Cs$_6$Nb$_4$Se$_{22}$ and K$_{12}$Nb$_6$Se$_{35.3}$: two new compounds containing the M_4Q_{22} building block

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The title compounds, namely hexacaesium tetraniobium docosaselenide and dodecapotassium hexaniobium pentatriacontaselenide, were formed from their respective alkali chalcogenide reactive flux and niobium metal. Both compounds fall into the larger family of solid-state compounds that contain the M_2Q_{11} building block (M = Nb, Ta; Q = Se, S), where the metal chalcogenide forms dimers of face-shared pentagonal bipyramids. Cs$_6$Nb$_4$Se$_{22}$ contains two Nb$_2$Se$_{11}$ building blocks linked by an Se—Se bond to form isolated Nb$_4$Se$_{22}$ tetrameric building blocks surrounded by caesium ions. K$_{12}$Nb$_6$Se$_{35.3}$ contains similar Nb$_4$Se$_{22}$ tetramers that are linked by an Se—Se—Se unit to an Nb$_2$Se$_{11}$ dimer to form one-dimensional anionic chains surrounded by potassium ions. Further crystallographic studies of K$_{12}$Nb$_6$Se$_{35.3}$ demonstrate a new M_2Se$_{12}$ building block because of disorder between an Se^{2-} site (85%) and an (Se—Se)$^{2-}$ unit (15%). The subtle differences between the structures are discussed.

Comment

The title compounds fall into a range of interesting tantalum and niobium chalcogenide compounds. The M_2Q_{11} building block offers a wide range of connectivity for new compounds and is observed as a monomer in K$_4$Nb$_2$S$_{11}$ (Bensch & Duerichen, 1996*a*), as extended finite units in A_6Nb$_4$S$_{22}$ (A = Rb, Cs; Bensch & Duerichen, 1996*b*), K$_4$Nb$_2$S$_{14}$ (Bensch & Duerichen, 1997) and K$_6$Nb$_4$S$_{22}$ (Stoll *et al.*, 2002), and as infinite anionic chains in Rb$_{12}$Nb$_6$Se$_{35}$ (Duerichen *et al.*, 1998) and K$_{12}$Nb$_6$Se$_{35}$ (Bensch *et al.*, 1999; Duerichen, 1998). Our work demonstrates that the connectivity of the niobium polyhedra in these structures is subtle and can easily be overlooked. New compounds are yet to be discovered in this composition space, including the novel M_2Se$_{12}$ unit.

Cs$_6$Nb$_4$Se$_{22}$ forms seven-coordinate pentagonal bipyramids where each niobium is coordinated by one Se^{2-} atom and six Se$^-$ atoms. The Se$^-$ atoms form Se—Se bonds [from 2.348 (2)

to 2.386 (1) Å]. The two polyhedra are face-shared through three Se$^-$ atoms to form the M_2Q_{11} dimeric building block (Fig. 1*a*). The dimer then forms an isolated tetrameric building block M_4Q_{22} through an Se1—Se1^i bond [2.361 (1) Å; symmetry code: (i) $-x + 2$, $-y$, $-z + 1$] (Fig. 2). The Cs$^+$ ions surround the tetramer for charge balance. The structure is isotypic with $A_6M_4Q_{22}$ (A = K, Cs, Rb; M = Ta, Nb; Q = S, Se) structures and all have similar face-shared polyhedra through an Se$^-$ atom in an Se—Se pair (Bensch *et al.*, 1999). The subtle differences between the structures are the angles at which two dimers are linked (Bensch & Duerichen, 1996*b*).
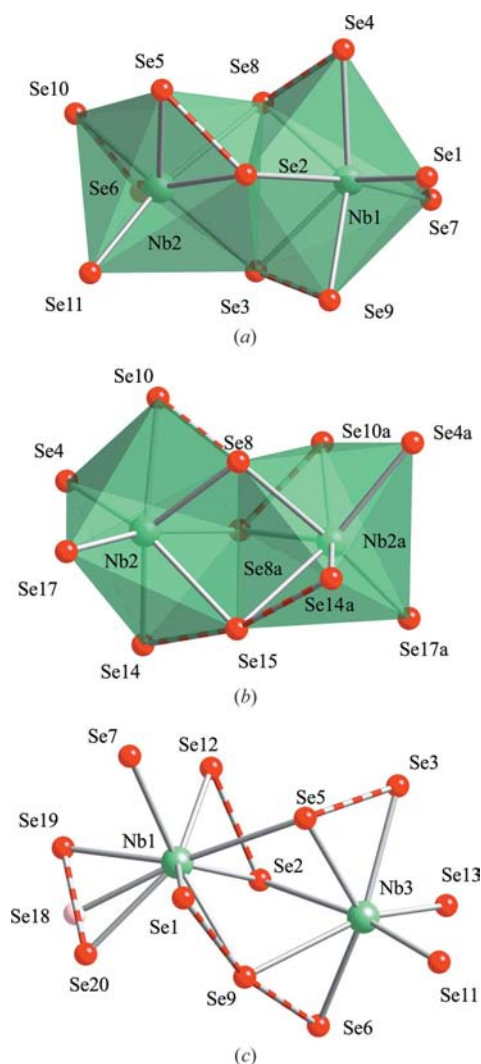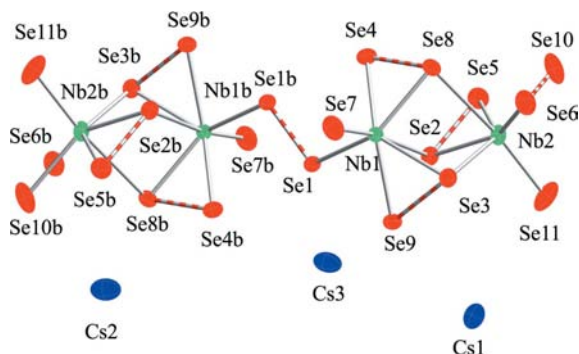

