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$Tl_4Nb_2Se_{11}$

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(Se–Se) = 0.003 Å
R factor = 0.055
wR factor = 0.161
Data-to-parameter ratio = 29.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The ternary compound tetrathallium diniobium undecaselenide, $Tl_4Nb_2Se_{11}$, was prepared by a molten flux method from a melt of Tl_2Se, elemental Se and Nb. The structure is composed of discrete Tl^+ cations and complex $[Nb_2Se_{11}]^{4-}$ anions. In the anion, the two crystallographically independent Nb atoms are sevenfold coordinated by Se atoms to form a distorted pentagonal bipyramid. Two $NbSe_7$ polyhedra have a face in common, thus yielding the $[Nb_2Se_{11}]^{4-}$ unit. The crystal structure of $Tl_4Nb_2Se_{11}$ is isotypic with the structure of the homologous tantalum compound $Tl_4Ta_2Se_{11}$ [Teske *et al.* (2002). *Z. Anorg. Allg. Chem.* **628**, 2651–2655], which was the first polyselenide with discrete complex $[M_2Se_{11}]^{4-}$ anions.

Comment

Until very recently compounds with discrete $[M_2Q_{11}]^{4-}$ anions (M = Nb and Ta, and Q = chalcogen) were reported only for sulfides, such as $Cs_4Nb_2S_{11}$ (Klepp & Gabl, 1998), $K_4Nb_2S_{11}$ (Bensch & Dürichen, 1996) and $K_4Ta_2S_{11}$ (Schreiner *et al.*, 1989; Herzog *et al.*, 1999), and for mixed chalcogenides, such as $K_4Nb_2S_{8.9}Se_{2.1}$, $K_4Nb_2S_{9.5}Se_{1.5}$ (Krause *et al.*, 2000) and $K_4Nb_2S_{10}O$ (Krause *et al.*, 1999). Common features of polyselenides with compositions such as $Rb_6Nb_4Se_{22}$ or $K_{12}Nb_6Se_{35}$ (Dürichen, 1998) are infinite ${}^1_\infty[Nb_xSe_y]^{z-}$ anionic chains containing Nb_2Se_{11} building blocks that are interconnected by $Se_2{}^{2-}$ or $Se_3{}^{2-}$ anions. Interestingly, a pure polyselenide comprising only the isolated binuclear anion $[M_2Se_{11}]^{4-}$ was reported only for M = Ta (Teske *et al.*, 2002). We report here the crystal structure of the homologous Nb compound that is isotypic with the aforementioned $Tl_4Ta_2Se_{11}$.

The $[Nb_2Se_{11}]^{4-}$ unit, which is composed of two distorted $NbSe_7$ pentagonal bipyramids sharing a common face, is displayed in Fig. 1. The coordination polyhedron of every Nb^{5+} ion consists of one terminal selenide Se^{2-}, one η^2-$Se_2{}^{2-}$ unit, a μ_2-Se^{2-} anion bridging the two metal centres and one additional $Se_2{}^{2-}$ anion, which is η^2 to one Nb^{5+} ion while one Se of this unit serves as a bridging atom to the second metal centre. Therefore, the complex molecular anion may be formulated as $[Nb_2(\mu\text{-}Se)(\mu\text{-}\eta^2,\eta^1\text{-}Se_2)_2(\eta^2\text{-}Se_2)_2(Se)_2]^{4-}$. The interatomic Nb—Se distances range from 2.409 (2) to 2.860 (3) Å (Table 1) and can be divided into three groups. The two short Nb—Se distances of 2.409 (2) and 2.437 (3) Å to the terminal Se^{2-} anions may be described as Nb═Se double bonds. Ten medium-long distances range from 2.559 (3) to 2.669 (3) Å, and two longer distances are 2.836 (3) and 2.860 (3) Å. The average Nb—Se distance of 2.62 Å is comparable to the sum of the ionic radii Σ = 2.62 Å [with $r(Nb^{5+})$ = 0.64 for sixfold coordination or Σ = 2.67 Å with $r(Nb^{5+})$ = 0.69 for sevenfold coordination and $r(Se^{2-})$ = 1.98 Å (Shannon, 1976)]. Since Ta^{5+} and Nb^{5+} have the same ionic

