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A new pseudo-two-dimensional niobium chloride selenide, $Nb_3Se_{10}Cl_3$

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(Se–Se) = 0.002 Å
R factor = 0.055
wR factor = 0.141
Data-to-parameter ratio = 24.7

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

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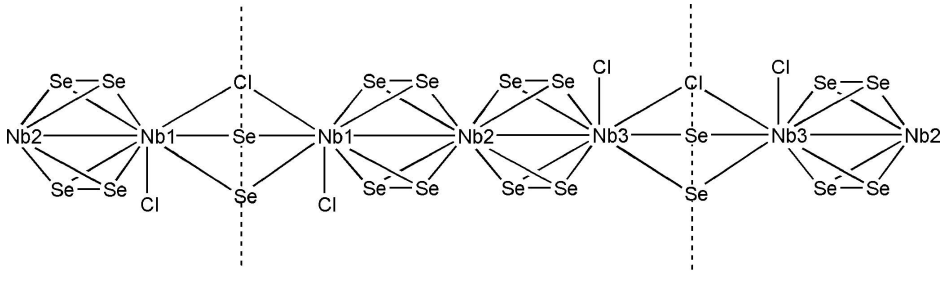
Triniobium decaselenide trichloride, $Nb_3Se_{10}Cl_3$, contains waved one-dimensional chains in which the Nb atoms are arranged in a sequence of two consecutive short bonds and one long distance. Two Nb atoms are each coordinated by three Se_2^{2-}, Cl^- and μ^2-Cl^-, whereas the third Nb atom is surrounded by four Se_2^{2-} to form distorted rectangular antiprisms of Se. Weak interchain interactions between Se and terminal Cl atoms connect the chains along the [101] direction to form a pseudo-two-dimensional layer. $Nb_3Se_{10}Cl_3$ is an insulator, in accordance with the charge-balanced formulation $[Nb^{5+}][Nb^{4+}]_2[Se_2^{2-}]_5[Cl^-]_3$.

Comment

During the search for new low-dimensional group 5 transition metal chalcogenides, single crystals of $Nb_3Se_{10}Cl_3$ were obtained. $Nb_3Se_{10}Cl_3$ is isostructural with low-temperature $Nb_3Se_{10}Br_3$ (Grenouilleau *et al.*, 1988), which transforms to a high-temperature form, $Nb_6Se_{20}Br_6$ (Meerschaut *et al.*, 1986). The existence of $Nb_6Se_{20}Cl_6$ has been mentioned (Grenouilleau *et al.*, 1988), but to our knowledge, no synthetic details or structural information have been reported.



(I)

$Nb_3Se_{10}Cl_3$ contains infinite one-dimensional chains in which the Nb atoms are arranged in a waved distribution with a sequence of two consecutive short bonds [Nb1—Nb2, 3.108 (2) Å; Nb2—Nb3, 3.105 (2) Å) and one long distance (Nb1—Nb1 or Nb3—Nb3, >3.8 Å) (Fig. 1). The short distances are slightly longer than the usual Nb—Nb bonding distances (Do & Yun, 1996; Kim & Yun, 2002; Meerschaut, 2006) but comparable to those found in $Nb_4Se_{16}Br_2$ (Grenouilleau *et al.*, 1987). Two types of Nb coordination polyhedra are found. Firstly, Se_2^{2-} pairs and μ^2-Cl^- ions bridge pairs of Nb atoms (Nb1—Nb1, Nb3—Nb3). An additional Cl^- ion and the rectangular [Se_4] plane are attached to the Nb1 and Nb3 atoms to complete the $NbSe_6Cl_2$ coordination. The imposed symmetry of the bridging atoms (Se9, Se10,

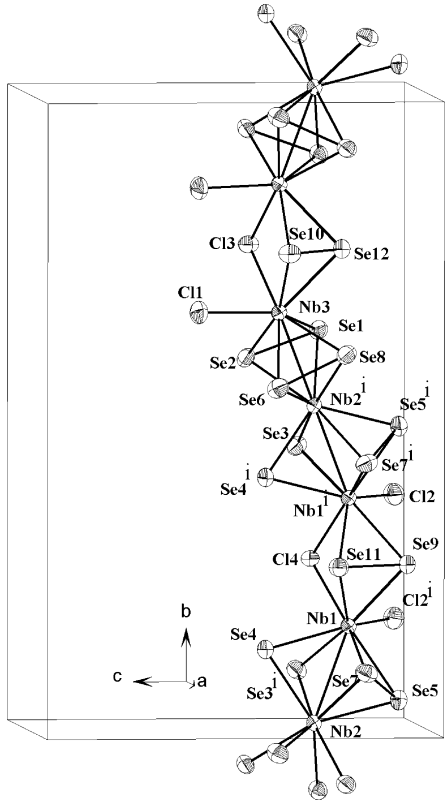


Figure 1
One $Nb_3Se_{10}Cl_3$ chain within the unit cell. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry code: (i) $x, \frac{1}{2} - y, z$.]

