

Protonated bis(quinuclidine) included in layered bis(urea)–bromide and -iodide hosts: new ternary urea inclusion compounds

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The synthesis, crystal structure, and properties of novel ternary inclusion compounds formed by the insertion of protonated bis(quinuclidine[†]) guests into urea–bromide and urea–iodide anionic hosts are reported. (Urea₂[quinuclidine₂H]⁺Br⁻), **1**, and (urea₂[quinuclidine₂H]⁺I⁻), **2**, are monoclinic, space group *C2*. ‡ The cell parameters for **1** are *a* = 19.323(8), *b* = 7.145(3), *c* = 8.566(4), β = 112.19(3), d_{calc} = 1.284 and *Z* = 4, considering 472 reflections; for **2** they are *a* = 20.51(11), *b* = 7.34(3), *c* = 8.17(4), β = 111.81(8), d_{calc} = 1.369, *Z* = 4, considering 716 reflections. In the two structures each urea molecule interacts with adjacent urea molecules *via* N–H \cdots O hydrogen bonds forming a ribbon-like arrangement. The ribbons are linked through halide ions by N–H \cdots X hydrogen bonds forming layered structures. The distances between the layers are 10.301 Å for **1** and 8.566 Å for **2**. The compounds may be described as commensurate species. Conductivity values determined for **1** and **2** at room temperature are 1.19×10^{-5} and 8.66×10^{-7} ($\Omega \text{ cm}$)⁻¹, and they increase with temperature. Aspects of the thermal stability of the products are discussed.

Introduction

Inclusion compounds are suitable systems for investigating the nature of molecular guest–host interactions; they have also received increasing attention as materials for applications in electronics and optoelectronics.^{1–3} Host materials such as urea, thiourea, cyclodextrins, calixarenes, zeolites and perhydrotriphenylene permit specific host–guest architectures, where guest molecules are incorporated along channels, within layers, or in isolated cages.^{4–6} Among these compounds, urea inclusion compounds have been particularly investigated. X-Ray diffraction studies have shown that typical binary compounds, such as those with hydrocarbons included in urea, lead to hexagonal channel structures.^{7–9} Guest species containing amine or azacyclo groups may also be included in urea and thiourea hosts.^{10–14} By using 1,2-diazabicyclo[2.2.2]octane or hexamethylenetetraamine as guest and thiourea as host, it has been possible to obtain binary layered inclusion compounds.^{14,15} The urea host is formed by hydrogen bonding, and a variety of guest molecules of appropriate size and shape can be included. However, the small urea channels are appropriate for storing, for example, only non-branched hydrocarbon chains. In this way, it is interesting to obtain derivatives of a urea matrix containing channels or layers large enough to accommodate bulky molecules. The synthesis of ternary compounds offers this possibility. Furthermore, if both host and guest are charged species, there is also the possibility of obtaining ion conductive materials.

Examples of ternary complexes of urea are scarce.^{16–18} The structural characterization of the isomorphous series of [(C₂H₅)₄N⁺X⁻](NH₂)₂CO·2H₂O (X = Cl, Br, CN) has been reported. In these compounds the cations are sandwiched between hydrogen-bonded urea–water–halide/pseudohalide puckered layers.¹⁷

We have chosen quinuclidine as a guest considering both its small cyclic structure and relatively mild basic properties. The proton affinity of quinuclidine is 236 kcal mol⁻¹; furthermore, a three-dimensional space occupation model indicates that there is no tension energy as in other pyramidal nitrogen compounds such as triethylamine.¹⁹

In this paper we describe the synthesis, characterization and conductivity properties of urea₂[quinuclidine₂H]⁺Br⁻ (**1**) and urea₂[quinuclidine₂H]⁺I⁻ (**2**).

