

Protonated Bis(quinuclidine) Included in Channel Thiourea-Bromide and Ribbons Thiourea-Iodide Lattice: New Thiourea Inclusion Compounds

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(Received: 17 October 2005; in final form: 13 March 2006)

Key words: Ternary inclusion compounds, thiourea-bromide, thiourea-iodide

Abstract

Host-guest supramolecular complexes are of special interest for understanding the chemistry in low dimensional spaces. The molecular recognition involved in the formation of such structures sometimes may be a relevant model for the kind of organized system usually found in living organisms. Matrix effects and anisotropic features which are habitual of the chemistry in restricted spaces also appear as useful for the development of new material of scientific and technological importance (Takemoto and Sonoda, 1984). Urea and thiourea clathrates constitute interesting systems in which the matrix being structured by hydrogen bond interactions has a relatively high liability to structural changes caused by the interaction with the host (Lehn, 1996). The syntheses and crystal structure of two novel ternary inclusion compounds having protonated bis (quinuclidine) as a guest into anionic thiourea-bromide and thiourea-iodide hosts are reported: (thiourea₂[quinuclidine₂H]⁺Br⁻), **1** and (thiourea₂[(quinuclidine₂H)⁺]₂(I⁻)₂), **2**. In the two structures thiourea molecules interact with each other via N–H...S hydrogen bonds to produce ribbon-like arrangements. In structure 1 these ribbons do not contain the halogen and define two non intersecting sets running along the *a* and *b* axis, linked through N–H...Br hydrogen bonds having the external halide ions as acceptors. This ribbon-crossover defines a channel structure along *c* with a cavity cross section of ca. 5.85 × 15.50 Å. In structure 2, ribbons contain iodide anions as well, bridging thiourea dimers into parallel 1D structures which align their flat side parallel to the (110) set of planes leaving a free spacing of ca. 8.25 Å.

Introduction

The nature of molecular guest-host interactions has received increasing attention due to its relevance in the behaviour of new materials with novel properties, viz., with applications in electronic and optoelectronics [1–3], etc. Host materials such as urea, thiourea, cyclodextrins, calixarenes, zeolites and perhydrotriphenylene allow for specific host-guest architectures, where guest molecules are incorporated along channels, within layers, or in isolated cages [1, 4–12]. Among such materials thiourea inclusion compounds (i.e. clathrates), have been extensively investigated. X-ray diffraction studies have shown that the typical binary compounds of thiourea are built up with an hexagonal channel structure [13–18]. Guest species containing amine or azacycle as functional groups are also included in urea and thiourea hosts. Using 1,2 diazabicyclo[2'2'2]octane or hexamethylenetetramine as

a guest and thiourea as a host it has been possible to obtain binary layered inclusion compounds [15, 19–21]. The thiourea host is formed by hydrogen bonding and a variety of guest molecules of appropriate size and shape can be included. The thiourea channel is appropriate, for example, to store branched hydrocarbon chains, as its characteristic diameter comprises values between 7 and 9 Å. In this way, it is interesting to obtain derivatives of a thiourea matrix containing channels or layers large enough as to accommodate more bulky molecules. The synthesis of ternary compounds offers this possibility and if in addition host and guest possess an anionic and a cationic character, respectively, it might be interesting to study their conductivity properties.

Examples of halogenated ternary ammonium inclusion complexes of thiourea are limited [17, 22–23]. We have recently reported the structure and some related properties (like conductivity, etc) of thiourea₂[quinuclidine₂H]⁺Cl⁻. [22–23]. Pedersen [24] and Hilgenfeld et al. [25] report a thiourea-iodide matrix structure formed by

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ribbons in a compound, containing dibenzo [18] crown-6, potassium iodide and thiourea. In the matrix the thiourea molecules are not involved in the complexation of the cation nor do they have any contact to the polyether, but form polymeric, hydrogen-bonded chains instead.

We chose quinuclidine as a guest considering its small cyclic structure and its basic properties. The proton affinity of quinuclidine is 236 Kcal/mol and the three-dimensional model with space occupation indicates that no tension energy exists as in other nitrogen pyramidal such triethylamine [26].

