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Preparation, Crystal Structure, and Properties of the Mixed-Valence Compound $Nb_3Se_5Cl_7$

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The new compound $Nb_3Se_5Cl_7$ was prepared by heating $2NbSe_2Cl_2 + 1NbCl_4$ at 530°C for 2–3 weeks. The compound is monoclinic with $a = 7.599$, $b = 12.675$, $c = 8.051$ Å; $\beta = 106.27°$; space group $P2_1/m$. The corresponding bromide, $Nb_3Se_5Br_7$ (obtained by decomposition of $NbSe_2Br_2$ under $NbSeBr_3$), is isotypic with $a = 7.621$, $b = 12.833$, $c = 8.069$ Å; $\beta = 106.21°$. from the crystal structure and XPS spectra it follows that $Nb_3Se_5Cl_7$ can be formulated as: $[Nb_2^{4+}\,Nb_1^{5+}\,(Se_2)_2^{2-}\,Se_1^{2-}\,Cl_7^-]$. The structure consists of chains of composition $[Nb_2^{4+}\,(Se_2)_2^{2-}\,Cl_5^-]$, to which side chains $[Nb^{5+}\,Se^{2-}\,Cl_2^-]$ are attached. The Nb^{4+} atoms form pairs (Nb–Nb = 2.94 Å) which explains that $Nb_3Se_5Cl_7$ is a diamagnetic semiconductor with a band gap (1.59 eV at 5°K, 1.49 eV at 300°K) very similar to that of $NbSe_2Cl_2$.

Introduction

In our study of the ternary system Nb–Se–Cl (*1*) we encountered a number of new phases. Among these phases was a compound of composition $Nb_3Se_5Cl_7$. Small brown bar-shaped crystals of this compound were obtained if mixtures of $NbSe_2Cl_2$ and $NbCl_4$ in mole ratio 2:1 were heated in sealed Pyrex glass tubes in a temperature gradient of 535/525°C for two to three weeks; the reaction tubes were cooled in air. Chemical analysis—found: Nb 29.90%; Se 43.23%; Cl 26.89%; calculated for $Nb_3Se_5Cl_7$: Nb 30.24%; Se 42.83%; Cl 26.93%. The reproducibility of the synthesis was rather poor.

Above 150°C $Nb_3Se_5Cl_7$ is stable only if it is kept under $NbSeCl_3$. If the compound is heated (under $NbSeCl_3$) it undergoes a transition at 209°C (from DTA and high-temperature X-ray diagrams). Probably, this is a phase transition, since quenching from high temperatures yielded only (the room temperature form of) $Nb_3Se_5Cl_7$.

Blue–black bar-shaped crystals of the corresponding bromide, $Nb_3Se_5Br_7$, were obtained by thermal decomposition of $NbSe_2Br_2$ under $NbSeBr_3$ in a closed system. The identity of the compound was established by its isotypism with $Nb_3Se_5Cl_7$.

In the present communication we report the crystal structure and some physical properties of $Nb_3Se_5Cl_7$ (room-temperature form).

Structure Determination

Accurate unit-cell dimensions of $Nb_3Se_5Cl_7$ were determined from Weissenberg photographs taken with CuKα radiation and calibrated with NaCl as an internal standard. Calculation by least squares gave the values (standard deviations in units of the last decimal are given in brackets): $a = 7.599(2)$ Å, $b = 12.675(2)$ Å; $c =$

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8.051(2) Å; $\alpha = \gamma = 90°$; $\beta = 106.27(1)°$. With a unit-cell content of $Nb_6Se_{10}Cl_{14}$ the density is calculated as 4.110 g cm^{-3}, in good agreement with the experimental value of 4.04 g cm^{-3}. For $Nb_3Se_5Br_7$ the following unit-cell dimensions were found: $a = 7.621(3)$ Å; $b = 12.833(4)$ Å; $c = 8.069(3)$ Å; $\alpha = \gamma = 90°$; $\beta = 106.21(3)°$.

