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The Crystal Structure of Ta₂S*

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The crystal structure of ditantalum sulfide, Ta₂S, has been determined from single-crystal X-ray diffraction data. The compound crystallizes in the orthorhombic system, space group *Pbcm*, with unit-cell dimensions: $a = 7.379$, $b = 5.574$, and $c = 15.19$ Å. The unit cell contains 12 formula units. Refinement of the structure was performed by a least-squares treatment of the positional parameters and the temperature factor coefficients. The Ta₂S structure is fundamentally different from other known metal-rich chalconide structures. The structure can be viewed as chains of body-centered pentagonal antiprisms of tantalum atoms sharing faces in one direction and interconnected *via* sulfur atoms in the other two directions.

Introduction

The crystal structures of the sulfides of tantalum have been reviewed by Jellinek (1963). It was concluded that an early claim of the preparation of a subsulfide of tantalum by Biltz & Kocher (1938) was incorrectly based on powder patterns of a mixture of phases. Preparations at relatively low temperatures (less than about 1000°C) have generally failed to produce metal-rich sulfides such as have been prepared by high-temperature techniques in recent years in the Hf-S system (Franzen & Graham, 1966), in the Ti-S system (Owens, Conard & Franzen, 1967), and in the Nb-S system (Franzen, Beineke & Conard, 1968). The work reported here was performed with the purpose of extending the application of high-temperature preparation techniques to the Ta-S system in order to prepare and determine the structure of a lower sulfide of tantalum.

Experimental

The ditantalum sulfide samples were prepared in a manner analogous to that previously described (Owens, Conard & Franzen, 1967). The sulfur obtained from the American Smelting and Refining Co. was 99.999% pure. The tantalum obtained from the National Research Corporation was 99.99% pure. The final annealing temperature in the case of the Ta₂S preparation was 1600°C. Single-crystal X-ray diffraction data were initially collected with a General Electric spectrometer and nickel filtered Cu $K\alpha$ radiation. Data were collected for 767 reflections in the range $0^\circ < 2\theta \leq 160^\circ$. A second set of data was collected using a Hilger-Watts diffractometer coupled with an SDS(910-IBM) (1401) computer configuration described elsewhere (Dahm, Benson, Nimrod, Fitzwater & Jacobson, 1967). Mo $K\alpha$ radiation was used with a Zr filter to collect data for 1104 reflections in the range $0^\circ < 2\theta \leq 60^\circ$. Lorentz and polarization corrections were applied to both sets of data. Absorption corrections, based on the crystal's approximately rectangular prismatic shape

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(about $15 \times 20 \times 140 \mu$) were made by use of a program written by Busing & Levy (1957) adapted to an IBM 360/65 computer. Total linear absorption coefficients of 1111 cm^{-1} and 1998 cm^{-1} for Mo and Cu radiation, respectively, were used to obtain the absorption corrections. The range in values for the transmission factor coefficients extends from 0.115 to 0.216 and 0.0140 to 0.171, respectively, for the Mo and Cu data. The lattice parameters were determined from a Guinier powder photograph at 25°C with KCl, $a = 6.29300 \pm 0.00009 \text{ \AA}$, (Hambling, 1953) as an internal standard and Cu $K\alpha$ radiation, $\lambda = 1.5405 \text{ \AA}$: $a = 7.379 \pm 3$, $b = 5.574 \pm 2$, $c = 15.19 \pm 1 \text{ \AA}$, $V = 624.8 \pm 9 \text{ \AA}^3$; with $Z = 12$ (cf. below) $D_x = 12.46 \text{ g.cc.}^{-1}$.

Structure determination

The conditions for reflection were observed to be:

$$\begin{array}{ll} hkl, \text{ no conditions;} & h00, \text{ no conditions;} \\ hk0, \text{ no conditions;} & 0k0, k=2n; \\ h0l, l=2n; & 00l, l=2n; \\ 0kl, k=2n. & \end{array}$$

These reflections indicate that the centrosymmetric space group is *Pbcm*. Two Ta atoms and one sulfur atom are in general eightfold positions, two Ta atoms are in the mirror plane, and one sulfur is in a glide plane. There are a total of 14 positional parameters for the structure.

