Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie

www.zaac.wiley-vch.de

ARTICLE

DOI: 10.1002/zaac.201400567

Synthesis and Crystal Structures of $Rb_4Al_2S_5$ and $Cs_4In_2S_5$

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Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of His 70th Birthday

Keywords: Thioaluminate; Thioindate; Azide method; Alkali metals; Crystal structure

Abstract. Two new alkali metal thiotrielates with the general composition $M_4T_2S_5$ (M = Rb, Cs; T = Al, In) were obtained via the *azide route* and their crystal structures were determined from single-crystal X-ray diffraction data. Highly air sensitive $Rb_4Al_2S_5$ crystallizes in pale red rods in the space group $Pna2_1$ (no. 33) with lattice constants a = 11.4450(5) Å, b = 11.4605(6) Å, c = 9.5727(4) Å, and a cell volume of V = 1255.6(1) Å^3 with Z = 4. To the best of our knowledge, $Rb_4Al_2S_5$ represents the first rubidium thioaluminate and a new structure type in the field of ternary alkali metal chalkogenometallates. $Cs_4In_2S_5$ crystallizes isotypic to $Rb_4In_2S_5$ in the space group $P\bar{1}$ (no. 2) with lattice constants a = 9.6871(3) Å, b = 11.1549(4) Å, c = 7.7879(3) Å, α = 110.731(3)°, β = 95.760(3)°, γ = 102.766(2)°, and a cell volume of V = 752.75(4) Å^3 with Z = 2. The crystal structures of both solids consist of edge-linked $[T_2S_6]^{6-}$ double tetrahedra, which build up one-dimensional, polymeric $^{1}_{\infty}[T_2S_5{}^{4-}]$ strands by trans-corner sharing. The anionic chains are separated by rubidium and cesium cations, respectively. Aluminum as well as indium has a slightly distorted tetrahedral surrounding by sulfur, and the four independent rubidium atoms in $Rb_4Al_2S_5$ feature distorted trigonal prismatic and distorted octahedral coordination spheres, respectively. In $Cs_4In_2S_5$ the four different cesium positions show coordination numbers of six and seven. $Cs_4In_2S_5$ was also characterized by Raman spectroscopy. The frequencies of In–S stretching modes are found in the range from 342 cm^{-1} to 292 cm^{-1}.

Introduction

Ternary alkali metal chalcogenometallates containing group 13 elements show a huge structural variety. Besides 3- (3D) and 2-dimensional (2D) network structures, infinite 1-dimensional (1D) polyanions as well as molecular units are familiar. A whole manifold of thio- and selenoborates with boron in trigonal planar and tetrahedral coordination have been investigated in the past.[1,2] On the other hand many examples for mixed-valent[3–5] compounds with In^{1+}, In$_2{}^{4+}$, and In^{3+} in different surroundings, and six fold coordinated[6,7] In^{3+} chalcogenides are known in the literature. Our investigations focus on ternary alkali metal chalcogenometallates containing the triel atoms in a tetrahedral coordination. Especially the lighter group 13 elements (B, Al, Ga) show a strong tendency for condensing the $[TQ_4]$ building blocks (T = triel, Q = S, Se) to various unique types of (poly)anionic motifs as for example $B_4S_{10}{}^{8-}$,[8,9] the smallest oligomer in case of B^{3+} ions. Besides many known polymeric anions[10–13] and layer structures[14–16] containing boron and indium in the oxidation state +III, exclusively In^{3+} features also isolated tetrahedral units InQ_4 in an alkali metal environment.[17]

Tetrameric anions are also found in $Cs_8Ga_4Se_{10}$.[18] The crystal structure is built up by four distorted $[GaSe_4]$ tetrahedra, which form condensed tetrameric units by edge-sharing. For ternary chalcogenogallates characteristic structural features are also 1D strands,[18] 2D layers, isolated $[Ga_2Q_6]$ double tetrahedra,[19] and the hexameric anion in $Cs_{10}Ga_6Se_{14}$.[18] Recently, a new structure motif was observed in $Cs_2Ga_2Q_5$ (Q = S, Se), which contains $^{1}_{\infty}[T_2Q_3(Q_2)^{2-}]$ anionic chains with dichalcogenide units substituting single chalcogenide ions.[20,21]

In contrast to the huge variety of ternary chalcogenometallates containing either boron or gallium and indium, the number of the hitherto known alkali metal chalcogenoaluminates is much smaller. The known compounds in the ternary system M-Al-Q (M = alkali metal; Q = S, Se, Te) are substitutes of the $M_6Al_2Q_6$ or of the $MAlQ_2$ composition,[22–32] consisting of isolated, edge-linked $[Al_2Q_6]$ double tetrahedra, e.g. in $M_6Al_2Q_6$, or infinite, 1D $^{1}_{\infty}[AlQ_2]$ polymeric anions in $MAlQ_2$. All representatives are located on the quasi binary section M_2Q-Al_2Q_3. $CsAlTe_3$,[33] the only exception, is located on the quasi binary section Al_2Te_5[34]-M_2Q. It represents a ternary alkali metal chalcogenoaluminate with a close relationship to $Cs_2Ga_2Q_5$ and to $RbBSe_3$.[35] It features five-membered rings, which form spiro-cyclic units with triel atoms as spiro center and the chalcogen atoms in oxidation states –I and –II. These units are condensed to polyanions $^{1}_{\infty}[AlTe_3{}^{-}]$.