The intensities of the X-ray reflections of $Nb_3Se_5Cl_7$ were measured with an Enraf–Nonius automatic three-circle diffractometer by the θ–2θ scan method; Zr-filtered MoKα radiation was used. The dimensions of the crystal were $0.04 \times 0.29 \times 0.04$ mm^3. Reliable intensities $[I > 3\sigma(I)]$ of 1309 independent reflections with $\sin\theta/\lambda < 0.88$ Å^{-1} were measured; they were corrected for Lorentz and polarization factors and for absorption $[\mu(\mathrm{Mo}) = 166\ \mathrm{cm}^{-1}]$. From the systematic absences ($0k0$ absent for k odd) the space group was derived as $P2_1$ or $P2_1/m$.

A Patterson synthesis was calculated; a number of possible (x, z) parameters were deduced from the $(u, \frac{1}{2}, w)$ maxima. Adopting space group $P2_1$ and assuming bonding distances of about 2.6 Å and nonbonding contacts of about 3.2 Å, a set of atomic positions were derived which could roughly explain the Patterson function. In this way a Nb_2Se_4 group similar to that in NbS_2Cl_2 (*2*) and $NbSe_2Cl_2$ (*1*) was found (repeated twice in the unit cell), together with four independent Cl atoms. The positions of the other atoms were derived from a difference Fourier synthesis.

Since the structure found was centrosymmetric, refinement (by full-matrix least squares) was carried out in space group $P2_1/m$. To each reflection a weight $w = 1/\sigma^2(F)$ was assigned. Atomic scattering factors were taken from Cromer and Mann (*3*) and corrected for anomalous dispersion (*4*). At the end of the refinement the discrepancy factor $R_w = \{\sum w\,(F_0 - |Fc|)^2/\sum wF_0^2\}^{1/2}$ was 0.047. The final positional and thermal parameters with their standard deviations are given in Table I; lists of observed and calculated structure factors are available from the authors on request. Three projections of the structure are shown in Fig. 1; bond distances are given in Table II.

Spectra and Physical Properties

The XPS spectrum of $Nb_3Se_5Cl_7$ was recorded with an AEI–ES 200 photoelectron spectrometer using MgKα radiation. It was compared with the spectra of $NbSe_2Cl_2$ and $NbSe_3$ which were recorded in the same way. In order to eliminate the effects of static charges on the high-ohmic compounds $Nb_3Se_5Cl_7$ and $NbSe_2Cl_2$ the binding energies of the core levels of Nb^{4+} were taken to be same as for the metallic compound $NbSe_3$. It was found that the core levels of Cl in both $Nb_3Se_5Cl_7$ and $NbSe_2Cl_2$ are sharp and appear at the same binding energies. In contrast, the signals due to the Se and Nb core levels of Nb_3Se_5Cl are more complex than those of $NbSe_2Cl_2$ (Fig. 2) and appear to consist of the double number of components. The Se-3*d* and Nb–3*d* signals of $Nb_3Se_5Cl_7$ were deconvoluted, assuming the signals to consist of a number of components with equal linewidth, but different intensities and binding energies; the results are given in Table III. It is found that the high-energy components of the Se signals of $Nb_3Se_5Cl_7$ correspond to the signals of $NbSe_2Cl_2$, as do the low-energy components of the Nb signals.

The optical absorption spectrum of $Nb_3Se_5Cl_7$ between 10 000 and 16 000 cm^{-1}, taken at 5.1 and 84.2°K (Fig. 3), shows only an allowed direct band–band transition. The absorption edges at these temperatures (1.59 eV and 1.58 eV, respectively) are similar to those of the allowed indirect transition of $NbSe_2Cl_2$ (*1*) (Table IV). The spectrum of $Nb_3Se_5Cl_7$ at 298.8°K is more complex; absorption starts at an energy similar to that of the forbidden direct

TABLE I

POSITIONAL AND THERMAL (IN 10^{-2} Å^2) PARAMETERS OF $Nb_3Se_5Cl_7$[a]

