

A New Extended Tetranuclear Titanium Cluster: $\text{Ti}_4\text{O}(\text{Te}_2)_4\text{TeI}_4$

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Received August 18, 1995; in revised form January 26, 1996; accepted January 30, 1996

A new one-dimensional compound $\text{TiO}_4(\text{Te}_2)_4\text{TeI}_4$ has been synthesized. Its important structural features are that of a distorted tetrahedral oxygen-centered cluster of Ti atoms bridged by Te_2 groups and that each μ_4 -Te atom connects two neighboring clusters to form a chain. It is found that the stable compounds with $M_4\text{O}$ cluster core meet $4n$ electron criterion. © 1996 Academic Press, Inc.

INTRODUCTION

Low-dimensional compounds have drawn much attention due to their particular properties and bonding (1, 2), such as a charge density wave, anisotropic behavior, and a van der Waals gap separating atomically identical slabs or fibers. But the synthesis of a low-dimensional solid is rather difficult and continues to impede the progress of the study of such solids.

Two quasi-one-dimensional compounds NbTe_4 and TaTe_4 were synthesized and structurally characterized (3–5). These two compounds exhibit charge density waves and easily produce modulated or incommensurate chain structures (4–6). Some one-dimensional earlier transitional metal chalcogenides with halogen ligands were prepared, for instance, $(MQ_4)_xY$ (7, 8), where $M = \text{Ta}, \text{Nb}$, $Q = \text{Se}$, $Y = \text{halogen}$, and $x = 2, 3$, and 3.33. They are semiconductors or insulators, depending on the Peierls distortion and the structural modulation in chain. They have a temperature dependence of diamagnetic susceptibility (9, 10). Recently, two $(MQ_4)Y$ compounds (11), $(\text{TaTe}_4)\text{I}$ and $(\text{NbTe}_4)\text{I}$, were also synthesized and their structures were determined. Some compounds, for example, $\text{Nb}_6\text{Se}_{20}\text{Br}_6$, have a wavy chain structure (12). Other compounds like $\text{Nb}_3\text{Se}_{10}\text{Br}_2$ are of mixed chain structures (13), while $(\text{TaTe}_4)_6\text{I}_4(\text{TaI}_6)$ and $(\text{TaTe}_4)_4\text{I}_2(\text{TaI}_6)$ (14) possess a chain structure with a complex ion.

Most compounds mentioned above have a common frame $MQ_4^{\delta+}$ ($1 \geq \delta > 0$), which goes through the chains or dominated the chains, and electrostatics–van der Waals contact between chains.

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Some compounds with more loose interchain contacts were prepared and characterized, $\text{Nb}_4\text{O}(\text{Te}_2)_4\text{TeI}_4$ with space group $C2/m$ (15) and $\text{Ta}_4\text{O}(\text{Te}_2)_4\text{TeI}_4$ (16). In this paper we report the synthesis and structure of $\text{Ti}_4\text{O}(\text{Te}_2)_4\text{TeI}_4$ and discuss the bonding of this type of compounds.

EXPERIMENT

The title compound was obtained from the reaction of a mixture of elements with the molar ratio $\text{Ti}:\text{Te}:\text{I} = 4:9:4.2$ at high temperature. A drop of water was added into the mixture before it was sealed in an evacuated quartz tube. The sample was heated at 673 K for 2 days, and at 923 K for 15 days. The sample was naturally quenched to room temperature. Shiny black needle crystals were formed at the low-temperature terminal of the tube. The composition of the crystal was measured by standardless electron spectrum analysis of a JEOL scanning electron microscope after the X-ray diffraction experiment. The result shows that there is a molar ratio of $\text{Ti}:\text{Te}:\text{I} = 1:2.48:1.1$ in the crystal. The oxygen element cannot be probed by this method, but X-ray structure analysis exhibits the existence of a light atom in the formula. Only the sample with a little water can yield the title compound crystal. Obviously, the atom may be oxygen and comes from the remainder of water.

