fill all or part of the tetrahedral and octahedral holes in these sublattices. All these structures are listed in Table 3 which gives the close packing of the sublattices and indicates which holes are filled and to what degree. The remaining structures are listed in Table 4.

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The Crystal Structures of α-V_3S and β-V_3S

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The structures of a new, dimorphous vanadium sulphide, V_3S, have been determined using single-crystal data.

α-V_3S, which is stable above 950 °C., has a body-centred, tetragonal structure with cell dimensions: $a = 9{\cdot}470$, $c = 4{\cdot}589$ Å. Space group $I\bar{4}2m$ with 8 V in (i) with $x_1 = 0{\cdot}0932$ and $z_1 = \frac{3}{4}$, 8 V in (i) with $x_2 = 0{\cdot}2000$ and $z_2 = \frac{1}{4}$, 8 V in (f) with $x_3 = 0{\cdot}3550$, 8 S in (g) with $x_4 = 0{\cdot}2851$.

β-V_3S, which is stable below 825 °C., has a tetragonal structure with cell dimensions: $a = 9{\cdot}381$, $c = 4{\cdot}663$ Å. Space group $P4_2/nbc$ with 8 V in (j) with $x_1 = 0{\cdot}4080$, 8 V in (j) with $x_2 = 0{\cdot}2028$, 8 V in (i) with $x_3 = 0{\cdot}1486$, 8 S in (h) with $x_4 = 0{\cdot}2171$. (Origin at $\bar{4}$).

Besides being closely related to β-V_3S, the structure of α-V_3S is closely related to that of Ni_3P. The structure of β-V_3S shows relationships to the β-W structure type.

Introduction

In a recent study of the vanadium sulphides (Pedersen, 1958) a subsulphide, V_3S, was identified by means of X-rays. This was unsuspected, as no vanadium sulphide richer in vanadium than VS had been observed by earlier investigators (Vogel & Wüstefeld, 1938; Biltz & Köcher, 1939).

The V_3S samples were made by melting weighed quantities of sulphur and vanadium in stoichiometric proportions at about 1400 °C. in crucibles of pure alumina, placed inside silica tubes which were evacuated and sealed. Depending upon the heat treatment two different forms of V_3S were obtained. Single crystals of the high temperature form (α-V_3S) were found in samples quenched from 1400 °C., and single crystals of the low temperature form (β-V_3S) were found in samples tempered at 825 °C. for about one month. They were probably formed from single crystals of the high temperature form. β-V_3S changed back into α-V_3S after heat treatment at 1150 °C. for six hours. Other experiments showed that α-V_3S was formed at 950 °C. and the transformation is therefore assumed to take place at a temperature between 825 and 950 °C.

Crystal data

The single crystals were needle-shaped with dimensions

$$0{\cdot}04 \times 0{\cdot}04 \times 0{\cdot}4 \text{ mm.}^3 \text{ for } \alpha\text{-}V_3S$$

and

$$0{\cdot}04 \times 0{\cdot}05 \times 0{\cdot}15 \text{ mm.}^3 \text{ for } \beta\text{-}V_3S\,.$$

Oscillation and Weissenberg photographs show that both forms have tetragonal symmetry, Laue symmetry $4/mmm$, with the c-axis along the needle axis. Cell dimensions determined from powder photographs taken with Cu K radiation ($\lambda_{\alpha_1} = 1{\cdot}5405$ Å) and densities, measured pycnometrically at 25·00 °C., are:

$$\alpha\text{-}V_3S \quad a = 9{\cdot}470,\ c = 4{\cdot}589 \text{ Å} \quad D_o = 5{\cdot}895 \text{ g.cm.}^{-3}$$
$$\beta\text{-}V_3S \quad a = 9{\cdot}381,\ c = 4{\cdot}663 \text{ Å} \quad D_o = 5{\cdot}939 \text{ g.cm.}^{-3}.$$

The observed densities indicate that the unit cell of both forms contain 8 V_3S-groups ($Z_c = 7{\cdot}90$ for α-V_3S and 7·95 for β-V_3S). Missing reflexions are:

		for α-V_3S	for β-V_3S
hkl	when	$h+k+l = 2n+1$	no conditions
$hk0$	when	$(h+k = 2n+1)$	$h+k = 2n+1$
$0kl$	when	$(k+l = 2n+1)$	$k = 2n+1$
hhl	when	$(l = 2n+1)$	$l = 2n+1$

Characteristic space groups for α-V_3S are accordingly: $I422$, $I4mm$, $I4/m2$, $I\bar{4}2m$ and $I4/mmm$. The characteristic space group for β-V_3S is $P4_2/nbc$. Both forms have symmetry $p4m$ in the 001-projection with $a'=b'=\frac{1}{2}\sqrt{(2)}a$.

