Cette description est relative aux premiers sels neutres de phosphites de terres rares. D'autres phases dans cette famille de sels neutres ont pu être isolées et font l'objet d'études cristallographique et structurale.

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Structure of a New Ternary Chalcogenide: FeTa(μ_4-Te)(μ_3-Te)$_2$

BY SHI-XIONG LIU,* GUAN-LIANG CAI AND JIN-LING HUANG

Institute of Structural Chemistry, Fuzhou University, Fuzhou, Fujian 350002, People's Republic of China

Abstract. Iron tantalum tritelluride, FeTaTe$_3$, M_r = 619.59, monoclinic, $P2_1/m$, a = 7.407 (4), b = 3.625 (3), c = 9.966 (3) Å, β = 109.16 (3)°, V = 252.8 (2) Å^3, Z = 2, D_x = 8.138 g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 410.98 cm^{-1}, $F(000)$ = 510, T = 295 K, final R = 0.051 for 1145 observed reflections. The new layered ternary chalcogenide FeTaTe$_3$ has been prepared by high-temperature reaction of the elements. FeTaTe$_3$ displays a new layered structure type. Every layer contains octahedral Ta atoms and tetrahedral Fe atoms each coordinated by Te atoms. These polyhedra, which are distinctly irregular, join *via* shared edges to form chains along the *b* axis. The Fe—Te bond in the title compound is the first to be characterized in the layered compounds.

Introduction. The study of materials in the ternary systems Ni/Co–Ta/Nb–S/Se with layered structures has been motivated by a general utilitarian interest, an assortment of unusual structure features, and an interesting anisotropic behaviour (Hulliger, 1976; Canadell & Whangbo, 1987; Sunshine & Ibers, 1985, 1986). Compared with many ternary sulfides and selenides, studies of only a few ternary tellurides have been reported (Liimatta & Ibers, 1988, 1989; Huang, Liu & Huang, 1991). Recently, we synthesized some new tellurides and have determined their

structure and properties. Here we present the crystal structure of FeTa(μ_4-Te)(μ_3-Te)$_2$, in which the coordination geometry of the Ta atom is different from that found in [Ni$_2$Ta$_2$Te$_4$] (Huang, Liu & Huang, 1991).

Experimental. FeTa(μ_4-Te)(μ_3-Te)$_2$ was obtained by direct combination of the elements. Fe powders (99.8%, Shanghai Chemicals Supply Service Station) were reduced in H$_2$ atmosphere for 20 min at 1123 K and then immediately sealed in a silica tube. Ta powders (99.98%, Zhuzhou Hard Alloy Plant) and Te powders (99.999%, Shanghai Chemicals Supply Service Station) were mixed with reduced Fe powders. The mixture was loaded in a silica tube, and a suitable amount of I$_2$ (99.99%, Beijing Chemicals Factory) was added as a transport agent for crystal growth. The tube was evacuated to ~0.0133 Pa and sealed. Then the tube was heated at 1213 K for 10 d. Some small shiny grey–black needle-like crystals formed. The composition of the crystal was proved by standardless electron spectrum analysis on a JEOL scanning electron microscope after data collection by X-ray single-crystal diffraction. The analytical results shown in Table 1 agree with those from crystal-structure refinement within the experimental e.s.d. range.

A grey–black crystal with dimensions 0.08 × 0.09 × 0.31 mm was selected and mounted on an

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* To whom correspondence should be addressed.

Table 1. *Standardless analysis results of JEOL scanning electron microscope*

ZAF correction, 25.00 kV, 32.22° angle of incidence.