Herein, we report on the synthesis and structural characterization of $Rb_4Al_2S_5$ and $Cs_4In_2S_5$. These new members of the family of chalcogenometallates consist of edge-sharing double tetrahedra, which form 1D polyanions by trans-corner sharing. Rubidium or cesium cations separate the anionic strands. To the best of our knowledge, $Rb_4Al_2S_5$ is the first example of a

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rubidium based chalcogenoaluminate. It also represents a new structure type in the field of ternary alkali metal chalcogenometallates. In contrast $Cs_4In_2S_5$ complements the row of chalcogenoindates with the general composition of $M_4In_2Q_5$ (M = alkali metal, Q = chalcogen). The new solid crystallizes isotypic to $Rb_4In_2S_5$, which was first described by *Deiseroth*.[36]

Results and Discussion

Crystal Structure of $Rb_4Al_2S_5$ (1)

Single-crystal X-ray diffraction reveals that highly air- and moisture sensitive tetrarubidium pentathio dialuminate(III) $Rb_4Al_2S_5$ crystallizes in the acentric space group $Pna2_1$ (no. 33) with a = 11.4450(5) Å, b = 11.4605(6) Å, c = 9.5727(4) Å, V = 1255.6(1) Å^3, and Z = 4 formula units per unit cell [single crystal data, T = 123(1) K]. The asymmetric unit contains four rubidium, two aluminum, and five sulfur sites, respectively.

The following description of the crystal structure is based on the coordination polyhedra of the first coordination sphere of the cations, the connection of these polyhedra, and the combination of all parts to a 3D crystal structure. To the best of our knowledge, $Rb_4Al_2S_5$ represents a new structure type. All relevant crystallographic data and details of the structure description as well as atom coordinates, equivalent isotropic displacement parameters, and anisotropic displacement param-

Table 1. Crystallographic data and details of the structure determination for $Rb_4Al_2S_5$ (**1**) and $Cs_4In_2S_5$ (**2**).

	1	**2**
Crystal data		
Empirical formula	$Rb_4Al_2S_5$	$Cs_4In_2S_5$
Formula weight /g·mol^{-1}	556.19	921.58
Crystal system	orthorhombic	triclinic
Space group	$Pna2_1$ (no. 33)	$P\bar{1}$ (no. 2)
Pearson code	$oP44$	$aP22$
Unit cell dimensions		
a /Å	11.4450(5)	9.6871(3)
b /Å	11.4605(6)	11.1549(4)
c /Å	9.5727(4)	7.7879(3)
α /°		110.731(3)
β /°		95.760(3)
γ /°		102.766(2)
Volume /Å^3	1255.6(1)	752.75(4)
Formula units/unit cell	4	2
F(000)	1016	796
Calculated density ρ /g·cm^{-3}	2.942	4.066
Wavelengthm λ /Å	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)
Cell parameters from	2117 reflections, θ = 3.3–26.5°	9413 reflections, θ = 3.4–30.3°
Color	red	pale yellow
Crystal size /mm^3	0.18 × 0.06 × 0.04	0.09 × 0.05 × 0.03
Data collection		
Diffractometer	Oxford Diffraction Gemini R Ultra	Agilent SuperNova
Monochromator	graphite	mirror
Scan type	ω scans	ω scans
Measuring temperature /K	123(1)	123(1)
Measured θ-range	$3.3° \leq \theta \leq 26.5°$	$3.24° \leq \theta \leq 30.56°$
Index ranges	$-14 \leq h \leq 12$	$-13 \leq h \leq 13$
	$-14 \leq k \leq 14$	$-15 \leq k \leq 15$
	$-12 \leq l \leq 12$	$-10 \leq l \leq 10$
Reflections collected	5655	15861
Independent reflections	2191	4243
Data averaging$^{a)}$	R_{int} = 0.0444, R_σ = 0.0585	R_{int} = 0.0323, R_σ = 0.0307
Reflections with $I > 2\sigma(I)$	1990	3847
Completeness to θ = 25°	97.2 %	99.8 %
Absorption coefficient μ /mm^{-1}	16.41	13.24
Absorption correction	analytical	analytical
Transmission factors	$0.145 \leq T \leq 0.608$	$0.356 \leq T \leq 0.584$
Refinement		
Structure solution, Refinement	Direct methods,[45] Full-matrix least-squares on F^2[46]	
Number of parameters	102	101
Number of restraints	1 (Floating origin restraints)	0
GooF on F^2	1.027	1.042
Weighting scheme$^{b)}$	A = 0.0189, B = 0	A = 0.0136, B = 0
R indices$^{a)}$ [$I > 2\sigma(I)$]	R_1 = 0.0324, wR_2 = 0.0582	R_1 = 0.0213, wR_2 = 0.0406
R indices$^{a)}$ [all Data]	R_1 = 0.0400, wR_2 = 0.0607	R_1 = 0.0250, wR_2 = 0.0419
Residual electron density /e·Å^{-3}	$-0.834 \leq \rho \leq 0.853$	$-0.944 \leq \rho \leq 0.863$
Extinction coefficient	0.030(2)	0.00051(6)
Flack parameter	0.410(9)[47]	–

a) Definition of R factors see Ref. [46]. b) $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP)]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Atom coordinates and equivalent isotropic displacement parameters U_{eq} /Å$^{2a)}$ of $Rb_4Al_2S_5$ and $Cs_4In_2S_5$.

Atom	x	y	z	U_{eq}
$Rb_4Al_2S_5$$^{b)}$				
S1	0.0079(1)	0.2456(2)	0.4044(2)	0.0139(6)
S2	0.0896(1)	0.1242(2)	0.0493(2)	0.0111(6)
S3	0.2076(2)	0.3890(2)	0.1430(2)	0.0103(5)
S4	0.2371(1)	0.7861(2)	0.2792(2)	0.0108(5)
S5	0.3979(2)	0.1191(2)	0.0722(2)	0.0120(6)
Al1	0.0398(2)	0.2799(2)	0.1809(2)	0.0094(6)
Al2	0.2504(2)	0.2368(2)	0.0001(2)	0.0083(7)
Rb1	0.01860(6)	0.60893(7)	0.23522(7)	0.0175(2)
Rb2	0.05308(6)	0.07678(7)	0.71374(8)	0.0180(2)
Rb3	0.25394(6)	0.07406(7)	0.36696(8)	0.0153(3)
Rb4	0.25636(5)	0.38898(6)	0.47463(7)	0.0104(2)
$Cs_4In_2S_5$$^{b)}$				
S1	0.15082(9)	0.56007(8)	0.3964(1)	0.0126(3)
S2	0.85458(9)	0.22943(8)	0.0488(1)	0.0119(2)
S3	0.51139(9)	0.04124(8)	0.2459(1)	0.0128(2)
S4	0.48321(9)	0.34361(8)	0.0672(1)	0.0160(3)
S5	0.10534(9)	0.18622(8)	0.4419(1)	0.0134(3)
In1	–0.00461(2)	0.34121(2)	0.37402(3)	0.0092(1)
In2	0.58940(2)	0.16712(2)	0.04788(4)	0.0095(1)
Cs1	0.21294(2)	0.91166(2)	0.41707(3)	0.0133(1)
Cs2	0.81468(2)	0.54717(2)	0.08701(3)	0.0140(1)
Cs3	0.82336(2)	0.90455(2)	0.03181(4)	0.0162(1)
Cs4	0.52698(2)	0.65943(2)	0.42633(4)	0.0248(1)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. b) All atom sites are fully occupied (*sof* = 1).

