similar environment of the O atoms of the sulphite groups. It is conceivable that the disparity between Fe—S distances in $Na_5[Fe(CN)_5(SO_3)] . 10\frac{1}{2}H_2O$ can be explained in a similar way.

Both the difference in Fe—S lengths between the two ions and the tendency towards long Fe(1)—C(12) and Fe(2)—C(22) bonds *cis* to sulphite were evident from a refinement based on data from a crystal of quality inferior (R = 0·059, 4060 reflections) to that finally used. This suggests that these trends are likely to be real effects.

The majority of the Na^+ ions have irregular environments of nearest neighbours comprising 5–7 N or O atoms at distances of 2·286 (3)–2·709 (4) Å. The shortest distance between two Na^+ ions is Na(7)··· Na(10) 3·251 (2) Å. As is apparent from Table 3, there are several O···O or O···N contacts of an order compatible with hydrogen bonding. Since the H atoms have not been located it is not, however, possible to describe the hydrogen-bonding network.

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The Structure of Tantalum Disulfide Thiophosphate $Ta[PS_4|S_2]$

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Abstract

Crystals of $Ta[PS_4|S_2]$ have been grown by vapor transport. They are tetragonal, space group $I4_1/acd$; a = 15·849 (3), c = 13·143 (4) Å; Z = 16. Final R = 0·030. Each Ta atom has eight nearest S neighbors, arranged in the form of a bicapped triangular prism. Two such prisms, sharing a common face, form $[Ta_2S_{12}]$ units. These units, linked by $[PS_4]$ tetrahedra, form endless chains, spiralling around the 4_1 and 4_3 axes. Rather large channels extend along these screw axes. One third of the S atoms are present as $[S—S]^{2-}$ pairs, two thirds as S^{2-} ions.

Introduction

In the course of an investigation of the system Ta—P—S, the formation of a new compound of overall

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composition $\mathrm{TaPS_6}$ was noted. This paper describes the structure of this compound whose strange stoichiometry is explained by the fact that two thirds of the S atoms occur as $\mathrm{S^{2-}}$ ions (forming $\mathrm{[PS_4]}$ tetrahedra, containing pentavalent P) whereas one third occur as $\mathrm{[S{-}S]^{2-}}$ pairs.

Experimental

Crystal data

Closed-tube iodine vapor transport of $\mathrm{Ta[PS_4|S_2]}$, synthesized from high-purity elements, yielded metal-grey single crystals, being combinations of {100} and {211}. Their composition was checked by chemical analysis for Ta and S; $M_r = 404{\cdot}31$. Lattice parameters (293 K) are $a = 15{\cdot}849\,(3)$, $c = 13{\cdot}143\,(4)$ Å, $V = 3301\,(2)$ Å^3, $Z = 16$, $D_m = 3{\cdot}20$, $D_c = 3{\cdot}25$ Mg m^{-3}. Reflection conditions were hkl $h + k + l = 2n$, $hk0$ $h, (k) = 2n$, $0kl$ $l, (k) = 2n$, hhl $2h + l = 4n$; space group $I4_1/acd$. Mo $K\alpha$ radiation was used ($\lambda = 0{\cdot}71069$ Å); μ(Mo $K\alpha$) = 15·6 mm^{-1}. Crystal size: ditetragonal bipyramid of 375 μm edge length. The cell parameters were obtained by least squares from 50 Guinier powder reflections [λ(Cu $K\alpha_1$) = 1·54051 Å; $\mathrm{As_2O_3}$ standard, $a_0 = 11{\cdot}0765\,(8)$ Å].

Data collection

The crystal was mounted with [001] parallel to the axis of the goniometer. Intensities were collected on a computer-controlled four-circle diffractometer (Enraf–Nonius CAD-4, Mo $K\alpha$ radiation, graphite monochromator) and measured with a scintillation counter. The ω–2θ scan method was used to explore one eighth of the sphere of reflection between $2\theta = 5{\cdot}14$ and 59·9°. Long-time drift of the primary beam was checked by measuring the intensities of two standard reflections after every 20 reflections. 1308 reflections (1202 of which are independent) were recorded. Of these, 927 had $I \geq 3\sigma(I)$, where $\sigma(I)$ is the variance of observations. The internal $R = \sum|I - I_m|/\sum I_m$ was 0·030 (I_m = mean intensity).

Data reduction

A Geneva version of XRAY 76 (Stewart, 1976) was used for data reduction, structure solution and refinement. Intensities were corrected for absorption with *ABSORB*. Scattering factors were taken from Cromer & Mann (1968).