Figure 1
The diverse face-shared connectivity of the pentagonal bipyramidal niobium is shown. The niobium sites are light (green in the electronic version of the paper), the selenium sites are dark (red) and Se—Se bonds are emphasized as striped lines. (*a*) In Cs$_6$Nb$_4$Se$_{22}$, the three shared Se atoms are part of an (Se—Se)$^{2-}$ pair. (*b*) In K$_{12}$Nb$_6$Se$_{35.3}$, two of the shared Se atoms are part of an (Se—Se)$^{2-}$ pair, but the third shared Se atom occurs in a rare (Se—Se—Se)$^{4-}$ unit [symmetry code: (*a*) $-x + 1$, *y*, $-z + \frac{1}{2}$]. (*c*) The disorder in K$_{12}$Nb$_6$Se$_{35.3}$ between atom Se18 (85%) and the Se19—Se20 pair (15%) is shown in the Nb1–Nb3 dimer. A discrete M_2Se$_{12}$ dimer has not been reported and is related to an Nb$_2$S$_{12}$ dimer (Wu & Bensch, 2009). Atom Se18 is emphasized as a white sphere.

inorganic compounds

The initial models of $K_{12}Nb_6Se_{35.3}$ indicate the structure is isotypic with $Rb_{12}Nb_6Se_{35}$ (Duerichen *et al.*, 1998). The Nb1 and Nb3 sites form face-shared pentagonal bipyramid dimers similar to $Cs_6Nb_4Se_{22}$, but the connectivity differs slightly. Two corners of the triangular face are shared through an Se^- atom from an $Se—Se$ pair; however, in $K_{12}Nb_6Se_{35.3}$, the third corner is shared through the central Se atom in a rare $(Se—Se—Se)^{4-}$ unit that contains longer $Se—Se$ bonds [$Se1—Se9 = 2.5794\,(11)$ Å and $Se9—Se6 = 2.6269\,(11)$ Å] than a typical $(Se—Se)^{2-}$ bonded pair (Fig. 1*b*). The Nb2 site forms a face-shared pentagonal bipyramidal dimer in the same manner as Nb1–Nb3. The Nb2 dimer connects to the Nb1–Nb3 tetramers through another $(Se—Se—Se)^{2-}$ [$Se4—Se16 = 2.3879\,(12)$ Å and $Se13—Se16^{ii} = 2.3911\,(11)$ Å; symmetry code: $x - 1, y, z$] linkage on each side to form an infinite linear chain (Fig. 3). The linear chains are surrounded by K^+ ions for charge balance. $K_{12}Nb_6Se_{35}$ has been reported (Bensch *et al.*, 1999; Duerichen, 1998), but a complete crystal structure has not been published. Another linear niobium chalcogenide chain was observed in $Rb_2BaNb_2Se_{11}$ (Wu *et al.*, 2007), where the M_2Q_{11} dimers have the same bonding as in the Nb2–Nb2($-x + 1, y, -z + \frac{1}{2}$) dimers in $K_{12}Nb_6Se_{35.3}$. The linear chain is formed only through $Se—Se$ bonds and there are no $Se—Se—Se$ units as seen in $K_{12}Nb_6Se_{35.3}$.

