

Synthesis and Crystal Structure of The New Selenogermanate, Cs₂CdGe₃Se₈

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Transition metal chalcogenosulfates form a wide and interesting class of compounds that have attracted attention because of their various structural chemistry and interesting properties.¹ Many ternary and quaternary compounds have been synthesized in this class. These materials have various phosphorus-sulfur/selenium polyanions and we found that the variability in the combination of these moieties with transition metals led us to find numerous new phases.²

In the case of chalcogenogermanate anions, various [Ge_xQ_yⁿ⁻] anions (Q=S or Se) are found in ternary or quaternary compounds, with mainly two types of building units of the trigonal pyramidal [GeQ₃³⁻] and tetrahedral [GeQ₄⁴⁻] being the most dominant.³ Condensed oligomers of [GeQ₃³⁻] are found in dimeric [Ge₂Se₄²⁻]⁴ and [Ge₂Q₅⁴⁻],⁵ trimeric [Ge₃Se₇⁵⁻],⁶ and hexameric [Ge₆Te₁₂⁶⁻] phases,⁷ whereas examples of the [GeQ₄⁴⁻] units are also found in the dimeric [Ge₂Q₆⁴⁻]⁸ and [Ge₂Q₇⁶⁻],⁹ trimeric [Ge₃S₉⁶⁻],¹⁰ and [Ge₄Q₁₀⁴⁻].¹¹ However their chemistry has not been abundant compared with their phosphate counterparts. This is probably due to the synthetic hindrance and we have exploited eutectic halide mixture as reactive fluxes to find new metal chalcogenogermanate phases. This synthetic technique proved to be of general utility in preparing crystalline metal chalcogenides.^{12,13}

As a guidepost toward a new compound, we have started from the known thiophosphate phases and anticipated substitution of PQ₄³⁻ for GeQ₄⁴⁻ (Q=S, Se) ions while the metal centered polyhedral structure are maintained. The mother structure can be modified by various factors such as radius ratios of each atom, preferred coordination of transition metals, reaction conditions, and stoichiometries of compounds. The GeS₄ units unlike PS₄ do not share two edges with metal centered octahedron because the ionic radii of Ge⁴⁺ is 0.390 Å while that of P⁵⁺ is only 0.17 Å. Usually the metal centered polyhedra connected by the tetrahedral GeS₄⁴⁻ unit adopt chain or layer structure and charges of these low-dimensional units form negative polyanions and the alkali metals play a role to balance the charge of the compounds and stabilize the structure through electrostatic interactions. As a result, the basic structure pattern is perturbed and the new structural type can be generated.

Experimental

Synthesis. The title compound, Cs₂CdGe₃Se₈ was prepared

by the reaction of elements with the use of the reactive halide-flux technique. A combination of the pure elements, Cd powder (Cerac, 99.5%), Ge powder (Cerac, 99.999%), Se powder (Aldrich) were mixed in a fused silica tube in molar ratio of Cd:Ge:Se = 1:1:4 and then CsCl (Sigma-Aldrich 99%) was added. The mass ratio of the reactants and the halide was 1:2. The tube was evacuated to 0.133 Pa, sealed, and heated gradually (14 K/h) to 923 K, where it was kept for 5 days. The tube was cooled to 373 K at the rate 5 K/h. The excess halide was removed with distilled water and dark green block-shaped crystals were obtained. The crystals are stable in air and water. A qualitative X-ray fluorescence analysis of the block indicated the presence of Cs, Cd, Ge, and Se. The composition of the compound was determined by single-crystal X-ray diffraction.

Crystallographic Studies. The structure of Cs₂CdGe₃Se₈ was determined by single crystal X-ray diffraction methods. Preliminary examination and data collection were performed

Table 1. Crystal data and structure refinement for Cs₂CdGe₃Se₈

Formula weight, amu	1227.67
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
a, Å	7.689(3)
b, Å	12.582(5)
c, Å	17.788(6)
V, Å ³	1721.0(10)
Z	4
T, K	150(1)
Radiation	Graphite monochromated MoKα (λ = 0.71073)
Linear absorption coefficient, mm ⁻¹	27.46
Crystal size, mm ³	0.30 × 0.07 × 0.05
Scan type	ω
θ limits, deg.	3.10° < θ < 27.47°
Data collected	± h, ± k, ± l
No. of unique data with F _o ² > 0	3905
Flack x parameter	0.59(1)
No. of unique data with F _o ² > 2σ (F _o ²)	3441
wR2 (F _o ² > 0)	0.0619
R(on F _o for F _o ² > 2σ (F _o ²))	0.0344
Goodness-of-fit on F ²	1.042
Min. and Max. residual	
Electron density (e/Å ³)	-0.995 and 1.088

