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Two inclusion compounds of guanylthiourea and 1,3,5-thiadiazole-5-amido-2-carbamate

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Abstract In the crystal structure of $[(n\text{-}C_4H_9)_4N]^+\cdot[NH_2(C_2N_2S)NHCOO^-]\cdot NH_2CSNC(NH_2)_2$ (**1**), guanylthiourea molecules and 1,3,5-thiadiazole-5-amido-2-carbamate ions are joined together by intermolecular N–H…O, N–H…N, and weak N–H…S hydrogen bonds to generate stacked host layers corresponding to the (110) family of planes, between which the tetra-n-butylammonium guest cations are orderly arranged in a sandwich-like manner. In the crystal structure of $[(n\text{-}C_3H_7)_4N]^+\cdot[NH_2(C_2N_2S)NHCOO^-]\cdot NH_2CSNC(NH_2)_2\cdot H_2O$ (**2**), the tetrapropyl ammonium cations are stacked within channels each composed of hydrogen bonded ribbons of guanylthiourea molecules, 1,3,5-thiadiazole-5-amido-2-carbamate ions and water molecules.

Introduction

Guanylthiourea is an important industrial and biological molecule. In conjunction with mercaptobenzothiazyl disulfide, it is used as an accelerator in sulfur vulcanization of natural rubber. In chemical synthesis, its special molecular skeleton and hydrogen-bonding capability has been utilized to synthesize anion-caged supermolecular compounds [1]. However, it is in the field of medicine that guanylthiourea finds the most important applications: it is a well-known stimulator of intestinal peristalsis and has been clinically applied to treat bowel paresis in peritonitis [2]; it has also shown promising use in clinical trials as an immunostimulant and tumor-cell inhibitor [3, 4]. Generally, organic compounds incorporating thioureido and guanidino units are useful as radioprotective agents [5]. In fact, guanylthiourea and its derivatives have been demonstrated to give a 66% survival rate when subjected to potentially lethal radiation doses.

In the field of supramolecular chemistry, research involving guanylthiourea mainly focuses on its coordination to transition metals, thereby generating molecular containers that may either enhance their Lewis acidity or introduce magnetic, electrochemical and/or luminescent properties into the host molecules. Guanylthiourea can coordinate to metal centers via (*N,N*) or (*N,S*) modes, yielding cationic host frameworks such as molecular squares and cages (**1**). Whilst anionic guests can be selectively encapsulated, the nature of such species has received much less attention [6, 7].

For nearly two decades, we have undertaken a systematic study on the construction of new urea/thiourea/selenourea-anion inclusion compounds and their hydrogen-bonding modes in the crystalline state [8, 9]. Our results have shown that such inclusion compounds can comprise quite different types, depending on their anionic host components and quaternary ammonium templates [10, 11]. On the other hand, a number of inclusion compounds have been synthesized based on aliphatic or aromatic poly-carboxylic acids, with or without the participation of urea or thiourea molecules [12, 13]. In this paper, we report the preparation and structural characterization of two new inclusion complexes formulated as $[(n\text{-}C_4H_9)_4N]^+\cdot[NH_2(C_2N_2S)NHCOO^-]\cdot NH_2CSNC(NH_2)_2$ (**1**)

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and $[(n\text{-}C_3H_7)_4N]^+\cdot[NH_2(C_2N_2S)NHCOO^-]\cdot NH_2CSNC$ $(NH_2)_2\cdot H_2O$ (**2**), in which guanylthiourea and the 1,3,5-thia-diazole-5-amido-2-carbamate ion constitute an anionic host lattice that accommodates the tetra-*n*-alkylammonium guest molecule. The synthesis of 1,3,5-thiadiazole-5-amido-2-car-bamic acid was reported a long time ago, but to our knowledge the literature hitherto contains no crystallographic structural information on this compound [14].

