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Manganese antimony diselenide iodide, $MnSbSe_2I$

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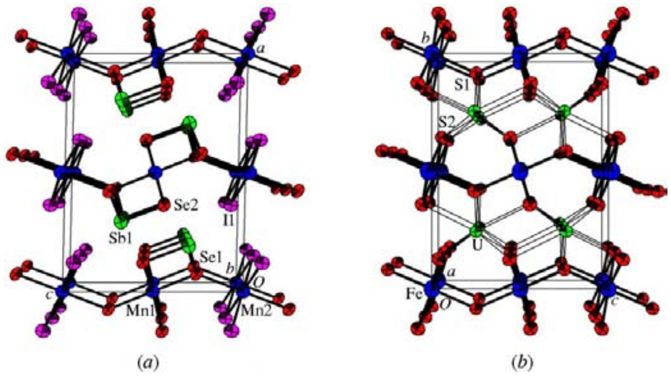
$MnSbSe_2I$ contains layers parallel to the *bc* plane that consist of edge- and corner-sharing $MnSe_{6/2}$ and $MnSe_{2/2}I_{4/2}$ octahedra. Sb atoms are located between these layers and form $SbSe_3$ trigonal pyramids. Owing to the off-center placement of the Sb atom and the inequivalence of the two crystallographically independent Mn atoms, the monoclinic $MnSbSe_2I$ structure is a distorted variant of the orthorhombic $UFeS_3$ structure type.

Comment

Quaternary phases consisting of a transition metal and several types of *p*-block elements in an ordered arrangement are relatively scarce. In TM*PnQX* systems (where TM is a transition metal; *Pn* = P, As, Sb or Bi; *Q* = S, Se or Te; and *X* = F, Cl, Br or I), the most prevalent examples contain Cu, for example, Cu_6PS_5Br (Haznar *et al.*, 1999), $(CuBr)_3P_4Se_4$ (Reiser *et al.*, 2003), $(CuI)P_4Se_4$ (Pfitzner *et al.*, 1999), $(CuI)_3P_4Se_4$ (Pfitzner & Reiser, 1999), $(CuI)_2P_8Se_3$ (Pfitzner *et al.*, 2000), $(CuI)_2Cu_3SbS_3$ (Pfitzner, 1997), $Cu_3Bi_2S_4Cl$ (Lewis & Kupčik, 1974) and $Cu_3Bi_2S_4Br$ (Mariolacos & Kupčik, 1975), or another late *d*-block element, for example, $CdSb_6S_8I_4$ (Sirota *et al.*, 1976) and Hg_3AsQ_4X (*Q* = S or Se, and *X* = Cl, Br or I; Beck *et al.*, 2000). In most cases, the metal adopts a tetrahedral coordination, as expected for these late *d*-block elements; an interesting exception is $CdSb_6S_8I_4$, in which the Cd atom adopts an octahedral coordination. There appear to be no examples of compounds of formula $TMPnQ_2X$.

$MnSbSe_2I$ represents a new layered structure type, as shown in Fig. 1(*a*). The layers are parallel to the *bc* plane and contain two kinds of Mn-centered octahedra: atom Mn1 is surrounded by four Se2 and two Se1 atoms, whereas atom Mn2 is surrounded by four I1 and two Se1 atoms. The octahedra share their corners along the *c* direction and share their edges along the *b* direction. The Mn—Se distances of 2.6590 (9), 2.7849 (6) and 2.7687 (9) Å, and the Mn—I distances of 2.8380 (5) Å (Table 1) are comparable to those found in olivine-type Mn_2SiSe_4 [2.671 (4)–2.756 (3) Å; Jobic *et al.*, 1995] and in $CsMnI_3$ [2.920 (2) Å; Zandbergen, 1980], respectively, where octahedrally coordinated Mn is present. Between the layers lie the Sb1 atoms, which are coordinated to three Se atoms, forming a trigonal pyramid, with Sb—Se distances [2.5995 (9) and 2.7277 (6) Å] that are similar to those in Sb_2Se_3 [2.589 (1)–2.803 (1) Å; Voutsas *et al.*, 1985]. The closest distance between an Sb1 atom in one layer and an Se atom in the adjacent layer is 3.1523 (8) Å, which is too long to be considered as a covalent bond.



