metal-organic papers

Bis(trimethylammonium) decaselenidotetragermanatomanganate(II)

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(Se–Mn) = 0.001 Å
H-atom completeness 91%
Disorder in solvent or counterion
R factor = 0.027
wR factor = 0.066
Data-to-parameter ratio = 14.6

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

Solvothermal reaction of Ge and Se with $Mn(CH_3COO)_2 \cdot 4H_2O$ in the presence of $[(CH_3)_3NH]Cl$ generates the open framework quaternary selenidogermanate(IV) $[(CH_3)_3NH]_2[MnGe_4Se_{10}]$, which contains corner-linked adamantanoid Ge_4Se_{10} cages and $MnSe_4$ tetrahedra. The trimethylammonium counter-cations are disordered and exhibit an S_4 crystallographic site symmetry. Whereas the Ge—Se distances within the Ge_4Se_6 core lie in the range 2.357 (1)–2.370 (1) Å, a significantly shorter Ge—Se bond length of 2.284 (1) Å is observed for the bridging Se atom to the $MnSe_4$ units.

Comment

We first reported the hydrothermal preparation and structural characterization of quaternary selenidogermanates(IV) of the type $A_3[AgGe_4Se_{10}] \cdot 2H_2O$ and $A_2[MnGe_4Se_{10}] \cdot 3H_2O$ (A = Rb and Cs) in 1997 (Loose & Sheldrick, 1997). These zeolite-like phases exhibit open framework anionic networks comprising corner-linked adamantanoid Ge_4Se_{10} cages and $AgSe_4$ or $MnSe_4$ tetrahedra. Interestingly, the alkali cations occupy a general position in the channels of the silver-bridged zinc blende-type of anionic framework $[AgGe_4Se_{10}]^{2-}$, but exhibit only site occupation factors of 0.75. In contrast, the counter-cations in the $[MnGe_4Se_{10}]^{2-}$ phases are disordered over general and special positions. Following our original report, Ahari *et al.* (1998) prepared the isostructural phases $[(CH_3)_4N]_2[MGe_4Se_{10}]$ (M = Mn and Fe) and confirmed their crystal structures by Rietveld analysis. In this case, however, both tetramethylammonium cations exhibit crystallographic S_4 symmetry. Subsequent investigations have shown that $[Ge_4S_{10}]^{4-}$ and $[Ge_4Se_{10}]^{4-}$ units can be bridged by a range of divalent metal ions ($M = Co^{2+}$, Ni^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}) in the presence of various surfactant cations to afford novel mesostructured phases (Wachhold, Rangan, Billinge *et al.*, 2000; Wachhold, Rangan, Lei *et al.*, 2000). Hexagonal ordered mesostructured chalcogenide frameworks are formed by linking $[Ge_4E_{10}]^{4-}$ (E = S and Se) cages with Sb^{III} or Sn^{IV} ions (Rangan *et al.*, 2001).

The $[(CH_3)_4N]^+$ and alkali metal cations (A = Rb and Cs) in the phases $A_2[MnGe_4Se_{10}] \cdot xH_2O$ (x = 0, 3) occupy fully or partially sites with S_4 symmetry. We therefore thought it would be of interest to establish whether lowering the symmetry of the structure-directing cation will affect the connectivity pattern and dimensionality of the resulting selenidogermante(IV). In fact, the title compound, (I), is isostructural with the above-mentioned phases, and its trimethylammonium cations occupy the same special positions of S_4 symmetry as do $[(CH_3)_4N]^+$ cations. The methyl groups of the $[(CH_3)_3NH]^+$ cations of (I) are accordingly disordered with site occupation

factors of 0.75. A particular aspect of the $[MnGe_4Se_{10}]^{2-}$ framework is its flexibility and the unit cell volumes of its isostructural phases vary from 1212.4 (3) $Å^3$ in $Cs_2[MnGe_4Se_{10}]\cdot3H_2O$ to 1415.0 (4) $Å^3$ in $[(CH_3)_4N][MnGe_4Se_{10}]$, with (I) exhibiting an intermediate cell volume of 1353.0 (7) $Å^3$.

(I)
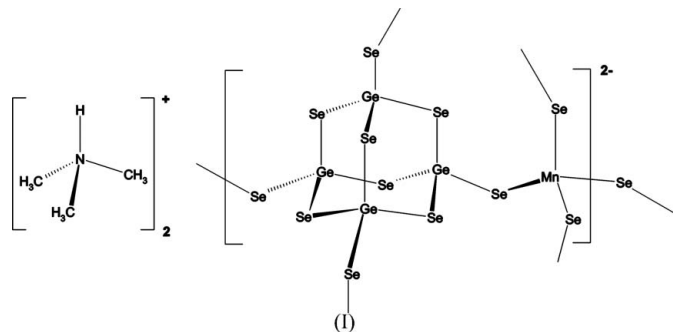
Experimental

Ge (76.22 mg, 1.05 mmol), Se (204.51 mg, 2.59 mmol), Mn(CH$_3$COO)$_2\cdot$4H$_2$O (61.28 mg, 0.25 mmol) and $[(CH_3)_3NH]Cl$ (95.57 mg, 1.0 mmol) were heated in a 1:1 mixture of CH$_3$OH and water (1 ml) to 423 K for 4 d. Cooling to 293 K at a rate of 1 K h^{-1} led to the formation of orange prismatic crystals of $[(CH_3)_3NH]_2[MnGe_4Se_{10}]$ in 65% yield.

