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Synthesis, Crystal Structure, and Properties of Polymeric $Rb_{12}Nb_6Se_{35}$, a Novel Ternary Niobium Selenide Consisting of Infinite Anionic Chains Built Up by Nb_2Se_{11} Units Containing an Uncommon Se_3^{4-}-Fragment

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$Rb_{12}Nb_6Se_{35}$ is the first ternary niobium polyselenide composed of infinite anionic chains. These are well separated by rubidium cations. It crystallizes in the orthorhombic space group *Pbcn* with unit cell dimensions $a = 8.5811(1)$ Å, $b = 13.7152(1)$ Å, $c = 56.5225(4)$ Å, and $Z = 4$. The least-squares refinement against F^2 with anisotropic displacement parameters for all atoms yields $R1 = 5.78$ and $wR2 = 12.81$. The anionic polymeric chains are arranged in layers parallel to the (010) plane, and successive planes are rotated by 35° against each other. Nb_2Se_{11} units composed of two face-sharing $NbSe_7$ pentagonal bipyramids are the building blocks of the structure. They are interconnected by Se_2^{2-} and Se_3^{2-} polyanions, giving rise to infinite $^1_\infty[Nb_6Se_{35}]^{12-}$ chains. Within the Nb_2Se_{11} units an unusual nearly linear Se_3 fragment is found which must be formulated as Se_3^{4-}. © 1998 Academic Press

INTRODUCTION

The reaction of metals in molten alkali polychalcogenide fluxes often referred to as the "reactive flux" method has proven to be an efficient synthetic route to new multinary transition metal and main group chalcogenides (1). The dimensionality of the structures of these compounds range from molecular anions to three-dimensional solid state compounds. The method is especially advantageous when oxophilic metals like Nb or Ta are used for which the preparation out of solution often leads to an incorporation of oxygen or oxygen-containing ligands into the complexes. When the reactive flux method is used, pure chalcogenometalates are easily accessible. Reaction of Nb or Ta in alkali metal chalcogenide melts led to a variety of new ternary $A/M^V/Q$ (A = K, Rb, Cs; M^V = Nb, Ta; Q = S, Se) compounds like $K_3Nb_2Se_{11}$ (2), $K_4M_2S_{11}$ (M = Nb, Ta) (2, 3), $A_6Nb_4S_{22}$ (A = Rb, Cs) (4), $K_6Nb_4S_{25}$ (5), or $K_4Nb_2S_{14}$ (6). All these compounds contain discrete complex molecular anions with a Nb_2Q_{11}-building unit of two face-sharing pentagonal bipyramids as a common feature.

Chalcogenides of the heavier group 5 metals prepared at elevated temperatures showing one-dimensional structural motifs are well known (7). For example, the binary compounds $NbSe_3$ (8) or $NbTe_4$ (9) can be regarded as being composed of infinite chains. In $NbSe_3$ the Nb centers are in a trigonal prismatic environment of Se atoms, and these prisms are connected via common trigonal faces forming infinite rods. $NbTe_4$ is built up in a similar fashion by Nb-centered quadratic antiprisms sharing common quadratic faces.

Compounds with the composition $(MQ_4)_nX$ (M = Nb, Ta; Q = Se,Te; X = Br, I; n = 1, 2, 3, 10/3) (10) exhibit one-dimensional cationic $^1_\infty[MQ_4]^{m+}$ chains separated by X^- anions. The M centers are eightfold coordinated by chalcogen atoms in a distorted square antiprismatic geometry. These compounds are remarkable with respect to their unusual electronic properties, i.e. charge density waves along the chains lead to outstanding electronic conductivity and transport properties.

Infinite anionic chains with alkali metals for charge balancing are found in the quaternary system $A/M^I/M^V/Q$ (A = K, Rb, Cs; M^I = Cu, Ag; M^V = V, Nb, Ta; Q = S, Se) and among the group 5 thiophosphates. $A_2M^IM^VQ_4$ (11) and $K_3CuNb_2Se_{12}$ (11a) are examples of the former compounds. The chains in $A_2M^IM^VQ_4$ are built up by alternating edge-sharing M^IQ_4 and M^VQ_4 tetrahedra. In $K_3CuNb_2Se_{12}$ the chains are composed of a combination of $CuSe_4$ tetrahedra and Nb_2Se_{11} units with Nb in a pentagonal bipyramidal environment. As a representative for the thiophosphates KNb_2PS_{10} (12) should be mentioned. Distorted tetracapped biprismatic $[Nb_2S_{12}]$ units with short Nb–Nb separations are joined via one prismatic edge and

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one capping S atom thus forming chains. The P atom is attached to two capping S atoms, one S atom from the prism edge and an additional S atom completing the tetrahedral S environment of the phosphorus. The only examples for ternary compounds with anionic chains separated by alkali cations are $CsTaQ_3$ (Q = S, Se, Te) (13) where the chains consist of face-sharing TaQ_6 octahedra and $NaNbS_6$ (14) with Nb in a ninefold coordination of S atoms.

