Synthesis and Crystal Structures of Two Novel Niobium Oxo-Selenides: $K_4Nb_2Se_{11}O$ Consisting of Infinite Anionic Chains and $Cs_4Nb_2Se_{11}O$ Being the First Example for the Coexistence of Molecular and Infinite Chainlike Transition Metal Polychalcogenide Anions in One Compound

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The new compounds $K_4Nb_2Se_{11}O$ and $Cs_4Nb_2Se_{11}O$ have been synthesized from a K_2Se_n and Cs_2Se_n flux, respectively. $K_4Nb_2Se_{11}O$ crsytallizes in the orthorhombic space group *Pbca* with lattice parameters $a = 15.946(4)$ Å, $b = 13.872(3)$ Å, $c = 18.622(3)$ Å, $V = 4119(2)$ Å^3, $Z = 8$. The structure has been refined to a $wR_2(F^2)$ of 0.1547 for 163 parameters and 4714 reflections. The $R_1(F)$ amounts to 0.0410. $Cs_4Nb_2Se_{11}O$ crsytallizes in the triclinic space group $P-1$ with unit cell dimensions $a = 12.023(4)$ Å, $b = 14.367(4)$ Å, $c = 14.571(4)$ Å, $\alpha = 76.90(2)°$, $\beta = 78.43(2)°$, $\gamma = 71.89(2)°$, $V = 2307(1)$ Å^3, $(Z = 4)$. Refinement against F^2 resulted in a wR_2 of 0.1075 for 326 parameters and 10542 unique reflections. The $R_1(F)$ amounts to 0.0411. The structures of both compounds consist of expanded and interconnected Nb_2Q_{11} units (Q = Se, O) which are built up of two face-sharing pentagonal $NbSe_6O$ and $NbSe_7$ bipyramids. In $K_4Nb_2Se_{11}O$ the Nb_2Q_{11} units are interconnected by Se_3^{2-} anions giving rise to infinite anionic $_\infty^1[Nb_2Se_{11}O]^{4-}$ chains which are separated by the K^+ cations. $Cs_4Nb_2Se_{11}O$ resembles a mixture of molecular $[Nb_2Se_{11}O]^{4-}$ anions and $_\infty^1[Nb_2Se_{11}O]^{4-}$ infinite anionic chains coexisting in one structure. Both compounds exhibit Se_n^{n-} anions with unusual bonding properties. In $K_4Nb_2Se_{11}O$, a nearly linear Se_3^{4-} anion is found, whereas $Cs_4Nb_2Se_{11}O$ contains a Se_6 fragment which carries six negative charges.

Introduction

The synthesis of new multinary transition metal polyselenides and tellurides is still a field of great interest, and many chemists are fascinated by the unusual crystal structures and interesting properties. One motivation for activities in this field is certainly the aim to learn more about the bonding properties and chemical behavior of such compounds, as the chemistry of the heavier chalcogenides is still underdeveloped compared to sulfur chemistry. This trend is impressingly documented in a number of recent reviews.[1] The synthetical routes to prepare such compounds are restricted to low-temperature syntheses, i.e., solution chemistry and solvothermal methods. Within the medium-temperature range (250−500 °C) the reactive flux method[2] is one of the most promising synthetical approaches to the preparation of new multinary selenides and tellurides.[3]

We are engaged in investigating the chalcogenide chemistry of group V metals. We synthesized a number of new molecular and one-dimensional ternary niobium sulfides ($K_4Nb_2S_{11}$, $A_6Nb_4S_{22}$ (A = Rb,Cs), $K_6Nb_4S_{25}$, K_4-Nb_2S_{14}, and $NaNbS_6^{4a-e}$), most of them comprised of pure and expanded Nb_2S_{11} units, by reaction of niobium in molten alkali polysulfide fluxes.

Using selenium instead of sulfur we succeeded in the preparation of two new alkali niobium polyselenides, $A_{12}Nb_6Se_{35}$ (A = K, Rb).[5] The crystal structures are based on interconnected Nb_2Se_{11} units leading to one-dimensional anionic chains with a repeating unit of about 56 Å. The cations are located between the chains. The basic M_2Q_{11} unit (M = V, Nb, Ta, Mo, W; Q = S, Se) of two face-sharing pentagonal bipyramids is a structural motif often encountered in the coordination chemistry of d^0 elements. In such molecular compounds obtained via classical solution chemistry, the two terminal chalcogen atoms are often substituted by oxygen.

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In contrast to oxysulfides, the number of oxyselenides and seleno oxometalates described in the literature is rather scant. Most of the oxyselenides occur in the chemistry of rare earth metals. The known ternary or quaternary rare earth oxyselenides are Ln_2O_2Se (Ln = La, Pr, Nd, Sm, Gd, Ho, Er, Yb),[6] $Ln_{10}Se_{14}O$ (Ln = La, Ce, Pr),[7] $La_4O_4Se_3$,[8] $UOSe$,[9] $ThOSe$,[10] $LaGaOSe_2$,[11] $La_4Ga_{1.88}O_4Se_{4.82}$,[12] $LaCrOSe_2$,[13] $Ln_2Ta_3Se_2O_8$ (Ln = La, Ce, Pr, Nd),[14] $Fe_2La_2O_3Se_2$,[15] $SmCuSeO$,[16] and $LnCuSeO$ (Ln = Gd, Dy).[17] The only examples for main group or transition metal oxyselenides are Bi_2O_2Se,[18] $BiCuOSe$,[19] and $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$.[20] From solution chemistry the following seleno oxometalate compounds were prepared: $(Ph_4P)_2[W_3Se_9]_{0.46}[W_3Se_8O]_{0.54}$,[21] $(Et_4N)_2[MoSe_8O]$,[22] $(2.2.2\text{-Cryptand-K})_2[Mo_2Se_6O_2]$,[23] $K_4[V_2O_2Se_{10}] \cdot 2MeOH$,[24] $K_4[V_2O_2Se_8] \cdot 0.65MeOH$,[24] $(Ph_4P)_2[NbOSe_2SeH]$,[25] $(Et_4N)_4[(NbO(Se_2)_2)_2Se_4]$,[25] and $(Et_4N)_4[(NbSe_3)_2O]$.[25]

In the present paper we present the preparation and structures of two new fascinating oxyselenides, $K_4Nb_2Se_{11}O$ and $Cs_4Nb_2Se_{11}O$, exhibiting new interconnection schemes between the Nb_2Q_{11} building units. $Cs_4Nb_2Se_{11}O$ is to the best of our knowledge the first example of a polychalcogenide in which molecular anions and infinite one-dimensional anionic chains coexist.

