layer is constructed from the third independent thiourea molecule and a centrosymmetric squarate dianion. All hydrogen atoms of the thiourea molecules **C**(**1**) and **C**(**2**) participate in the construction of the hydrogen-bonded type I layer. Two pairs of donor and acceptor hydrogen bonds are used to produce an infinitely extended thiourea ribbon while the third pair of donor and acceptor hydrogen bond is used to cross-link the adjacent thiourea ribbons.

Two independent thiourea molecules **C**(**1**) and **C**(**2**), which are alternately linked together by pairs of N–H···S hydrogen bonds in shoulder-to-shoulder fashion to form zigzag and puckered ribbons directed along the *a*-axis. The relevant torsion angles in each thiourea ribbon are: C1–S1···N3–C2=−56.6°, C2–S2···N2–C1=−51.6°, C1–S1···N4a–C2a=69.8° and C1–N1···S2a–C2a=65.0°. With these ribbons arranged side by side, atom S3 of molecule **C**(**1**) forms two acceptor hydrogen bonds with atoms N2 and N1

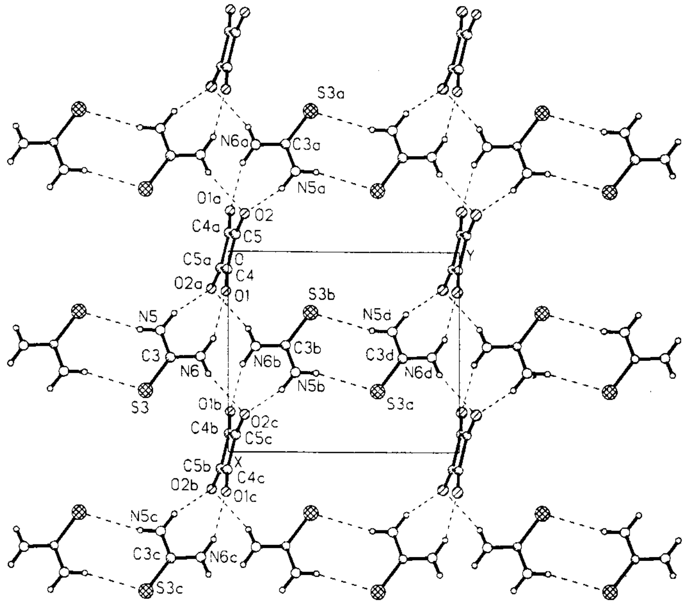

Figure 6. Type II layer in (**2**) resulting from the cross-linkage between adjacent ribbons built of the centrosymmetric squarate dianion and the third independent thiourea molecule **C**(**3**); the mean plane of this layer is at $z=0$. Broken lines represent hydrogen bonds and atom types are distinguished by size and shading. Symmetry transformations: (a) $(-x, -y, -z)$; (b) $(1-x, -y, -z)$, (c) $(1+x, y, z)$; and (d) $(x, 1+y, z)$.

of molecule **C**(**3**) belonging to the adjacent ribbon, such that this type of cross-linkage yields a puckered layer that is normal to the *c*-axis, Fig. 5. The dihedral angles between adjacent ribbons are quite large, as can be seen from the relevant torsion angles: C1–N1···S2b–C2b=88.3° and C1–N2···S2b–C2b=−98.6°. It is noted that this kind of linkage mode of thiourea molecules also exists in (**1**) and $(n\text{-}C_3H_7)_4N^+HCO_2^-\cdot 3(NH_2)_2CS\cdot H_2O$,[18] as it offers two opposite walls to facilitate the direct linkage of a wide variety of inter-layer structural moieties to form large uni-directional channel systems, provided that such inter-layer linkers have optimal sizes and compatible hydrogen bonding sites.