Experimental

Commercially available reagents were used as received. The products were obtained from solutions of urea, quinuclidine and lithium halide in a 2:2:1 molar ratio in methanol, by slow evaporation of the solvent at room temperature. After about 24 h, well formed thin plate crystals could be separated. The products were washed with cold methanol and dried under vacuum. The crystals, showing characteristic behaviour by polarized light microscopy, may be rapidly distinguished and separated from lithium halide, quinuclidine or pure urea; the purity was also verified by polycrystalline powder diffraction analysis of the samples. The crystals decompose in water producing a characteristic, visually observable dynamic effect.²⁰

¹³C CP-MAS NMR spectra were recorded on a Bruker AMX-300 spectrometer at a frequency of 75.47 MHz for ¹³C. The number of scans was 4096 with 5.0 μ s 90° pulses; 5 ms cross-polarisation contact time; 50 ms acquisition time during proton decoupling; and 5 s recycle delay. The samples were spun at a frequency of 4 kHz. The chemical shifts are given with respect to TMS using glycine (175 ppm) as an external standard.

Single crystals were selected for X-ray diffraction analysis. Data were collected on a Siemens R3m/V diffractometer with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 293 K. Intensity data were corrected for **1** and **2** for Lorentz polarization, and for **2** also for absorption. The crystals

[†] Quinuclidine corresponds to 1-azabicyclo[2.2.2]octane.

[‡] The compounds can be refined in the symmetry space group *C2/m* but attempts to do this proved fruitless due to disorder problems.

correspond to space group *C2*. The structures were solved by direct methods using the SHELXS-97 program.²¹ The positions of the hydrogen atoms were calculated geometrically using the riding model with fixed isotropic temperature factors. Complete CIF file sets have been deposited at the Cambridge Crystallographic Data Centre. §

For conductivity measurements in the 1–10⁵ Hz range, a Parc electrochemical impedance analyzer model 6310 was used.

Results and discussion

The synthesis of the compounds was carried out in methanol; the partial hydrolysis of lithium bromide and lithium iodide produced protons and halide ions necessary for obtaining both the ionic guest and host. Moreover, this method of synthesis allows the removal of water from the solvent, so the crystals do not contain water, as seen in the only known ternary urea compounds reported up to now.¹⁷

The structure of the compounds was determined. As shown in Fig. 1, the urea molecules and bromide ions form nearly

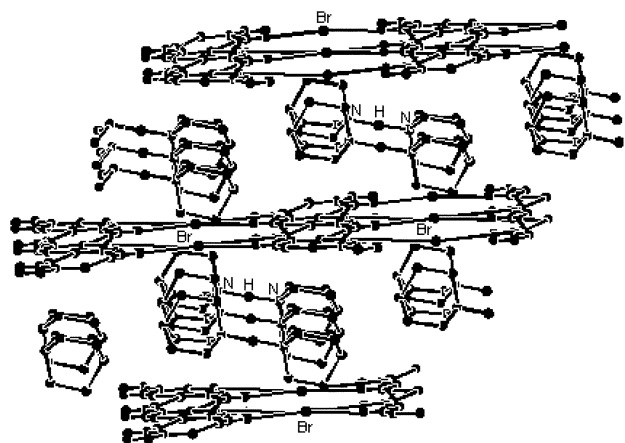


Fig. 1 Layer structure of **1**, urea₂[quinuclidine₂H]⁺Br⁻. Diquinuclidinium ions are sandwiched between the host layers of parallel hydrogen bonded urea ribbons cross-bridged by Br⁻ and I⁻ anions.

planar layers with the diquinuclidinium ions sandwiched between them. The layers result from parallel hydrogen-bonded urea ribbons cross-bridged by Br⁻ or I⁻ anions. Each urea molecule interacts with adjacent urea molecules via N–H···O hydrogen bonds to give a ribbon-like arrangement, forming four N–H···X hydrogen bonds with a halide ion in **1** and two in **2**; this results in an anionic framework ribbon as a component in the crystal packing.

Structural parameters as well as most relevant bond distances and angles are given in Table 1. The H-bond lengths of N···H···N within the bridged quinuclidine moieties are 1.36 Å for **1** and 1.38 Å for **2**, and the angles are 177.1° and 149.5° for **1** and **2**, respectively. The distances between the layers are 10.301 Å for **1** and 8.566 Å for **2**.