Experimental Section

Synthesis. *$K_4Nb_2Se_{11}O$.* K_2Se_3, Nb, and Se, in a 2/1/4 molar ratio, were thoroughly mixed in a drybox. The Nb (<65 μm) was stored in a dry but not completely O_2 free glovebox for over 1 year and must have been contaminated by oxygen. K_2Se_3 was prepared by the reaction of stoichiometric amounts of K and Se in liquid ammonia under an argon atmosphere. The mixture was then loaded into a Pyrex glass ampule which

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was subsequently evacuated ($4 \cdot 10^{-4}$ mbar) and sealed. The ampule was heated to 350 °C, held at this temperature for 6 days, and afterward was cooled to room temperature at 3 °C/h. The resulting black melt was washed with DMF and ether and dried in a vacuum. The product consisted of rhombic platelike black brown crystals of $K_4Nb_2Se_{11}O$ together with contaminations of selenium. The X-ray powder pattern of manually selected crystals could successfully be indexed on the basis of the cell of $K_4Nb_2Se_{11}O$. Additionally, EDAX investigations performed on selected single crystals yielded $K_{3.87}Nb_{2.11}Se_{10.21}$ as the approximate composition, which is in good agreement with the composition derived from the crystallographic structure determination. $K_4Nb_2Se_{11}O$ is stable to dry air for a long time. Under humid conditions it slowly decomposes.

It must be noted that using fresh Nb led to the oxygen-free product $K_{12}Nb_6Se_{35}$ (see Discussion).

The preparation of $K_4Nb_2Se_{11}O$ can also be achieved by using NbO as educt. The reaction of K_2Se_3, NbO, and Se in a 2/1/4 molar ratio at 350 °C using the preparation procedure described above resulted in $K_4Nb_2Se_{11}O$ together with potassium oxoniobates as byproducts. The yield of $K_4Nb_2Se_{11}O$ was approximately 30% based on Nb. For all spectroscopic measurements manually selected single crystals were used.

$Cs_4Nb_2Se_{11}O$. For the preparation of the cesium compound the procedure described for $K_4Nb_2Se_{11}O$ was applied. As in the case of $K_4Nb_2Se_{11}O$, it was first obtained accidentally with old Nb as educt (see above), but it can also be prepared from the reaction of a mixture of Cs_2Se_3, NbO, and Se (2/1/5 molar ratio). The educts were heated in an evacuated Pyrex glass ampule at 350 °C for 6 days and then cooled to room temperature with 3 °C/h. The product was isolated by washing the resulting black melt with DMF and ether. The residue consisted of black multifaced crystals of $Cs_4Nb_2Se_{11}O$ together with selenium and cesium oxoniobates as byproducts. The yield was approximately 20%.

The X-ray powder pattern of manually selected crystals could successfully be indexed on the basis of the cell of $Cs_4Nb_2Se_{11}O$. EDAX analysis on selected single crystals yielded $Cs_{4.1}Nb_{2.04}Se_{10.15}$ as an approximate composition. $Cs_4Nb_2Se_{11}O$ is stable under dry conditions for a long period but decomposes slowly when exposed to humid air.

Precaution must be taken during the preparation of Cs_2Se_3 because Cs and Se may already react vigorously in the solid state. The Cs should be dissolved in liquid NH_3 first and then the Se should be added in small portions.

Physical Measurements. *Infrared/Raman Spectroscopy.* An 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 both compounds were prepared as KBr pellets. far-IR was recorded between 80 and 550 cm^{-1} (resolution = 2 cm^{-1}) on a ISF-66 device (Bruker) with $K_4Nb_2Se_{11}O$ and $Cs_4Nb_2Se_{11}O$ 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). $K_4Nb_2Se_{11}O$ and $Cs_4Nb_2Se_{11}O$ were ground and prepared on Al sample holders. The measuring range was -1000 to 3500 cm^{-1} with a resolution of 2 cm^{-1}.

UV/Vis/NIR Diffuse Reflectance. UV/vis/NIR diffuse reflectance spectra were recorded on a Cary 5 spectrometer (Varian Techtron Pty.). The spectrometer was equipped with a Ulbricht sphere (Diffuse reflectance accessory; Varian Techtron Pty.). The inner wall of the Ulbricht sphere (diameter = 110 mm) was covered with a PTFE layer of 4 mm thickness. A PbS detector (NIR) and a photomultiplier (UV/vis) were attached to the Ulbricht sphere.

The samples were ground together with $BaSO_4$ and prepared as a flat specimen of approximate 2 mm thickness. Resolution was 1 nm for the UV/vis range and 2 nm for the NIR range. The measuring range was 250−2000 nm. $BaSO_4$ was used as standard for 100% reflectance. Absorption data were calculated from the reflectance data using the Kubelka−

Table 1. Crystallographic Data for K₄Nb₂Se₁₁O and Cs₄Nb₂Se₁₁O

	$K_4Nb_2Se_{11}O$	$Cs_4Nb_2Se_{11}O$
crystal size (mm³)	0.06 × 0.08 × 0.2	0.2 × 0.2 × 0.1
a (Å)	15.946(4)	12.023(4)
b (Å)	13.872(3)	14.367(4)
c (Å)	18.622(4)	14.571(4)
α (deg)		76.90(2)
ss (deg)		78.43(2)
γ (deg)		71.89(2)
volume (Å³)	4119(2)	2307(1)
crystal system	orthorhombic	triclinic
space group	$Pbca$ (No. 61)	$P-1$ (No. 2)
Z	8	4
MW	1226.78	1602.02
μ (mm⁻¹)	21.344	24.558
(g/cm³)	3.956	4.613
2Θ (deg)	5−55	3−55
index ranges	−1 < h < 20	0 < h < 15
	0 < k < 18	−17 < k < 18
	−24 < l < 0	−18 < l < 18
reflections collected	5077	11232
unique data	4714	10542
unique data ($I > 2.0\sigma(I)$)	3723	7563
min./max. transmission	0.18045/0.31347	0.038/0.088
R_{int} (%)	4.77	7.31
k^a	no extinction corr	0.01391(2)
x^a		0.00018(3)
y^b	0.0390	0.0518
z^b	56.39	21.01
parameters refined	163	326
R_1 ($I > 2\sigma I$) (%)^c	4.10	4.11
wR_2 (all data) (%)^d	15.47	10.75
R_1 (all data) (%)	7.24	7.70
GOOF	1.600	1.015
difference peaks (e Å⁻³)	1.58/−1.39	2.90/−1.83

^{a} Extinction correction: $F^* = F_c k(1 + 0.001 x F_c^2 \lambda^3/\sin 2\Theta)^{-1/4}$; k = OSF. ^{b} Weighting scheme: $w^{-1} = \sigma^2(F_o^2) + (yP)^2 + zP$, $P = [\max. (0 \text{ or } F_o^2) + 2F_c^2]/3$ $^c R_1 = \Sigma[||F_o| - |F_c||/\Sigma|F_o|]$. $^d wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Munk function.[26] 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 a $(F(R))^2$ plot.

Single-Crystal X-ray Diffraction. Single-crystal X-ray investigations were performed on a STOE AED II diffractometer (=0.7107 Å, graphite monochromator). The intensities were reduced to F_o. Lorentz and polarization corrections as well as an empirical absorption correction using φ scan data for Cs₄Nb₂Se₁₁O and a numerical absorption correction (indexed faces) in the case of K₄Nb₂Se₁₁O were applied. 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 93 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.

