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Niobium selenide trichloride, $NbSeCl_3$

Alain Meerschaut

Institut des Matériaux Jean Rouxel, UMR6502 CNRS–Université de Nantes, 2 rue de la Houssinière, 44322 Nantes, France

Correspondence e-mail: meerschaut@cnrs-imn.fr

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The structure of the title compound, $NbSeCl_3$, was determined by single-crystal X-ray diffraction. The structure consists of $NbSeCl_3$ chains centred on the Nb atoms. These chains, with a zigzag development along the *c* direction, show a regular alternation of short and long Nb—Nb distances. $NbSeCl_3$ is isostructural with $NbSeBr_3$; it may be described as $2(Nb^{4+})(Se_2^{2-})\ 6(Cl^-)$, with the presence of both $(Nb—Nb)^{8+}$ and $(Se—Se)^{2-}$ dimers.

Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(e–Se) = 0.001 Å
R factor = 0.039
wR factor = 0.073
Data-to-parameter ratio = 37.5

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

Comment

The MXY_3 (M = Nb or Ta, X = S or Se, and Y = Cl, Br or I) compounds were extensively studied some years ago, particularly with regard to their optical properties (IR and Raman spectroscopies) [for review articles on chalcohalides of the transition metals, see Rice (1978), Atherton & Holloway (1979) and Fenner *et al.* (1980)]. To the best of our knowledge, the first report on the structure of a member of the MXY_3 family of compounds was for $NbSeBr_3$ (Franzen *et al.*, 1983). Thereafter, we also reported the structure determination of the same $NbSeBr_3$ compound (Meerschaut *et al.*, 1994), ignoring at that time the pioneering work of Franzen *et al.*. According to the ICSD (2005), there is no report to date of a determination of the crystal structure of $NbSeCl_3$. However, the existence of $NbSeCl_3$ was mentioned as early as 1966 (Schäfer & Beckmann, 1966). The reaction of niobium pentachloride with both antimony triselenide and selenium was the method used to obtain $NbSeCl_3$, and this compound was known to be sensitive to humidity.

$NbSeCl_3$ is isostructural with $NbSeBr_3$. Fig. 1 shows the projection of the structure on to the *ac* plane. The Nb atoms are seven-coordinate (five Cl atoms and two Se atoms). The Nb atoms are associated in pairs which are alternately sepa-

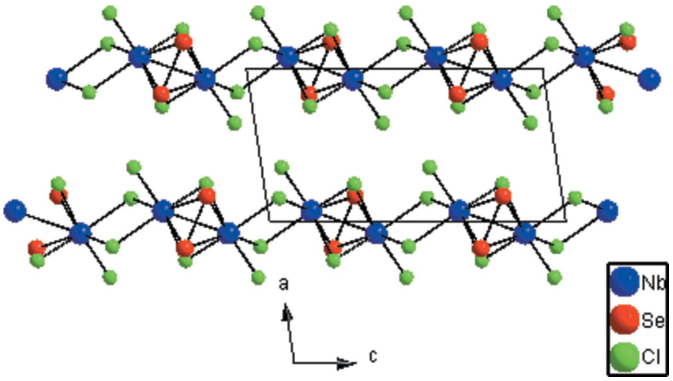

Figure 1
Projection of the structure of $NbSeCl_3$ on to the *ac* plane.

rated by a very long Nb—Nb distance [3.9573 (8) Å] along the *c* direction. The Nb—Nb dimer defines an [$Nb_2Se_2Cl_2$] structural unit in which an Se—Se pairing is observed, with a bond length slightly less than the shortest Se—Se bond found in $NbSe_3$ [*i.e.* 2.37 Å, as representative of an Se—Se pairing (Nb^{4+}) (Se_2^{2-}) (Se^{2-}); Hodeau *et al.*, 1978]. On both sides of this structural unit, there are two Cl atoms, which connect two adjacent units between them along the *c* direction. Thus, the title compound may be described as $(Nb—Nb)^{8+}$ (Se_2^{2-}) 6(Cl^-) with a strong Nb—Nb pairing (d^1–d^1), for which an electron cannot move along the *c* direction because of the very large Nb—Nb separation between these pairs.

Experimental

$NbSeCl_3$ was obtained as a side-product from a solid-state reaction of $NbCl_5$, Nb and Se in an approximate ratio of 5:4:13, respectively. The starting materials were placed in a Pyrex tube, which was evacuated to 10^{-2} Torr (1 Torr = 133.322 Pa), sealed and then placed in a computer-controlled furnace. The reactants were gradually heated up to 750 K, kept at this temperature for one week, and then slowly cooled (the furnace was switched off). The final product appeared very inhomogeneous, with thin white–grey needles, yellow transparent crystals and a dark powder and, in a small amount (less than 2%), some dark-red crystals of the title compound. The other phases were not identified. $NbSeCl_3$ is air-sensitive and so the selected crystal was glued to a glass capillary with nail varnish and then soaked in mineral oil (nujol), in an attempt to protect the crystal from humidity during data collection (3 h).

Crystal data

$NbSeCl_3$
$M_r = 278.22$
Monoclinic, $P2/c$
$a = 6.2993$ (13) Å
$b = 6.7205$ (13) Å
$c = 11.962$ (2) Å
$\beta = 98.71$ (3)°
$V = 500.56$ (17) Å^3
$Z = 4$
$D_x = 3.692$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 11.09$ mm^{-1}
$T = 293$ (2) K
Lath, dark-red
0.22 × 0.04 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: Gaussian integration (Sheldrick, 2001)
$T_{min} = 0.157$, $T_{max} = 0.839$
10058 measured reflections
1725 independent reflections
1251 reflections with $I > 2\sigma(I)$
$R_{int} = 0.161$
$\theta_{max} = 32.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.073$
$S = 0.99$
1725 reflections
46 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0233P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.36$ e Å^{-3}
$\Delta\rho_{min} = -1.35$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Nb1—Cl1	2.3587 (12)	Nb1—Se1	2.5795 (7)
Nb1—Cl2^{i}	2.4296 (12)	Nb1—Se1^{i}	2.6610 (7)
Nb1—Cl3^{ii}	2.5077 (12)	Nb1—Nb1^{i}	2.7913 (9)
Nb1—Cl2	2.5508 (12)	Se1—Se1^{i}	2.2995 (12)
Nb1—Cl3	2.5744 (12)		

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

The highest peak is located 0.53 Å from atom Nb1 and the deepest hole 0.75 Å from Nb1.

Data collection: *XPREP* in *SHELXTL* (Sheldrick, 2003); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *XPREP* in *SHELXTL*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2001).

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