

Syntheses and structures of six compounds in the A_2LiMS_4 ($A = K, Rb, Cs; M = V, Nb, Ta$) family

Fu Qiang Huang, Bin Deng, James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA

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Abstract

Six new compounds in the A_2LiMS_4 ($A = K, Rb, Cs; M = V, Nb, Ta$) family, namely K_2LiVS_4 , Rb_2LiVS_4 , Cs_2LiVS_4 , Rb_2LiNbS_4 , Cs_2LiNbS_4 , and Rb_2LiTaS_4 , have been synthesized by the reactions of the elements in $Li_2S/S/A_2S_3$ ($A = K, Rb, Cs$) fluxes at 773 K. The A and M atoms play a role in the coordination environment of the Li atoms, leading to different crystal structures. Coordination numbers of Li atoms are five in K_2LiVS_4 , four in A_2LiVS_4 ($A = Rb, Cs$) and Cs_2LiNbS_4 , and both four and five in Rb_2LiMS_4 ($M = Nb, Ta$). The A_2LiVS_4 ($A = Rb, Cs$) structure comprises one-dimensional chains of ${}^1_{\infty}[LiVS_4]$ tetrahedra. The Rb_2LiMS_4 ($M = Nb, Ta$) structure is composed of two-dimensional ${}^2_{\infty}[LiMS_4]$ layers. The Cs_2LiNbS_4 structure contains one-dimensional ${}^1_{\infty}[LiNbS_4]$ chains that are related to the Rb_2LiMS_4 layers. The K_2LiVS_4 structure contains a different kind of ${}^1_{\infty}[LiVS_4]$ layer.

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1. Introduction

Since its discovery, the reactive-flux method [1] has led to the syntheses of about 40 new $A/M/M'/Q$ ($A = Na, K, Rb, Cs, Tl; M = Cu, Ag; M' = V, Nb, Ta; Q = S, Se, Te$) quaternary compounds. Examples include $K_3CuNb_2Se_{12}$ [2], $CsCu_2MTe_4$ ($M = Nb, Ta$) [3], A_2AgTaS_4 ($A = Tl, Rb$) [4,5], $NaCu_2NbS_4$ [6], and Rb_2CuVS_4 [7]. In most of these compounds, the M and M' atoms are tetrahedrally coordinated by four Q atoms. The dimensionality of these structures is reduced as the ratio of alkali metal A to the transition metal (M, M') increases [8]. Take the $K/Nb/Cu/Se$ system as an example: as one goes from Cu_3NbSe_4 [9,10] to KCu_2NbSe_4 [11] to $K_2CuNbSe_4$ [2] to K_3NbSe_4 [12] the dimensionality of the structures reduces from three-dimensional to two-dimensional to one-dimensional and finally to a zero-dimensional salt. Conceptually, the series presents the progressive substitution of K for Cu.

Concomitant dimensional reduction occurs owing to the predilection of K^+ to achieve higher coordination numbers than Cu^+ .

Among ternary and quaternary metal chalcogenides containing alkali metals, those incorporating Li are the least common. Li generally adopts a lower coordination number than do its higher congeners. In sulfides, the coordination number of Li is often four ($ALiS$ ($A = K, Rb$) [13,14], $KLiMS_2$ ($M = Mn, Zn$) [15], $LiGaS_2$ [16]); occasionally five (Li_4GeS_4 [17–19], Li_3AsS_3 [20]); and often six ($LiBiS_2$ [21,22], $LiTiS_2$ [23]). Here we investigate the substitution of Li for Cu in the $K_2CuNbSe_4$ structure type [2], which consists of one-dimensional ${}^1_{\infty}[CuNbSe_4^{2-}]$ chains of edge-sharing $CuSe_4$ and $NbSe_4$ tetrahedra. Six new compounds, namely K_2LiVS_4 , Rb_2LiVS_4 , Cs_2LiVS_4 , Rb_2LiNbS_4 , Cs_2LiNbS_4 , and Rb_2LiTaS_4 , have been synthesized. Li shows coordination numbers four or five in these compounds. Among these compounds three are one-dimensional and three are two-dimensional; three different space groups are represented. Only Rb_2LiVS_4 and Cs_2LiVS_4 belong to the $K_2CuNbSe_4$ structure type.