Determination of the structures

The intensities of the $hk0$ and $hk1$-reflexions for both α-V_3S and β-V_3S were estimated visually from 'multiple film' Weissenberg photographs taken with CuK-radiation. The intensities were corrected for Lorentz and polarization factors, but not for absorption and extinction. A temperature correction was not applied since B (in $\exp(-B\sin^2\theta/\lambda^2)$) for the $hk0$-material of α-V_3S was calculated as only 0·05, which shows that the absorption and temperature effects nearly balance each other.

Throughout this paper the agreement between F_o and F_c is expressed by the reliability index, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. F_c-values corresponding to undetected reflexions have been added with their half value.

The structure of α-V_3S

On the basis of the corrected $F(hk0)^2$-values a Patterson map was computed. Its interpretation was not easy as about one hundred larger and smaller maxima were present (Fig. 1). Related compounds were therefore looked for, and among the Me_3B compounds the Ni_3P and β-W(W_3O) structure types found to be rather common. Of these, the Ni_3P-structure, which was worked out by Aronsson (1955) from single-crystal data, showed relationships with the α-V_3S structure.

Both Ni_3P and α-V_3S are body-centred tetragonal with eight Me_3B groups in the unit cell and have about the same lattice dimensions ($a=8{\cdot}952$, $c=4{\cdot}388$ Å for Ni_3P). There is, however, an important difference between them, as Ni_3P has Laue symmetry $4/m$, while α-V_3S has Laue symmetry $4/mmm$.

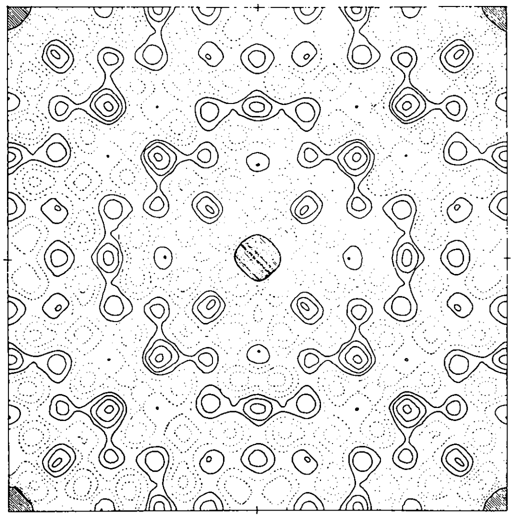

Fig. 1. Patterson projection of α-V_3S on (001). The contours are at equal but arbitrary intervals. Zero and negative contours are broken.

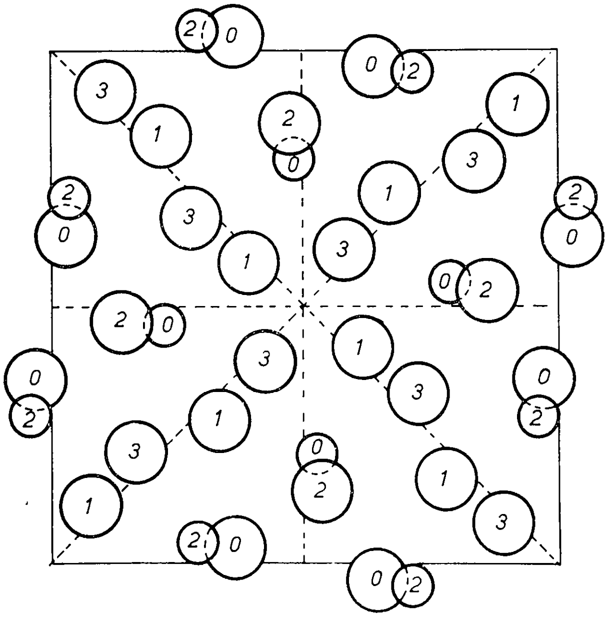

Fig. 2. The structure of Ni_3P viewed along the c-axis. Large circles indicate the nickel atoms and small circles the phosphorus atoms. Numbers in the circles give the z-parameters of the atoms in fourths.

