

Additional short intermolecular distances are 2.73 Å between O(21) and H(51) of the molecule at $2-x, 2-y, 1-z$ and 2.35 Å between H(25) and H(43) of the molecule at $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

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Preparation and Structure Determination of Ti_8S_3

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Ti_8S_3 is monoclinic $C2/m$, $a=32.69$ (1), $b=3.327$ (2), $c=19.36$ (2) Å, $\beta=139.9$ (5)°, $V=1356$ (7) Å³. The structure was determined by single-crystal methods and refined to $R=0.08$ by least-square calculations. The composition was deduced from the structure. There are a great many structural similarities between Ti_8S_3 and Ti_2S .

Introduction

Ti_8S_3 was first prepared by heating 150 mg of a pelletized mixture of TiS and titanium metal with an overall Ti/S ratio of 3.0 to 1125°C. The small single crystal used in structure determination was obtained from the partially melted pellet which was a mixture of Ti_8S_3 and Ti_2S . Rotation and zero and first-layer Weissenberg patterns indicated that the crystal was C -centered monoclinic with the crystal-rotation axis coincident with the unique crystallographic b axis of the unit cell. The conditions for reflection were observed to be

$$\begin{aligned} hkl: & h+k=2n \\ h0l: & h=2n \\ 0k0: & k=2n \end{aligned}$$

The possible space groups consistent with this observation are $C2$, Cm , and $C2/m$. $C2$ was ruled out because the unitary structure factors for the $h0l$ and $h2l$ reflections were essentially equal, indicating that the atoms are located in mirror planes perpendicular to the b axis.

Single-crystal X-ray diffraction data were collected with a Hilger-Watts four-circle automated diffractometer, coupled with an SDS 910 computer as described by Dahm, Bensen, Nimrod, Fitzwater & Jacobson

(1967). Peak-height intensities were measured. Zirconium-filtered Mo $K\alpha$ radiation was used to obtain data for non-extinguished reflections in the first two octants with $\theta \leq 30^\circ$. Lorentz and polarization corrections were applied, but owing to the very small size of the crystal, no absorption correction was made. The crystal dimensions were approximately $10\mu \times 10\mu \times 50\mu$.

The fluctuation level of the counter was assumed to be proportional to the square root of the total counts and the statistical uncertainties of the intensity data were taken to be $(A+B)^{1/2}/(A-B)$, where A and B are peak and background counts respectively. Of the 2351 intensity data collected 713 had uncertainties less than 33%.

A Howells, Phillips & Rogers plot proved to be an inconclusive test for a center of symmetry. The structure was determined by *MULTAN* techniques (Germain, Main & Woolfson, 1971) for the non-centrosymmetric space group Cm . The criteria of this technique for judgement of the probable correctness of the various calculated solutions permitted the selection of a most probable solution. This trial structure placed atoms in 44 independent point sets. The titanium and sulfur positions were distinguished by examining the atomic coordination polyhedra. It was noted that a center of symmetry was present in the trial structure which implied that $C2/m$ rather than Cm was the cor-

rect space group. The structure was refined by least-squares computation (Busing, Martin & Levy, 1962), with atomic scattering factors by Hansen, Herman, Lea & Skillman (1964), and the assumed space group $C2/m$. Isotropic temperature factors were assumed in the refinement. All of the original titanium and sulfur positions from the *MULTAN* solution were within 0.5 \AA of the final refined positions given in Table 1. The structure was refined by use of the data with uncertainties $\leq 33\%$; the unweighted R index calculated from $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.080 , and the positional uncertainties less than 0.014 \AA for titanium and less than 0.020 \AA for sulfur.*

Table 1. Final atomic parameters for Ti_8S_3

All atoms occupy fourfold positions (i) $x, 0, z$ of space group $C2/m$.