In this work we describe the syntheses, structure characterization and properties of thiourea₂[quinuclidine₂H]⁺Br⁻ (**1**) and (thiourea₂[(quinuclidine₂H)⁺]₂(I⁻)₂) (**2**).

Experimental

Commercially available reagents were used as received. The products were obtained at room temperature by slow evaporation of the solvent from methanolic solutions of thiourea, quinuclidine and lithium halide in 2:2:1 molar ratio. After about 48 h, well formed hexagonal crystals for **1** and thin plates for **2** could be separated. Products were washed with cold methanol and dried under vacuum. Crystals of **1** and **2** showed under the polarizing microscope a characteristic behaviour which allowed to distinguish them from lithium halide, quinuclidine and pure thiourea, as verified by X-ray powder diffraction analysis of the products samples. Crystals decompose in water producing a characteristic visually observable dynamic effect [27]. Single crystals were selected for X-ray diffraction analysis. Data were collected at room temperature on a Siemens R3m/V diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods using SHELXS-97 [28]. Hydrogen atoms were located geometrically and allowed to ride both in coordinates as in their isotropic temperature factors. H1's in the cations were located in the difference Fourier map and conventionally refined with isotropic temperature factors.

A fully completed CIF was deposited in the Cambridge Crystallographic Data Centre: for **1** CCDC 229895 and for **2** CCDC 229896.

Results and discussion

The synthesis of the compounds was carried up in methanol as solvent, where the partial hydrolysis of lithium bromide and lithium iodide produced the protons and halides necessary to obtain the ionic guest and host. Moreover, this synthesis method allowed to remove the water contained in the solvent and as a result the crystals structures obtained do not contain water as often occurs in ternary thiourea compounds [17].

The structural determination of **1** and **2** shows the presence of supramolecular structures which allow describing them as host-guest inclusion compounds. Crystal data and relevant refinement parameters are presented in Table 1. Selected H-bonding interactions are shown in Tables 2 and 3.

In spite of being quite different, the structures share some common aspects, like the fact of being constituted by polyanionic matrices composed of neutral thiourea and Br/I anions, in which voids the cationic [Q₂H]⁺ entities lodge.

In the case of **1**, the polyanionic array is a 3D mesh conformed by two sets of non intersecting planar ribbons normal to the *c* axis, each one made up of H-bonded thiourea molecules linked along the chain to neighbouring sulphur atoms through their *syn* N–H protons [17]. Figure 1 shows a view of such an elemental chain and Table 2 gives details of the H-bonding interactions. One of these sets runs along [110] at a height $z = 0.50$ and the other one, along $[-110]$ at $z = 0$ and 1. The interaction between the quasi-orthogonal chains is provided by H-bonds having the bromine anions, which lie in between, as common acceptors. This chain-crossover defines a set of cavities approximately 5.85 by 15.50 Å, in which the [Q₂H]⁺ complex species are stacked with a periodicity of ca. 11.4 Å, Figure 2. Besides the omnipresent coulombian forces due to the ionic character of the structure, the only other interaction holding the cationic groups seem to be van der Waals interactions, as suggested by the distances between the outermost hydrogens in the complex and the matrix, which are always longer than 3 Å. Nevertheless, these interactions are strong enough as to prevent free rotation of the cation, which appears very well resolved, with no trace of disorder.

In the case of **2** the elemental unit of the anionic network consists of hydrogen-bonded thiourea dimers bridged by iodide anions through N–H...I⁻ bonding (Figure 3, Table 3) and which define ribbons running in the *c* direction at $x = 0, 1, y = 0.50$. These ribbons, which do not have any kind of direct interaction with each other, align their flat side parallel to the (110) set of planes (Figure 4), leaving a free spacing of ca. 8.25 Å, where the diquinuclidinium cations [Q₂H]⁺ reside. Here again there is not direct linkage between the anionic network and the embedded cations, the interactions taking part being the coulombian as well as van der Waal's.