Element	K-ratio	Z	A	F	At. %	Wt%
Ta—L	0.344	1.041	1.041	1.000	25.64	36.15
Ta—M	0.009	1.029	1.305	0.998	0.87	1.23
Fe—K	0.080	0.846	1.219	0.966	18.53	8.07
Te—L	0.492	0.999	1.223	0.995	54.58	54.28
Nb—L	0.002	0.916	1.841	0.995	0.38	0.27
I—K	0.000	0.977	1.195	0.993	0.00	0.00
						Total = 100.00%

AFC-5R diffractometer. A least-squares fit of 20 reflections in the range $12 < \theta < 20°$ yielded the unit cell and orientation matrix. Intensities of reflections with indices h 0 to 12, k 0 to 6, l -16 to 15 with $2\theta < 74°$ were measured by θ–2θ scans of scan width $(1.575 + 3.000\tan\theta)°$, and with graphite-monochromated Mo $K\alpha$ radiation. Intensities of three standard reflections measured every 150 reflections showed no evidence of crystal decay. 1532 reflections were measured, of which 1450 were unique. Of these 1145 with $I > 3\sigma(I)$ were used in structure solution and refinement; $R_{int} = 0.05$. Data were corrected for Lorentz and polarization factors, and DIFABS absorption effect, maximum and minimum transmission factors 1.331 and 0.594 (Walker & Stuart, 1983; Coppens, Leiserowitz & Rabinovich, 1965). Gaussian integration grid $6 \times 6 \times 6$. Data collection showed systematic absences typical of the space groups $P2_1$ and $P2_1/m$. The space group $P2_1/m$ was chosen and confirmed by the successful structure solution and refinement.

The crystal structure was solved by direct methods. Refinement was by full-matrix least-squares calculations with anisotropic thermal parameters. The final cycle of refinement included 31 variable parameters, and gave $R = 0.051$, $wR = 0.068$, $w = 1/\sigma^2(F_o)$, goodness of fit = 1.77. Maximum shift/e.s.d. = 0.002, and the final residual electron density was 14.23 (-7.08) e Å^{-3}; no chemically significant features. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were made on a MicroVAX II computer using the TEXSAN software package (Molecular Structure Corporation, 1985). Atomic coordinates* and details of molecular geometry are listed in Tables 2 and 3, respectively.

Discussion. A view of the $[FeTa(\mu_4\text{-Te})(\mu_3\text{-Te})_2]$ structure down the [101] direction (Fig. 1) clearly shows the layered nature of the title compound. The

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55329 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0023]

Table 2. *Positional parameters and equivalent isotropic thermal parameters* (Å^2)

$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}]$.

	x	y	z	B_{eq}
Ta(1)	0.3340 (1)	$\frac{1}{4}$	0.30049 (7)	0.59 (2)
Fe(1)	0.1151 (4)	$-\frac{1}{4}$	0.0891 (3)	0.66 (7)
Te(1)	-0.0608 (2)	$\frac{1}{4}$	0.1864 (1)	0.76 (3)
Te(2)	0.4837 (2)	$-\frac{1}{4}$	0.1590 (1)	0.67 (3)
Te(3)	0.7178 (2)	$\frac{1}{4}$	0.4971 (1)	0.59 (3)

Table 3. *Selected bond distances* (Å) *and bond angles* (°)

Ta(1)—Te(1)	2.768 (1)	Fe(1)—Te(1^f)	2.599 (2)
Ta(1)—Te(2)	2.744 (1)	Fe(1)—Te(1^c)	2.641 (3)
Ta(1)—Te(2^a)	2.744 (1)	Fe(1)—Te(2)	2.587 (3)
Ta(1)—Te(3)	2.875 (2)	Ta(1)—Fe(1)	2.848 (2)
Ta(1)—Te(3^b)	2.830 (1)	Ta(1)—Fe(1^a)	2.848 (2)
Ta(1)—Te(3^c)	2.830 (1)	Fe(1)—Te(1^c)	2.713 (4)
Fe(1)—Te(1)	2.599 (2)	Fe(1)—Fe(1^d)	2.713 (4)