(*a*) (*b*)

Figure 1
(*a*) $MnSbSe_2I$ viewed along the *b* axis and (*b*) $UFeS_3$ viewed along the *a* axis. Displacement ellipsoids are drawn at the 99% probability level in both cases.

The structure of monoclinic $MnSbSe_2I$ (space group *C*2/*m*) is a distorted variant of orthorhombic $UFeS_3$ (*Cmcm*; Fig. 1*b*; Noël & Padiou, 1976). In the latter structure, layers of Fe-centered octahedra are also evident, but the intervening U atoms are arranged more symmetrically, residing in tricapped trigonal-prismatic sites. The lower monoclinic symmetry ($\beta = 91.27°$) of $MnSbSe_2I$ arises from the absence of mirror and glide planes associated with the displacement of the Sb atoms, as well as the chemical inequivalence of the two types of Mn-centered octahedra. The irregular position of the Sb atom is indicative of Sb^{3+}, implying the presence of a lone pair. This assignment is consistent with the charge-balanced formulation $(Mn^{2+})(Sb^{3+})(Se^{2-})_2(I^-)$. Comparison with the analogous formulation $(U^{3+})(Fe^{3+})(S^{2-})_3$ shows that replacement of one of the chalcogen atoms in $UFeS_3$ by a halogen atom in $MnSbSe_2I$ is compensated by substitution with a transition-metal ion of lower charge.

Experimental

Single crystals of $MnSbSe_2I$ were obtained as a by-product of the reaction of Sm (1.20 mmol, Alfa, 40 mesh, 99.9%), Mn (0.20 mmol, Alfa, 100 mesh, 99.9%), Sb (0.20 mmol, Alfa, 325 mesh, 99.5%) and Se (2.40 mmol, Alfa, 325 mesh, 99.99%) in a fused-silica tube containing a small amount of I_2. The reaction tube was heated at 1223 K for 4 d before being cooled to 973 K at a rate of 3 K h^{-1}, at which point the furnace was turned off. The product consisted mainly of golden plate-like crystals of $SmSe_3$ and a few black prisms of $MnSbSe_2I$. Qualitative energy-dispersive X-ray analysis performed

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on several of these prisms revealed an average composition (atomic %) of 19 (2)% Mn, 22 (2)% Sb, 39 (2)% Se and 21 (2)% I, in good agreement with that deduced from the single-crystal X-ray analysis. No trace of Sm was detected.

Crystal data

$MnSbSe_2I$
M_r = 461.51
Monoclinic, $C2/m$
a = 13.319 (3) Å
b = 4.0359 (8) Å
c = 10.105 (2) Å
β = 91.27 (3)°
V = 543.08 (19) Å^3
Z = 4

D_x = 5.645 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2097 reflections
θ = 3.1–28.6°
μ = 26.21 mm^{-1}
T = 153 (2) K
Prism, black
0.19 × 0.04 × 0.02 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: numerical (*XP* in *SHELXTL*; Sheldrick, 1997)
$T_{\min}$ = 0.145, $T_{\max}$ = 0.656
2404 measured reflections

737 independent reflections
709 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.026
$\theta_{\max}$ = 28.6°
$h = -17 \rightarrow 17$
$k = -5 \rightarrow 5$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R(F)$ = 0.026
$wR(F^2)$ = 0.071
S = 1.37
737 reflections
34 parameters

$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 2.11 e Å^{-3}
$\Delta\rho_{\min}$ = −1.63 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0022 (3)

Table 1
Selected interatomic distances (Å).

Sb1—Se2	2.5995 (9)	Mn1—Se2$^{\rm iii}$	2.7849 (6)
Sb1—Se1$^{\rm i}$	2.7277 (6)	Mn2—Se1$^{\rm iv}$	2.7687 (9)
Mn1—Se1$^{\rm ii}$	2.6590 (9)	Mn2—I1$^{\rm iii}$	2.8380 (5)

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1033). Services for accessing these data are described at the back of the journal.

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