In both structures the guest species corresponds to an adduct of a heterocyclic base with its conjugated cation. In the case of **1** there are no differentiated roles for the base/cation as the proton lays on a symmetry centre and the group displays a [Q–H–Q]⁺ linear arrangement similar to one reported for diquinuclidinone [29]. The considerably short 1.341(3) Å N–H distance in the compound here described is similar to that determined by neutron diffraction studies for the perchlorate salt of the diquinuclidinium homoconjugated cation ($d(\text{N–H}) = 1.317 \text{ \AA}$, $\text{N–H–N angle} = 175.7^\circ$) [29].

Table 1. Crystal data and structure refinement for **1** and **2**

| Identification code | 1 | 2 |
|---|---|---|
| Formula | 2(C ₄ H ₄ N ₂ S)Br ⁻¹ (C ₁₄ H ₂₇ N ₂) ⁺¹ | (C ₄ H ₄ N ₂ S)I ⁻¹ (C ₇ H ₁₄ N) ⁺¹ (C ₇ H ₁₃ N) |
| Formula weight | 455.53 | 426.40 |
| Temperature | 293(2) K | 293(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å |
| Crystal system | Monoclinic | Triclinic |
| Space group | C2/c | P-1 |
| a/Å | 13.418(10) | 10.1003(15) |
| b/Å | 11.546(6) | 10.1148(15) |
| c/Å | 14.916(10) | 10.9033(16) |
| α/° | 90 | 63.889(2) |
| β/° | 99.09(6) | 83.889(2) |
| γ/° | 90 | 77.779(2) |
| Volume/Å ³ | 2282(3) | 977.4(3) |
| Z | 4 | 2 |
| D _c /g cm ⁻³ | 1.326 | 1.449 |
| Absorption coefficient/mm ⁻¹ | 1.996 | 1.746 |
| F(000) | 960 | 436 |
| Crystal size/mm ³ | 0.14 × 0.05 × 0.02 | 0.10 × 0.04 × 0.01 |
| Theta range for data collection | 2.34 to 25.06° | 2.06 to 23.24 |
| Index ranges | 0 < = h < = 15, 0 < = k < = 13, -17 < = l < = 17 | -11 < = h < = 11, -11 < = k < = 9, -12 < = l < = 12 |
| Reflections collected | 2099 | 12774 |
| Independent reflections | 1993 [R(int) = 0.0913] | 2760 [R(int) = 0.0458] |
| Absorption correction | Psi-scan | Multi-scan |
| Max. and min. transmission | 0.9612 and 0.7675 | 0.9828 and 0.8448 |
| Data/parameters | 1993 / 117 | 2760 / 195 |
| Goodness-of-fit on F ² | 1.055 | 1.044 |
| Final R indices [I > 2σ(I)] | R1 = 0.0494, wR2 = 0.1181 | R1 = 0.0443, wR2 = 0.1252 |
| R indices (all data) | R1 = 0.0749, wR2 = 0.1323 | R1 = 0.0447, wR2 = 0.1258 |
| Extinction coefficient | 0.0087(11) | 0.020(3) |
| Largest diff. peak and hole / e.Å ⁻³ | 0.882 and -0.677 | 0.887 and -1.175 |

Table 2. Hydrogen bonds for **1** [Å and °]

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------|--------|----------|----------|--------|
| N(2)-H(2A)...Br(1) | 0.86 | 2.63 | 3.426(4) | 155.1 |
| N(2)-H(2B)...S(1)#1 | 0.86 | 2.63 | 3.476(4) | 167.6 |
| N(3)-H(3A)...Br(1) | 0.86 | 2.59 | 3.396(4) | 156.9 |
| N(3)-H(3B)...S(1)#2 | 0.86 | 2.64 | 3.470(4) | 161.5 |

Symmetry transformations used to generate equivalent atoms: #1 -x + 1/2, -y + 1/2, -z + 1 #2 -x + 1, -y + 1, -z + 1 #3 -x + 1, y, -z + 3/2.

The [Q₂H]⁺ group in **2**, instead, is clearly differentiated into a well defined QH⁺ cation and a neutral Q base to which it is strongly H-bonded, (N1A-H1: 0.99(9), H1...N1B: 1.71(9) Å, N1A-H1...N1B: 175(7)°) as shown in Figure 3.

