

Pu-Zhou Hu, Jian-Ge Wang, Lu Wang, Jun-Qing Chen and Bang-Tun Zhao*

Department of Chemistry, Luoyang Normal University, Luoyang 471022, People's Republic of China

Correspondence e-mail: zbt@lynu.edu.cn

Key indicators

Single-crystal X-ray study
 $T = 291\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.024
 wR factor = 0.068
Data-to-parameter ratio = 18.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

4,5-Bis(carboxymethylsulfanyl)-1,3-dithiole-2-thione monohydrate

In the crystal structure of the title compound, $\text{C}_7\text{H}_6\text{O}_4\text{S}_5 \cdot \text{H}_2\text{O}$, a chain forms along the b axis *via* weak $\text{S} \cdots \text{S}$ interactions. The structure is further stabilized by an extensive network of $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds in the ac plane, giving an interleaved supramolecular architecture.

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Comment

Tetrathiafulvalene (TTF) and its derivatives are the subject of intense interest in materials chemistry, crystal engineering and supramolecular chemistry (Segura & Martin, 2001). 1,3-Dithiole-2-thiones, important precursors to TTF derivatives, have also attracted attention (Chen *et al.*, 2005; Fabre, 2004). We report here the structure of the title compound (I) (Fig. 1), which was prepared by the reaction of di(tetraethylammonium) bis(1,3-dithiol-2-thione-4,5-dithiolate)zincate and BrCH_2COOH in the presence of NaOH (Wang *et al.*, 1998).

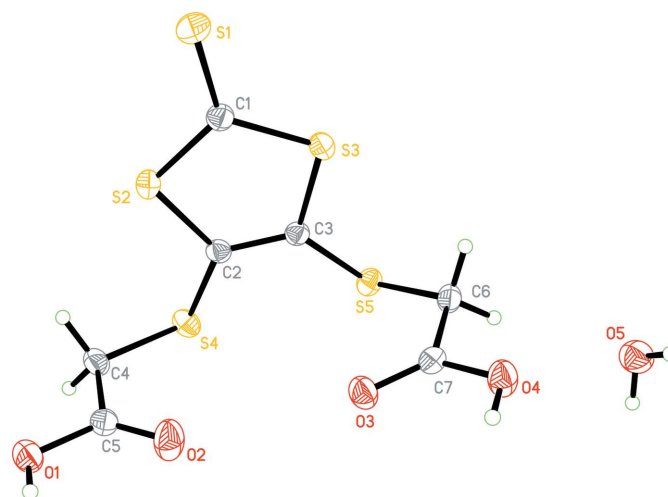
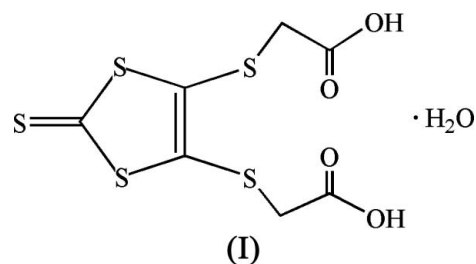


Figure 1

A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

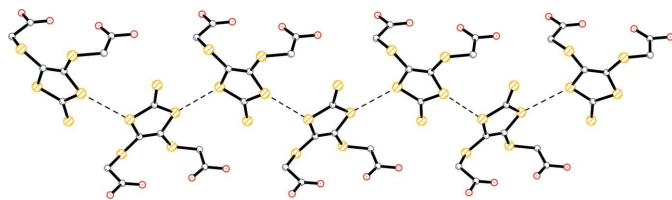


Figure 2
The one-dimensional chain-like structure of (I), formed by S...S interactions (dashed lines) along the *b* axis.

In the crystal structure, intermolecular S...S interactions [$S3 \cdots S4 = 3.5551(5) \text{ \AA}$] link the molecules into a chain along the *b* axis (Fig. 2). In addition, an extensive network of hydrogen bonds stabilizes the crystal packing in (I) (Table 1). Each carboxylate group forms inversion-related dimers through intermolecular O—H...O hydrogen bonds. These are further interconnected by hydrogen bonds to and between the solvent water molecules (Fig. 3). This hydrogen-bonding network combines with the weak S...S interactions to build an interleaved three-dimensional supramolecular architecture (Fig. 4).

Experimental

Di(tetraethylammonium) bis(1,3-dithiol-2-thione-4,5-dithiolate)-zincate (700 mg, 1.0 mmol) in acetonitrile (15 ml) was mixed with BrCH_2COOH (0.84 g, 6 mmol), NaOH (0.26 g, 6.5 mmol) and H_2O (7.5 ml) and heated under reflux for about 20 h. CH_3CN was removed *in vacuo* and HCl (36%, 25 ml) was added with cooling to give red crystals. These were dissolved in dilute NH_3 and then HCl (36%) was added slowly to give the product (yield 74.4%, m.p. 445–447 K). $^1\text{H NMR}$ (250 MHz, $\text{DMSO}-d_6/\text{TMS}$, δ , p.p.m.): 4.37 (broad, COOH), 3.84 (*s*, CH_2). Recrystallization from ethanol at room temperature over a week gave red block-shaped crystals suitable for X-ray analysis.