	Nb(1)	Nb(2)	Se(1)	Se(2)	Se(3)	Cl(1)	Cl(2)	Cl(3)	Cl(4)	Cl(5)
x	0.0233(2)	0.4061(4)	0.1850(3)	0.2870(3)	0.4303(5)	0.9455(10)	0.8238(11)	0.2892(11)	0.1460(6)	0.6094(7)
y	0.3900(1)	0.25	0.4735(2)	0.5303(2)	0.25	0.25	0.25	0.25	0.3818(4)	0.3836(4)
z	0.0608(2)	0.4777(4)	0.8430(3)	0.1244(3)	0.7631(5)	0.8181(9)	0.1468(10)	0.1250(9)	0.4017(6)	0.4596(6)
u_{11}	1.37(9)	1.99(15)	2.36(12)	1.75(12)	4.68(24)	2.29(38)	1.93(42)	2.13(43)	2.12(25)	2.82(26)
u_{22}	0.42(7)	0.87(13)	0.93(10)	0.88(10)	3.41(22)	0.71(31)	0.80(35)	0.68(34)	1.66(25)	1.02(22)
u_{33}	1.06(8)	1.07(14)	1.67(12)	1.80(12)	2.51(20)	1.41(36)	1.64(40)	0.97(38)	1.36(23)	1.84(23)
u_{12}	−0.06(8)	0	0.10(9)	−0.21(9)	0	0	0	0	0.37(23)	−0.52(23)
u_{13}	0.28(7)	0.11(11)	1.11(10)	0.11(9)	1.31(18)	0.52(30)	0.96(33)	0.52(32)	0.24(19)	0.96(19)
u_{23}	0.10(9)	0	0.09(9)	0.18(9)	0	0	0	0	−0.02(24)	−0.03(21)

[a] Atoms lie in positions $4(f)$: $\pm(x\ y\ z;\ x, \frac{1}{2}-y, z)$ and $2(e)$: $\pm(x \frac{1}{4} z)$ of space group $P2_1/m$; standard deviations in units of the last decimal are given in brackets.

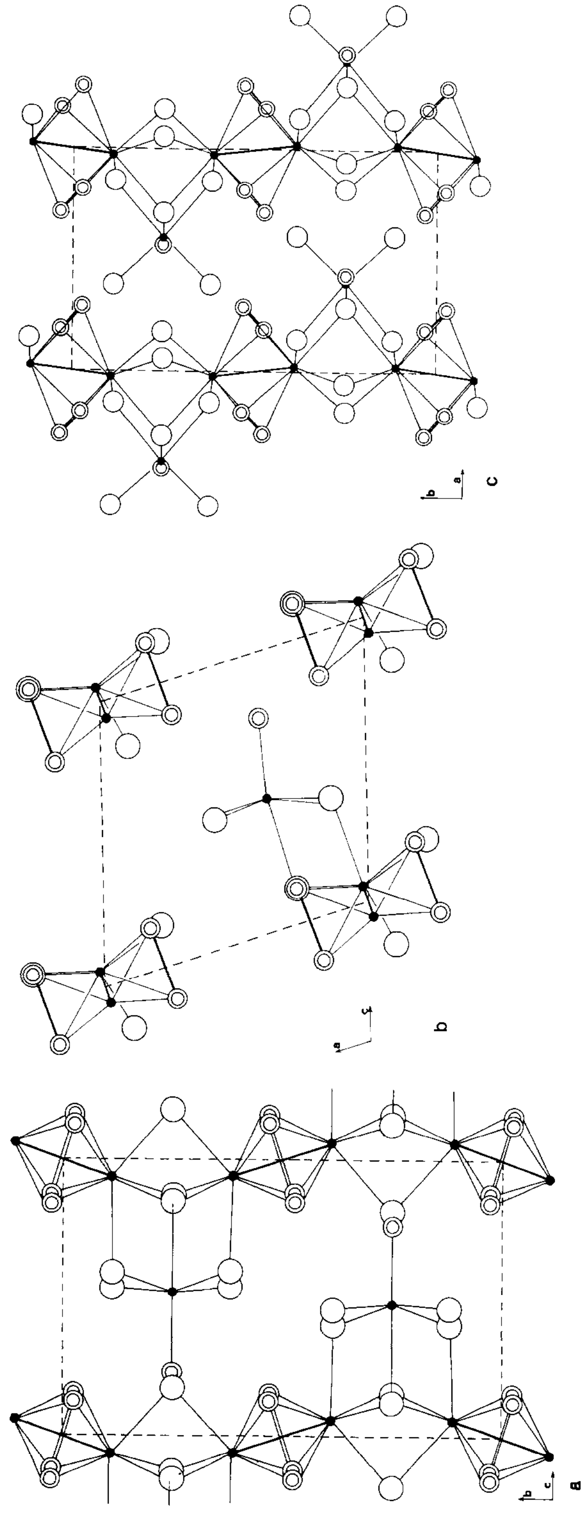

FIG. 1. Three projections of the structure of $Nb_3Se_5Cl_7$. Niobium atoms are indicated by black circles, selenium atoms are indicated by double circles, chlorine by open circles; Nb–Nb and Se–Se bonds are shown by thick lines. (a) Projection along the *a* axis; (b) Projection along the *b* axis; for clarity only atoms with $-0.115 < y < 0.385$ are shown; (c) Projection along the *c* axis.