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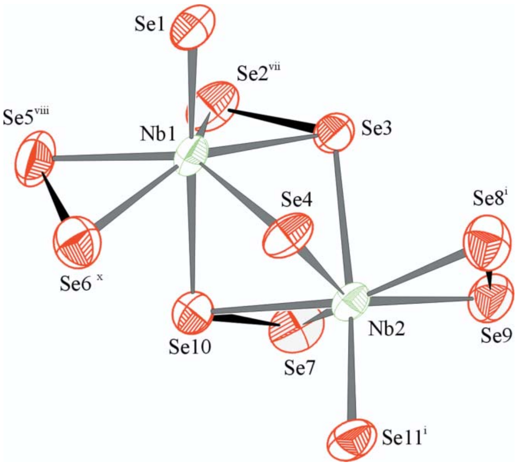

Figure 1
The Nb_2Se_{11} unit in $Tl_4Nb_2Se_{11}$, with displacement ellipsoids drawn at the 90% probability level. Symmetry codes are as in Table 1.

radius, these are very similar to the corresponding distances in the structure of the homologuous Ta compound. Likewise, the distortion of the bipyramidal MQ_7 units is very similar to those of $Tl_4Ta_2Se_{11}$. In the title compound, the Nb···Nb distance of 3.560 (3) Å is too long for metal-to-metal interaction. The mean Se—Se bond length in the Se_2^{2-} anions of about 2.36 Å (see Table 1) is typical for Se—Se single bonds. The displacements of the Nb^{5+} ions from the mean planes defined by the equatorial atoms Se4/Se6/Se5/Se2/Se3 and Se4/Se8/Se9/Se7/Se10 are 0.3596 (16) Å for Nb2 and 0.4223 (16) Å for Nb1, respectively, with an angle between the two pentagonal planes of 49.23 (7)°. The corresponding values for $Tl_4Ta_2Se_{11}$ are 0.36 Å for Ta2 and 0.41 Å for Ta1 and 57.5°, respectively. [Note that these values were wrongly reported in the original paper (Teske *et al.*, 2002) and are now recalculated correctly.] The coordination numbers (CN) for the Tl^+ ions are CN(Tl2) = 7, CN(Tl4) = 8, CN(Tl1) = 9 and CN(Tl3) = 9, with Tl—Se distances ranging from 3.024 (3) to 3.849 (3) Å (Table 1.) The average Tl—Se value of about 3.40 Å is nearly 5% shorter than the sum of the ionic radii (Shannon, 1976) for CN = 8. The arrangement of the anions is shown in Fig. 2. Within the *ac* plane the anions are packed in a hexagonal fashion to form pseudo-layers. These layers are stacked perpendicular to [001].

Experimental

For the synthesis of $Tl_4Nb_2Se_{11}$, mixtures of Tl_2Se, Nb and Se in the molar ratio 2:2:9 were sealed in a Duran glass ampoule under an argon atmosphere. The starting materials were Nb powder (99.7%, Riedel-De Haën AG), Se (99.5%, Riedel-De Haën AG) and Tl (99.99%, Sigma–Aldrich). Tl_2Se was prepared by direct reaction of Tl and Se. The ampoule was transferred to a preheated furnace at 493 K, heated to 753 K with a heating rate of 3 K min^{-1}, held at that temperature for 12 h and heated to 833 K within 1 h, which produced a black melt. The ampoule was removed from the furnace and shaken (until solidification after some seconds) to homogenize the black liquid. This was repeated once a day during a heating period of one week. Finally, the ampoule was cooled to 623 K (3 K min^{-1}) and opened at room temperature. The black crystals obtained are stable in air for a long time.

Crystal data

$Tl_4Nb_2Se_{11}$
M_r = 1871.86
Triclinic, $P\overline{1}$
a = 7.974 (4) Å
b = 9.147 (5) Å
c = 13.626 (7) Å
α = 73.11 (4)°
β = 89.26 (4)°
γ = 85.76 (6)°
V = 948.4 (9) Å^3
Z = 2
D_x = 6.555 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 70 reflections
θ = 10–25°
μ = 56.11 mm^{-1}
T = 295 (2) K
Column, black
0.24 × 0.16 × 0.12 mm

Data collection

Philips PW1100 four-circle diffractometer
ω/θ scans
Absorption correction: numerical [*X-SHAPE* (Stoe & Cie, 1998) and *X-RED* (Stoe & Cie, 1998)]
T_{min} = 0.005, T_{max} = 0.035
4895 measured reflections
4572 independent reflections
3582 reflections with $I > 2\sigma(I)$
R_{int} = 0.092
θ_{max} = 28.0°
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.161
S = 1.07
4572 reflections
155 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1091P)^2 + 9.5978P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.011
$\Delta\rho_{max}$ = 5.28 e Å^{-3}
$\Delta\rho_{min}$ = −4.33 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0021 (2)

Table 1
Selected bond lengths (Å).

