

Replacement of selenium by antimony in MoSe₂: interconnection of the MoSbSe layers by Sb–Sb bonding

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The replacement of every other Se atom in layered MoSe₂ by two Sb atoms led to the formation of MoSb₂Se; within its lattice, Sb atoms interconnect the MoSbSe sheets to form a truly three-dimensional structure, thereby enlarging the octahedral cavities.

The layered dichalcogenides of the valence-electron-poor transition metal atoms have attracted the interest of various different interdisciplinary research groups owing to potential applications such as solid lubricants, and intercalation reactions and electronic instabilities leading to energy storage applications¹ and charge density waves.² Consequently, extensive theoretical work (based on the Extended Hückel calculations) was performed to investigate the different physical properties³ as well as the different metal clustering which are both dependent upon the electron count.⁴

For packing considerations, metal atoms, M, fill the octahedral voids of every other layer in the hexagonal close-packing of chalcogen atoms, Q, (realized in the CdI₂ lattice type, as observed for ZrSe₂⁵); different electron configurations of the M atoms bring about different distortions in the structures. For example, in going from ZrSe₂ through the polymorph NbSe₂⁶ to MoSe₂,⁷ the d electron configuration of the M⁴⁺ atom changes from 4d⁰ to 4d¹ to 4d²: this leads to significant shifts of the atomic positions in the layers of NbSe₂ and MoSe₂, which produce in part bonding M–M contacts that do not occur in the undistorted CdI₂ type structure. MoSe₂ and α-MoTe₂⁸ crystallize as the MoS₂ type, with Mo atoms surrounded in a trigonal prismatic arrangement. This is—for d² ions—one of the two energetically favorable deviations from ideal hexagonal close-packing of the chalcogen atoms. Here, the electronic stabilization results from lowering of the one filled d orbital in the trigonal prismatic ligand field. The other favorable configuration, realized in β-MoTe₂ and WTe₂,⁹ is the formation of M–M zigzag chains, stabilized by the occurrence of two single bonds per M atom, *i.e.* by lowering the one filled d orbital of the t_{2g} set. Linearly linked rhomboidal clusters would be favorable for a d³ count as in ReSe₂.¹⁰ The latter two distortions can be deduced to arise from a Peierls distortion associated with the partially filled t_{2g} band.

The intercalation chemistry of the layered chalcogenides, MQ₂, known to date is substantive.¹¹ Usually, intercalation of cations increases the number of M-centered d electrons and thus enhances M–M bonding within the MQ₂ layers. Examples include M'_{0.5}NbSe₂ (M' = Ti, V, Cr)¹² and Cu_xNbTe₂,¹³ while Zr_{1+x}Te₂ represents a notable exception.¹⁴

Intercalation of anions is less favorable due to anion–anion repulsions. The problem can be avoided by connecting the anions to the MQ₂ layers *via* covalent bonds. To achieve this, one must either oxidize the Q²⁻ anions or exchange Q for less electronegative atoms, such as the heavier pnictogen atoms like antimony. Since the Sb atoms tend to form Sb–Sb bonds even in metal-rich antimonides of the valence-electron-poor transition metals, *e.g.* in (Hf,Ti)₇Sb₄,¹⁵ (Zr,V)₁₁Sb₈,¹⁶ (Zr,V)₁₃Sb₁₀¹⁷ and (Zr,Ti)Sb,¹⁸ and the only known molybdenum antimonide, Mo₃Sb₇, comprises Sb–Sb bonds as well,¹⁹ it seemed most

promising to use the latter method with Sb atoms as replacements for the chalcogen atoms, Q.

Subsequently, reactions aimed at hypothetical Sb_xMo(Sb,Se)₂ were carried out by heating the elements in the stoichiometric ratios in sealed silica tubes at 800 °C with addition of traces of iodine to promote crystal growth. Thereby, the new antimonide selenide MoSb₂Se formed and was characterized by EDX and crystal structure analysis.²⁰ MoSb₂Se crystallizes in its own structure type, which can be described based on MoSbSe layers being interconnected by additional Sb atoms (Sb3 and Sb4), as depicted in Fig. 1.

The MoSbSe layers closely resemble the MoTe₂ layers of β-MoTe₂, with the Sb atoms capping the longer Mo–Mo distances > 450 pm and the smaller Se atoms capping the Mo–Mo bonds of 281 pm (Mo–Mo in β-MoTe₂: 289–290 pm). This suggests a d² configuration of the Mo atoms, *i.e.* Mo⁴⁺, as in Mo⁴⁺(Se²⁻)₂. Correspondingly, the Mo–Se distances are very similar in both compounds, ranging from 250–252 pm in MoSb₂Se, compared to 253 pm in MoSe₂. Also, the Mo–Sb distances in MoSb₂Se (282–284 pm) compare well to the longer one in Mo₃Sb₇ (285 pm), to which the Sb atoms with Sb–Sb bonding contribute.

