$wR = 0.038$
$S = 1.95$
1789 reflections
119 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.0053$
$\Delta\rho_{\max} = 0.9$ e Å^{-3}
$\Delta\rho_{\min} = -0.7$ e Å^{-3}
Extinction coefficient: $1.17(4) \times 10^{-6}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Ba(1)—O(13$^{\rm i}$)	2.641 (2)	Mg—O(11$^{\rm ix}$)	2.046 (3)
Ba(1)—O(12$^{\rm ii}$)	2.702 (2)	Mg—O(21)	2.048 (2)
Ba(1)—O(22$^{\rm iii}$)	2.703 (2)	Mg—O(23$^{\rm ii}$)	2.059 (2)
Ba(1)—O(22)	2.732 (2)	Mg—O(14$^{\rm x}$)	2.061 (2)
Ba(1)—O(24$^{\rm iv}$)	2.823 (3)	Mg—O(13)	2.084 (3)
Ba(1)—O(11$^{\rm v}$)	2.917 (3)	Mg—O(12)	2.390 (3)
Ba(1)—O(14$^{\rm v}$)	2.952 (2)	P(1)—O(12)	1.512 (2)
Ba(1)—O(23$^{\rm iii}$)	3.114 (3)	P(1)—O(11)	1.513 (2)
Ba(2)—O(12)	2.731 (3)	P(1)—O(13)	1.534 (2)
Ba(2)—O(21$^{\rm vi}$)	2.732 (2)	P(1)—O(14)	1.552 (2)
Ba(2)—O(23)	2.733 (3)	P(2)—O(21)	1.515 (2)
Ba(2)—O(13$^{\rm vi}$)	2.747 (2)	P(2)—O(22)	1.517 (2)
Ba(2)—O(14)	2.776 (2)	P(2)—O(23)	1.545 (2)
Ba(2)—O(24$^{\rm vii}$)	2.789 (2)	P(2)—O(24)	1.549 (2)
Ba(2)—O(24$^{\rm viii}$)	2.898 (2)		
O(11$^{\rm ix}$)—Mg—O(21)	173.88 (9)	O(21)—Mg—O(12)	88.01 (8)
O(11$^{\rm ix}$)—Mg—O(23$^{\rm ii}$)	85.98 (8)	O(23$^{\rm ii}$)—Mg—O(14$^{\rm x}$)	112.27 (8)
O(11$^{\rm ix}$)—Mg—O(14$^{\rm x}$)	89.44 (8)	O(23$^{\rm ii}$)—Mg—O(13)	99.03 (8)
O(11$^{\rm ix}$)—Mg—O(13)	86.27 (8)	O(23$^{\rm ii}$)—Mg—O(12)	164.35 (7)
O(11$^{\rm ix}$)—Mg—O(12)	95.34 (8)	O(14$^{\rm x}$)—Mg—O(13)	148.02 (8)
O(21)—Mg—O(23$^{\rm ii}$)	89.42 (8)	O(14$^{\rm x}$)—Mg—O(12)	83.35 (8)
O(21)—Mg—O(14$^{\rm x}$)	96.04 (8)	O(13)—Mg—O(12)	65.56 (7)
O(21)—Mg—O(13)	90.48 (8)		

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, 1 - y, -z$; (iv) $-x, 1 - y, -z$; (v) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (viii) $1 + x, y, z$; (ix) $1 - x, 1 - y, 1 - z$; (x) $x - 1, y, z$.

Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *ORXFLS* (Busing, 1971, locally modified by P. Laruelle). Molecular graphics: *ORTEP*III (Burkett & Johnson, 1996); *MOLVIEW* (Cense, 1990). Geometric calculations: *ORFFE* (Busing, Martin & Levy, 1964).

The authors thank A. Mazurier (Laboratoire de Physique de la Faculté des Sciences pharmaceutiques et biologiques, Université René Descartes, Paris) for intensity data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1147). Services for accessing these data are described at the back of the journal.

