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Bis(2-aminoethylammonium) (ethylenediammonium) (di-μ-sulfido-κ^2S:S)bis[dithiostannate(IV)]

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Key indicators

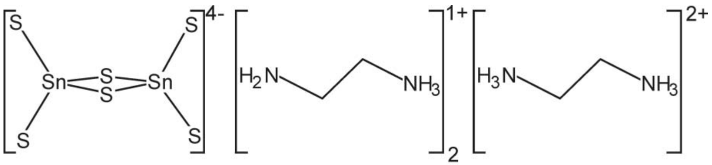
Single-crystal X-ray study
T = 170 K
Mean σ(C–C) = 0.005 Å
R factor = 0.029
wR factor = 0.076
Data-to-parameter ratio = 25.9

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

The crystal structure of the title compound, $(C_2H_{10}N_2)(C_2H_9N_2)_2[Sn_2S_6]$, consists of discrete $[Sn_2S_6]^{4-}$ anions and mono- as well as diprotonated ethylenediamine molecules. The anion and the monoprotonated cation occupy general positions, whereas the dications are located on centres of inversion. In the crystal structure, the anions and cations are connected *via* N—H···S and N—H···N hydrogen bonds.

Comment

In the last few years, several compounds containing the $[Sn_2S_6]^{4-}$ anion have been reported. Examples with protonated organic amines as counterions are $(CHAH)_2[Sn_2S_6]$ (CHA is cyclohexylamine; Jiang *et al.*, 1998), $(C_{12}H_{25}NH_3)_4[Sn_2S_6]\cdot 2H_2O$ (Li *et al.*, 1997), $(C_6H_{20}N_4)_2[Sn_2S_6]\cdot 2H_2O$ (Näther *et al.*, 2003) and $(enH)_4[Sn_2S_6]$ (en = ethylenediamine) (Dehnen & Zimmermann, 2002). There are also some compounds containing transition metal complexes as charge-compensating cations, *e.g.* $[Ni(en)_3]_2[Sn_2S_6]$, $[Ni(dap)_3]_2[Sn_2S_6]\cdot 2H_2O$ (dap is 1,2-diaminopropane), $[Co(tren)_3]_2[Sn_2S_6]$ [tren is tris(2-aminoethyl)amine] and $[Ni(tren)_3]_2[Sn_2S_6]$ (Behrens *et al.*, 2003), and $C_{12}H_{44}N_8O_2[S_6Sn_2][M(en)_3]_2[Sn_2S_6]$ (M is Mn, Co or Zn; Jia *et al.*, 2004). Many of these compounds were prepared under solvothermal conditions. We are interested in the syntheses, structures and properties of thiostannates containing protonated organic amines. We now report the synthesis and crystal structure of the title novel thiostannate, (I), prepared under solvothermal conditions.


(I)

The asymmetric unit of (I) consists of one crystallographically independent $[Sn_2S_6]^{4-}$ anion, two crystallographically independent monoprotonated ethylenediamine ions and half each of two crystallographically independent diprotonated ethylenediammonium dications (Fig. 1). The two diprotonated cations are each located on centres of inversion, whereas the $[Sn_2S_6]^{4-}$ anion and the two monoprotonated cations occupy general positions. The $[Sn_2S_6]^{4-}$ anions are formed by two edge-sharing SnS_4 tetrahedra.

The Sn—S distances to the terminal S atoms range from 2.3337 (9) to 2.3509 (8) Å, shorter than the Sn—S bond lengths to the bridging S atoms [2.4409 (9)–2.4868 (8) Å]

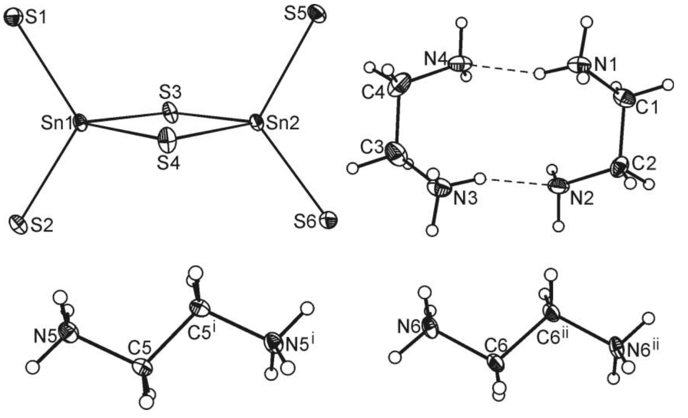


Figure 1
The structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i) $-x + 2$, $-y + 1$, $-z + 2$; (ii) $-x + 1$, $-y + 1$, $-z + 1$.]