Crystal data

$\text{C}_7\text{H}_6\text{O}_4\text{S}_5 \cdot \text{H}_2\text{O}$	$Z = 4$
$M_r = 332.43$	$D_x = 1.765 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.5548(10) \text{ \AA}$	$\mu = 0.93 \text{ mm}^{-1}$
$b = 10.8325(8) \text{ \AA}$	$T = 291(2) \text{ K}$
$c = 9.5073(7) \text{ \AA}$	Block, red
$\beta = 104.577(1)^\circ$	$0.30 \times 0.19 \times 0.17 \text{ mm}$
$V = 1251.37(16) \text{ \AA}^3$	

Data collection

Bruker APEX-2 CCD area-detector diffractometer	6519 measured reflections
φ and ω scans	2859 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2569 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.767$, $T_{\max} = 0.857$	$R_{\text{int}} = 0.011$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.2783P]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
2859 reflections	$\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$
156 parameters	
H-atom parameters constrained	

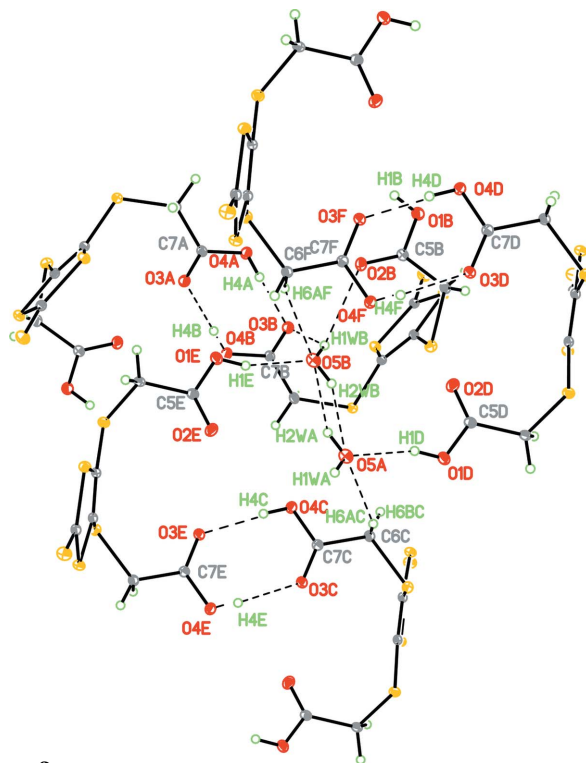


Figure 3
The extensive network of interpenetrating O—H...O hydrogen bonds (dashed lines) in the *ac* plane. Atoms labelled with the suffixes A–F are at the symmetry positions (A) x, y, z ; (B) $-x + 1, -y + 1, -z + 1$; (C) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (D) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (E) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (F) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

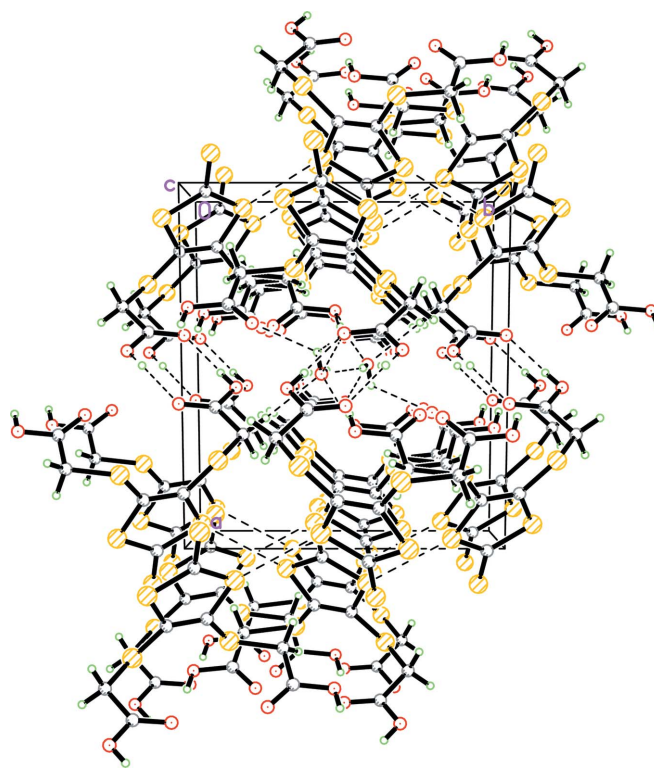


Figure 4
The crystal packing in (I). Hydrogen bonds and intermolecular S...S interactions are drawn as dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O5-H2W\cdots O5^i$	0.87	2.01	2.782 (3)	147
$O5-H1W\cdots O2^{ii}$	0.87	2.47	3.111 (2)	131
$O5-H1W\cdots O3^{ii}$	0.87	2.24	2.8797 (19)	130
$O4-H4\cdots O3^{iii}$	0.82	1.91	2.7236 (16)	172
$O1-H1\cdots O5^{iv}$	0.82	1.87	2.6553 (19)	161

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, y-1, z$.

H atoms in the solvent water molecule were located in a difference Fourier map and their distances were subsequently restrained to $O-H = 0.85$ Å and $H\cdots H = 1.45$ Å. Other H atoms were refined using a riding model, with $C-H = 0.97$ Å and $U_{iso} = 1.2U_{eq}(C)$, and $O-H = 0.82$ Å and $U_{iso} = 1.5U_{eq}(O)$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2004); software used to prepare material for publication: *SHELXTL*.

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