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Bis{2,2′-[(2-aminoethyl)azanediyl]-diethanaminium} di-μ-sulfido-bis-(disulfidogermanate)

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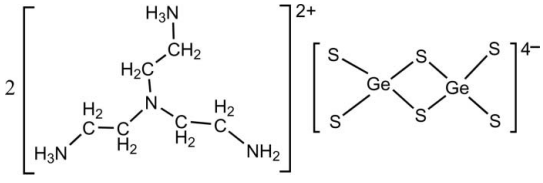
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.006 Å; R factor = 0.042; wR factor = 0.111; data-to-parameter ratio = 18.6.

In the title compound, $(C_6H_{20}N_4)_2[Ge_2S_6]$, the dimeric $[Ge_2S_6]^{4-}$ anion is formed by two edge-sharing GeS_4 tetrahedral units. The average terminal and bridging Ge—S bond lengths are 2.158 (14) and 2.276 (6) Å, respectively. The anions and the diprotonated ammonium cations are organized into a three-dimensional network by N—H···S and N—H···N hydrogen bonds.

Related literature

For background to main group metal–chalcogenide compounds, see: Bowes & Ozin (1996); Zheng *et al.* (2002, 2005). For a related structure, see: Jia *et al.* (2005).



Experimental

Crystal data

$(C_6H_{20}N_4)_2[Ge_2S_6]$
M_r = 634.06
Monoclinic, $C2/c$
a = 25.2845 (17) Å
b = 7.3173 (4) Å
c = 16.6001 (9) Å
β = 122.637 (4)°
V = 2586.3 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.83 mm^{-1}
T = 296 K
0.19 × 0.16 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.616, T_{max} = 0.677
11988 measured reflections
2952 independent reflections
2243 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.111
S = 1.03
2952 reflections
159 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.05 e Å^{-3}
$\Delta\rho_{min}$ = −1.08 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1N···S3^{i}	0.85 (4)	2.61 (5)	3.445 (4)	170 (4)
N2—H2N···S2	0.73 (8)	2.91 (8)	3.470 (4)	136 (6)
N2—H2N···S3	0.73 (8)	2.89 (8)	3.514 (4)	145 (7)
N2—H3N···N3^{ii}	0.99 (4)	1.95 (4)	2.897 (5)	159 (4)
N4—H6N···S3^{i}	0.90 (5)	2.44 (5)	3.311 (4)	163 (4)
N4—H7N···S2^{iii}	0.87 (4)	2.50 (4)	3.357 (4)	170 (3)
N4—H8N···S3^{iv}	0.90 (4)	2.47 (4)	3.362 (4)	171 (3)

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2497).

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Bis{2,2′-[(2-aminoethyl)azanediyl]diethanaminium} di-μ-sulfido-bis(disulfidogermanate)

Chao Xu, Jing-Jing Zhang, Taike Duan, Qun Chen and Qian-Feng Zhang

S1. Comment

There has been an extensive interest in main group metal–chalcogenide compounds because of their unique structures and potential applications in areas such as semiconductors and photocatalysis (Zheng *et al.*, 2005). To synthesize related compounds, many attempts have been made to the reaction of metal-sulfur fluxes at high temperature (Bowes & Ozin, 1996). Compared to the harsh conditions, solvothermal synthesis in a lower temperature is the most efficient choice for the synthesis of metal–chalcogenide complexes (Zheng *et al.*, 2002). In this paper, we report the hydrothermal synthesis and crystal structure of a new thiogermanate, $[taeaH_2]_2[Ge_2S_6]$ (taea = tris(2-aminoethyl)amine).

The title compound is composed of a dimeric $[Ge_2S_6]^{4-}$ anion and two diprotonated $[taeaH_2]^{2+}$ cations (Fig. 1). The dimeric anion is constructed by two edge-sharing tetrahedral GeS_4 units, forming a planar four-membered Ge_2S_2 ring. The S—Ge—S angles from the tetrahedral unit display a range from 94.68 (3) to 115.75 (4)°. The Ge—S—Ge angle in the four-membered Ge_2S_2 ring is 85.32 (3)°. The average bond length of Ge—S_t (terminal bond) is shorter than that of Ge—S_b (bridging bond) by 0.118 Å. The bond parameters in the title compound are similar to those found in the other thiogermmanates (Jia *et al.*, 2005). Two terminal amine groups from the taea molecule are protonated to balance negative charges of the dimeric anion. The anions and cations are organized into an extended three-dimensional network by N—H···N and N—H···S hydrogen bonds (Fig. 2 and Table 1).