(Table 1). The S—Sn—S angles in the Sn_2S_2 ring [93.46 (3) and 94.34 (3)°] are smaller than those to the terminal S atoms [106.50 (3)–117.06 (3)°]. The geometric parameters found in the $[Sn_2S_6]^{4-}$ anion are comparable with those in other thiostannates (Behrens *et al.*, 2003).

Between the anions and cations, N—H···S hydrogen bonds are found (Fig. 2). The N···S distances are in the range 3.228 (3)–3.683 (3) Å and the H···S distances are between 2.40 and 2.83 Å; the N—H···S angles range from 147 to 174°. The two monoprotonated cations are also connected *via* N—H···N hydrogen bonds into dimers (Fig. 1). The two diprotonated cations are each. In these dimers, each of the cations acts as a hydrogen-bond donor and acceptor. The N···N distances are 2.833 (4) and 2.849 (5) Å, the H···N distances are 1.95 and 1.97 Å, and the N—H···N angles are both 162°. We note that a thiostannate with four monoprotonated ethylenediamine molecules has been obtained using a room-temperature solvent route (Dehnen & Zimmermann, 2002).

Experimental

The title compound was prepared by the reaction of elemental Sn (275.4 mg) and S (48.2 mg) in a 20% solution of ethylenediamine in methanol (3.75 ml), in a Teflon-lined steel autoclave under solvothermal conditions. The reaction mixture was heated for 3 d at 433 K, tempered for 12 h at 363 K and cooled. The product was washed with water and ethanol (yield 10%, based on Sn) and was contaminated with large amounts of SnS_2.

Crystal data

$(C_2H_{10}N_2)(C_2H_9N_2)_2[Sn_2S_6]$
$M_r = 614.08$
Triclinic, $P\overline{1}$
$a = 8.7638$ (7) Å
$b = 10.729$ (1) Å
$c = 12.222$ (1) Å
$\alpha = 74.85$ (1)°
$\beta = 73.00$ (1)°
$\gamma = 88.98$ (1)°
$V = 1058.54$ (16) Å^3

$Z = 2$
$D_x = 1.927$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
$\theta = 2.5$–28°
$\mu = 2.95$ mm^{-1}
$T = 170$ (2) K
Block, colourless
0.09 × 0.09 × 0.08 mm

Data collection

Stoe IPDS-1 diffractometer
φ scans
Absorption correction: none
11 088 measured reflections
4820 independent reflections
3926 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.044$
$\theta_{\rm max} = 28.0°$
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.077$
$S = 0.97$
4820 reflections
186 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.91$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.80$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0039 (5)

Table 1
Selected geometric parameters (Å, °).