Results and discussion

Crystal structure of 1

The hydrogen-bonding interactions in the host lattice of **1** are best described with the aid of Fig. 1; Table 1. The guanylthiourea molecule (referred to as **S2** for conve-nience) exhibits intramolecular hydrogen bonding (motif **A**), and symmetry-related molecules are joined together by pairs of strong N–H…N hydrogen bonds to form dimer **B** in a nearly co-planar manner, as indicated by the torsion angle of 7.6°. Symmetry-related 1,3,5-thiadiazole-5-amido-2-carbamate ions (referred to as S1 for convenience) are linked together by pairs of strong N–H…N hydrogen bonds to form dimer **C**. Adjacent S1 dimers related by simple translation along the *c*-axis are further connected together by charge-assisted N–H…O$^-$ hydrogen bonds [motif **D** = $R_2^2(8)$] to form an infinite chain running parallel to the [001] direction. Thus, S1 dimers are located in the midst of adjacent chains. In detail, the amidinium groups of
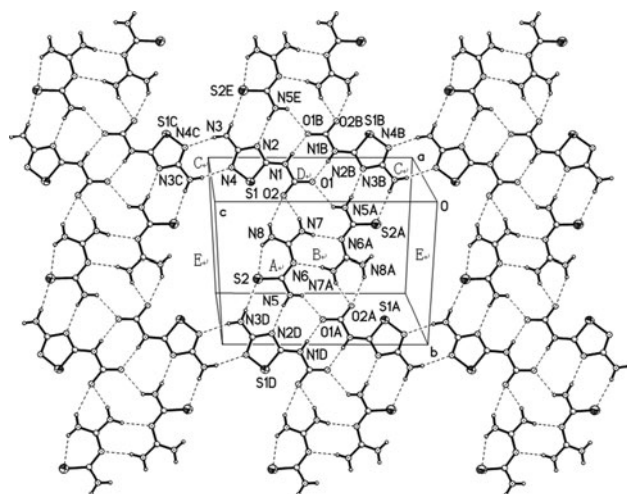

Fig. 1 Projection showing the hydrogen-bonding interactions in the host lattice of **1** constructed with guanylthiourea and the 1,3,5-thiadiazole-5-amido-2-carbamate ion. The host layer structure matches the (110) family of planes. Symmetry transformations: **a** $1-x$, $1-y$, $1-z$; **b** $2-x$, $-y$, $1-z$; **c** $2-x$, $-y$, $2-z$; **d** $-1+x$, $1+y$, z; **e** $1+x$, $-1+y$, z

Table 1 Selected bond distances (Å) and bond angles (°) for the host molecules of **1**

C(1)–O(1)	1.241(2)	S(2)–C(4)	1.715(1)
C(1)–O(2)	1.245(2)	C(3)–N(4)	1.307(2)
C(1)–N(1)	1.411(2)	C(3)–N(3)	1.362(2)
N(1)–C(2)	1.351(2)	C(4)–N(5)	1.331(2)
S(1)–N(4)	1.678(1)	C(4)–N(6)	1.341(2)
S(1)–C(2)	1.723(1)	C(5)–N(8)	1.316(2)
C(2)–N(2)	1.316(2)	C(5)–N(7)	1.316(2)
N(2)–C(3)	1.374(2)	C(5)–N(6)	1.343(2)
O(1)–C(1)–O(2)	127.8(1)	N(4)–C(3)–N(2)	119.4(1)
O(1)–C(1)–N(1)	116.8(1)	N(3)–C(3)–N(2)	118.0(1)
O(2)–C(1)–N(1)	115.4(1)	N(5)–C(4)–N(6)	113.6(1)
C(2)–N(1)–C(1)	121.9(1)	N(5)–C(4)–S(2)	116.8(1)
N(4)–S(1)–C(2)	91.50(6)	N(6)–C(4)–S(2)	129.6(1)
N(2)–C(2)–N(1)	123.2(1)	C(3)–N(4)–S(1)	108.2(1)
N(2)–C(2)–S(1)	112.4(1)	N(8)–C(5)–N(7)	116.7(1)
N(1)–C(2)–S(1)	124.5(1)	N(8)–C(5)–N(6)	126.9(1)
C(2)–N(2)–C(3)	108.6(1)	N(7)–C(5)–N(6)	116.4(1)
N(4)–C(3)–N(3)	122.6(1)	C(4)–N(6)–C(5)	125.3(1)