	x	y	z	$B (\text{\AA}^2)$
Ti(1)	0.5795 (4)	0.0	0.5867 (7)	1.0 (2)
Ti(2)	0.5943 (4)	0.0	0.7732 (7)	1.1 (2)
Ti(3)	0.5680 (4)	0.0	0.0804 (7)	1.0 (2)
Ti(4)	0.6223 (4)	0.0	0.3128 (7)	1.0 (2)
Ti(5)	0.6712 (4)	0.0	0.0034 (7)	0.9 (2)
Ti(6)	0.6956 (4)	0.0	0.6419 (7)	1.0 (2)
Ti(7)	0.7180 (4)	0.0	0.8292 (7)	0.9 (2)
Ti(8)	0.7033 (4)	0.0	0.2776 (7)	0.7 (2)
Ti(9)	0.8001 (4)	0.0	0.0692 (7)	1.2 (2)
Ti(10)	0.7658 (4)	0.0	0.5729 (7)	0.9 (2)
Ti(11)	0.8363 (4)	0.0	0.5171 (7)	1.0 (2)
Ti(12)	0.8476 (4)	0.0	0.8980 (7)	0.9 (2)
Ti(13)	0.9410 (4)	0.0	0.1633 (7)	1.0 (2)
Ti(14)	0.0105 (4)	0.0	0.5945 (7)	1.0 (2)
Ti(15)	0.9904 (4)	0.0	0.8926 (7)	0.9 (2)
Ti(16)	0.4485 (4)	0.0	0.6199 (7)	1.1 (2)
S(1)	0.5719 (6)	0.0	0.9517 (9)	0.9 (2)
S(2)	0.7430 (6)	0.0	0.2061 (10)	1.1 (2)
S(3)	0.8933 (6)	0.0	0.4711 (10)	0.9 (2)
S(4)	0.8722 (6)	0.0	0.7755 (10)	1.0 (2)
S(5)	0.8710 (6)	0.0	0.2704 (10)	0.9 (2)
S(6)	0.9462 (6)	0.0	0.7152 (10)	1.3 (3)

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30243 (4 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

A difference Fourier electron density map obtained from these data was void of significant maxima. The highest values in this difference map occurred on atom positions and were less than $0.5 e$.

Discussion

There exist in Ti_8S_3 structural units which are similar to those found in Ti_2S . These units are linked in such a way as to yield a relatively large and complex unit cell, as can be seen in Fig. 1. Thus, a reduction in complexity is accomplished by considering the similarities between the Ti_8S_3 and Ti_2S structures.

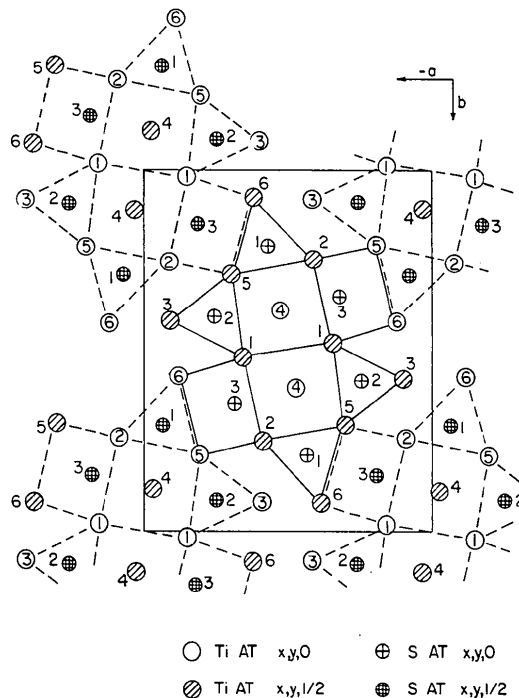


Fig. 2. The crystal structure of Ti_8S_3 viewed along the c axis.

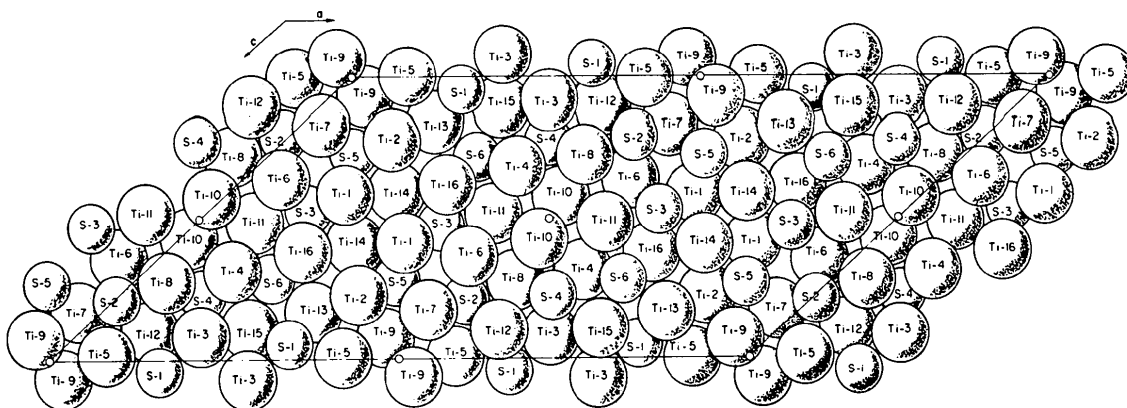


Fig. 1. The crystal structure of Ti_8S_3 viewed along the b axis.