A crystal was mounted on an AFC5R diffractometer. A least-square fit of 25 reflections in the range $15^\circ < 2\theta < 20^\circ$ yields the unit cell and orientation matrix. Intensities of reflections with $2\theta < 64.2^\circ$ and indices h from 0 to 36, k from -10 to 10, and l from -32 to 32 were measured by ω scans with graphite monochromatic $\text{MoK}\alpha$ radiation. Intensities of three standard reflections measured every 150 reflections showed no evidence of crystal decay.

The crystal structure was solved by direct methods and refined by full matrix least-squares calculation with anisotropic temperature parameters on a Micro VAX II computer using the TEXSAN software package. The final cycle of refinement included 84 variable parameters. The crystal data are given in Table 1. The final atomic parameters are

TABLE 1
Crystallographic Data

Formula	Ti ₄ O(Te ₂) ₄ TeI ₄
MW	1863.62
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> (Å)	22.144(7)
<i>b</i> (Å)	6.230(1)
<i>c</i> (Å)	19.726(8)
β (°)	125.51(2)
<i>V</i> (Å ³)	2215(1)
<i>Z</i>	4
<i>D</i> _{calc.} (mg/mm ⁻³)	5.59
<i>F</i> (000)	3104
μ (MoK α) (mm ⁻¹)	1.849
λ (MoK α)(Å)	0.71069
<i>T</i>	298 K
Diffractometer	AFC5R
Scan type	ω
θ _{max} (°)	32.1
Standard reflection	(150)
Decay	None
No. of reflections	
Total	7935
Unique	4194
<i>R</i> _{int}	0.022
Observed (<i>I</i> > 3.00 σ (<i>I</i>))	2128
Weighting scheme	$w = 1/(\sigma^2(F))$
<i>R</i>	0.043
<i>R</i> _w	0.054
<i>s</i>	1.21

TABLE 3
Selected Interatomic Distances (Å) and Bond Angles (°)

Ti(1)–O(1)	2.050(6)	Ti(2)–Te(4a)	2.774(3)
Ti(1)–I(1)	2.726(3)	Ti(2)–Te(3)	2.792(3)
Ti(1)–Te(3)	2.817(3)	Ti(2)–Te(1d)	2.930(3)
Ti(1)–Te(1)	2.921(3)	Te(1)–Ti(2c)	2.930(3)
Ti(2)–O(1)	2.074(6)	Te(2)–Te(3)	2.707(2)
Ti(2)–I(2)	2.710(3)	Te(4)–Te(5)	2.710(2)
Ti(1)–Ti(2)	3.166(4)	O(1b)–Te(1)	3.10(2)
O(1)–Te(2)	3.447(5)	T(1)–Te(5b)	3.588(2)
O(1)–Te(1)	3.13(1)	Te(5)–Te(5g)	3.712(2)
Te(2)–Te(2f)	3.757(2)	I(2)–Te(4e)	3.571(2)
Ti(1)–Te(1)–Ti(1a)	78.8(1)	I(1)–Ti(1)–Te(5)	93.95(8)
Ti(1)–Te(1)–Ti(2b)	126.30(8)	I(1)–Ti(1)–Te(2)	95.7(1)
Ti(1)–Te(2)–Ti(2)	69.07(8)	Te(5)–Ti(1)–Te(3)	133.8(1)
Te(4)–Te(5)–Ti(1)	61.77(6)	Te(2)–Ti(1)–Te(1)	139.8(1)
O(1)–Ti(1)–Ti(2)	40.1(1)	Te(1)–Ti(1)–Ti(2a)	93.0(1)
Te(1)–Ti(1)–Ti(2)	92.84(9)	Te(4a)–Ti(2)–Ti(1)	99.4(1)
O(1)–Ti(2)–Te(4a)	90.2(3)	Te(3)–Ti(2)–Ti(1a)	100.0(1)
O(1)–Ti(2)–Te(5a)	89.0(1)	Te(2)–Ti(2)–Te(1d)	83.24(7)
O(1)–Ti(2)–Te(1d)	74.4(3)	Te(2)–Ti(2)–Ti(1a)	126.6(1)
I(2)–Ti(2)–Te(4a)	95.52(8)	Te(5a)–Ti(2)–Ti(1a)	55.08(7)
Te(4a)–Ti(2)–Te(2)	134.4(1)	Ti(1)–O(1)–Ti(1a)	129.6(7)
Symmetry codes			
(a)	1 – <i>x</i> , <i>y</i> , $\frac{3}{2}$ – <i>z</i>	(b)	<i>x</i> , –1 + <i>y</i> , <i>z</i>
(c)	1 – <i>x</i> , –1 + <i>y</i> , $\frac{3}{2}$ – <i>z</i>	(d)	<i>x</i> , 1 + <i>y</i> , <i>z</i>
(e)	1 – <i>x</i> , 1 + <i>y</i> , $\frac{3}{2}$ – <i>z</i>	(f)	1 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>
(g)	$\frac{1}{2}$ – <i>x</i> , $\frac{3}{2}$ – <i>y</i> , 1 – <i>z</i>		