S2. Experimental

GeO_2 (104.6 mg, 1.0 mmol) and S (128.0 mg, 4.0 mmol) were mixed with tris(2-aminoethyl)amine (2.0569 g) in a 23 ml Teflon-lined stainless steel autoclave and stirred for 20 min. The vessel was sealed and heated to 190°C for 6 d and then cooled to room temperature. Colorless flake crystals were obtained and air dried. The yield based on GeO_2 is about 40%. Analysis, calculated for $C_{12}H_{40}Ge_2N_8S_6$: C 22.7, H 6.36, N 17.7%; found: C 22.5, H 6.31, N 17.6%.

S3. Refinement

C-bound H atoms were positioned geometrically and refined as riding atoms. with C—H = 0.97 (CH_2) Å and with U_{iso}(H) = 1.2U_{eq}(C). N-bound H atoms were located from a difference Fourier map and refined isotropically.

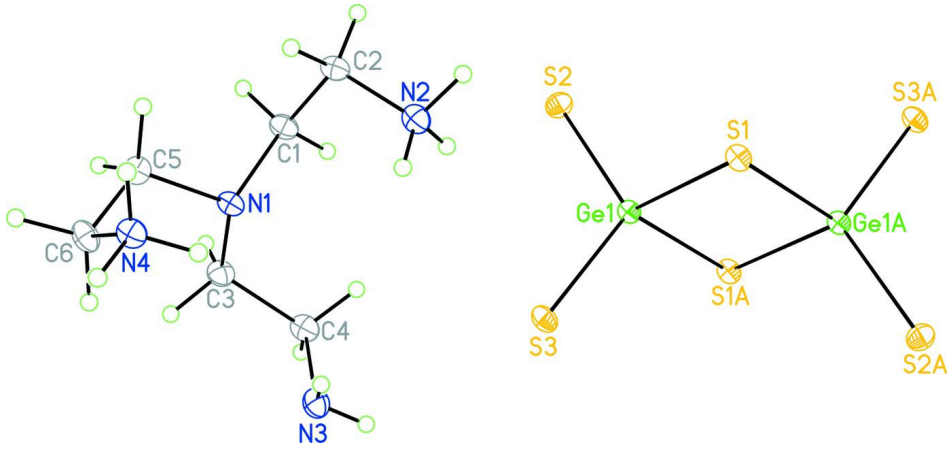

Figure 1

The structure of the title compound, showing displacement ellipsoids at the 50% probability level.

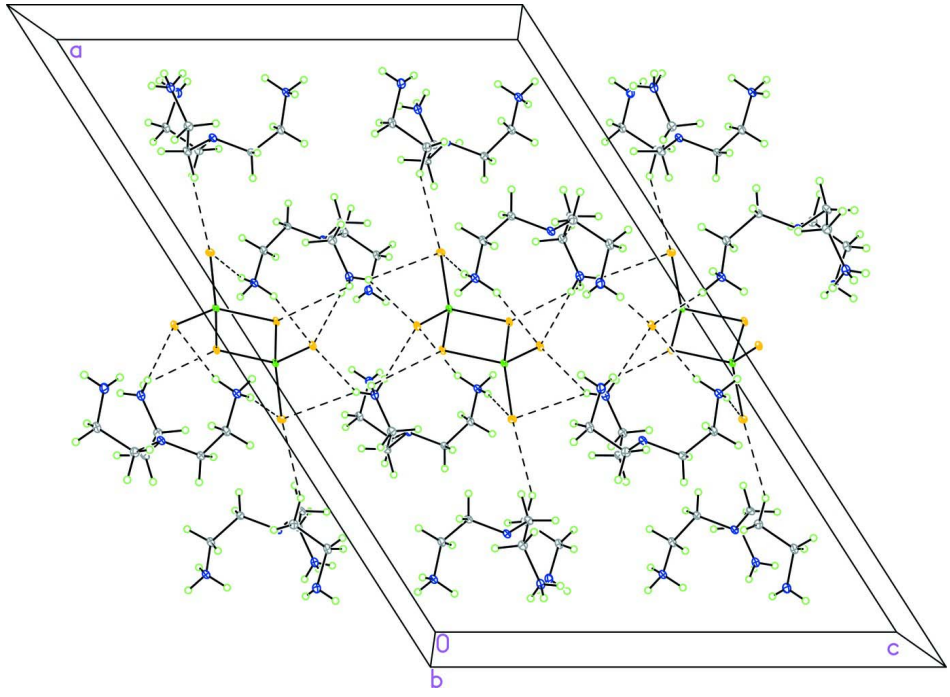

Figure 2

Packing diagram of the title compound. Dashed lines denote hydrogen bonds.