Results and Discussion

The structures of both compounds are based on Nb₂-Se₁₀O building blocks. To make the structural discussion easier, we first want to give a general description of the Nb₂Q₁₁ unit. Because the differences between Nb₂Q₁₁ units in different compounds are only evident in the pentagonal planes, we introduce a simplified projection of the Nb₂Q₁₁ unit onto two dimensions. This projection should serve as a pictorial aid for a better distinction between different types of bipyramids. Every Nb₂Q₁₁ unit is composed of *two* face-sharing pen-

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Table 2. Atomic Coordinates (10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for K₄Nb₂Se₁₁O and Cs₄Nb₂Se₁₁O

atom	x	y	z	$U_{eq}a$
	$K_4Nb_2Se_{11}O$			
Nb(1)	1248(1)	757(1)	1284(1)	20(1)
Nb(2)	1712(1)	1062(1)	3239(1)	20(1)
Se(1)	940(1)	−648(1)	627(1)	42(1)
Se(2)	1481(1)	2037(1)	269(1)	28(1)
Se(3)	−135(1)	1697(1)	1452(1)	27(1)
Se(4)	186(1)	531(1)	2342(1)	24(1)
Se(5)	2836(1)	961(1)	1083(1)	33(1)
Se(6)	2266(1)	−126(1)	2230(1)	29(1)
Se(7)	1437(1)	−787(1)	3279(1)	35(1)
Se(8)	1963(1)	2267(1)	2188(1)	24(1)
Se(9)	1105(1)	2780(1)	3162(1)	29(1)
Se(10)	679(1)	781(1)	4344(1)	31(1)
Se(11)	207(1)	2285(1)	4774(1)	33(1)
O	2666(4)	1196(5)	3742(4)	32(2)
K(1)	842(2)	4066(2)	1248(2)	44(1)
K(2)	944(2)	−2371(2)	1950(1)	43(1)
K(3)	3245(2)	2451(2)	−464(1)	40(1)
K(4)	1291(2)	240(2)	−969(1)	41(1)
	$Cs_4Nb_2Se_{11}O$			
Nb(1)	2058(1)	6534(1)	5067(1)	24(1)
Nb(2)	640(1)	7667(1)	2874(1)	24(1)
Nb(3)	2630(1)	13435(1)	−43(1)	20(1)
Nb(4)	4714(1)	12298(1)	1838(1)	23(1)
Se(1)	1635(1)	6802(1)	6649(1)	36(1)
Se(2)	3404(1)	4701(1)	5320(1)	40(1)
Se(3)	1400(1)	4922(1)	5257(1)	36(1)
Se(4)	3989(1)	7034(1)	4315(1)	34(1)
Se(5)	2181(1)	8237(1)	4032(1)	28(1)
Se(6)	−195(1)	7289(1)	4710(1)	27(1)
Se(7)	−611(1)	9063(1)	3810(1)	37(1)
Se(8)	2066(1)	5910(1)	3281(1)	28(1)
Se(9)	2659(1)	6933(1)	1865(1)	39(1)
Se(10)	1024(1)	9214(1)	1614(1)	35(1)
Se(11)	−615(1)	10518(1)	2074(1)	47(1)
Se(12)	2850(1)	13088(1)	−1584(1)	34(1)
Se(13)	962(1)	15135(1)	−172(1)	26(1)
Se(14)	1001(1)	12726(1)	1020(1)	29(1)
Se(15)	2968(1)	11654(1)	977(1)	26(1)
Se(16)	3751(1)	14764(1)	−300(1)	32(1)
Se(17)	4929(1)	13057(1)	−18(1)	28(1)
Se(18)	3038(1)	13944(1)	1790(1)	29(1)
Se(19)	3048(1)	12763(1)	3227(1)	43(1)
Se(20)	5818(1)	10937(1)	823(1)	36(1)
Se(21)	5162(1)	10434(1)	2777(1)	47(1)
Se(22)	4244(1)	10405(1)	4522(1)	58(1)
O(1)	−458(6)	7402(6)	2363(5)	32(2)
O(2)	5905(7)	12678(5)	2086(5)	32(2)
Cs(1)	4238(1)	8806(1)	1699(1)	38(1)
Cs(2)	3096(1)	8632(1)	6159(1)	39(1)
Cs(3)	8529(1)	9001(1)	687(1)	39(1)
Cs(4)	2009(1)	7357(1)	−555(1)	45(1)
Cs(5)	1226(1)	11064(1)	3419(1)	45(1)
Cs(6)	7014(1)	7807(1)	3843(1)	45(1)
Cs(7)	−84(1)	15127(1)	2310(1)	40(1)
Cs(8)	5239(1)	14731(1)	2839(1)	49(1)

^{a} The equivalent isotropic displacement parameter U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

tagonal NbQ₇ bipyramids. One axial bond in each bipyramid is short and resembles a Nb=Q double bond; the axial counterbond is long, representing only weak interactions. The two axial chalcogen atoms with the long Nb−Q bonds are bridging atoms and do *always* belong to a Se₂²⁻ anion η^2 bound to the second Nb center. The third bridging Se atom lies within the pentagonal plane and has "normal" bonds (about 2.6 Å) to both Nb centers. For a projection, the two long bonds were disregarded and the two pentagonal planes were opened to planarity. This results in a view onto two corner-sharing pentagonal planes where the axial posi-

Table 3. Selected Interatomic Bond Distances (Å) and Angles (deg) in $K_4Nb_2Se_{11}O$ and $Cs_4Nb_2Se_{11}O$

	$K_4Nb_2Se_{11}O$		
Nb(1)−Se(1)	2.353(2)	Nb(1)−Se(5)	2.574(2)
Nb(1)−Se(3)	2.582(2)	Nb(1)−Se(4)	2.618(2)
Nb(1)−Se(2)	2.619(2)	Nb(1)−Se(6)	2.690(2)
Nb(1)−Se(8)	2.918(2)	Nb(2)−O	1.796(7)
Nb(2)−Se(9)	2.577(2)	Nb(2)−Se(7)	2.603(2)
Nb(2)−Se(8)	2.605(2)	Nb(2)−Se(6)	2.651(2)
Nb(2)−Se(10)	2.664(2)	Nb(2)−Se(4)	3.043(2)
Se(2)−Se(11)e	2.421(2)	Se(3)−Se(4)	2.373(2)
Se(5)−Se(6)	2.768(2)	Se(6)−Se(7)	2.530(2)
Se(8)−Se(9)	2.380(2)	Se(10)−Se(11)	2.358(2)
Se(11)−Se(2)b	2.421(2)	Nb(1)−Nb(2)	3.739(3)
⟨K(1)−Se⟩ (CN10)	3.58(12)	⟨K(2)−Se⟩ (CN9)	3.51(18)
⟨K(3)−Se⟩ (CN6)	3.41(16)	⟨K(4)−Se⟩ (CN6)	3.43(19)
K(3)−O	2.561(8)	K(4)−O	2.650(7)
Se(7)−Se(6)−Se(5)	164.70(5)	Se(10)−Se(11)−Se(2)b	101.82(5)