In the type II layer, each thiourea molecule utilizes three donor N–H···O hydrogen bonds in building the infinite thiourea-squarate chains while a pair of donor and acceptor hydrogen bonds is used to cross-link the adjacent thiourea-squarate ribbons. The third thiourea molecule **C**(**3**), together with its centrosymmetrically related partner **C**(**3a**), is

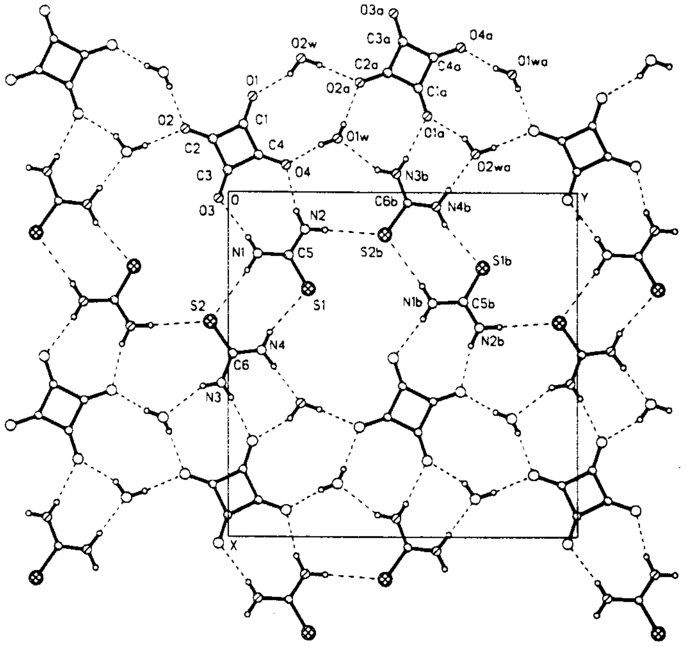

Figure 7. Projection diagram along the *c*-axis showing the hydrogen bonding interaction within a host layer in the crystal structure of (**3**); the mean plane of this layer is at $z=3/8$. Broken lines represent hydrogen bonds and atom types are distinguished by size and shadings. Symmetry transformations: (a) $(-0.5-x, 0.5+y, z)$; (b) $(0.5-x, 0.5+y, z)$.

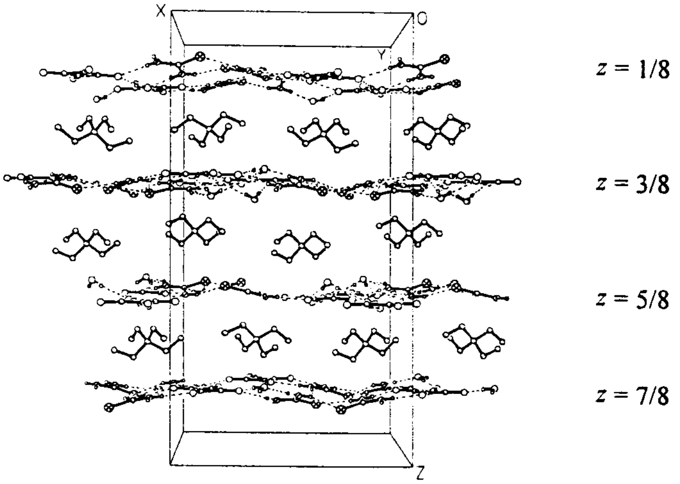

Figure 8. Perspective view of the crystal structure of (**3**) showing that the well-ordered $(C_2H_5)_4N^+$ cations are sandwiched between adjacent puckered squarate–thiourea–water layers. The origin of the unit cell lies on the upper right corner, with *a* pointing from right to left, *b* away from the reader, and *c* downward.

hydrogen-bonded to the squarate dianion at $\bar{1}$ via pairs of N–H···O hydrogen bonds to form a twisted bow-tie-like (or two-wing propeller-like) cyclic trimer which serves as a repeating unit in generating the infinite thiourea-squarate chains. The relevant torsion angles are C3–N5···O2a–C5a=−88.3° and C3–N6···O1–C4=−56.0°, respectively. The lower half of the twisted bow-tie-like trimer is interlocked with the upper half of the preceding one via an additional pairs of N–H···O (squarate) hydrogen bonds to form an infinitely extended thiourea-squarate chain along the *a*-axis. With these ribbons lying side by side, cross-linkage between adjacent thiourea molecules via pairs of N–H···S hydrogen bonds in a shoulder-to-shoulder fashion generates a puckered layer containing large peanut-shaped voids with cross-sectional area somewhat less than $a\times b$ Å^2 (see Fig. 6). The relevant torsion angle is C3b–S3b···N5d–C3d=14.7°. This thiourea-squarate layer links two adjacent zigzag and puckered thiourea layers together by forming two pairs of donor N–H···O (squarate) hydrogen bonds (N3–H···O1=2.844 Å, N4–H···O2=2.823 Å) from two centrosymmetrically related **C**(**2**) type thiourea molecules to generate a three-dimensional host framework with open-channels running parallel to the *a*-axis. Note that the thiourea molecules of type **C**(**2**) stretch out from both sides of each thiourea layers to facilitate their linkage to the thiourea-squarate puckered layers. The well-ordered tetraethylammonium cations almost attain idealized 222 molecular symmetry and are stacked densely within each channel with cross-sectional dimensions of about 9.42 Å×8.96 Å.