Here we report on the crystal structure and properties of $Rb_{12}Nb_6Se_{35}$, prepared via the reactive flux route. It is the first ternary niobium polyselenide exhibiting $^1_\infty[Nb_6Se_{35}]^{12-}$ anionic chains built up by Nb_2Se_{11} units which are interconnected by Se_2 and Se_3 fragments.

EXPERIMENTAL

1. *Synthesis*

Rb_2Se_3, Nb, and Se, in a 2:1:4 molar ratio, were thoroughly mixed in a drybox. Rb_2Se_3 was prepared by the reaction of stoichiometric amounts of Rb and Se in liquid ammonia under an argon atmosphere. The mixture was then loaded into a Pyrex glass ampoule which was subsequently evacuated (4×10^{-4} mbar) and sealed. The ampoule was heated to 350°C, held at this temperature for 3 days, and afterward lowered to room temperature at 3°/h. The resulting black melt was washed with DMF and ether and dried in vacuo. The product consisted of black-brown non-transparent platelets. The X-ray powder pattern could successfully be indexed on the basis of the cell of $Rb_{12}Nb_6Se_{35}$ indicating a homogenous product. Additionally, EDAX investigations performed on selected single crystals yielded $Rb_{12.3}Nb_6Se_{34.6}$ as an approximate composition, which is in good agreement with the composition derived from the crystallographic structure determination.

2. *Physical Measurements*

Infrared/Raman spectroscopy. A MIR spectrum was collected on a Genesis FT-spectrometer (ATI Mattson) in the range between 400 and 4000 cm^{-1}. Resolution was 2 cm^{-1}, and $Rb_{12}Nb_6Se_{35}$ was prepared as KBr pellets. A FIR was recorded between 80 and 550 cm^{-1} (resolution = 2 cm^{-1}) on an ISF-66 device (Bruker) with $Rb_{12}Nb_6Se_{35}$ pressed in polyethylene pellets. The FT-Raman spectrum was measured on an ISF-66 spectrometer (Bruker) with an additional FRA 106 Raman module. A Nd:YAG laser was used as source for excitation ($\lambda = 1064$ nm). $Rb_{12}Nb_6Se_{35}$ was ground and prepared on Al sample holders. The measuring range was -1000 to 3500 cm^{-1} with a resolution of 2 cm^{-1}.

Solid state UV/vis spectroscopy. Diffuse reflectance measurements were carried out by means of a homemade optical bench. It was equipped with a 100 W tungsten halogen lamp and an integrating sphere. Spectra were recorded by parallel operation of a 0.275 and a 0.5 m monochromator (SpectraPro-275 and SpectraPro-500, Acton Research) between 700 and 1200 nm. A liquid nitrogen cooled InGaAs photodiode (Electro-optical Instruments) was used for detection. The $Rb_{12}Nb_6Se_{35}$ crystals were ground before the measurement, and $BaSO_4$ of high optical quality was used as a reflectance standard. Absorption data were calculated from the reflectance data using the Kubelka–Munk function. The approximate band gap was determined as the intersection point between the energy axis and the line extrapolated from the linear part of the absorption edge in the $(F(R))^2$ plot.

Single crystal X-ray diffraction. The cell parameters of $Rb_{12}Nb_6Se_{35}$ were first determined by a search in reciprocal space on a conventional STOE AED II four-circle diffractometer. Due to the large c axis the collection of the intensities was carried out at room temperature on a Siemens CCD three-circle diffractometer (using monochromated Mo$K\alpha$ radiation; $\lambda = 0.7107$ Å) which was capable of resolving the close lying reflections. Lorentz, polarization, and an absorption correction using equivalent reflections using the program SADABS (15) were applied to all data. A full-matrix least-squares refinement against F^2 with anisotropic displacement parameters for all atoms was performed. All calculations were carried out using the SHELXL 96 software package. Crystallographic data as well as the refinement results are summarized in Table 1. Atomic coordinates are listed in Table 2, and Table 3 contains selected distances and angles.

