

(LiI)₂Li₃SbS₃: A mixed Alkali Metal Halide Thioantimonate with a novel Tetrahedron Network

Arno Pfitzner*, Christian Preitschaft, and Franz Rau

Regensburg, Institut für Anorganische Chemie der Universität

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Dedicated to Professor Klaus-Jürgen Range on the Occasion of his 65th Birthday

Abstract. (LiI)₂Li₃SbS₃ was prepared by solid-state reaction of stoichiometric amounts of LiI, Li, Sb, and S in the ratio 2 : 3 : 1 : 3. The product is air and moisture sensitive. The crystal structure was determined from single crystals at room temperature. Colourless to pale yellow (LiI)₂Li₃SbS₃ crystallizes in the orthorhombic system, space group Pnmm (no. 58) with $a = 10.436(1) \text{ \AA}$, $b = 13.509(1) \text{ \AA}$, $c = 7.530(1) \text{ \AA}$, $V = 1061.6(1) \text{ \AA}^3$, and $Z = 4$ (data at 20 °C). The crystal structure of (LiI)₂Li₃SbS₃ is closely related to that of (CuI)₂Cu₃SbS₃ and (AgI)₂Ag₃SbS₃, at least for the positions of I, Sb, and S. Thus, iodine forms an eutactic arrangement which resembles the structure of hexagonal diamond. [SbS₃]³⁻ units are embedded in this framework in a way that the sulphur atoms of

two adjacent trigonal pyramids form distorted octahedral voids. The lithium ions are tetrahedrally coordinated and fully ordered within the anionic framework. The three-dimensional connectivities in (LiI)₂Li₃SbS₃ are significantly different from the homologous copper and silver compound due to the bonding necessities of Li and slightly different radii of the monovalent cations. Thus, a novel three-dimensional network of edge sharing tetrahedra is observed in (LiI)₂Li₃SbS₃. It exhibits strands of eight-membered rings of edge sharing tetrahedra which are linked by common vertices and cross linked by double tetrahedra.

Keywords: Lithium; Antimony; Chalcogens; Halogens; Crystal structures

(LiI)₂Li₃SbS₃: Ein gemischtes Alkalimetall-Halogenid-Thioantimonat

Inhaltsübersicht. (LiI)₂Li₃SbS₃ wurde durch Festkörperreaktion stöchiometrischer Mengen von LiI, Li, Sb und S im Verhältnis 2 : 3 : 1 : 3 erhalten. Die Verbindung ist luft- und feuchtigkeitsempfindlich. Die Kristallstruktur wurde bei Raumtemperatur an Einkristallen bestimmt. Farbloses bis leicht gelbliches (LiI)₂Li₃SbS₃ kristallisiert orthorhombisch, Raumgruppe Pnmm (Nr. 58) mit $a = 10.436(1) \text{ \AA}$, $b = 13.509(1) \text{ \AA}$, $c = 7.530(1) \text{ \AA}$, $V = 1061.6(1) \text{ \AA}^3$ und $Z = 4$. Die Kristallstruktur von (LiI)₂Li₃SbS₃ entspricht hinsichtlich der Positionen von I, Sb und S den Strukturen von (CuI)₂Cu₃SbS₃ bzw. (AgI)₂Ag₃SbS₃. Die Iodidionen liegen in einer eutaktischen Anordnung vor, die an diejenige von hexagonalem Diamant erinnert. Darin sind [SbS₃]³⁻-Einheiten so eingelagert,

dass die Schwefelatome jeweils zweier gegenüberliegender trigonaler Pyramiden verzerrte Oktaederlücken ausbilden. Die Lithiumionen sind tetraedrisch koordiniert und voll ausgeordnet. Die dreidimensionalen Konnektivitäten in (LiI)₂Li₃SbS₃ unterscheiden sich deutlich von denen der homologen Kupfer- und Silberverbindung, was auf das verschiedene Bindungsverhalten von Lithium und die leicht unterschiedlichen Ionenradien der einwertigen Kationen zurückzuführen ist. In (LiI)₂Li₃SbS₃ liegt ein bisher nicht bekanntes Netzwerk kantenverknüpfter Tetraeder vor. Achtgliedrige Ringe kantenverknüpfter Tetraeder sind untereinander über Ecken zu Bändern verknüpft. Diese Bänder sind durch kantenverknüpfte Doppeltetraeder untereinander verbunden.

