Refinement

Refinement on F
Final $R = 0.0298$
$wR = 0.0213$
$S = 1.21$
316 reflections
16 parameters
$w = 1/[\sigma^2(F)+0.0001F^2]$
$(\Delta/\sigma)_{\max} \leq 0.001$
$\Delta\rho_{\max} = 1.33$ e Å^{-3}
$\Delta\rho_{\min} = -1.52$ e Å^{-3}
Extinction correction: $F^* = F(1+0.002xF^2/\sin 2\theta)^{-1/4}$
Extinction coefficient: $x = 0.0028$ (6)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement coefficients* (Å^2)

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$.

	x	y	z	$U_{\rm eq}$
295 K				
V	0.4874 (1)	0.1216 (1)	0.2500	0.06 (1)
S(1)	0.3474 (1)	0.2971 (1)	0.2500	0.06 (1)
S(2)	0.3333	0.6666	0.2500	0.05 (1)
170 K				
V	0.4874 (1)	0.1215 (1)	0.2500	0.04 (1)
S(1)	0.3472 (1)	0.2969 (1)	0.2500	0.04 (1)
S(2)	0.3333	0.6666	0.2500	0.04 (1)
100 K				
V	0.4875 (1)	0.1214 (1)	0.2500	0.03 (1)
S(1)	0.3473 (1)	0.2967 (1)	0.2500	0.03 (1)
S(2)	0.3333	0.6666	0.2500	0.03 (1)

Table 2. *Selected bond lengths* (Å) *for* V_3S_4 *determined at different temperatures*

	295 K	170 K	100 K
V—2V	2.864(1)	2.859(1)	2.856(1)
V—2V	3.120(1)	3.115(1)	3.114(1)
V—2S(2)	2.444(1)	2.440(1)	2.440(1)
V—S(1)	2.358(1)	2.355(1)	2.354(1)
V—S(1)	2.497(1)	2.493(1)	2.490(1)
V—2S(1)	2.340(1)	2.337(1)	2.338(1)
V—S(av.)	2.404	2.400	2.400

Lists of structure factors, anisotropic displacement parameters and selected bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55842 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1019]

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A New Type of One-Dimensional Compound: Structure of $Nb_4(Te_2)_4Te_4I$

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Abstract

The new infinite-chain niobium telluride iodide has been prepared by reaction of the elements at 893 K. $Nb_4(Te_2)_4Te_4I$ represents a new one-dimensional structure type. The structure consists of $[Nb_4(Te_2)_4Te_4I]_\infty$ chains which are formed by the four-nuclear butterfly cluster units '$Nb_4(Te_2)_4Te_4$' with the I atoms bridging between different cluster units.

Comment

Low-dimensional niobium and tantalum chalcogenide compounds have received much attention in the last few years (Rouxel, 1986*a*; Badding & Disalvo, 1990; Liimatta & Ibers, 1987, 1988, 1989). The main interests lie in the synthesis, structure and especially the unusual properties such as superconductivity (Shenoy, Dunlap & Fradin, 1981), charge-density waves (Rouxel, 1986*b*; Mihaly, Chen, Kim & Gruner, 1988), anisotropic electrical conductivity and optical behaviour (Wilson, Disalvo & Mahajan, 1975). Although numerous investigations have been conducted on niobium/tantalum chalcogenides, examples of low-dimensional niobium/tantalum telluride compounds are still very limited. Here we report on the structure determination of a new one-dimensional compound $Nb_4(Te_2)_4Te_4I$. The compound was obtained by solid-state reactions of the approximate stoichiometric elements at about 893 K. Single crystals used in the structure determination

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were obtained by vapour transport methods with iodine as the transport agent. Details of synthetic work and physical properties, along with a theoretical consideration will be published elsewhere (Shuiquan, Honghui, Jinshun & Jingling, 1992).

A perspective view of the structure along the *c* axis is shown in Fig. 1. The atom-labelling scheme is illustrated in Fig. 2. As shown in Fig. 1, the structure of the title compound is based on the $Nb_4(Te_2)_4Te_4I$ monomers, stacked in a head-to-tail manner to form the $[Nb_4(Te_2)_4Te_4I]_\infty$ chains, which are held together by van der Waals interactions and pack in a monoclinic unit cell. One I atom bridges two different '$Nb_4(Te_2)_4Te_4$' cluster units. Nb atoms in the cluster unit bond together to form the four-nuclear butterfly cluster core, to our knowledge hitherto not found in the niobium or tantalum cluster chemistry.

Te atoms coordinate the Nb atoms in two ways: one in the form of Te_2 dimers which coordinate over the edge of the Nb_4 butterfly core; the other simply as the terminal coordinating atoms; this leads to the formula $Nb_4(Te_2)_4Te_4I$.