References

Becker, P. J. & Coppens, P. (1975). *Acta Cryst.* A**31**, 417–425.
Brown, I. D. & Wu, K. K. (1976). *Acta Cryst.* B**32**, 1957–1959.
Burkett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Busing, W. R. (1971). *Acta Cryst.* A**27**, 683–684.
Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.
Cense, J. M. (1990). *Stud. Phys. Theor. Chem.* **71**, 763–766.
Debaerdemaeker, T., Germain, G., Main, P., Refaat, L. S., Tate, C. & Woolfson, M. M. (1988). *Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
Elbali, B., Boukhari, A., Aride, J., Belaiche, M., Abraham, F. & Drillon, M. (1994). *Eur. J. Solid State Inorg. Chem.* **31**, 61–73.
Elbali, B., Boukhari, A., Holt, E. M. & Aride, J. (1993). *Acta Cryst.* C**49**, 1131–1133.
Hoffman, M. V. (1965). *J. Electrochem. Soc.* **110**, 1223–1227.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Acta Cryst. (1997). C**53**, 1743–1745

A New Structural Variation of Nb_3YX_7 Compounds: Monoclinic Nb_3SI_7

Peter Josef Schmidt and Gerhard Thiele

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21a, D-79104 Freiburg, Germany. E-mail: schmidt@sapphire.chemie.uni-freiburg.de

(*Received 18 March 1997; accepted 2 June 1997*)

Abstract

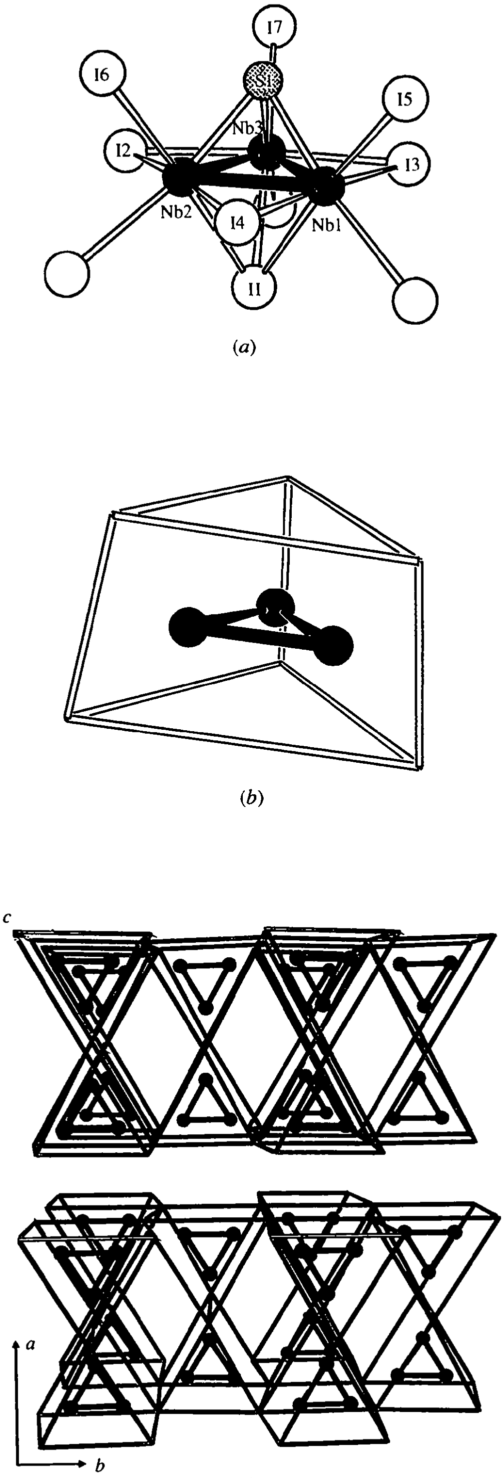
Monoclinic triniobium sulfide heptaiodide, *m*-Nb_3SI_7, was obtained by reaction of the elements in evacuated sealed fused silica tubes at 1105 K. The structure comprises $[Nb_3SI_{10}]^{3-}$ clusters containing Nb triangles bicapped by μ_3-I and μ_3-S atoms. The clusters are linked by terminal I atoms to form dimeric units with a crystallographic center of symmetry. These dimeric units are cross-linked by the remaining terminal I atoms to form a novel two-dimensional structure.

Comment

Triangular Nb_3 cluster compounds Nb_3X_8 and Nb_3YX_7 (X = Cl, Br, I; Y = S, Se, Te) are well known (Simon & von Schnering, 1966; Furuseth, Hönle, Miller & von Schnering, 1988; Miller, 1995). Compounds with composition Nb_3SI_7 show a remarkable structural diversity with different cluster units (Miller & Lin, 1994; Miller, 1995). The bicapped 42 electron cluster $[Nb_3SI_{10}]^{3-}$, in contrast to the 42 electron clusters in $[Nb_3SI_{12}]^{5-}$ and $[Nb_3S_2I_{11}]^{6-}$, could only be stabilized in the solid state by co-condensation with NbI_5 monomers to form a further two-dimensional network of composition Nb_3SI_7.

