INORGANIC COMPOUNDS

An Oxygen-Centred Tetranuclear Tantalum Cluster: Ta4O(Te2)4TeI4

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Abstract

Tetratantalum nonatellurium tetraiodide oxide exhibits a one-dimensional structure containing distorted tetrahedral oxygen-centred tetranuclear clusters of Ta atoms. Each of the four shorter Ta—Ta bonds is bridged by a Te_2 group, and each Ta atom is also bonded to a terminal I atom and a μ_4 O atom. A μ_4 Te atom connects two neighbouring clusters to form a one-dimensional chain along the b axis. The chains are held together by van der Waals interactions.

Comment

One-dimensional transition metal tellurides are of special interest in materials chemistry and theoretical chemistry because of their particular properties and bonding (Cheetham & Day, 1992). The centre atom is especially important in supporting and stabilizing the metal cluster in some chalcogenide compounds, such as the molecular cluster $Ti_4O(S_2)_4Cl_6$ (Cotton et al., 1989). One-dimensional clusters of this type include $Nb_4OTe_9I_4$, prepared by Tremel (1992), and $Ti_4O(Te_2)_4TeI_4$, synthesized and structurally characterized by Liu et al. (1996). We report here the structure of another new compound, $Ta_4O(Te_2)_4TeI_4$.

The title compound exhibits a chain structure containing distorted tetrahedral oxygen-centred tetranuclear clusters of Ta atoms. Each cluster has four short Ta—
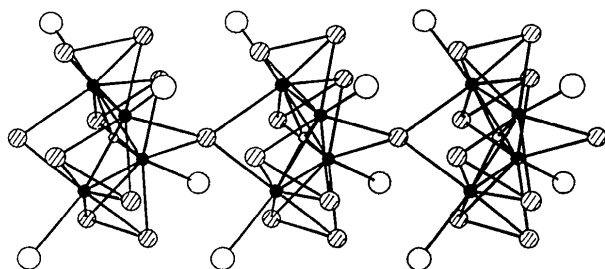
Ta contacts. Each pair of Ta atoms is bridged by a Te_2 group and each Ta atom is also bonded to a terminal I atom. Each μ_4 Te atom in the monomer unit is shared with a neighbouring cluster to form a chain structure along the b axis. This interesting intrachain structure exhibits C_2 symmetry as shown in Fig. 1.

The $Ta_4O(Te_2)_4(Te_{0.5})_2I_4$ monomer cluster is shown in Fig. 2. The O atom and the μ_4 Te atom in the monomer cluster are located on a twofold axis. The interstitial O atom is in the centre of the cage of a flattened tetrahedral Ta_4 nucleus, which has four short Ta—Ta contacts in the range 3.042 (4)–3.046 (6) Å [Ta(1)—Ta(2), Ta(1)—Ta(2^{iii}), Ta(2^{iii})—Ta(1^{iii}) and Ta(1^{iii})—Ta(2)]. These values are longer than the Ta—Ta contact in Ta metal (2.86 Å; Pauling, 1960), but are close to the average of the shorter and longer Ta—Ta distances in Ta_4Te_4Si (3.238–3.261 and 2.970–2.979 Å; Badding & DiSalvo, 1990). However, the Ti—Ti distances in $Ti_4O(Te_2)_4TeI_4$ are 3.166 and 3.160 Å, even though the atomic radii of Ta and Ti are almost the same. The short Ta—Ta contacts are considered to be weak covalent bonds. Each short Ta—Ta edge is bridged by a Te_2 group in which the Te—Te bond lengths, 2.719 (2) and 2.713 (2) Å, are close to the Te—Te covalent contact of 2.70 Å. They are shorter than in $TaTe_4$ (2.90–2.95 Å; Bronsema et al., 1987) but are the same as in $Ti_4O(Te_2)_4TeI_4$ (2.710–2.707 Å). The double-bridged Ta—Te_2 bonds are strong enough to distort the tetrahedral Ta_4 cluster to form four shorter Ta—Ta contacts. Eight slightly different Te_2—Ta distances are found. The μ_4 Te atom connects neighbouring clusters via Te—Ta bonds of 2.991 (3) and 3.021 (3) Å. Only a few transition metal iodine chalcogenides with low-dimensional structures, like this type of compound, contain metal-iodine bonds. The Ta—I bond lengths, 2.807 (4) and 2.814 (4) Å, are longer than the covalent contact, 2.67 Å, but obviously shorter than the sum of the ionic radii of
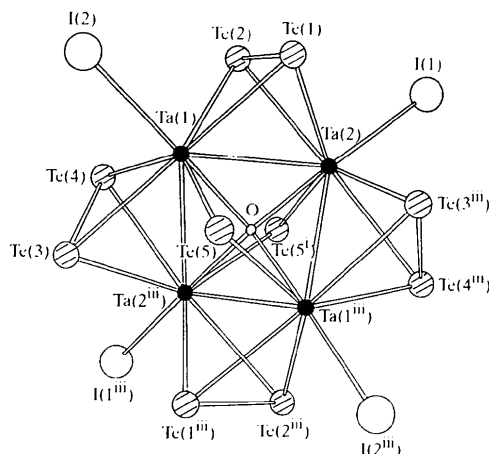