S2 and S1 anions are joined together by pairs of N–H…O hydrogen bonds; the thioureido groups of S2 and **S1** anions are joined together by pairs of N–H…O$^-$, N–H…N imparted hydrogen bonds and a pair of N–H…S hydrogen bonds, thus enabling S2 to act as a hydrogen-bond donor and acceptor simultaneously. As a result, an essentially planar host layer with large voids **E** is generated. The mean planes of the host layer structure matches the (110) family of planes, with an interlayer spacing of about 8.78 Å to accommodate the tetra-*n*-butylammonium cations (Fig. 2). Apart from the traditional strong hydrogen bonds that consolidate the host lattice, the weak C–H…N intermo-lecular interaction [H…N = 2.59 Å, being shorter than the van der Waals contact of H…N = 2.75 Å)] also plays an important role in providing additional stabilization.

Crystal structure of 2

The hydrogen-bonding scheme in the host lattice of **2** can be described with the aid of Figs. 3, 4; Table 2. The 1,3,5-thiadiazole-5-amido-2-carbamate ion (referred to as S1 for convenience) and the guanylthiourea molecule (referred to as S2) are joined together by pairs of strong N–H…O hydrogen bonds to form dimer A [motif **A** = $R_2^2(8)$], as indicated by the torsion angle of 54.8°. S1–S2 dimers related by glide plane (001) and bridging water molecules are interconnected by hydrogen bonds to generate an infi-nite chain running parallel to the [001] direction (Fig. 3). In detail, the thioureido groups of S2 and imino group of S1B are joined together by three hydrogen bonds (N–H…O and a pairs of N–H…N), thus enabling S2 to act simultaneously
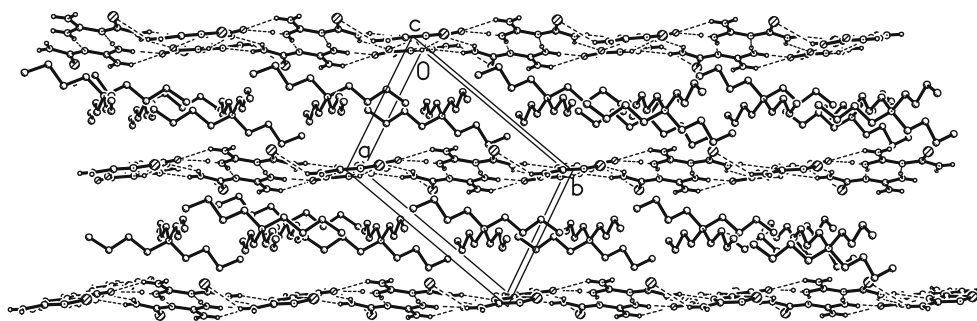
Fig. 2 Perspective view of a portion of the crystal structure of **1** showing the well-ordered tetra-*n*-butylammonium cations sandwiched between the anionic host layers. The hydrogen atoms of the organic cations are omitted for clarity
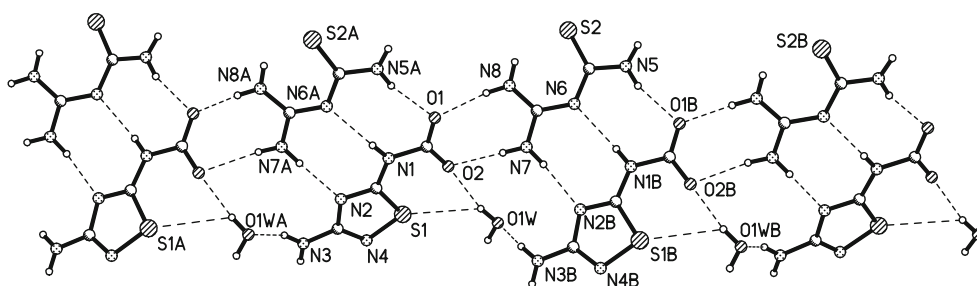

