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Synthesis and Crystal Structure of Tetraamminelithium-Rubidiumtriselenide, $Li(NH_3)_4RbSe_3$, and Pentaamminesodium-Rubidiumtriselenide-Ammonia(1/3), $Na(NH_3)_5RbSe_3 \cdot 3NH_3$

Tobias Hanauer, Florian Kraus, and **Nikolaus Korber**[*]

Universität Regensburg, Institut für Anorganische Chemie, Germany

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Summary. The ammoniates $Li(NH_3)_4RbSe_3$ and $Na(NH_3)_5RbSe_3 \cdot 3NH_3$ were prepared by the reduction of Rb_2Se_5 with lithium or sodium in liquid ammonia. Single crystals were isolated and characterized by X-ray structure analysis using low temperature techniques. Both compounds contain triselenide anions Se_3^{2-}, which coordinate to rubidium cations forming ${}^1_\infty[RbSe_3]^-$ or ${}^1_\infty[Rb(NH_3)_2Se_3]^-$ chains. The chains are separated in the crystal structures by the homoleptic ammine complexes $Li(NH_3)_4^+$ and $Na(NH_3)_5^+$.

Keywords. Alkali metal; Ammoniate; Crystal structure; Liquid ammonia; Selenide.

Introduction

Binary alkali metal selenides are known in large numbers today. In addition to the monoselenides A_2Se, polyselenides A_2Se_n with chain-like anions are easily accessible by melt reactions of the elements. *Klemm et al.* made the first systematic investigations in these systems in the thirties of the past century [1]. By now, the crystal structures of compounds like Rb_2Se_2 [2], Rb_2Se_3 [3], Rb_2Se_5 [4] are known, as well as those of compounds like $[Na(15\text{-crown-}5)]_2Se_5$ [5] and $[Na(12\text{-crown-}4)_2]_2Se_8 \cdot (Se_6, Se_7)$ [6], in which the use of alkali metal ligands leads to larger polyanions. Additionally, non-chain-like polyselenides have been reported, which are formed when the valence of some selenium atoms is extended from two to four. Spiro-cyclic Se_{11}^{2-} in $(NPr_4)_2Se_{11}$ [7] (NPr_4 = tetrapropyl ammonium, $N(C_3H_7)_4^+$) or Se_{16}^{4-} in Cs_4Se_{16} [8] are examples from this group. The compound $(NPr_4)_2Se_{11}$ illustrates that polyselenides also exist with metal-free, organic counter ions.

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[*] Corresponding author. E-mail: nikolaus.korber@chemie.uni-regensburg.de

Further examples are the compounds (*PP*N)$_2$(Se$_4$)$\cdot$4CH$_3$CN [9] (*PP*N = bis (triphenyphosphine)iminium ion, (P*Ph*$_3$)$_2$N$^+$) and (P*Ph*$_4$)$_2$Se$_5$ [10] (P*Ph*$_4$ = tetraphenyl phosphonium, P(C$_6$H$_5$)$_4{}^+$). A slightly different approach to the structural variation of selenides is the investigation of mixed alkali metal cation phases. Mixed alkali metal monoselenides like RbLiSe [11], KLiSe [12], KNaSe [12], and CsNaSe [13] have been reported, but there seems to be no information on the respective polyselenides. Our approach to mixed cation polyselenides is the reductive cleavage of larger binary polyselenides with a solution of the second, lighter alkali metal in liquid ammonia. The new cations are thus introduced as ammine complexes, and usually retain their ligand sphere in the thermally labile ammoniates which crystallize directly from the reaction solution. In this contribution, we report on the results of the reduction of Rb$_2$Se$_5$ with lithium and sodium in liquid ammonia.

