

Carbonate and oxalate dianions as prolific hydrogen-bond acceptors in supramolecular assembly†‡

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Received (in Columbia, MO, USA) 10th June 2003, Accepted 18th September 2003

First published as an Advance Article on the web 8th October 2003

In the new inclusion compound $[(C_2H_5)_4N^+]_2 \cdot CO_3^{2-} \cdot 7(NH_2)_2CS$, the carbonate ion is surrounded by twelve convergent NH donor groups from six thiourea molecules to form a hydrogen-bonded aggregate shaped like two concave three-leaved propellers sharing a common core, whereas in $[(n-C_3H_7)_4N^+]_2 \cdot C_2O_4^{2-} \cdot 4(NH_2)_2CS$ the oxalate ion serves as a hub for binding four thiourea molecules to generate a cross-shaped structural motif.

Recently we carried out *in situ* generation of the non-benzenoid aromatic D_{6h} and enediolate C_{2v} valence tautomers of the relatively unstable rhodizonate dianion $C_6O_6^{2-}$ and stabilized them with convergent N–H hydrogen bond donor sites provided by (3-hydroxyphenyl)urea and 1,1'-ethylenediurea, respectively, in two novel crystalline inclusion compounds.¹ Guided by this design strategy, we proceeded to explore the two simplest oxocarbon dianions, namely carbonate and oxalate, as hubs for supramolecular assembly. Our study was further motivated by the fact the carbonyl oxygen atom in the tetragonal phase of urea forms four acceptor hydrogen bonds,² and that the squarate ion in $[(C_2H_5)_4N^+]_2 \cdot C_4O_4^{2-} \cdot 6(NH_2)_2CS$ forms an unusually large number of ten acceptor hydrogen bonds with six neighboring thiourea molecules,³ and hence it would be of interest to see if the smaller acyclic oxocarbon ions can better this record. Experimentation with various peralkylated ammonium ions as structure-inducing agents and different molar ratios has led to the isolation of the new inclusion compounds $[(C_2H_5)_4N^+]_2 \cdot CO_3^{2-} \cdot 7(NH_2)_2CS$ **1** and $[(n-C_3H_7)_4N^+]_2 \cdot C_2O_4^{2-} \cdot 4(NH_2)_2CS$ **2**,† the characterization§ of which are described in the present report.

In the crystal structure of **1**, the carbonate ion occupies a site of symmetry 2. The independent thiourea molecules **C(1)** and **C(2)** each (conveniently referred to by naming only its carbon atom) generate a centrosymmetric dimer, and the rings labeled by **A** and **B** in Fig. 1 have the same motif described by the graph-set notation $N_2 = R_2^2(8)$.⁴ These thiourea dimers are directly connected to the carbonate ion by strong charge-assisted N–H \cdots O[−] hydrogen bonds with ring motifs **C** and **D**, $N_2 = R_2^2(8)$ to form a highly puckered hydrogen-bonded layer. The layer is further consolidated by additional N–H \cdots S hydrogen bonds to form a new ring motif **E**, $N_4 = R_4^2(8)$.

With these hydrogen-bonded layers arranged parallel to the (100) family of planes, interlayer linkage by the thiourea dimers derived from **C(3)** (ring motif **F**, $N_2 = R_2^2(8)$) in ring motif **G**, $N_2 = R_2^2(8)$, defines the square shape of the channel system extending along the *b*-axis (Fig. 2). The resulting three-dimensional host lattice also has narrower channels along the [011] and [0 $\bar{1}$ 1] directions.

The most prominent feature of the host framework in **1** is the formation of the $[CO_3^{2-} \cdot 6(NH_2)_2CS]$ aggregate, which may be described as two concave three-leaved propellers attached to the same core. All three independent thiourea molecules **C(1)**, **C(2)** and **C(3)** are hydrogen-bonded on the same side to the trigonal planar carbonate ion, which has a two-fold axis passing through

atoms C(5) and O(2), whereas their symmetry-related partners are bound to the opposite face (Fig. 3a). The stability of the host framework is further strengthened by the presence of additional thiourea molecules derived from **C(4)** (Fig. 3b). Besides pulling a pair of two neighboring $[CO_3^{2-} \cdot 6(NH_2)_2CS]$ building blocks together by two strong N–H \cdots S hydrogen bonds, each **C(4)** rides on two **C(1)** type thiourea molecules (the dihedral angle is 79.6°) and forms two weak N–H \cdots π (thioamido) hydrogen bonds (NH \cdots NH₂CS, $D = 3.367$ Å, $d = 2.601$ Å and $\theta = 149.0^\circ$) with two thiourea molecules of a third building block. Two columns of well-ordered tetraethylammonium cations are arranged in staggered fashion and accommodated within each channel [see Fig. 5 in ESI].