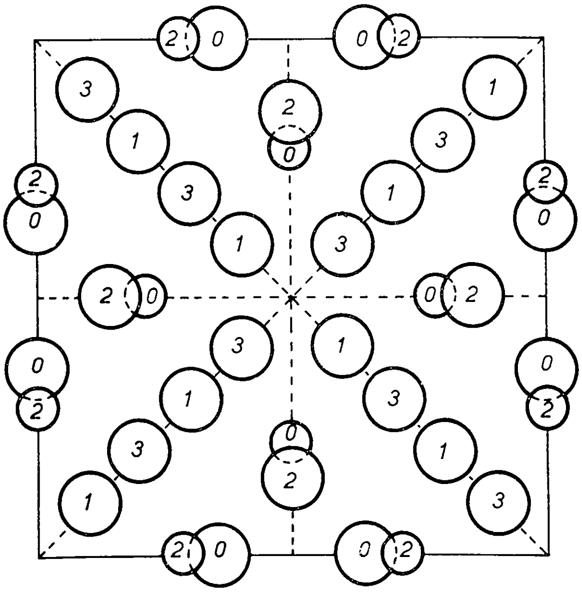

Fig. 3. The structure of α-V_3S viewed along the c-axis. Large circles indicate the vanadium atoms and small circles the sulphur atoms. Numbers in the circles give the z-parameters of the atoms in fourths.

In α-V_3S $\frac{1}{5}\sqrt{(2)}a$ is 2·68 Å, i.e., $\frac{1}{5}$ of the diagonal is thus equal to the distance between two vanadium atoms in twelve coordination (2·68 Å (Pauling, 1947)). Furthermore, the highest peaks in the Patterson map lie along this diagonal. From the projection of the structure of Ni_3P, shown in Fig. 2, it can be seen that eight metal atoms are located close to each diagonal. It seems then reasonable to assume that in α-V_3S the metal atoms lie on the diagonal, and that the remaining atoms are aligned parallel to the *a*- and *b*-axes. This would give α-V_3S the necessary higher symmetry as indicated in Fig. 3. The suggested structure is in agreement with the Patterson map, and on its basis preliminary parameters for the atomic positions were deduced. Structure factors were calculated, and after adjusting F_o and F_c to the same scale, the R-value obtained was 0·31. This agreement gives an indication that the main features of the proposed structure are correct.

The atomic parameters were refined further by means of two Fourier and one difference synthesis. R decreased to 0·22 after the second Fourier synthesis and to 0·12 after the difference synthesis. This reflects the large effect associated with the termination of the Fourier series. The observed and calculated $F(hk0)$-values are listed in Table 1, and the second Fourier map is shown in Fig. 4. The final parameters, referred to the body-centered axes, are:

1. 8 V in $x=0·0932$ $y=0·0932$, etc.
2. 8 V in $x=0·2000$ $y=0·2000$, etc.
3. 8 V in $x=0·3550$ $y=0$, etc.
4. 8 S in $x=0·2851$ $y=0$, etc.

It might be assumed that the z-coordinates in α-V_3S are the same as for the corresponding atoms in Ni_3P. To test this assumption an attempt was made to obtain data for a new projection, but this was unsuccessful. The crystals were needle-shaped with the *c*-axis as needle axis, and the intensities for other projections than 001 were therefore subject to absorption errors which are very difficult to correct for. The only possibility left was to evaluate intensities of higher layer lines with the *c*-axis as rotation axis. The assumed z-coordinates were tested by comparing $|F(hk1)|_o$ with $|F(hk1)|_c$. The agreement was so good, $R=0·13$, that the selection of equal z-coordinates for α-V_3S and Ni_3P seems justified, see Table 1.

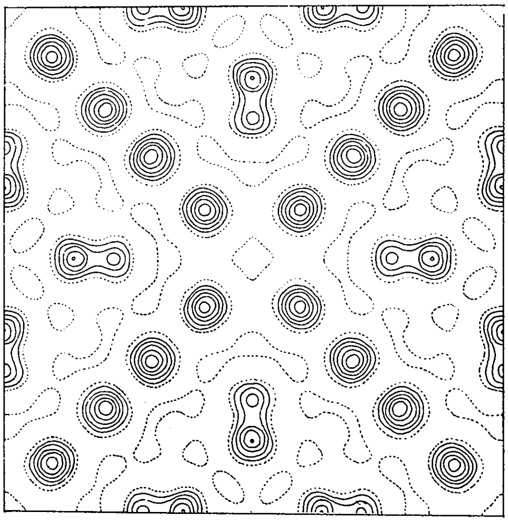

Fig. 4. Fourier projection of α-V_3S on (001). Contours are at intervals of 10 e.Å^{-2}. The zero contour is broken.