Te(1)—Ta(1)—Te(2)	109.85 (4)	Te(1)—Fe(1)—Te(1^f)	88.5 (1)
Te(1)—Ta(1)—Te(2^a)	109.85 (4)	Te(1)—Fe(1)—Te(1^c)	117.64 (7)
Te(1)—Ta(1)—Te(3)	162.76 (4)	Te(1)—Fe(1)—Te(2)	120.91 (7)
Te(1)—Ta(1)—Te(3^b)	85.46 (4)	Te(1^f)—Fe(1)—Te(1^c)	117.64 (7)
Te(1)—Ta(1)—Te(3^c)	85.46 (4)	Te(2)—Fe(1)—Te(1^f)	120.91 (7)
Te(2)—Ta(1)—Te(2^a)	82.68 (6)	Te(2)—Fe(1)—Te(1^c)	93.8 (1)
Te(2)—Ta(1)—Te(3)	82.77 (4)		
Te(2)—Ta(1)—Te(3^b)	96.62 (5)	Fe(1)—Ta(1)—Fe(1^a)	79.06 (8)
Te(2)—Ta(1)—Te(3^c)	164.04 (4)	Ta(1)—Fe(1)—Fe(1^d)	98.16 (6)
Te(2^a)—Ta(1)—Te(3)	82.77 (4)	Ta(1)—Fe(1)—Fe(1^c)	173.0 (2)
Te(2^a)—Ta(1)—Te(3^b)	164.04 (4)	Ta(1)—Fe(1)—Ta(1^f)	79.06 (8)
Te(2^a)—Ta(1)—Te(3^c)	96.62 (5)	Ta(1^f)—Fe(1)—Fe(1^d)	173.0 (2)
Te(3)—Ta(1)—Te(3^b)	81.32 (4)	Ta(1^f)—Fe(1)—Fe(1^c)	98.16 (6)
Te(3)—Ta(1)—Te(3^c)	81.32 (4)	Fe(1^c)—Fe(1)—Fe(1^d)	83.9 (1)
Te(3^b)—Ta(1)—Te(3^c)	79.67 (5)		

Symmetry code: (a) x, $1 + y$, z; (b) $1 - x$, $-\frac{1}{2} + y$, $1 - z$; (c) $1 - x$, $\frac{1}{2} + y$, $1 - z$; (d) $-x$, $\frac{1}{2} + y$, $-z$; (e) $-x$, $-\frac{1}{2} + y$, $-z$; (f) x, $-1 + y$, z.

structure can be described as a series of zigzag chains. There are two unique chains that run parallel to the b axis. One chain consists of Ta-centred octahedra that share Te—Te edges; the distance between two Ta atoms from two neighbouring Ta octahedra is 3.625 Å (the b repeat). On the other hand, the other chain is made up of Fe-centred edge-sharing tetrahedra; every two neighbouring Fe-centred tetrahedra are related to each other by a screw axis 2_1 [010] and the closest distance between Fe atoms in adjacent tetrahedra is 2.713 (4) Å, indicating that there are Fe—Fe bonds between neighbouring tetrahedra in this crystal. The Fe—Fe distance of 2.713 Å is 0.28 and 0.04 Å longer than the Fe—Fe bond lengths in $[Cp_2Mo_2Fe_2Te_2(CO)_7]$ (Bogan, Rauchfuss & Rheingold, 1985) and in $[(\eta^5\text{-}C_5Me_5)MnFe_2Te(CO)_8]$ (Herrmann, Hecht, Ziegler & Zahn, 1984), respectively. The Fe—Fe bond length is near the longer limit of measured Fe—Fe bond lengths (Churchill, 1967).

Fig. 2 displays the geometry around the Ta and Fe atoms. The coordination about Ta and Fe atoms, as observed, is distorted from ideal geometry. The dis-

tortion may be owing to the Fe—Fe bonds in the crystal. The Ta—Te distances in the octahedron range from 2.744 (1) to 2.875 (2) Å. These distances compare well with the Ta—Te distances of 2.664 (4)–2.894 (4) Å found in [Ta$_3$Pd$_3$Te$_{14}$] (Liimatta & Ibers, 1989). However, the Ta atom is tetrahedrally coordinated with four Te atoms in [Ni$_2$Ta$_2$Te$_4$] (Huang, Liu & Huang, 1991).