Structure determination and refinement

Peaks in the Patterson map revealed occupancy of the 16-fold equipoint (f) by the Ta atoms. Fourier maps calculated with these positions suggested the P atoms on the 16-fold equipoint (e) and the 96 S atoms on three different 32-fold equipoints (g). A subsequent refinement of the extinction (Becker & Coppens, 1975), with non-averaged data, yielded an extinction parameter $G = 0{\cdot}98\,(3) \times 10^{-4}$ (Lorentzian distribution of mosaic spread). Then the extinction-corrected data were averaged (*SORTAV*) and a least-squares refinement was carried out with anisotropic temperature factors for all atoms. Anomalous-dispersion corrections f' and f'' were taken from *International Tables for X-ray Crystallography* (1974). The final $R = \sum|F_o - F_c|/\sum F_o$ was 0·028; $R_w = \sum w|F_o - F_c|/\sum wF_o$ [with $w = \sigma(F_o)^{-1}$] was 0·030.* The goodness of fit was $[\sum w(F_o - F_c)^2/(n - m)]^{1/2} = 2{\cdot}74$. This non-ideal value was attributed to the occurrence of multiple diffraction, leading to substantial differences between F_c and F_o for high-angle reflections. This was indicated by the fact that the condition $2h + l = 4n$, required by $I4_1/acd$, appeared to be slightly violated in diffractograms taken on the four-circle diffractometer. Weak reflections of the type hhl were recorded additionally. They were not detectable on single-crystal photographs. Refinements based on space group $Ibca$ (a subgroup of $I4_1/acd$), which would allow these additional reflections, did not (within the limit of error) lead to different atomic coordinates, nor did R or the goodness of fit improve.

Table 1. *Fractional coordinates* (*origin at* $\bar{1}$) *of* $\mathrm{Ta[PS_4|S_2]}$

All values are ×10^4. E.s.d.'s are in parentheses. W = Wyckoff position.

	W	x	y	z
Ta	16(f)	751 (1)	3251 (1)	1250
P	16(e)	4308 (2)	0	2500
S(1)	32(g)	4530 (1)	2944 (1)	2506 (2)
S(2)	32(g)	3531 (1)	3947 (2)	190 (2)
S(3)	32(g)	−3 (2)	314 (1)	1255 (3)

Table 2. *Interatomic distances* (Å)

E.s.d.'s are in parentheses.

Ta–Ta	3·365 (1)	S(1)–S(1)	2·048 (4)
Ta–P	3·219 (1)	S(1)–S(2)	3·451 (4)
Ta–S(1)	2·540 (2)	S(1)–S(2)	3·410 (4)
Ta–S(1)	2·578 (3)	S(1)–S(3)	3·288 (4)
Ta–S(2)	2·465 (3)	S(1)–S(3)	3·251 (4)
Ta–S(3)	2·562 (2)	S(2)–S(3)	3·174 (4)
P–S(2)	2·039 (4)	S(2)–S(3)	3·218 (4)
P–S(3)	2·027 (4)		

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35427 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The atomic parameters are listed in Table 1, interatomic distances in Table 2.

Structural results and discussion

The structure consists of $[Ta_2S_{12}]$ units, linked by $[PS_4]$ tetrahedra into a three-dimensional network. It is best understood by first considering these $[Ta_2S_{12}]$ units (Fig. 1). The Ta atoms occur always in pairs. The vectors between the atoms of these pairs point either in the [110] or $[1\bar{1}0]$ directions. The interatomic distance within a pair is 3·37 Å. The smallest Ta—Ta distance between adjacent $[Ta_2S_{12}]$ units is 6·44 Å.

