INORGANIC COMPOUNDS

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Cs_3NbSe_4

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Abstract

Tricaesium niobium tetraselenide, Cs_3NbSe_4, was obtained in the form of single crystals by the reaction of Cs_2Se_3, NbO and Se. The compound crystallizes in the K_3VS_4-type structure and is isotypic with previously reported K and Rb analogues. The crystal structure is based on discrete tetrahedral $[NbSe_4]^{3-}$ anions, which are connected *via* Cs^+ cations.

Comment

During our investigations of the $A/M^V/Q/O$ system (A = alkali metal, M^V = V, Nb or Ta, and Q = S or Se), the title compound, tricaesium niobium tetraselenide, Cs_3NbSe_4, was obtained in the form of single crystals as a by-product of the reaction of Cs_2Se_3 with NbO and Se. To date, only the lattice parameters of this compound have been reported in the literature, as determined by X-ray and neutron powder diffraction techniques, and Cs_3NbSe_4 was claimed to be isostructural with Cs_3TaSe_4 (Yun *et al.*, 1988).

Alkali metal chalcogenometallates of composition A_3BX_4 (A = alkali metal, B = V, Nb or Ta, and X = S or Se) crystallize in the K_3VS_4-type structure (van den Berg & de Vries, 1964). To date, the following compounds exhibiting the K_3VS_4 structure have been reported: K_3NbS_4, K_3NbSe_4, K_3TaS_4 and K_3TaSe_4 (Latroche & Ibers, 1990), Rb_3NbS_4 (Krause *et al.*, 1998), Cs_3TaSe_4 (Yun *et al.*, 1988) and $(NH_4)_3VS_4$ (Schäfer, Moritz & Weiss, 1965). Only one isostructural oxometallate, with the composition K_3FeO_4 (Hoppe & Mader, 1990), has been reported. Further related compounds of this type of structure are found in the S and Se salts of group 15 elements, such as K_3PS_4 (Schäfer, Schäfer & Weiss, 1965), K_3SbS_4 (Bensch & Dürichen, 1997), Rb_3AsSe_4 and Cs_3AsSe_4 (Wachhold & Sheldrick, 1996), Rb_3SbS_4 (Bensch & Dürichen, 1996), Rb_3SbSe_4 and Cs_3SbSe_4 (Wachhold & Sheldrick, 1996) and $(NH_4)_3AsS_4$ (Schäfer *et al.*, 1963; Graf & Schäfer, 1976), and one group 13 thiophosphate, Tl_3PS_4 (Taffoli *et al.*, 1981).

Cs_3NbSe_4 crystallizes in the centrosymmetric space group *Pnma*. The crystal structure contains discrete tetrahedral complex anions which are connected by Cs^+ cations. The average Nb—Se distance of 2.3923 (11) Å and the Se—Nb—Se angles of 108.43 (3) to 112.06 (5)° are in the range observed in other niobium(V) selenides. There are two crystallographically independent Cs^+ cations in the asymmetric unit. The Cs1 ion is coordinated by seven Se atoms from four symmetry-related $[NbSe_4]^{3-}$ anions within an irregular polyhedron. The average Cs1—Se distance is 3.6957 (10) Å. In contrast, the Cs2 ion is fivefold coordinated by the Se atoms of five symmetry-related $[NbSe_4]^{3-}$ anions. The average Cs2—Se distance is 3.7303 (13) Å.

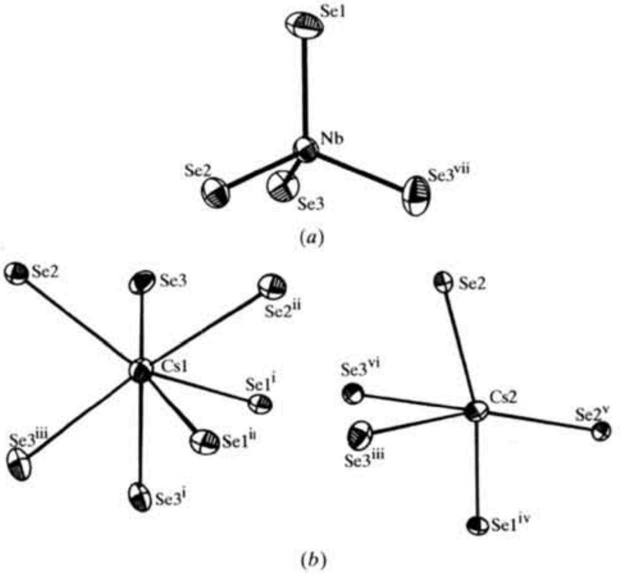

Fig. 1. The structure of Cs_3NbSe_4, showing the coordination spheres of (*a*) the Nb^+ and (*b*) the Cs^+ cations, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes are as given in Table 2.