TABLE II

BONDING DISTANCES IN $Nb_3Se_5Cl_7$ (IN Å)[a]

Nb(1)–1 Nb(1)	2.944(3)	Nb(2)–1 Se(3)	2.254(4)
–1 Se(1)	2.605(3)	–1 Cl(3)	2.727(8)
–1 Se(1)	2.629(3)	–2 Cl(4)	2.529(7)
–1 Se(2)	2.615(3)	–2 Cl(5)	2.323(7)
–1 Se(2)	2.620(3)		
–1 Cl(1)	2.582(5)	Cl(1)–2 Nb(1)	2.582(5)
–1 Cl(2)	2.553(7)		
–1 Cl(3)	2.629(9)	Cl(2)–2 Nb(1)	2.553(7)
–1 Cl(4)	2.642(5)		
		Cl(3)–2 Nb(1)	2.629(9)
Se(1)–1 Se(2)	2.295(3)	–1 Nb(2)	2.727(8)
–1 Nb(1)	2.605(3)		
–1 Nb(1)	2.629(3)	Cl(4)–1 Nb(1)	2.642(5)
		–1Nb(2)	2.529(7)
Se(2)–1 Se(1)	2.295(3)		
–1 Nb(1)	2.615(3)	Cl(5)–1 Nb(2)	2.323(7)
–1 Nb(1)	2.620(3)		
Se(3)–1 Nb(2)	2.254(4)		

[a] Standard deviations in units of the last decimal are given in brackets.

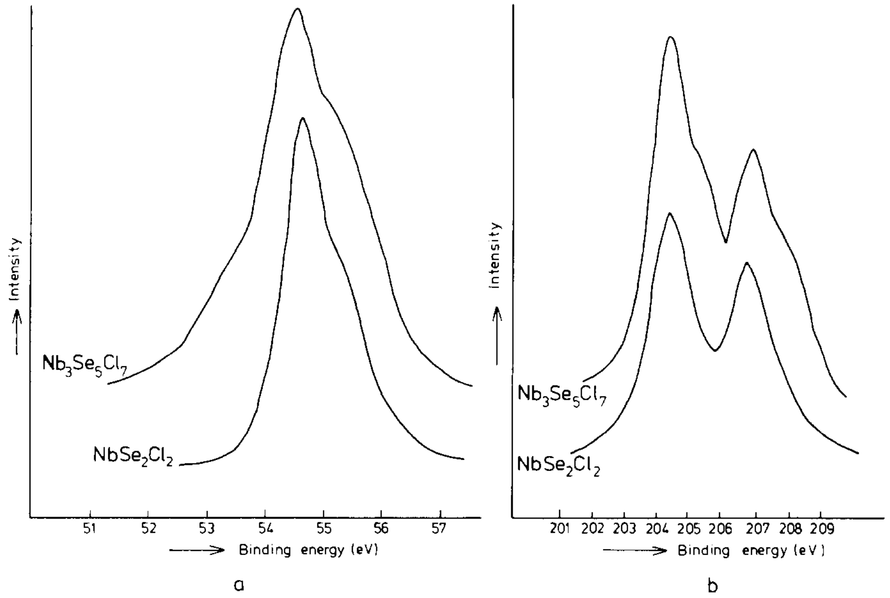

FIG. 2. Computer fits of the XPS signals due to (a) Se-3d and (b) Nb-3d of $Nb_3Se_5Cl_7$ and $NbSe_2Cl_2$.