A fundamental issue for conventional binary channel urea inclusion compounds is to know the correlation between the position of the guest molecules in different tunnels and the overall three-dimensional ordering of the guest molecules.^{22–24} In commensurate systems there is a well defined positioning of the guest molecules at specific locations within each channel, which thus gives rise directly to a three-dimensionally ordered arrangement of guest molecules controlled by the three-dimensional periodicity of the host structure. Most binary inclusion compounds of urea are incommensurate,²³ however,

Table 1 Structural parameters for **1**, urea₂[quinuclidine₂H]⁺Br⁻ and **2**, urea₂[quinuclidine₂H]⁺I⁻

	1	2
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2</i>	<i>C2</i>
Empirical formula	C ₈ H _{17.5} Br _{0.5} N ₃ O	C ₈ H _{17.5} I _{0.5} N ₃ O
<i>a</i> /Å	19.323(8)	20.51(11)
<i>b</i> /Å	7.145(3)	7.34(3)
<i>c</i> /Å	8.566(4)	8.17(4)
β/°	112.19(3)	111.81(8)
Cell volume/Å ³	1095.0(8)	1095.0(8)
<i>Z</i> (formula units/cell)	4	4
Density (calculated)/g ml ⁻¹	1.284	1.369
Absorption coefficient μ/mm ⁻¹	1.897	1.423
<i>F</i> (000)	448	484
Radiation source	Mo Kα	Mo Kα
Wavelength/Å	0.71073	0.71073
Data collection temperature/K	293(2)	293(2)
Two-theta range/°	4.56–50.04 –22 < <i>h</i> < 21	4.28–49.98 –24 < <i>h</i> < 24
Index ranges	0 < <i>k</i> < 8 0 < <i>l</i> < 10	–8 < <i>k</i> < 0 –9 < <i>l</i> < 9
Reflections collected	1046	1094
Observed reflections	472	716
Residuals (observed data)	0.0607	0.0409
Residuals (all data)	0.1787	0.0708

Table 2 *c_g*, *c_h* and *c_g/c_h* values of **1**, urea₂[quinuclidine₂H]⁺Br⁻ and **2**, urea₂[quinuclidine₂H]⁺I⁻

Compound	<i>c_g</i> /Å	<i>c_h</i> /Å	<i>c_g/c_h</i>
1	7.9353	8.57	0.93
2	7.5852	8.17	0.93

amine–urea binary inclusion compounds have commensurate properties.¹⁰ In incommensurate systems the host substructure can be considered in terms of a basic structure with a period *c_h* along the channel, which is subjected to an incommensurate modulation with period *c_g* along the channel through its interaction with the guest substructure.

The positional relationship between molecules in adjacent channels is conveniently described in terms of the offset, denoted by Δ_g, along the channel axis between the centres of mass of guest molecules in adjacent channels. An inclusion compound is described as incommensurate if there are no sufficiently small integers *p* and *q* for which *pc_g* = *qc_h*, while it is considered to be commensurate if sufficiently small integers *p* and *q* to satisfy this equality can be found. We apply these concepts developed for channel structures to the urea layered structures **1** and **2**. From crystallographic studies we can obtain *c_g* and *c_h*; the former corresponds to the distance associated with *h k l*, *i.e.* 0 0 1, and the latter to lattice parameter *c*. In the layered compounds **1** and **2**, the axis *c* coincides with the inter-layer axis. Table 2 shows the *c_g* and *c_h* values and the *c_g/c_h* ratios for **1** and **2**. They clearly indicate that both compounds are commensurate; *i.e.* around each guest molecule there is the same host structural conformation. A schematic comparison of the typical incommensurate situation of most urea binary compounds and the commensurate behaviour of **1** and **2** is shown in Fig. 2.

Compounds **1** and **2** do not present topotactic properties. Obviously, the anionic matrix structure needs the presence of the cationic guest, so the escape of the guest leads to the destruction of the host structure. Differential thermal analysis of **1**, illustrated in Fig. 3, shows a relatively wide, slightly asymmetric strong peak centred at 107.7 °C, corresponding to the melting point. The loss of mass due to the rupture of the matrix hydrogen bonds and the simultaneous escape of the guest begin at exactly this temperature. At 260 °C, when 27.5% of the total mass is lost, a clear change of the mass loss rate is observed.

§ CCDC reference numbers 177892 and 177893. See <http://www.rsc.org/suppdata/p2/b2/b201053b/> for crystallographic files in .cif or other electronic format.