Introduction

Copper(I) and silver halides and chalcogenides are well known to show high ionic conductivity at elevated temperatures whereas a mixed electronic and ionic conductivity is discussed for copper compounds in the room temperature regime [1–6]. The preparation of composite materials having both, halide ions and chalcogenide ions in their anionic sublattice should provide an enhanced ionic conductivity of the resulting compounds. The systems CuX–Cu₂Q (X = Cl,

Br, I, Q = S, Se, Te) just show an eutectic behaviour but no formation of a ternary compound. Thus, numerous efforts to synthesize copper and silver ion conducting materials with a mixed anion arrangement consisting both of halide ions and thiometalate units have been made in the last years [7–11]. At least the copper compounds belong to the best ionic conductors in their class [12]. This work is part of a project to prepare ionic conducting compounds by providing only weak bonding partners to the mobile ions, i.e. highly polarizable anions or neutral elemental fragments [13].

We recently started to transfer the findings concerning the mixed halide thiometalate ion conductors of copper and silver to homologous lithium compounds. A progress in the development of new lithium respectively alkali metal ion conducting quaternary composites can be expected from this approach. Herein we report the synthesis and the struc-

* Prof. Dr. A. Pfitzner
Institut für Anorganische Chemie
Universität Regensburg
D-93040 Regensburg
Fax: +49 941 943 4983
E-mail: arno.pfitzner@chemie.uni-regensburg.de

Table 1 Crystallographic data for the structure analysis of $(\text{LiI})_2\text{Li}_3\text{SbS}_3$

Compound	$(\text{LiI})_2\text{Li}_3\text{SbS}_3$
Formula weight/(g mol ⁻¹)	506.43
Crystal size/mm ³ and colour	0.08 x 0.08 x 0.10, colourless
Crystal system	orthorhombic
Space group	<i>Pnmm</i> (No. 58)
Lattice constants (Å)	<i>a</i> = 10.436(1)
from single crystal	<i>b</i> = 13.509(1)
	<i>c</i> = 7.530(1)
Cell volume, <i>Z</i>	1061.6(1) Å ³ , 4
$\rho_{\text{calc}}/(\text{g cm}^{-3})$	3.169
Diffractometer	STOE IPDS, MoK α , λ = 0.710743 Å, oriented graphite monochromator
φ -range/ $\Delta\varphi^\circ$	0.0 \leq φ \leq 360.0, 1.0
Absorption correction	numerical, crystal description with 15 faces, shape optimizes with X-SHAPE [15]
No. of measured images	360
Irradiation time/image (min)	10
Temperature/ $^\circ\text{C}$	20
2θ -range/ $^\circ$	4.2 \leq 2θ \leq 58.6
<i>hkl</i> -range	-14 \leq <i>h</i> \leq 14 -18 \leq <i>k</i> \leq 18 -10 \leq <i>l</i> \leq 10
No. of reflections, R_{int}	15461, 0.0648
No. of independent reflections	1504
No. of parameters	58
Program	SHELX 97 [16]
Final <i>R</i> / <i>wR</i> (<i>I</i> > 2 σ)	0.0300, 0.0568
Final <i>R</i> / <i>wR</i> (all reflections)	0.0448, 0.0584
Goof	0.880
Largest difference peak $\Delta\rho_{\text{max}}$ and hole $\Delta\rho_{\text{min}}/(\text{e \AA}^{-3})$	1.013 -1.047

Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), Fax: 0049 7247 808 666, E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-413355, the name of the authors, and the reference of the publication.

tural characterization of $(\text{LiI})_2\text{Li}_3\text{SbS}_3$, the first quaternary alkali metal halide thiometalate. It is closely related to $(\text{CuI})_2\text{Cu}_3\text{SbS}_3$ and $(\text{AgI})_2\text{Ag}_3\text{SbS}_3$.