TABLE III

BINDING ENERGIES, LINEWIDTH AND RELATIVE INTENSITIES OF THE COMPONENTS OF THE Se-3*d* AND Nb-3*d* XPS SIGNALS OBTAINED BY A COMPUTER FIT; ERRORS ARE 0.1 eV

	$Nb_3Se_5Cl_7$				$NbSe_2Cl_2$			
Component	Binding energy eV	Width eV	I_{obs}	I^a_{calc}	Binding energy eV	Width eV	I_{obs}	I_{calc}
Se^{2-}–$3d_{5/2}$	53.3	1.2	2.8	3				
Se^{2-}–$3d_{3/2}$	(54.4)	1.2	13.7	2				
Se_2^{2-}–$3d_{5/2}$	54.6			12	54.7	1.4	3.1	3
Se_2^{2-}–$3d_{3/2}$	55.5	1.2	8.4	8	55.6	1.4	2.0	2
Nb^{4+}–$3d_{5/2}$	204.3	1.3	5.9	6	204.2	1.5	2.9	3
Nb^{5+}–$3d_{5/2}$	205.3	1.3	3.2	3				
Nb^{4+}–$3d_{3/2}$	207.0	1.3	4.0	4	206.8	1.5	2.0	2
Nb^{5+}–$3d_{3/2}$	208.0	1.3	1.9	2				

[a] From formula [Nb_2^{4+} Nb_1^{5+} $(Se_2)_2^{2-}$ Se_1^{2-} Cl_7^-].

transition of $NbSe_2Cl_2$, while the slope of the absorption curve increases at an energy close to that of the allowed indirect transition of $NbSe_2Cl_2$ at 300°K.

$Nb_3Se_5Cl_7$ shows nearly temperature-independent diamagnetism with $\chi_m = -340 \times 10^{-6}$ c.g.s. units per mole of $Nb_3Se_5Cl_7$ (not corrected for core diamagnetism) in the range 100–300°K. Some of the crystals of $Nb_3Se_5Cl_7$ were large enough to allow a study of the electrical properties by a four-point contact method. Semiconducting behavior was found with an activation energy of 0.63 eV (probably almost intrinsic conduction) and a resistivity of ~10^8 ohm cm at room temperature.

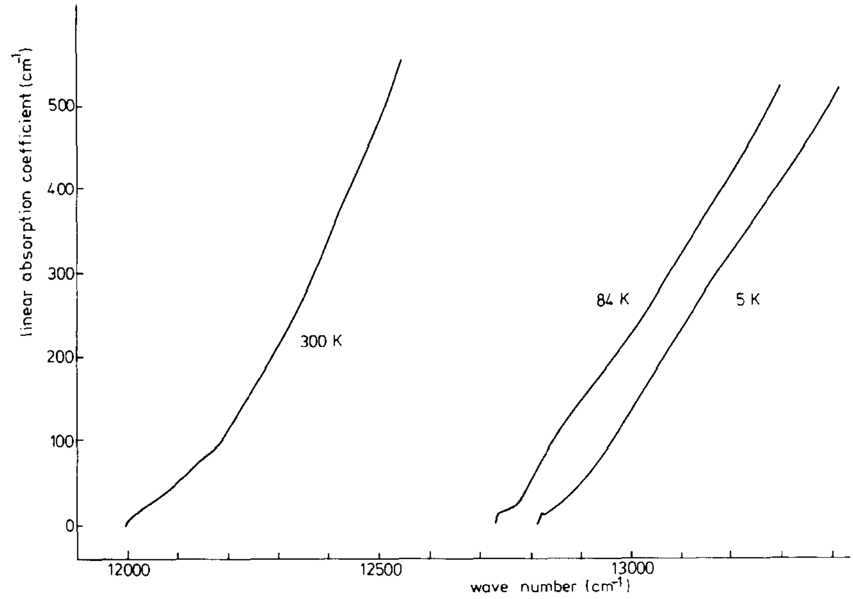

FIG. 3. The optical absorption edge of $Nb_3Se_5Cl_7$ at various temperatures.

TABLE IV

WAVE NUMBERS (cm^{-1}) OF THE THRESHOLD ENERGIES DERIVED FROM THE ABSORPTION SPECTRA OF $Nb_3Se_5Cl_7$ AND $NbSe_2Cl_2$[a]

$Nb_3Se_5Cl_7$		$NbSe_2Cl_2$		
T (K)	E	T (K)	E_i	E_f
5.1	12 811	5.6	12 760	12 936
84.2	12 764	78.6	12 709	12 786
298.8	11 998; ca 12 200	300.2	12 147	11 998

[a] E_i refers to the indirect gap, E_f to the forbidden direct gap of $NbSe_2Cl_2$.