The refinement resulted in relatively large R factors and a residual electron density of 6.14 e Å^{-3}. A close inspection of the structural parameters, standard deviations, and anisotropic displacement parameters gave no hints for any errors or inconsistencies in the structure determination.

RESULTS AND DISCUSSION

The crystal structure of $Rb_{12}Nb_6Se_{35}$ is composed of $^1_\infty[Nb_6Se_{35}]^{12-}$ anionic chains running along the c axis. They are well separated by the Rb^+ cations. The main structural "building block" of the chains is a Nb_2Se_{11} unit, being composed of two distorted face-sharing $NbSe_7$ pentagonal bipyramids. Within the bipyramids one apical position is occupied by a terminal Se center and the second by a Se atom of a Se_2 group of the neighboring polyhedron. The pentagonal plane is composed of one Se_2 group showing a μ-η^2, η^1 coordination mode, two Se atoms of a μ-η^2, η^2 -bridging Se_3 fragment, and one Se center of a terminally bound Se_n polyselenide anion (n = 2 or 3). These Se_2^{2-} and Se_3^{2-} anions interconnect the Nb_2Se_{11} building blocks in a 3-3-2 fashion giving rise to infinite chains as shown in Fig. 1. With this coordination the repeat unit of the chains may

TABLE 1
Crystallographic Data for $Rb_{12}Nb_6Se_{35}$

Crystal size [mm^3]	$0.22 \times 0.18 \times 0.16$
a [Å]	8.5811(1)
b [Å]	13.7152(1)
c [Å]	56.5225(4)
Volume [Å^3]	6652.2(1)
Crystal system	orthorhombic
Space group	*Pbcn*
Z	4
MW	4346.7
μ [mm^{-1}]	28.888
ρ [g/cm^3]	4.340
2θ [deg]	9.5–53
Index ranges	$-10 < h < 10$
	$-17 < k < 16$
	$-70 < l < 59$
No. of reflections collected	58465
No. of unique data	6779
No. of unique data ($I > 2.0\sigma(I)$)	4546
Min/max transmission	0.3678/1.0000
R_{int} [%]	14.82
k^a	0.01781(4)
x^a	0.00056(3)
y^b	0.0627
No. of parameters refined	243
$R1$ ($I > 2\sigma I$) [%]^c	5.78
w$R2$ (all data) [%]^d	12.81
$R1$ (all data) [%]	10.34
GOOF	1.005
No. of difference peaks [e Å^{-3}]	6.138/–2.336

[a] Extinction correction: $F^* = F_c k(1 + 0.001xF_c^2\lambda^3/\sin 2\Theta)^{-1/4}$; k = OSF.
[b] Weighting scheme: $w^{-1} = \sigma^2(F_o^2) + (yP)^2$; $P = [\max(0, F_o^2) + 2F_c^2]/3$.
[c] $R1 = \sum[||F_o| - |F_c||/\sum|F_o|]$.
[d] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for $Rb_{12}Nb_6Se_{35}$

	X	Y	Z	U_{eq}^a
Nb(1)	4617(1)	3682(1)	471(1)	14(1)
Nb(2)	4625(1)	4500(1)	1106(1)	15(1)
Nb(3)	10571(1)	2959(1)	2183(1)	16(1)
Se(1)	4819(2)	2140(1)	292(1)	45(1)
Se(2)	3866(2)	4812(1)	114(1)	20(1)
Se(3)	7294(2)	4512(1)	428(1)	23(1)
Se(4)	6892(2)	3596(1)	778(1)	19(1)
Se(5)	1650(2)	3975(1)	507(1)	23(1)
Se(6)	3046(2)	3150(1)	860(1)	20(1)
Se(7)	5018(2)	2689(1)	1197(1)	24(1)
Se(8)	3813(2)	5461(1)	734(1)	19(1)
Se(9)	5852(2)	6151(1)	966(1)	22(1)
Se(10)	2640(2)	4998(1)	1371(1)	29(1)
Se(11)	7148(2)	4743(1)	1365(1)	26(1)
Se(12)	7514(2)	3314(1)	1600(1)	29(1)
Se(13)	9318(2)	4076(1)	1863(1)	30(1)
Se(14)	8228(2)	1824(1)	2123(1)	28(1)
Se(15)	0	1543(1)	2500	23(1)
Se(16)	7897(2)	3598(1)	2451(1)	21(1)
Se(17)	11567(2)	4743(1)	2247(1)	26(1)
Se(18)	12582(2)	2186(1)	1971(1)	35(1)
Rb(1)	5000	1791(1)	2500	31(1)
Rb(2)	5461(2)	1267(1)	1665(1)	29(1)
Rb(3)	4903(2)	4699(1)	1922(1)	55(1)
Rb(4)	3921(2)	7577(1)	1391(1)	36(1)
Rb(5)	−218(2)	5648(1)	857(1)	44(1)
Rb(6)	0	5000	0	23(1)
Rb(7)	5848(2)	7030(1)	325(1)	45(1)