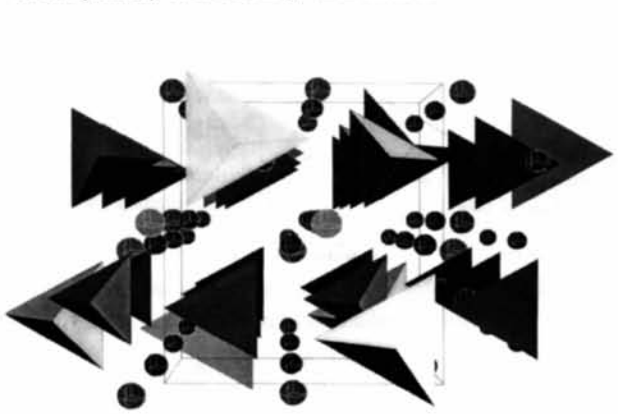

Fig. 2. The crystal structure of Cs_3NbSe_4 viewed along the *c* axis.

Experimental

For the preparation of single crystals of Cs_3NbSe_4 (all manipulations were performed under nitrogen using a glove-box and conventional Schlenk techniques), the starting compounds Cs_2Se_3, NbO and Se were mixed thoroughly in a 2:1:4 ratio and sealed into a Pyrex ampoule which was evacuated to 6×10^{-8} Pa. Cs_2Se_3 was prepared by the reaction of stoichiometric amounts of Cs and Se in liquid ammonia under an argon atmosphere. The ampoule containing the three starting materials was heated to 623 K and held at that temperature for a period of 6 d and afterwards cooled to room temperature at the rate of $3\ \mathrm{K\,h^{-1}}$. The resulting melt was washed with dimethylformamide and ether, and the residue was dried *in vacuo*.

Crystal data

Cs_3NbSe_4
$M_r = 807.48$
Orthorhombic
Pnma
$a = 10.293\ (2)$ Å
$b = 11.909\ (2)$ Å
$c = 10.252\ (2)$ Å
$V = 1256.7\ (4)$ Å^3
$Z = 4$
$D_x = 4.268$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 80 reflections
$\theta = 26\text{–}39°$
$\mu = 21.043$ mm^{-1}
$T = 293\ (2)$ K
Block
$0.04 \times 0.03 \times 0.03$ mm
Brown–black

Data collection

Stoe AED-II diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*XEMP* in *SHELXTL/PC*; Siemens, 1990)
$T_{\min} = 0.305$, $T_{\max} = 0.532$
3198 measured reflections
1926 independent reflections
1482 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.027$
$\theta_{\max} = 30.01°$
$h = 0 \rightarrow 14$
$k = -16 \rightarrow 9$
$l = 0 \rightarrow 14$
4 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.095$
$S = 1.056$
1926 reflections
44 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 1.7791P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.898$ e Å^{-3}
$\Delta\rho_{\min} = -1.431$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0027 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Nb	0.22072 (7)	1/4	0.48176 (6)	0.02341 (17)
Se1	0.20648 (10)	1/4	0.24971 (8)	0.0334 (2)
Cs1	0.04599 (4)	0.54173 (4)	0.70678 (4)	0.03477 (14)
Cs2	0.14774 (7)	1/4	0.90911 (6)	0.0497 (2)
Se2	0.00504 (9)	1/4	0.57121 (8)	0.0308 (2)
Se3	0.33211 (8)	0.41657 (8)	0.54877 (8)	0.0433 (2)

Table 2. *Selected geometric parameters (Å, °)*

Nb—Se1	2.3834 (12)	Cs1—Se2	3.7656 (8)
Nb—Se3	2.3920 (9)	Cs1—Se2$^{\rm ii}$	3.8144 (9)
Nb—Se2	2.4019 (12)	Cs2—Se1$^{\rm iv}$	3.5438 (13)
Cs1—Se1$^{\rm i}$	3.5829 (10)	Cs2—Se2$^{\rm v}$	3.6833 (13)
Cs1—Se1$^{\rm ii}$	3.6199 (10)	Cs2—Se2	3.7627 (12)
Cs1—Se3$^{\rm iii}$	3.6536 (10)	Cs2—Se3$^{\rm vi}$	3.8309 (12)
Cs1—Se3	3.6769 (10)	Cs2—Se3$^{\rm iii}$	3.8309 (12)
Cs1—Se3$^{\rm i}$	3.7567 (11)		
Se1—Nb—Se3	108.43 (3)	Se1—Nb—Se2	108.92 (4)
Se1—Nb—Se3$^{\rm vii}$	108.43 (3)	Se3—Nb—Se2	109.47 (3)
Se3—Nb—Se3$^{\rm vii}$	112.06 (5)	Se3$^{\rm vii}$—Nb—Se2	109.47 (3)

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (ii) $-x, 1 - y, 1 - z$; (iii) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (iv) $x, y, 1 + z$; (v) $\frac{1}{2} + x, y, \frac{3}{2} - z$; (vi) $x - \frac{1}{2}, \frac{1}{2}\ \ y, \frac{3}{2} - z$; (vii) $x, \frac{1}{2} - y, z$.

All Cs, Nb and Se atoms were refined with anisotropic displacement parameters. The highest residual electron-density peak is located 1.27 Å from Se3. In view of the large absorption coefficient, a face-indexed absorption correction was attempted, however, no improvement of the structure model or of the *R* values was obtained.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *CIFTAB* in *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1211). Services for accessing these data are described at the back of the journal.

