Cs$_4$Ge$_2$S$_8$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(S–S) = 0.001 Å
R factor = 0.021
wR factor = 0.051
Data-to-parameter ratio = 34.6

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

The reaction of Cs$_2$S$_3$, Ge and S yields single crystals of tetracesium digermanium octasulfide, Cs$_4$Ge$_2$S$_8$. The structure contains the novel dinuclear anion [Ge$_2$S$_8$]$^{4-}$, and is another example of a chalcogenidogermanate(IV) exhibiting S$_2$ bridging units. Two GeS$_4$ tetrahedra in the anion are linked *via* S—S bonds, yielding a six-membered ring which displays a chair conformation and crystallographic C_{2h} symmetry. The anions are connected *via* Cs$^+$ ions. The compound crystallizes with the Cs$_4$Ge$_2$Se$_8$ structure.

Comment

The hitherto-known ternary alkali chalcogenido-germanates with composition A_2GeQ_4, where A is K, Rb or Cs and Q is Se or Te (Eisenmann, Schrod & Schäfer, 1984; Sheldrick & Schaaf, 1994, 1995) crystallize in three different structure types characterized by GeQ_4 units that are interconnected by covalent Q—Q bonding. Attempts to prepare the analogous ternary germanium sulfides yielded the title compound, Cs$_4$Ge$_2$S$_8$.

The crystal structure of Cs$_4$Ge$_2$S$_8$ is based on discrete [Ge$_2$S$_8$]$^{4-}$ anions, which are connected by Cs$^+$ cations. The [Ge$_2$S$_8$]$^{4-}$ anion is composed of two GeS$_4$ tetrahedra which are bridged *via* two S—S bonds, thus forming a six-membered Ge$_2$S$_4$ ring (Fig. 1). This ring shows a chair conformation and crystallographic C_{2h} symmetry. The terminal Ge—S distances are 2.1428 (11) and 2.1528 (12) Å, which are shorter than the Ge—S bonds to the S atom of the bridging S$_2^{2-}$ anions [2.2891 (8) Å]. The S—S distance of 2.0767 (15) Å is typical for an S—S single bond (Table 1). The S—Ge—S angles are in the range 100.40 (3)–125.13 (5)° (Table 1), indicating a strong distortion of the GeS$_4$ tetrahedron. The Ge—S bond lengths
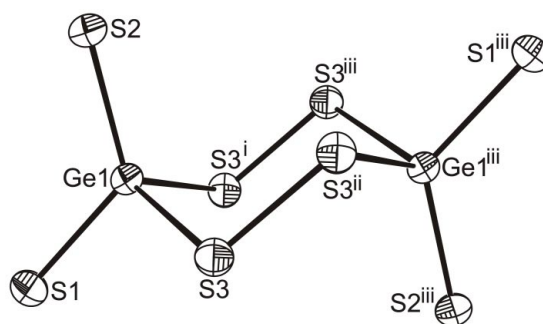

Figure 1
A view of the dimeric [Ge$_2$S$_8$]$^{4-}$ anion of Cs$_4$Ge$_2$S$_8$ with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level [symmetry codes: (i) x, $-y$, z; (ii) $-x$, y, $1-z$; (iii) $-x$, $-y$, $1-z$].
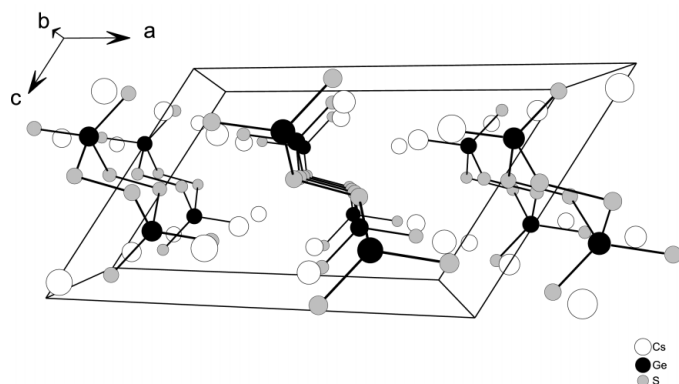
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Figure 2
The crystal structure of $Cs_4Ge_2S_8$ viewed parallel to the crystallographic b axis.

and S—Ge—S angles are within the ranges found for other thiogermanates (Eisenmann, Kieselbach *et al.*, 1984; Klepp & Fabian, 1999; Klepp, 2000).