	$Cs_4Nb_2Se_{11}O$		
Nb(1)−Se(1)	2.352(2)	Nb(1)−Se(5)	2.596(2)
Nb(1)−Se(4)	2.602(2)	Nb(1)−Se(3)	2.612(2)
Nb(1)−Se(2)	2.615(2)	Nb(1)−Se(6)	2.695(2)
Nb(1)−Se(8)	2.935(2)	Nb(2)−O(1)	1.811(7)
Nb(2)−Se(7)	2.585(2)	Nb(2)−Se(8)	2.589(2)
Nb(2)−Se(9)	2.616(2)	Nb(2)−Se(10)	2.640(2)
Nb(2)−Se(6)	2.658(2)	Nb(2)−Se(5)	3.125(2)
Nb(3)−Se(12)	2.356(2)	Nb(3)−Se(14)	2.565(2)
Nb(3)−Se(16)	2.585(2)	Nb(3)−Se(15)	2.605(2)
Nb(3)−Se(13)	2.631(2)	Nb(3)−Se(17)	2.653(2)
Nb(3)−Se(18)	3.088(2)	Nb(4)−O(2)	1.806(8)
Nb(4)−Se(18)	2.584(2)	Nb(4)−Se(20)	2.585(2)
Nb(4)−Se(19)	2.590(2)	Nb(4)−Se(21)	2.659(2)
Nb(4)−Se(17)	2.670(2)	Nb(4)−Se(15)	3.103(2)
Se(2)−Se(3)	2.347(2)	Se(4)−Se(5)	2.363(2)
Se(6)−Se(7)	2.534(2)	Se(8)−Se(9)	2.369(2)
Se(10)−Se(11)	2.364(2)	Se(13)−Se(13)k	2.401(2)
Se(14)−Se(15)	2.385(2)	Se(16)−Se(17)	2.411(2)
Se(18)−Se(19)	2.377(2)	Se(20)−Se(21)	2.788(2)
Se(21)−Se(22)	2.557(2)	Se(22)−Se(22)b	2.359(3)
Se(7)−Se(11)	2.893(2)		
Nb(1)−Nb(2)	3.723(3)	Nb(3)−Nb(4)	3.827(3)
⟨Cs(1)−Se⟩ (CN10)	3.80(15)	⟨Cs(2)−Se⟩ (CN8)	3.62(11)
⟨Cs(3)−Se⟩ (CN7)	3.71(7)	⟨Cs(4)−Se⟩ (CN7)	3.73(17)
⟨Cs(5)−Se⟩ (CN10)	3.82(14)	⟨Cs(6)−Se⟩ (CN8)	3.79(12)
⟨Cs(7)−Se⟩ (CN8)	3.69(18)	⟨Cs(8)−Se⟩ (CN8)	3.82(14)
Cs(2)−O(2)	3.027(7)	Cs(3)−O(1)	3.104(7)
Cs(4)−O(2)	2.999(8)	Cs(6)−O(1)	3.327(7)
Cs(7)−O(1)	3.175(8)	Cs(8)−O(2)	3.192(7)
Se(22)−Se(21)-Se(20)	166.19(7)	Se(22)b-Se(22)−Se(21)	108.3(1)
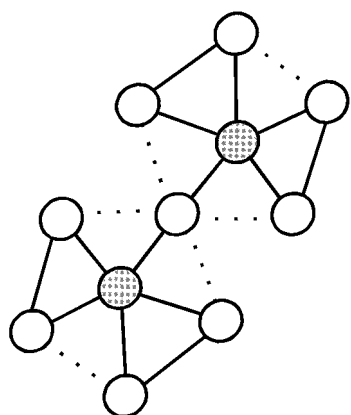
Figure 1. Projection of a Nb_2Q_{11} unit onto two dimensions.[4a] (Only continuous lines resemble bonds.)

tions are not visible (Figure 1). In the following, only the pentagonal planes and their differences will be discussed.

$K_4Nb_2Se_{11}O$. The crystal structure of $K_4Nb_2Se_{11}O$ is composed of $_\infty^1[Nb_2Se_{11}O]^{4-}$ anionic chains running along the *c*-axis which are well-separated by the K^+ cations. The main structural motive of the chains is a
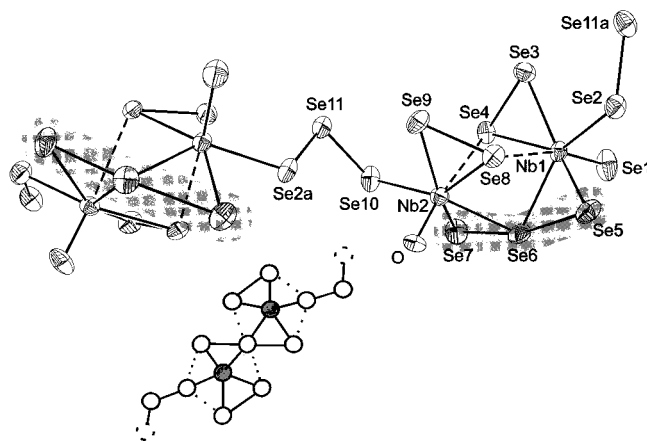
Figure 2. Two $Nb_2Se_{10}O$ units interconnected by a Se_3^{2-} anion as a part of the infinite $_\infty^1[Nb_2Se_{11}O]^{4-}$ chains in $K_4Nb_2Se_{11}O$. The Se_3^{4-} anion is highlighted (see Discussion). Probability ellipsoids are drawn at the 70% level.
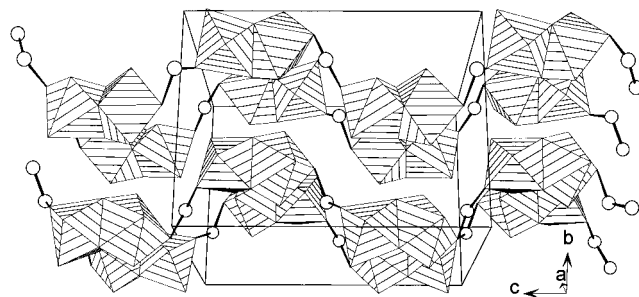
Figure 3. View of the unit cell of $K_4Nb_2Se_{11}O$ with infinite anionic $_\infty^1[Nb_2Se_{11}O]^{4-}$ chains. The Nb_2Q_{11} units are represented as polyhedra. Open circles are selenium (cations are omitted for clarity).

$Nb_2Se_{10}O$ unit (Figure 2). In one bipyramid the terminal position is occupied by an O atom. The pentagonal planes of both bipyramids are composed of one Se_2 group showing a $\mu\text{-}\eta^2,\eta^1$ coordination mode, two Se atoms of a $\mu\text{-}\eta^2, \eta^2$ bridging Se_3 fragment, and one Se atom of a terminally bound Se_3^{2-} polyselenide anion. These Se_3^{2-} anions interconnect the $Nb_2Se_{10}O$ building blocks, giving rise to infinite $_\infty^1[Nb_2Se_{11}O]^{4-}$ chains (Figure 3). Taking this coordination into account the chains may be described as $_\infty^1[(Nb_2(\mu\text{-}\eta^2,\eta^2\text{-}Se_3)(\mu\text{-}\eta^2,\eta^1\text{-}Se_2)_2(Se)_2)(\mu\text{-}\eta^1,\eta^1\text{-}Se_3)]^{4-}$.

The $_\infty^1[Nb_2Se_{11}O]^{4-}$ chains are not linear but corrugated. They are arranged in layers parallel to the (120) plane (Figure 3).