Fig. 1. The chain structure of $Ta_4O(Te_2)_4TeI_4$.

Fig. 2. The $Ta_4O(Te_2)_4(Te_{0.5})_2I_4$ cluster unit in $Ta_4O(Te_2)_4TeI_4$.

Ta^{4+} and I^-. The O atom in the Ta_4 cage is almost equidistant from the Ta atoms, with Ta—O distances of 2.04 (1) and 2.010 (8) Å. These distances are very close to the sum of the radii of Ta^{4+} and O^{2-} (2.06 Å). This shows that the centre O atom is very important in supporting the Ta_4 cage.

The smallest Ta—(μ_4-Te)—Ta angle, 77.5 (1)°, is larger than the smallest Ta—Te_2—Ta angle, 64.8 (1)°. This is a result of differences in the Te-atom coordination numbers and valences: the coordination number and valence for the μ_4 Te atom are 4 and −2, respectively, compared with 3 and −1, respectively, for a Te atom in a Te_2 group.

The chains are held together by van der Waals forces. The shortest interchain Te⋯I contact is 3.540 (4) Å, which is longer than a bonding contact but a little shorter than in $Ti_4O(Te_2)_4TeI_4$ [3.571 (2) Å].

The title compound can be formulated as $Ta_4^{4+}O^{2-}$-$(Te_2)_4^{2-}Te^{2-}I_4^-$. Band-structure calculations clearly show that the Ta—Ta contact is weak, and that the four shorter Ta—Ta contacts in the title compound are stronger than the Ti—Ti contacts in $Ti_4O(Te_2)_4TeI_4$, in which there are no Ti—Ti bonds. This supports the postulated valence for Ta.

Experimental

The title compound was prepared by solid-state reaction of the appropriate amounts of elemental Ta, Te and I. After exposure to air for 30 min, the mixture was sealed in an evacuated quartz tube, slowly heated to 1273 K and then cooled to 773 K for two days.

Crystal data

$Ta_4O(Te_2)_4TeI_4$
$M_r = 2395.80$
Monoclinic
$C2/c$
$a = 21.97 (4)$ Å
$b = 6.155 (3)$ Å
$c = 19.98 (4)$ Å
$\beta = 122.08 (9)°$
$V = 2289 (2)$ Å^3
$Z = 4$
$D_x = 6.95$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12-20°$
$\mu = 35.458$ mm^{-1}
$T = 298$ K
Needle
$0.3 \times 0.03 \times 0.02$ mm
Black

Data collection

Rigaku AFC-5R diffractometer
ω scans
Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
$T_{min} = 0.227$, $T_{max} = 0.415$
8832 measured reflections
4674 independent reflections

2817 reflections with $I \geq 3\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 33°$
$h = 0 \rightarrow 33$
$k = -9 \rightarrow 9$
$l = -30 \rightarrow 30$
3 standard reflections every 150 reflections intensity decay: 2%

Refinement

Refinement on F
$R = 0.033$
$wR = 0.043$
$S = 1.072$
2817 reflections
84 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.15$
$\Delta\rho_{max} = 3.55$ e Å^{-3}
$\Delta\rho_{min} = -3.69$ e Å^{-3}
Extinction correction: none
Scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\AA^2$)*