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cs}_2\text{CdGe}_3\text{Se}_8$

	x	y	z	U(eq)
Cs1	2454(1)	3787(1)	4489(1)	17(1)
Cs2	-2325(1)	8127(1)	6529(1)	19(1)
Cd	-198(1)	-12(1)	3466(1)	14(1)
Ge1	2401(1)	-627(1)	5165(1)	10(1)
Ge2	2636(1)	519(1)	6756(1)	11(1)
Ge1	4808(1)	266(1)	3457(1)	10(1)
Se1	2392(1)	1340(1)	3417(1)	13(1)
Se2	-14(1)	5991(1)	5520(1)	12(1)
Se3	2314(1)	1205(1)	5505(1)	12(1)
Se4	2807(1)	-1316(1)	6404(1)	13(1)
Se5	-151(1)	-1268(1)	4657(1)	14(1)
Se6	4965(1)	4119(1)	2629(1)	13(1)
Se7	83(1)	3738(1)	2717(1)	15(1)
Se8	2231(1)	3642(1)	6503(1)	12(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

with Mo $K\alpha_1$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a RIGAKU R-ASXIS RAPID diffractometer. The cell constants and an orientation matrix were determined from least-squares, using the setting angles in the range $3.0^\circ < \theta < 27.5^\circ$. The crystallographic details are described in Table 1. Intensity data were collected with the ω scan technique.

The intensity statistics and systematic absences are consistent with the orthorhombic space group, $P2_12_12_1$. The initial positions for all atoms were obtained by using direct methods of the SHELXS-86 program.¹⁴ The structure was refined by full-matrix least-squares techniques with the use of the SHELXL-97 program.¹⁴ The data for $\text{Cs}_2\text{CdGe}_3\text{Se}_8$ were corrected for absorption using the multi-scan method.¹⁵ The final cycle of refinement performed on F_o^2 with 3905 unique reflections afforded residuals $wR2 = 0.0619$ and the conventional R index based on the reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.0344.

A difference Fourier synthesis calculated with phases based on the final parameters shows no peak heights greater than 1.09 e/\AA^3 . No unusual trends were found in the goodness of fit as a function of F_o , $\sin\theta/\lambda$ and Miller indices. Final values of the atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. Anisotropic displacement parameters and complete tabulations on the X-ray studies can be found in CIF format in the Supporting Information Section.

Result and Discussion

The general features of the structure of $\text{Cs}_2\text{CdGe}_3\text{Se}_8$ indicate that this phase is a new member of the previously characterized type II $A_2MM'_3Q_8$ family ($A=K, Rb, Cs, M=\text{transition metals}, M'=\text{Si, Ge, Q}=\text{S, Se, Te}$).¹⁶ Selected bond distances and angles are listed in Table 3. A view down the **a** axis, given in Figure 1 shows the two-dimensional nature of the compound. The structure of $\text{Cs}_2\text{CdGe}_3\text{Se}_8$ consists of two-dimensional $[\text{CdGe}_3\text{Se}_8]^{2-}$ layers separated by Cs^+

Table 3. Bond lengths [\AA] and angles [deg] for $\text{Cs}_2\text{CdGe}_3\text{Se}_8$