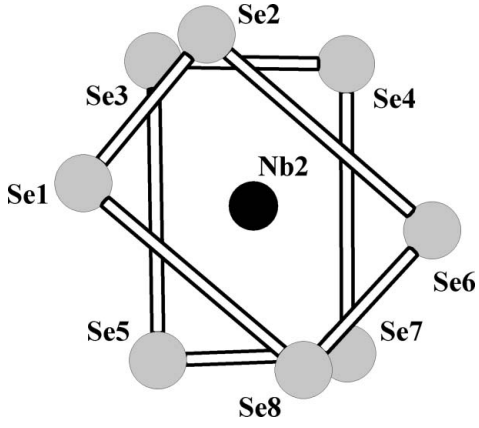


Figure 2
Relative orientation of adjacent $[Se_4]$ units of the $NbSe_8$ antiprism.

Se11, Se12, Cl3 and Cl4) is *m*. Secondly, the rectangular $[Se_4]$ planes are perpendicular to the Nb1—Nb2 and Nb2—Nb3 bonds, which leads to a distorted rectangular antiprismatic arrangement around Nb2 (Fig. 2). The sharing of the rectangular faces allows for the formation of the short Nb—Nb distances. The dihedral angle of the rectangular $[Se_4]$ planes is 48.6 (1)°, which is significantly smaller than 54° found in $Nb_3Se_{10}Br_2$ (Meerschaut *et al.*, 1987). Weak interactions between the Se atoms of one chain with the terminal Cl atoms of neighboring chains [Cl1—Se4, 2.968 (1) Å; Cl2—Se1, 3.011 (2) Å] connect the chains along the [101] direction to form a pseudo-two-dimensional layer (Fig. 3). The charge-balanced formulation $[Nb^{5+}][Nb^{4+}]_2[Se_2^{2-}]_5[Cl^-]_3$ is consistent with the observed insulating behavior of this compound.

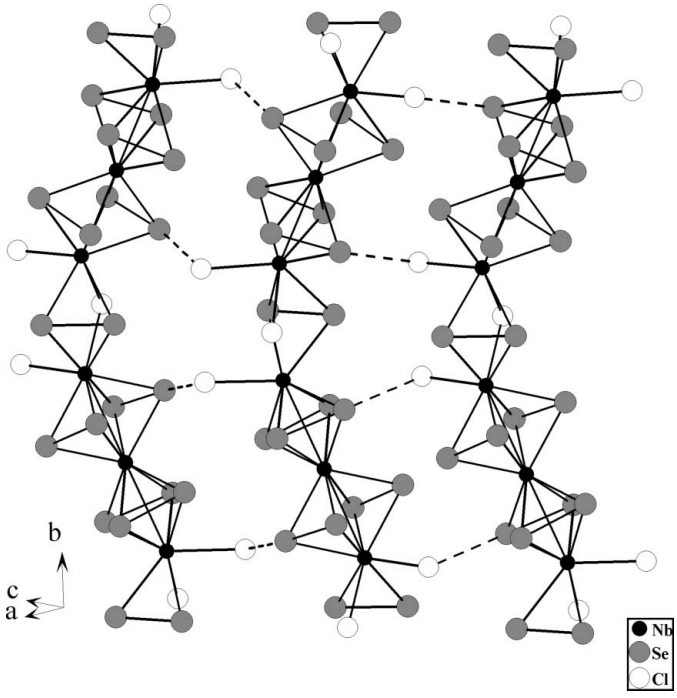


Figure 3
One layer in $Nb_3Se_{10}Cl_3$ formed by Se···Cl interchain connections.

