References

Aurivillius, K. & Nilsson, B. A. (1974). *Z. Kristallogr.* **141**, 1–10.
Calvo, C. (1968). *Am. Mineral.* **53**, 742–750.
Calvo, C. & Stephens, J. S. (1968). *Can. J. Chem.* **46**, 903–915.
Engel, G. & Klee, W. E. (1970). *Z. Kristallogr.* **132**, 332–339.
Kostiner, E. & Rea, J. R. (1974). *Inorg. Chem.* **13**, 2876–2883.
Lidin, S., Fogden, A. & Larsson, A.-K. (1993). To be published.
Lundgren, J.-O. (1982). Report No. UUIC-BB-4-05. Univ. of Uppsala, Sweden.
Stephens, J. S. (1967). Dissertation. McMaster Univ., Hamilton, Canada.

Acta Cryst. (1993). C**49**, 786–788

A New One-Dimensional Compound: Synthesis and Structure of $InNb_3(Se_2)_6$

Deng Shuiquan,* Zhuang Honghui,
Huang Jinshun and Huang Jingling

Fujian Institute of Research on the Structure of Matter,
State Key Laboratory of Structural Chemistry,
Chinese Academy of Sciences, Fuzhou, Fujian 350002,
People's Republic of China

(*Received* 3 *July* 1992; *accepted* 13 *October* 1992)

Abstract

The new one-dimensional compound, indium niobium selenide, was synthesized by high-temperature solid-state reactions. The structure is composed of $[Nb_3(Se_2)_6]_\infty$ chains running along the *c* axis with In atoms intercalated between these chains. All the Nb atoms have rectangular antiprismatic coordination environments. All the Se atoms in the structure are in the form of Se_2 dimers with Se—Se distances of 2.325 (2) and 2.356 (2) Å.

Comment

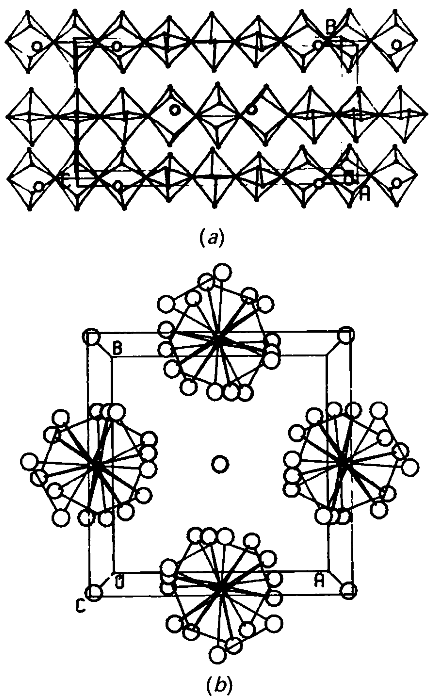
Chemical investigations in the field of chalcogen-rich niobium and tantalum chalcogenides have led to the characterization of many new one-dimensional or quasi-one-dimensional compounds. These include, for example, MX_3 (M = Nb, Ta; X = S, Se) (Sambong *et al.*, 1977; Rijnsdorp & Jellinek, 1978; Hodeau, *et al.*, 1978; Bjerkelund, Fermor & Kjerkshus, 1966), $(MX_4)_nY$ (M = Nb, Ta; X = S, Se; Y = Br, I) (Gressier, Meerschaut, Guemas, Rouxel & Monceau, 1984), Nb_2Se_9 (Meerschaut, Guemas, Berger & Rouxel, 1979) *etc.* The structures and properties of low-dimensional metal chalcogenides have been reviewed by Rouxel (1986) and Gressier *et al.* (1984). Low-dimensional materials are of great interest, because they exhibit some remarkable properties such as the Peierls transition, charge-density wave (CDW) *etc.* Studies of the collective dynamics of charge-density waves and other low-dimensional phenomena have promoted the need for the new materials to support experimentally the growing development of theories. During the investigations of ternary Nb and Ta selenides, we have recently synthesized a new pseudo-one-dimensional compound, $InNb_3(Se_2)_6$.

Crystals of $InNb_3(Se_2)_6$ were obtained initially from a reaction mixture of Nb_2Se_9 and In in approximately stoichiometric proportions at 773–873 K. Better-quality single crystals used in the struture determination were obtained by a vapour transport method at 923 K with a small amount of selenium as the transport agent.