Bond lengths			
Cd-Ge1	2.612(1)	Ge2-Ge7#1	2.301(1)
Cd-Ge8#2	2.623(1)	Ge2-Ge6#2	2.371(1)
Cd-Ge7#10	2.629(1)	Ge2-Ge4	2.397(2)
Cd-Ge(5)	2.644(1)	Ge2-Ge3	2.399(1)
Ge1-Ge4	2.389(1)	Ge3-Ge1	2.298(1)
Ge1-Ge(5)	2.306(1)	Ge3-Ge8#1	2.316(1)
Ge1-Ge2#1	2.376(1)	Ge3-Ge2#1	2.416(1)
Ge1-Ge3	2.384(2)	Ge3-Ge6#12	2.416(1)
Bond Angles			
Se1-Cd-Ge8#2	98.47(5)	Se3-Ge1-Ge4	96.92(4)
Se1-Cd-Ge7#10	109.65(4)	Se4-Ge2-Ge3	96.32(4)
Se1-Cd-Ge(5)	113.86(4)	Se5-Ge1-Ge2#1	116.34(5)
Se7#10-Cd-Ge(5)	106.44(5)	Se5-Ge1-Ge3	114.44(5)
Se8#2-Cd-Ge7#10	115.78(4)	Se5-Ge1-Ge4	110.20(5)
Se8#2-Cd-Ge(5)	112.74(4)	Se6#2-Ge2-Ge3	105.66(5)
Se1-Ge3-Ge8#1	107.62(6)	Se6#2-Ge2-Ge4	110.65(5)
Se1-Ge3-Ge2#1	116.97(5)	Se7#1-Ge2-Ge6#2	116.25(5)
Se1-Ge3-Ge6#12	112.63(5)	Se7#1-Ge2-Ge4	116.94(5)
Se2#1-Ge1-Ge3	109.88(5)	Se7#1-Ge2-Ge3	108.44(5)
Se2#1-Ge1-Ge4	107.11(5)	Se8#1-Ge3-Ge2#1	108.64(5)
Se2#1-Ge3-Ge6#12	101.95(5)	Se8#1-Ge3-Ge6#12	108.72(5)

Symmetry transformations used to generate equivalent atom:

#1 $x+1/2, -y+1/2, -z+1$ #2 $x-1/2, -y+1/2, -z+1$ #3 $x+1/2, -y+3/2, -z+1$
 #4 $-x, y+1/2, -z+3/2$ #5 $x, y+1, z$ #6 $-x-1/2, -y+1, z+1/2$
 #7 $x-1, y+1, z$ #8 $-x+1/2, -y+1, z+1/2$ #9 $x-1/2, -y+3/2, -z+1$
 #10 $-x, y-1/2, -z+1/2$ #11 $-x-1/2, -y+1, z-1/2$ #12 $-x+1, y-1/2, -z+1/2$
 #13 $x+1, y-1, z$ #14 $x, y-1, z$ #15 $-x+1, y+1/2, -z+1/2$
 #16 $-x+1/2, -y+1, z-1/2$ #17 $-x, y+1/2, -z+1/2$ #18 $-x, y-1/2, -z+3/2$

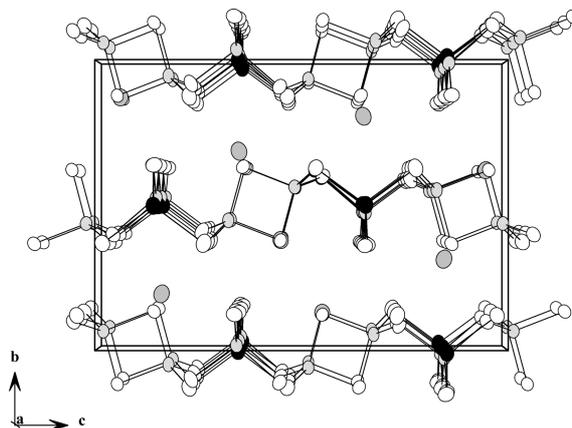


Figure 1. View of $\text{Cs}_2\text{CdGe}_3\text{Se}_8$ down the **a**-axis showing the stacking of the layers. Displacement ellipsoids are drawn at the 90% probability level. Filled circles are Cd atoms, hatched circles are Ge atoms, open circles are Se atoms, and gray circles are Cs atoms.

cations.

There is only one crystallography distinct Cd atom in this compound. The Cd atom is tetrahedrally coordinated by four Se atoms. The Ge atom is also surrounded by four Se atoms in a tetrahedral fashion. These alternating CdSe_4 and GeSe_4 tetrahedra are connected by sharing corners to form an

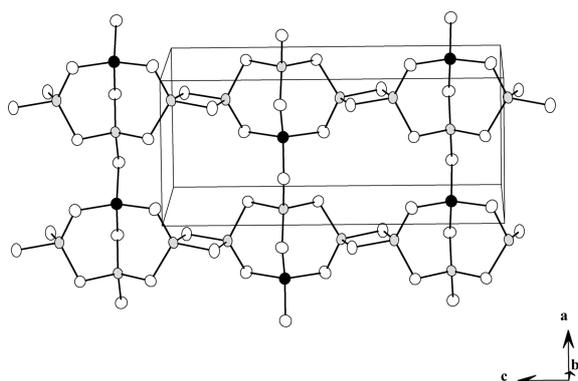


Figure 2. View of $\text{Cs}_2\text{CdGe}_3\text{Se}_8$ down the *b*-axis showing an individual layer and the coordination around the Cd and Ge atoms. Atoms are as marked in Figure 1.

infinite linear chain, ${}_2^2[\text{CdGeSe}_6]$ along the *a* axis. These chains are linked together through the Ge_2Se_6 units by sharing edges to form the two-dimensional ${}_2^2[\text{CdGe}_3\text{Se}_8^{2-}]$ along the *c* axis (Figure 2).