The title compound, monoclinic Nb_3SI_7, which was discovered during our search for suitable layered materials to investigate electronic surface structures, is built up exclusively from bicapped $[Nb_3SI_{10}]^{3-}$ clusters with 42 electrons. The double capping by S and I atoms leads to marked shortening of the Nb—Nb distances within the clusters [2.767 (1)–2.780 (1) Å] in comparison with the single-capped clusters in hexagonal Nb_3SI_7

Acta Crystallographica Section C
ISSN 0108-2701 © 1997



(*a*)

(*b*)

(*c*)

Fig. 1. (*a*) The $[Nb_3SI_{10}]^{3-}$ cluster unit in monoclinic Nb_3SI_7. (*b*) The trigonal prism formed by connecting the terminal I atoms, which can be used to illustrate the cross-linking of the cluster units. (*c*) [001] projection of the structure of monoclinic Nb_3SI_7. The formal prisms form dimeric units *via* edge sharing along [100]. These units are cross-linked *via* corners to form a layered structure.

(Furuseth *et al.*, 1988) and orthorhombic Nb_3SI_7 (Miller, 1995) (2.995 and 2.96–3.05 Å, respectively). This shortening corresponds to the transition from the edge-sharing to the face-sharing connection of the octahedral coordination polyhedra surrounding the Nb atoms. Except for the lower symmetry, this and the other geometrical details of the $[Nb_3SI_{10}]^{3-}$ cluster units agree well with those in $[Nb_3SI_7]_2[NbI_5]$ (Miller, 1995).

To elucidate the arrangement of the $[Nb_3SI_{10}]^{3-}$ clusters (Fig. 1*a*) in the structure it is convenient to see the six terminal I atoms with their free coordination sites as corners of a formal trigonal prism (Fig. 1*b*). Each prism shares one edge with another prism including a crystallographic center of symmetry to form dimeric units $[(Nb_3SI_9)_2]^{4-}$. These dimeric units are cross-linked by the remaining corners to form a novel two-dimensional structure motif (Fig. 1*c*).

Experimental

Single crystals of the title compound were obtained by heating a mixture of the elements (molar ratio Nb:S:I = 3:1:8.5) in evacuated sealed fused silica tubes (V = 6 ml) at 1105 K for two weeks. After rapid quenching, higher niobium iodides were separated from the product by sublimation before the tubes were opened.

Crystal data

Nb_3SI_7
M_r = 1199.09
Monoclinic
$P2_1/c$
a = 15.564 (3) Å
b = 12.441 (2) Å
c = 7.800 (2) Å
β = 99.49 (3)°
V = 1489.7 (5) Å^3
Z = 4
D_x = 5.347 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 10.11–19.00°
μ = 16.872 mm^{-1}
T = 293 (2) K
Plate
0.09 × 0.09 × 0.02 mm
Metallic black

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: numerical (*SHELXTL/PC*; Sheldrick, 1994)
T_{min} = 0.145, T_{max} = 0.515
3588 measured reflections
3588 independent reflections

2955 reflections with $I > 2\sigma(I)$
θ_{max} = 27.96°
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 10$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.092
S = 1.082
3576 reflections

$\Delta\rho_{max}$ = 1.66 e Å^{-3}
$\Delta\rho_{min}$ = −1.94 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)

101 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 13.9960P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
Extinction coefficient: 0.00037 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

I1—Nb3	2.8196 (12)	Nb1—Nb3	2.7801 (10)
I1—Nb1	2.8241 (9)	Nb2—S1	2.435 (2)
I1—Nb2	2.8382 (10)	Nb2—Nb3	2.7671 (10)
Nb1—S1	2.420 (2)	Nb3—S1	2.413 (2)
Nb1—Nb2	2.7759 (10)		
Nb3—I1—Nb1	59.02 (2)	Nb3—Nb2—Nb1	60.21 (2)
Nb3—I1—Nb2	58.56 (2)	Nb3—S1—Nb1	70.23 (5)
Nb1—I1—Nb2	58.71 (2)	Nb3—S1—Nb2	69.61 (5)
Nb2—Nb1—Nb3	59.74 (2)	Nb1—S1—Nb2	69.74 (6)