[a] The equivalent isotropic displacement parameter U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

be described as $^1_\infty[(Nb_2(\mu\text{-}\eta^2, \eta^2\text{-}Se_3)\ (\mu\text{-}\eta^2, \eta^1\text{-}Se_2)_2(Se)_2)_3\ (\mu\text{-}\eta^1\text{-}Se_3)_2(\mu\text{-}\eta^1\text{-}Se_2)]^{12-}$.

The Se(15) atom is located on a twofold axis, and therefore two different Nb_2Se_{11} units are in the crystal structure. The differences between the two units are very small as evidenced by fitting the fragments onto each other. The minimum and maximum deviations are 0.025 Å (Nb2–Nb3a) and 0.442 Å (Se2–Se13), the weighted RMS deviation amounts to 0.16 Å.

The $^1_\infty[Nb_6Se_{35}]^{12-}$ chains are not linear but corrugated. They are arranged in layers parallel to the (0 1 0) plane. Successive planes are rotated by 35° against each other as depicted in Fig. 2. The shortest interchain Se $\cdots$ Se distance amounts to 3.768 Å which is just the sum of the van der Waals radii of Se.

The Nb–Se distances range from 2.35 to 2.94 Å with mean values of $\langle$Nb(1)–Se$\rangle$ = 2.624 Å, $\langle$Nb(2)–Se$\rangle$ = 2.629 Å and $\langle$Nb(3)–Se$\rangle$ = 2.616 Å. The individual Nb–Se bond lengths can be divided into three groups. Every Nb has one apical Se at about 2.35 Å, indicating appreciable double bonding character. Normally such short Nb–Se separations are found for Nb in tetrahedral environment of Se atoms (16). Five intermediate Nb–Se bond distances within the pentagonal plane scatter around 2.6 Å and are comparable to data given in the literature (17). In addition the three crystallographically independent Nb atoms have each a second apical Se at a distance between 2.886(2) and 2.961(2) Å (marked as dotted lines in Fig. 1). It must be noted that there is no simple correlation between the short and the very long distance, i.e., the shortest Nb–Se bond is not accompanied by the longest Nb–Se distance.

The Rb^+ cations (Rb(1) to Rb(6)) are in irregular environments of Se with coordination numbers between 5 and 8 with a cutoff of 3.7 Å. Rb(7) is coordinated by 10 Se atoms (cutoff = 3.9 Å) with a mean Rb–Se distance of 3.706 Å. The other mean Rb–Se distances range from 3.385 Å for Rb(2) ($CN = 7$) to 3.573 Å for Rb(4) ($CN = 8$).

The Se–Se distances within the Se_2 dumbbells and within the Se_3 units interconnecting the Nb_2Se_{11} fragments are typical for Se–Se single bonds (2.36 to 2.39 Å).

The two different Nb_2Se_{11} units show an unusual Se_3 fragment, in contrast to the other compounds with the

TABLE 3
Selected Interatomic Bond Distances (Å) and Angles (deg) in $Rb_{12}Nb_2Se_{35}$