Fig. 3 An infinite chain running parallel to the [001] direction in the host lattice of **2** constructed by hydrogen-bonding interactions between guanylthiourea, 1,3,5-thiadiazole-5-amido-2-carbamate and the water molecule. Symmetry transformations: **a** x, $3/2 - y$, $-1/2 + z$; **b** x, $3/2 - y$, $1/2 + z$

as a donor and acceptor (motif **B** = $R_2^2(8)$). The amino group N7 of **S2** and the central atom N2 of five-membered ring **S1B** form a N7–H...N2B hydrogen bond (motif **C** = $R_2^2(8)$). Water molecule O1 W located between adjacent dimers behaves as a hydrogen-bond donor (forming O–H...O and O–H...S; motif **D**) and acceptor (with amino group N3 of adjacent dimer S1B; motif **E** = $R_4^3(10)$). Thus with the participation of water molecules and its inherent hydrogen-bonding capacity, the **S1**–**S2** dimer serves as a vertex of a lozenge pipeline to generate an infinite chain along the c-axis (Fig. 3). Adjacent infinite chains are interlinked by two kinds of connections: one involves S1 and water molecules O1 W and their symmetry-equivalents (motif **F** = $R_4^4(10)$, Fig. 5a); the other involves the thioamino groups of **S2** across an inversion center (motif **G** = $R_2^2(8)$, Fig. 5b). Hence four vertices are connected together like a lozenge pipe through these two kinds of connections, yielding a channel-type host lattice that are neatly filled by rows of tetrapropyl ammonium guest cations (Fig. 4).

Discussion of crystal structure

In inclusion complex **1**, 1,3,5-thiadiazole-5-amido-2-carbamate S1 and guanylthiourea S2 each forms a conventional cyclic, planar hydrogen-bonded dimer, and these two kinds of dimer are connected to yield a layer-type anionic host lattice. In contrast, S1 and **S2** in inclusion complex **2** form non-planar S1–S2 hydrogen-bonded dimers with large torsion angles, and the water molecule also participates in the construction of the host lattice, resulting in a three-dimensional tubular structure.

Structural features of **1** and **2**

The crystal structure of commercially available guanylthiourea (Scheme 1a: **II**; Aldrich, CAS No. 2114-02-05) was previously reported as 2-imino-4-thiobiuret, and the authors concluded that it exists in the tautomeric form 1-(diaminomethylene)thiourea (Scheme 1a: **I**), which is in agreement with that found in the present X-ray structure of **1**. On the other hand, re-crystallization of guanylthiourea from water yielded crystals of **I**, not the imino tautomer **II** [15]. Moreover, guanylthiourea can exist in a third tautomeric form (Scheme 1a: **III**) [16]. Although the hydrogen atoms of the three tautomeric forms are positioned differently, they have the same conjugate anion (Scheme 1b). In a word, the three tautomers are potentially interesting compounds that can be used in crystal engineering to build up extended frameworks, since they contain complementary arrays of hydrogen-bonding sites.

As revealed by the present X-ray structure analysis, the guanylthiourea molecules in both inclusion compound