Crystal structure of $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 2(NH_2)_2CS\cdot 2H_2O$ (3)

When a smaller stiochiometric ratio of squaric acid to thiourea was employed the layer-type inclusion complex (**3**) was obtained. In the crystal structure of (**3**), all of the hydrogen-bond donating sites on the thiourea molecules participate in the construction of the anionic host lattice which contains puckered layers generated by the cross-linkage of zigzag $(C_4O_4^{2-}\cdot 2H_2O)_\infty$ chains and thiourea ribbons. The hydrogen-bonding scheme is conveniently described with reference to Fig. 7.

Neighboring squarate dianions are bridged by two independent water molecules via two pairs of fairly strong hydrogen bonds (O1w–H···O4=2.767 Å, O2w–H···O1=2.668 Å, O1w–H···O2a=2.837 Å and O2w–H···O2a=2.725 Å) to generate a zigzag $(C_4O_4^{2-}\cdot 2H_2O)_\infty$ chain extending along the *b*-axis. Each zigzag $(C_4O_4^{2-}\cdot 2H_2O)_\infty$ chain contains 11-membered rings which are constituted by four crystallographically independent hydrogen bonds. The pattern can be described by the 'chain of rings' notation $\boldsymbol{C_4^4(15)[R_3^4(11)]}$. On the other hand, two independent thiourea molecules **C5** (containing atoms of C5, S1, N1 and N2) and **C6** are joined together by a pair of N–H···S hydrogen bonds (N1–H···S2=3.591 Å and N4–H···S1=3.345 Å) to form a slightly twisted thiourea dimer in a typical shoulder-to-shoulder fashion, as revealed from the torsion angles C5–N1···S2–C6=−26.5° and C6–N4···S1–C5=−53.2°. Neighboring thiourea dimers are further connected to each other by a single N–H···S hydrogen bond (N2–H···S2b=3.490 Å) to produce a zigzag 'dimeric thiourea ribbon' running parallel to the $(C_4O_4^{2-}\cdot 2H_2O)_\infty$ chain. With these zigzag $(C_4O_4^{2-}\cdot 2H_2O)_\infty$ chains and dimeric thiourea ribbons lying alternately side by side, five additional hydrogen bonds (N1–H···O3=2.904 Å, N2–H···O4=2.838 Å; N3b–H···O1a=2.886 Å, N4b–H···O2wa=2.880 and N3b–H···O1w=2.936 Å) are formed to inter-link them together to yield a puckered layer normal to the *c*-axis. The puckered layers lie close to the planes z=1/8, 3/8, 5/8 and 7/8, and the well-ordered tetraethylammonium cations are alternately arranged and sandwiched between them, as shown in Fig. 8.

Structural features and topological correlation of the host lattices

By varying the stiochiometric ratio of thiourea to squarate and the crystallization medium, three different inclusion complexes were obtained. The host structure of complex $[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 4(NH_2)_2CS\cdot 2H_2O$ (**1**) is found to be