The space group for the deduced atomic arrangement is $I\bar{4}2m$ with

1. 8 V in (*i*) with $x_1=0·0932$ and $z_1=\frac{3}{4}$
2. 8 V in (*i*) with $x_2=0·2000$ and $z_2=\frac{1}{4}$
3. 8 V in (*f*) with $x_3=0·3550$
4. 8 S in (*g*) with $x_4=0·2851$

Table 1. *Observed and calculated structure factors for* α-V_3S

hkl	F_o	$\frac{1}{4}F_c$	*hkl*	F_o	$\frac{1}{4}F_c$	*hkl*	$\|F\|_o$	$\frac{1}{4}\|F\|_c$	*hkl*	$\|F\|_o$	$\frac{1}{4}\|F\|_c$
200	0	+3·1	530	7·4	−4·8	101	2·3	2·6	431	10·9	11·5
400	6·9	+6·4	730	31·6	+29·1	301	12·2	14·9	631	16·2	16·9
600	13·1	+12·3	930	0	+3·7	501	11·1	15·2	831	31·0	28·2
800	0	+4·5	11,3,0	15·9	+15·1	701	15·4	16·0	10,3,1	13·8	10·5
10,0,0	47·3	+48·0	440	—	(+3·5)	901	13·2	14·4	541	8·2	7·8
110	0	+1·2	640	21·6	+18·5	11,0,1	10·2	6·0	741	32·1	32·7
310	4·3	−4·3	840	7·5	−5·2	211	2·3	2·9	941	33·4	29·3
510	27·1	−31·4	10,4,0	14·7	−14·7	411	46·3	47·7	11,4,1	15·4	18·8
710	28·0	−30·2	550	39·3	+35·7	611	23·8	28·2	651	21·5	18·0
910	0	+0·2	750	15·4	−13·2	811	0	2·3	851	19·4	14·9
11,1,0	21·4	+21·0	950	12·5	−11·1	10,1,1	20·6	17·8	10,5,1	8·6	5·3
220	0	−1·3	660	36·9	+31·7	321	48·3	41·4	761	13·9	9·9
420	30·4	−35·7	860	7·6	+5·2	521	15·9	15·6	961	24·0	27·1
620	20·3	−19·9	10,6,0	7·7	−9·3	721	28·6	29·4	871	25·5	25·2
820	9·2	+8·9	770	18·7	+13·2	921	14·5	14·3			
10,2,0	19·9	−22·0	970	14·4	−14·6	11,2,1	14·3	10·2			
330	58·5	+62·4	880	15·4	+18·5						

The structure of β-V_3S

As previously mentioned, the symmetry of β-V_3S in the 001-projection is the same as for α-V_3S. Furthermore, the intensities of the *hk*0-reflexions of β-V_3S are almost equal to those of the corresponding reflexions of α-V_3S. The projection of β-V_3S and α-V_3S in the 001-plane must therefore be nearly the same. This assumption was supported by the value 0·21 for the reliability index, obtained on the basis of F_o-values from β-V_3S and F_c-values from α-V_3S. A further refinement of the atomic parameters by means of one Fourier and two difference syntheses resulted in $R=0{\cdot}16$, see Table 2, and the following parameters:

1. 8 V in (*j*) with $x_1=0{\cdot}4080$
2. 8 V in (*j*) with $x_2=0{\cdot}2028$
3. 8 V in (*i*) with $x_3=0{\cdot}1486$
4. 8 S in (*h*) with $x_4=0{\cdot}2171$

According to the systematic absences, the characteristic space group of β-V_3S is $P4_2/nbc$ (the parameters given refer to the origin at $\bar{4}$). The Fourier projection then shows that the atoms are in special positions with fixed *z*-coordinates. The structure of β-V_3S is thus completely determined by its 001-projection. Further support for the correctness of the structure is found in the good agreement between observed and calculated *F*(*hk*1)-values, $R=0{\cdot}18$, see Table 2. The structure of β-V_3S is shown in Fig. 5 with origin at 4_2, 0, $\frac{1}{2}$, $\frac{1}{4}$ from $\bar{4}$, which makes it easy to compare with that of α-V_3S.