shown in Table 2 and the selected interatomic distances and bond angles in Table 3, respectively.

DISCUSSION

Ti₄O(Te₂)₄TeI₄ has one-dimensional chain structure, and the space group *C2/c*. Figure 1 is a packing diagram down the *b* axis showing the stacking of chain.

TABLE 2
Positional Parameters and *B*_{eq}

Atom	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>B</i> _{eq} ^a
Ti(1)	0.4521(1)	0.3070(4)	0.6355(2)	1.09(7)
Ti(2)	0.5928(1)	0.5851(4)	0.7662(2)	1.12(8)
I(1)	0.39076(6)	0.0794(2)	0.49167(7)	1.78(3)
I(2)	0.70609(6)	0.8133(2)	0.78563(8)	1.99(4)
Te(1)	$\frac{1}{2}$	–0.0552(2)	$\frac{3}{4}$	1.09(4)
Te(2)	0.51236(5)	0.6289(2)	0.59340(6)	1.41(3)
Te(3)	0.59278(5)	0.2677(2)	0.66632(6)	1.44(3)
Te(4)	0.31843(5)	0.2651(2)	0.62129(6)	1.41(3)
Te(5)	0.34300(5)	0.6223(3)	0.56222(6)	1.47(3)
O	$\frac{1}{2}$	0.447(2)	$\frac{3}{4}$	0.8(4)

^a $B_{eq} = \left(\frac{1}{3}\right)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos \alpha)\beta_{12} + 2ac(\cos \beta)\beta_{13} + 2bc(\cos \gamma)\beta_{23}]$.

The cluster unit of Ti₄O(Te₂)₄TeI₄ is shown in Fig. 2. The Ti₄O core is a distorted tetrahedron with four short edges. The interstitial oxygen atom is located in the center of Ti₄ cage. Each of four pairs of Te₂ groups bonds with a short edge Ti–Ti. Every two Ti₄O cores are joined by a shared μ_4 -Te to form a chain structure, as shown in Fig. 3. The shortest interchain contact Te $\cdot\cdot$ I is 3.571 Å and it is longer than that in Ta₄O(Te₂)₄TeI₄, 3.540 Å. However, the shortest Te $\cdot\cdot$ I distances between chains in (*MQ*₄)_{*x*}Y-type compounds (*M* = Nb, Ta; *Q* = Se, Te; *Y* = I, Br) are in the range 3.1–3.3 Å (10).