Table 3. Anisotropic displacement parameters U_{ij} ($\times 10^3$) /Å$^{2a)}$ of $Rb_4Al_2S_5$ and $Cs_4In_2S_5$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Rb_4Al_2S_5$						
S1	116(8)	238(14)	63(8)	–28(9)	–1(7)	8(8)
S2	114(9)	94(11)	126(9)	–16(8)	29(7)	–20(8)
S3	132(9)	104(11)	72(8)	–22(8)	21(7)	–20(8)
S4	127(9)	125(11)	71(8)	–8(8)	0(7)	20(8)
S5	106(9)	133(11)	122(9)	–1(8)	–47(7)	21(8)
Al1	110(10)	100(13)	72(10)	8(9)	2(8)	2(9)
Al2	85(10)	103(13)	61(11)	–8(9)	2(8)	10(10)
Rb1	127(3)	163(4)	235(4)	–10(3)	–38(3)	–47(4)
Rb2	175(3)	209(4)	155(4)	–20(3)	–50(4)	–37(4)
Rb3	187(4)	155(5)	116(4)	25(3)	18(3)	14(4)
Rb4	116(3)	130(4)	66(3)	1(3)	0(3)	1(3)
$Cs_4In_2S_5$						
S1	117(4)	112(4)	133(5)	13(3)	57(3)	32(3)
S2	96(4)	126(4)	112(4)	23(3)	14(3)	25(3)
S3	147(4)	128(4)	83(4)	0(3)	16(3)	36(3)
S4	115(4)	111(4)	263(6)	42(3)	25(4)	79(4)
S5	122(4)	127(4)	172(5)	53(3)	33(3)	69(4)
In1	92(1)	85(1)	91(1)	22(1)	18(1)	26(1)
In2	86(1)	87(1)	108(1)	22(1)	18(1)	36(1)
Cs1	130(1)	162(1)	121(1)	42(1)	29(1)	67(1)
Cs2	143(1)	129(1)	141(1)	37(1)	24(1)	48(1)
Cs3	120(1)	130(1)	229(1)	26(1)	54(1)	63(1)
Cs4	134(1)	212(1)	265(2)	7(1)	61(1)	–41(1)

a) Coefficients U_{ij} of the anisotropic displacement factor tensor of the atoms are defined by $\exp[-2\pi^2(h^2a^{*2}U_{11} +..+ 2hka^{*}b^{*}U_{12} +..)]$.

eters are listed in Table 1, Table 2, and Table 3, respectively. Selected interatomic distances and angles in $Rb_4Al_2S_5$ are summarized in Table 4.

Coordination Polyhedra

The structure of $Rb_4Al_2S_5$ is characterized by the tetrahedral coordination of the two crystallographic independent aluminium atoms Al1 and Al2 by sulfur, and the four crystallographically independent rubidium atoms Rb1–Rb4, which are sixfold coordinated by sulfur in the first coordination sphere (Figure 1).

The interatomic distances of the AlS_4 tetrahedra are in the range from 2.194(2) to 2.320(3) Å [$\bar{d}$(Al–S) = 2.258 Å] and thus correspond well to distances found in the hitherto known