It was arbitrarily decided to accept those data as 'observed' for which $\sqrt{A+B}/(B-A) \leq 0.25$ in which B and A equal, respectively, the integrated peak intensity and the background intensity for a given reflection, and to consider the remainder as 'unobserved'. According to this criterion, there were, in the case of the Cu data, 366 observed reflections, or about 17 data per variable, in the final refinement. For the Mo data, there were 435 observed reflections, or about 21 data per variable, in the final refinement. Unitary structure

factors were obtained from the observed structure factors from the Cu data by a graphical method (Woolfson, 1961). The 41 unitary structure factors with magnitudes greater than or equal to 0.40, comprising approximately 11% of the 'observed' reflections, were examined. The triple-product sign relation was used to obtain the signs of these structure factors with one variable sign. Two electron density maps were obtained with the use of 41 signed F_{obs} values, one with the variable sign positive, the other with the variable sign negative. Both maps contained five strong peaks per asymmetric unit; however, the tantalum atoms in the full unit cell obtained with the variable sign positive were separated by unreasonably short distances (2.38 \AA). Accordingly, the atomic positions implied by the peak positions in the map with the variable sign negative were used as atomic positions in a trial structure. The electron density maps calculated on the basis of this trial structure clearly showed two possible sulfur positions in the asymmetric unit. The structure obtained from the tantalum and sulfur positions thus obtained was refined by least-squares computation (Busing, Martin & Levy, 1962), with atomic scattering factors by Hansen, Herman, Lea & Skillman (1964). The scattering factors were corrected for anomalous dispersion by use of the corrections given in *International Tables for X-ray Crystallography*. (1962)

Results

In the case of the data obtained with Cu radiation and refinement with isotropic temperature factor coefficients, the structure refined until the unweighted reliability index, defined by $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, was 0.100. The data obtained with Mo radiation were refined with isotropic temperature factor coefficients; the final unweighted reliability index was 0.095. A weighting scheme based on statistical counting errors was used in the least-squares treatment of both sets of data. The

Table 1(a) *Positional and thermal parameters from Mo radiation*

	Wyckoff notation	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	B
Ta(1)	<i>e</i>	966 ± 4	8933 ± 8	901 ± 2	$0.36 \pm 5 \text{ \AA}^2$
Ta(2)	<i>e</i>	2843 ± 4	3945 ± 8	1542 ± 2	0.28 ± 5
Ta(3)	<i>d</i>	-93 ± 7	6307 ± 11	2500	0.22 ± 6
Ta(4)	<i>d</i>	3526 ± 6	8742 ± 11	2500	0.41 ± 7
S(1)	<i>c</i>	1834 ± 33	2500	0	0.29 ± 31
S(2)	<i>e</i>	4092 ± 29	7724 ± 42	939 ± 12	1.13 ± 28

Table 1(b). *Positional and thermal parameters from Cu radiation*

	Wyckoff notation	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	B
Ta(1)	<i>e</i>	969 ± 4	8930 ± 9	900 ± 2	$1.01 \pm 7 \text{ \AA}^2$
Ta(2)	<i>e</i>	2841 ± 5	3952 ± 9	1541 ± 2	1.06 ± 8
Ta(3)	<i>d</i>	-90 ± 7	6306 ± 15	2500	0.94 ± 8
Ta(4)	<i>d</i>	3528 ± 7	8709 ± 13	2500	1.09 ± 9
S(1)	<i>c</i>	1809 ± 38	2500	0	1.36 ± 39
S(2)	<i>e</i>	4132 ± 27	7651 ± 49	955 ± 14	1.63 ± 29

weights were assigned by calculating a relative error in the observed structure factor for each reflection, namely, the weights were taken to be σ_F^{-2} , where

$$\sigma_F = [\partial F / \partial I]^2 (\sigma_I)^2 + (\partial F / \partial A)^2 (\sigma_A)^2 + (\partial F / \partial \overline{LP})^2 (\sigma_{\overline{LP}})^2]$$