Table 2. *The nearest neighbors and their interatomic distances in Ti₈S₃*

(Deviations for Ti-S and Ti-Ti distances are 0.050 and 0.035 Å respectively.)

Central atom	Type of neighbors	Number of neighbors	Distances	Central atom	Type of neighbors	Number of neighbors	Distances	Central atom	Type of neighbors	Number of neighbors	Distances
Ti(1)	S(5)	2	2.486	Ti(8)	S(4)	2	2.460	Ti(15)	S(6)	1	2.499
	S(3)	2	2.513		S(2)	1	2.529		S(1)	2	2.554
	Ti(14)	2	2.820		Ti(10)	2	2.767		S(4)	1	2.574
	Ti(14)	2	2.901		Ti(6)	2	2.875		Ti(3)	2	2.868
	Ti(6)	1	3.049		Ti(3)	1	2.884		Ti(3)	2	2.881
	Ti(7)	1	3.159		Ti(12)	2	2.910		Ti(4)	2	3.120
					Ti(11)	1	3.091		Ti(13)	1	3.145
Ti(2)	S(5)	2	2.497	Ti(9)	Ti(4)	1	3.196	Ti(16)	S(3)	2	2.521
	Ti(14)	2	2.783		S(5)	1	2.591		S(6)	2	2.532
	Ti(13)	2	2.793		Ti(9)	2	2.696		Ti(14)	2	2.942
	Ti(9)	2	2.803		Ti(5)	2	2.770		Ti(11)	2	2.995
	Ti(5)	1	3.010		Ti(2)	2	2.803		Ti(2)	1	3.149
	Ti(16)	1	3.149		Ti(7)	2	2.955		Ti(13)	2	3.202
					Ti(7)	1	3.124				
Ti(3)	S(4)	2	2.454	Ti(10)	Ti(7)	1	3.124	S(1)	Ti(12)	2	2.535
	S(1)	1	2.586		S(4)	1	2.576		Ti(13)	2	2.541
	Ti(15)	2	2.868		Ti(10)	2	2.710		Ti(15)	2	2.554
	Ti(3)	1	2.879		Ti(8)	2	2.767		Ti(5)	1	2.560
	Ti(15)	2	2.881		Ti(11)	2	2.843		Ti(3)	1	2.586
	Ti(8)	1	2.884		Ti(11)	2	2.843				
	Ti(12)	2	2.960		Ti(4)	2	2.943				
Ti(4)	S(4)	2	2.488	Ti(11)	Ti(8)	1	3.091	S(2)	Ti(7)	2	2.489
	S(6)	2	2.490		S(6)	1	2.563		Ti(8)	1	2.529
	Ti(11)	2	2.938		S(3)	1	2.605		Ti(6)	2	2.533
	Ti(10)	2	2.943		Ti(10)	2	2.843		Ti(12)	2	2.544
	Ti(15)	2	3.120		Ti(6)	2	2.903		Ti(5)	1	2.603
	Ti(8)	1	3.196		Ti(4)	2	2.938				
					Ti(16)	2	2.995				
Ti(5)	S(1)	1	2.560	Ti(12)	Ti(8)	1	3.091	S(3)	Ti(6)	2	2.509
	S(2)	1	2.603		Ti(8)	1	3.091		Ti(1)	2	2.513
	Ti(9)	2	2.770		S(1)	2	2.535		Ti(14)	1	2.520
	Ti(7)	2	2.905		S(2)	2	2.544		Ti(16)	2	2.521
	Ti(13)	2	2.922		Ti(8)	2	2.910		Ti(11)	1	2.605
	Ti(12)	2	2.930		Ti(5)	2	2.930				
	Ti(2)	1	3.010		Ti(3)	2	2.960				
Ti(6)	S(3)	2	2.509	Ti(13)	S(6)	1	2.418	S(4)	Ti(3)	2	2.454
	S(2)	2	2.533		S(1)	2	2.541		Ti(8)	2	2.460
	Ti(8)	2	2.875		Ti(2)	2	2.793		Ti(4)	2	2.488
	Ti(11)	2	2.903		Ti(5)	2	2.922		Ti(15)	1	2.574
	Ti(1)	1	3.049		Ti(15)	1	3.145		Ti(10)	1	2.576
	Ti(7)	1	3.097		Ti(16)	2	3.202		Ti(12)	1	3.032
Ti(7)	S(2)	2	2.489	Ti(14)	S(5)	1	2.520	S(5)	Ti(1)	2	2.486
	S(5)	2	2.520		S(3)	1	2.520		Ti(2)	2	2.497
	Ti(5)	2	2.905		Ti(2)	2	2.783		Ti(14)	1	2.520
	Ti(9)	2	2.955		Ti(1)	2	2.820		Ti(7)	2	2.520
	Ti(6)	1	3.097		Ti(1)	2	2.901		Ti(9)	1	2.591
	Ti(9)	1	3.124		Ti(16)	2	2.942				
	Ti(1)	1	3.159		Ti(14)	1	3.165				