Fig. 4 Perspective view of a portion of the crystal structure of **2** showing the well-ordered tetrapropylammonium cations filling the anionic host channels. For clarity the $[(C_3H_7)_4N]^+$ cations are represented by large shaded spheres
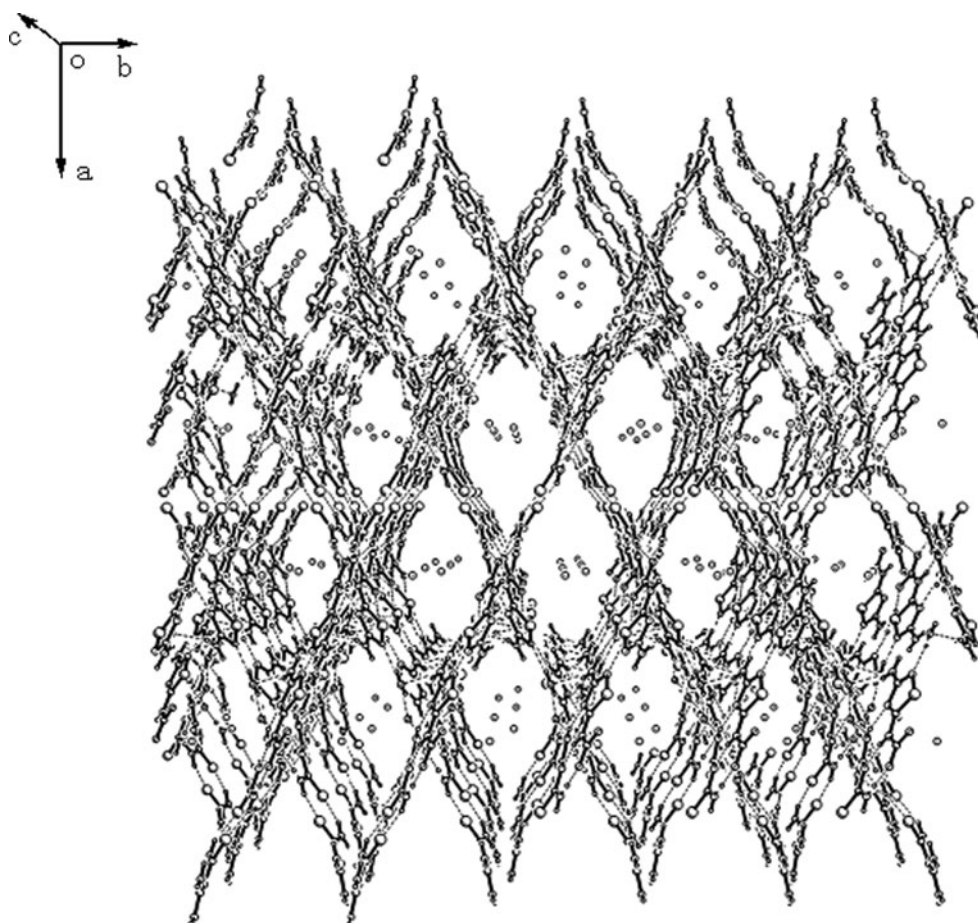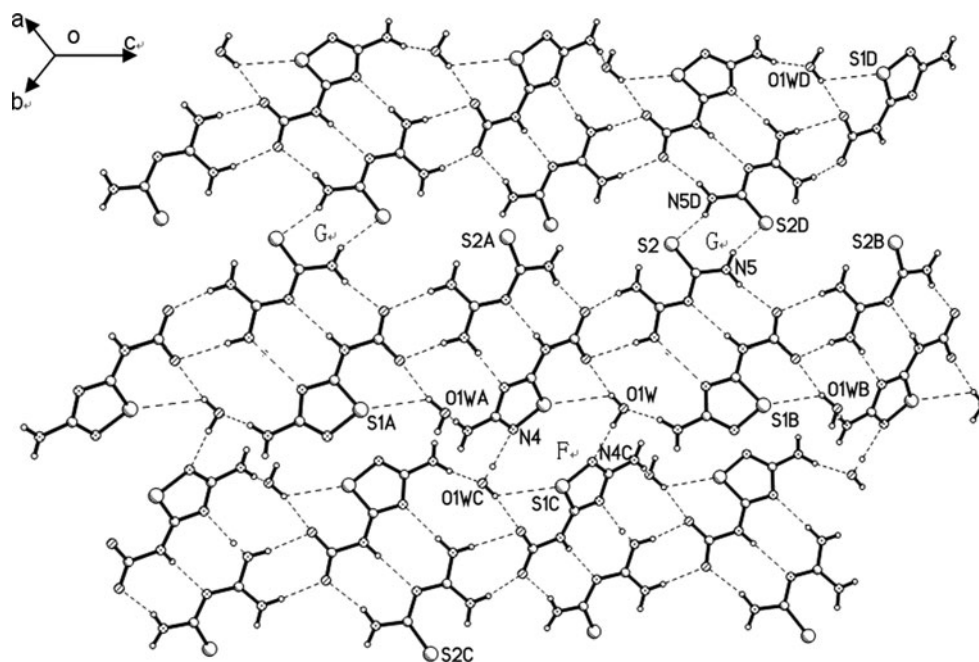