Nb(1)–Se(1)	2.352(2)	Nb(1)–Se(3)	2.575(2)
Nb(1)–Se(5)	2.585(2)	Nb(1)–Se(4)	2.615(2)
Nb(1)–Se(2)	2.624(2)	Nb(1)–Se(6)	2.680(2)
Nb(1)–Se(8)	2.938(2)	Nb(2)–Se(10)	2.368(2)
Nb(2)–Se(7)	2.559(2)	Nb(2)–Se(8)	2.580(2)
Nb(2)–Se(9)	2.619(2)	Nb(2)–Se(11)	2.634(2)
Nb(2)–Se(6)	2.685(2)	Nb(2)–Se(4)	2.961(2)
Nb(3)–Se(18)	2.355(2)	Nb(3)–Se(14)	2.565(2)
Nb(3)–Se(16)a	2.600(2)	Nb(3)–Se(13)	2.603(2)
Nb(3)–Se(17)	2.617(2)	Nb(3)–Se(15)	2.686(2)
Nb(3)–Se(16)	2.886(2)	Se(2)–Se(2)b	2.391(3)
Se(3)–Se(4)	2.369(2)	Se(5)–Se(6)	2.586(2)
Se(6)–Se(7)	2.625(2)	Se(8)–Se(9)	2.384(2)
Se(11)–Se(12)	2.389(2)	Se(12)–Se(13)	2.387(2)
Se(14)–Se(15)	2.644(2)	Se(15)–Se(14)a	2.644(2)
Se(16)–Se(17)a	2.361(2)	Se(17)–Se(16)a	2.361(2)
Se(2)b–Se(2)–Nb(1)	110.0(1)	Se(12)–Se(11)–Nb(2)	108.3(1)
Se(13)–Se(12)–Se(11)	94.2(1)	Se(12)–Se(13)–Nb(3)	116.3(1)
Se(5)–Se(6)–Se(7)	164.4(1)	Se(14)a–Se(15)–Se(14)	163.2(1)

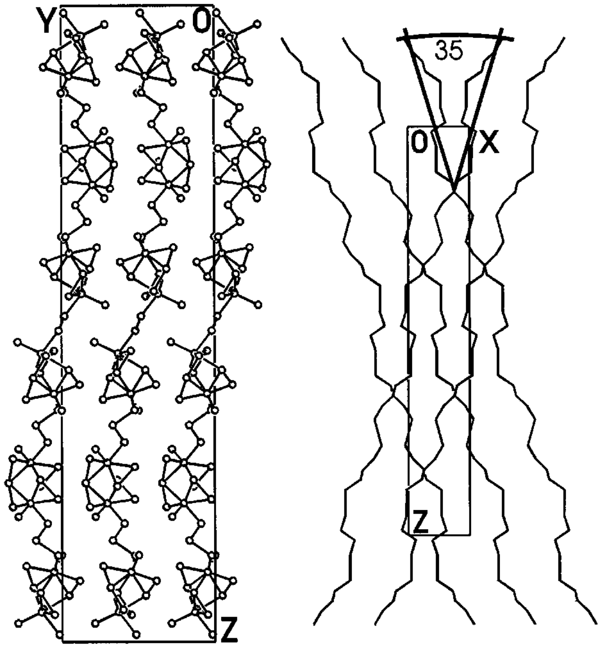

FIG. 2. Left side: Projection onto the (100) plane (Rb cations are omitted for clarity). Right side: "Backbone" (build up by the Nb atoms and the interconnecting Se_2 and Se_3 units) of the $^1_\infty[Nb_6Se_{35}]^{12-}$ chains projected onto the (010) plane.

M_2Q_{11} unit. The Se_3 unit exhibits two long Se–Se bonds of 2.586(2) and 2.625(2) Å for Se(5)–Se(6)–Se(7) and twice 2.644(2) Å in case of Se(14)–Se(15)–Se(14a) (Fig. 1). It coordinates to two Nb centers in a μ-η^2, η^2 fashion with Nb–Se distances ranging from 2.565 to 2.686 Å. The Se–Se distances of about 2.62 Å are significantly longer than for a single bond of 2.38 Å as found in the Se_3^{2-} anion of A_2Se_3 ($A = K, Rb, Cs$) (18) or other Se_3 fragments like in K_3AuSe_{13} (19). The Se–Se–Se angles are 163.2(1) and 164.4(1)°. In other polyselenides the angles around the Se centers are in the range expected for a tetrahedral environment.