Crystal data

(C$_3$H$_{10}$N)$_2$[MnGe$_4$Se$_{10}$]
$M_r = 1255.14$
Tetragonal, $I\bar{4}$
$a = 9.559$ (2) Å
$c = 14.808$ (6) Å
$V = 1353.0$ (7) Å^3
$Z = 2$
$D_x = 3.081$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 4.9–12.9°$
$\mu = 18.29$ mm^{-1}
$T = 293$ (2) K
Prism, orange
$0.16 \times 0.14 \times 0.12$ mm

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction: ψ scan (*XPREP* in *SHELXTL-Plus*; Sheldrick, 1995)
$T_{min} = 0.069$, $T_{max} = 0.117$
945 measured reflections
859 independent reflections

790 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 11$
$l = -1 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.066$
$S = 1.09$
859 reflections
59 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}
Absolute structure: Flack (1983), 242 Friedel pairs
Flack parameter: 0.00 (5)

Table 1
Selected geometric parameters (Å, °).

Ge—Se3	2.2843 (12)	Ge—Se2	2.3699 (13)
Ge—Se1	2.3574 (11)	Se3—Mn	2.5512 (10)
Se3—Ge—Se2^{ii}	110.26 (5)	Ge—Se1—Ge^i	105.21 (6)
Se3—Ge—Se1	108.89 (5)	Ge^{iii}—Se2—Ge	104.76 (5)
Se2^{ii}—Ge—Se1	111.80 (4)	Ge—Se3—Mn	110.58 (4)
Se3—Ge—Se2	102.29 (5)	Se3^{vi}—Mn—Se3	127.73 (5)
Se2^{ii}—Ge—Se2	111.93 (4)	Se3^v—Mn—Se3	101.19 (2)
Se1—Ge—Se2	111.23 (4)		

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

The trimethylammonium cations are disordered with the four symmetry-equivalent C atoms exhibiting a site occupation factor of 0.75. The H atom is accordingly also disordered over four equivalent sites and was not included in the refinement. The methyl H atoms
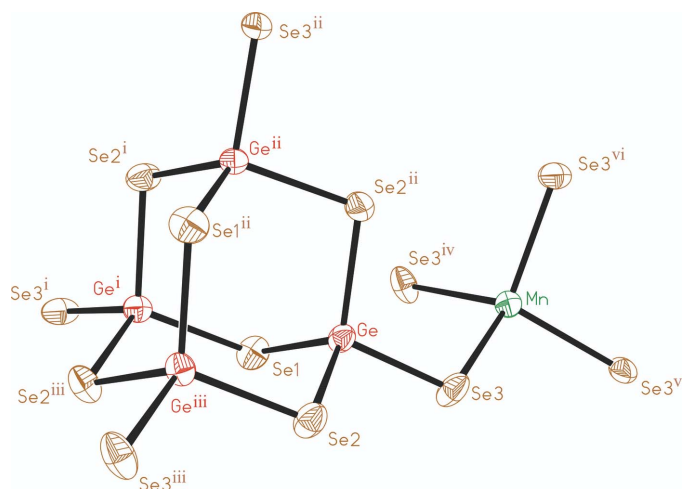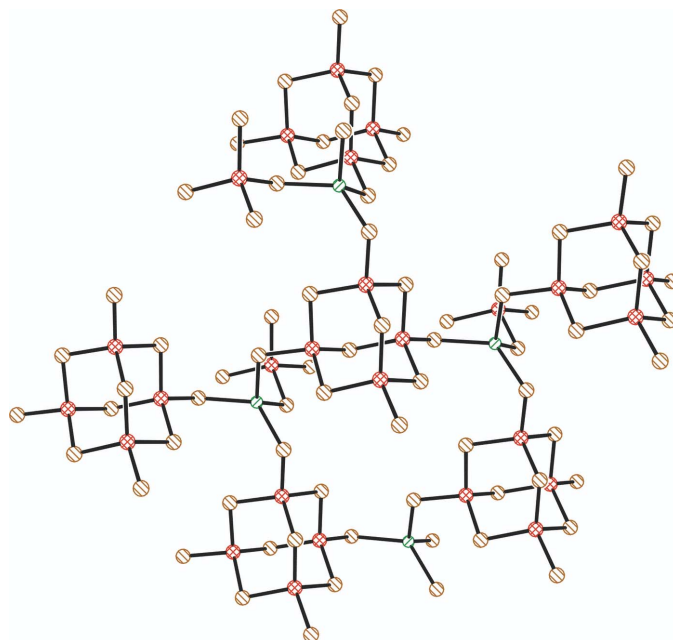

Figure 1
Part of the framework $[MnGe_4Se_{10}]^{2-}$ polyanion of (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry operators: (i) $-x, 2-y, z$; (ii) $1-y, x+1, 2-z$; (iii) $y-1, 1-x, 2-z$; (iv) $y-\frac{1}{2}, \frac{3}{2}-x, \frac{3}{2}-z$; (v) $\frac{3}{2}-y, x+\frac{1}{2}, \frac{3}{2}-z$; (vi) $1-x, 2-y, z$.]

Figure 2
The framework anionic network of (I), illustrating the channels in the [100] direction, which host the disordered trimethylammonium counter-cations. Colour codes: Ge: red; Se: brown; Mn: green.

were constrained to idealized positions using a riding model, with C–H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *R3m/V* (Siemens, 1989); cell refinement: *R3m/V*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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