and σ_I is the estimated error in the intensity, σ_A is the estimated error in the reciprocal of the transmission factor correction, and $\sigma_{\overline{LP}}$ is the estimated error in the reciprocal of the combined Lorentz and polarization correction, and where the structure factor F , the intensity I , and the transmission factor coefficient A ² are related by the familiar expression $I = kA^2LP(F)$,

with k a proportionality constant. The weights were revised so that the slope of the straight line obtained when $|F_o - F_c|/\sigma_F^2$ was plotted versus $|F_o|^2$ had approximately zero slope. After refinement, the goodness of fit defined by $(\sum |F_o - F_c|^2/\sigma_F^2)/(m-n)$ where m is the number of observed reflections and n is the number of variables, was equal to 1.051 for Mo data and 0.871 for the Cu data.

Tables 1(a) and 1(b) list the values obtained for the positional parameters and temperature factor coefficients obtained from both sets of data and the uncertainties computed for these quantities. Attempts

Table 2. Observed and calculated structure factors for Ta₂S

(Mo K α data) (*='Unobserved').

K	L	FD	FC	K	L	FD	FC	K	L	FD	FC	K	L	FD	FC	K	L	FD	FC	K	L	FD	FC	K	L	FD	FC	K	L	FD	FC	K	L	FD	FC																																																																																																																																																																																																																																																																																																																																																																																																																																				
0	4	175	-222	2	6	152	-158	1	1	193	-177	4	4	306	280	0	6	149	-157	1	0	161	141	3	0	185	-177	3	1	0	7*	3	3	210	-178	3	4	130	119	3	4	249	243	3	9	191	159	3	10	151	-115	3	11	42	-57*	4	0	127	-115	4	1	59	96*	4	2	154	138	4	4	101	84*	4	5	140	-115	4	6	368	-331	4	7	146	156*	4	8	230	412	4	9	343	302	4	10	1143	-128*	4	11	41	25*	4	12	347	302	4	13	225	-239	4	14	28	-28*	4	15	121	121*	4	16	55	-57*	4	17	0	-3*	4	18	25	-239	4	19	196	196	4	20	191	191	4	21	191	191	4	22	191	191	4	23	191	191	4	24	191	191	4	25	191	191	4	26	191	191	4	27	191	191	4	28	191	191	4	29	191	191	4	30	191	191	4	31	191	191	4	32	191	191	4	33	191	191	4	34	191	191	4	35	191	191	4	36	191	191	4	37	191	191	4	38	191	191	4	39	191	191	4	40	191	191	4	41	191	191	4	42	191	191	4	43	191	191	4	44	191	191	4	45	191	191	4	46	191	191	4	47	191	191	4	48	191	191	4	49	191	191	4	50	191	191	4	51	191	191	4	52	191	191	4	53	191	191	4	54	191	191	4	55	191	191	4	56	191	191	4	57	191	191	4	58	191	191	4	59	191	191	4	60	191	191	4	61	191	191	4	62	191	191	4	63	191	191	4	64	191	191	4	65	191	191	4	66	191	191	4	67	191	191	4	68	191	191	4	69	191	191	4	70	191	191	4	71	191	191	4	72	191	191	4	73	191	191	4	74	191	191	4	75	191	191	4	76	191	191	4	77	191	191	4	78	191	191	4	79	191	191	4	80	191	191	4	81	191	191	4	82	191	191	4	83	191	191	4	84	191	191	4	85	191	191	4	86	191	191	4	87	191	191	4	88	191	191	4	89	191	191	4	90	191	191	4	91	191	191	4	92	191	191	4	93	191	191	4	94	191	191	4	95	191	191	4	96	191	191	4	97	191	191	4	98	191	191	4	99	191	191	4	100	191	191