The charge of the Se_3 polyselenide anion is not clear because the assignment of the formal oxidation states in $Rb_{12}Nb_6Se_{35}$ is not straightforward. Using the normal electron counting rules the Nb centers should be in the oxidation state +4, leading to the formulation $\{Rb^+\}_{12}\{Nb^{4+}\}_6\{Se_3^{2-}\}_3\{Se_2^{2-}\}_6\{Se^{2-}\}_6\{Se_3^{2-}\}_2\{Se_2^{2-}\}$. But it is well documented that Nb(IV) centers tend to form Nb–Nb bonds with typical distances of about 3 Å. Such Nb–Nb bonds are found in $Nb_2Y_2X_6$ (Y = Se, Te; X = Br, I) (20), KNb_2PS_{10} (12), or Nb_2Se_9 (21). The Nb–Nb distances of about 3.7 Å in $Rb_{12}Nb_6Se_{35}$ are too long to be treated as Nb–Nb bonds

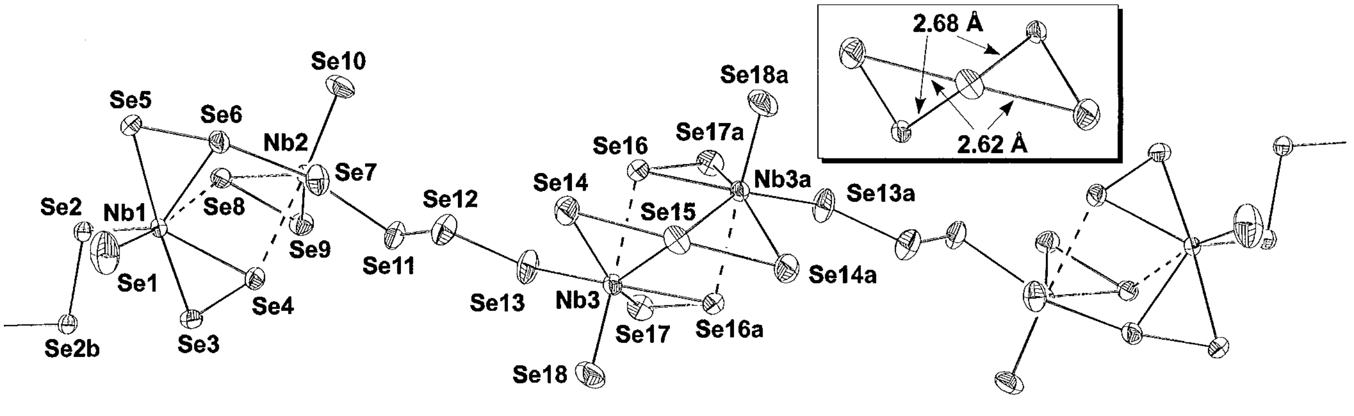

FIG. 1. Nb_2Se_{11} units in the structure of $Rb_{12}Nb_6Se_{35}$ interconnected to infinite $^1_\infty[Nb_6Se_{35}]^{12-}$ chains. The inset shows the Se_3^{4-} anion.

which makes the assignment of $+4$ for the Nb centers highly unreasonable.

If Se spirocycle anions are excluded, then to the best of our knowledge only two other examples with Se_n units showing such long Se–Se distances are known. In Nb_2Se_9 (21) a Se_5 fragment is observed which exhibits two unusual large inner Se–Se distances of 2.643 and 2.663 Å and two normal terminal Se–Se bond lengths of about 2.36 Å. The angle between the three central Se atoms of 143° is nearly as large as in the title compound. The Nb–Nb distance in Nb_2Se_9 amounts to 2.895 Å typical for a single bond between Nb (d^1) centers. With Nb in the d^1 configuration the Se_5 unit must be considered as a Se_5^{4-} anion and Nb_2Se_9 can be formulated as $\{Nb^{4+}\}_2\{Se_2^{2-}\}_2\{Se_5^{4-}\}$ (21b).

The second example is $K_3CuNb_2Se_{12}$ (11a) containing a Se_4 fragment with one short (2.389 Å) and two long Se–Se distances of 2.726 and 2.542 Å. Again the angle of 165.7° between the three Se atoms connected via the two long bonds is close to linearity, and it is not clear whether the fragment should be formulated as Se_4^{2-} or as Se_4^{4-}. The authors mentioned the arbitrariness of defining the formal oxidation state for Nb, i.e., Nb(IV) or Nb(V) but did not want to put themselves to a final decision.