Positions 1 and 2 above are the same as for α-V_3S,

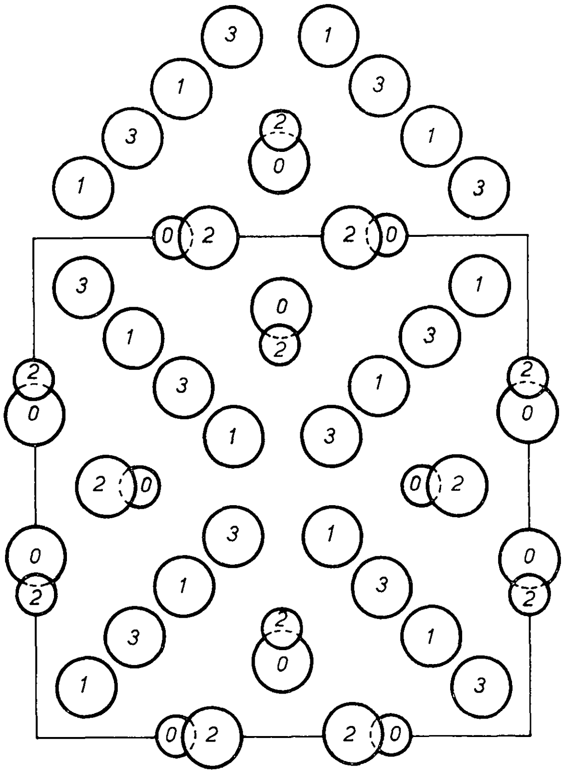

Fig. 5. The structure of β-V_3S viewed along the *c*-axis. Large circles indicate the vanadium atoms and small circles the sulphur atoms. Numbers in the circles give the *z*-parameters of the atoms in fourths.

Table 2. *Observed and calculated structure factors for* β-V_3S

hkl	F_o	$\frac{1}{4}F_c$
200	0	−1·9
400	8·2	+10·4
600	12·4	+9·8
800	0	+4·3
10,0,0	43·5	+45·5
12,0,0	9·6	+9·4
110	0	+2·2
310	0	−2·5
510	28·2	−32·8
710	26·5	−30·7
910	0	+1·9
11,1,0	24·7	+19·6
220	0	−1·4
420	31·0	−37·4
620	17·0	−18·4
820	0	+4·9
10,2,0	23·5	−24·0
330	53·3	+61·2
530	8·2	−5·8
730	30·0	+29·8
930	0	+3·5
11,3,0	19·2	+17·7
440	—	(+6·0)
640	22·6	+19·1
840	9·6	−5·9
10,4,0	14·7	−13·3
550	35·8	+33·1
750	17·0	−14·6
950	8·3	−6·6
660	39·0	+32·0
860	10·7	+7·0
10,6,0	9·9	−11·6
770	21·0	+16·6
970	16·9	−15·4
880	15·2	+14·7

hkl	$\|F\|_o$	$\frac{1}{4}\|F\|_c$
101	0	0
201	0	0·1
301	0	0
401	23·6	25·0
501	0	0
601	7·2	8·5
701	0	0
801	0	1·2
901	0	0
10,0,1	19·3	15·6
11,0,1	0	0
111	0	0
211	0	0·1
311	14·3	17·3
411	34·3	39·2
511	17·2	15·7
611	25·2	28·0
711	14·0	14·0
811	0	2·6
911	15·9	16·6
10,1,1	10·0	9·9
11,1,1	6·6	5·1
221	0	0
321	36·6	40·1
421	20·2	16·5
521	0	4·8
621	6·6	9·4
721	24·3	22·7
821	0	1·1
921	9·2	6·3
10,2,1	19·6	15·1
11,2,1	12·4	8·4
331	0	0
431	8·0	4·1
531	0	0·8
631	10·6	7·2
731	25·9	24·5
831	29·9	29·8
931	0	6·1
10,3,1	12·1	6·7
11,3,1	0	3·4
441	0	0
541	10·6	6·5
641	27·5	26·6
741	0	3·0
841	24·6	17·7
941	31·7	28·4
10,4,1	0	0·1
11,4,1	16·2	16·4
551	0	0
651	0	3·8
751	28·5	23·9
851	0	3·7
951	0	5·0
10,5,1	0	2·4
661	0	0
761	0	4·4
861	0	5·4
961	21·4	20·6
771	0	0
871	25·6	20·1
971	20·1	24·3