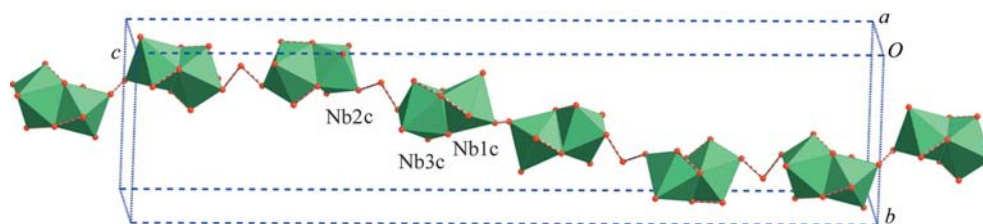Using the $Rb_{12}Nb_6Se_{35}$ structure, the structure solution refines anisotropically to about 6%. Two larger than expected residual electron-density peaks (10 and 11 e$^-$) are found near Se18 (1.42 and 0.93 Å therefrom). The three electron-density peaks are modeled so that the structure is disordered between an Se18 atom (85%) or an Se19—Se20 pair (15%) (Fig. 1*c*). The Se18 and the Se19—Se20 pair both have a -2 charge so that the structure remains charge balanced. The disorder occurs in the Nb1 coordination polyhedron, creating an eight-coordinate distorted monocapped pentagonal bipyramid. The Nb1 polyhedron is still face-shared with the Nb3 polyhedron and represents the first time a discrete M_2Se_{12} building block has been reported. A sulfur analog of the building block, *viz.* Nb_2S_{12}, has been reported with a distorted monocapped pentagonal bipyramid; however, the structure only contains a pair of bridging $S—S$ and no $S—S—S$ fragments (Wu & Bensch, 2009). Nb_2PS_{10} (Brec *et al.*, 1983) also contains eight-coordinate niobium sites, but the structure is a bicapped trigonal prism that forms extended linear chains, not discrete M_2Q_{12} building blocks.

The new building block is Se rich and the stoichiometry of $K_{12}Nb_6Se_{35.3}$ is formally $K_{12}Nb_6Se_{35.3}$. In a separate reaction (described in the *Experimental* section), the same compound was found and the disorder refined to a similar percentage (82 and 18%). The selenium content in the precursor was higher in this case and, in the future, more systematic studies could be performed to examine whether the disorder correlates with increased selenium in the precursor.

Our work shows the diverse bonding in the M_2Q_{11} building block that can lead to new structures that seem to be isostructural to known compounds but have subtle differences that are only seen from full data collections. In both structures, the oxidation state for niobium can be assigned as +5. Our future work will continue to examine this ternary composition space to search for magnetically interesting chalconiobates. The reactions require compositions with less oxidizing power in our flux reactions: lower molar ratios of selenium or higher molar ratios of niobium.

Experimental

The alkali chalcogenide fluxes (A_2Se_2, where A = K or Cs) were prepared by reacting stoichiometric amounts of the respective alkali metal (K from Aldrich 99.5%; Cs from Strem 99.5+%) and selenium (Alfa Aesar 99.999+%) in liquid ammonia (Sunshine *et al.*, 1987). For the preparation of $Cs_6Nb_4Se_{22}$, Cs_2Se_2 (0.0930 g), Nb (Aldrich 99.8%,

Figure 2
The displacement ellipsoid plot of the Nb_4Se_{22} anion in (I) at the 50% probability level. The discrete dimers are connected through an $Se—Se$ bond to form the tetrameric M_4Q_{22} building block. The $Se—Se$ bonds are emphasized as striped lines. [Symmetry code: (*b*) $-x + 2, -y, -z + 1$.]

Figure 3
The linear anionic chains in $K_{12}Nb_6Se_{35.3}$ are shown and form an $A'AA$ type of repeating structure, with A' as an Nb2 dimer and A as the Nb1–Nb3 dimer. The connectivity between A' and A is through an $(Se—Se—Se)^{2-}$ linkage. Niobium sites are polyhedra (green in the electronic version of the paper), selenium sites are spheres (red) and $Se—Se$ bonds are emphasized as striped lines. [Symmetry code: (*c*) $-x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.]