The crystal quality, initial cell parameters and symmetry information were determined from DeJong photographs taken at 298 K. This was useful because the crystals show a tendency towards twinning. The lattice metrics ($a/c = 2$ with $\cos\beta^* = 1/6$) provide a geometrical condition for partial merohedric twinning of index 3. This leads to coincidental reciprocal lattice points for $l = 3n$ ($n = 0, 1, 2, \ldots$). For the crystal structure analysis an untwinned specimen was selected. Intensity data were processed (Keller, 1981) and corrected for absorption (Sheldrick, 1994). The final refinement included anisotropic displacement parameters and an extinction parameter. The largest feature in a final difference electron-density map was 1.66 e Å^{-3} at a distance of 0.81 Å from I6.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4/*CAD*-6 (Keller, 1981). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SCHAKAL*92 (Keller, 1992).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1212). Services for accessing these data are described at the back of the journal.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
Furuseth, S., Hönle, W., Miller, G. J. & von Schnering, H. G. (1988). 9th International Conference of Transition Elements, Abstracts. London: The Royal Society of Chemistry.
Keller, E. (1981). *CAD*-4/*CAD*-6. University of Freiburg, Germany.
Keller, E. (1992). *SCHAKAL*92. *A Computer Program for the Graphic Representation of Molecular and Crystallographic Models*. University of Freiburg, Germany.
Miller, G. J. (1995). *J. Alloys Compd.* **229**, 93–106.
Miller, G. J. & Lin, J. (1994). *Angew. Chem.* **106**, 357–359; *Angew. Chem. Int. Ed. Engl.* **33**, 334–336.
Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Simon, A. & von Schnering, H. G. (1966). *J. Less Common Met.* **11**, 31–46.

Acta Cryst. (1997). C**53**, 1745–1748

Fe_3W_3N: a Rietveld Refinement Using X-ray Powder Diffraction

Kenneth S. Weil and Prashant N. Kumta

Department of Materials Science and Engineering, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, PA 15213, USA. E-mail: kumta@cmu.edu

(*Received 12 February 1997; accepted 3 June 1997*)

Abstract

A new ternary nitride, triiron tritungsten nitride, has been synthesized by the ammonolysis of a metal-organic precursor. The structure, found to be face-centered cubic ($Fd\bar{3}m$), was determined by powder X-ray diffraction and Rietveld refinement of the resulting diffraction pattern. The ideal structure of Fe_3W_3N is similar to the η-carbide structure exhibited by many ternary transition metal carbides.

Comment

A growing number of new ternary transition metal–transition metal nitride compounds have been synthesized over the past several years. Thus far, the crystal structures of these compounds fall predominantly into one of two categories: (*a*) layered hexagonal or rhombohedral structures such as $FeWN_2$ and $MnMoN_2$ (Bem, Lampe-Önnerud, Olsen & zur Loye, 1996), $CrWN_2$ (Weil & Kumta, 1997), $CoWN_2$ and $NiWN_2$ (Herle, Vasanthacharya, Hegde & Gopalakrishnan, 1995), and $MnWN_2$ (Bem, Houmes & zur Loye, 1993); and (*b*) cubic, η-carbide-like structures such as Fe_3Mo_3N and Co_3Mo_3N (Houmes, Bem & zur Loye, 1993). We have recently synthesized a new intermetallic tungsten nitride with the η-carbide structure, Fe_3W_3N, which has been characterized by X-ray diffraction and Rietveld analysis (Rietveld, 1969). The results of this analysis are reported in this paper.

The η-carbide structure has been previously described in detail by Westgren (1933) for the stoichiometry $T^{\rm I}{}_3T^{\rm II}{}_3C$ (where $T^{\rm I}$ and $T^{\rm II}$ represent two different transition metals) and by Kislyakova (1943) for the stoichiometry $T^{\rm I}{}_2T^{\rm II}{}_4C$. These structures have been observed for carbides, such as Fe_3W_3C (Westgren & Phragmen, 1928) and Co_6Mo_6C (Fraker & Stadelmaier, 1969), and for nitrides and oxides, such as Fe_2Ta_4N and Ni_2Nb_4O (Holleck & Thummler, 1967). Both structural descriptions are derived from that for the Ti_2Ni intermetallic structure (Yurko, Barton & Parr, 1959) with the interstices at the 16*c* Wyckoff positions filled by C atoms. As shown in Fig. 1, separate clusters of $T^{\rm II}$ and $T^{\rm I}$ atoms in the Westgren $T^{\rm I}{}_3T^{\rm II}{}_3C$ structure essentially

Acta Crystallographica Section C
ISSN 0108-2701 © 1997