Tl1—Se1^{i}	3.071 (3)	Tl4—Se11^{i}	3.099 (2)
Tl1—Se4^{i}	3.099 (3)	Tl4—Se9^{i}	3.261 (3)
Tl1—Se8^{ii}	3.422 (3)	Tl4—Se7	3.310 (3)
Tl1—Se1^{iii}	3.426 (3)	Tl4—Se7^{vii}	3.389 (3)
Tl1—Se9^{iv}	3.453 (3)	Tl4—Se5	3.402 (3)
Tl1—Se3^{i}	3.459 (3)	Tl4—Se8	3.536 (3)
Tl1—Se2	3.505 (3)	Tl4—Se6^{vii}	3.849 (3)
Tl1—Se3^{iv}	3.526 (3)	Nb1—Se1	2.409 (2)
Tl1—Se8	3.811 (3)	Nb1—Se2^{vii}	2.568 (3)
Tl2—Se4^{i}	3.044 (2)	Nb1—Se6^{x}	2.594 (3)
Tl2—Se11	3.160 (3)	Nb1—Se5^{viii}	2.606 (3)
Tl2—Se10^{v}	3.203 (3)	Nb1—Se4	2.625 (2)
Tl2—Se5^{v}	3.263 (3)	Nb1—Se3	2.636 (3)
Tl2—Se11^{vi}	3.274 (3)	Nb1—Se10	2.860 (3)
Tl2—Se10^{vii}	3.340 (3)	Nb2—Se11^{i}	2.437 (3)
Tl2—Se6	3.825 (3)	Nb2—Se7	2.559 (3)
Tl3—Se5	3.144 (2)	Nb2—Se7	2.559 (3)
Tl3—Se5	3.144 (2)	Nb2—Se8^{i}	2.584 (3)
Tl3—Se1^{viii}	3.193 (3)	Nb2—Se9	2.591 (3)
Tl3—Se1^{iv}	3.297 (3)	Nb2—Se4	2.656 (2)
Tl3—Se2^{ix}	3.313 (3)	Nb2—Se10	2.669 (3)
Tl3—Se8	3.463 (3)	Nb2—Se3	2.836 (3)
Tl3—Se7^{vii}	3.523 (3)	Se2—Se3^{vii}	2.355 (3)
Tl3—Se3^{vii}	3.526 (3)	Se5—Se6^{vii}	2.365 (3)
Tl3—Se6^{vii}	3.673 (3)	Se7—Se10	2.361 (3)
Tl3—Se2	3.711 (3)	Se8—Se9^{i}	2.373 (3)
Tl4—Se11	3.024 (3)		

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, -y+1, -z+2$; (iii) $x, y+1, z+1$; (iv) $x, y, z+1$; (v) $x, y+1, z$; (vi) $-x, -y+2, -z+1$; (vii) $-x+1, -y+1, -z+1$; (viii) $-x+1, -y, -z+1$; (ix) $-x+1, -y+1, -z+2$; (x) $x, y-1, z$.

The atomic coordinates of the isotypic Ta compound (Teske *et al.*, 2002) were used as a starting model. The highest peak is sited 0.88 Å from Tl2 and the deepest hole 0.87 Å from Tl4.

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: coordinates taken from the isotypic Ta compound; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 1999); software used to prepare material for publication: *SHELXL97*.

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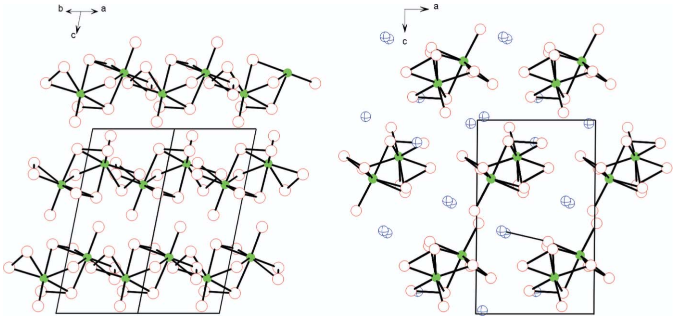

Figure 2
Arrangement of the $[Nb_2Se_{11}]^{4-}$ anions in the structure of $Tl_4Nb_2Se_{11}$. Projections along [110] (left) and along [001] (right). Colour code: Se red open spheres, Nb green filled spheres, Tl blue cross-hatched spheres. For clarity, Tl atoms have been omitted on the left.

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