The title compound is isostructural with $I_{0.33}NbSe_4$ (Meerschaut, Palvadeau & Rouxel, 1977). The atomic coordinates and selected distances and angles are given in Tables 1 and 2, respectively. As shown in Fig. 1, the structure is composed of $[Nb_3(Se_2)_6]_\infty$ chains with the In atoms intercalated between them. There exists a periodic sequence of distances (in Å) $\cdots Nb(1^{ii})$—3.037—$Nb(1^i)$—3.248—Nb(2)—3.248—Nb(1)$\cdots$ in a $[Nb_3(Se_2)_6]_\infty$ chain (see Fig. 2). The bonding between the chains is very weak and is of typical van der Waals type. The $Nb(1^i)$—$Nb(1^{ii})$ bonding distance of 3.037 Å is somewhat longer than the values found in NbS_2Cl_2 (2.871 Å), $NbSe_2Cl_2$ (2.973 Å) (Rijnsdorp, de Lange & Wiegers, 1979) and $Nb_3Se_5Cl_7$ (2.94 Å) (Rijnsdorp & Jellinek, 1979), but a Nb—Nb bond of similar length (3.029 Å) has been found in $NbCl_4$ (Taylor, Calabrese & Larsen, 1977) and even longer Nb—Nb bonds (3.12–3.16 Å) in the oxide halides $NbOX_2$ (X = Cl, Br, I; Schafer & Schnering, 1964). In comparison with the much longer Nb—Nb bonds (3.308 Å) in α-NbI_4 (Dahl & Wampler, 1962), the Nb(1)—Nb(2) distance of 3.248 Å should also involve chemical bonding. According to the periodic sequence of Nb—Nb distances along the *c* axis, the $Nb_3(Se_2)_6$ unit can be viewed formally as the building block of a chain. The reason for our not choosing the $NbSe_4$ unit as the building block is that there are two crystallographically independent Nb atoms in each chain and the coordination polyhedra $[Nb(1)(Se_2)_4$ and $Nb(2)(Se_2)_4]$ have crystallographic C_2 and D_2 symmetry, respectively; a simple $NbSe_4$ unit cannot therefore represent the basic unit from which the chain is constructed. The $Nb_3(Se_2)_6$ units are linked together through bridging $(Se_2)^{2-}$ ligands as well as through Nb—Nb bonding to form infinite $[Nb_3(Se_2)_6]_\infty$ chains parallel to the *c* axis. Considering the long distance (6.69 Å) between the centre lines of different chains, the metal–metal interaction is very anisotropic and typical of the one-dimensional character.

0108-2701/93/040786-03\$06.00

The Nb—Se and Se—Se bond lengths are in agreement with the reported values for other niobium selenides such as $\mathrm{NbSe_3}$ (Hodeau *et al.*, 1978) and $\mathrm{I_{0.33}NbSe_4}$ (Meerschaut, Palvadeau & Rouxel, 1977).


(*a*)

(*b*)

Fig. 1. (*a*) Perspective view of $\mathrm{InNb_3(Se_2)_6}$ along the *a* axis. Atoms corresponding to $x < 0.25$ have been omitted. (*b*) Perspective view of $\mathrm{InNb_3(Se_2)_6}$ along the *c* axis. Atoms corresponding to $z < 0.5$ have been omitted. The large isolated circles are In atoms.

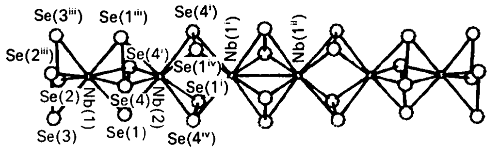


Fig. 2. Section of an infinite $[\mathrm{Nb_3(Se_2)_6}]_\infty$ chain with atom labelling.

It is interesting to notice the vacant one-dimensional channels between different chains in which the In atoms are intercalated. All the In atoms are located on the centre lines of the channels along the *c* axis; every In atom has a tetragonal pyramidal configuration with four equidistant Se atoms contributed by four different $[\mathrm{Nb_3(Se_2)_6}]_\infty$ chains. The height of the tetragonal pyramid $\mathrm{InSe_4}$ is 0.364 Å, while that of $\mathrm{ISe_4}$ is 0.592 Å; this is the main difference between the structures of $\mathrm{InNb_3(Se_2)_6}$ and $\mathrm{I_{0.33}NbSe_4}$. Along the centre line, the In atoms are well separated from one another [$d(\mathrm{In—In}) \geq 5.345$ Å]. The In—Se distance of 3.233 Å is much larger than the normal In—Se bond length (~ 2.6 Å) (Benoit, Charpin & Djega-Mariadassou, 1983), which indicates very weak interaction between Se and In atoms and may explain the large thermal motion of the In atom. As in $\mathrm{In_{\sim3}Mo_{15}Se_{19}}$ [In(1)—Se ≥ 3.162 Å] (Gruttner & Yvon, 1979), the guest In atoms can reasonably be considered as intercalated into the host one-dimensional framework. Considering the large difference between the electronegativities of indium and iodine, which will have different effects on the electronic states in the $[\mathrm{Nb_3(Se_2)_6}]_\infty$ chain, different electrical behaviour may be expected in the two compounds, and appropriate studies are being conducted at the present time.

