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Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{Se}-\text{Ge}) = 0.003$ Å
 R factor = 0.056
 wR factor = 0.145
Data-to-parameter ratio = 15.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Reinvestigation of Hg_2GeSe_4 based on single-crystal data

Dimercury(II) germanium(IV) tetraselenide, Hg_2GeSe_4 , adopts a cation-deficient diamond-like structure. It crystallizes in space group $\bar{I}4$ of the tetragonal system. The structure consists of tetrahedral $[\text{HgSe}_4]$ and $[\text{GeSe}_4]$ groups. These groups are interconnected by sharing common corners. The previous structure report on Hg_2GeSe_4 based on powder diffraction data [Parasyuk *et al.*, (2003). *J. Alloys Compd.*, **351**, 135–144] is comparable with our results except for the absolute configuration determination. In the asymmetric unit, the site symmetries of the Hg and Ge atoms are $\bar{4}$.

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Comment

The synthesis and crystal structure of Hg_2GeSe_4 have been reported, but with limited precision (Parasyuk *et al.*, 2003). Single crystals of reasonable quality and size suitable for X-ray diffraction studies have not been obtained with traditional solid-state synthetic techniques. Consequently, the X-ray diffraction data have been collected from powders and structural analysis has been carried out by the Rietveld profile refinement technique. The previously reported crystal structure of Hg_2GeSe_4 has been refined in the non-centrosymmetric space group $\bar{I}4$ and the initial positional parameters were taken from cadmium thiogallate, CdGa_2S_4 (Krämer *et al.*, 1983). We have used halide mixtures to prepare single crystals of metal chalcogenides, and this synthetic technique appears to be of general utility in preparing crystalline chalcogenides (Do & Yun, 1996; Kim *et al.*, 1997). We describe here the synthesis and structural characterization of Hg_2GeSe_4 single crystals.

The general features of the structure of Hg_2GeSe_4 are the same as previously reported (Parasyuk *et al.*, 2003). Fig. 1

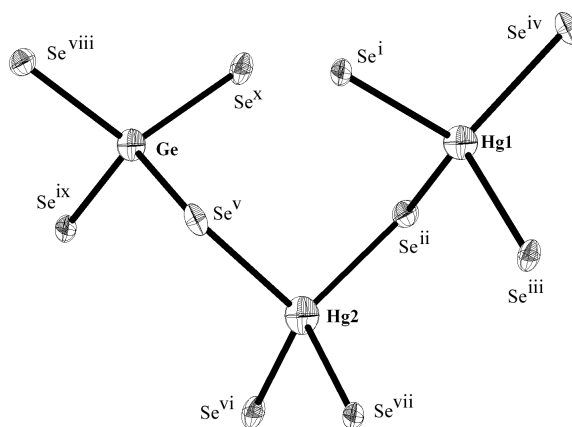


Figure 1
Interconnection of the tetrahedral $[\text{HgSe}_4]$ and $[\text{GeSe}_4]$ groups through sharing common Se atoms. Displacement ellipsoids are drawn at the 90% probability level. Symmetry codes are as given in Table 1.

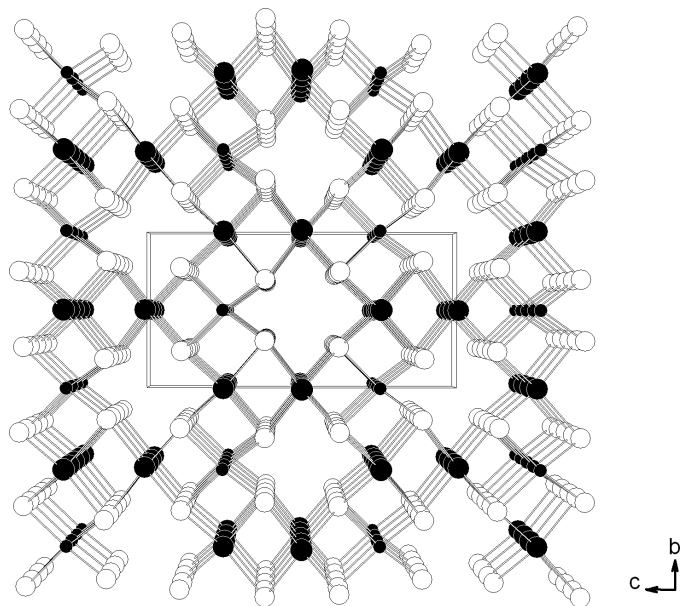


Figure 2
The structure of Hg_2GeSe_4 , viewed down [100]. Large filled circles are Hg atoms, small filled circles are Ge atoms and open circles are Se atoms.

shows the interconnection of the $[\text{HgSe}_4]$ and $[\text{GeSe}_4]$ tetrahedra. There are two crystallographically independent mercury sites in the structure. The Hg–Se separations [2.658 (3) Å for Hg1–Se and 2.646 (3) Å for Hg2–Se] are in good agreement with those calculated from the covalent radii of Hg and Se (1.49 and 1.16 Å, respectively; radii taken from Webelements, 2004). While the bond distances between Hg and Se atoms are almost the same, the Hg_2Se_4 tetrahedron is significantly distorted compared to the Hg_1Se_4 tetrahedron. The Ge–Se distance [2.374 (2) Å] also agrees well with the sum of the covalent radii (Ge: 1.22 Å) and is comparable with those of other selenogermanates such as $\text{SrCu}_2\text{GeSe}_4$ [2.345 (5)–2.370 (4) Å; Tampier & Johrendt, 2001]. These tetrahedra are connected by sharing common corners, forming a three-dimensional network. As a result, the title compound belongs to the class of cation-deficient diamond-like structures, where one out of the four cationic sites is empty.