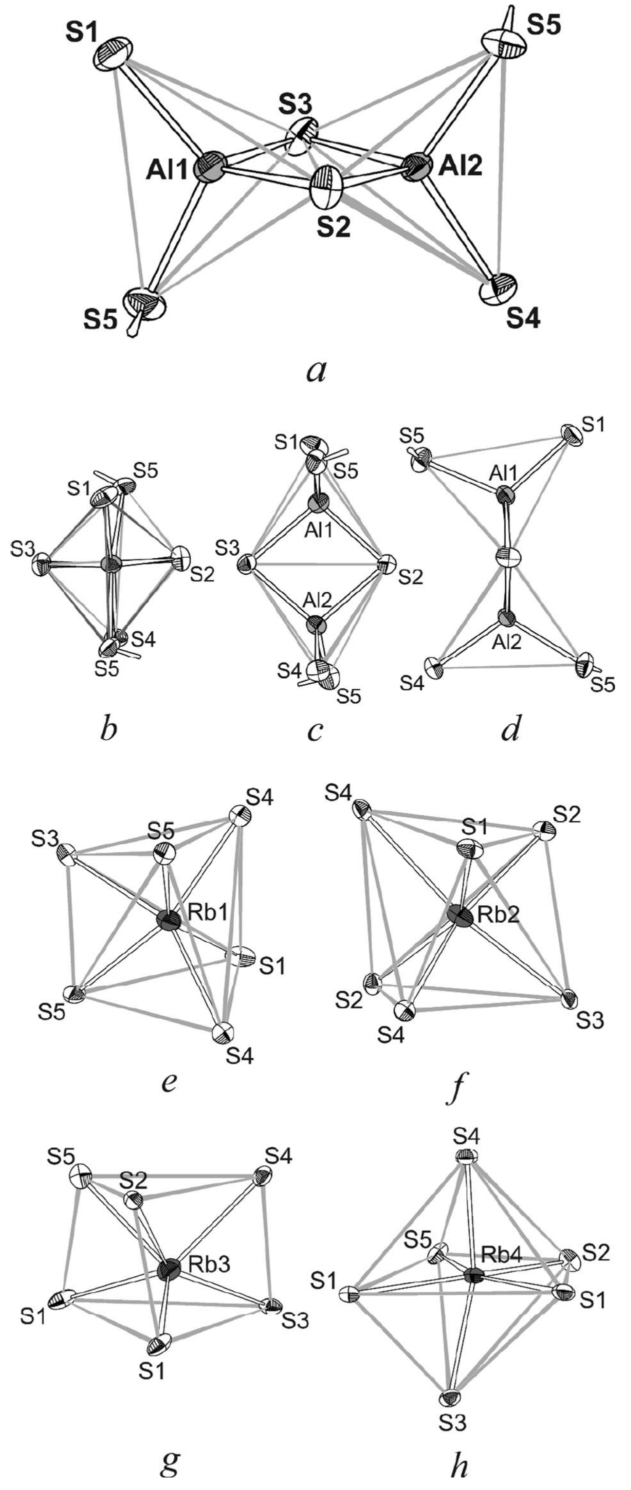

Figure 1. $Rb_4Al_2S_5$: (a–d) Two edge sharing tetrahedra $(AlS_{1/2}S_{1/1}S_{2/2})_{2n}$ shown in different viewing directions, and (e–h) coordination polyhedra of the four crystallographic independent rubidium atoms.

alkali metal thioaluminates $LiAlS_2$[22] [d(Al–S) = 2.246–2.324 Å, $\bar{d}$(Al–S) = 2.280 Å], and α-$Na_6Al_2S_6$[37] [d(Al–S) = 2.194–2.312 Å, $\bar{d}$(Al–S) = 2.273 Å]. However, considering only the averaged atomic distances of the AlS_4 tetrahedra, the value for $\bar{d}$(Al–S) in $Rb_4Al_2S_5$ is slightly smaller than in the above mentioned reference substances, probably because of the low temperature measurement, but still slightly longer than the sum of the tabulated ionic radii[38] $d(^{IV}Al^{+3} + {}^{VI}S^{2-})$ = 2.23 Å).

As already mentioned, the four crystallographic independent rubidium atoms are sixfold coordinated by sulfur in the first coordination sphere. In the case of Rb1, Rb2, and Rb3 the resulting polyhedra can be regarded as highly distorted trigonal prisms. The observed $Rb4S_6$ polyhedron can be described as a distorted octahedron (Figure 1). The average Rb–S distances (Table 4) of the "prisms" and "octahedra" herein correspond quite well to similar compounds, e.g. trigonal prismatic coordination spheres in $RbInS_2$ with average distances of $\bar{d}$(Rb1–S) = 3.43 Å and $\bar{d}$(Rb4–S) = 3.38 Å, and distorted octahedral polyhedra in $Rb_4In_2S_5$ [$\bar{d}$(Rb1–S) = 3.408 Å, $\bar{d}$(Rb4–S) = 3.516 Å] and $Rb_6In_2S_6$ [$\bar{d}$(Rb1–S) = 3.431 Å, $\bar{d}$(Rb3–S) = 3.532 Å].

Table 4. Selected interatomic distances /Å and angles /° in $Rb_4Al_2S_5$ (**1**).

Atom	–Q	Distance		Angle
Al1	–S1	2.206(3)	S1–Al1–S5^i	114.9(1)
	–S5	2.250(3)	S1–Al1–S2	116.2(1)
	–S2	2.257(3)	S5^i–Al1–S2	109.3(1)
	–S3	2.320(3)	S1–Al1–S3	112.6(1)
	$\bar{d}$(Al1–S)	2.258	S5^i–Al1–S3	104.3(1)
			S2–Al1–S3	97.5(1)
Al2	–S4	2.194(2)	S4^{ii}–Al2–S3	113.4(1)
	–S5	2.269(3)	S4^{ii}–Al2–S5	113.4(1)
	–S3	2.270(3)	S3–Al2–S5	115.7(1)
	–S2	2.296(3)	S4^{ii}–Al2–S2	113.3(1)
	$\bar{d}$(Al2–S)	2.257	S3–Al2–S2	97.8(1)
			S5–Al2–S2	101.5(1)
Al1	–Al2	3.008(3)	Al1–S5–Al2	110.63(4)
S2	–S3	3.441(3)		
Rb1	–S	3.249(2)–3.592(2), $\bar{d}(Rb1–S_6)$ = 3.408		
Rb2	–S	3.233(2)–3.575(2), $\bar{d}(Rb2–S_6)$ = 3.470		
Rb3	–S	3.309(2)–3.622(2), $\bar{d}(Rb3–S_6)$ = 3.466		
Rb4	–S	3.145(2)–3.352(2), $\bar{d}(Rb4–S_6)$ = 3.277		

Symmetry codes: (i) x–1/2, –y+1, z; (ii) –x+1/2, y–1/2, z–1/2.

The distances Rb–S in $Rb_4Al_2S_5$ are also slightly larger than the sum of the tabulated ionic radii[38] $d(^{VI}Rb^+ + {}^{VI}S^{2-})$ = 3.36 Å.

Linked Polyhedra

The sulfur atoms in the AlS_4 tetrahedra of $Rb_4Al_2S_5$ span angles between 97.5(1)° and 116.3(1)° and thus deviate significantly from the ideal tetrahedral angle (109.47°). These deviations are caused by the condensation of the $Al1S_4$ and $Al2S_4$ tetrahedra to edge sharing $[Al_2S_6]^{6-}$ double tetrahedra (Figure 1a) and the further linkage of these units via *trans*-corners to linear infinite $^1_\infty[Al_2S_5{}^{4-}]$ polyanions along [100] (Figure 2).