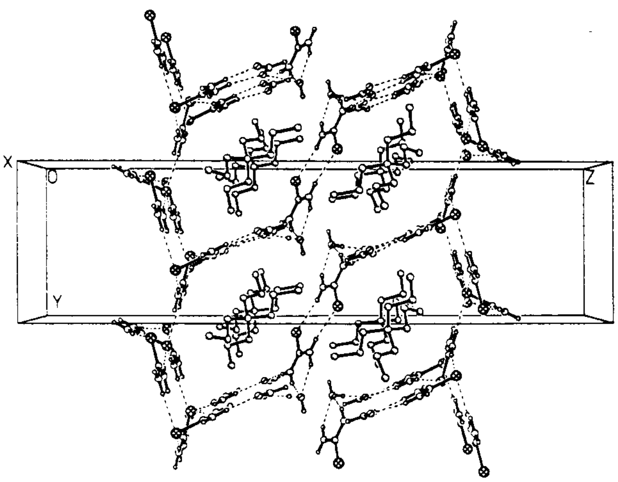

Figure 9. Channel-type crystal structure of $(n\text{-}C_3H_7)_4N^+HCO_2^-\cdot 3(NH_2)_2CS\cdot H_2O$.[18] The origin of the unit cell lies at the upper left corner, with *a* pointing towards the reader, *b* downward and *c* from left to right. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. The peanut-shape channels are viewed end-on.

closely related to that of another inclusion complex $(n\text{-}C_3H_7)_4N^+HCO_2^-\cdot 3(NH_2)_2CS\cdot H_2O$.[18] Both of them contain a uni-directional open-channel system. Although the channels are completely different in shape, the replacement of squarate–water chains with the large cyclic linker composed of two pairs of centrosymmetric thiourea dimers cyclized by another pair of centrosymmetrically related formate and water molecules modifies the cross-section of the channel from lunch-box (about 16.96 Å×7.73 Å) to peanut (about 25.38 Å×8.77 Å). As a result of this expansion in channel size, two columns of larger and well-ordered $(n\text{-}C_3H_7)_4N^+$cations can be accommodated within each peanut-shaped channel in the latter complex, as shown in Fig. 9. Detailed hydrogen bonding interactions and structural characteristics of the squarate–water chain and the large cyclic linker are compared in Figs. 3 and 10.

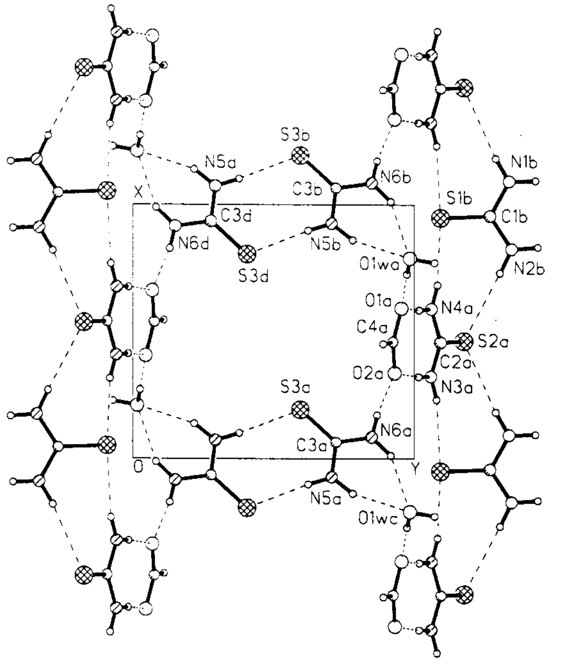

Figure 10. Projection diagram of a portion of a host lattice in $(n\text{-}C_3H_7)_4N^+HCO_2^-\cdot 3(NH_2)_2CS\cdot H_2O$[18] showing the cyclic linker that inter-links two adjacent puckered thiourea layers via two pairs of N–H···O (formate) hydrogen bonds. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. Symmetry transformations: (a) (*x*, 1+*y*, *z*); (b) (1+*x*, 1+*y*, *z*); (c) (−1+*x*, 1+*y*, *z*); (d) (1−*x*, −*y*, −*z*).

Although the squarate dianion is an electron-rich chemical species with high molecular symmetry, it does not always utilize its hydrogen bonding acceptor sites to the maximum extent in the construction of host lattices. In the present three new crystal structures, each squarate forms different numbers of acceptor hydrogen bond with its surrounding hydrogen-bond donating molecular species. In the host lattice of (**1**), each squarate dianion forms eight acceptor hydrogen bonds. Four of them are used to generate a linear $(C_4O_4^{2-}\cdot 2H_2O)_\infty$ chain, while another two pairs of hydrogen bonds are used to cross-link two adjacent puckered thiourea layers to produce a large uni-directional rectangular channel system.