In order to tackle the problem of oxidation state assignment we conducted bond-valence calculations for the Nb–Se bonds using the equation given by Pauling, $S_{ij} = \exp((r_0 - D_{ij}/b)$. The parameter b is usually taken to be an universal constant of 0.37. An appropriate bond valence parameter r_0 of 2.51 for Nb–Se compounds was suggested in Ref. (22). When these values are used, the sums of the valences in $Rb_{12}Nb_6Se_{35}$ adopt unreasonably high values from 5.56 to 5.68 for the three crystallographically independent Nb atoms. New calculations with Monte Carlo methods as well as least-squares refinements on a basis of 8 compounds with 14 crystallographically independent Nb atoms yielded for $b = 0.28$ and $r_0 = 2.48$ Å. Using these new values the sums of bond valences for $Rb_{12}Nb_6Se_{35}$ and $K_3CuNb_2Se_{12}$ range from 4.8 to 4.9 for the crystallographically independent Nb atoms and to about 4.3 in Nb_2Se_9, in nice accordance with Nb(V) in the two former compounds and Nb(IV) in the latter.

It is further noted that the alkalipolychalcogenide melts are strongly oxidizing agents. All niobium sulfides and selenides (2–6, 11) prepared by this method unambiguously contain Nb in the highest oxidation state. Hence, there is no reason why this should be different in $Rb_{12}Nb_6Se_{35}$.

Because there is no example of such a linear Se_3^{4-} fragment in the literature a short excursion into the chemistry of Te with its nonclassical behavior will demonstrate that Se might also exhibit unusual bonding properties. For Te a number of different Te–Te–Te bonding modes with bonding angles of about 90, 109 and 180° are reported (23). A hypothetical Te_3^{4-} anion and its linear geometry is discussed in (24) in terms of a VSEPR model. The Te_3^{4-} anion is described as pseudotrigonal bipyramidal with three lone pairs in the equatorial plane. In NaTe (25) a linear Te_3 unit is found as a part of a Z-shaped Te_5^{4-} anion. Like in the Se_3^{4-} anion of the title compound, it shows elongated Te–Te bonds of 3.08 Å (single bond 2.75 Å).

The existence of four negative charges on a Se_3 fragment is also plausible from simple electronic considerations. The linear combination of the three p orbitals of the Se atoms leads to the three σ orbitals, one bonding (σ), one nonbonding (n), and an antibonding (σ^*). The σ as well as the n orbitals should be able to accommodate two electrons. As a result the Se_3 can accommodate four negative charges.

As a consequence of the investigations and considerations presented above, the existence of the Se_3^{4-} anion seems to be highly plausible. This means that polyselenides clearly show the gradual change in the properties of anionic fragments and arrays from sulfur with its pure classical behavior to tellurium, where a number of different networks with a wide range of Te–Te distances were observed.

The optical properties of $Rb_{12}Nb_6Se_{35}$ were investigated with UV/vis diffuse reflectance measurements. The resulting spectra showed a steep absorption edge from which an optical band gap of about 1.4 eV is calculated. This value is in agreement with the dark-brown color of $Rb_{12}Nb_6Se_{35}$.

The FIR spectrum is very complex. It shows a number of only poorly resolved absorptions between 425 and 340 cm^{-1} and between 320 and 200 cm^{-1} together with two sharp peaks at 142 and 101 cm^{-1}, respectively. No attempts were undertaken to assign these absorptions. No peaks were observed in the MIR range above 500 cm^{-1}. The Raman spectrum shows sharp peaks at 319 (vw), 262 (w), 236 (s), and 144 (w) cm^{-1}. A comparison with the spectra reported for Nb in tetrahedral environment of Se (26) led to the assignment of the 236 cm^{-1} peak to Nb–Se stretching modes.

$Rb_{12}Nb_6Se_{35}$ (27) is another example with a $M_2^VQ_{11}$ "building block" ($M^V = Nb, Ta$; $Q = S, Se$) as the basic unit creating the structure. As mentioned above, this unit is also found in several other ternary and quarternary alkali group 5 chalcogenides. In fact, $Rb_{12}Nb_6Se_{35}$ is the first ternary niobium selenide with infinite anionic chains which was prepared using the "reactive flux" method. The preparation of $Rb_{12}Nb_6Se_{35}$ gives rise to the assumption that the variability of the connection modes for this $M_2^VQ_{11}$ "building block" has not yet come to an end and that one will still find new types of bridging modes leading to unprecedented and interesting new structures.

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27. By the time we finished writing this paper, we successfully prepared the isostructural potassium compound $K_{12}Nb_6Se_{35}$. It crystallizes in the space group *Pbcn* with cell parameters of $a = 8.3679(5)$ Å, $b = 13.3516(7)$ Å, and $c = 56.2140(34)$ Å. $K_{12}Nb_6Se_{35}$ was synthesized under the same conditions (educt ratio and temperature) like the title compound.