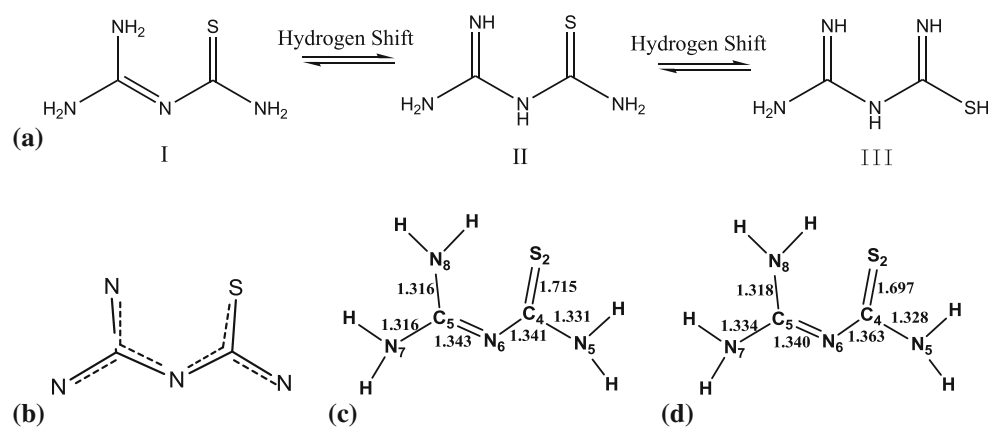**Table 2** Selected bond distances (Å) and bond angles (°) for the host molecules of **2**

C(1)–O(1)	1.236(3)	C(3)–N(2)	1.367(3)
C(1)–O(2)	1.247(3)	C(4)–N(5)	1.328(3)
C(1)–N(1)	1.406(3)	C(4)–N(6)	1.363(3)
C(2)–N(2)	1.314(3)	C(4)–S(2)	1.697(3)
C(2)–N(1)	1.347(3)	C(5)–N(8)	1.318(3)
C(2)–S(1)	1.711(3)	C(5)–N(7)	1.334(3)
C(3)–N(4)	1.307(3)	C(5)–N(6)	1.340(3)
C(3)–N(3)	1.358(3)	N(4)–S(1)	1.669(2)
O(1)–C(1)–O(2)	127.5(2)	N(5)–C(4)–S(2)	117.7(2)
O(1)–C(1)–N(1)	116.9(2)	N(6)–C(4)–S(2)	129.1(2)
O(2)–C(1)–N(1)	115.7(2)	N(8)–C(5)–N(7)	116.6(2)
N(2)–C(2)–N(1)	122.0(2)	N(8)–C(5)–N(6)	126.9(2)
N(2)–C(2)–S(1)	113.0(2)	N(7)–C(5)–N(6)	116.5(2)
N(1)–C(2)–S(1)	125.0(2)	C(2)–N(1)–C(1)	123.5(2)
N(4)–C(3)–N(3)	122.4(3)	C(2)–N(2)–C(3)	107.9(2)
N(4)–C(3)–N(2)	119.6(2)	C(3)–N(4)–S(1)	108.1(2)
N(3)–C(3)–N(2)	117.9(3)	C(5)–N(6)–C(4)	122.9(2)
N(5)–C(4)–N(6)	113.2(2)	N(4)–S(1)–C(2)	91.4(1)