The Nb−Se distances range from 2.353(2) to 3.043(2) Å and can be divided into three groups. One short axial bond [Nb(1)−Se(1)] and two very long axial bonds being trans to the short Nb=Se bond and trans to the Nb=O bond [Nb(1)−Se(8) and Nb(2)−Se(4)] and medium distances of about 2.6 Å (see Table 3). The Nb−O distance amounts to 1.796(7) Å and can be regarded as a Nb=O double bond. This distance is significantly shorter than the sum of the ionic radii of Nb(V) in 7-fold coordination (0.69 Å) and O(−II) (1.35 Å)[27] and it is only slightly longer than the Nb=O distances in $R_4[(Nb(O)(Se_2)_2)_2\text{-}Se_4]$ and $R_4[(Nb(Se)_3)_2)O]$ (with R = Ph_4P^+, Et_4N^+),[25] which are 1.67 (1) and 1.68 (2) Å, respectively. In NbO and NbO_2, the reported bond lengths are about 2.105
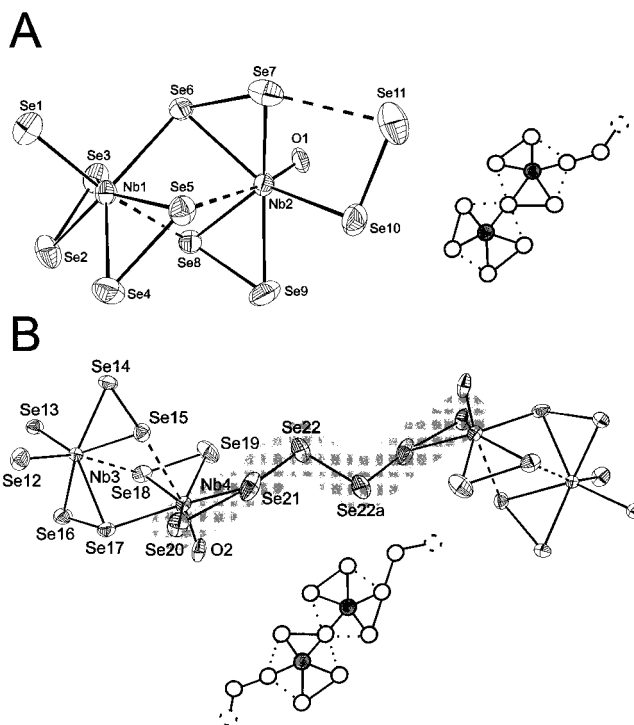
(27) Shannon, R. D. *Acta Crystallogr. Sect. A* **1976**, *32*, 751.

and 2.046 Å, respectively, with niobium being in a quadratic planar environment. The average tetrahedral Nb−O distance in Nb_2O_5 is 1.725 Å.[28a] We note that Nb−O distances scatter over a wide range, even for NbO_6 octahedra (e.g. 1.751−2.554 Å in $Nb_{12}O_{29}$,[28b] 1.635−2.331 Å in $NaNbO_3$,[28c] 1.867−2.107 Å in Rb_4-$Nb_{11}O_{30}$[28d]) and NbO_7 pentagonal bipyramidal coordination (e.g. 1.896−2.435 Å and 1.761−2.161 Å in La-Nb_5O_{14}[28e]).

The potassium cations are coordinated by 7 to 10 chalcogen atoms in irregular environments. The mean K−Se and the K−O distances are given in Table 3. Coordination numbers are given in parentheses. These values correspond very well to the sum of the ionic radii (K, 1.51 Å (CN = 8); Se, 1.98 Å).[27]

The Se−Se distances within the Se_2 dumbbells and within the Se_3 units interconnecting the $Nb_2Se_{10}O$ fragments are typical for Se−Se single bonds (2.36−2.39 Å). Both Nb atoms are not exactly located within the pentagonal plane but are shifted 0.52 Å [Nb(1)] and 0.51 Å [Nb(2)] toward the short axial bond. The shortest Se−Se intrachain contact amounts to 3.032(3) Å [Se(2)−Se(5)], and the shortest interchain distance is 3.482(3) Å [Se(1)−Se(11)], both being shorter than the sum of the van der Waals radii of selenium.

One remarkable feature of the structure is the μ-η^2,η^2-coordinating Se_3 fragment [Se(5)−Se(6)−Se(7)] within the bipyramids. It exhibits two relatively long Se−Se distances of 2.530(2) and 2.768(2) Å (Figure 2). These distances are significantly longer than a single bond of 2.38 Å, as found in the Se_3^{2-} anion of A_2Se_3 (A = K, Rb, Cs)[29] or other Se_3 fragments such as in K_3AuSe_{13}.[30] The angle between the three Se atoms is 164.70(5)°. In other polyselenides Se−Se−Se angles adopt values near the tetrahedral angle. Assuming a formal oxidation state of +5 for niobium, the charge on the Se_3 polyselenide anion must be −4. There are several arguments which support this assignment. First we note that the Nb−Nb distance in $K_4Nb_2Se_{11}O$ of 3.739(3) Å is much longer than Nb−Nb bond lengths of about 2.8 Å found in compounds with Nb(IV) (d[1]), which is known to undergo metal metal bonding. Such a Nb−Nb bond formation is found in $Nb_2Y_2X_6$ (Y=Se,Te; X=Br,I),[31] KNb_2PS_{10}[32] or Nb_2Se_9.[33] Another argument is the angle of 164.7° close to linearity. This geometry is known from analogous Te anions such as in $NaTe$,[34] where a linear Te_3 unit is found as part of a Z-shaped Te_5^{4-} anion. 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 three σ orbitals, one bonding (σ), one

(28) (a) Gatehouse, B. M.; Wadsley, A. D. *Acta Crystallogr.* **1964**, *17*, 1545. (b) Norin, R. *Acta Chem. Scand.* **1966**, *20*, 871. (c) von der Muehl, R.; Sadel, A.; Hagenmueller, P. *J. Solid State Chem.* **1984**, *51*, 176. (d) Dewan, J. C.; Edwards, A. J.; Jones, G. R. *J. Chem. Soc., Dalton Trans.* **1978**, *1978*, 968. (e) Hofmann, R.; Gruehn, R. *Z. Anorg. Allg. Chem.* **1990**, *590*, 81.
(29) (a) Böttcher, P. *Z. Anorg. Allg. Chem.* **1977**, *432*, 167. (b) Böttcher, P. *Z. Anorg. Allg. Chem.* **1980**, *461*, 13.
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(31) Franzen, H. F.; Hönle, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1983**, *497*, 13.
(32) Do, J., Yun, H. *Inorg. Chem.* **1996**, *35*, 3729.
(33) (a) Meerschaut, A.; Guemas, L.; Berger, R.; Rouxel, J. *Acta Crystallogr.* **1979**, *B35*, 1747; (b) Sunshine., S.A.; Ibers, J. A. *Acta Crystallogr.* **1987**, *C43*, 1019.
(34) Böttcher, P. *J. Less Common Met.* **1985**, *109*, 311.