Until now Fe—Te bonds have only been found in some metal carbonyl telluride clusters. The Fe—Te bond lengths are in the range 2.587–2.641 Å in FeTaTe$_3$. This is somewhat longer than correspond-
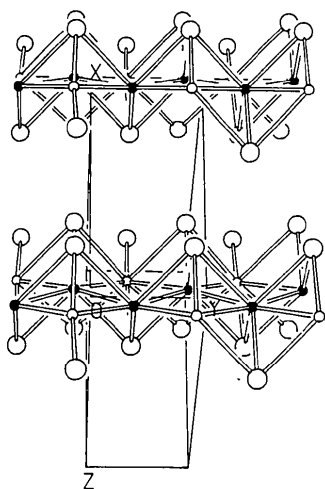

Fig. 1. View of the FeTaTe$_3$ structure down the direction [101]. Here and in Fig. 2, small filled circles are Fe atoms, small open circles are Ta atoms, and large open circles are Te atoms.
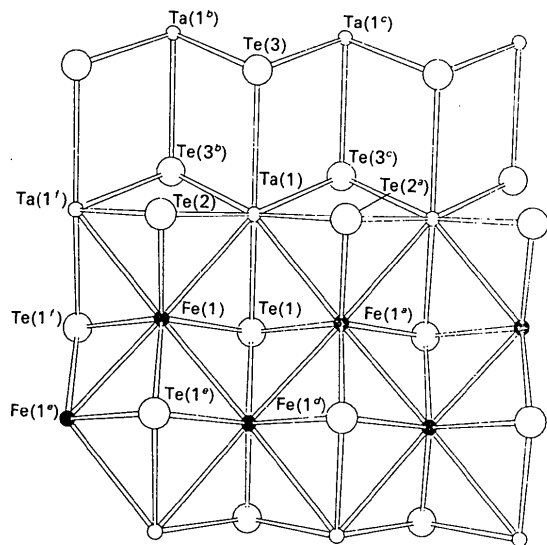

Fig. 2. View of the FeTaTe$_3$ structure down the c axis showing the coordination around the Ta and Fe atoms. Symmetry code is given in Table 3.

ing values in the metal carbonyl telluride clusters, e.g. 2.466–2.467 Å in [FeCo$_2$(CO)$_9$Te] (Strouse & Dahl, 1971), 2.472–2.476 Å in [(η^5-C$_5$Me$_5$)MnFe$_2$-Te(CO)$_8$] (Herrmann, Hecht, Ziegler & Zahn, 1984), 2.554–2.586 Å in [Fe$_2$Te$_3$(CO)$_6$]$^{2-}$ (Eichhorn, Haushalter & Merola, 1990), 2.562–2.567 Å in [Cp$_2$Mo$_2$FeTe$_2$(CO)$_3$(C$_2$H$_2$)] (Bogan, Clark & Rauchfuss, 1986).

This structure can also be described as a series of sandwiches, shown in Fig. 1. The neighbouring sandwiches are held together by weak van der Waals interaction between Te atoms. As shown in Fig. 2, in each sandwich, the metal atoms are packed between layers of Te atoms, each Fe atom is bonded to two adjacent Fe atoms, forming an Fe$_n$ chain along the b axis with Fe—Fe bonds (2.713 Å), and every Ta atom in one of the two sides of the Fe$_n$ chain is connected with two neighbouring Fe atoms in the Fe$_n$ chain, forming two Ta—Fe bonds (2.848 Å). The Ta—Fe bond length is longer than most of the Ta—Te distances but shorter than the longest Ta—Te distance (2.875 Å) in this crystal.