Through the substitution of bridging water molecules in (**1**) by thiourea molecules in (**2**), each squarate dianion in the later host lattice forms an unusually large number of ten acceptor hydrogen bonds with six neighboring thiourea molecules, as shown in Fig. 11. The twisted dimeric thiourea linkers connect the squarate dianions in an end-to-end fashion, hence facilitating the formation of thiourea-squarate ribbons and the cross-linkage between similar ribbons on adjacent floors, as illustrated in Fig. 6. Moreover, this substitution effectively slices each large rectangular channel in (**1**) that accommodates a double column of tetraethylammonium cations (see Fig. 1) length-wise into two equal parts in (**2**) (see Fig. 4), as the additional adjacent thiourea molecules are cross-linked by pairs of N–H···S hydrogen bonds to create the partitions. Each smaller 'halved' channel in (**2**), with a cross-section of about 9.42×8.96 Å^2, thus accommodates a single column of well-ordered tetraethylammonium cations with nearly 222 molecular symmetry.

In contrast to (**1**) and (**2**), each squarate forms only seven acceptor hydrogen bonds in the host layer of (**3**) (see Fig. 7). Four of them involve two pairs of bridging water molecules to form a zigzag $(C_4O_4^{2-}\cdot 2H_2O)_\infty$ ribbon. Another pair of acceptor hydrogen bonds are used to directly join with an adjacent thiourea dimer, and the seventh acceptor hydrogen bond is used to consolidate the squarate–thiourea–water anionic host layer.

The most prominent structural feature of the present channel-type inclusion complexes is their analogous linkage mode of thiourea molecules which leads to the same type of hydrogen-bonded puckered thiourea layer (see Fig. 2 and Fig. 5). Two independent thiourea molecules are joined together in a shoulder-to-shoulder fashion to form a twisted thiourea ribbon. Ribbons that lie side-by-side in different orientations are further cross-linked by forming pairs of N–H···S hydrogen bonds in a head-to-tail fashion. In this way, a pair of N–H hydrogen-bond donating sites are made available for direct connection to the linkers to generate large uni-directional channel systems with distinct sizes and shapes.

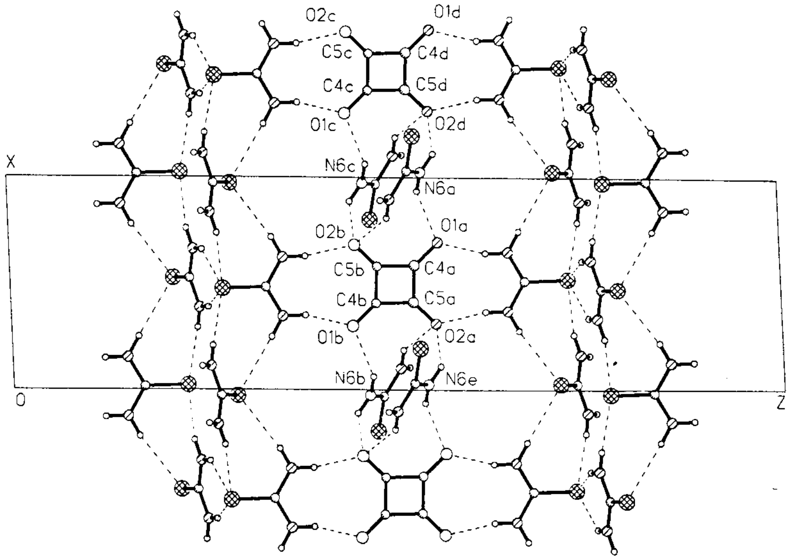

Figure 11. Projection diagram of the hydrogen-bonded squarate–thiourea chain in (**2**). Each squarate ion cross-link two thiourea molecules protruding from two adjacent puckered thiourea layers to form a wide platform, while another two pairs of thiourea molecules bridge the squarate dianions and inter-link parallel squarate–thiourea chains. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. Symmetry transformations: (a) (0.5+x, 0.5−y, 0.5+z); (b) (0.5−x, 0.5+y, 0.5−z); (c) (1.5−x, 0.5+y, 0.5−z); (d) (1.5+z, 0.5−y, 0.5+z); and (e) (−0.5+x, 0.5−y, 0.5+z).