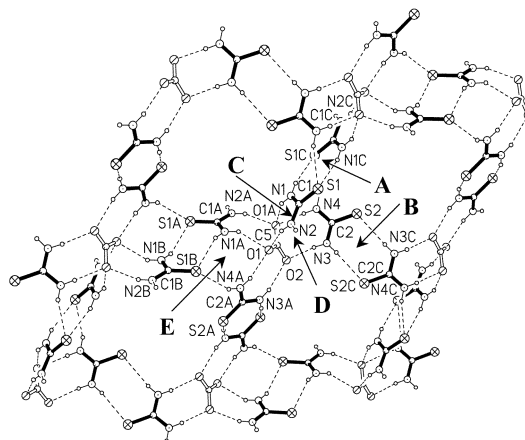


Fig. 1 In the host structure of **1**, the carbonate ions are linked to thiourea dimers derived from **C(1)** and **C(2)** to form a hydrogen-bonded layer parallel to (100). Symmetry transformations: A ($-x, y, 1/2 - z$); B ($x, -y, z - 1/2$); C ($-x, 1 - y, 1 - z$).

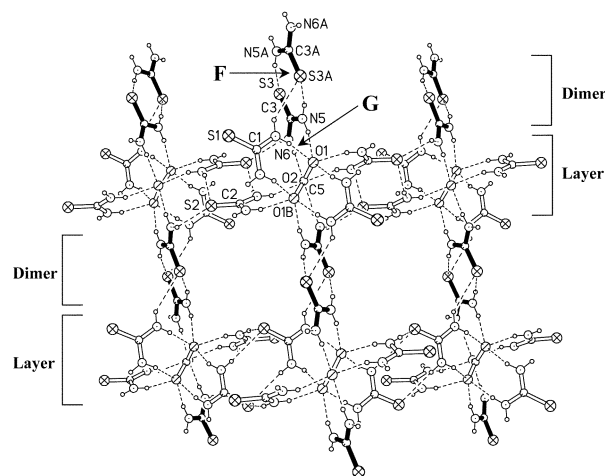


Fig. 2 Perspective view along the *b*-axis showing the channel-type host framework of **1** built of carbonate–thiourea layers cross-linked by thiourea dimers derived from **C(3)**. Symmetry transformations: A ($1/2 - x, 1/2 - y, 1 - z$); B ($-x, y, 1/2 - z$).

† Electronic supplementary information (ESI) available: synthesis details for **1** and **2**; Figs. 5 and 6. See <http://www.rsc.org/suppdata/cc/b3/b306649e/>
‡ Dedicated to Prof. James Trotter on the occasion of his 70th birthday.

In the host lattice of **2**, the two-fold disordered oxalate anion is bound by strong N–H···O[−] hydrogen bonds to two pairs of independent thiourea molecules in nearly orthogonal directions, forming an essentially planar cross-shaped structural building block (Fig. 4a) displaying two types of ring motifs: **A** and **B**, $N_2 = R_2^2(8)$; **C** and **D**, $N_2 = R_2^2(9)$. Adjacent cross-shaped building blocks related by simple axial translation are further interlinked to generate the ring motifs **E** and **F**, $N_2 = R_2^2(8)$ and **G**, $N_4 = R_4^2(8)$, yielding a wavy layer corresponding to the plane $z = \frac{1}{4}$ (Fig. 4b). This hydrogen-bonded host layer is characterized by the large and unsymmetrical void **H**, $N_4 = R_{10}^7(28)$, and well-ordered tetra-*n*-propylammonium cations are accommodated between these puckered layers with interlayer spacing of $c/2 = 8.2 \text{ \AA}$ [see Fig. 6 in ESI].

The carbonate and oxalate ions are known to form six⁵ to ten⁶ and eight⁷ to twelve⁸ acceptor hydrogen bonds, respectively, in their crystalline compounds. In the present work, the carbonate ion in **1** forms a record number of twelve acceptor hydrogen bonds with the convergent N–H donor sites from six thiourea