Around each Ta, six S atoms [S(1) and S(2) of Table 1] are arranged, forming the vertices of a triangular prism. The two prisms originating from each Ta—Ta pair have a common, rectangular face which is nearly perpendicular to and divides the line connecting the Ta atoms. Additional S atoms, S(3), 2·56 Å from the Ta are found above the centers of the non-common prism faces. Each atom of a Ta—Ta pair thus has eight nearest S neighbors, arranged in the form of a bicapped, triangular prism and each Ta—Ta pair is the origin of a $[Ta_2S_{12}]$ unit, arising by face-sharing of two such prisms. Another striking feature of the structure is the occurrence of disulfide $[S{-}S]^{2-}$ ions in addition to normal sulfide ions S^{2-} as revealed by examining the S—S distances within and between the $[Ta_2S_{12}]$ units. One third of the S atoms, namely the S(1) of the triangular prisms, have such short distances ($d = 2{\cdot}05$ Å) that they have to be identified as $[S{-}S]^{2-}$ pairs (Fig. 1). Above and below each Ta—Ta pair such paired S(1) atoms are found, forming the common face between the S prisms around each Ta atom. The S(1)—S(1) vectors are nearly perpendicular to the Ta—Ta vectors. Such anion pairs are known to exist in a number of chalcogenides, *e.g.* in pyrite, FeS_2, $d_{S-S} = 2{\cdot}17$ (Wyckoff, 1968); in patronite, VS_4, $d_{S-S} = 2{\cdot}04$ (Allmann, Baumann, Kutoglu & Rösch, 1964); in NbS_2Cl_2, $d_{S-S} = 2{\cdot}03$ (von Schnering & Beckmann, 1966) and in $NbSe_3$, $d_{Se-Se} = 2{\cdot}22$ Å (Meerschaut & Rouxel, 1975).

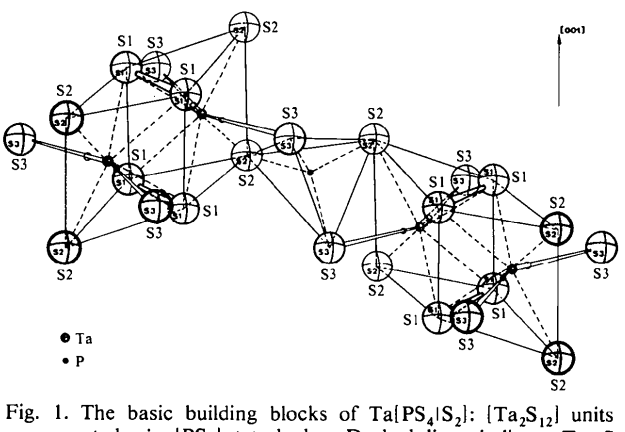

Fig. 1. The basic building blocks of $Ta[PS_4|S_2]$: $[Ta_2S_{12}]$ units connected *via* $[PS_4]$ tetrahedra. Dashed lines indicate Ta—S bonds within the double prisms of S atoms and P—S bonds within the tetrahedron. Bonds between Ta and S(3) (capping the prism faces) are drawn in perspective. $(S{-}S)^{2-}$ pairs formed by S(1) atoms are indicated by thick lines.

The remaining two thirds of the S atoms, S(2) and S(3), are present as S^{2-}. Of these, the S(2) form the remaining vertices of the S prisms. They have an average distance of 3·43 Å from the atoms of a $[S{-}S]^{2-}$ pair. The S(3) atoms, capping the prism faces, have average distances of 3·27 to the S(1) and of 3·20 Å to the S(2) atoms. The $[Ta_2S_{12}]$ unit therefore should be written more correctly $[Ta_2(S{-}S)_2S_8]$. Each of these units is crosslinked to four adjacent ones by four $[PS_4]$ tetrahedra. The interconnection is such that two vertices of a $[PS_4]$ tetrahedron are formed by a S(2) and a S(3) atom of one $[Ta_2(S{-}S)_2S_8]$ unit, the other two by corresponding S(2) and S(3) atoms of a neighboring unit (Fig. 1). The average edge length of

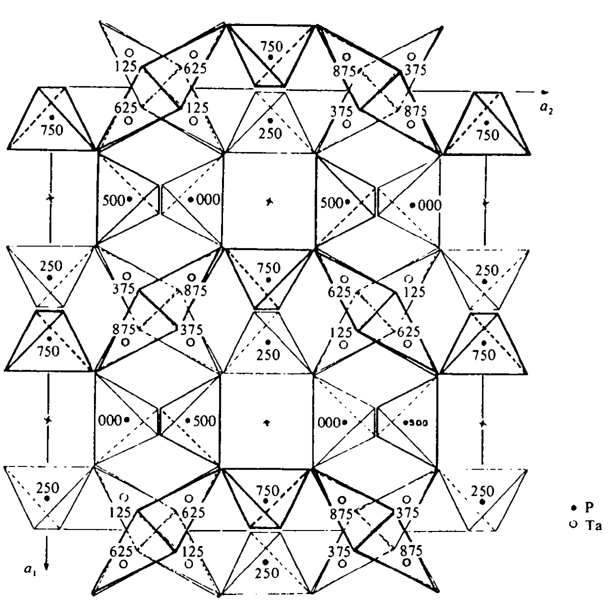

Fig. 2. Projection of the $Ta[PS_4|S_2]$ structure along $[00\bar{1}]$ showing the arrangement of $[Ta_2S_{12}]$ units linked by $[PS_4]$ tetrahedra and channels along 4_1 and 4_3 axes.