Sn1—S2	2.3337 (9)	Sn2—S5	2.3434 (9)
Sn1—S1	2.3474 (8)	Sn2—S6	2.3509 (8)
Sn1—S3	2.4549 (9)	Sn2—S4	2.4409 (9)
Sn1—S4	2.4868 (8)	Sn2—S3	2.4659 (8)
S2—Sn1—S1	117.06 (3)	S5—Sn2—S4	113.84 (3)
S2—Sn1—S3	111.51 (3)	S6—Sn2—S4	112.12 (3)
S1—Sn1—S3	112.48 (3)	S5—Sn2—S3	106.50 (3)
S2—Sn1—S4	109.00 (3)	S6—Sn2—S3	113.35 (3)
S1—Sn1—S4	110.79 (3)	S4—Sn2—S3	94.34 (3)
S3—Sn1—S4	93.46 (3)	Sn1—S3—Sn2	86.14 (3)
S5—Sn2—S6	114.80 (3)	Sn2—S4—Sn1	85.98 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···N4	0.91	1.95	2.833 (4)	162
N1—H2N1···S2$^{\rm i}$	0.91	2.40	3.228 (3)	151
N1—H3N1···S5	0.91	2.49	3.390 (3)	168
N2—H1N2···S6$^{\rm ii}$	0.91	2.65	3.477 (3)	152
N2—H2N2···S1$^{\rm iii}$	0.91	2.83	3.683 (3)	157
N3—H1N3···N2	0.91	1.97	2.849 (5)	162
N3—H2N3···S5$^{\rm ii}$	0.91	2.36	3.271 (3)	174
N3—H3N3···S6	0.91	2.55	3.436 (4)	164
N4—H1N4···S1$^{\rm i}$	0.91	2.68	3.523 (3)	155
N4—H2N4···S2$^{\rm iii}$	0.91	2.72	3.533 (3)	150
N5—H1N5···S2$^{\rm iv}$	0.91	2.41	3.263 (3)	157
N5—H2N5···S1$^{\rm v}$	0.91	2.44	3.303 (3)	159
N5—H3N5···S6$^{\rm vi}$	0.91	2.35	3.260 (3)	174
N6—H1N6···S5	0.91	2.40	3.293 (3)	167
N6—H2N6···S6$^{\rm vii}$	0.91	2.60	3.399 (3)	147
N6—H3N6···S1$^{\rm iv}$	0.91	2.35	3.250 (3)	173

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

All H atoms were located in difference maps. C-bound H atoms were positioned with idealized geometry, with C—H = 0.99 Å, and refined with fixed isotropic displacement parameters [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)] using a riding model. The positions of the N-bound H atoms of the tertiary amino group were idealized with N—H distances of 0.91 Å, and they were then refined as rigid groups allowed to rotate but not tip, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(N). N-bound H atoms of the secondary amino groups were located in difference maps, and they were refined as riding with N—H 0.91 Å and $U_{\rm iso}$(H)

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= $1.2U_{eq}$(N). The deepest hole in the difference map is −1.80 e/Å^3, located 0.78 Å from Sn2.

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXL97*.

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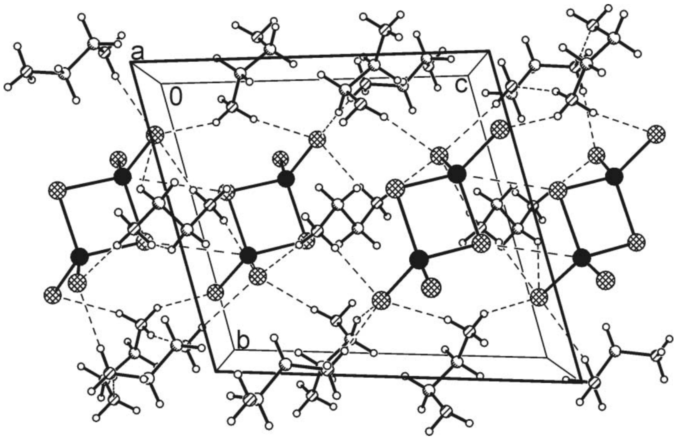

Figure 2
The crystal structure of (I), viewed in the direction of the crystallographic *a* axis. Hydrogen bonds are shown as dashed lines.

References

Behrens, M., Scherb, S., Näther, C. & Bensch, W. (2003). *Z. Anorg. Allg. Chem.* **629**, 1367–1373.

Bruker (1998) *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Dehnen, S. & Zimmermann, C. (2002). *Z. Anorg. Allg. Chem.* **628**, 2463–2469.

Jiang, T., Lough, A., Ozin, G. A. & Bedard, R. L. (1998). *J. Mater. Chem.* **8**, 733–741.

Li, J., Marler, B., Kessler, H., Soulard, M. & Kallus, S. (1997). *Inorg. Chem.* **36**, 4697–4701.

Jia, D. X., Zhang, Y., Dai, J., Zhu, Q. Y. & Gu, X. M. (2004). *Z. Anorg. Allg. Chem.* **630**, 313–318.

Näther, C., Scherb, S. & Bensch, W. (2003). *Acta Cryst.* E**59**, m280–m282.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Stoe & Cie (1998). *IPDS*. Version 2.89. Stoe & Cie, Darmstadt, Germany.