Bis{2,2′-[(2-aminoethyl)azanediyl]diethanaminium} di-μ-sulfido-bis(disulfidogermanate)

Crystal data

$(C_6H_{20}N_4)_2[Ge_2S_6]$
$M_r = 634.06$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 25.2845\ (17)$ Å
$b = 7.3173\ (4)$ Å
$c = 16.6001\ (9)$ Å
$\beta = 122.637\ (4)°$
$V = 2586.3\ (3)$ Å^3
$Z = 4$
$F(000) = 1312$
$D_x = 1.628$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3750 reflections
$\theta = 2.9–26.8°$
$\mu = 2.83$ mm^{-1}

T = 296 K
Block, colorless

0.19 × 0.16 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.616, T_{max} = 0.677

11988 measured reflections
2952 independent reflections
2243 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.5°, θ_{min} = 1.9°
h = −28→32
k = −9→9
l = −21→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.111
S = 1.03
2952 reflections
159 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.05 e Å^{-3}
$\Delta\rho_{min}$ = −1.08 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ge1	0.046082 (16)	0.40953 (4)	0.47830 (2)	0.02516 (14)
S1	−0.02392 (4)	0.64364 (11)	0.40812 (6)	0.0284 (2)
S2	0.14075 (4)	0.50236 (13)	0.53795 (7)	0.0368 (2)
S3	0.01711 (4)	0.17923 (11)	0.38125 (6)	0.0322 (2)
N1	0.16919 (14)	0.0976 (3)	0.2936 (2)	0.0291 (7)
N2	0.10013 (18)	0.4325 (5)	0.3045 (3)	0.0375 (8)
H1N	0.074 (2)	0.358 (6)	0.263 (3)	0.042 (12)*
H2N	0.096 (3)	0.399 (9)	0.342 (6)	0.11 (3)*
H3N	0.0834 (19)	0.559 (6)	0.295 (3)	0.043 (11)*
N3	0.08225 (18)	−0.1798 (5)	0.3167 (3)	0.0411 (8)
H4N	0.061 (2)	−0.179 (7)	0.340 (4)	0.062 (17)*
H5N	0.066 (2)	−0.111 (6)	0.277 (3)	0.040 (14)*
N4	0.09320 (16)	0.0946 (5)	0.0738 (2)	0.0344 (7)

H6N	0.070 (2)	0.112 (6)	0.100 (4)	0.054 (14)*
H7N	0.1009 (18)	0.199 (6)	0.058 (3)	0.038 (11)*
H8N	0.0691 (18)	0.031 (5)	0.019 (3)	0.034 (10)*
C1	0.19669 (17)	0.2513 (5)	0.3611 (3)	0.0353 (8)
H1A	0.2403	0.2653	0.3812	0.042*
H1B	0.1957	0.2233	0.4174	0.042*
C2	0.16258 (18)	0.4298 (5)	0.3188 (3)	0.0370 (9)
H2A	0.1874	0.5293	0.3610	0.044*
H2B	0.1584	0.4496	0.2578	0.044*
C3	0.18437 (18)	−0.0753 (5)	0.3472 (3)	0.0375 (9)
H3A	0.2283	−0.0737	0.3987	0.045*
H3B	0.1784	−0.1755	0.3048	0.045*
C4	0.14468 (19)	−0.1096 (5)	0.3891 (3)	0.0396 (9)
H4A	0.1659	−0.1972	0.4409	0.048*
H4B	0.1401	0.0035	0.4152	0.048*
C5	0.19364 (17)	0.0959 (5)	0.2311 (3)	0.0342 (8)
H5A	0.2350	0.0400	0.2652	0.041*
H5B	0.1983	0.2209	0.2165	0.041*
C6	0.15200 (18)	−0.0063 (5)	0.1386 (3)	0.0372 (8)
H6A	0.1745	−0.0252	0.1070	0.045*
H6B	0.1419	−0.1252	0.1526	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ge1	0.0285 (2)	0.0261 (2)	0.0180 (2)	0.00119 (14)	0.01058 (16)	0.00061 (12)
S1	0.0353 (5)	0.0292 (4)	0.0177 (4)	0.0043 (3)	0.0123 (4)	0.0038 (3)
S2	0.0288 (5)	0.0419 (6)	0.0347 (5)	−0.0023 (4)	0.0138 (4)	0.0004 (4)
S3	0.0412 (5)	0.0293 (5)	0.0231 (4)	0.0015 (4)	0.0153 (4)	−0.0034 (3)
N1	0.0328 (16)	0.0249 (14)	0.0219 (14)	0.0012 (12)	0.0097 (12)	0.0013 (11)
N2	0.045 (2)	0.036 (2)	0.0295 (18)	0.0025 (16)	0.0191 (17)	0.0009 (15)
N3	0.047 (2)	0.043 (2)	0.035 (2)	0.0016 (17)	0.0230 (18)	−0.0023 (16)
N4	0.0356 (18)	0.0358 (18)	0.0248 (16)	0.0000 (15)	0.0116 (15)	0.0001 (14)
C1	0.0354 (19)	0.0322 (19)	0.0274 (18)	−0.0033 (15)	0.0097 (15)	−0.0042 (14)
C2	0.041 (2)	0.0298 (19)	0.037 (2)	−0.0050 (16)	0.0187 (18)	−0.0034 (15)
C3	0.044 (2)	0.0283 (19)	0.039 (2)	0.0064 (16)	0.0216 (18)	0.0079 (15)
C4	0.050 (2)	0.036 (2)	0.029 (2)	−0.0008 (17)	0.0186 (18)	0.0017 (15)
C5	0.0314 (19)	0.038 (2)	0.0273 (18)	0.0032 (15)	0.0119 (16)	0.0041 (14)
C6	0.044 (2)	0.035 (2)	0.0268 (18)	0.0076 (16)	0.0151 (16)	−0.0008 (15)