*Corresponding author. Fax: +847 491 2976.

E-mail address: ibers@chem.northwestern.edu (J.A. Ibers).

2. Experimental

2.1. Syntheses

The following reagents were used as obtained: K (Alfa, 98%), Rb (Aldrich, 98 + %), Cs (Aldrich, 99.5%), V (Strem, 99.5%), Nb (Johnson Matthey, 99.8%), Ta (Aldrich, 99.9%), S (Alfa, 99.5%), and Li₂S (Aldrich, 98%). A₂S₃ (A = K, Rb, Cs), the reactive fluxes employed in the syntheses, were prepared by the stoichiometric reactions of the elements in liquid NH₃. All these compounds were synthesized by the reaction of 1.0 mmol of *M* (*M* = V, Nb, Ta), 1.0 mmol of S, 0.5 mmol of Li₂S, and 1.0 mmol of A₂S₃ (A = K, Rb, Cs). A reaction mixture was loaded into a fused-silica tube under an Ar atmosphere in a glove box. The tube was sealed under a 10⁻⁴ Torr atmosphere and then placed in a computer-controlled furnace. The sample was heated to 773 K in 8 h, kept at 773 K for 72 h, cooled at 3 K/h to 375 K, and then the furnace was turned off. The reaction mixture was washed with *N,N*-dimethylformamide. The products in the V reactions were composed of red needles and plates; those in the Nb and Ta reactions were pink blocks. Yields for the V reactions were greater than 90%; those for the Nb and Ta reactions were about 20%. Examination of selected crystals with an EDX-equipped Hitachi S-3500 SEM led to results consistent with the stated compositions. The compounds are extremely air-sensitive. They decompose in water and acetone.

2.2. Structure determinations

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [24]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in four groups of 606 frames at φ settings of 0°, 90°, 180°, and 270°. The exposure time was 5–15 s/frame. The collection of the intensity data was carried out with the program SMART [24]. Cell refinement and data reduction were carried out with the use of the program SAINT [24] and face-indexed absorption corrections were performed numerically with the use of the program XPREP [25]. Then the program SADABS [24] was employed to make incident beam and decay corrections.

The structures were solved with the direct methods program SHELXS and refined with the full-matrix least-squares program SHELXL of the SHELXTL suite of programs [25]. Each final refinement included anisotropic displacement parameters. One of the three independent K atoms in the K₂LiVS₄ structure is disordered over two sites. None of the other structures displays any disorder. Additional experimental details are shown in Table 1 and in the Supplementary material. Tables 2–5 present selected metrical data.

Table 1

Crystal data and structure refinements for K₂LiVS₄, Rb₂LiVS₄, Cs₂LiVS₄, Rb₂LiNbS₄, Cs₂LiNbS₄, and Rb₂LiTaS₄^a

Compound	K ₂ LiVS ₄	Rb ₂ LiVS ₄	Cs ₂ LiVS ₄	Rb ₂ LiNbS ₄	Cs ₂ LiNbS ₄	Rb ₂ LiTaS ₄
Formula mass	264.32	357.06	451.94	399.03	493.91	487.07
Space group	C2/c	Fddd	Fddd	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
Z	8	8	8	4	2	4
<i>a</i> (Å)	10.4788(7)	5.813(1)	5.8316(5)	7.0285(4)	6.9186(8)	7.0452(5)
<i>b</i> (Å)	8.4250(6)	13.083(2)	13.610(1)	11.3919(7)	7.2518(8)	11.3929(9)
<i>c</i> (Å)	17.9897(12)	23.164(4)	24.177(2)	11.8129(7)	9.761(1)	11.8205(9)
α (°)	90	90	90	71.761(1)	96.650(2)	71.747(1)
β (°)	94.748(1)	90	90	87.877(1)	92.239(2)	87.766(1)
γ (°)	90	90	90	83.876(1)	91.279(2)	83.652(1)
<i>V</i> (Å ³)	1582.8(2)	1761.7(5)	1918.8(3)	893.18(9)	485.9(1)	895.5(1)
ρ_c (g/cm ³)	2.218	2.692	3.129	2.967	3.376	3.613
μ (cm ⁻¹)	32.5	129.56	92.93	130.14	93.93	239.11
<i>T</i> _{min} / <i>T</i> _{max}	0.582/0.789	0.067/0.247	0.108/0.445	0.072/0.302	0.117/0.310	0.017/0.130
<i>q</i>	0.04	0.02	0.03	0.03	0.025	0.025
<i>R</i> (<i>F</i>) ^b	0.0337	0.0145	0.0219	0.0293	0.0253	0.0353
<i>R</i> _w (<i>F</i> _o ²) ^c	0.0823	0.0356	0.058	0.086	0.0629	0.1083
<i>S</i> ^d	1.27	1.17	1.45	1.28	1.16	1.44

