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Bis[2,2′-(2-aminoethylimino)di(ethylammonium)] hexasulfidodistannate(IV) dihydrate

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The crystal structure of the title compound, $(C_6H_{20}N_4)_2[Sn_2S_6]\cdot 2H_2O$, consists of discrete $[Sn_2S_6]^{4-}$ anions, diprotonated tris(2-aminoethyl)amine dications and hydrate water molecules. The cations and water molecules occupy general positions, whereas the anions are located on centres of inversion. In the crystal structure, the anions, cations and water molecules are connected *via* hydrogen bonds.

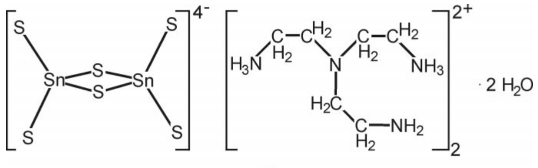
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.019
wR factor = 0.054
Data-to-parameter ratio = 28.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Recently the synthesis and structural characterization of new thiostannates has become of increasing interest (Sheldrick & Wachold, 1997; Sheldrick, 2000). Most of these compounds were prepared by solvothermal methods, some of them crystallizing as open-framework materials (Scott *et al.*, 1999). These compounds contain two-dimensional layered anions with compositions such as $[Sn_3S_7]^{2-}$ and $[Sn_4S_9]^{2-}$. In such compounds, tetraalkylammonium cations or protonated organic amines, such as tetramethylammonium (TMA) (Parise *et al.*, 1994), tetraethylammonium (TEA) or protonated 1,8-diazabicyclooctane (DABCO-H) (Jiang, Lough *et al.*, 1998), act as charge-compensating cations. The main interest in such compounds are their interesting properties, such as adsorption, molecular sensing (Jiang, Ozin *et al.*, 1998) or ion-exchange (Bowes *et al.*, 1998). In our own investigations, we are also interested in the synthesis, structures and properties of thiostannates containing protonated organic amines as cations, and, in addition, in the incorporation of transition metals into the thiostannate frameworks (Behrens *et al.*, 2003). As a first result, we report the synthesis and crystal structure of a new thiostannate, (I), prepared by solvothermal synthesis.



(I)

The crystal structure of (I) consists of discrete $[Sn_2S_6]^{4-}$ anions, diprotonated tris(2-aminoethyl)amine dications and hydrate water molecules. The $[Sn_2S_6]^{4-}$ anions are formed by two edge-sharing SnS_4 tetrahedra and are located on centres of inversion. The Sn—S distances to the terminal S atoms, of 2.3211 (10) and 2.3398 (10) Å, are shorter than the Sn—S bond lengths to the bridging S atoms, 2.4477 (8) Å. The S—Sn—S angle in the Sn_2S_2 ring, 93.74 (3)°., is smaller than the S—Sn—S angles to the terminal S atoms, which lie between 108.55 (4) and 121.44 (4)°. The geometrical parameters found in the $[Sn_2S_6]^{4-}$ anion are comparable to those in other thio-

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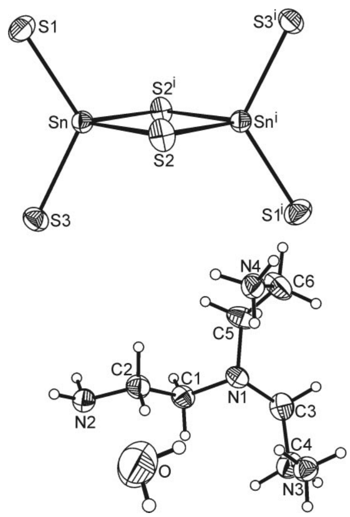

Figure 1
The structure of (I), excluding water, with the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x$, $-y+2$, $-z$].

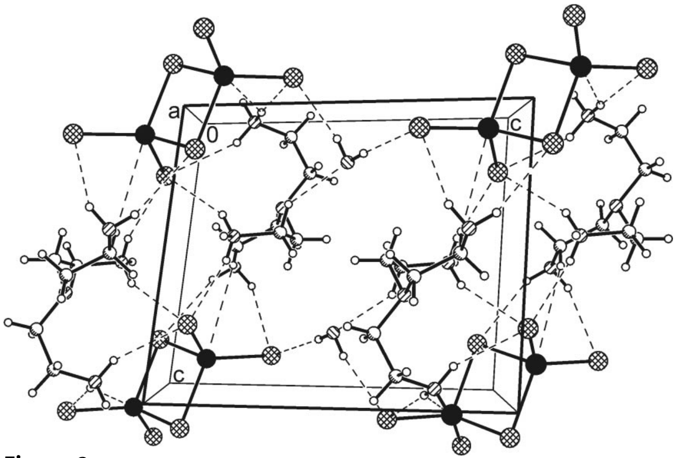

Figure 2
The structure of the title compound, viewed along the *a* axis (hydrogen bonding is indicated by dashed lines).