Geometric parameters (Å, º)

Ge1—S2	2.1482 (10)	N4—H8N	0.90 (4)
Ge1—S3	2.1677 (9)	C1—C2	1.514 (5)
Ge1—S1^{i}	2.2715 (9)	C1—H1A	0.9700
Ge1—S1	2.2804 (9)	C1—H1B	0.9700
N1—C5	1.466 (5)	C2—H2A	0.9700
N1—C1	1.471 (4)	C2—H2B	0.9700

N1—C3	1.473 (4)	C3—C4	1.519 (6)
N2—C2	1.465 (5)	C3—H3A	0.9700
N2—H1N	0.85 (4)	C3—H3B	0.9700
N2—H2N	0.73 (8)	C4—H4A	0.9700
N2—H3N	0.99 (4)	C4—H4B	0.9700
N3—C4	1.467 (5)	C5—C6	1.511 (5)
N3—H4N	0.81 (5)	C5—H5A	0.9700
N3—H5N	0.75 (5)	C5—H5B	0.9700
N4—C6	1.479 (5)	C6—H6A	0.9700
N4—H6N	0.90 (5)	C6—H6B	0.9700
N4—H7N	0.87 (4)		

S2—Ge1—S3	115.74 (4)	N2—C2—C1	112.4 (3)
S2—Ge1—S1^{i}	112.57 (4)	N2—C2—H2A	109.1
S3—Ge1—S1^{i}	110.36 (4)	C1—C2—H2A	109.1
S2—Ge1—S1	111.28 (4)	N2—C2—H2B	109.1
S3—Ge1—S1	110.26 (3)	C1—C2—H2B	109.1
S1^{i}—Ge1—S1	94.69 (3)	H2A—C2—H2B	107.9
Ge1^{i}—S1—Ge1	85.31 (3)	N1—C3—C4	113.4 (3)
C5—N1—C1	109.8 (3)	N1—C3—H3A	108.9
C5—N1—C3	110.4 (3)	C4—C3—H3A	108.9
C1—N1—C3	109.5 (3)	N1—C3—H3B	108.9
C2—N2—H1N	116 (3)	C4—C3—H3B	108.9
C2—N2—H2N	120 (6)	H3A—C3—H3B	107.7
H1N—N2—H2N	94 (6)	N3—C4—C3	111.6 (3)
C2—N2—H3N	112 (2)	N3—C4—H4A	109.3
H1N—N2—H3N	113 (4)	C3—C4—H4A	109.3
H2N—N2—H3N	101 (5)	N3—C4—H4B	109.3
C4—N3—H4N	108 (4)	C3—C4—H4B	109.3
C4—N3—H5N	109 (3)	H4A—C4—H4B	108.0
H4N—N3—H5N	102 (5)	N1—C5—C6	113.3 (3)
C6—N4—H6N	112 (3)	N1—C5—H5A	108.9
C6—N4—H7N	111 (3)	C6—C5—H5A	108.9
H6N—N4—H7N	109 (4)	N1—C5—H5B	108.9
C6—N4—H8N	110 (2)	C6—C5—H5B	108.9
H6N—N4—H8N	107 (4)	H5A—C5—H5B	107.7
H7N—N4—H8N	107 (4)	N4—C6—C5	111.6 (3)
N1—C1—C2	112.9 (3)	N4—C6—H6A	109.3
N1—C1—H1A	109.0	C5—C6—H6A	109.3
C2—C1—H1A	109.0	N4—C6—H6B	109.3
N1—C1—H1B	109.0	C5—C6—H6B	109.3
C2—C1—H1B	109.0	H6A—C6—H6B	108.0
H1A—C1—H1B	107.8		

Symmetry code: (i) $-x, -y+1, -z+1$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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N4—H8*N*···S3^{v}	0.90 (4)	2.47 (4)	3.362 (4)	171 (3)

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