^a *T* = 153(2) K and $\lambda = 0.71073$ Å.^b $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.^c $R_w(F_o^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4 \}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (qP)^2$ and $P = [2F_c^2 + \max(F_o^2, 0)]/3$.^d Least-squares goodness of fit: $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n-p) \}^{1/2}$, where *n* = number of reflections and *p* = number of parameters refined.

Table 2
Selected bond lengths (Å) and angles (°) for K₂LiVS₄

Li–S2	2.496(5)	S3–V–S4	110.70(3)
Li–S4	2.497(5)	S1–V–S2	110.96(3)
Li–S2	2.536(5)	S2–Li–S4	82.7(1)
Li–S3	2.661(5)	S2–Li–S3	84.8(2)
Li–S4	2.711(5)	S4–Li–S4	88.7(3)
V–S3	2.1326(8)	S4–Li–S3	93.1(2)
V–S1	2.1414(7)	S2–Li–S4	95.2(2)
V–S2	2.1573(8)	S2–Li–S3	95.4(2)
V–S4	2.1613(8)	S4–Li–S2	112.7(2)
S2–V–S4	106.85(3)	S2–Li–S2	121.1(2)
S3–V–S2	108.42(3)	S2–Li–S4	126.1(2)
S3–V–S1	109.66(3)	S3–Li–S4	177.8(2)
S1–V–S4	110.21(3)		

Table 3
Selected bond lengths (Å) and angles (°) for Rb₂LiVS₄, and Cs₂LiVS₄

Bond/angle	Rb ₂ LiVS ₄	Cs ₂ LiVS ₄
Li–S × 4	2.4030(4)	2.3988(6)
V–S × 4	2.1595(4)	2.1548(6)
S–Li–S × 2	93.63(2)	93.18(3)
S–Li–S × 2	117.61(2)	118.09(3)
S–Li–S × 2	118.24(2)	118.27(3)
S–V–S × 2	108.47(2)	107.94(3)
S–V–S × 2	109.61(2)	110.13(4)
S–V–S × 2	110.34(2)	110.35(3)

Table 4
Selected bond lengths (Å) and angles (°) for Rb₂LiNbS₄ and Rb₂TaVS₄

Bond/angle	Rb ₂ LiNbS ₄	Rb ₂ LiTaS ₄	Angle	Rb ₂ LiNbS ₄	Rb ₂ LiTaS ₄
Li1–S3	2.381(8)	2.39(1)	S1–Li2–S6	80.0(3)	80.0(4)
Li1–S2	2.446(9)	2.45(1)	S6–Li2–S6	82.8(3)	82.5(4)
Li1–S7	2.481(9)	2.47(1)	S6–Li2–S1	89.5(3)	89.3(5)
Li1–S2	2.505(8)	2.50(1)	S1–Li2–S1	92.7(3)	92.9(5)
Li2–S8	2.466(9)	2.47(1)	S8–Li2–S6	97.9(3)	97.8(5)
Li2–S1	2.511(9)	2.49(2)	S8–Li2–S1	98.2(3)	98.5(5)
Li2–S6	2.528(9)	2.53(1)	S8–Li2–S6	113.2(4)	112.9(5)
Li2–S1	2.620(10)	2.63(2)	S8–Li2–S1	122.1(4)	122.6(6)
Li2–S6	3.013(10)	3.05(2)	S1–Li2–S6	123.7(4)	123.4(6)
M1–S5	2.257(1)	2.257(2)	S1–Li2–S6	163.8(4)	163.6(5)
M1–S6	2.264(1)	2.265(2)	S6–M1–S1	106.00(5)	106.05(7)
M1–S3	2.272(1)	2.269(2)	S6–M1–S3	108.51(3)	108.58(8)
M1–S1	2.276(1)	2.274(2)	S5–M1–S1	108.57(5)	108.69(8)
M2–S4	2.254(1)	2.257(2)	S5–M1–S3	110.00(5)	110.07(7)
M2–S7	2.259(1)	2.258(2)	S5–M1–S6	111.26(5)	111.22(8)
M2–S8	2.268(1)	2.264(2)	S3–M1–S1	112.45(5)	112.18(8)
M2–S2	2.288(1)	2.284(2)	S7–M2–S2	105.27(5)	105.48(7)
S7–Li1–S2	92.9(3)	93.3(4)	S4–M2–S2	108.79(5)	108.73(8)
S2–Li1–S2	101.8(3)	102.2(5)	S7–M2–S8	108.90(5)	108.81(8)
S3–Li1–S2	108.9(4)	109.1(6)	S4–M2–S7	110.60(5)	110.63(8)
S3–Li1–S7	110.5(3)	110.7(5)	S8–M2–S2	111.14(5)	111.17(8)
S3–Li1–S2	113.6(3)	113.1(5)	S4–M2–S8	111.93(5)	111.84(7)
S2–Li1–S7	125.2(4)	125.0(6)			