1 (Scheme 1c) and **2** (Scheme 1d) have the same 1-(diaminomethylene)thiourea structure **I**, and their bond lengths and bond angles are compared in Table 2. The C4=S2 bond is longer by ~ 0.05 Å than typical C=S double bonds in thiourea derivatives (mean value 1.663 Å) [17]. However, thioformaldehyde, $H_2C=S$, in the gas-phase has a value of 1.6109 (8) Å for its C=S bond distance, which represents 100% double-bond character, while C=S bond lengths of ca 1.74 Å are cited as representing 50% double-bond character, as observed in dithiolate anions [18, 19]. Therefore in the crystal structure of **1**, the C4=S2 bond order is 1–2. The C–N bond lengths involving the central N6 atom are significantly longer than the other C–N bond lengths linking the amine groups. The planarity of the amine groups indicates sp^2-hybridization for the amine N atoms, and the lone-pair electrons occupy a p orbital, which lies perpendicular to the plane of the NH_2 groups. The p orbitals of the C and S atoms, being the π components of the C5=N6 and C4=S2 double bonds, also lie perpendicular to the plane; therefore, partial delocalization, due to the symmetry of the p orbitals, of the π electrons over the whole molecule is possible, hence leading to elongation of the C4=S2 and C5=N6 double bonds and to

Fig. 5 Two kinds of linkage between neighboring molecules in the channel-type host lattice. Symmetry transformations: **a** x, $\frac{1}{2} - y$, $1/2 + z$; **b** x, $\frac{1}{2} - y$, $-1/2 + z$; **c** $2 - x$, $-y$, $2 - z$; **d** $1 - x$, $-y$, $1 - z$
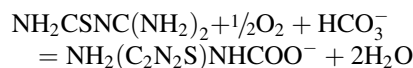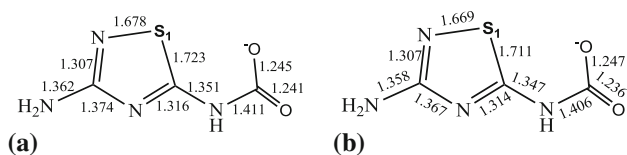

Scheme 1

shortening of the other C–N single bonds. Thus the bond order of the C4=S2 and C5=N6 bonds is smaller than 2, and the bond order of the C–N bonds linking the amine groups exceeds one. Moreover, the bond order of the C–N bonds joining the amine groups is larger than the bond order of the C–N bonds involving the central N6 atom. The repulsion between the S2 atom and the amine group at N8 causes rotation of both arms of the molecule around the C–N6 bonds, which accounts for the twisted conformation of the molecule. This interaction decreases the overlap of the p orbitals of atoms C5 and N6 and of atoms N6 and C4, leading to elongation of the C5–N6 and N6–C4 bonds as compared with the other C–N amine bonds [20]. The steric interaction between atom S2 and amine atom N8 makes the N8–C5–N6, C5–N6–C4 and N6–C4–S2 angles greater than the standard 120° angle for sp^2 hybridization.

The other molecular component of the host lattice in both inclusion compound **1** and **2** is 1,3,5-thiadiazole-5-amido-2-carbamate, whose parent carbamic acid is not known in the free state, and the carbamate ester is a fugitive species among the oldest organic compounds recorded in the literature [21]. In the present study, formation of the carbamate anion from guanylthiourea and tetra-*n*-butyl-ammonium hydroxide or tetrapropyl ammonium hydroxide likely involves oxidative ring closure in aqueous methanol followed by condensation with the bicarbonate ion, which is produced by absorption of atmospheric CO_2 in the alkaline medium:

$$NH_2CSNC(NH_2)_2 + \tfrac{1}{2}O_2 + HCO_3^- = NH_2(C_2N_2S)NHCOO^- + 2H_2O$$

The measured C–N bond lengths of 1,3,5-thiadiazole-5-amido-2-carbamate from the terminal amino group toward the carbamate (Scheme 2a, b) are in accord with the alternate single- and double-bond character as depicted by their structural formulas.