As demonstrated in the structures of these new inclusion complexes and those reported previously,[16,17] the squarate dianion plays an important role in providing hydrogen-bonding acceptor sites for other molecular species, such as urea, thiourea and water molecules, in the construction of a rich variety of hydrogen bonding patterns. The present examples further demonstrate that the geometry of the thiourea-anion host lattice can be modified in interesting ways by substitution of appropriate hydrogen-bonded synthons through the variation of molecular building blocks, thus providing another interesting example of isostructurality (i.e. structural similarities)[22] in the context of supramolecular architecture.

Experimental

Complex (**1**), (**2**) and (**3**) were prepared by mixing tetra-

Table 1. Crystal data and refinement parameters of inclusion complexes (**1**), (**2**) and (**3**)

Inclusion Complex	(**1**)	(**2**)	(**3**)
Structural formula	$[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 4(NH_2)_2CS\cdot 2H_2O$	$[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 6(NH_2)_2CS$	$[(C_2H_5)_4N^+]_2C_4O_4^{2-}\cdot 2(NH_2)_2CS\cdot 2H_2O$
CCDC deposit no.	CCDC-137067	CCDC-137068	CCDC-137069
Chemical formula	$C_{24}H_{60}N_{10}O_6S_4$	$C_{26}H_{64}N_{14}O_4S_6$	$C_{22}H_{52}N_6O_6S_2$
Formula weight	713.06	829.27	560.82
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1$/n (No. 14)	$P2_1$/n (No. 14)	*Pbca* (No. 61)
T, °C	20	20	18
a, Å	8.070(1)	8.149(1)	14.592(3)
b, Å	28.365(2)	9.419(1)	14.825(4)
c, Å	8.622(1)	29.552(2)	29.473(5)
α, deg	90	90	90
β, deg	91.28(1)	92.54(1)	90
γ, deg	90	90	90
V, Å^3	1973.1(4)	2266.0(4)	6376(2)
Z	2	2	8
Crystal size, mm^3	0.50×0.50×0.54	0.48×0.50×0.52	0.40×0.48×0.50
Melting point, °C	199.2–200.4	202.3–202.5	200.6–200.9
ρ_{calcd}, g cm^{-3}	1.200	1.215	1.168
μ, mm^{-1}	0.287	0.347	0.209
Reflections measured	3477	4459	6519
Reflections observed with $I>2\sigma(I)$	1466	2631	4232
No. of variables	200	227	362
Goodness-of-fit (all)	1.061	1.022	1.013
R1	0.0748(obs), 0.1925(all)	0.0548(obs), 0.1119(all)	0.0448(obs), 0.0750(all)
WR2	0.1124(obs), 0.1532(all)	0.0980(obs), 0.1260(all)	0.1274(obs), 0.1407(all)
Largest diff. peak and hole, e Å^{-3}	0.213 and −0.186	0.227 and −0.224	0.337 and −0.178
Maximun shift/e.s.d.	0.001	0.001	0.001

ethylammonium hydroxide (35% wt. solution in water, Aldrich), squaric acid (99%, Aldrich) and thiourea (Riedel-de Haën) in a molar ratio of 2:1:6, 2:1:6 (recrystallized in 95% ethanol) and 2:1:3, respectively. In each case, a minimum amount of water was added to dissolve the solid. The solution was stirred for 15 minutes and then placed in a desiccator charged with anhydrous calcium chloride for slow evaporation at room temperature. Colorless crystals in the form of rectangular prisms were obtained after several weeks. Single crystals of suitable dimensions were selected and subjected to X-ray analysis. Information concerning the crystallographic data is summarized in Table 1.

Intensities were collected with MoK$_\alpha$ radiation (λ= 0.71073 Å) at 291(2) K using the variable ω-scan technique on a Siemens P4 diffractometer for (**1**) and (**2**), and on a Bruker SMART 1000 CCD diffractometer for (**3**). Absorption correction from psi scan was omitted for (**1**) and (**2**), but applied using SADABS for (**3**).[23,24] All three structures were solved by direct phase determination, and the atomic parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method.[25] The atomic coordinates, bond lengths and angles, and thermal parameters of (**1**), (**2**) and (**3**) have been deposited at the Cambridge Crystallographic Data Centre as CCDC deposit reference number 137067-9.

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