3. Results

3.1. Synthesis

K₂LiVS₄, Rb₂LiVS₄, Cs₂LiVS₄, Rb₂LiNbS₄, Cs₂LiNbS₄, and Rb₂LiTaS₄ have been synthesized by the reactions of the elements in Li₂S/S/A₂S₃ (A = K, Rb, Cs) fluxes at 773 K. The yields of the V compounds were over 90%; those of the Nb and Ta compounds were about 20%. Attempts to prepare the other three compounds in this series, namely K₂LiNbS₄, K₂LiTaS₄, and Cs₂LiTaS₄, were unsuccessful. Failure to prepare K₂LiNbS₄ or K₂LiTaS₄ as opposed to K₂LiVS₄ may be a manifestation of the relatively small ionic radius of V⁵⁺ compared with those of Nb⁵⁺ or Ta⁵⁺. But given the minimal difference in ionic radii of the latter two cations it is not clear why Cs₂LiNbS₄ could be prepared but not Cs₂LiTaS₄.

3.2. Crystal structures

There are no S–S bonds in the structures of the compounds A₂LiMS₄ (A = K, Rb, Cs; M = V, Nb, Ta). Accordingly, the formal oxidation states of A, Li, V, and S are 1+, 1+, 5+, and 2–, respectively.

The crystal structure of K₂LiVS₄ (space group C2/c) comprises two-dimensional ∞ [LiVS₄^{2–}] layers separated by K atoms. Each layer is built from edge-sharing tetrahedra NbS₄ and slightly distorted LiS₅ trigonal bipyramids (Fig. 1). The unit cell is displayed in Fig. 2.

Table 5
Selected bond lengths (Å) and angles (°) for Cs₂LiNbS₄

Li–S1	2.426(7)	S1–Li–S4	110.5(3)
Li–S4	2.468(7)	S1–Li–S3	111.5(3)
Li–S3	2.494(7)	S1–Li–S4	114.4(3)
Li–S4	2.538(7)	S4–Li–S2	122.7(3)
Nb–S2	2.258(1)	S3–Nb–S4	105.69(4)
Nb–S3	2.262(1)	S2–Nb–S4	109.20(4)
Nb–S1	2.271(1)	S3–Nb–S1	109.38(4)
Nb–S4	2.292(1)	S2–Nb–S1	109.87(4)
S3–Li–S4	92.3(2)	S2–Nb–S3	110.43(4)
S4–Li–S4	101.7(3)	S1–Nb–S4	112.19(4)

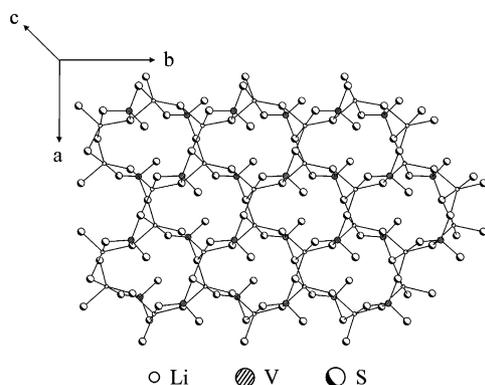


Fig. 1. The ${}^2_{\infty}[\text{LiVS}_4]^{2-}$ layer in K₂LiVS₄.