at refinement with anisotropic temperature factor coefficients yielded negative values for some of the β_{ii} components of the temperature factor coefficients obtained from both sets of data. This fact suggests that the absorption corrections were only approximate, and that refinement with anisotropic temperature factor coefficients is not justified. Accordingly, only isotropic temperature factor coefficients were used in the final refinements. The values of the temperature factor coefficients obtained with Mo radiation are subject to less error than those obtained with Cu data owing to the fact that the linear absorption coefficient for Mo radiation is significantly smaller than that for Cu radiation. Table 2 lists the 'observed' and about 40% of the 'unobserved' structure factors for the Mo data. The unweighted reliability index for this set of 623 data is 9.8%, the goodness of fit for these data is 0.938. The positional and thermal parameters from this refinement agree within the standard deviations of those given in Table 1(a). All signs of the structure factors assigned by the direct method agreed with those obtained for the refined structure.

A difference Fourier synthesis was performed for each set of data with all observed reflections. In the case of Mo data, the synthesis indicated an approxi-

mately 2 electron peak above the position occupied by Ta(1), *i.e.* $x=0.097$, $y=0.893$, $z=0.090$ and a second peak of the order of 1.8 electrons at $x=0.328$, $y=0.611$, $z=0.032$. All other residual peak heights were less than 1.7 electrons in magnitude. In the case of Cu data, there were two peaks at $x=0.109$, $y=0.889$, and $z=0.145$ and at $x=0.297$, $y=0.389$, and $z=0.097$, corresponding to a peak height of about 3 electrons. Each of these peaks was within 1 Å of the center of a Ta atom. All other peak heights from the Cu data corresponded to scattering by less than 2.6 electrons. A comparison of the two difference Fourier syntheses for both Mo and Cu data indicated the absence of common peaks attributable to scattering by more than 1.2 electrons. It was concluded from the absence of common residual peaks in the difference Fourier syntheses for the Cu and Mo data that the residual peaks in the difference electron density maps were the result of errors in the data.

The *Thermal Ellipsoid Plot* computer program written by Johnson (1965) was used to draw a projection of the structure down the b axis. This view is illustrated in Fig. 1. The interatomic distances given in Table 3 were also obtained with this program. The upper limits to the uncertainties in these interatomic

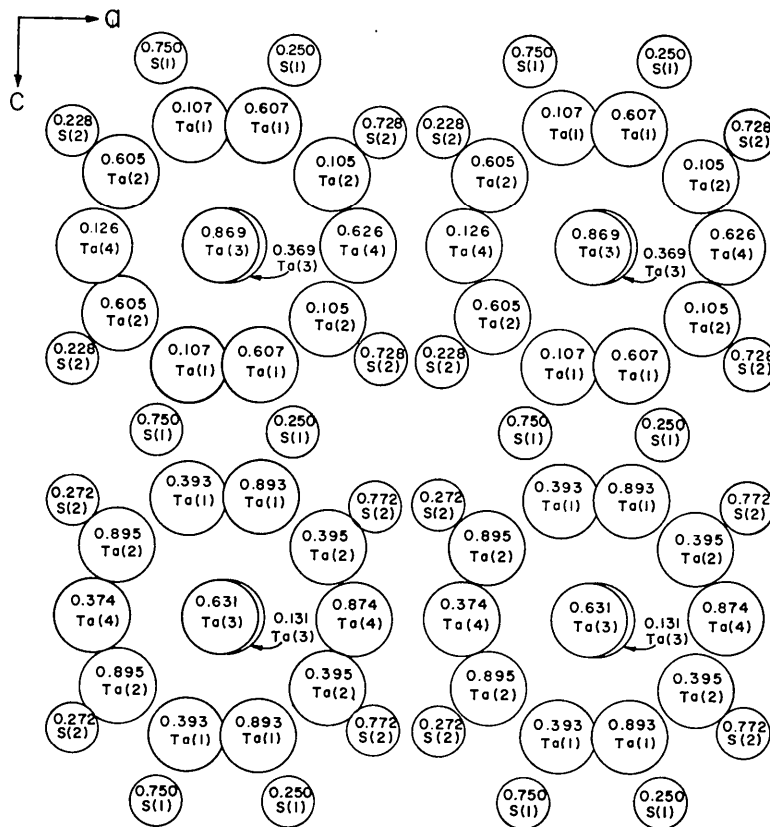


Fig. 1. Projection of the Ta₂S structure on to the xz plane.

distances are estimated to have the following values: 0.008 Å (Ta-Ta), 0.02 Å (Ta-S), 0.03 Å (S-S). The results from the Mo data were used for these calculations.