The Ti_2S structure is shown in projection onto the ab plane in Fig. 2 (Conard, 1969). The solid lines trace out the projection of a structural unit which is repeated indefinitely in the c direction. It consists of the trigonal prismatic coordination polyhedra around S(1) and S(2) (prism axes parallel to the crystallographic c axis) and around S(3) (prism axis perpendicular to the c axis), and two cubic coordination polyhedra around Ti(4), which share faces to form the structural unit.

The 2_1 screw operation implicit in the space group ($Pnmm$) of Ti_2S causes repetition of this unit centered on the origin, as shown by the dashed outline of the unit in Fig. 2. The Ti(5)–Ti(6) prism edge is shared between the units. It also results that Ti(3) of the dashed unit is a capping atom for the triangular prism around S(1).

Ti_8S_3 has two basic structural units which are similar to that found in Ti_2S . These are illustrated in solid outline in Fig. 3(a) and (b). Each of these shares only three cube faces with trigonal prisms as compared to six in Ti_2S . The unit of Fig. 3(a) differs from that of Fig. 3(b) inasmuch as one of the trigonal prisms has its axis parallel to the plane of the figure [the prism around S(6)].

Each of the basic units is inverted through a center of symmetry as shown by the dashed outlines in Fig. 3(a) and (b). There result fused units as shown and these in large measure provide the building blocks of the structure. The units are centered at $(\frac{1}{2}, \frac{1}{4}, \frac{1}{2})$ and at $(\frac{1}{2}, \frac{3}{4}, 0)$ respectively as can be seen in Fig. 1. The nearly complete structure results from the translation of these units by $\frac{1}{2}, \frac{1}{2}, 0$. This repetition produces cubes which are filled by Ti(14). The two basic units of Ti_8S_3 are linked *via* edge sharings and capping of polyhedra, including the Ti(13)–Ti(15) edge which is shared like the edge in Ti_2S . The similarity between the Ti_8S_3 and Ti_2S structures is further emphasized by the similarities of the interatomic distances as can be seen by comparing the interatomic distances given in Table 2 with those given for Ti_2S in a previous publication (Owens, Conard & Franzen, 1967). Atoms at similar positions in the two structures have distances of the same length within experimental error.

Thus, there are remarkable similarities between the two metal-rich sulfides of titanium despite the difference in stoichiometry. The two compounds can be regarded as modifications of a structure class.

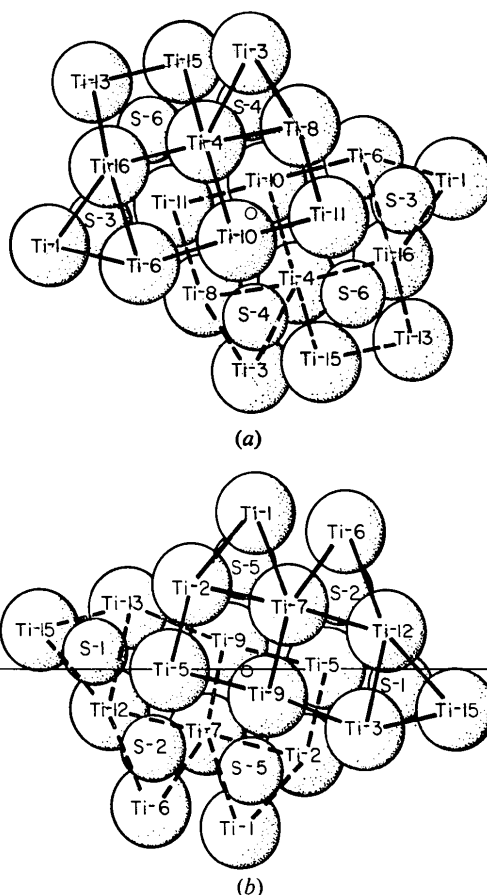


Fig. 3. (a) One of the basic structure units of Ti_8S_3 . (b) The second basic structure unit of Ti_8S_3 .

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