Some oxygen-centered tetranuclear cluster compounds [Ti₄O(S₂)₄Cl₆] (17), [Ti₄O(S₂)₄Cl₆·2S₈] (17), [R₄Ti₄O₂(S₂)₄] (18), [R₄Ti₄O(S₂)₄] (18), [Cp₄Ti₄OSe₇] (19), [V₄O(ett)₄Cl₈]²⁻ (20), and chain compounds *M*₄O(Te₂)₄TeI₄ (*M* = Ti, Nb, Ta) contain a common *M*₄O frame, which may be very important in stabilizing the clusters. The compounds [Ti₄O(S₂)₄Cl₆] and [Ti₄O(S₂)₄Cl₆·2S₈] also have similar cluster units as the chain compounds *M*₄O(Te₂)₄TeI₄. The unit is labeled as *M*₄O(*Q*₂)₄T₄ (*Q* = S, Te; *T* = Cl, Te) and *T* is shared by two neighboring clusters within the chain. Although the *M*–*M* distances in the *M*₄O core of these compounds are different (15–20), the *M*–O distances are the same, 2.03 ± 0.03 Å, and are almost equal to the sum of effective ion radii of *M*⁴⁺ and

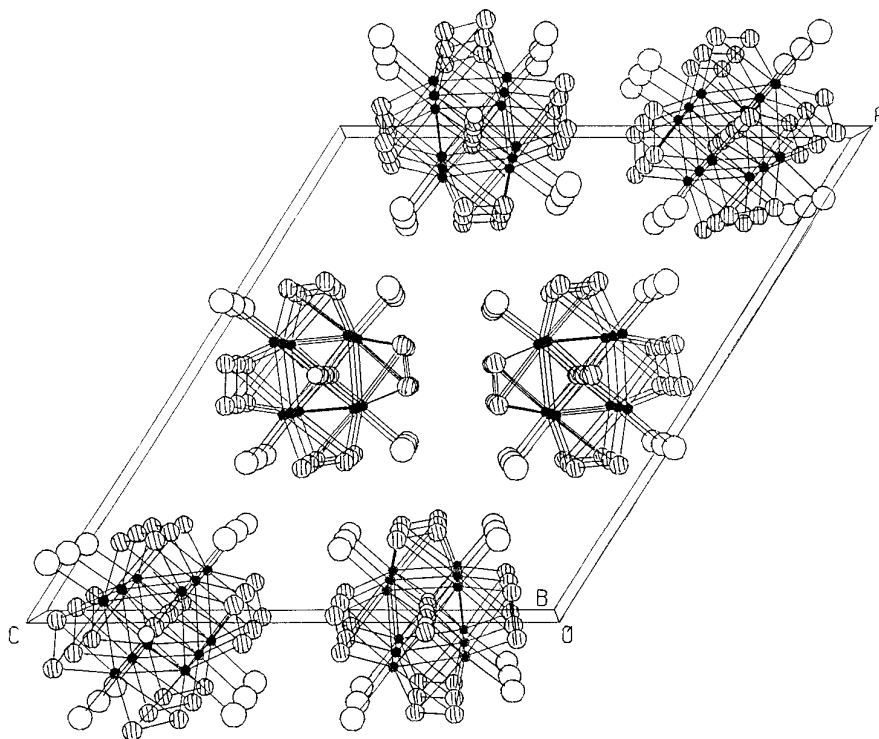


FIG. 1. A perspective view of $\text{Ti}_4\text{O}(\text{Te}_2)_4\text{TeI}_4$ along the b axis.

O^{2-} (21). The $M\text{-O}$ contacts must be the closest contact. The compounds with the $M_4\text{O}$ frame mentioned above contain $4n$ electrons and are stable, except $[\text{R}_4\text{Ti}_4\text{O}(\text{S}_2)_4]$ which does not meet the $4n$ electron criterion and which

is rapidly oxidized to the stable compound $[\text{R}_4\text{Ti}_4\text{O}_2(\text{S}_2)_4]$ (18).