Experimental

$Nb_3Se_{10}Cl_3$ was obtained from a reaction of Ag, Nb and Se in an elemental ratio of 1:1:3 in the presence of a eutectic mixture of AgCl/LiCl. The starting materials were placed in a fused-silica tube. The tube was evacuated to 10^{-3} Torr, sealed and heated to 903 K, where it was kept for 72 h. The tube was cooled at a rate of 28 K h^{-1} to 573 K and the furnace was shut off. Air- and water-stable black needle-shaped crystals were isolated after the flux was removed. Qualitative analysis of the crystals with an EDAX-equipped scanning electron microscope indicated the presence of Nb, Se and Cl. No other element was detected.

Crystal data

$Nb_3Se_{10}Cl_3$
M_r = 1174.68
Monoclinic, $P2_1/m$
a = 7.207 (3) Å
b = 18.974 (8) Å
c = 11.834 (7) Å
β = 95.60 (2)°
V = 1610.6 (14) Å^3
Z = 4
D_x = 4.844 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 25.17 mm^{-1}
T = 150 (2) K
Needle, black
0.30 × 0.10 × 0.05 mm

Data collection

Rigaku R-AXIS Rapid diffractometer
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 2000)
T_{min} = 0.053, T_{max} = 0.278
15892 measured reflections
3799 independent reflections
2794 reflections with $I > 2\sigma(I)$
R_{int} = 0.080
θ_{max} = 27.5°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 20.4571P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.141$	$\Delta\rho_{max} = 3.51$ e Å^{-3}
$S = 1.07$	$\Delta\rho_{min} = -2.66$ e Å^{-3}
3799 reflections	
154 parameters	

Table 1
Selected geometric parameters (Å, °).

Nb1—Cl2^{i}	2.497 (3)	Nb3—Cl1	2.492 (4)
Nb1—Cl4	2.549 (3)	Nb3—Cl3	2.563 (3)
Nb1—Se3^{i}	2.5761 (19)	Nb3—Se2	2.5741 (18)
Nb1—Se7	2.5942 (19)	Nb3—Se8	2.589 (2)
Nb1—Se4	2.623 (2)	Nb3—Se1	2.6311 (19)
Nb1—Se5	2.6654 (19)	Nb3—Se6	2.6586 (19)
Nb1—Se11	2.6975 (18)	Nb3—Se12	2.686 (2)
Nb1—Se9	2.7047 (19)	Nb3—Se10	2.7114 (19)
Nb2—Se4	2.6234 (19)	Nb1—Nb2	3.1075 (18)
Nb2—Se1^{i}	2.6283 (18)	Nb2—Nb3^{i}	3.1053 (19)
Nb2—Se5	2.639 (2)	Se1—Se2	2.338 (2)
Nb2—Se6^{i}	2.6423 (19)	Se3—Se4^{i}	2.339 (2)
Nb2—Se8^{i}	2.6649 (18)	Se5—Se7	2.308 (2)
Nb2—Se3^{i}	2.6837 (19)	Se6—Se8	2.307 (2)
Nb2—Se2^{i}	2.6861 (19)	Se9—Se11	2.309 (3)
Nb2—Se7	2.6895 (19)	Se10—Se12	2.317 (3)
Nb3^{i}—Nb2—Nb1	179.08 (5)	Nb1^{i}—Cl4—Nb1	96.85 (17)
Nb3^{ii}—Cl3—Nb3	96.62 (15)		

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

The highest peak in the final Fourier map is 1.21 Å from Cl4 and the deepest hole is 0.76 Å from Nb1.

Data collection: *RAPID-AUTO* (Rigaku, 2005); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: locally modified version of *ORTEP* (Johnson, 1965); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Do, J. & Yun, H. (1996). *Inorg. Chem.* **35**, 3729–3730.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Grenouilleau, P., Guemas, L. & Meerschaut, A. (1988). *Eur. J. Solid State Inorg. Chem.* **25**, 341–350.
Grenouilleau, P., Meerschaut, A., Guemas, L. & Rouxel, J. (1987). *J. Solid State Chem.* **66**, 293–303.
Higashi, T. (2000). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Kim, C.-K. & Yun, H.-S. (2002). *Acta Cryst.* C**58**, i53–i54.
Meerschaut, A. (2006). *Acta Cryst.* E**62**, i131–i132.
Meerschaut, A., Grenouilleau, P., Guemas, L. & Rouxel, J. (1987). *J. Solid State Chem.* **70**, 36–47.
Meerschaut, A., Grenouilleau, P. & Rouxel, J. (1986). *J. Solid State Chem.* **61**, 90–97.
Rigaku (2005). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.