Table 3. Bond distances for Ta₂S

Reference atom	Neighbor	No. of neighbors	Distance	
Ta(1)	S(2)	1	2.403 Å	
	S(1)	1	2.497	
	S(1)	1	2.604	
	Ta(3)	1	2.840	
	Ta(3)	1	2.942	
	Ta(2)	1	2.975	
	Ta(4)	1	3.079	
	Ta(1)	2	3.131	
	Ta(1)	1	3.169	
	Ta(2)	1	3.255	
	Ta(2)	1	3.267	
	Ta(1)	1	3.307	
	Ta(2)	S(2)	1	2.475
		S(2)	1	2.534
S(1)		1	2.587	
Ta(3)		1	2.897	
Ta(2)		1	2.910	
Ta(3)		1	2.923	
Ta(1)		1	2.975	
Ta(4)		1	3.051	
Ta(4)		1	3.085	
Ta(1)		1	3.255	
Ta(1)		1	3.267	
Ta(4)		1	3.284	
Ta(3)		2	2.790	
Ta(1)		2	2.840	
Ta(2)	2	2.897		
Ta(4)	1	2.908		
Ta(2)	2	2.923		
Ta(1)	2	2.942		
Ta(4)	1	2.995		
Ta(4)	S(2)	2	2.474	
	Ta(3)	1	2.908	
	Ta(3)	1	2.995	
	Ta(2)	2	3.051	
	Ta(1)	2	3.079	
	Ta(2)	2	3.085	
S(1)	Ta(1)	2	2.497	
	Ta(2)	2	2.587	
	Ta(1)	2	2.604	
S(2)	Ta(1)	1	2.403	
	Ta(4)	1	2.474	
	Ta(2)	1	2.475	
	Ta(2)	1	2.534	

Discussion

The Ta atoms are all contained in chains of slightly distorted body-centered pentagonal antiprisms. These chains run in the **b** direction. The average Ta-Ta distance from the central atom to atoms in the pentagonal antiprism is 2.91 Å, and the distance from a central Ta atom to the next such atom is 2.79 Å. Thus each central Ta atom is surrounded by 12 Ta atoms in a slightly distorted icosahedron, and each central Ta atom is also an apical Ta atom in the next icosahedron in the chain. The average Ta-Ta distance on the faces of the antiprisms is 3.14 Å. The chains of Ta antiprisms are

bridged in the **a** and **c** directions by two types of sulfur atoms. The first type, S(1), is bonded to six Ta atoms forming faces of two of the antiprisms, with an average Ta-S(1) distance of 2.56 Å. The second type of sulfur atom, S(2), is bonded to three Ta atoms forming the face of one antiprism and to a Ta atom at the corner of another antiprism; the average Ta-S(2) distance is 2.47 Å.

The shortest S-S distance is 2.86 Å, and the average S-S distance for S-S distances less than 4 Å is 3.41 Å. The sum of two Slater radii for sulfur is 2.00 Å.

Valences were obtained from bond orders which were calculated with the empirical relation due to Pauling (1960),

$$D(n) = D(1) - 0.60 \log n,$$

relating a bond distance, *D*, to its order, *n*. The calculated valences for Ta(1), Ta(2), and Ta(4) are all approximately 4. Ta(3), however, has a calculated valence of 5.6, emphasizing its dissimilarity to the other Ta's in the structure. The calculated valence for both S atoms is about 3. This value is significantly lower than that found in other transition metal lower sulfides, *e.g.* Ti₂S (Owens, Conard & Franzen, 1967), Nb₂₁S₈ (Franzen, Beineke & Conard, 1967), and Hf₂S (Franzen & Graham, 1966), in which the calculated sulfur valences are approximately 4.