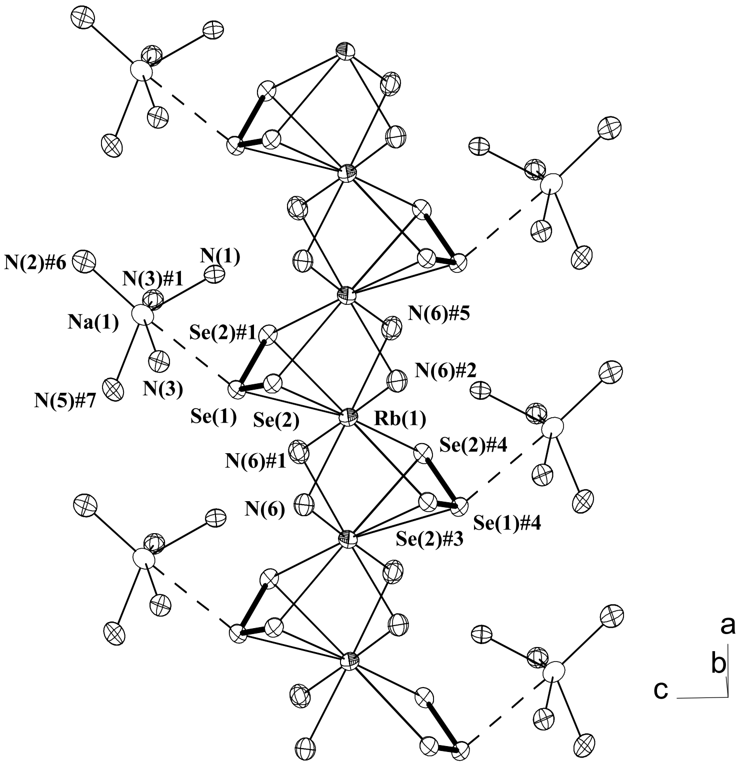

Fig. 1. Section of one chain in Na(NH$_3$)$_5$RbSe$_3\cdot$3NH$_3$, showing the coordination of both rubidium and sodium cations; ellipsoids are drawn with a probability factor of 70% [19]; selected distances (in Å) and angles (in °): Rb(1)–N(6) 3.149(3), Rb(1)–N(6)#1 3.149(3), Rb(1)–N(6)#2 3.164(3), Rb(1)–N(6)#5 3.164(3), Rb(1)–Se(1) 3.6341(5), Rb(1)–Se(2) 3.6062(4), Rb(1)–Se(2)#1 3.6062(4), Rb(1)–Se(2)#3 3.6177(4), Rb(1)–Se(2)#4 3.6177(4), Se(1)–Se(2) 2.3634(3), Na(1)–Se(1) 3.771(1), Na(1)–N(1) 2.564(3), Na(1)–N(2)#6 2.479(4), Na(1)–N(3) 2.503(2), Na(1)–N(5)#7 2.453(4), Se(2)–H(3C) 2.88(1), Se(2)–H(1A)#1 2.843(8); Se(2)–Se(1)–Se(2)#1 107.63(2), N(3)–H(3C)–Se(2) 159.44(1), N(1)–H(1A)#1–Se(2) 155.36(1); symmetry operations: #1 $x, -y+1/2, z$; #2 $x+1/2, y, -z+1/2$; #3 $x-1/2, y, -z+1/2$; #4 $x-1/2, -y+1/2, -z+1/2$; #5 $x+1/2, -y+1/2, -z+1/2$; #6 $-x+2, -y, -z-1$; #7 $-x+1, -y, -z+1$

Results and Discussion

Rb_2Se_5 was reduced with an excess of lithium and sodium in liquid ammonia and the resulting solvate crystals were characterized by low-temperature X-ray structure analysis. The products are the mixed alkali metal triselenides $Na(NH_3)_5RbSe_3 \cdot 3NH_3$ (**1**) and $Li(NH_3)_4RbSe_3$ (**2**). Both contain Se_3^{2-} anions, which coordinate to rubidium cations resulting in infinite ${}^1_\infty[RbSe_3]^-$ chains separated by homoleptic ammine complexes of the lighter alkali metal cations. The chains are built up only by triselenide anions and rubidium cations in **2**, but contain additional ammonia molecules in **1**.