The $M\text{-M}$ distances directly reflect the bonding between the metal atoms. The effective ion radii of Ti^{4+} , Nb^{4+} , and Ta^{4+} are almost the same, but the $M\text{-M}$ distances of short M_4 edges are different. The $\text{Ti}\text{-Ti}$ distances of short edges are always longer than those of $\text{Nb}\text{-Nb}$ or $\text{Ta}\text{-Ta}$. This difference simply arises from the bonding between metal atoms, because Nb^{4+} and Ta^{4+} still have one electron available for bonding with neighboring metal atoms, and Ti^{4+} has not. The bond order of each $\text{Ta}\text{-Ta}$ bond and $\text{Nb}\text{-Nb}$ is 0.5.

The kind of metal atoms is limited, because the increasing number of d electrons of metal increases the $M\text{-M}$ bond order and shortens the $M\text{-M}$ distance, because the

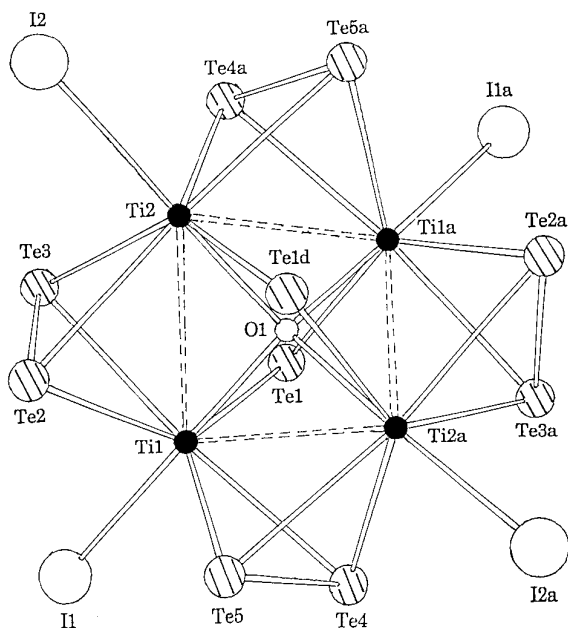


FIG. 2. The cluster unit $\text{Ti}_4\text{O}(\text{Te}_2)_4(\text{Te}_{0.5})_2\text{I}_4$ of $\text{Ti}_4\text{O}(\text{Te}_2)_4\text{TeI}_4$.

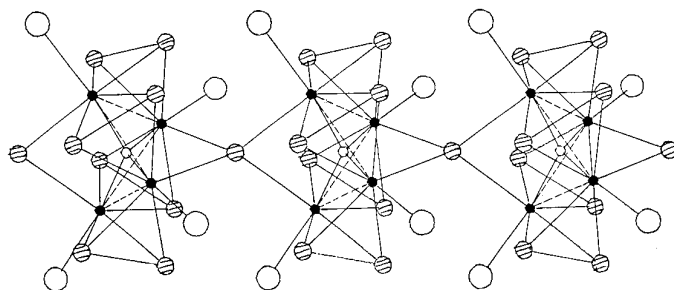


FIG. 3. The chain structure of $\text{Ti}_4\text{O}(\text{Te}_2)_4\text{TeI}_4$ compound.

oxygen in M_4O impedes the $M-M$ closer contact and keeps the four short edges of M_4O .