Results

Structure determination

Single crystals suitable for a structure determination were obtained from a stoichiometric reaction mixture (for details see Experimental). X-ray intensities were collected on a STOE IPDS using MoK α radiation. An orthorhombic cell with lattice constants of *a* = 10.436(1) Å, *b* = 13.509(1) Å, *c* = 7.530 Å (1), and *V* = 1061.6(1) Å³ was found. The space group *Pnmm* (No. 58) was derived from systematic extinctions and was confirmed by the subsequent refinement. Direct methods were applied to solve the structure and provided the positions of I, Sb, and S. Li atoms were located from difference fourier maps. The structure refinement converged to *R* = 0.0300 and *wR* = 0.0568 (*I* > 2 σ (*I*)) for 1504 independent reflections and 58 parameters. All atoms were refined with anisotropic displacement parameters and a parameter for extinction was included during the last cycles. Further crystallographic details are summarized in Table 1. Atomic coordinates and isotropic displacement parameters are collected in Table 2. Table 3 lists the anisotropic displacement parameters, and Table 4 shows selected interatomic distances and angles.

Table 2 Atomic coordinates and equivalent isotropic displacement parameters U_{eq} for $(\text{LiI})_2\text{Li}_3\text{SbS}_3$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^{a}
Li1	0.0590(9)	0.0979(7)	0.230(1)	0.036(2)
Li2	0.187(1)	0.461(1)	0	0.036(3)
Li3	0.305(1)	0.2524(7)	0.242(2)	0.051(3)
Sb	0.3011(1)	-0.0052(1)	0	0.019(1)
I1	0.5686(1)	0.2620(1)	0	0.025(1)
I2	0.0576(1)	0.6426(1)	0	0.030(1)
S1	0.2018(2)	0.1592(1)	0	0.020(1)
S2	0.3271(1)	0.4331(1)	0.2530(2)	0.021(1)

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

Table 3 Anisotropic displacement parameters U^{ij} for $(\text{LiI})_2\text{Li}_3\text{SbS}_3$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Li1	0.025(5)	0.038(4)	0.046(6)	-0.009(4)	0.006(4)	-0.005(4)
Li2	0.028(7)	0.053(8)	0.027(7)	0	0	0.003(6)
Li3	0.076(8)	0.022(4)	0.056(7)	-0.001(4)	-0.033(6)	-0.002(5)
Sb	0.016(1)	0.019(1)	0.022(1)	0	0	0(1)
I1	0.027(1)	0.026(1)	0.024(1)	0	0	0.003(1)
I2	0.027(1)	0.025(1)	0.038(1)	0	0	-0.001(1)
S1	0.023(1)	0.015(1)	0.022(1)	0	0	-0.003(1)
S2	0.022(1)	0.019(1)	0.020(1)	-0.003(1)	0(1)	0.001(1)

Table 4 Selected interatomic distances (in Å), and angles (in degrees) for $(\text{LiI})_2\text{Li}_3\text{SbS}_3$ at room temperature