There are one μ_4-Te atom [Te(1)] and two μ_3-Te atoms [Te(2) and Te(3)] in the title molecule, although there are only μ_4-Te atoms in [Ni$_2$Nb$_2$Te$_4$] and [Ni$_2$Ta$_2$Te$_4$] (Huang, Liu & Huang, 1991). The majority of the Te—Te distances in this crystal range from 3.760 to 3.952 Å. These distances are significantly longer than the Te—Te bond of 2.928 Å found in [TaTe$_4$] (Bronsema, van Smaalen, de Boer, Wiegers, Jellinek & Mahy, 1987), and Te—Te distances of 3.125–3.812 Å found in [TaNiTe$_5$], [Ta$_3$Pd$_3$Te$_{14}$] and [NbPdTe$_5$] (Liimatta & Ibers, 1988, 1989), but they are similar to the 3.794 Å distance found in [Cp$_2$Mo$_2$FeTe$_2$(CO)$_3$(C$_2$H$_2$)] (Bogan, Clark & Rauchfuss, 1986). The closest distance between two Te atoms from the neighbouring layers is 3.727 (1) Å. However, all Te—Te distances in the title compound are still shorter than twice the ionic radius of Te^{2-} (4.4 Å) (Shannon, 1976).

On the other hand, [FeTa(μ_4-Te)(μ_3-Te)$_2$] can also be considered as an intercalation compound; that is, the Fe atoms are intercalated into a layered structure formed by TaTe$_2$ building blocks, as found in the corresponding sulfides and selenides. However, the situation of the tellurides is remarkably different from that of sulfides and selenides. For the series M'_xMX_2 (M' = Ti, V, Fe, Co, Ni, etc.; M = Nb, Ta; X = S, Se, $x < 0.33$) (Beal, 1979), the ternary atom, M', occupies octahedral sites between sheets consisting of M atoms bonded to two layers of chalcogens. It is noteworthy, therefore, that in [FeTa(μ_4-Te)(μ_3-Te)$_2$] the ternary atom, Fe, inserts into the tetrahedral cavities within the sheet in which Ta atoms have occupied octahedral caverns instead of holes between the sheets. This particular structural characteristic of tellurides has been seen in

$[Ni_2Nb_2Te_4]$ and $[Ni_2Ta_2Te_4]$ (Huang, Liu & Huang, 1991).

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Structure of Disulfuryl Difluoride at 100 K

BY ALEXANDER J. BLAKE*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

AND ZDIRAD ŽÁK

Department of Inorganic Chemistry, Masaryk University, Kotlářská (Street) 2, 61137 Brno, Czechoslovakia

Abstract. $S_2O_5F_2$, $M_r = 182.07$, tetragonal, $P\bar{4}2_1c$, $a = 7.5214 (5)$, $c = 9.2610 (10)$ Å, $V = 523.9$ Å^3, $Z = 4$, $D_x = 2.308$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 0.975$ mm^{-1}, $F(000) = 360$, $T = 100$ K, $R = 0.024$ for 433 unique observed reflections. Molecules of $S_2O_5F_2$ occupy special positions on twofold axes. Principal bond lengths and angles are: S—O 1.6108 (11); S=O 1.3947 (20), 1.4021 (18); S—F 1.5215 (16) Å; S—O—S 123.44 (7); O—S=O 109.82 (8), 104.46 (9); O—S—F 98.34 (7); O=S—F 107.42 (9), 108.16 (10); O=S=O 125.35 (11)°. The molecule adopts a different conformation in the crystal from that previously observed in the gas phase.

Introduction. Disulfuryl difluoride was first prepared by the reaction of SbF_5 with SO_3 (Hayek & Koller, 1951). It is a liquid at room temperature (m.p. 225 K, b.p. 324 K) and is sensitive to moisture. Although the structure of the free molecule is known from gas-phase electron diffraction (Hencher & Bauer, 1973), its solid-state structure was unknown. We undertook the determination of the crystal structure in part to allow comparison between the molecule in the two phases.

Experimental. The title compound was prepared by the reaction of SbF_5 with SO_3 (Hayek & Koller, 1951). The crude product was purified by repeated distillation and its purity checked by Raman spectroscopy (Toužin & Černik, 1992). A sample of the liquid was sealed in a Pyrex capillary tube and slow cooling on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986) yielded a single crystal which was held at 100.0 (1) K for the duration of the