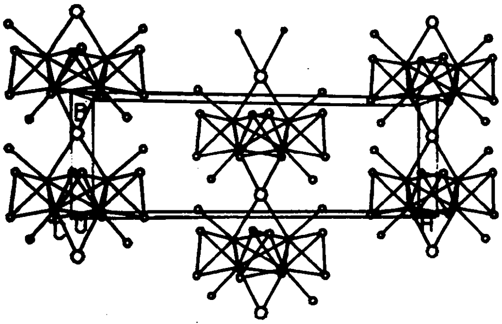

Fig. 1. Perspective view of the structure of $Nb_4(Te_2)_4Te_4I$ along the *c* axis. Atoms corresponding to $z < 0.5$ have been omitted.

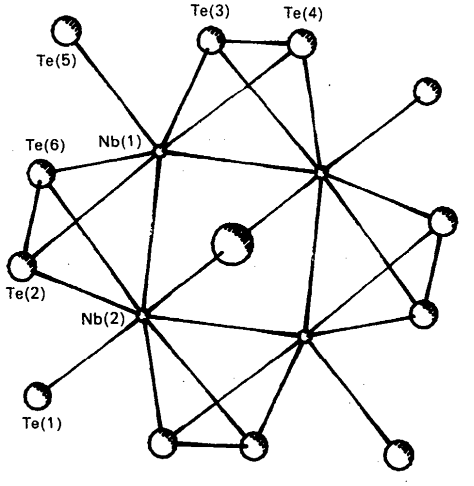

Fig. 2. Projection of a '$Nb_4(Te_2)_4Te_4I$' monomer along the *b* axis, showing the atom labelling.

The shortest Nb—Nb distance in the cluster core averages 3.046 (3) Å, and is consistent with the reported values of Nb—Nb bond lengths [2.986 Å, $Nb_4Se_4I_4$ (Ben Yaich, Jegaden, Potel & Sergent, 1984)]. The long distances between the Nb atoms at the opposite corners of the butterfly core (3.765 Å average) indicate no chemical bonding and suggest that the core is a butterfly rather than a tetrahedron. The Nb—Te bond lengths range from 2.771 (3) to 2.889 (2) Å in the '$Nb_4(Te_2)_4Te_4$' cluster unit. These distances are similar to the values found in $NbTe_4$ [2.902 Å (Selte & Kjekshus, 1964)]. The Te—Te bond lengths range from 2.705 (3) to 2.717 (3) Å, which are shorter than found in $NbTe_4$ [2.867 Å (Selte & Kjekshus, 1964)], and in Te crystals [2.835 (2) Å (Cherin & Unger, 1967)]. The Nb—I distance is 2.998 Å (average), which is a little larger than the Nb—I^{a-a} distance [2.958 (3) Å] in Nb_6I_{11} (Imoto & Simon, 1982), and indicates weaker Nb—I bonding. The weak Nb—I bonding shows that the '$Nb_4(Te_2)_4Te_4$' cluster units are relatively independent with respect to each other. Therefore, the title compound may be viewed as in the molecular state with the formula $Nb_4(Te_2)_4Te_4I$. The title compound is indeed much different from other families of one-dimensional compounds that have extended metal–metal interactions, for example: Ta_4ZTe_4 (Z = stabilizing heteroatom) (Badding & Disalvo, 1990); $(MX_4)_nY$ (M = Nb, Ta; X = S, Se; Y = Br, I) (Gressier, Meerschaut, Guemas, Rouxel & Monceau, 1984). A new member belonging to the same family, $Ta_4(Te_2)_4Te_4I$, has been synthesized. The structure determination is in progress.

In summary, the title compound represents a new one-dimensional class with typical molecular characteristics, especially the novel Nb_4/Ta_4 butterfly cluster core. Further studies of the properties of these phases, through breaking the I-atom bridges and/or substituting I atoms for other ligands, are being conducted.

Experimental

Crystal data

$Nb_4(Te_2)_4Te_4I$
M_r = 2029.73
Monoclinic
$C2/c$
a = 21.957 (5) Å
b = 6.147 (3) Å
c = 19.925 (4) Å
β = 122.40 (1)°
V = 2270.6 Å^3
Z = 4
D_m = 5.8 (5) Mg m^{-3}
Density measured by micropycnometry in toluene

Mo radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14–15°
μ = 18.38 mm^{-1}
T = 296 K
Rectangular
0.12 × 0.08 × 0.06 mm
Black
Crystal source: vapour transport methods

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans of rate 1-5° min^{-1} and width (0.45 + $0.35\tan\theta$)°
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\text{min}} = 0.53$, $T_{\text{max}} = 1.00$
2269 measured reflections
2202 independent reflections
1375 observed reflections [$I > 3\sigma(I)$]
$R_{\text{int}} = 0.038$
$\theta_{\text{max}} = 25.0°$
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 7$
$l = -23 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity variation: 2.2%