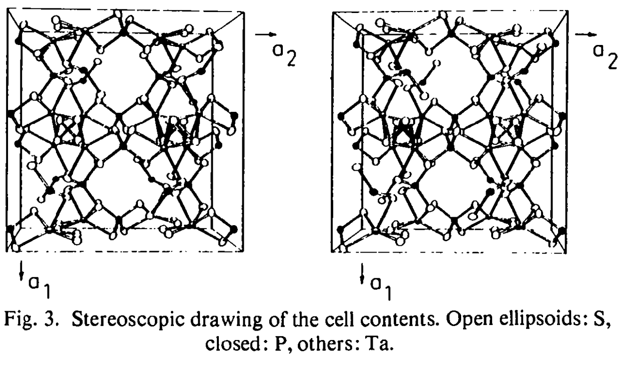

Fig. 3. Stereoscopic drawing of the cell contents. Open ellipsoids: S, closed: P, others: Ta.

the $[PS_4]$ tetrahedra is 3·32 Å, the P—S distances ranging between 2·03 and 2·04 Å. Such $[PS_4]$ tetrahedra occur in various thiophosphates, *e.g.* in $GaPS_4$, $d_{S-S} = 3{\cdot}34$, $d_{P-S} = 2{\cdot}05$ (Buck & Carpentier, 1973); $InPS_4$, $d_{S-S} = 3{\cdot}36$, $d_{P-S} = 2{\cdot}04$ (Diehl & Carpentier, 1978); $Cd_{13}P_4S_{22}I_2$, $d_{S-S} = 3{\cdot}35$, $d_{P-S} =$ 2·05 Å (Bubenzer, Nitsche & Grieshaber, 1976).

From a formal, electrochemical point of view, the compound therefore can be envisaged as containing two cations Ta^{5+} and P^{5+} (1:1) and two anions, namely $[S—S]^{2-}$ and S^{2-} (1:4), resulting in the formula $Ta[PS_4|S_2]$.

Fig. 2 is a projection along $[00\bar{1}]$, Fig. 3 a stereoscopic drawing of the unit-cell contents. The $[Ta_2S_{12}]$ units, linked by the $[PS_4]$ tetrahedra, form endless chains, spiralling around the 4_1 and 4_3 axes. Spiral chains around adjacent screw axes of opposite sense do not interfere with each other and have no common units. Spiral chains around adjacent screw axes of the same sense are interconnected by common $[Ta_2S_{12}]$ units.

Similar metal chalcogen units, $[Nb_2Se_{12}]$, are found in Nb_2Se_9 (Meerschaut, Guémas, Berger & Rouxel, 1979). However, in this compound they are crosslinked by common Se atoms into parallel chains. In $ZrSe_3$ on the other hand (Krönert & Plieth, 1965) and in $NbSe_3$ (Meerschaut & Rouxel, 1975) the bicapped triangular-prismatic arrangement of eight Se around each metal is still present, but these prisms have no common rectangular prism faces. Instead they are connected *via* common triangular endfaces into infinite chains.

A similar arrangement of metal–metal and (perpendicular) $[S—S]^{2-}$ pairs as in $Ta[PS_4|S_2]$ is present in $Nb_2S_2Cl_2$ (von Schnering & Beckmann, 1966) and in VS_4 (Allmann, Baumann, Kutoglu & Rösch, 1964).

Another interesting feature of the $Ta[PS_4|S_2]$ structure is the existence of rather large channels extending along the fourfold screw axes (Fig. 3). It appears probable that foreign atoms or small molecules can be inserted into and move in these channels, the free diameter of which is about 4·65 Å.

One of us (SF) is indebted to K. Scheunemann for introducing him to XRAY 76 and for help in interpreting the Patterson maps. All calculations were carried out on the Univac 1100/81 computer of the Rechenzentrum der Universität Freiburg.

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The Structure of Pentaindium Tetrasulfide

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Abstract

The structure of the new compound In_5S_4 has been determined by direct methods using single-crystal X-ray diffractometer data and refined to $R = 0{\cdot}046$. The symmetry is $Pa3$ and the cell edge is 12·340 (10) Å. There are eight formula units in the cell. The structure consists of a three-dimensional network of corner-

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