The cell parameters [$a = 5.6786$ (2) Å and $c = 11.2579$ (5) Å] and interatomic distances [Hg1–Se = 2.672 (4) Å, Hg2–Se = 2.671 (4) Å and Ge–Se = 2.384 (4) Å] determined from the room temperature powder data are slightly larger than those of the present work performed at 150 K based on single-crystal data. The difference is probably due simply to the temperature difference.

Experimental

Hg_2GeSe_4 was prepared by the reaction of HgSe, elemental Ge, and Se with the use of the reactive halide flux technique. A combination of HgSe (CERAC 99.8%), Ge powder (CERAC 99.5%) and Se powder (Aldrich 99.999%) was loaded in a quartz tube in a molar ratio of HgSe:Ge:Se = 1:1:5 and an $\text{ErCl}_3/\text{NaCl}$ eutectic mixture was then added in a weight ratio of $\text{HgGeSe}_6:\text{ErCl}_3/\text{NaCl} = 1:2$. The tube

was evacuated to 10^{-2} Torr, sealed, and heated gradually (50 K h^{-1}) to 1123 K in a tube furnace where it was kept for 24 h. The tube was cooled slowly to 373 K at a rate of 4 K h^{-1} and quenched. Black shiny needle-shaped crystals up to 0.40 mm in length were found. The excess halides were removed with distilled water. The crystals are stable in air and water. Analysis of these crystals with the microprobe of an EDAX-equipped AMRAY 1200 C scanning electron microscope indicated the presence of Hg, Ge and Se. No other element was detected.

Crystal data

Hg_2GeSe_4	Mo $K\alpha$ radiation
$M_r = 789.63$	Cell parameters from 22 reflections
Tetragonal, $I\bar{4}$	$\theta = 12.0\text{--}14.5^\circ$
$a = 5.6741$ (17) Å	$\mu = 66.39 \text{ mm}^{-1}$
$c = 11.249$ (5) Å	$T = 150$ (2) K
$V = 362.2$ (2) Å ³	Needle, black
$Z = 2$	$0.40 \times 0.02 \times 0.01 \text{ mm}$
$D_x = 7.241 \text{ Mg m}^{-3}$	

Data collection

MacScience MXC3 diffractometer	$R_{\text{int}} = 0.066$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.4^\circ$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$h = 0 \rightarrow 7$
$T_{\text{min}} = 0.220$, $T_{\text{max}} = 0.520$	$k = 0 \rightarrow 7$
288 measured reflections	$l = 0 \rightarrow 14$
263 independent reflections	2 standard reflections every 100 reflections
260 reflections with $I > 2\sigma(I)$	intensity decay: 0.5%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.056$	$\Delta\rho_{\text{max}} = 3.24 \text{ e \AA}^{-3}$
$wR(F^2) = 0.145$	$\Delta\rho_{\text{min}} = -5.17 \text{ e \AA}^{-3}$
$S = 1.08$	Extinction correction: <i>SHELXL97</i>
263 reflections	Extinction coefficient: 0.027 (4)
17 parameters	Absolute structure: Flack (1983), 38 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.12P)^2 + 19.6039P]$	Flack parameter = -0.01 (6)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (Å, °).

Hg1–Se ⁱ	2.658 (3)	Ge–Se ⁱⁱⁱ	2.374 (2)
Hg2–Se ⁱⁱ	2.646 (3)		
Se ⁱ –Hg1–Se ^{iv}	108.29 (5)	Se ⁱⁱ –Hg2–Se ^v	104.49 (5)
Se ⁱ –Hg1–Se ^v	111.86 (11)	Se ⁱⁱⁱ –Ge–Se ^{vii}	102.34 (13)
Se ⁱⁱ –Hg2–Se ^{vi}	119.97 (12)	Se ⁱⁱⁱ –Ge–Se ^{viii}	113.15 (7)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} + y, z - \frac{1}{2}$; (ii) $\frac{1}{2} - y, x - \frac{1}{2}, \frac{3}{2} - z$; (iii) $1 - x, 1 - y, z$; (iv) $y, 1 - x, 1 - z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $y - \frac{1}{2}, \frac{1}{2} - x, \frac{3}{2} - z$; (vii) $x - 1, y, z$; (viii) $y - \frac{1}{2}, \frac{3}{2} - x, \frac{3}{2} - z$.

The absolute structure for this particular crystal was found to be the opposite of that represented by the published coordinates from the previous powder study (Parasyuk *et al.*, 2003) gave a value of $x = 0.85$ (9) for the Flack (1983) parameter ($wR2 = 0.1913$), which suggests that the absolute structure may not be correct. Refinement of the inverse structure which is in agreement with the selected setting of this work leads to $x = -0.01$ (6) and significantly improved the reliability factor ($wR2 = 0.1449$). The highest residual electron density is 2.32 \AA^{-3} from the Hg1 site and the deepest hole is 0.95 \AA^{-3} from the Se site.

Data collection: *MXC3 Diffractometer Control Software* (MacScience, 1994); cell refinement: *MXC3 Diffractometer Control Software*; data reduction: *MXC3 Diffractometer Control Software*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985);

program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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