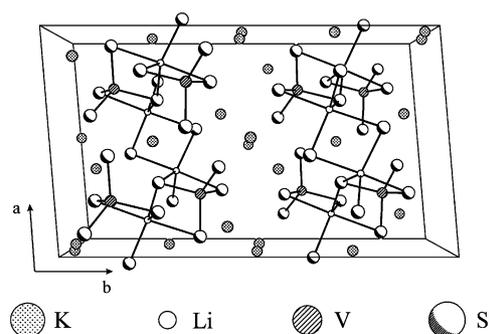


Fig. 2. The unit cell of K₂LiVS₄ down [010].

Rb₂LiVS₄ and Cs₂LiVS₄ are isostructural and of the K₂CuNbSe₄ structure type (space group *Fddd*). The structure of Rb₂LiVS₄ is displayed in Fig. 3. It consists of one-dimensional ${}^1_{\infty}[\text{LiVS}_2]^{2-}$ chains separated by Rb atoms. Each chain is built from LiS₄ and VS₄ tetrahedra that share edges to form a ${}^1_{\infty}[\text{LiVS}_2]^{2-}$ chain along [100], as shown in Fig. 4.

Rb₂LiNbS₄ and Rb₂LiTaS₄ are isostructural, crystallizing in a new structure type (space group *P1̄*) different from the structure of A₂LiVS₄ (A = Rb, Cs; space group *Fddd*). The unit cell of Rb₂LiNbS₄ is shown in Fig. 5. The structure is composed of two-dimensional

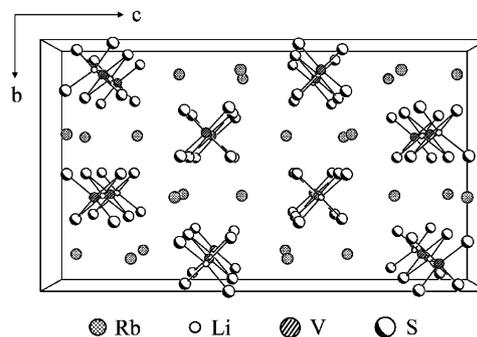


Fig. 3. The unit cell of Rb₂LiVS₄ down [100].

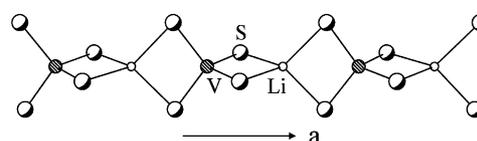


Fig. 4. The ${}^1_{\infty}[\text{LiVS}_4]^{2-}$ chain in Rb₂LiVS₄.

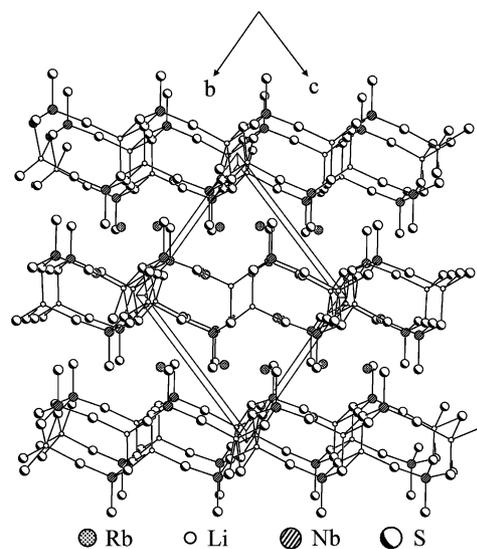


Fig. 5. The unit cell of Rb₂LiNbS₄ down [100].

${}^2_{\infty}[\text{LiNbS}_4]$ layers (Fig. 6) separated by Rb atoms. Each ${}^2_{\infty}[\text{LiNbS}_4]$ layer is built from vertex- and edge-sharing NbS₄ tetrahedra, LiS₄ tetrahedra, and distorted Li₂S₅ trigonal bipyramids.