Considering this fact, it is interesting to note that, whereas Ti₂S, Ti₂Se, Zr₂S, and Zr₂Se (Franzen, Smeggil & Conard, 1967) are all isostructural with Ta₂P (Nylund, 1966), Ta₂S adopts a radically different structure type. Since the radii of S and P are nearly equal (Slater, 1964), it seems likely that the explanation for this difference lies in a difference in electron concentration. It thus might be that the additional electron (relative to phosphorus) from each sulfur would go into an antibonding band (Rundle, 1967) in the Ta₂P structure type. This conjecture is supported by the fact that neither V₂S nor Nb₂S is known with the Ta₂P structure type, as well as the fact that the Ta₂S structure is unique.

It is clear that the sulfur atoms in Ta₂S do not have the same high coordination (between seven and nine) characteristic of phosphorus in Ta₂P, and thus it seems reasonable to suppose that the role of the non-metal in bonding is different in the two structure types, presumably for the reason given above. However, the Ta₂S structure provides a conceptual link between the structures of the metal-rich compounds of phosphorus, sulfur, and selenium and those of the cluster compounds of Ta with halogens, *e.g.* Ta₆Cl₁₅ (Cotton, 1966). In the cluster compounds the bonding electrons are delocalized within the clusters, whereas in the metal-rich compounds the bonding electrons are obviously delocalized over the whole solid. The Ta₂S structure lies somewhere between these extremes in that the metal-metal bonding is predominantly restricted to the icosahedral clusters; but the icosahedra interpenetrate to give rise to linear chains.

There also exist some moderately short metal-metal distances between the columns: 3.5 Å in the *a* direction and 3.10 Å in the *c* direction. The previously mentioned bridging sulfur atoms also connect the columns in these directions. Thus Ta₂S might be a three-dimensional metal, either as a result of metal-metal interactions or because of the involvement of sulfur in the conduction process.

It is thus proposed that this structure, while highly unusual in detail, in broad outline is simply another example of delocalized directional bonding in a metal-rich sulfide. Bonding of this type has been proposed for lower sulfides of transition metals in general (Franzen, 1966).

According to a recent private communication from Professor F. Jellinek the Ta₂S phase has also been prepared in the Laboratory of Inorganic Chemistry, University of Groningen, by Dr G. A. Wiegers and Drs P. T. van Emmerik.

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The Crystal Structure of *p,p'*-Bitolyl

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Crystals of *p,p'*-bitolyl are monoclinic, space group $P2_1/c$, with $a = 9.77$, $b = 13.67$, $c = 18.25$ Å, $\beta = 118.3^\circ$ and 8 molecules in the unit cell. Intensity data were collected from Weissenberg photographs about two crystal axes and measured with a microdensitometer. The crystal structure has been solved by the use of information from direct methods and Patterson syntheses. After least-squares refinement the final *R* index is 0.083. Both molecules in the asymmetric unit lie with their H₃C...CH₃ axes nearly parallel to the *b* axis; the angle of twist between the phenyl rings assumes values of 36° and 40° for the two molecules. These values correspond to a definite minimum in a semi-empirical calculation of conformational energy in the crystal.

Introduction

The behaviour of the biphenyl molecule in different environments has been reviewed in a preceding paper (Casalone, Mariani, Mugnoli & Simonetta, 1968) where the theoretical geometry is also given, both for the gas phase and for 'model' crystals. The present work was undertaken to establish a comparison with the crystal structure of biphenyl, in which the coplanarity of the phenyl rings was first suggested by crystallo-

graphic symmetry (Hengstenberg & Mark, 1929; Clark & Pickett, 1930, 1931), and more recently confirmed by two independent two-dimensional structure determinations (Trotter, 1961; Hargreaves & Rizvi, 1962).

Experimental

Crystals of *p,p'*-bitolyl (m. p. 121°C) are white paral-lelepeds elongated along *a*. The crystal data are collected in Table 1. The conventional cell leads to the