Refinement

Refinement on F
Final $R = 0.052$
$wR = 0.062$
$S = 1.26$
1375 reflections
79 parameters
$w = 1/[\sigma^2(F_o) + (0.03|F_o|)^2 + 1.0]$
$(\Delta/\sigma)_{\text{max}} = 0.01$
$\Delta\rho_{\text{max}} = 0.86$ e Å^{-3}
$\Delta\rho_{\text{min}} = 0.81$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 0.61×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\text{eq}} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
I	0.0000	−0.3225 (4)	0.7500	4.35 (6)
Nb(1)	0.07816 (6)	0.2970 (2)	0.73611 (6)	0.53 (2)
Nb(2)	−0.06469 (6)	0.0562 (2)	0.63875 (6)	0.59 (3)
Te(1)	−0.1432 (1)	−0.1965 (4)	0.5011 (1)	3.32 (5)
Te(2)	−0.02309 (9)	0.3595 (4)	0.56782 (9)	3.00 (4)
Te(3)	0.18146 (9)	0.0047 (4)	0.8362 (1)	3.01 (4)
Te(4)	0.17261 (9)	0.3635 (4)	0.9049 (1)	2.94 (4)
Te(5)	0.17463 (9)	0.5548 (4)	0.7199 (1)	3.36 (5)
Te(6)	0.05870 (9)	−0.0065 (4)	0.62339 (9)	3.03 (4)

Table 2. *Geometric parameters* (Å, °)

Nb(1)—Nb(2)	3.045 (2)	Nb(1)—Nb(2)^{i}	3.047 (3)
Nb(1)—Te(2)	2.889 (2)	Nb(1)—Te(3)	2.777 (2)
Nb(1)—Te(4)	2.882 (2)	Nb(1)—Te(5)	2.800 (3)
Nb(1)—Te(6)	2.771 (3)	Nb(2)—Te(1)	2.800 (2)
Nb(2)—Te(2)	2.774 (3)	Nb(2)—Te(6)	2.911 (3)
Nb(2)—Te(3)^{i}	2.887 (3)	Nb(2)—Te(4)^{i}	2.780 (2)
Te(3)—Te(4)	2.705 (3)	Te(2)—Te(6)	2.717 (3)
I—Nb(2)	2.996 (2)	I—Nb(1)^{ii}	3.000 (3)
Te(2)—Nb(1)—Te(3)	138.31 (8)	Te(2)—Nb(1)—Te(5)	87.13 (7)
Te(3)—Nb(1)—Te(4)	57.09 (6)	Te(4)—Nb(1)—Te(5)	86.49 (6)
Te(2)—Nb(1)—Te(6)	57.33 (7)	Te(4)—Nb(1)—Te(6)	138.02 (7)
Te(3)—Nb(1)—Te(5)	94.79 (8)	Te(3)—Nb(1)—Te(6)	81.05 (7)
Te(2)—Nb(1)—Te(4)	163.91 (8)	Te(5)—Nb(1)—Te(6)	94.87 (8)
Te(1)—Nb(2)—Te(2)	94.12 (7)	Te(1)—Nb(2)—Te(3)^{i}	87.69 (8)
Te(1)—Nb(2)—I	95.32 (7)	Te(1)—Nb(2)—Te(4)^{i}	95.52 (6)
Te(1)—Nb(2)—Te(6)	86.73 (7)	Te(2)—Nb(2)—Te(3)^{i}	137.81 (7)
Te(2)—Nb(2)—I	138.10 (6)	Te(2)—Nb(2)—Te(4)^{i}	80.93 (7)
Te(2)—Nb(2)—Te(6)	57.04 (7)	Te(3)^{i}—Nb(2)—I	83.34 (5)
Te(3)^{i}—Nb(2)—Te(4)^{i}	56.99 (7)	Te(3)^{i}—Nb(2)—Te(6)	164.58 (8)
I—Nb(2)—Te(4)^{i}	138.24 (8)	I—Nb(2)—Te(6)	82.87 (6)
Te(4)^{i}—Nb(2)—Te(6)	137.95 (8)	Nb(2)—I—Nb(2)^{i}	78.03 (7)
Nb(1)^{ii}—I—Nb(1)^{iii}	77.55 (8)	Nb(2)—Nb(1)—Nb(2)^{i}	76.51 (5)
Nb(1)—Nb(2)—Nb(1)^{i}	76.18 (5)		

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

The crystals of $Nb_4(Te_2)_4Te_4I$ are black and show metallic lustre. Microprobe analysis of the single crystals was made with the Jeol scanning electron microscope. The experimental values are: Nb 19.6(7), Te 75.2(4), I 5.1(7) wt %. Calculated for $Nb_4(Te_2)_4Te_4I$: Nb 18.31, Te 75.44, I 6.25 wt %. These results are within the accuracy of the microprobe of ±20%. Data collection and cell refinement: Enraf-Nonius (1977) CAD-4 diffractometer control software. Programs used to solve structure: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Programs used for full-matrix least-squares refinement and other calculations: Enraf-Nonius *SDP* package (Frenz, 1978). Calculations were performed on a VAX 785 computer.

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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 55906 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1041]

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