The structure of Cs₂LiNbS₄ belongs to a new structure type (space group *P1̄*), as displayed in Fig. 7. The structure consists of one-dimensional ${}^1_{\infty}[\text{LiNbS}_4]^{2-}$ chains separated by Cs atoms, as shown in Fig. 8. Each chain is composed of vertex- and edge-sharing NbS₄ and LiS₄ tetrahedra, different from the chain in Cs₂LiVS₄, which is built solely from edge-sharing VS₄ and LiS₄ tetrahedra. The structure of Cs₂LiNbS₄ is related to that of Rb₂LiNbS₄. The shape of the chain in Cs₂LiNbS₄

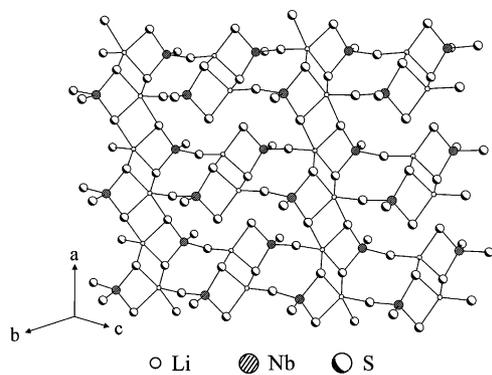


Fig. 6. The ${}^2_{\infty}[\text{LiNbS}_4]^{2-}$ layer in $\text{Rb}_2\text{LiNbS}_4$.

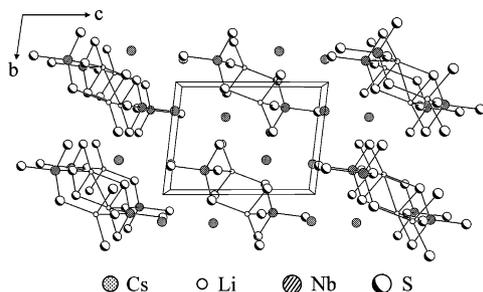


Fig. 7. The unit cell of $\text{Cs}_2\text{LiNbS}_4$ down [100].

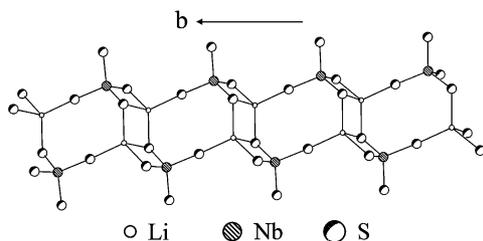


Fig. 8. The ${}^2_{\infty}[\text{LiNbS}_4]^{2-}$ chain in $\text{Cs}_2\text{LiNbS}_4$.

(Fig. 8) is somewhat similar to that of the ${}^2_{\infty}[\text{LiNbS}_4]$ layers in $\text{Rb}_2\text{LiNbS}_4$ (Fig. 6).

The VS_4 tetrahedra in K_2LiVS_4 , Rb_2LiVS_4 , and Cs_2LiVS_4 (Tables 2 and 3) are minimally distorted. The range of V–S distances is 2.1326(8)–2.1613(8) Å and the range of S–V–S angles is 106.85(3)–110.96(3)°. These may be compared to V–S distances of 2.141(1)–2.170(1) Å and S–V–S angles of 108.54(4)–111.86(6)° in AVS_4 ($A = \text{Rb}, \text{Cs}$) [26]. Similarly, the MS_4 ($M = \text{Nb}, \text{Ta}$) tetrahedra in $\text{Rb}_2\text{LiNbS}_4$, $\text{Cs}_2\text{LiNbS}_4$, and $\text{Rb}_2\text{LiTaS}_4$ (Tables 4 and 5) are nearly regular with M –S distances ranging from 2.254(1) to 2.292(1) Å and S– M –S angles ranging from 105.27(5) to 112.45(5)°. These may be compared to M –S distances of 2.262(6)–2.287(6) Å and S– M –S angles of 107.71(4)–112.4(3)° in A_3MS_4 ($A = \text{Na}, \text{Rb}; M = \text{Nb}, \text{Ta}$) [27]. The LiS_4 tetrahedra in Rb_2LiVS_4 , Cs_2LiVS_4 ,