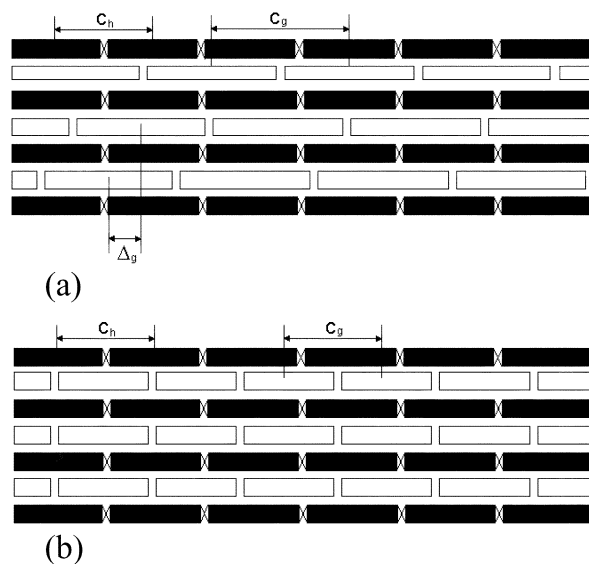


Fig. 2 Schematic comparison between (a) an incommensurate structure corresponding to most binary channel urea inclusion compounds and (b) the commensurate structure for **1** and **2** here described, with c as the interlayer axis.

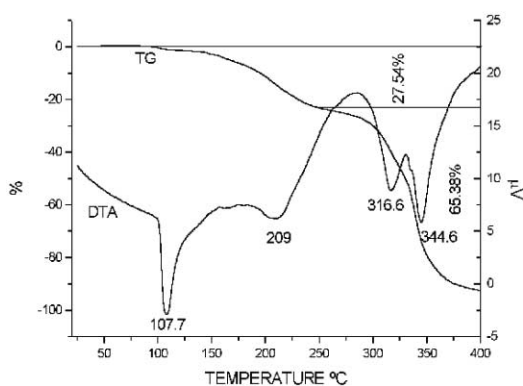


Fig. 3 Thermal analysis, DTA and TG of **1**, urea₂[quinuclidine₂H]⁺Br⁻.

If the crystals of the products are left in contact with a high polarity solvent such as DMSO or water,²⁰ the quinuclidine appears to be rapidly extracted from the solid, propelling the crystal through the liquid surface. The evolution of the quinuclidine may be observed visually 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 the rupture of the host structure producing urea, X⁻ (I⁻ or Br⁻), protons, and quinuclidine in solution.

The room-temperature ¹³C CP-MAS NMR spectra of the studied compounds, illustrated in Fig. 4, show a wide signal centred at 164.7 ppm (line width ≈250 Hz) for **1** and 164.3 ppm (line width ≈197 Hz) for **2**, corresponding to the carbonyl carbon. Similar chemical shift values have been reported previously for urea in binary inclusion compounds.²⁵ Relatively narrow signals corresponding to the carbon nuclei (C_α) bonded directly to the nitrogen atom in the diquinuclidinium ion appear at 46.94 ppm (line width ≈77.6 Hz) and 47.07 ppm (line width ≈79.9 Hz) for **1** and **2**, respectively. For ¹³C directly bonded to nitrogen (¹⁴N, $I = 1$), MAS frequently gave a powder pattern consisting of a doublet because the ¹³C and ¹⁴N residual dipolar interaction is not averaged to zero by MAS-NMR.^{26–28} In spite of low amplitude motions of the diquinuclidinium guest between the host layers, at room temperature these doublets are not observed. Table 3 shows the chemical shifts in the ¹³C CP-MAS NMR of urea, quinuclidine and compounds **1** and **2**. The influence of hydrogen bonding on the ¹³C chemical shifts

Table 3 ¹³C CP-MAS NMR chemical shifts of urea, quinuclidine, compound **1**, urea₂[quinuclidine₂H]⁺Br⁻ and compound **2**, urea₂[quinuclidine₂H]⁺I⁻

Compound	¹³ C Urea (ppm)	¹³ C Quinuclidine (ppm)		
		α	β	γ
Urea	174			
Quinuclidine		49.02	28.34	22.26
1	164.74	46.94	24.82	20.31
2	164.29	47.07	24.50	20.02

Table 4 Conductivity data (Ω cm)⁻¹ for urea, **1**, urea₂[quinuclidine₂-H]⁺Br⁻ and **2**, urea₂[quinuclidine₂H]⁺I⁻ measured for pellets and showing dependence on temperature