while positions 3 and 4 differ in the two structures by a translation of $c/2$ along the c-axis for the atoms grouped around $x=0$, $y=\frac{1}{2}$ only. Accordingly, the $F(hkl)$-values for the two structures are equal when l is even. This is just what has been observed, as the Weissenberg photographs of α-V_3S and β-V_3S are equal for $hk0$ and $hk2$, the only accessible layer lines with l even for Cu-radiation. It follows from the geometrical structure factors* that when l is odd only atoms in positions No. 1 and 2 cause reflexions with $h+k=2n+1$, while atoms in positions 3 and 4 cause the remaining reflexions. It is therefore interesting to note, that in the first layer the former reflexions are sharp, while the latter are more diffuse. A reasonable explanation of this is that the crystals of β-V_3S are formed from those of α-V_3S by movement of the atoms in positions 3 and 4.

Discussion of the structures

The structures of α-V_3S and β-V_3S can be said to consist of vanadium atoms in the diagonal planes parallel to the c-axis. Between these are located columns of interwoven tetrahedra of vanadium and sulphur atoms in equal proportions. Each vanadium in the column is surrounded by sulphur atoms at the corners of a tetrahedron. The only difference between the structure of α-V_3S and β-V_3S is a translation, of magnitude $c/2$, of the column around $x=0$, $y=\frac{1}{2}$. The interatomic distances between nearest neighbours calculated for the final parameters found for α-V_3S and β-V_3S are listed in Table 3.

Table 3. *Interatomic distances*

Interatomic distances in α-V_3S (Å)

1. V	−12 V	2·50; 2·70 (2); 2·77; 2·87 (2); 2·90 (4); 2·96 (2)
	− 2 S	2·32 (2)
2. V	− 9 V	2·66 (4); 2·70 (2); 2·77; 2·96 (2)
	− 2 S	2·36 (2)
3. V	− 9 V	2·66 (2); 2·75; 2·87 (2); 3·00 (4)
	− 4 S	2·39 (2); 2·46 (2)
4. S	− 8 V	2·32 (2); 2·36 (2); 2·39 (2); 2·46 (2)
	− 0 S	

Interatomic distances in β-V_3S (Å)

1. V	−12 V	2·44; 2·76 (2); 2·83 (2); 2·85; 2·90 (4); 2·95 (2)
	− 2 S	2·31 (2)
2. V	− 9 V	2·63 (2); 2·65 (2); 2·76 (2); 2·85; 2·95 (2)
	− 2 S	2·35 (2)
3. V	− 9 V	2·63 (2); 2·79; 2·83 (2); 3·03 (4)
	− 4 S	2·42 (2); 2·47 (2)
4. S	− 8 V	2·31 (2); 2·35 (2); 2·42 (2); 2·47 (2)
	− 0 S	

The standard deviation in the interatomic distances calculated according to Cruickshank (1949) is about 0·017 Å.

In both structures the vanadium–vanadium distances are of the same magnitude as in metallic vanadium, where each vanadium atom is surrounded by eight vanadium atoms at the distance 2·66 Å and six at the distance 3·03 Å (Seybolt & Sumsion, 1953). One vanadium–vanadium distance within each unit cell is, however, definitely shorter than in metallic vanadium.

The vanadium–sulphur distances are considerably shorter than the sum of the Pauling (1947) metallic radii, $1\cdot34+1\cdot22=2\cdot56$ Å for vanadium in twelve coordination and sulphur in eight coordination. Similarly short vanadium–sulphur distances have been observed for the V_5S_4-phase and the $V_{1-x}S$-phase (Pedersen, 1958). In α-V_3S the shortest sulphur–sulphur distances between atoms in the same columns are 3·68 Å, and between atoms in different columns 3·81 Å. In β-V_3S the corresponding distances are 3·71 Å and 4·42 Å.