$\text{Rb}_2\text{LiNbS}_4$, $\text{Rb}_2\text{LiTaS}_4$, and $\text{Cs}_2\text{LiNbS}_4$ (Tables 3–5) are somewhat less regular than the MS_4 tetrahedra with Li–S distances ranging from 2.381(8) to 2.538(7) Å and S–Li–S angles ranging from 92.9(3) to 125.2(4)°. The Li–S distances in the LiS_4 tetrahedra in Li_3AsS_3 range from 2.39(2) to 2.58(2) Å [20] whereas they are 2.52(2) and 2.53(1) Å in LiAuS [28]. Not surprisingly, the LiS_5 trigonal bipyramids in K_2LiVS_4 , $\text{Rb}_2\text{LiNbS}_4$, and $\text{Rb}_2\text{LiTaS}_4$ are more distorted: Li–S distances range from 2.466(9) to 3.013(10) Å, $\text{S}_{\text{eq}}\text{–Li–S}_{\text{eq}}$ angles range from 112.7(2) to 126.1(2)°, and $\text{S}_{\text{eq}}\text{–M–S}_{\text{ax}}$ angles range from 80.0(3) to 98.5(5)°. The $\text{S}_{\text{ax}}\text{–M–S}_{\text{ax}}$ angles range from 163.6(5) to 177.8(2)° (Tables 2 and 4).

The A–S coordination numbers and distance ranges are: 7, 3.021(7)–3.772(6) Å (K_2LiVS_4); 8, 3.3981(6)–3.7259(6) Å (Rb_2LiVS_4); 8, 3.5222(7)–3.8246(7) Å (Cs_2LiVS_4); 7, 3.388(1)–3.638(1) Å ($\text{Rb}_2\text{LiNbS}_4$); 9, 3.491(1)–4.069(1) Å ($\text{Cs}_2\text{LiNbS}_4$); and 7, 3.390(2)–3.645(2) Å ($\text{Rb}_2\text{LiTaS}_4$). These are comparable to those in A_2AgMS_4 ($A = \text{K}, \text{Rb}, \text{Cs}; M = \text{Nb}, \text{Ta}$) [7].

4. Conclusions

The substitution of Li for Cu in the $\text{K}_2\text{CuNbSe}_4$ structure type [2], which consists of one-dimensional ${}^1_{\infty}[\text{CuNbSe}_4]^{2-}$ chains of edge-sharing CuSe_4 and NbSe_4 tetrahedra, has generally affected not only the dimensionality of the structure but also the structure type and space group. Only Rb_2LiVS_4 and Cs_2LiVS_4 belong to the $\text{K}_2\text{CuNbSe}_4$ structure type. In fact, among the six compounds, namely K_2LiVS_4 , Rb_2LiVS_4 , Cs_2LiVS_4 , $\text{Rb}_2\text{LiNbS}_4$, $\text{Cs}_2\text{LiNbS}_4$, and $\text{Rb}_2\text{LiTaS}_4$, three are one-dimensional and three are two-dimensional structures; there are three different space groups; there are four different structure types; there is one compound in which Li is five-coordinate; there are three in which Li is four-coordinate; and there are two in which Li is both four- and five-coordinate. It appears that the smaller the transition metal the lower the dimensionality, and the smaller the alkali metal the higher the dimensionality. One wonders whether structural information on the three other possible compounds in the series, namely K_2LiNbS_4 , K_2LiTaS_4 , and $\text{Cs}_2\text{LiTaS}_4$, which we were unable to synthesize, would have simplified or further complicated these results.

5. Supplementary material available

Crystallographic data in CIF format have been deposited with FIZ Karlsruhe with the following CSD numbers: K_2LiVS_4 , 414184; Rb_2LiVS_4 , 414185; Cs_2LiVS_4 , 414186; $\text{Rb}_2\text{LiNbS}_4$, 414189; $\text{Cs}_2\text{LiNbS}_4$, 414187; and $\text{Rb}_2\text{LiTaS}_4$, 414186. These data may be obtained free of charge by contacting FIZ Karlsruhe at

+49 7247 808 666 (fax) or crysdata@fiz-karlsruhe.de (E-mail).

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