The two crystallographically independent Cs^+ cations are coordinated by nine S atoms within irregular polyhedra, with Cs—S distances in the range 3.4979 (13)–3.7200 (9) Å. The average of these distances is 3.666 (1) Å, which well matches the sum of the ionic radii [1.84 Å for S^{2-} and 1.78 Å for Cs^+ (CN9); Shannon, 1976]. The anions are stacked in a rod-like manner parallel to [010], with the Cs^+ ions located between the rods (Fig. 2). We note that $Cs_4Ge_2S_8$ is isotypic with $Cs_4Ge_2Se_8$ (Sheldrick & Schaaf, 1994).

Experimental

The title compound, $Cs_4Ge_2S_8$, was initially synthesized from a mixture of Cs_2S_3, Ge, Sb and S in the ratio 2:2:1:7. Cs_2S_3 was prepared from stoichiometric amounts of Cs and S in liquid ammonia under an argon atmosphere. The starting materials were thoroughly mixed and loaded into a silica tube in a nitrogen-filled glove box. After evacuating to 10^{-3} mbar (1 mbar = 100 Pa) the tube was flame-sealed, placed in a computer-controlled furnace and heated to 853 K within 24 h. After 3 d the tube was cooled at a rate of 2 K h^{-1} to 373 K, followed by rapid cooling to room temperature. The resulting product was washed with dry *N,N*-dimethylformamide and diethyl ether and the residue dried *in vacuo*. The product consisted of orange platelet-like crystals which were slightly contaminated with transparent colourless crystals that have been identified as Cs_2SO_4. A reaction without Sb (Cs_2S_3:Ge:S 2:2:7) also gave a single phase of $Cs_4Ge_2S_8$. The crystals are stable in air for several weeks.

Crystal data

$Cs_4Ge_2S_8$	$D_x = 3.450$ Mg m^{-3}
$M_r = 933.42$	Mo $K\alpha$ radiation
Monoclinic, $C2/m$	Cell parameters from 108
$a = 14.721$ (2) Å	reflections
$b = 7.364$ (1) Å	$\theta = 14$–19°
$c = 9.820$ (1) Å	$\mu = 12.23$ mm^{-1}
$\beta = 122.43$ (1)°	$T = 293$ (2) K
$V = 898.5$ (2) Å^3	Polyhedron, orange
$Z = 2$	$0.12 \times 0.08 \times 0.06$ mm

Data collection

Phillips PW1100 four-circle diffractometer	$R_{int} = 0.034$
	$\theta_{max} = 30°$
ω/θ scans	$h = -20 \rightarrow 18$
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)	$k = -10 \rightarrow 10$
	$l = -13 \rightarrow 13$
$T_{min} = 0.322$, $T_{max} = 0.480$	4 standard reflections
4059 measured reflections	frequency: 120 min
1417 independent reflections	intensity decay: none
1244 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.021$	$\Delta\rho_{max} = 0.92$ e Å^{-3}
$wR(F^2) = 0.051$	$\Delta\rho_{min} = -0.87$ e Å^{-3}
$S = 1.08$	Extinction correction: *SHELXL*97
1417 reflections	(Sheldrick, 1997)
41 parameters	Extinction coefficient: 0.00151 (12)
$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2 + 2.6105P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Cs1—S2^i	3.6229 (13)	Cs2—S3^{iv}	3.6289 (8)
Cs1—S2^{ii}	3.6256 (12)	Cs2—S3^{vi}	3.6289 (8)
Cs1—S3	3.6866 (8)	Cs2—S3^{viii}	3.7040 (9)
Cs1—S3^{iii}	3.6866 (8)	Cs2—S3^{ix}	3.7040 (9)
Cs1—S1	3.7132 (13)	Cs2—S2^v	3.7176 (5)
Cs1—S1^{iv}	3.7170 (5)	Cs2—S2^{iv}	3.7176 (5)
Cs1—S1^v	3.7170 (5)	Ge1—S2	2.1428 (11)
Cs1—S3^{iv}	3.7200 (9)	Ge1—S1	2.1528 (12)
Cs1—S3^{vi}	3.7200 (9)	Ge1—S3^{iii}	2.2891 (8)
Cs2—S1^{ii}	3.4979 (13)	Ge1—S3	2.2891 (8)
Cs2—S1^{vii}	3.5177 (13)	S3—S3^x	2.0767 (15)
Cs2—S2^{ii}	3.6241 (14)		
S2—Ge1—S1	125.13 (5)	S2—Ge1—S3	112.65 (3)
S2—Ge1—S3^{iii}	112.65 (3)	S1—Ge1—S3	100.40 (3)
S1—Ge1—S3^{iii}	100.40 (3)	S3^{iii}—Ge1—S3	102.71 (4)

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

Data collection: *DIF*4 (Stoe & Cie, 1990); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1990); 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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