(a)

(b)

Scheme 2

then stirred for about 1.5 h. The mixed reactant was subsequently heated at 80 °C under stirring for another 1.5 h. The pH of the solution was 11.0, which is favorable to the absorption of atmospheric CO_2. Then the solution was subjected to slow evaporation in open air at room temperature. Large colorless block-like crystals were obtained about 10 days later.

Experimental

Synthesis of 1

Guanylthiourea and tetra-n-butylammonium hydroxide were mixed in a molar ratio of 2:1. The mixture was dissolved in a minimum amount of methanol and water, and

Synthesis of 2

This compound was prepared by a procedure similar to that used for the preparation of **1** except that tetrapropyl ammonium hydroxide was employed instead of tetra-n-butylammonium hydroxide. Large colorless block-like crystals of **2** were obtained after about 10 days.

Table 3 Crystal data and structure refinement

Complex	1	2
Molecular formula	$[(n\text{-}C_4H_9)_4N]^+\cdot[NH_2(C_2N_2S)NHCOO^-]\cdot NH_2CSNC(NH_2)_2$	$[(n\text{-}C_3H_7)_4N]^+\cdot[NH_2(C_2N_2S)NHCOO^-]\cdot NH_2CSNC(NH_2)_2\cdot H_2O$
Formula weight	518.27	481.69
Temperature (K)	293(2)	296(2)
$\lambda(\text{Mo}K\alpha)$ (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a (Å)	8.7801(1)	18.2044(3)
b (Å)	12.1955(1)	8.5037(2)
c (Å)	14.2657(2)	17.0979(3)
α (°)	89.865(1)	90
β (°)	82.842(1)	96.3840(10)
γ (°)	75.605(1)	90
V (Å^3)	1467.40(3)	2630.42(9)
Z, D_{calc}(g/cm^{-3})	2,1.173	4, 1.216
μ (Mo-Kα) (mm^{-1})	0.215	0.237
$F(000)$	561	1,040
Crystal size (mm)	0.50 × 0.40 × 0.20	0.21 × 0.15 × 0.04
θ range (°)	2.21–27.50	2.40–23.88
Index ranges	$-11 \leq h \leq 11$ $-15 \leq k \leq 15$ $-18 \leq l \leq 18$	$-20 \leq h \leq 16$ $-9 \leq k \leq 9$ $-19 \leq l \leq 18$
Reflections collected	17,694	9,158
Independent refl./R_{int}	6,723/0.0204	4,046/0.0271
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.9584 and 0.9003	0.9906 and 0.9519
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6,723/179/361	4,046/0/282
Goodness-of-fit on F^2	1.012	1.018
$R_1/wR_2[I > 2\sigma(I)]$	0.0403/0.1056	0.0439/0.1025
R_1/wR_2 (all data)	0.0519/0.1126	0.0704/0.1157
Residual extrema (e/Å^3)	0.305 and −0.240	0.182 and −0.185

Crystallography

Intensity data were collected on a Siemens P4 four-circle diffractometer (monochromatized Mo-Kα X-ray source, $\lambda = 0.71073$ Å). Crystallographic data are summarized in Table 3. The structures were solved by the directed method and refined with anisotropic non-hydrogen atoms by full-matrix least-squares on F_0^2 using the SHELX-97 package [22]. Hydrogen atoms were located in their expected positions and refined using the rigid-body approximation. Two terminal carbon atoms on the same alkyl chain of the tetra-n-butylammonium cation are found to be disordered over two positions. These disordered carbon atoms were refined with equivalent anisotropic displacement parameters. Crystallographic details have been deposited at the Cambridge Crystallographic Data Centre; reference CCDC numbers 856079 and 856080.

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