stannates (Behrens *et al.*, 2003). The organic cations are located in general positions with two of the three terminal amino groups protonated. Between the anions and cations, N—H···S hydrogen bonds are found. The N···S distances lie between 3.230 (2) and 3.619 (2) Å, the H···S distances are between 2.40 and 2.93 Å and the N—H···S angles range from 114 to 169°. In the structure, N—H···N hydrogen bonding is also found. The anions are also connected by hydrate water molecules. The O···S distances of 3.295 (3) and 3.418 (2) Å, the H···S distances of 2.49 and 2.60 Å and the O—H···S angles of 169 and 177° show these to be strong interactions.

Experimental

The title compound was prepared by the reaction of elemental Co (59 mg), Sn (119 mg) and S (129 mg) in 3 ml of tris(2-aminoethyl)-amine in a Teflon-lined steel autoclave under solvothermal conditions. The reaction mixture was heated at 413 K for 7 d and cooled. The product consists of small crystals of the title compound.

Crystal data

$(C_6H_{20}N_4)_2[Sn_2S_6]\cdot 2H_2O$
$M_r = 762.29$
Triclinic, $P\overline{1}$
$a = 7.7499$ (15) Å
$b = 9.7054$ (19) Å
$c = 10.908$ (2) Å
$\alpha = 89.22$ (3)°
$\beta = 75.27$ (3)°
$\gamma = 67.40$ (3)°
$V = 729.3$ (2) Å^3

$Z = 1$
$D_x = 1.736$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 96 reflections
$\theta = 10$–15°
$\mu = 2.17$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.16 × 0.12 × 0.06 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
$T_{min} = 0.699$, $T_{max} = 0.875$
4132 measured reflections
3858 independent reflections
3767 reflections with $I > 2\sigma(I)$

$R_{int} = 0.007$
$\theta_{max} = 29.0°$
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.054$
$S = 1.35$
3858 reflections
138 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 0.348P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.69$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn—S1	2.3211 (10)	Sn—S2	2.4477 (8)
Sn—S3	2.3398 (10)	Sn—S2^i	2.4576 (7)
S1—Sn—S3	121.44 (4)	S3—Sn—S2^i	108.55 (4)
S1—Sn—S2	113.23 (4)	S2—Sn—S2^i	93.74 (3)
S3—Sn—S2	106.59 (4)	Sn—S2—Sn^i	86.26 (3)
S1—Sn—S2^i	109.71 (3)		

Symmetry code: (i) $-x, 2-y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O—H2O···S1	0.82	2.60	3.418 (3)	177
O—H1O···S1^i	0.82	2.49	3.295 (3)	169
N2—H1N2···S1^{ii}	0.89	2.93	3.619 (2)	135
N2—H2N2···S2^{iii}	0.89	2.82	3.611 (2)	148
N3—H1N3···S1^i	0.89	2.45	3.323 (2)	169
N3—H3N3···S3^{iv}	0.89	2.58	3.415 (2)	156
N4—H1N4···S3^{ii}	0.89	2.40	3.230 (2)	155
N4—H2N4···N2^v	0.89	2.08	2.873 (3)	147
N4—H2N4···S2^i	0.89	2.95	3.421 (3)	115
N4—H3N4···S3^{iv}	0.89	2.67	3.501 (2)	156

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

The positions of the H atoms were found from difference maps. The H atoms bonded to carbon were positioned with idealized geometry and refined with fixed isotropic displacement parameters [$U_{iso}(H) = 1.2U_{eq}$C(methylene)], using a riding model with C—H(methylene) = 0.97 Å. The positions of N—H H atoms bonded to the tertiary amino groups were idealized with N—H distances of

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0.89 Å, then refined as rigid groups allowed to rotate but not tip. These H atoms were refined with fixed isotropic displacement parameters [$U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(N)]. The H atoms of the water molecules and the H atoms of the secondary amino group were identified from difference syntheses but refined as rigid groups with an idealized O—H bond length of 0.82 Å and an N—H bond length of 0.89 Å. These H atoms were refined with fixed isotropic displacement parameters [$U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O) or 1.2$U_{\rm eq}$(N)].

Data collection: *Structure Determination Package* (Enraf–Nonius, 1985); cell refinement: *Structure Determination Package*; data reduction: *Structure Determination Package*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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