0.0210 g) and Se (0.0866 g) were loaded into a fused silica ampoule in a nitrogen glove-box. For the preparation of $K_{12}Nb_6Se_{35.3}$, K_2Se_2 (0.1036 g), Nb (0.0272 g) and Se (0.0693 g) were loaded into a fused silica ampoule in a nitrogen glove-box. Ampoules were evacuated and flame sealed. Samples were placed in a computer-controlled tube furnace and heated to 773 K at a rate of 35 K h^{-1}. $Cs_6Nb_4Se_{22}$ was held at 773 K for 75 h and cooled to room temperature at a rate of 5 K h^{-1}. $K_{12}Nb_6Se_{35.3}$ was held at 773 K for 120 h and cooled at a rate of 1 K h^{-1}. Excess flux was removed by washing with dimethyl-formamide (Aldrich 99.8%) to release the crystals, which in the case of $Cs_6Nb_4Se_{22}$ contained black needles and in the case of $K_{12}Nb_6Se_{35.3}$ contained black plates and red plates. The red plates were identified as K_3NbSe_4 by unit cell (Latroche & Ibers, 1990) The crystals appeared to be moisture sensitive over time. Crystals of $Cs_6Nb_4Se_{22}$ were handpicked and coated liberally with epoxy for data collection at room temperature. Crystals of $K_{12}Nb_6Se_{35.3}$ were mounted in mineral oil and placed in a 100 K nitrogen coldstream for data collection. $K_{12}Nb_6Se_{35.3}$ was also found in a reaction between K_2Se_2 (0.0930 g), Nb (0.0210 g) and Se (0.0866 g) as black blocks only. The heating profile was the same as above for $Cs_6Nb_4Se_{22}$.

$Cs_6Nb_4Se_{22}$

Crystal data

$Cs_6Nb_4Se_{22}$	$V = 2113.72\,(18)$ Å^3
$M_r = 2906.22$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.5887\,(6)$ Å	$\mu = 25.10$ mm^{-1}
$b = 8.5127\,(4)$ Å	$T = 296$ K
$c = 20.3151\,(10)$ Å	$0.2 \times 0.08 \times 0.06$ mm
$\beta = 103.853\,(1)°$	

Data collection

Bruker APEXII CCD diffractometer	35929 measured reflections
	4844 independent reflections
Absorption correction: empirical (using intensity measurements) (*SADABS*; Bruker, 2008)	3550 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.065$
$T_{min} = 0.347$, $T_{max} = 0.746$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	145 parameters
$wR(F^2) = 0.089$	$\Delta\rho_{max} = 4.93$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -2.29$ e Å^{-3}
4844 reflections	

$K_{12}Nb_6Se_{35.3}$

Crystal data

$K_{12}Nb_6Se_{35.30}$	$Z = 4$
$M_r = 3810.00$	Mo $K\alpha$ radiation
Orthorhombic, $Pbcn$	$\mu = 22.69$ mm^{-1}
$a = 8.3290\,(4)$ Å	$T = 100$ K
$b = 13.2559\,(7)$ Å	$0.16 \times 0.12 \times 0.02$ mm
$c = 55.974\,(3)$ Å	
$V = 6180.0\,(5)$ Å^3	

Data collection

Bruker APEXII CCD diffractometer	53662 measured reflections
	5107 independent reflections
Absorption correction: empirical (using intensity measurements) (*SADABS*; Bruker, 2008)	4470 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.074$
$T_{min} = 0.380$, $T_{max} = 0.745$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	263 parameters
$wR(F^2) = 0.063$	$\Delta\rho_{max} = 1.96$ e Å^{-3}
$S = 1.12$	$\Delta\rho_{min} = -0.97$ e Å^{-3}
5107 reflections	

In the structure refinement of $Cs_6Nb_4Se_{22}$, a larger than expected residual electron-density peak (4.93 e Å^{-3}) was found 0.96 Å from Cs2 and attributed to absorption of the heavy Cs atom.

The initial structure model for $K_{12}Nb_6Se_{35.3}$ refined to a 6% R value. At this point, two large electron-density peaks (11 and 10 e Å^{-3}) were found 1.42 and 0.93 Å from atom Se18. The peaks were modeled as disordered Se atoms (Se19 and Se20). At first, the site-occupation factors of the three sites were given individual free variables. The occupancy of atom Se18 converged to 85%. Se19 and Se20 converged to similar occupancies (12%). Examining the structure, Se19 and Se20 were determined to be an Se—Se bonded pair. The disorder was fixed to 85% for Se18 and 15% for Se19—Se20, so the overall space is 100% occupied and the refinement continued to convergence. Twinning was not observed even with a larger than expected weighting scheme. Unit-cell determinations using *CELL_NOW* (Sheldrick, 2004) showed 92% of the reflections (out of 660 reflections) fell into a single domain. The remaining reflections were attributed to a minor second crystal that was not refined. With a long c axis, spot overlap could have been a problem. The data images were observed with the unit-cell overlay and diffraction spots were well resolved. An examination of the *SAINT-Plus* (Bruker, 2008) output (1-PKFRAC; the fraction of the intensity which had to be estimated from the model profiles because of overlap with neighboring spots) showed none of the intensities overlapped with neighboring spots.

For both compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (CrystalMaker Software, 2009); software used to prepare material for publication: *APEX2*.

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