Li1-S4	2.43(1)	S4-Li1-S5	134.3(4)
Li1-S5	2.46(1)	S4-Li1-S5	92.6(3)
Li1-S5	2.53(1)	S5-Li1-S5	108.1(3)
Li1-I1	2.778(9)	S4-Li1-I1	105.4(3)
Li2-S5	2x 2.430(9)	S5-Li1-I1	96.6(3)
Li2-I2	2.80(1)	S5-Li1-I1	123.1(4)
Li2-I2	2.92(1)		
Li3-S5	2.456(9)	S5-Li2-S5	103.3(5)
Li3-S4	2.47(1)	S5-Li2-I2	2x 115.3(4)
Li3-I2	2.83(1)	S5-Li2-I2	2x 116.9(4)
Li3-I1	3.15(1)	I2-Li2-I2	89.9(4)
Sb-S5	2x 2.438(1)		
Sb-S4	2.450(2)	S5-Li3-S4	124.9(4)
		S5-Li3-I2	116.9(4)
		S4-Li3-I2	117.5(3)
		S5-Li3-I1	96.5(4)
		S4-Li3-I1	94.7(4)
		I2-Li3-I1	86.7(3)
		S5-Sb-S5	99.45(6)
		S5-Sb-S4	2x 94.46(4)

Structure description and discussion

The crystal structure of $(\text{LiI})_2\text{Li}_3\text{SbS}_3$ is closely related to that of $(\text{CuI})_2\text{Cu}_3\text{SbS}_3$ and $(\text{AgI})_2\text{Ag}_3\text{SbS}_3$, i.e., the positions of I, Sb, and S are the same for all three compounds. Figure 1 shows the arrangement of the I ions in $(\text{LiI})_2\text{Li}_3\text{SbS}_3$. From a topological point of view the iodine part of the anionic substructure can be derived from the hexagonal diamond structure (*d*(I-I) < 4.303 Å). Thus, the iodide ions form an eutactic network of six-membered rings

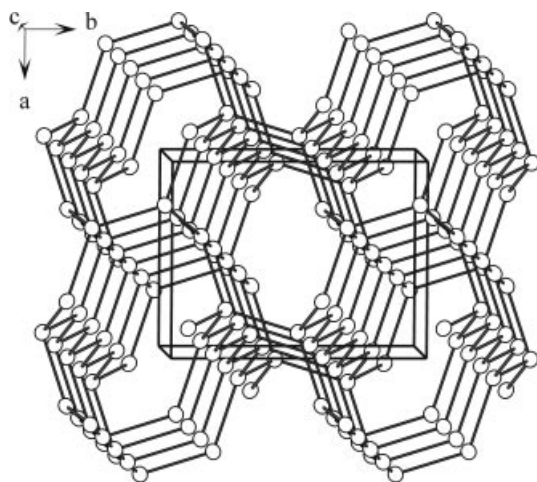


Figure 1 Section of the crystal structure of (LiI)₂Li₃SbS₃ showing the arrangement of I⁻ ions (Li atoms and [SbS₃]³⁻ units are omitted). Iodine atoms are connected to emphasize the relation of their eutactic packing to the hexagonal diamond structure.

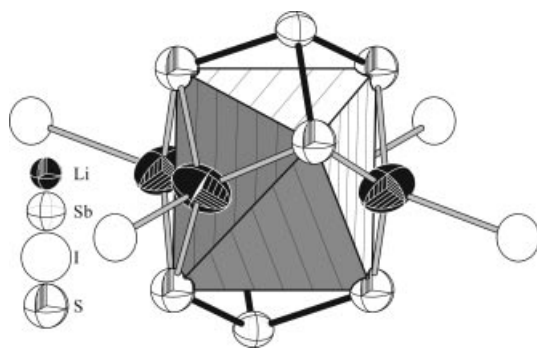


Figure 2 Section of the crystal structure of (LiI)₂Li₃SbS₃ showing a distorted empty S₆ octahedron formed by two thioantimonate (III) ions. Li1 atoms are located on the octahedral faces connected with three sulphur and one iodine atom. Ellipsoids are drawn at the 90% level.

in chair and boat conformation. Some of the iodine atoms are replaced by trigonal-pyramidal (ψ -tetrahedral) [SbS₃]³⁻ units. As a consequence I2 has four iodine atoms as neighbours, whereas I1 is surrounded only by three further iodine atoms. Distorted S₆ octahedra are formed by two adjacent thioantimonate(III) ions (Figure 2). No additional sulphur atoms are found for antimony as next neighbours within a 4 Å sphere. The thiometalate ions can be regarded as isolated from each other in a lithium iodide matrix.