Vibrational analysis of a [Q-H-Q]⁺ linear arrangement as the one in **1** predicts absorption at 668 cm⁻¹ for the symmetric N...N stretching mode, and 1260 cm⁻¹ for the antisymmetric ion transfer vibrations. Corresponding features are indeed apparent in the IR spectrum of [Q₂H]⁺, in which a characteristic frequency at 2937 cm⁻¹ has been observed [30]. Thus, for **1** beside the

Table 3. Hydrogen bonds for **2** [Å and °]

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------|---------|----------|----------|--------|
| N(2)-H(2A)...I(1)#1 | 0.86 | 2.92 | 3.723(4) | 155.9 |
| N(2)-H(2B)...S(1)#2 | 0.86 | 2.60 | 3.433(4) | 164.6 |
| N(3)-H(3A)...I(1)#1 | 0.86 | 2.89 | 3.695(5) | 157.2 |
| N(3)-H(3B)...I(1) | 0.86 | 2.89 | 3.723(4) | 163.5 |
| N(1A)-H(1)...N(1B) | 0.99(9) | 1.71(9) | 2.704(5) | 175(7) |

Symmetry transformations used to generate equivalent atoms: #1 -x, -y + 1, -z + 1 #2 -x, -y + 1, -z.

quinuclidine absorption (at 2930 cm⁻¹) and the characteristic stretching modes of the thiourea network (observed normally at 1470 and between 3169 and 3367 cm⁻¹) [31], a relatively intense absorption band at 1433 cm⁻¹ and a weak absorption at 659 cm⁻¹ are clearly seen. Relative absorption values for thiourea, quinuclidine, **1** and **2**, are shown in Table 4.

If crystals of the products are left in contact with a highly polar solvent as DMSO or water [27], the quinuclidine appears to be rashly extracted from the solid propelling the crystal through the liquid surface. The evolution of the quinuclidine may be visually

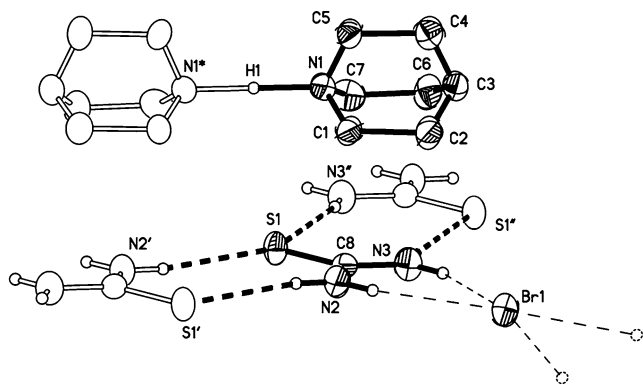


Figure 1. Molecular ellipsoid diagram of **1**, drawn at a 40% probability label. The independent part has been drawn in full ellipsoids; empty ellipsoids denote symmetry related moieties. Note the way in which thiourea chains build up, through N–H...S interactions (heavy broken lines). In thin broken lines, N–H...Br contacts linking chains and defining the anionic network (See text).

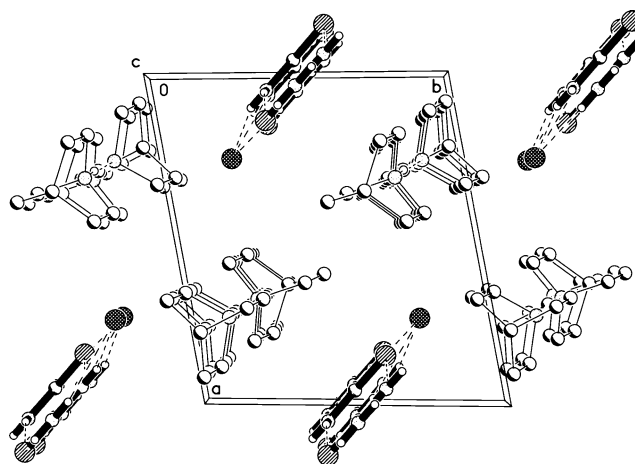


Figure 4. Schematic packing diagram of **2** drawn along (001) and showing the non-interacting anionic ribbons (in heavy full lines) coming out of the figure. In thin lines, the included $[Q_2H]^+$ cations.