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Lithium barium arsenide, $Li_4Ba_3As_4$, containing isolated As^{3-} and As_2^{4-} anions

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Abstract

$Li_4Ba_3As_4$ crystallizes in the orthorhombic space group *Immm* and is isostructural with $Li_4Sr_3Sb_4$ and $Li_4Ba_3Sb_4$ [Liebrich, Schäfer & Weiss (1970). *Z. Naturforsch. Teil B*, **25**, 650–651]. The structure contains two anionic moieties, namely As_2^{4-} dumbbells [As1—As1 2.487 (2) Å] and As^{3-}.

Comment

The structure of $Li_4Ba_3As_4$ has been determined in the centrosymmetric space group *Immm* (No. 71) and is isostructural with $Li_4Sr_3Sb_4$ and $Li_4Ba_3Sb_4$ (Liebrich *et al.*, 1970). The structure contains two anionic moieties, namely As_2^{4-} dumbbells [As1—As1 2.487 (2) Å] and isolated As^{3-} anions. This structure is best described by visualizing coordination polyhedra around the Ba atoms. Ba1 lies at the center of a pseudo-octahedron (symmetry *mmm*) formed by four As1 atoms at 3.320 (1) Å and two As2 atoms at 3.319 (1) Å. Ba2 is coordinated by six Li atoms [four at 3.28 (1) Å and two at 3.29 (2) Å] and six As atoms [four As1 and two As2 at 3.363 (1) and 3.392 (1) Å, respectively]. The large $BaAs_6$ octahedra are condensed along the [100] direction into a linear framework by edge sharing. These columns form a two-dimensional array through the As1—As1 dumbbell parallel to [010]. Interestingly, the planes of the octahedra are separated from each other by corrugated sheets of electropositive Li and Ba atoms. The As1 atoms that form the As_2^{4-} dumbbells are coordinated by six Li atoms [two at 2.75 (2) Å and four at 2.80 (1) Å]. The As1—As1 distance of 2.487 (2) Å is slightly longer than the single-bond length given by Pauling (2.42 Å; Pauling, 1947, 1949). This compound can be described using the Zintl formalism as the ionic compound: 4 Li^+, 3 Ba^{2+}, As_2^{4-}, 2 As^{3-}.

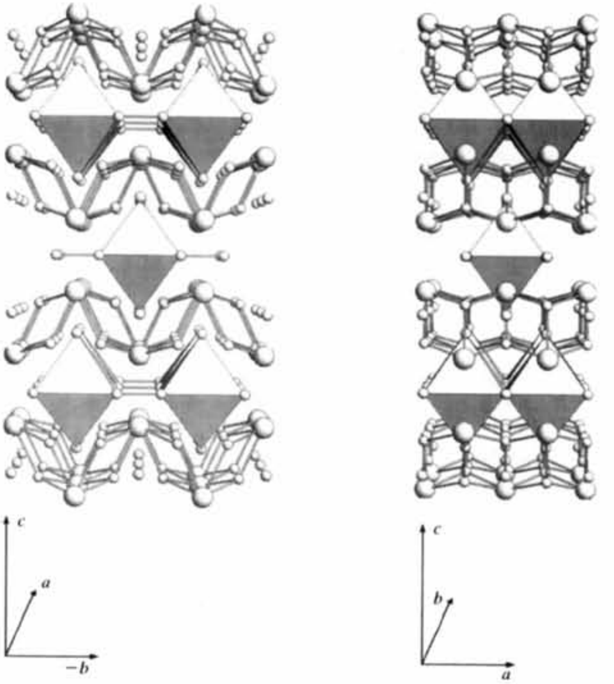

Fig. 1. Two views of the structural packing of $Li_4Ba_3As_4$. Ba1 lies at the center of the octahedron and the origin of the cell, Ba2 is represented by large circles, As1 is in the equatorial plane of the octahedron and forms dumbbells between adjoining octahedra, As2 is axial with respect to the octahedron and Li is represented by small circles between Ba2 atoms.

Experimental

With the aim of obtaining the quaternary phase $Li_3Ba_2VAs_4$, which is closely related to the recently discovered Li_7VAs_4 phase (Monconduit, 1999), Li_3As, As, Ba and V (ratio 1:3:2:1) were inserted into a niobium reactor weld-sealed under argon. The niobium reactor was protected in a quartz ampoule sealed under vacuum. Single crystals of $Li_4Ba_3As_4$ were obtained by heating to 1273 K for 10 h, heating for 8 d at 1123 K and then cooling the mixture at a rate of 150 K h^{-1}. The product contained a large amount of $Li_4Ba_3As_4$. Elemental analyses (SEM) of flat crystals confirmed the presence of barium and arsenic in a Ba/As ratio of 0.77, and the absence of vanadium. Atomic absorption analyses showed an Li/Ba ratio of 1.21.

Crystal data

$Li_4Ba_3As_4$
$M_r = 739.46$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å