T/°C	Urea _{amb} ^a	1 _{amb}	1 _{vac} ^b	2 _{amb}	2 _{vac}
25	6.84 e ⁻⁸	1.19 e ⁻⁵	1.13 e ⁻⁷	8.66 e ⁻⁷	2.58 e ⁻⁶
40	3.64 e ⁻⁸	2.73 e ⁻⁵	3.55 e ⁻⁷	1.10 e ⁻⁶	3.13 e ⁻⁶
60	1.81 e ⁻⁸	3.21 e ⁻⁵	7.09 e ⁻⁶	1.81 e ⁻⁶	5.40 e ⁻⁶
77	1.95 e ⁻⁸	1.13 e ⁻⁴	3.64 e ⁻⁶	4.88 e ⁻⁶	

^a amb = ambient. ^b vac = vacuum.

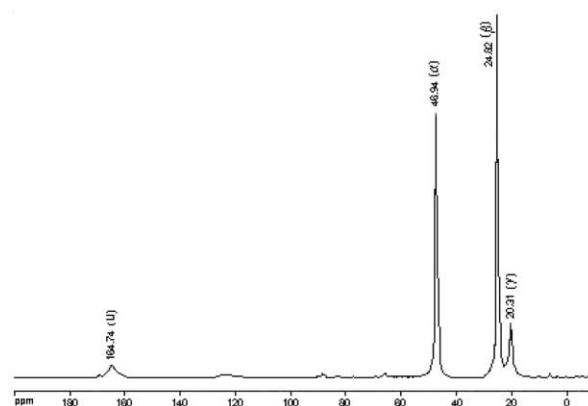


Fig. 4 ¹³C CP-MAS NMR spectrum of inclusion compound **1**, urea₂[quinuclidine₂H]⁺Br⁻.

may be understood in general by the sigma electron push-pull effects^{19,27,29} produced, in our case, by the charge displacements from quinuclidinium ions toward the polyanionic acceptor matrix *via* hydrogen bonding. According to the isovalent hybridization concept,¹⁹ the interaction of the basic quinuclidine nitrogen atom with the protons should induce an increment of the s-character of the C_α hybrid orbitals directed toward its neighbours, but the N-atom produces a high field shift of its ¹³C NMR signal. The ¹H CP-MAS NMR signal corresponding to the proton bridge to quinuclidine that appears at 1.68 ppm for **1** and at 2.82 ppm for **2**, is probably overlapped with the signal of the proton linked to the γ-carbon, which can be determined by the integration values of the signals.

Ionic conductivity studies for compounds **1** and **2** were also carried out using a diffuse impedance instrument. Measurements were made using composed polycrystalline samples, since obtaining crystals of adequate size for anisotropic measurements was unsuccessful. The conductivity in these samples, which is probably produced by proton displacement, depends on the conditions of the measurements. It increases noticeably with temperature. The presence of humidity permits greater cohesion of the crystalline powder, facilitating the formation of better press pellets. Table 4 shows the temperature dependence of the conductivity of urea, **1** and **2**.

Conclusions

In summary, the synthesis, crystal structure, conductivity and thermal properties of the novel ternary inclusion compounds

urea₂[quinuclidine₂H]⁺Br⁻ and urea₂[quinuclidine₂H]⁺I⁻ have been investigated systematically with a wide range of characterisation and analytical methods (¹³C and ¹H CP-MAS NMR spectra, X-ray diffraction analysis, electrochemical impedance spectroscopy, DTA/TG).

In the structure of both compounds the urea molecules and bromide or iodide ions form nearly planar layers with the diquinuclidinium ions sandwiched between them. The layers result from parallel hydrogen-bonded urea ribbons cross-bridged by Br⁻ or I⁻ anions.

Both inclusion compounds are commensurate, *i.e.* around each guest molecule there is the same host structural conformation.

The conductivity of polycrystalline samples of the synthesised inclusion compounds depends on the measurement conditions, increasing with temperature and humidity. At room temperature the values are 1.19×10^{-5} and 8.66×10^{-7} ($\Omega \text{ cm}$)⁻¹, respectively, for the bromide and iodide derivatives.

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