Especially the angles S2–Al1–S3 and S2–Al2–S3 of 97° show a striking deviation from the tetrahedral angle in case of the bridging atoms. Similar deformations are observed in all known structurally related compounds containing double tetrahedra, e.g. $Rb_4In_2S_5$[36] and $Cs_4In_2S_5$ (in this publication) with 91° and 95°, $Rb_4Fe_2O_5$[39] with 93° or $Cs_8Ga_4Se_{10}$[18] with 94°

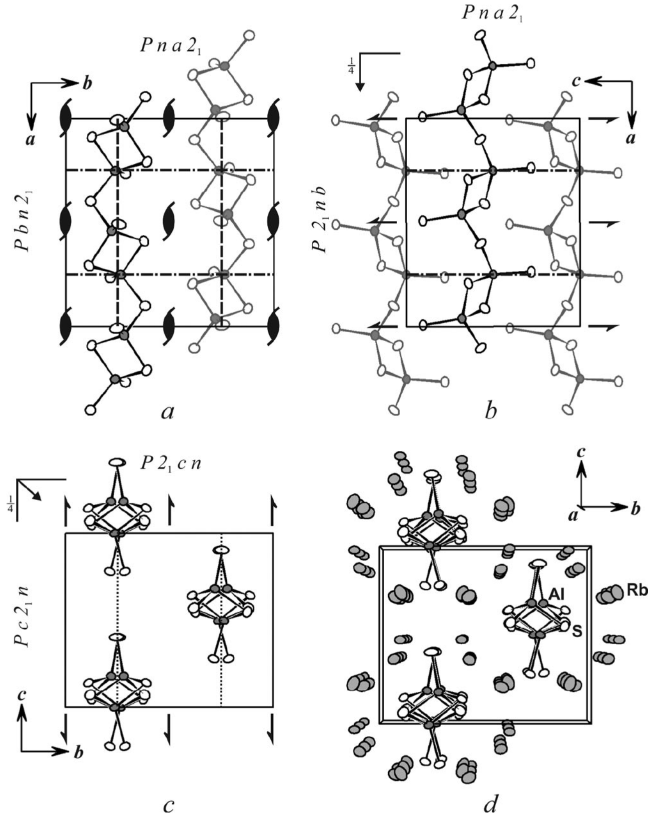

Figure 2. Arrangement of the anionic partial structure of $Rb_4Al_2S_5$ illustrated by projections along (a) [001], (b) [010], and (c) [100]. The symmetry elements are included to clarify the symmetry relations between the anionic chains within the crystal structure. The perspective view (d) shows the alkali metal substructure and the anionic chains embedded therein.

to 97°. These deviations are due to the formation of four-membered rings in these compounds, and are the result of an optimization of counteracting forces, as bonding necessities and repulsive forces due to electrostatic interactions.

The linear infinite $^{1}_{\infty}[Al_2S_5{}^{4-}]$ polyanion can be classified as "*zweier single chain*", following a modified Liebau nomenclature, in which the whole double tetrahedron is defined as the repeating unit, in contrast to the single tetrahedron as shortest identity period of *Liebau's* original classification.[40]

The arrangement of these *single chains* within the crystal structure of $Rb_4Al_2S_5$ is depicted in Figure 2 by projections along the three crystallographic directions. The symmetry elements are included to explain the symmetry relations.

3D Crystal Structure

The projection along [100] as shown in Figure 3a illustrates a hypothetical separation of the crystal structure of $Rb_4Al_2S_5$ in an alkali metal framework structure as host with inserted polyanionic strands by dint of a 4.8^2 net (truncated square tiling). The linear infinite $^{1}_{\infty}[Al_2S_5{}^{4-}]$ polyanions are positioned within the octagons of the 4.8^2 net and are thus arranged with the motif of a *tetragonal rod packing*.

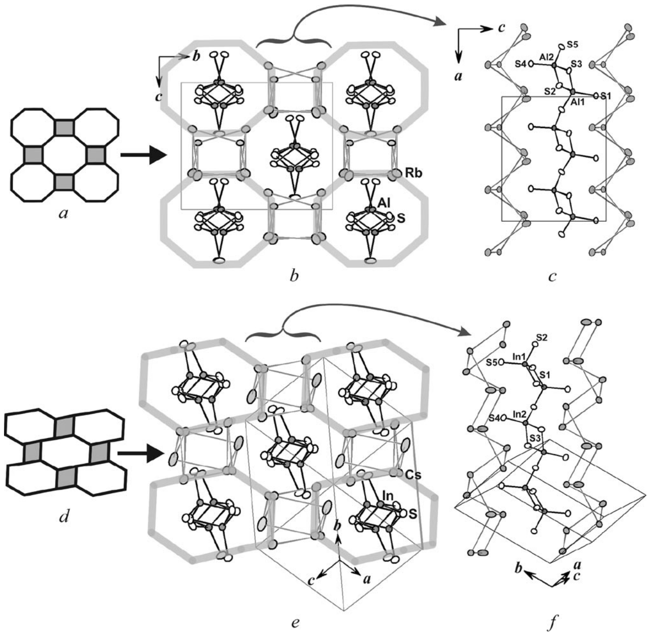

Figure 3. Comparison of the crystal structure of (a–c) $Rb_4Al_2S_5$ and of (d–f) $Cs_4In_2S_5$: (a) 4.8^2 net, (d) distorted 4.8^2 net, (b, e) superposition of the crystal structure with (a) and (d), (c) and (f) double-chained staircase-like (or zigzag) arrangement of the alkali metal atoms.

A topological linkage of the rubidium atoms located on the edge of the squares of the 4.8^2 net, wherein only distances between 3.7 and 4.4 Å are considered, illustrates a double-chained staircase-like (or zigzag) arrangement of the rubidium atoms (Figure 3c). This reduction of the graphical representation of the rubidium subnet into these strands simplifies the comparison of the two title compounds (see below). The zigzag arrangement of the rubidium strands provides optimal space for the polyanions.