In compound **1**, the rubidium cation Rb(1) is surrounded by five selenium atoms and by four molecules of ammonia (N(6), N(6)#1, N(6)#2, N(6)#5) (Fig. 1). The rubidium–selenium distances are in the range of 3.6062(4) to 3.6341(5) Å and the rubidium–nitrogen distances lie between 3.149(3) and 3.164(3) Å.

The Se_3^{2-} ion is situated on a special position and has two crystallographically independent selenium atoms, the selenium–selenium bond lengths are 2.3634(3) Å and the bond angle is 107.63(1)°. In other triselenides [3, 17] the selenium–selenium bonds range from 2.358(1) to 2.383(7) Å, which compares well with the observed value. However, the Se–Se–Se angles of the other known triselenides are 102.5(1) (K_2Se_3) [17], 103.1(3) (Rb_2Se_3) [3], and 103.6(5)° (Cs_2Se_3) [3], with a mean value significantly smaller than in **1**. In the binary compounds, the triselenide anions are completely surrounded by eight cations, whereas a distinctly one sided coordination of Se_3^{2-} by Rb(1) is observed in **1**, which may explain the larger bond angle of the anion. A similar phenomenon has

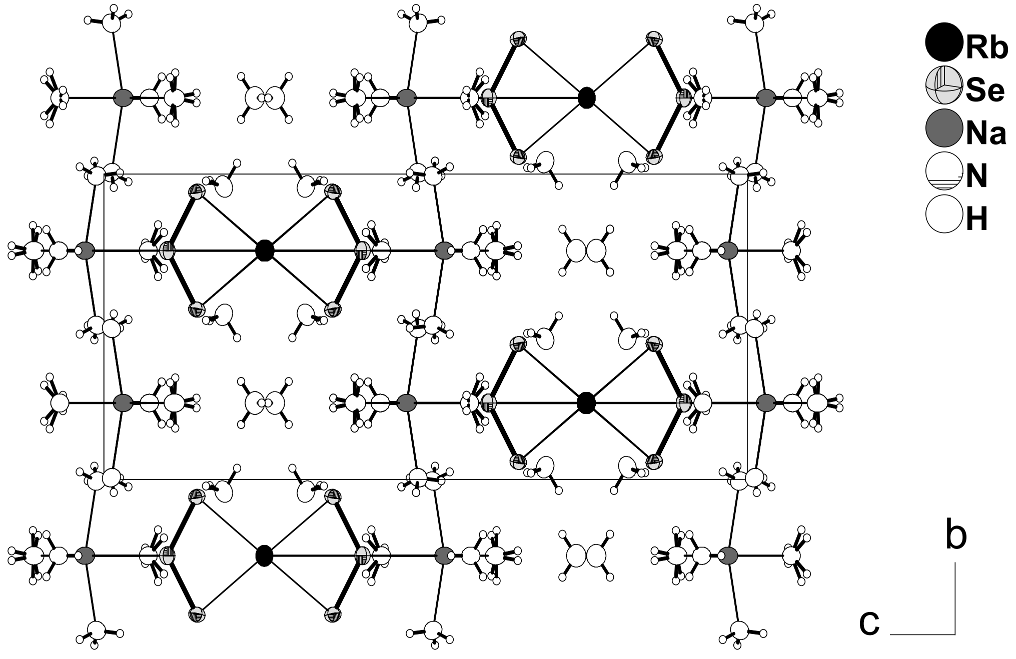

Fig. 2. Projection of the structure of $Na(NH_3)_5RbSe_3 \cdot 3NH_3$ on the *bc*-plane; ellipsoids are drawn with a probability factor of 70%

been reported for the *catena*-$P_3H_3^{3-}$-anion in $[Na(NH_3)_5][Na(NH_3)_3(P_3H_3)]$ [18]. In this compound, the two terminal P-atoms coordinate to a $[Na(NH_3)_3]^+$-fragment in an η^2-like fashion, and the bond angle is also enlarged compared to free triphosphorus species.