The major difference between (LiI)₂Li₃SbS₃ and the homologous copper and silver compound is the ordering scheme for the monovalent cations. Contrary to Cu⁺ and Ag⁺ in (CuI)₂Cu₃SbS₃ and (AgI)₂Ag₃SbS₃, respectively, the Li ions in (LiI)₂Li₃SbS₃ are well located at room temperature. As we have shown earlier, copper and silver ions are mobile in the anionic framework even at -80 °C and the corresponding compounds show some temperature dependent disorder and reorientation processes [8, 11].

The crystal structure of (LiI)₂Li₃SbS₃ can be rationalized as two-dimensional (2D) polyanionic layers $\frac{2}{3}$ [Li₃SbS₃I₂]²⁻, see (Figure 3 c), which are stacked along [100] (Figure 4). [SbS₃] and [Li₂I₂] (Li2, Li3) units are located in these layers. Adjacent [SbS₃] units form distorted octahedral voids S₆ and Li1 ions are located on the triangular faces of these octahedra. This results in a [LiS₃I] coordination mode. However, contrary to (CuI)₂Cu₃SbS₃ [8] and (AgI)₂Ag₃SbS₃ [11] Li ions are not delocalized on the octahedral faces, *vide infra*. The coordination sphere of Li3 is best described as a 3+1 coordination since one of the iodine atoms has a considerably large distance to the lithium atom, ($d(\text{Li3-I1}) = 3.14 \text{ \AA}$), which is in the typical range for six-coordinate Li. From the Shannon radii [14] one expects a distance $d(\text{Li-I})$ of about 2.8 Å for a four-coordinate Li ion. This fits the other distances in the title compound quite good, cf. Table 4. The description of the crystal structure as a 2D layer structure is derived from the homologous copper and silver compound. A closer inspection of the atomic coordinates, and the sections of the crystal structures shown in Figure 3 a-c, and having in mind that all Li atoms are well localized makes an alternative description of the crystal structure desirable. This description is best based on the network of vertex and edge sharing Li centred tetrahedra. At a first glance it becomes obvious that Li2 is located in double tetrahedra [Li₂S₄I₂] with linking iodine edges, see Figure 5. The second basic building units are eight-membered rings of edge sharing tetrahedra which consist of Li1 and Li3 centred tetrahedra, see Figure 5. Corner sharing between the eight-membered rings leads to ribbons of tetrahedra extending along [001], cf. Figure 6. These ribbons of tetrahedra are interlinked to result in a three-dimensional (3D) network by the above mentioned vertex sharing double tetrahedra [Li₂S₄I₂]. Antimony atoms are embedded in this 3D arrangement. To the best of our knowledge a similar arrangement of edge sharing tetrahedra is not yet known even from silicate chemistry.

Experimental Part

(LiI)₂Li₃SbS₃ was prepared by reaction of LiI (LiI anhydrous, Merck), Li (Merck), Sb (99.9999%, Chempur) and S (99.9995%, Alfa Aesar) in the ratio 2 : 3 : 1 : 3. Before using anhydrous LiI it was purified additionally from crystal water by refluxing with 2,2-Dimethoxypropane. [17] The resulting greyish powder (LiI · 4 CH₃OH) was separated from the solution by distillation and then dried in a vacuum for several hours. The starting mixtures were filled within a glove box under an atmosphere of argon in small closed graphite crucibles and then put in evacuated silica ampoules. After heating the starting materials to 450 °C for five days the crude product was homogenized by grinding and then annealed at 350 °C for three weeks. Single crystals of suitable size for a single crystal X-ray structure determination could be separated from the colourless to pale yellow reaction product. (LiI)₂Li₃SbS₃ is extremely air sensitive. For the structure determination at room temperature single crystals were filled in a closed glass capillary and mounted on a IPDS (Stoe) single crystal diffractometer providing monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Crystallographic data are collected in Table 1. Absorption was corrected