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

	x	*y*	*z*	B_{eq}
Ta(1)	0.07799 (2)	0.29502 (7)	0.73638 (3)	1.10 (1)
Ta(2)	0.06446 (2)	0.05602 (7)	0.86114 (3)	1.12 (1)
I(1)	0.14303 (5)	−0.1975 (1)	0.99857 (5)	1.85 (3)
I(2)	0.17519 (5)	0.5516 (1)	0.72037 (6)	2.01 (3)
Te(1)	0.17204 (4)	0.3634 (1)	0.90449 (5)	1.54 (2)
Te(2)	0.18157 (4)	−0.0059 (1)	0.83644 (5)	1.53 (2)
Te(3)	−0.02239 (5)	0.3579 (1)	0.56848 (5)	1.57 (2)
Te(4)	0.05881 (5)	−0.0084 (1)	0.62398 (5)	1.53 (2)
Te(5)	0	0.6740 (2)	3/4	1.08 (3)
O	0	0.164 (4)	3/4	3.7 (7)

Table 2. *Selected geometric parameters (Å, °)*

Ta(1)—O	2.04 (1)	Ta(1)—Ta(2)	3.042 (4)
Ta(1)—I(2)	2.807 (4)	I(2)—Te(2^v)	3.532 (3)
Ta(1)—Te(3)	2.900 (6)	Ta(1)—Te(4)	2.776 (3)
Ta(2)—Te(5^i)	3.021 (3)	Ta(1)—Te(1)	2.891 (6)
I(1)—Te(3^{ii})	3.540 (4)	Ta(1)—Te(5)	2.991 (3)
Ta(2)—O	2.010 (8)	Te(1)—Te(2)	2.713 (2)
Ta(2)—I(1)	2.814 (4)	I(2)—Te(4^v)	3.514 (4)
Ta(2)—Te(4^{iii})	2.904 (6)		
O—Ta(1)—Te(4)	93.7 (4)	O—Ta(1)—Te(2)	93.8 (5)
O—Ta(1)—I(2)	169.0 (6)	O—Ta(1)—Te(1)	92.0 (2)
O—Ta(1)—Ta(2)	40.9 (2)	O—Ta(1)—Ta(2^{iii})	40.9 (2)
Te(4)—Ta(1)—Te(2)	81.3 (1)	Te(4)—Ta(1)—I(2)	94.83 (9)
Te(4)—Ta(1)—Ta(2^{iii})	59.6 (1)	Te(2)—Ta(1)—I(2)	94.3 (1)
Te(2)—Ta(1)—Te(1)	57.0 (1)	Te(2)—Ta(1)—Te(3)	138.40 (6)
Te(2)—Ta(1)—Te(5)	137.86 (9)	Te(2)—Ta(1)—Ta(2)	59.3 (1)
I(2)—Ta(1)—Te(3)	87.1 (1)	I(2)—Ta(1)—Te(5)	94.5 (1)
I(2)—Ta(1)—Ta(2)	140.95 (8)	I(2)—Ta(1)—Ta(2^{iii})	141.6 (1)
Te(1)—Ta(1)—Te(3)	163.72 (5)	Te(1)—Ta(1)—Te(5)	82.6 (1)
Te(5)—Ta(1)—Ta(2^{iii})	89.5 (1)	Ta(2)—Ta(1)—Ta(2^{iii})	77.1 (1)
O—Ta(2)—Te(3^{iii})	96.3 (5)	O—Ta(2)—Te(1)	95.9 (5)
O—Ta(2)—Ta(1)	41.6 (2)	O—Ta(2)—Ta(1^{iii})	41.5 (2)
Te(3^{iii})—Ta(2)—Te(1)	81.0 (1)	Te(3^{iii})—Ta(2)—I(1)	94.2 (1)
Te(3^{iii})—Ta(2)—Ta(1^{iii})	59.6 (1)	Te(1)—Ta(2)—I(1)	95.4 (1)
Te(1)—Ta(2)—Te(2)	57.1 (1)	Te(1)—Ta(2)—Te(4^{iii})	138.17 (8)
Te(1)—Ta(2)—Te(5^i)	138.35 (6)	Te(1)—Ta(2)—Ta(1)	59.3 (1)
I(1)—Ta(2)—Te(4^{iii})	86.9 (1)	I(1)—Ta(2)—Te(5^i)	95.2 (1)
I(1)—Ta(2)—Ta(1)	142.3 (1)	I(1)—Ta(2)—Ta(1^{iii})	141.38 (7)
Te(2)—Ta(2)—Te(4^{iii})	164.21 (4)	Te(2)—Ta(2)—Te(5^i)	83.3 (1)
Te(2)—Ta(2)—Ta(1)	55.99 (8)	Te(2)—Ta(2)—Ta(1^{iii})	131.3 (1)
Te(2)—Te(1)—Ta(2)	63.5 (1)	Te(2)—Te(1)—Ta(1)	59.57 (7)
Ta(2)—Te(1)—Ta(1)	64.8 (1)	Te(1)—Te(2)—Ta(1)	63.4 (1)
Te(1)—Te(2)—Ta(2)	59.43 (5)	Ta(1)—Te(2)—Ta(2)	64.8 (1)
Ta(2^{iii})—Te(3)—Ta(1)	65.0 (1)	Te(3)—Te(4)—Ta(1)	63.7 (1)
Te(3)—Te(4)—Ta(2^{iii})	58.88 (8)	Ta(1)—Te(4)—Ta(2^{iii})	64.8 (1)
Ta(1)—Te(5)—Ta(1^{iv})	77.5 (1)	Ta(1)—Te(5)—Ta(2^v)	127.3 (1)
Ta(1)—Te(5)—Ta(2^i)	127.42 (8)	Ta(1^{iv})—Te(5)—Ta(2^v)	127.42 (8)
Ta(2^{iii})—O—Ta(1^{iii})	97.4 (2)	Ta(1)—O—Ta(1^{iii})	133 (1)