Crystal Structure of $Cs_4In_2S_5$ (2) in Comparison with 1

The crystal structure of moderate air stable $Cs_4In_2S_5$ is *isotypic* to the already known rubidium thioindate $Rb_4In_2S_5$[36] and structurally related to the title compound $Rb_4Al_2S_5$. The cesium thioindate crystallizes in the space group $P\bar{1}$ (no. 2) with lattice constants $a = 9.6871(3)$ Å, $b = 11.1549(4)$ Å, $c = 7.7879(3)$ Å, $\alpha = 110.731(3)°$, $\beta = 95.760(3)°$, $\gamma = 102.766(2)°$, $V = 752.75(4)$ Å^3, and $Z = 2$. For a detailed structure description of the $Rb_4In_2S_5$ structure type see Ref. [36].

All relevant crystallographic data and details of the structure description as well as atom coordinates and equivalent isotropic displacement parameters of $Cs_4In_2S_5$ are listed in Table 1 and Table 2, respectively. Selected interatomic distances and angles in $Cs_4In_2S_5$ are summarized in Table 5.

Figure 3 shows the structural relationship of $Cs_4In_2S_5$ to $Rb_4Al_2S_5$ by a direct comparison of the two structure types. The discussed hypothetical separation of the crystal structure in an alkali metal framework as a host with inserted polyanionic strands as shown for the thioaluminate is also evident in the thioindate $Cs_4In_2S_5$. In contrast to $Rb_4Al_2S_5$ the superposition of an ideal 4.8^2 net is impossible in case of $Cs_4In_2S_5$

Table 5. Selected interatomic distances /Å and angles /° in $Cs_4In_2S_5$ (**2**).

Atom	–Q	Distance		Angle
In1	–S5	2.3982(8)	S5–In1–S2^{i}	107.99(3)
	–S2^{i}	2.4800(9)	S5–In1–S1^{ii}	114.66(3)
	–S1^{ii}	2.4939(9)	S2^{i}–In1–S1^{ii}	112.50(3)
	–S1	2.5058(9)	S5–In1–S1	119.65(3)
	$\bar{d}$(In1–S)	2.470	S2^{i}–In1–S1	106.03(3)
			S1^{ii}–In1–S1	95.45(3)
In2	–S4	2.3819(8)	S4–In2–S3	115.69(3)
	–S3	2.4939(9)	S4–In2–S2	112.78(3)
	–S2	2.5072(9)	S3–In2–S2	116.26(3)
	–S3^{iii}	2.5248(9)	S4–In2–S3^{iii}	114.80(3)
	$\bar{d}$(In2–S)	2.477	S3–In2–S3^{iii}	90.99(3)
			S2–In2–S3^{iii}	103.81(3)
In1	–In1^{ii}	3.3633(5)	In1–S2–In2	111.8(1)
In2	–In2^{iii}	3.5179(5)		
S1	–S1	3.699(1)		
S3	–S3	3.580(1)		

Symmetry codes: (i) x–1, y, z; (ii) –x, –y+1, –z+1; (iii) –x+1, –y+1, –z+1

(see Figure 3). However, this overlay can be achieved by a slight rotation and compression of the net. This deformation of the net becomes evident in the crystal structure of $Cs_4In_2S_5$. In comparison to $Rb_4Al_2S_5$ the linear infinite strands ${}^{1}_{\infty}[In_2S_5{}^{4-}]$ are rotated about 19° along their propagation axis (cf. Figure 3e) and the coordination spheres of the four crystallographic independent Cs atoms now show sixfold (Cs1, Cs4) and sevenfold (Cs2, Cs3) irregular coordination. In addition, the angles of the bridging atoms between the double tetrahedra differ by 1.2° [Al1–S5–Al2 = 110.63(4)°; In1–S2–In2 = 111.8(1)°]. The deformation of the thioindate structure in comparison to the thioaluminate structure is also evident in the double-chained staircase-like (or zigzag) arrangement of the alkali metal atoms (cf. Figure 3c and f)

The linear infinite strand can be classified as "*zweier single chain*", following the modified *Liebau* nomenclature of this paper as in case of the thioaluminate.

From a more general viewpoint these two compounds with an equivalent formula type show up the influence of the combination of ions with different radii upon the resulting crystal structures. Thus, the overall arrangement of the chains depends on the ratio T:Q. According to this ratio both polyanions show the formation of edge-sharing double-tetrahedra $[TQ_{1/2}Q'_{1/1}Q''_{2/2}]_2$ (Q = bridging chalcogen atom linking the double-tetrahedra, Q' = terminating chalcogen atoms, and Q'' = chalcogen atoms forming the common edge within the double tetrahedron). This means, that the arrangement of T and Q atoms depends mainly on the ratio T:Q, or popular speaking the chalcogen atoms act as chemical scissors cutting the 3D structure of the corresponding T_2Q_3 compounds. The higher symmetry of $Rb_4Al_2S_5$ can therefore be regarded as a result of a better fit of the ionic radius of Rb^+ and the polyanion ${}^{1}_{\infty}[Al_2S_5{}^{4-}]$ as compared to the combination of Cs^+ or Rb^+ and ${}^{1}_{\infty}[In_2S_5{}^{4-}]$. As already mentioned in the introduction we can obtain different polyanions when the ratio T:Q is varied.