The coordinative interactions between rubidium cations, triselenide anions, and the ammonia molecule N(6) lead to a ${}^1_\infty[Rb(NH_3)_2Se_3]^-$ chain running parallel to the *a*-axis (Fig. 2), in which the closest Rb–Rb distance is only 3.7228(2) Å. The ammonia molecules which arise from the nitrogen atom N(6) in the asymmetric unit serve as bridging ammine ligands.

The second cation sodium forms a pentaammine complex of roughly square-pyramidal shape with four of the remaining ammonia molecules in the asymmetric unit (Fig. 1). The closest distance to the anion is 3.771(1) Å (Se(1)), which at best represents a very weak interaction. One ammonia molecule of solvation (N(4)) coordinates neither to sodium nor to rubidium. Atoms Rb(1), Se(1), Na(1), N(1),

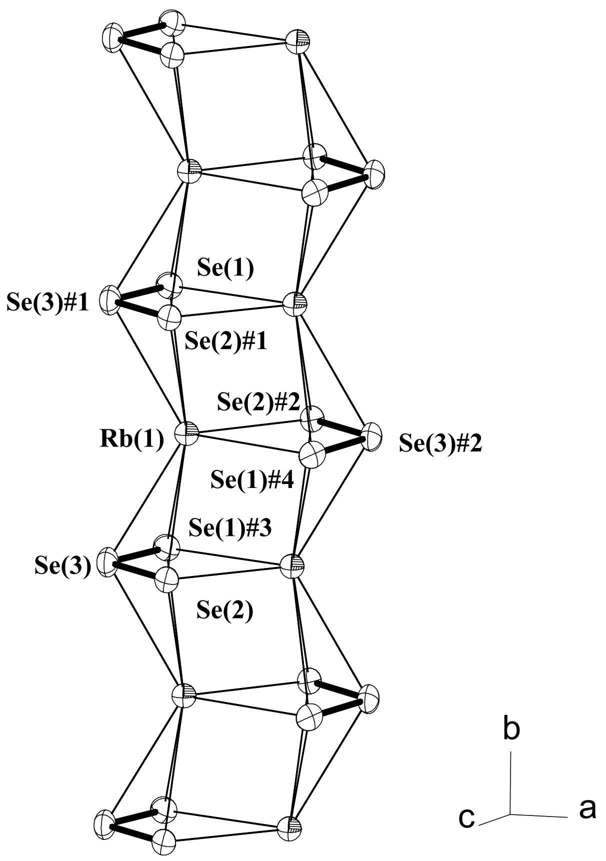

Fig. 3. Section of one ${}^1_\infty[RbSe_3]^-$ chain in $Li(NH_3)_4RbSe_3$; ellipsoids are drawn with a probability factor of 70% [19]; selected distances (in Å) and angles (in °): Rb(1)–Se(1) 3.5807(7), Rb(1)–Se(2) 3.4764(7), Rb(1)–Se(3) 3.5410(6), Rb(1)–Se(1)#4 3.7006(7), Rb(1)–Se(2)#1 3.5033(7), Rb(1)–Se(2)#2 3.5370(6), Rb(1)–Se(3)#1 3.5542(6), Rb(1)–Se(1)#3 3.6322(7), Se(1)–Se(3)#1 2.3628(7), Se(2)–Se(3) 2.3611(7); Se(2)–Se(3)–Se(1)#3 104.05(2); symmetry operations: #1 x, y + 1, z; #2 −x + 1/2, y + 1/2, −z + 1/2; #3 x, y − 1, z; #4 −x + 1/2, y − 1/2, −z + 1/2

N(2), N(4), N(5), as well as H(3) and H(5) (bound to N(5) and N(4), respectively) occupy the special position *4c*, all others the general position *8d* of the space group *Pnma*.