These layers then stack on top of each other to complete the three-dimensional structure with an undulating van der Waals gap shown in Figure 1. There is no bonding interaction, only van der Waals forces, between the layers. The Cd-Se distances range from 2.612(1) to 2.644(1) Å and the Ge-Se distances range from 2.298(1) to 2.416(1) Å. They are in good agreement with those calculated from crystal radii typical for these atoms.¹⁷ There is no bonding interactions between the Cd and Ge atoms. According to the bond valence calculations,¹⁸ the global instability index of the structure, $G_{ii} = 0.1518\text{v.u}$ and the charge balance can be described by $[\text{Cs}^+]_2[\text{Cd}^{2+}][\text{Ge}^{4+}]_3[\text{Se}^{2-}]_8$.

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Supporting Information. Crystallographic data for the structures reported here have been deposited with FIZ (Deposition No. CSD-425592). These data can be obtained free of charge from FIZ, D-76344, Eggenstein-Leopoldshafen, Germany, E-mail: crysdata@fiz-karlsruhe.de.

References

- Do, J.; Lee, K.; Yun, H. *J. Solid State Chem.* **1996**, *125*, 30.
- Do, J.; Yun, H. *Inorg. Chem.* **1996**, *35*(18), 5283.
- (a) Vincent, H.; Bertaut, E. *Acta Crystallogr.* **1976**, *B32*, 1749. (b) Mazurier, A.; Etienne, J. *Acta Crystallogr.* **1974**, *B30*, 759. (c) Eisenmann, B.; Kieselbach, E.; Schaefer, H.; Schrod, H. *Z. Anorg. Allg. Chem.* **1984**, *516*, 49.
- Tampier, M.; Johrendt, D.; Poettgen, R.; Kotzyba, G.; Rosenhahn, C.; Mosel, B. D. *Z. Naturforsch.* **2002**, *57b*, 133.
- (a) Eisenmann, B.; Schaefer, H.; Schwerer, H. *Z. Naturforsch.* **1983**, *38b*, 924. (b) Eisenmann, B.; Hansa, J.; Schaefer, H. *Mater. Res. Bull.* **1985**, *20*, 1339.
- Eisenmann, B.; Hansa, J.; Schaefer, H. *Z. Naturforsch.* **1985**, *40b*, 450.
- Eisenmann, B.; Schwerer, H.; Schaefer, H. *Mater. Res. Bull.* **1983**, *18*, 1189.
- (a) Eulenberger, G. *Acta Crystallogr.* **1978**, *B34*, 2614. (b) van Almsick, T.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1746.
- Eisenmann, B.; Hansa, J.; Schaefer, H. *Rev. Chim. Miner.* **1986**, *23*, 8.
- Bugli, G.; Carre, D.; Barnier, S. *Acta Crystallogr.* **1978**, *B34*, 3186.
- (a) Klepp, K. O.; Fabian, F. *Z. Naturforsch.* **1999**, *54b*, 1499. (b) Eisenmann, B.; Hansa, J. *Z. Kristallogr.* **1993**, *205*, 325. (c) Klepp, O. K.; Zeitlinger, M. *Z. Kristallogr.* **2000**, *215*, 7.
- (a) Do, J.; Dong, Y.; Kim, J.; Hahn, S.; Yun, H. *Bull. Kor. Chem. Soc.* **2005**, *26*(8), 1260. (b) Dong, Y.; Do, J.; Yun, H. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2676.
- Dong, Y.; Kim, S.; Yun, H.; Lim, H. *Bull. Kor. Chem. Soc.* **2005**, *26*(2), 309.
- Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.
- Rigaku *RAPID-AUTO Manual*, Rigaku Corporation, Tokyo, Japan, 2006.
- Hahn, S., Thesis, Ajou University, 2006.
- Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
- Adams, S. *Acta Crystallogr.* **2001**, *B57*, 278.