Experimental

Crystal data

$\mathrm{InNb_3(Se_2)_6}$
$M_r = 1341.06$
Tetragonal
$P4/mnc$
$a = 9.450$ (1) Å
$c = 19.068$ (9) Å
$V = 1703$ (1) Å^3
$Z = 4$
$D_x = 5.23$ Mg m^{-3}
$D_m = 5.2$ (1) Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 9$–$11°$
$\mu = 28.57$ mm^{-1}
$T = 300$ K
Square prism
$0.14 \times 0.05 \times 0.05$ mm
Black

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min} = 0.618$, $T_{\max} = 0.967$
1284 measured reflections
1284 independent reflections

499 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 30°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 26$
3 standard reflections monitored every 150 reflections intensity variation: 3.6%

Refinement

Refinement on *F*
Final $R = 0.045$
$wR = 0.051$
$S = 1.15$
499 reflections
43 parameters
$w = 1/[\sigma^2(F_o) + (0.02|F_o|)^2 + 1.0]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 1.35$ e Å^{-3}
$\Delta\rho_{\min} = 1.65$ e Å^{-3}

Extinction correction: Zachariasen (1963)
Extinction coefficient: $g = 8.9 \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
In	0.0000	0.0000	0.1402 (1)	2.12 (4)
Nb(1)	0.0000	0.5000	0.0796 (1)	0.71 (2)
Nb(2)	0.0000	0.5000	0.2500	0.63 (3)
Se(1)	0.1259 (1)	0.3151 (1)	0.16147 (7)	1.00 (2)
Se(2)	0.2249 (2)	0.4836 (2)	0.0000	0.62 (3)
Se(3)	−0.1075 (2)	0.3003 (2)	0.0000	1.30 (4)
Se(4)	−0.2148 (1)	0.4529 (1)	0.17180 (8)	1.11 (2)

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°)

Nb(1^{i})—Nb(1^{ii})	3.037 (3)	Nb(1)—Nb(2)	3.248 (2)
Nb(1)—Se(1)	2.627 (2)	Nb(1)—Se(2)	2.617 (2)
Nb(1)—Se(3)	2.627 (2)	Nb(1)—Se(4)	2.721 (2)
Nb(2)—Se(1)	2.705 (1)	Nb(2)—Se(4)	2.558 (1)
Se(1)—Se(4^{iii})	2.356 (2)	Se(2)—Se(3^{iii})	2.325 (2)
In—Se(1)	3.233 (1)		
Nb(1)—Nb(2)—Nb(1^{i})	180.00	Nb(2)—Nb(1^{i})—Nb(1^{ii})	180.00
Se(1)—Nb(1)—Se(1^{iii})	107.15 (8)	Se(1)—Nb(1)—Se(2)	86.42 (4)
Se(1)—Nb(1)—Se(2^{iii})	138.74 (4)	Se(1)—Nb(1)—Se(3)	92.32 (4)
Se(1)—Nb(1)—Se(3$^{i(1)ii}$)	130.24 (4)	Se(1)—Nb(1)—Se(4)	81.12 (6)
Se(1)—Nb(1)—Se(4^{iii})	52.23 (4)	Se(2)—Nb(1)—Se(2^{iii})	109.05 (8)
Se(2)—Nb(1)—Se(3)	86.34 (6)	Se(2)—Nb(1)—Se(3^{iii})	52.62 (5)
Se(2)—Nb(1)—Se(4)	116.15 (5)	Se(2)—Nb(1)—Se(4^{iii})	77.21 (4)
Se(3)—Nb(1)—Se(3^{iii})	109.37 (7)	Se(3)—Nb(1)—Se(4)	88.13 (4)
Se(3)—Nb(1)—Se(4^{iii})	141.18 (4)	Se(4)—Nb(1)—Se(4^{iii})	99.57 (7)
Se(1)—Nb(2)—Se(1^{iii})	102.78 (4)	Se(1)—Nb2—Se(1^{i})	79.70 (4)
Se(1)—Nb(2)—Se(1^{iv})	163.26 (3)	Se(1)—Nb(2)—Se(4)	82.70 (4)
Se(1)—Nb(2)—Se(4^{iii})	53.09 (3)	Se(1)—Nb(2)—Se(4^{i})	143.12 (3)
Se(1)—Nb(2)—Se(4^{iv})	85.84 (4)	Se(4)—Nb(2)—Se(4^{iii})	108.68 (4)
Se(4)—Nb(2)—Se(4^{i})	128.02 (4)	Se(4)—Nb(2)—Se(4^{iv})	93.66 (4)