Compound **2** also contains chains built from rubidium cations and triselenide anions, but in this case the rubidium cation is exclusively coordinated by eight selenium atoms with Rb–Se distances ranging from 3.4764(7) to 3.7006(7) Å (Fig. 3). The Se_3^{2-} anion has two almost identical Se–Se bond lengths of 2.3628(7) and 2.3611(7) Å, which agree well with the values from the literature [3, 17] and compound **1**. In this case, the bond angle is 104.05(2)°, and thus is not significantly larger than the angles reported previously. The $^{1}_{\infty}[RbSe_3]^-$ chains are separated by the approximately tetrahedral tetraammine lithium cations, which are generally found in lithium containing ammoniates (Fig. 4).

The rubidiumpolyselenide substructures found in compounds **1** and **2** closely resemble previously reported substructures built from heavier alkali metals and polyphosphides, the first example of which was $^{1}_{\infty}[RbP_7]^{2-}$ in the compound $(NMe_4)_2RbP_7 \cdot NH_3$ [20]. Generally, in ammoniates of mixed cation polyphosphides like $BaCsP_{11} \cdot 11NH_3$ [21] or $[Li(NH_3)_4]_2RbP_7 \cdot NH_3$ [22], a structural

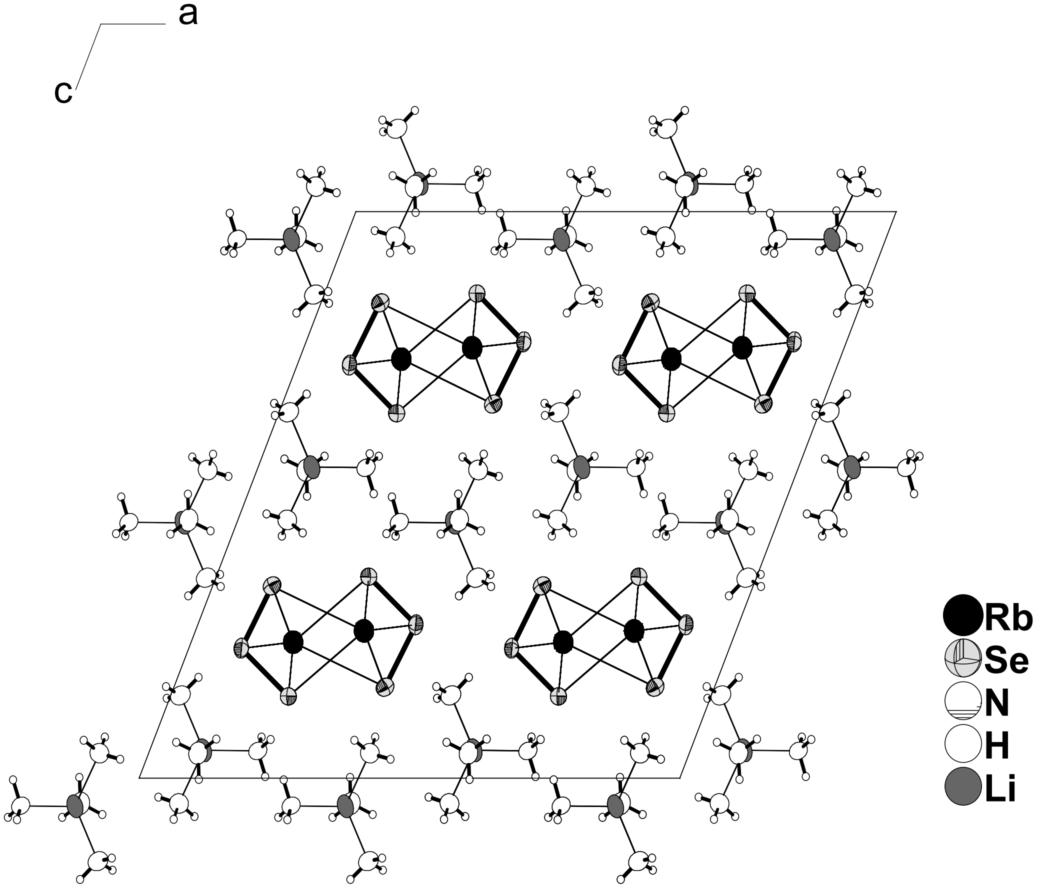

Fig. 4. Projection of the structure of $Li(NH_3)_4RbSe_3$ on the *ac*-plane; ellipsoids are drawn with a probability factor of 70%