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

The structure was solved by direct methods (Gilmore, 1983) and difference Fourier techniques, and refined by full-matrix least-squares methods (Peterse & Palm, 1966). Refined absorption corrections were compared to the cylindrical corrections and were deemed reliable for this fine needle crystal. The

maximum and minimum peaks in the final difference Fourier map are near Ta sites. All calculations were performed on a MicroVAXII computer using *TEXSAN* software (Molecular Structure Corporation, 1985).

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A New One-Dimensional Compound: (TaTe4)6I4(TaI6)

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Abstract

The title compound, hexakis(tetratelluriotantalum) tetraiodide hexaiodotantalate, has a $[TaTe_4]_n$ chain structure with TaI_6^- complex anions and I^- anions between the chains. The $[TaTe_4]_n$ chain contains rectangular antiprismatic $TaTe_8$ polyhedra, each Ta atom being

coordinated by four Te_2 groups. The Ta atom in the TaI_6^- complex anion is octahedrally coordinated by I^- anions.

Comment

Transition metal chalcogenides with chain structures have attracted growing interest in recent years (Whittingham & Jackson, 1982) owing to their physical properties, such as superconductivity, magnetic ordering at low temperatures, charge-density wave properties and anisotropic behaviour (Li *et al.*, 1990; Minton & Brill, 1987). Recently, the study of compounds with MQ_4 chains (M = Ta, Nb; Q = chalcogen) has increased markedly. The compounds $(MTe_4)I$ (Huang, 1994) and $(MSe_4)_yX$ (y = 2, 3, 3.33, 4; X = Br, I) (King, 1994) have been synthesized and structurally characterized. A compound with TaI_6 complex anions, $(TaTe_4)_4I_2(TaI_6)$, has been obtained (Liu *et al.*, 1996). In this paper, we report the structure of a new compound, $(TaTe_4)_6I_4(TaI_6)$.

The structure of the title compound can be considered as consisting of $[TaTe_4]_n$ chains, TaI_6^- complex anions and I^- anions. The TaI_6^- complex anions and I^- anions are relatively isolated.

The configuration of the $[TaTe_4]_n$ chain is shown in Fig. 1, in which each Ta atom is coordinated by four Te_2 groups in the form of a rectangular antiprism. The dichalcogen group acts as a ligand and bridges two neighbouring metal atoms along the chain, as found in the binary compound VS_4 (Allmann *et al.*, 1964). The Ta—Te bond lengths are in the range 2.831 (1)–2.866 (1) Å, while the $(TaTe_4)_4I_2(TaI_6)$ compound exhibits longer Ta—Te bond lengths, from 2.81 to 2.96 Å. The Te—Te bond lengths of the Te_2 groups are in the range 2.752 (1)–2.812 (1) Å, which
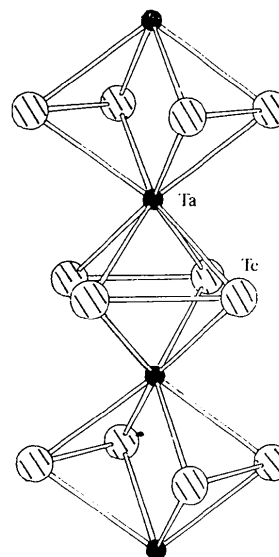

Fig. 1. The structure of a $[TaTe_4]_n$ chain.