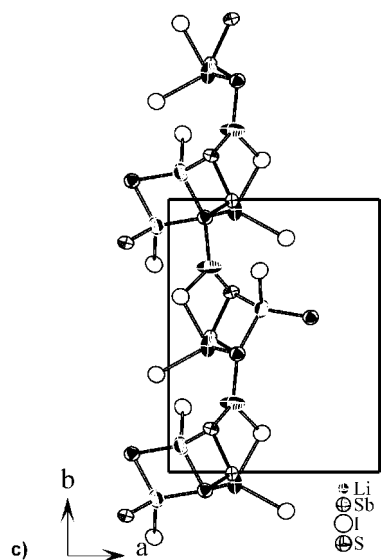
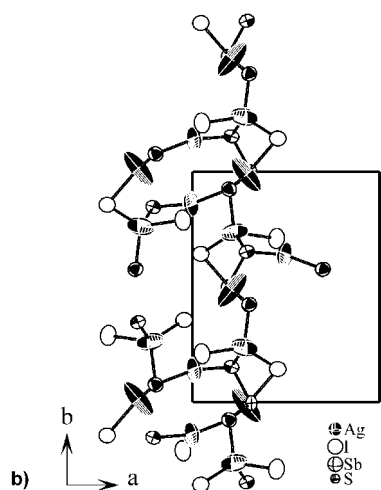
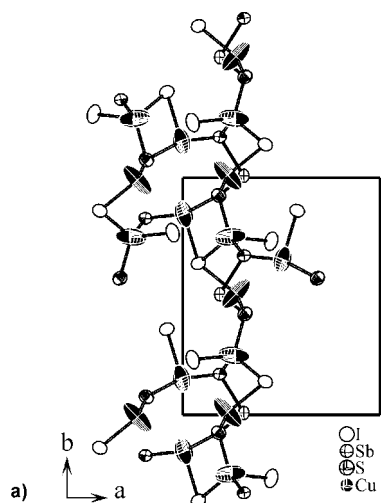


Figure 3 Polyanionic layers $\frac{2}{3}[\text{M}_3\text{SbS}_3\text{I}_2]^{2-}$ ($\text{M} = \text{Li}, \text{Cu}, \text{Ag}$) formed by $[\text{SbS}_3]$ -, $[\text{MS}_2\text{I}_{1+1}]$ - and $[\text{MS}_2\text{I}_2]$ -units in a) $(\text{CuI})_2\text{Cu}_3\text{SbS}_3$, b) $(\text{AgI})_2\text{Ag}_3\text{SbS}_3$, and c) $(\text{LiI})_2\text{Li}_3\text{SbS}_3$. Note the gradual shift of the monovalent cations from a) to c).

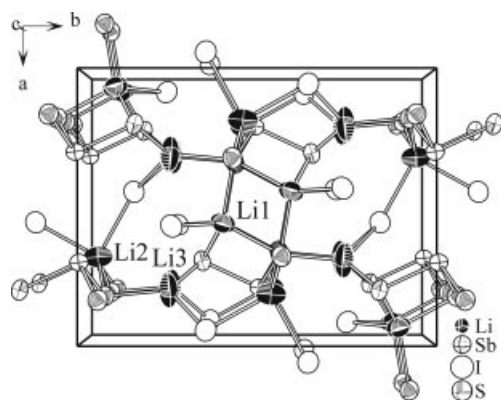


Figure 4 Projection of the structure along $[001]$. $\frac{2}{3}[\text{Li}_3\text{SbS}_3\text{I}_2]^{2-}$ -layers are stacked along $[100]$. Distorted octahedral voids are formed by sulphur of two adjacent $[\text{SbS}_3]$ -units. (Li1) is located on the octahedral faces.