differentiation very similar to the situation reported here is observed, with one kind of cations forming homoleptic ammine complexes, and the other kind forming metal cation–polyanion substructures with only a minimum, if at all, number of ammonia-cation contacts. This behaviour may readily be explained by the well-known HSAB principle [23], which calls for coordination of the hard base ammonia to the – in comparison – harder acids Li^+ and Na^+, while the softer base Se_3^{2-} coordinates exclusively to the larger, softer Rb^+ ion.

Experimental

All manipulations were performed under dry argon or vacuum using standard *Schlenk* techniques. In Schlenk tubes, 0.446 g (0.788 mmol) or 0.354 g (0.626 mmol) of Rb_2Se_5, and 0.028 g (1.218 mmol) of sodium or 0.007 g (1.009 mmol) of lithium were placed. About 20 ml of NH_3 were condensed onto the educts at 238 K. After a few days, dark red, air and moisture sensitive, block-shaped crystals had formed in both cases, which turn black and decompose rapidly if they are removed from the ammonia solutions. Single crystals were isolated directly from the ammonia solutions and measured on an IPDS (STOE & Cie, graphite monochromized MoKα-radiation) at 123 K. More information on structure

Table 1. Crystal data and structure refinement for $Na(NH_3)_5RbSe_3 \cdot 3NH_3$ and $Li(NH_3)_4RbSe_3$

Empirical formula	$H_{24}N_8NaRbSe_3$	$H_{12}N_4LiRbSe_3$
Formula weight/g mol^{-1}	481.62	397.43
Measuring range/°	0–360	0–211.2
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma* (No. 62)	*C*12/*c*1 (No. 15)
Cell parameter	$a = 7.4453(4)$ Å	$a = 19.924(2)$ Å
	$b = 9.8923(7)$ Å	$b = 5.9664(4)$ Å
	$c = 23.064(1)$ Å	$c = 20.476(2)$ Å
		$\beta = 112.92(1)°$
	$V = 1698.7(1)$ Å^3	$V = 2241.9(3)$ Å^3
Formula units per unit cell	$Z = 4$	$Z = 8$
Calculated density/Mg m^{-3}	1.883	2.355
Absorption coefficient/mm^{-1}	9.353	14.102
Absorption correction	DELrefABS [14]	
F (000)	920 electrons	1456 electrons
θ-range/°	2.87–25.86	2.22–25.86
Total number of reflections	22649	8705
Independent reflections	1738	2109
R_{int}	0.0617	0.0640
Structure solution	Direct methods, SHELXS-97 [15]	
Structure refinement	Least square refinement (F^2), Full Matrix, SHELXL-97 [16]	
Parameters	99	86
Goodness-of-fit (F^2)	1.001	0.893
R_1 ($I > 2\sigma(I)$)	0.0215	0.0269
wR_2 ($I > 2\sigma(I)$)	0.0512	0.0650
R_1 (all reflections)	0.0262	0.0392
wR_2 (all reflections)	0.0523	0.0683
Largest difference peaks/e Å^{-3}	0.537/−0.648	0.740/−0.620

solution and refinement can be found in Table 1. Hydrogen atoms were found by difference *Fourier* analysis and refined isotropically. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, on quoting the deposition numbers CSD-413743 ($Na(NH_3)_5RbSe_3 \cdot 3NH_3$) and CSD-413744 ($Li(NH_3)_4RbSe_3$).

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