Figure 4. (A) The $[Nb_2Se_{11}O]^{4-}$ anion in $Cs_4Nb_2Se_{11}O$. (B) Two $Nb_2Se_{10}O$ units connected via a Se_6^{6-} anion (highlighted) as part of an infinite anionic $_\infty^1[Nb_2Se_{11}O]^{4-}$ chain in Cs_4Nb_2-$Se_{11}O$. Probability ellipsoids are drawn at the 70% level.

nonbonding (n), and one antibonding (σ^*). The σ as well as the n orbital should be able to accommodate two electrons each. As a result, the Se_3 can accommodate four negative charges. A similar unusual anionic fragment will be encountered below in $Cs_4Nb_2Se_{11}O$.

Interestingly, the configuration of the $Nb_2Se_{10}O$ bipyramids is nearly identical to the configuration of the analogous Nb_2Se_{11} unit in $A_{12}Nb_6Se_{35}$.[5] The different crystal structures arise from the connection of the Nb_2Q_{11} units with Se_n^{2-} anions (n = 2, 3). In the title compound, it is an n = 3−3−3 connection scheme, whereas n = 3−3−2 is observed in $A_{12}Nb_6Se_{35}$, leading to the remarkable long repeating distance of about 56 Å. The total number of atoms in the unit cell of K_4Nb_2-$Se_{11}O$ amounts to 144 and to 212 in $K_{12}Nb_6Se_{35}$, which is a ratio of about 2/3. The unit cell volumes of the two compounds V = 4119 and 6281 Å[3] show roughly the same ratio, demonstrating the strong relationship between these two structures. At the moment, it is difficult to give an explanation why the substitution of one Se by O leads to the different connection modes of the Nb_2Q_{11} units.

$Cs_4Nb_2Se_{11}O$. The structure of $Cs_4Nb_2Se_{11}O$ is again based on expanded and interconnected $Nb_2Se_{10}O$ units and resembles a framework of alternating complex $[Nb_2Se_{11}O]^{4-}$ anions and infinite anionic $_\infty^1[Nb_2Se_{11}O]^{4-}$ chains. These two structural motifs will be first discussed separately and then combined to create the entire structure. It should be mentioned here that in each Nb_2Q_{11} unit only *one* selenium is substituted by an oxygen atom.

Within the molecular $[Nb_2Se_{11}O]^{4-}$ anions (Figure 4a) the pentagonal plane of the oxygen-free bipyramid contains two η^2-Se_2^{2-} anions (one bridging) and one Se atom from a neighboring μ-η^2,η^1-Se_2^{2-} anion. The

second bipyramid with the axial Nb=O bond shows a pentagonal plane of two $\mu\text{-}\eta^2,\eta^1\text{-Se}_2{}^{2-}$ anions and a fifth Se atom of a terminal bound $\text{Se}_2{}^{2-}$ anion. The complete anion can be described as $[\text{Nb}_2(\mu\text{-}\eta^2,\eta^1\text{-Se}_2)_3(\eta^2\text{-Se}_2)(\text{Se})(\text{O})(\eta^1\text{-Se}_2)]^{4-}$. The end-on $\text{Se}_2{}^{2-}$ anion is directed toward another Se_2 dumbbell so that Se(11) is coming close to Se(7). This results in a short Se(7)–Se(11) distance of 2.893(3) Å, which is significantly shorter than the sum of the van der Waals radii and should be considered as a weak bonding interaction. This assumption is further supported by the weakened Se(6)–Se(7) bond, which is enlarged to 2.534(2) Å. Another unexpected short intramolecular distance of only 2.979-(2) Å is observed between Se(8) and Se(3). In this case the intramolecular Se–Se interaction does not affect the Se–Se bond strengths within the $\text{Se}_2{}^{2-}$ anions, as is evidenced by the Se(2)–Se(3) and Se(8)–Se(9) distances of 2.347(2) and 2.369(2) Å, respectively.

The other Se–Se ($\langle\text{Se–Se}\rangle = 2.36$ Å), axial Nb=Se (2.352(2) Å), and equatorial Nb–Se distances ($\langle\text{Nb–Se}\rangle = 2.62(3)$ Å) are in normal ranges found in related compounds. The Nb–O bond length amounts to 1.811-(7) Å and as discussed above should be treated as a Nb=O double bond. The two long axial Nb–Se separations of 2.935(2) and 3.125(2) Å represent only weak bonding interactions.

The $\text{Nb}_2\text{Se}_{10}\text{O}$ units of the $^1_\infty[\text{Nb}_2\text{Se}_{11}\text{O}]^{4-}$ chains reveal a different configuration (Figure 4b). In the oxygen-free bipyramid, the pentagonal plane accommodates a $\mu\text{-}\eta^2,\eta^1\text{-Se}_2{}^{2-}$ and an $\eta^2\text{-Se}_2{}^{2-}$ anion together with a Se atom of a terminal $\mu\text{-}\eta^1,\eta^1\text{-Se}_2{}^{2-}$ dumbbell which is connected to another Nb_2Q_{11} unit. In the other pentagonal plane, a $\mu\text{-}\eta^2,\eta^1\text{-Se}_2{}^{2-}$ dumbbell, one atom of a bridging $\mu\text{-}\eta^2,\eta^1\text{-Se}_2{}^{2-}$ unit, and two Se atoms of an η^2-bound Se_6 fragment are found. It must be noted that the configuration found here is very similar to that in $\text{K}_3\text{CuNb}_2\text{Se}_{12}$.[35] The Se_6 chain is certainly a very fascinating feature of the structure. The inner Se–Se distance of 2.360(3) Å is typical for a Se–Se single bond. The outer two bond lengths [Se(20)–Se(21) and Se(21)–Se(22)] are significantly enlarged [2.788(2) and 2.557-(2) Å]. The larger distance is found between the two Se atoms which coordinate to the Nb center. The reason for this enlargement might be the proximity of the oxygen, which draws electron density from the Se–Se bond and therefore weakens it. Additionally, the angle between the three outer Se atoms is 166.20(7)°, whereas the angle around Se(22) is near the tetrahedral angle [108.3(1)°]. The observation of two enlarged Se–Se bonds combined with an angle close to linearity is also made in $\text{A}_{12}\text{Nb}_6\text{Se}_{35}$ ($\text{Se}_3{}^{4-}$ anion), $\text{K}_3\text{CuNb}_2\text{Se}_{12}$ ($\text{Se}_4{}^{4-}$ anion), Nb_2Se_9 ($\text{Se}_5{}^{4-}$ anion),[33] and $\text{K}_4\text{Nb}_2\text{Se}_{11}\text{O}$ ($\text{Se}_3{}^{4-}$ anion; see above). Assuming a charge of +5 for Nb (see Discussion for $\text{K}_4\text{Nb}_2\text{Se}_{11}\text{O}$), the Se_6 fragment should contain six negative charges. Until now, no example for such a Se polyanion fragment has been observed. The $\text{Se}_6{}^{6-}$ anion is also bridging to another $\text{Nb}_2\text{Se}_{10}\text{O}$ unit. The adequate description for the chain should therefore be $^1_\infty[((\text{Nb}_2)(\mu\text{-}\eta^2,\eta^1\text{-Se}_2)_3(\text{Se})(\text{O}))_2(\mu\text{-}\eta^2,\eta^2\text{-Se}_6)(\mu\text{-}\eta^1,\eta^1\text{-Se}_2)]^{4-}$.