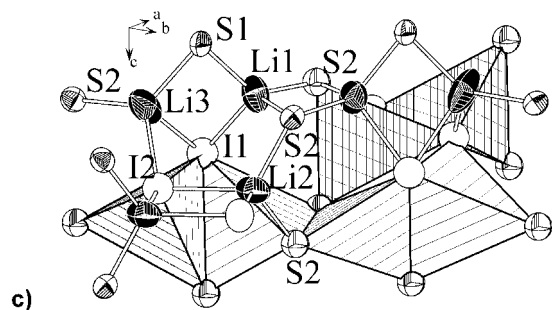
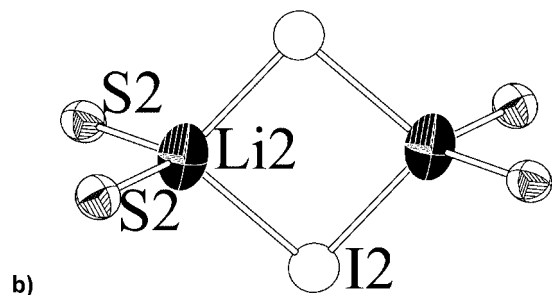
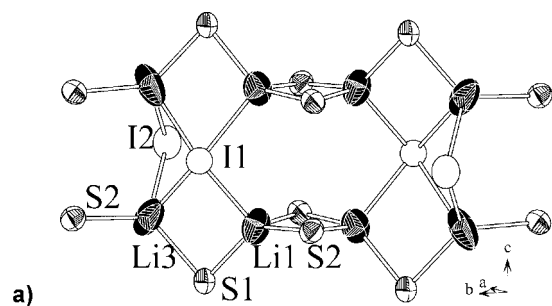


Figure 5 Coordination schemes for Li1 and Li3 in a) a ring of eight edge sharing tetrahedra, b) of Li2 in double tetrahedra, and c) the linkage between these building groups.

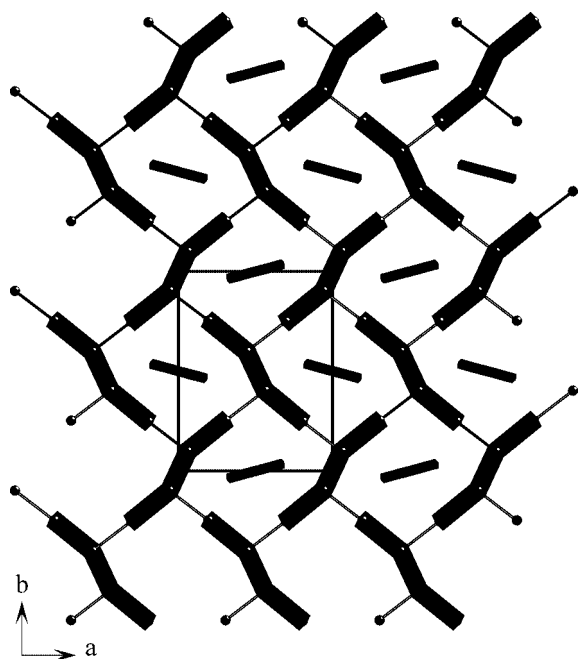


Figure 6 3D network of ribbons of tetrahedra extending along [001] (fat bars corresponding to the edge sharing tetrahedra [Li₄S₆I₄] in Figure 5a). These ribbons are interlinked by double tetrahedra (small bars corresponding to double tetrahedra [Li₂S₄I₂] in Figure 5b). Only Li atoms are linked by the bars, and Sb, S, and I are omitted for clarity.

numerically and the description of the crystal shape was optimized with the X-SHAPE [15] routine.

Differential thermal analysis measurements were performed on a SETARAM TG-DTA 92-16 in evacuated silica tubes. (LiI)₂Li₃SbS₃ decomposes peritectically at 433 °C (onset temperature).

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