Vibration Spectroscopy of $Cs_4In_2S_5$ (2)

The Raman spectrum of selected crystals of $Cs_4In_2S_5$ is characterized by bands at 342, 317, 287, 174, and 154 cm^{-1} (Figure 4) These bands are in good accordance with frequencies observed for monoclinic $CsInS_2$, regardless the different arrangement of the tetrahedral units $[InS_4]$ therein.[49] The stretching vibrations In–S were assigned to bands in the range from 342 cm^{-1} to 292 cm^{-1}, and the corresponding stretching vibrations Cs–S to bands at 306 and 277 cm^{-1}, respectively. The peaks at 154 cm^{-1} and 174 cm^{-1} are tentatively assigned to Cs–S or In–S bending modes or lattice vibrations, respectively.[49]

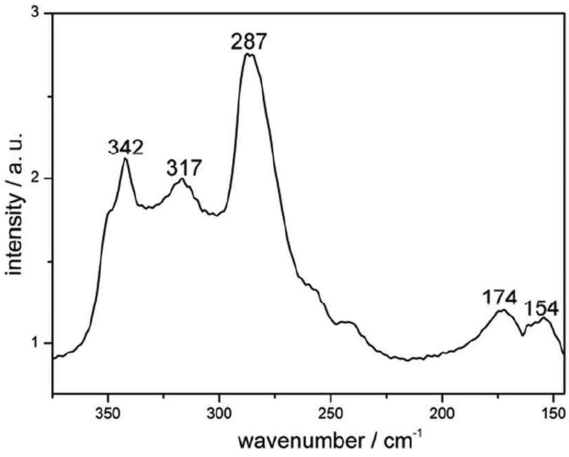

Figure 4. Raman spectrum of $Cs_4In_2S_5$.

Conclusions

In comparison to classic solid state reactions, the *azide route*[7,21,41,42] allows the handling of the highly reactive heavy alkali metals rubidium and cesium in an elegant and easy way. Two new heavy alkali metal thiotrielates were obtained by this *azide route*.[7,21,41,42] Highly air sensitive $Rb_4Al_2S_5$ represents up to now the only ternary chalcogenoaluminate with rubidium and crystallizes in a new structure type. $Cs_4In_2S_5$ is isotypic to $Rb_4In_2S_5$[36] and is a new member of the group of $M_4In_2Q_5$ solids. The crystal structures of both solids consist of edge-sharing $[T_2S_6]^{6-}$ double tetrahedra (T = Al, In), which build up polymeric ${}^{1}_{\infty}[T_2S_5{}^{4-}]$ strands by trans-corner sharing. The anionic chains are separated by rubidium and cesium, respectively. Although the interatomic distances $d(T–Q)$ in $Rb_4Al_2S_5$ ($d \approx 2.2$ Å) and $Cs_4In_2S_5$ ($d \approx 2.4$ Å) differ for about 0.2 Å the same structural motif is observed in both crystals. Interestingly, the well-known $Cs_8Ga_4Se_{10}$[18] features tetrameric units, which are built up by edge-sharing $[GaSe_4]$ tetrahedra as mentioned before.

The structural chemistry of such $M_4T_2Q_5$ compounds will be investigated in more detail in the near future. Several attempts to synthesize "$Cs_4Al_2S_5$" failed up to now. Currently a partial substitution of cesium with rubidium is attempted in order to get some more insight and to obtain a isostructural tetrameric anion $[Al_4Q_{10}]^{8-}$ as in $Cs_8Ga_4Se_{10}$.[18]

Experimental Section

Synthesis: Both title compounds were synthesized by use of the *azide route*.[7,21,41,42] With this method, the highly reactive heavier alkali metals (M = Rb, Cs) can be added to a reaction mixture without working with the pure and extremely reactive elements.

All starting materials were used as purchased and handled on air. The alkali metal azides RbN_3 and CsN_3 were synthesized from NaN_3 (99.0 %, Sigma-Aldrich) and Rb_2CO_3 (99 %, Sigma-Aldrich) or Cs_2CO_3 (99.9 %, Sigma-Aldrich) according to *Suhrmann* and *Clusius*.[43] The freshly synthesized azides were recrystallized several times from water.

Attention: Condensed HN_3 is highly explosive. Tools made from transition metals must be avoided.

The respective alkali metal azide (powder or pre-melted regulus) was added into the reaction container, typically an approximately 20 cm long quartz ampoule (Ø 10 mm), together with elemental sulfur (99.999 %, Chempur) and aluminum grit (99+ %, Chempur) or indium shots (99.999 %, Chempur) corresponding to a molar ratio of $4M$:$2T$:5S. The reaction temperature was subsequently increased under dynamical vacuum conditions. The beginning of the controlled thermal decomposition of the respective azide under release of elemental alkali metal M and nitrogen was observed at 270 °C for $Cs_4In_2S_5$ and at 350 °C for $Rb_4Al_2S_5$, respectively. The reaction process was monitored directly by the pressure evolving during the reaction. The alkali metal formed in situ and reacted immediately with sulfur and the triel under generation of a homogeneous melt for both compounds. Subsequently, the reaction mixtures were heated up to about 450 °C to ensure complete decomposition of the azide. The raw products were sealed in dry and evacuated quartz ampoules and annealed for 8–10 d at 500 °C. In case of the aluminum compound a dark red powder, containing red single crystals suitable for X-ray structure analysis, were observed already after this first heating period. For the synthesis of the indium compound and especially for the growth of single crystals a second step was necessary. Thus, the intermediate product was homogenized in an agate mortar under inert gas atmosphere and finally heat treated for 15 d at 500 °C, resulting in a yellow crystalline powder containing pale yellow crystals of the targeted compound.

Crystal Structure Determination: Single crystals suitable for X-ray diffraction studies were selected in an argon filled glove-box, stored in mineral oil, and were then mounted on a CryoLoop. Diffraction intensities were collected with an Agilent Technologies Gemini R Ultra ($Rb_4Al_2S_5$), and on an Agilent Technologies Supernova ($Cs_4In_2S_5$) diffractometer. In both cases the measurements were performed at 123(1) K, using Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator).

For data collection, data processing, and an analytical absorption correction, the Agilent Technologies Crysalis Pro software[44] was used. Structure solution was possible by direct methods (SHELXS 97[45]), the structure refinement (full-matrix least-squares on F_o^2) was done by SHELXL 97.[46] In case of $Rb_4Al_2S_5$ the Flack parameter[47] is 0.410(9). However, a structure refinement in a centrosymmetric space group was not successful.