Q_2 bridges are common in one-dimensional earlier transitional metal chalcogenides (22). The $Q-Q$ distances are within the bonding range, 2.77–2.82 Å for Te–Te and 2.30–2.40 Å for Se–Se (7, 8, 11, 12). The valence of the bridged Q_2 group is considered to be Q_2^{2-} . In the $M_4O(Te_2)_4TeI_4$, each of four Te_2 groups bridges a short $M-M$ edge of the M_4 cage. The Te–Te bond crosses over the short $M-M$ bond. The two Te_2 groups and the μ_4 -Te atom are almost in the same plane. So are the molecular clusters. The average $Y_{\text{terminal}}-M$ -Bridge bond angle, M -Bridge- M bond angle (here Y is terminal halogen and Bridge means bridge atom in catenation cluster or molecular cluster), M -Bridge bond length, and $M-M$ bond length (15–20) are closely related; the longer the M -Bridge and $M-M$ bond, the larger the $Y_{\text{terminal}}-M$ -Bridge and M -Bridge- M bond angles. Since the $M-M$ bond is almost constant, if the bridge atom is S, the radius of which is smaller than that of Te, then the M -Bridge bond length is shorter and the $Y_{\text{terminal}}-M$ -Bridge and M -Bridge- M angles are larger. The situation is the same when one of the bridge atoms is Cl in the molecular case, but the effect of the terminal atom Y on the $Y_{\text{terminal}}-M$ -Bridge bond angle cannot be neglected. The larger electronegativity of atom Y exerts a larger dispersive force on the bridge atoms and makes the $Y_{\text{terminal}}-M$ -Bridge bond angle larger.

ACKNOWLEDGMENT

The authors thank the financial support of the National Natural Science Foundation of China.

REFERENCES

1. A. K. Cheetham and P. Day, "Solid State Chemistry: Compounds." Clarendon Press, Oxford, 1992.
2. F. W. Boswell, A. Proden, and J. K. Brandon, *J. Phys. C: Solid State Phys.* **16**, 1067 (1983).
3. K. Selte and A. Kjekshus, *Acta Chem. Scand. Navica* **18**, 690 (1964).
4. K. D. Bronsema, S. van Smaalen, J. L. de Boer, G. A. Wiegers, and F. Jellinek, *Acta Crystallogr. B* **43**, 305 (1987).
5. S. van Smaalen and K. D. Bronsema, *Acta Crystallogr. B* **42**, 43 (1987).
6. J. C. Bennett, F. W. Boswell, A. Product, J. M. Corbett, and S. Ritchie, *J. Phys. C: Solid State Phys.* **18**, 2145 (1985).
7. P. Gressier, A. Meerschaut, L. Guemas, and J. Rouxel, *J. Solid State Chem.* **51**, 141 (1984).
8. P. Gessier, L. Guemas, and A. Meerschaut, *Acta Crystallogr. B* **38**, 2877 (1982).
9. M. Sato and H. Nishihava, *J. Phys. C: Solid State Phys.* **18**, 2145 (1985).
10. M. Servin and H. R. Salva, *Solid State Commun.* **83**(7), 457 (1992).
11. Chang-Cang Huang, Doctoral dissertation of Fuzhou University, China, 1995.
12. A. Meerschaut, P. Grenouilleau, and J. Rouxel, *J. Solid State Chem.* **61**, 90 (1986).
13. P. Grenouilleau A. Meerschaut, L. Guemas, and J. Rouxel, *J. Solid State Chem.* **66**, 293 (1987).
14. S.-X. Liu, D.-P. Huang, C.-C. Huang, and J.-L. Huang, *Polyhedron* in press (1996).
15. W. Tremel, *J. Chem. Soc. Commun.* 709 (1992).
16. D.-P. Huang, C.-C. Huang, S.-X. Liu, H.-D. Xu, and J.-L. Huang, *Acta Crystallogr.* in press.
17. F. A. Cotton, X.-J. Feng, P. A. Kibala, and R. B. W. Sandor, *J. Am. Chem. Soc.* **111**, 2148 (1989).
18. G. A. Zank, C. A. Jones, T. B. Ranchfuss, and A. L. Rheingold, *Inorg. Chem.* **25**, (1986).
19. P. G. Maue and D. Fenske, *Z. Naturforsch.* **436**, 1213 (1988).
20. Joe R. Rambo, J. C. Huffmman, and G. Christou, *J. Am. Chem. Soc.* **111**, 8027 (1989).
21. R. C. Weast (Ed.), "CRC Handbook of Chemistry and Physics," 66th ed., pp. 1985–1986 F-164. CRC Press, Boca Raton, FL.
22. R. B. King, "Encyclopedia of Inorganic Chemistry," Vol. 2.