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

The crystals of $InNb_3(Se_2)_6$ show metallic lustre and are stable in air. A microanalysis of single crystals was made with a Jeol scanning electron microscope. The experimental values in molar ratio are 1.1:2.7:11.7 (In:Nb:Se). The density was measured by the micropycnometer method in toluene.

The data were collected using scan rates of 5–16° min^{-1} and a scan width of (1.5+0.35tanθ)°. Refinement was by full-matrix least-squares methods. Programs used to solve structure: *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Other programs used: *SDP* (Frenz, 1978). Calculations performed on a VAX 785 computer.

This work was supported financially by the National Science Foundation of China.

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55752 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1022]

References

Benoit, P., Charpin, P. & Djega-Mariadassou, C. (1983). *Mat. Res. Bull.* **18**, 1047–1057.

Bjerkelund, E., Fermor, J. H. & Kjerkshus, A. (1966). *Acta Chem. Scand.* **20**, 1836–1842.

Dahl, F. L. & Wampler, D. L. (1962). *Acta Cryst.* **15**, 903–911.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Gressier, P., Meerschaut, A., Guemas, L., Rouxel, J. & Monceau, P. (1984). *J. Solid State Chem.* **51**, 141–151.

Gruttner, A. & Yvon, K. (1979). *Acta Cryst.* **B35**, 285–292.

Hodeau, J. L., Marezio, M., Roucau, C., Ayroles, R., Meerschaut, A., Rouxel, J. & Monceau, P. (1978). *J. Phys. C*, **11**, 4117–4134.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Meerschaut, A., Guemas, L., Berger, R. & Rouxel, J. (1979). *Acta Cryst.* **B35**, 1747–1750.

Meerschaut, A., Palvadeau, P. & Rouxel, J. (1977). *J. Solid State Chem.* **20**, 21–27.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Rijnsdorp, J. & Jellinek, F. (1978). *J. Solid State Chem.* **25**, 325–328.

Rijnsdorp, J. & Jellinek, F. (1979). *J. Solid State Chem.* **28**, 149–156.

Rijnsdorp, J., de Lange, G. J. & Wiegers, G. A. (1979). *J. Solid State Chem.* **30**, 365–373.

Rouxel, J. (1986). *J. Solid State Chem.* **64**, 305–321.

Sambong, T., Tsutsumi, K., Shiozaki, K., Yamamoto, M., Yamaya, K. & Abe, Y. (1977). *Solid State Commun.* **22**, 729–731.

Schafer, H. & Schnering, H. G. (1964). *Angew. Chem.* **76**, 833.

Taylor, D. R., Calabrese, J. C. & Larsen, E. M. (1977). *Inorg. Chem.* **16**, 721–722.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1993). C**49**, 788–790

Structure of 1-Benzhydryl-4-(2-benzoylethyl)piperazinium Tetrachlorocuprate(II) Hydrate

JOSEF MACÍČEK

Bulgarian Academy of Sciences, Institute of Applied Mineralogy, Rakovski Str. 92, 1000 Sofia, Bulgaria

JOVKA TCHOLAKOVA AND MILENA PARVANOVA

Sofia Technology University, Bul. Kl. Ohridski 8, 1156 Sofia, Bulgaria

(*Received* 24 *April* 1992; *accepted* 17 *November* 1992)

Abstract

The structure consists of bulky $Ph_2CH(C_4H_{10}N_2)CH_2CH_2(CO)Ph^{2+}$ cations extended along the *c* axis, isolated $[CuCl_4]^{2-}$ anions and a disordered water molecule scattered in a channel running parallel to the *a* axis through the centre of the unit cell. Both the tertiary-amine-group

0108-2701/93/040788-03$06.00