The $^1_\infty[\text{Nb}_2\text{Se}_{11}\text{O}]^{4-}$ chains are corrugated and lie within the (212) plane. Between the chains the complex

(35) Lu, Y.-J.; Ibers, J. A. *Inorg. Chem.* **1991**, *30*, 3317.
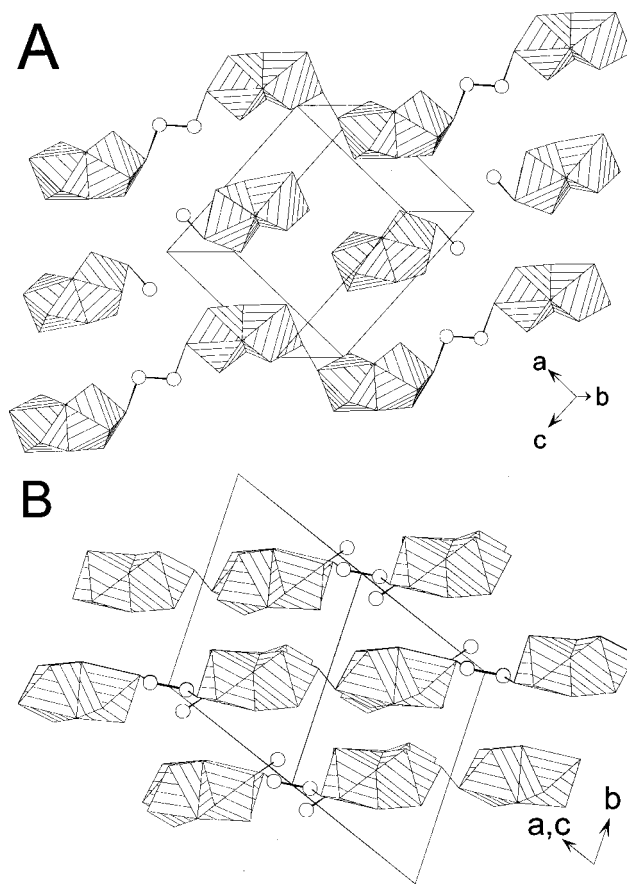
Figure 5. Coexistence of $[\text{Nb}_2\text{Se}_{11}\text{O}]^{4-}$ anions and infinite anionic $^1_\infty[\text{Nb}_2\text{Se}_{11}\text{O}]^{4-}$ chains in $\text{Cs}_4\text{Nb}_2\text{Se}_{11}\text{O}$. The Nb_2Q_{11} units are represented as polyhedra. Open circles are selenium. (A) View on the (212) plane. (B) View perpendicular to the (212) plane (cations are omitted for clarity).

$[\text{Nb}_2\text{Se}_{11}\text{O}]^{4-}$ anions are situated in a fashion so that one terminal $\text{Se}_2{}^{2-}$ anion is directed toward the same anion of the next $[\text{Nb}_2\text{Se}_{11}\text{O}]^{4-}$ anion (Figure 5).

The shortest Se–Se distance between the isolated anion and the chain is 3.540 Å (Se(9)–Se(17)). The shortest distance between two adjacent chains in different layers amounts to 4.070 Å [Se(16)–Se(17)]. The other bonding Se–Se ($\langle\text{Se–Se}\rangle = 2.38$ Å), axial Nb=Se = 2.356(2) Å) and equatorial Nb–Se distances ($\langle\text{Nb–Se}\rangle = 2.63(3)$ Å) are in normal ranges. The Nb=O bond is 1.806(8) Å and the two long axial Nb–Se separations are 3.088(2) and 3.103(2) Å, respectively. All four Nb centers are shifted out of the pentagonal plane toward the short axial bond (Nb(1), 0.52 Å; Nb(2), 0.54 Å; Nb(3), 0.54 Å; Nb(4), 0.50 Å)

The cesium cations are coordinated by 8–10 chalcogen atoms in irregular environments. The mean Cs–Se and the Cs–O distances are given in Table 3 (coordination numbers are given in parentheses) and are just the sum of the ionic radii.

$\text{K}_4\text{Nb}_2\text{Se}_{11}\text{O}$ and $\text{Cs}_4\text{Nb}_2\text{Se}_{11}\text{O}$ are good examples for demonstrating an effect which was discussed in ref 25. It was argued that the strength of the axial M=Q bond determines the tendency to undergo axial bonding trans to this M=Q bond and hence the stability of a pentagonal bipyramidal environment. In the title compounds two types of axial bonds are found, i.e., Nb=O and Nb=Se. The Nb=O distances lie between 1.796 and 1.811 Å. The related trans Nb–Se bonds range from 3.043

Two Novel Niobium Oxo-Selenides

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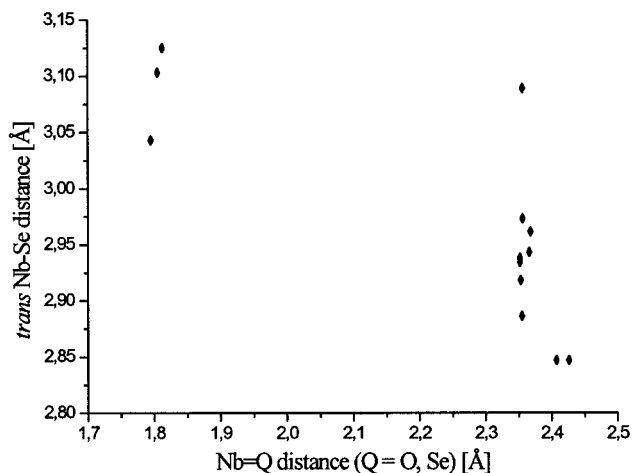
Figure 6. Correlation of axial Nb=Q distances (Q = O, Se) with trans axial Nb−Se distances in compounds exhibiting pentagonal bipyramidal Se environment for Nb.

to 3.125 Å. The Nb=Se bonds between 2.352 and 2.356 Å have trans counterbonds in the range of 2.918−3.088 Å. By including data from the literature ($K_6Nb_4Se_{22}$, $Rb_{12}Nb_6Se_{35}$, $K_3CuNb_2Se_{12}$), an analysis of the bonding properties is possible (see Figure 6). It is obvious that short Nb=Q bonds result in long Nb−Se distances. We note that in the anions $[Nb(O)(Se_2)SeH]^{2-}$ and $[(Nb(O)-(Se_2)_2)_2Se_4]^{4-}$ with very short Nb=O distances of 1.68 Å, no trans Nb−Q bonds are formed.[25] The analysis gives a hint for a generalization of this "rule". But one must keep in mind that packing or electronic effects can have a strong influence on the bond lengths and the formation of the trans bonds. Additionally, the correlation discussed above is only reliable for one system, like, for example, Nb=Q (Q = O, S(hypothetical), Se)/Nb−Se.