Discussion

From Fig. 1 and Table II it is evident that the Nb(1) atoms form pairs (Nb–Nb = 2.94 Å), while Nb(2) is isolated. Similarly, the atoms Se(1) and Se(2) form a Se_2 group, the Se(1)–Se(2) distance (2.30 Å) corresponding to a single bond; Se(3) is coordinated to one metal atom only, at a remarkably short distance. The Cl atoms are bonded to one, two, or three Nb atoms, the bond distances increasing with the coordination number (Table II).

In an ionic formalism the Se_2 groups may be described as $(Se_2)^{2-}$, Se(3) as Se^{2-} and the chlorines as Cl^-; the total charge on the anions then is −13 per formula unit. Electroneutrality then requires that two Nb per formula unit have an ionic charge of +4, the third Nb a charge of +5. The compound may thus be described as: $[Nb_2^{4+}\,Nb_1^{5+}\,(Se_2)_2^{2-}\,Se_1^{2-}\,Cl_7^-]$, in good agreement with the XPS spectrum (Table III).

There are several reasons to identify the Nb(1) atoms as Nb^{4+}, the Nb(2) atom as Nb^{5+}. In the first place a charge of −3.83 is observed for the coordination sphere of Nb(1) and a charge of −5.33 for the coordination sphere of Nb(2); (a Cl^- ion coordinated to two metal atoms is taken as contributing a charge of −0.50 to each coordination sphere, etc.). The electrostatic valence rule (*5*) thus suggests Nb(1) to be Nb^{4+} and Nb(2) Nb^{5+}. Moreover, the occurrence of Nb_2 pairs is quite common for Nb^{4+} compounds, such as $NbSe_2Cl_2$ (*1*) and many other compounds (*6*). Indeed, the "cage" formed by the Nb(1) pairs and Se(1)–Se(2) groups of $Nb_3Se_5Cl_7$ (Fig. 1) is very similar to the cages found in the Nb^{4+} compounds NbS_2Cl_2 (*2*) and $NbSe_2Cl_2$ (*1*). Due to the presence of Nb^{4+} ($4d^1$) in pairs, these compounds are diamagnetic semiconductors, as is $Nb_3Se_5Cl_7$.

Although $Nb_3Se_5Cl_7$ is a mixed-valence compound, its optical absorption spectrum closely resembles that of $NbSe_2Cl_2$; no charge-transfer band which could be assigned to an electron transfer from Nb^{4+} to Nb^{5+} or Se^{2-} to Se^- is observed below 2.0 eV. This is ascribed to the occurrence of Nb^{+} and Se^- in pairs. In the case of $(Se_2)^{2-}$ the σ_u^* ($4p$) level, which is the possible acceptor level, is antibonding and thus, destabilized by the pair formation (*7*). For Nb^{4+}, in contrast, it is the potential donor level $4d^1$ which is stabilized by the formation of a metal–metal bond. In both cases the net result is that the energy required for an electron transfer $Se^{2-} \rightarrow Se^-$ or $Nb^{4+} \rightarrow Nb^{5+}$ is increased. This phenomenon has been known for compound containing an anion in two valences, such as ZrS_3 and $ZrSe_3$ (*7*), but to our knowledge this is the first case where it has been considered for mixed-valence cation compounds.

From Fig. 1 it is evident that the structure of $Nb_3Se_5Cl_7$ consists of chains. The elements of the chain are formed by Nb_2Se_4 cages consisting of a Nb(1) pair perpendicular to the plane of two Se(1)–Se(2) pairs, as in NbS_2Cl (*2*) and $NbSe_2Cl_2$ (*1*); these elements are linked to chains by sharing Cl(1, 2, 3) triangles. Moreover, each Nb(1) atom carries a Cl(4) ligand, resulting in a coordination number of six ($2Se_2^{2-} + 4Cl^-$). The chains described carry side tails formed by the Nb(2), Se(3) and Cl(5) atoms; these side tails are linked to the backbone of the chains by sharing Cl(3, 4, 4) triangles. The coordination of Nb(2) is approximately octahedral; the remarkably short Nb(2)–Se(3) distance (2.25 Å) suggests the existence of a selenoniobyl group.

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