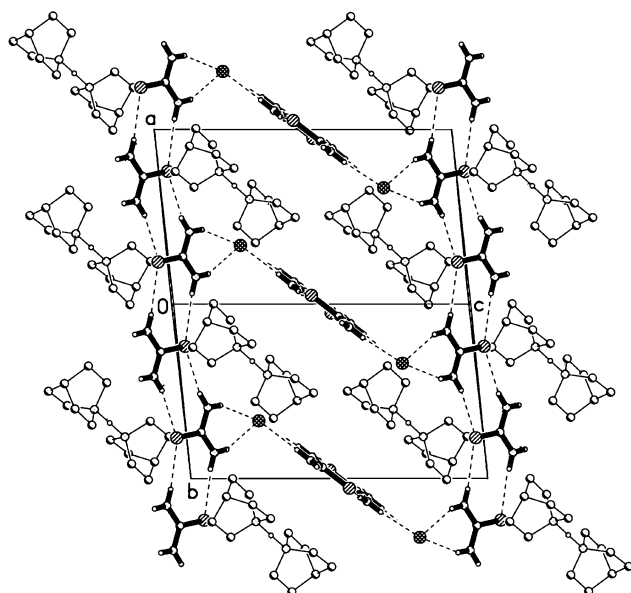


Figure 2. Schematic packing diagram of **1** drawn along (110) and showing the structural cavities defined by the two different orientations of thiourea ribbons (in heavy full lines) connected by N–H...Br interactions. In thin lines, the included $[Q_2H]^+$ cations.

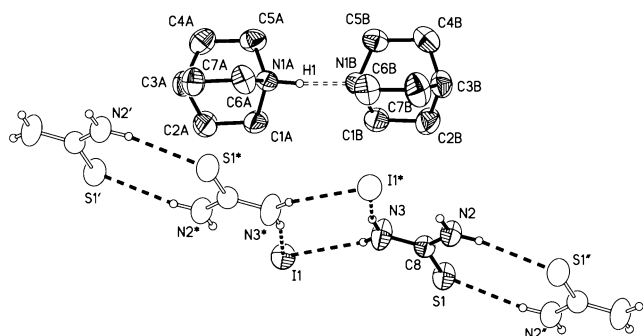


Figure 3. Molecular ellipsoid diagram of **2**, drawn at a 40% probability label. The independent part has been drawn in full ellipsoids; empty ellipsoids denote symmetry related moieties. Note the way in which anionic chains, including iodine ions, build up through N–H...S and N–H...I interactions (heavy broken lines) (See text).

Table 4. Characteristic vibrational frequencies $[cm^{-1}]$ of thiourea, **1**, thiourea $_2$ [quinclidine $_2H$] $^+ Br^-$ and **2**, thiourea $_2$ [quinclidine $_2H$] $_2^+ I_2^-$

| | Thiourea | Q...Q | 1 | 2 |
|--------------------------|----------|-------|----------|----------|
| $\nu(N-H)_{asym.}$ | 3367 | | 3314 | 3308 |
| $\nu(N-H)_{sim.}$ | 3169 | | 3147 | 3144 |
| $\nu(C-N)$ | 1470 | | 1433 | 1449 |
| $\nu(C-H_2)$ | | 2937 | 2930 | 2933 |
| $\nu(N\cdots N)_{asym.}$ | | 1260 | 1334 | 1317 |
| $\nu(N\cdots N)_{sym.}$ | | 668 | 659 | 652 |

observed by adding phenolphthalein to the solution. The motion effect is thus accompanied by the formation of a beautiful red “wake” in the liquid. This experiment suggests that the hosts structures experiment a rupture and it produces thiourea, Br^- or I^- , proton and quinclidine in dissolution.

Acknowledgement

Research financed by FONDECYT (1050287)

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