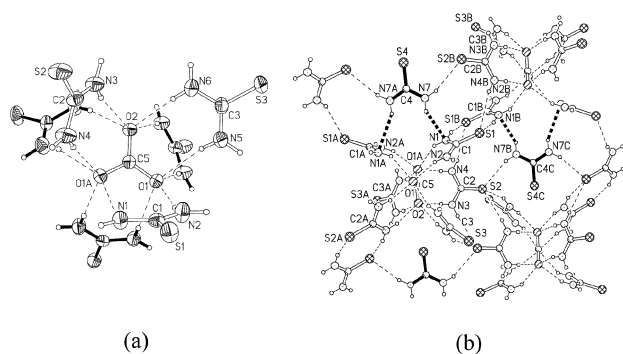


Fig. 3 (a) Biconcave, twin propeller-like $[\text{CO}_3^{2-}\cdot 6(\text{NH}_2)_2\text{CS}]$ molecular aggregate in **1**. Thiourea molecules lying above and below the plane of the carbonate ion are depicted by open and filled bond types, respectively. Thermal ellipsoids are drawn at the 30% probability level. Symmetry transformation: A $(-x, y, 1/2 - z)$. (b) Linkage between $[\text{CO}_3^{2-}\cdot 6(\text{NH}_2)_2\text{CS}]$ building blocks with thiourea molecules derived from **C(4)**. The weak N–H··· π (thioamido) interactions between thiourea molecules are indicated by thick broken lines. Symmetry transformations: A $(-x, y, 1/2 - z)$; B $(-x, -y, 1 - z)$; C $(x, -y, 1/2 + z)$.

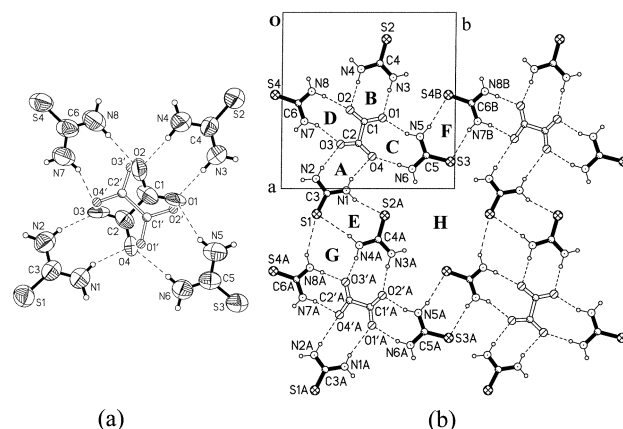


Fig. 4 (a) Two-fold disordered oxalate anion in **2**; one of the two possible orientations is highlighted by the open-bond type. Thermal ellipsoids are plotted at the 50% probability level. (b) Hydrogen-bonding interactions in the host layer of **2**. The two-fold disordered oxalate anions are shown in only one orientation in each site. Symmetry transformations: A $(1 + x, y, z)$; B $(x, 1 + y, z)$.

Furthermore, the presence of the **C(4)** type thiourea molecule in the host lattice of **1** also plays a significant role, as its almost perpendicular orientation to the **C(1)** type thiourea molecule facilitates weak N–H··· π (thioamido) interaction⁹ between them (Fig. 3b). Interestingly, the crystal structure of **2** shows that a two-fold disordered oxalate ion may be considered as a structural equivalent of the squarate ion in supramolecular assembly *via* hydrogen bonding, thus providing an elegant example of isostructurality.¹⁰

Recent studies have established that novel polynuclear complexes and coordination polymeric networks can be constructed with the carbonate¹¹ or oxalate¹² dianion as a multi-dentate building block. The present work complements this by showing that these two ubiquitous species, considered as hubs each bearing a divergent set of hydrogen-bond acceptor sites, may serve as versatile component modules for the *de novo* crystal engineering of supramolecular networks and organic–inorganic hybrid materials.¹³

This work was supported by Hong Kong Research Grants Council Earmarked Grants CUHK 4206/99P and 4268/00P.

Notes and references

§ Crystal data for **1**: $[(\text{C}_2\text{H}_5)_4\text{N}^+]_2\text{CO}_3^{2-}\cdot 7(\text{NH}_2)_2\text{CS}$, monoclinic, space group $C2/c$ (no. 15), $a = 25.462(4)$, $b = 12.901(2)$, $c = 17.355(3) \text{ \AA}$, $\beta = 124.009(3)^\circ$, $Z = 4$, 4656 unique MoK α reflections ($R_{\text{int}} = 0.0212$), final $R_1 = 0.0430$, $wR_2 = 0.1270$, 3592 observed reflections [$I > 2\sigma(I)$]. Crystal data for **2**: $[(n\text{-C}_3\text{H}_7)_4\text{N}^+]_2\text{C}_2\text{O}_4^{2-}\cdot 4(\text{NH}_2)_2\text{CS}$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.8476(7)$, $b = 12.0889(7)$, $c = 16.397(1) \text{ \AA}$, $\alpha = 74.427(1)$, $\beta = 87.521(1)$, $\gamma = 89.893(2)^\circ$, $Z = 2$, 7933 unique MoK α reflections ($R_{\text{int}} = 0.0176$), final $R_1 = 0.0516$, $wR_2 = 0.1594$ for 4093 observed reflections [$I > 2\sigma(I)$]. CCDC 212432 and 212433. See <http://www.rsc.org/suppdata/cc/b3/b306649e/> for Figs. 5 and 6 and the crystallographic data in CIF or other electronic format.

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