Every Sb atom of the MoSbSe layers forms one homonuclear bond to one interlayer Sb atom, the length of which (285 pm) suggests a typical single bond, as also found in KSb (283 and 285 pm),²¹ *cyclo*-Sb₅⁵⁻ (between 281–291 pm),²² and Sb₁₁³⁻ (276–285 pm).²³ Furthermore, each of these intralayer Sb atoms takes part in four longer bonds (325–330 pm, dashed lines in Figs. 1 and 2). These distances are indicative of weak but clearly present interactions.²⁴ Ignoring them in a first approximation and applying the (8 – N) rule, we assign the oxidation state of 2– to the intralayer Sb atoms, which leads to neutral interlayer Sb atoms, *i.e.* Sb⁰Mo⁴⁺Sb²⁻Se²⁻. The latter readily explains the presence of three Sb–Sb single bonds per interlayer Sb atom

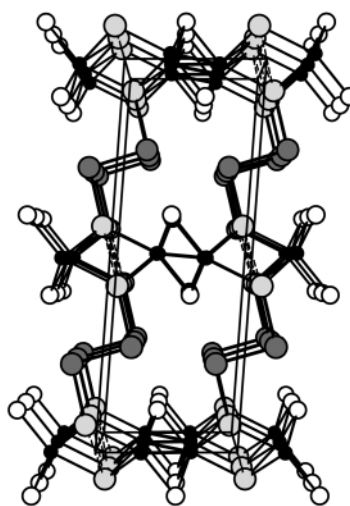


Fig. 1 Projection of the structure of MoSb₂Se along [010]. Horizontal, *a* axis; Mo (●), Se (○), Sb1, Sb2 (⊙), Sb3, Sb4 (⊗); dashed lines, 325 < *d*_{Sb–Sb} < 330 pm.

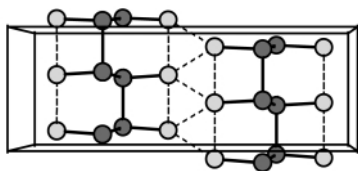


Fig. 2 Projection of the Sb atom substructure along [100]. Horizontal, c axis; solid lines, $285 < d < 292$ pm; dashed lines, $325 < d < 330$ pm.

(bond lengths 285–292 pm), which requires doubling of the monoclinic axis (Fig. 2). The doubling of the b axis led to only weak superstructure reflections because only the Sb3 and Sb4 atoms were shifted to form alternating short and long distances of 292 and 357 pm. These shifts are reflected in the differences in the y parameters of Sb3 and Sb4, while all other atoms are pairwise related, e.g. Mo1 x, y, z , Mo2 $x, y + \frac{1}{2}, z$.

The situation is somewhat more complicated as discussed above, since the Sb–Sb bonds classified as single bonds are up to 10 pm longer than regular single bonds, and because of the presence of the four weaker bonds per intralayer Sb atom. These details suggest the oxidation states of the different Sb atoms being more similar, leading to a formulation of $\text{Sb}^x\text{–Mo}^{4+}\text{Sb}^{(2-x)}\text{–Se}^{2-}$ with $0 < x < 1$.

Although interlayer atoms are already present in MoSb_2Se , the structure is still susceptible for intercalation of cations. The distances between the layers increase by going from MoSe_2 through MoTe_2 to MoSb_2Se , i.e. from 366, to 386, to 561 pm, measured between the Se and Te atoms, respectively. As a consequence, an octahedral void remains, which is even larger in MoSb_2Se than in MoSe_2 .

Therefore, we are currently investigating possible intercalation reactions for MoSb_2Se . Reducing MoSb_2Se might lead to reduced interlayer Sb atoms thus breaking the Sb–Sb bonds parallel to the b axis, which would eliminate the superstructure. Also of interest are attempts to place more Sb atoms between the MoSbSe layers by forming (hypothetical) compounds like MoSb_3Se or MoSb_4Se .

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- 20 *Crystal data*: MoSb_2Se , $M = 418.4$, space group $P2_1/c$, $a = 657.28(4)$, $b = 649.41(3)$, $c = 1829.9(1)$ pm, $\beta = 94.246(8)^\circ$, $Z = 8$; $\mu = 26.0$ mm⁻¹, 2214 independent reflections, $R(F) = 0.021$, $R_w(F^2) = 0.044$ for 1403 observed reflections [$I > 2\sigma(I)$]. Atomic positions [atom x, y, z , U_{eq} (pm²)]: Mo1 0.32480(4), 0.1251(3), 0.99414(2), 32.4(8); Mo2 0.32494(4), 0.6247(3), 0.99426(2), 31.7(8); Sb1 0.07475(3), 0.3744(3), 0.07598(1), 47.1(7); Sb2 0.07472(3), 0.8747(3), 0.07582(1), 48.4(7); Sb3 0.20296(7), **0.3499(2)**, 0.22816(3), 119(2); Sb4 0.20267(7), **0.8999(2)**, 0.22806(3), 122(2); Se1 0.41395(5), 0.6249(4), 0.39800(2), 53.0(8); Se2 0.41440(5), 0.1247(4), 0.39798(2), 53.2(8). CCDC 182/1764. See <http://www.rsc.org/suppdata/cc/b0/b005062h/> for crystallographic files in .cif format.
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