One point must be stressed again: both compounds were first obtained accidently during the attempt to prepare ternary alkali niobium selenides. We used niobium powder which had been stored in a drybox (not completely oxygen free) for over 1 year. The synthesis

with fresh Nb resulted in the oxygen-free compound $K_{12}Nb_6Se_{35}$ (see above). By using NbO as the educt together with freshly prepared A_2Se_3 and Se, it is possible to reproduce the synthesis of $K_4Nb_2Se_{11}O$ and $Cs_4Nb_2Se_{11}O$.

It is surprising that in both compounds only one axial Se within the Nb_2Se_{11} unit is substituted by O. In all other anions with the M_2Q_{11} unit either none or both positions are substituted. An explanation for this observation cannot be given at this time. We are currently investigating the reactions in reactive fluxes and the role of the oxygen sources on product formation to get a better understanding of the reaction mechanisms involved. One goal is to find an oxygen source suitable for preparation of a doubly exchanged Nb_2Q_{11} unit.

In the two title compounds two different modes for an expansion of the Nb_2Q_{11} units in two directions were observed. In $K_4Nb_2Se_{11}O$, terminal-bound Se_3^{2-} anions act as links to other bipyramids, whereas in $Cs_4Nb_2Se_{11}O$, only one terminal-bound Se_2^{2-} anion together with an η^2-bound Se_6^{6-} anion helps connecting Nb_2Q_{11} units to chains. So far, no other connecting mode has been observed, but this does not exclude the existence other possible configurations. It would be of special interest to achieve a third or fourth coupling position within the pentagonal planes which could lead to new two or even three-dimensional frameworks all composed of interconnected Nb_2Q_{11} building blocks.

Spectroscopy. *$K_4Nb_2Se_{11}O$.* The MIR spectrum shows only one strong absorption at 879.72 cm^{-1}. It can can be assigned to the Nb=O bond present in the structure. The absorption is shifted significantly toward lower frequencies compared to values reported for similar complexes such as $[Nb(O)(Se_2)SeH]^{2-}$ (910 cm^{-1}) and $[(Nb(O)(Se_2)_2)_2Se_4]^{4-}$ (903 cm^{-1}). This shift to lower energies is in agreement with the elongated bond length caused by the trans Nb−Se bond, as discussed above. The absorptions in the far-IR are ν/cm^{-1} 316.1 (s), 307.6 (s), 294.7 (s), 247.1 (s), 235.6 (s). It is difficult to make
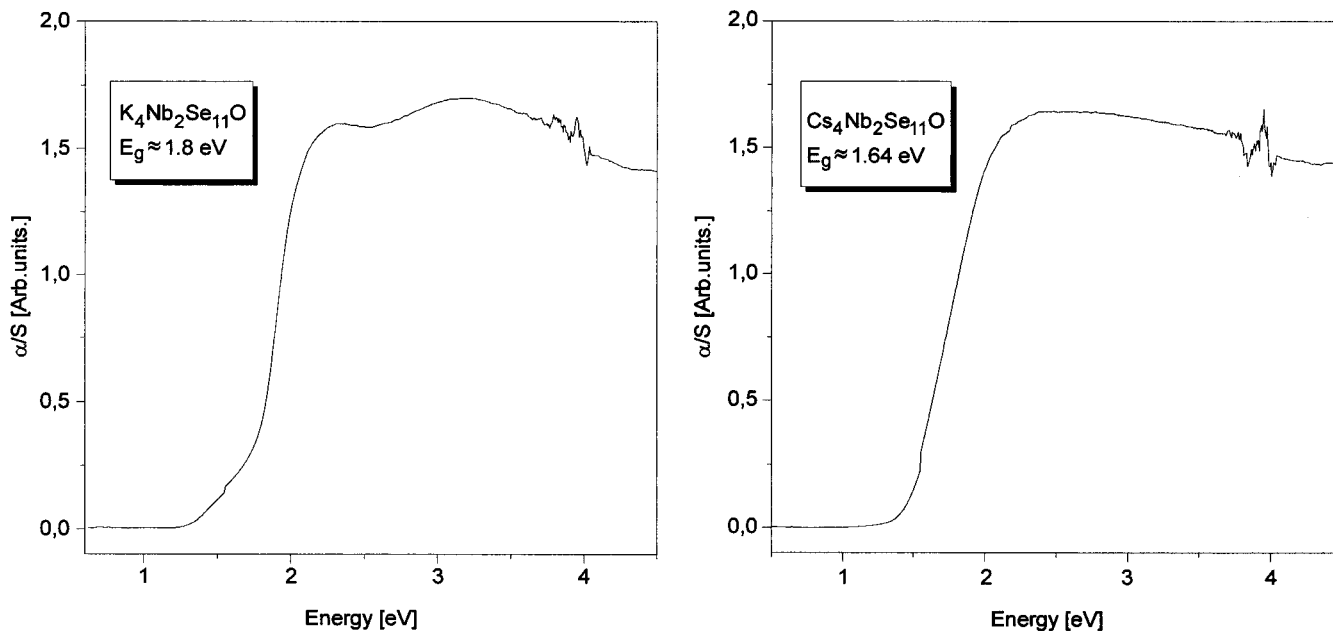
Figure 7. Diffuse reflectance spectra of $K_4Nb_2Se_{11}O$ and $Cs_4Nb_2Se_{11}O$. α is the absorption coefficient, S the scattering coefficient.

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assignments as Nb−Se and Se−Se frequencies are in the same range and a number of different groups are present in the structure. The Raman absorptions are ν/cm^{-1} 877.9 (w) (Nb=O), 320.3 (m), 296.5 (w), 263.6 (s), 236.8 (vs), 188.2 (m), 143.9 (m).

The diffuse reflectance spectrum shows a steep absorption edge (Figure 7). From the spectrum an optical band gap of approximately 1.8 eV was estimated. This value corresponds to the dark brown-black color of the material.

$Cs_4Nb_2Se_{11}O$. The MIR spectrum shows two strong absorptions at 865.88 and 853.35 cm^{-1} which can again be clearly assigned to the two distinct Nb=O bonds. The absorptions are shifted about 20 cm^{-1} toward lower frequencies compared to $K_4Nb_2Se_{11}O$, being in accordance with the slightly larger Nb=O bond lengths. The absorptions in the far-IR are ν/cm^{-1} 318.1 (vs), 301.9 (vs), 274.6 (s), 268.6 (s), 257.2 (m), 247.3 (s), 231.4 (m), 196.9 (m), 159.3 (w), 123.5 (m), 112.1 (m). No assignment was made due to the difficulties mentioned above. The Raman absorptions are ν/cm^{-1} 864.6 (w) and 852.2 (w) (Nb=O), 309.9 (m), 284.5 (s), 258.6 (vs), 243.7 (s), 235.0 (s), 184.6 (ms), 166.1 (ms), 153.2 (ms), 118.7 (s).

The diffuse reflectance spectrum of $Cs_4Nb_2Se_{11}O$ also shows a steep absorption edge. The corresponding optical band gap was estimated to 1.64 eV, which is shifted 0.16 eV toward lower energies compared to K_4-$Nb_2Se_{11}O$.

Supporting Information Available: Tables of X-ray diffraction structural data for $K_4Nb_2Se_{11}O$ and $Cs_8Nb_4Se_{22}O_2$ (7 pages); oberved and calculated structure factors for the novel compounds (34 pages). Ordering information is given on any current masthead page.

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