Table 1 summarizes the crystallographic data for both solids and selected experimental parameters. The atomic coordinates and isotropic displacement parameters are given in Table 2. Table 3 lists the anisotropic displacement parameters.

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-429147 ($Rb_4Al_2S_5$) and CSD-429148 ($Cs_4In_2S_5$).

RAMAN Spectroscopy: Raman spectra were recorded by a Varian FTS 7000e spectrometer with a Varian FT-Raman module equipped with a Nd:YAG laser (λ = 1064 nm). A liquid nitrogen cooled germanium detector was used in the back-scattering mode. The software Varian Resolutions Pro[48] was used for processing the scattering intensities. A small amount of single crystals of $Cs_4In_2S_5$ was deposited in mineral oil for the Raman measurements.

Acknowledgements

A.P. and *M.S.* thank *H. J. Deiseroth* for his continuous support and a long lasting friendship.

References

[1] S. Pütz, M. Döch, B. Krebs, *Z. Kristallogr.* **2004**, *21*, 179.
[2] B. Krebs, *Angew. Chem.* **1983**, *95*, 113.
[3] H. J. Deiseroth, H. Pfeifer, A. Stupperich, *Z. Kristallogr.* **1993**, *207*, 45.
[4] R. Walther, H. J. Deiseroth, *Z. Kristallogr. NCS* **1995**, *210*, 359.
[5] H. J. Deiseroth, C. Reiner, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1839.
[6] C. Reiner, *Dissertation*, Universität Siegen, Siegen, Germany, **1999**.
[7] C. Reiner, H. J. Deiseroth, M. Schlosser, L. Kienle, *Z. Anorg. Allg. Chem.* **2002**, *628*, 249.
[8] P. Hagenmüller, F. Chopin, B. Castagna, *C R. Acad. Sci. C* **1966**, *262*, 418.
[9] A. Hardy, *Bull. Soc. Fr. Mineral. Cristallogr.* **1968**, *91*, 111.
[10] A. Hammerschmidt, J. Küper, L. Stork, B. Krebs, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1898.
[11] C. Püttmann, F. Hiltmann, W. Hamann, C. Brendel, B. Krebs, *Z. Anorg. Allg. Chem.* **1993**, *619*, 109.
[12] H. J. Deiseroth, *Z. Kristallogr.* **1986**, *177*, 307.
[13] L. Kienle, V. Duppel, A. Simon, H. J. Deiseroth, *Z. Anorg. Allg. Chem.* **2003**, *629*, 443.
[14] F. Chopin, B. Capdepuy, *Bull. Soc. Chim. Fr.* **1970**, 505.
[15] C. Püttmann, W. Hamann, B. Krebs, *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 857.
[16] Z. Huiyi, Z. Fakun, C. Ruiping, D. Zhenchao, G. G. Cong, H. Jinshun, *J. Alloys Compd.* **2007**, *432*, 69.
[17] B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *197*, 169.
[18] H. J. Deiseroth, *Z. Kristallogr.* **1984**, *166*, 283.
[19] A. Kyas, *Dissertation*, TH Aachen, Aachen, Germany, **1981**.
[20] D. Friedrich, M. Schlosser, A. Pfitzner, *Z. Anorg. Allg. Chem.* **2014**, *640*, 826.
[21] D. Friedrich, F. Pielnhofer, M. Schlosser, R. Weihrich, A. Pfitzner, *Chem. Eur. J.* **2015**, *21*, 1811.
[22] E. E. Hellstrom, R. A. Huggins, *Mater. Res. Bull.* **1979**, *14*, 881.
[23] J. Kim, T. Hughbanks, *Inorg. Chem.* **2000**, *39*, 3092.
[24] B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *197*, 139.
[25] J. Weis, R. Schäfer, G. Schön, *Z. Naturforsch.* **1976**, *31b*, 1336.
[26] J. Kim, T. Hughbanks, *J. Solid State Chem.* **2000**, *149*, 242.
[27] B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *197*, 161.
[28] B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *197*, 141.
[29] B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *197*, 139.
[30] B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *197*, 173.
[31] B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *197*, 157.
[32] B. Eisenmann, A. Jäger, *Z. Kristallogr.* **1991**, *197*, 253.
[33] B. Eisenmann, A. Jäger, *Z. Kristallogr.* **1991**, *197*, 251.

[34] H. J. Deiseroth, P. Amann, H. Thurn, *Z. Anorg. Allg. Chem.* **1996**, *622*, 985.
[35] A. Lindemann, J. Küper, W. Hamann, J. Kuchinke, C. Köster, B. Krebs, *J. Solid State Chem.* **2001**, *157*, 206.
[36] H. J. Deiseroth, *Z. Naturforsch.* **1980**, *35b*, 953.
[37] A. P. Brown, B. S. Tani, *Mater. Res. Bull.* **1987**, *22*, 1029.
[38] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751.
[39] G. Frisch, C. Röhr, *Z. Kristallogr.* **2005**, *220*, 135.
[40] F. Liebau, *Structural Chemistry of Silicates - Structure, Bonding, and Classification*, Springer-Verlag Berlin Heidelberg New York Tokyo, **1985**.
[41] U. Zachwieja, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1095.
[42] M. Jansen, *Z. Anorg. Allg. Chem.* **2012**, *638*, 1910.
[43] R. Suhrmann, K. Clusius, *Z. Anorg. Allg. Chem.* **1926**, *152*, 52.
[44] *CrysAlisPro*, Agilent Technologies, XRD Products, Darmstadt, Germany, **2010**.
[45] G. M. Sheldrick, *SHELXS-97*, University of Göttingen, Göttingen, Germany, **1997**.
[46] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany **1997**.
[47] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876.
[48] *Resolutions Pro* (Version 4.1.0.101), Varian, **1993–2006**.
[49] H. Zeng, R. Chen, Y. Zheng, J. Mao, Z. Dong, G. Guo, J. Huang, *Guangpuxue Yu Guangpu Fenxi* **2000**, *20*, 697.

Received: November 29, 2014