It is remarkable that vanadium forms a considerable number of V_3B compounds, where $B=$ Ir, Pt, Rh, Co, Ni, Au, Si, Ge, Sn, As, Sb or P. All these, with the possible exception of V_3P, are of the β-W (A–15)-type structure (see Geller, 1956; Pauling, 1957). The one rather short vanadium–vanadium distance found in each of these compounds varies from 2·36 Å in V_3Si to 2·47 Å in V_3Sn. By comparing the β-V_3S structure with the β-W structure one finds that they have characteristic features in common. In both structures similar V–B columns are found with the same relative orientation. The difference between the two structures lies thus only in the ordering of the remaining metal atoms. In β-W the metal atoms form chains and

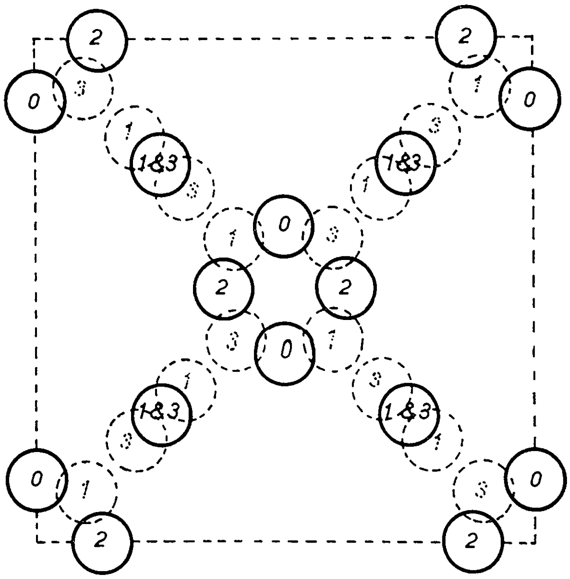

Fig. 6. Surplus metal atoms in the β-V_3S (broken lines) and in the β-W structure (solid lines). Numbers in the circles give the z-parameters in fourths.

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* The expression for B (origin at $\bar{4}$) given in the *International Tables* (1935, 1952) contains an error in sign. It should read:

$$B=-8\sin^2 2\pi(h+k+l/4)\sin 2\pi lz \times(\sin 2\pi(hx-l/4)\sin 2\pi(ky+l/4) + \sin 2\pi(kx+l/4)\sin 2\pi(hy+l/4))$$

columns, while in β-V_3S they form nets. This is apparent from Fig. 6 and one can easily see how the metal atoms in the β-W structure must be moved to give the atomic arrangement in β-V_3S (the V–*B* columns have been omitted for the sake of clarity). It seems reasonable to suppose that this rearrangement causes little change in bond distance between the metal atoms in the V–V column. It is between these metal atoms that the short bond distance is observed in the β-W structure, and it is also between these atoms that the short V–V distance, 2·44 Å, is found in β-V_3S.

The structures of α-V_3S and Ni_3P are closely related, but α-V_3S has higher symmetry than Ni_3P. It might therefore seem natural to describe the structure of Ni_3P as a somewhat deformed α-V_3S structure. The Ni_3P structure is related to the β-W structure via the structures of α-V_3S and β-V_3S. That such a relationship might be expected is indicated by the remarks of Schønberg (Aronsson, 1955) that V_3P is isotypic with Ni_3P, and by Mathias *et al.* (1957) that V_3P has a slightly distorted β-W structure.

The authors wish to thank Prof. Haakon Haraldsen for his interest in this study and for placing laboratory facilities at their disposal.

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X-ray Studies on the Metal Complexes with the Glyoximes. II.

Structure of the Pt-Dimethyl-Glyoxime

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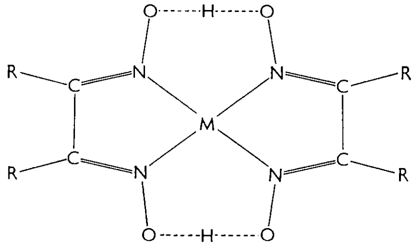
During a systematic investigation of the metal complexes of the glyoximes, the structure of Pt-dimethyl-glyoxime has been examined. It has the same space group *Ibam* as Ni-dimethyl-glyoxime. The lattice constants are $a = 16{\cdot}73$, $b = 10{\cdot}59$, $c = 6{\cdot}47$ Å; $Z = 4$. Such values are similar to those found in Ni-dimethyl-glyoxime.

The molecule is planar and the Pt–Pt distances between metallic atoms of overlying molecules are 3·23 Å. The intramolecular distance of 3·03 Å between the oxygen atoms bound by a hydrogen bond, is significantly longer than the one in Ni-dimethyl-glyoxime (2·44 Å) and in Cu-dimethyl-glyoxime (2·57–2·70 Å).

Introduction

In this Centro di Strutturistica Chimica we have examined a series of compounds having the following general formula:



This work has shown a variety of possibilities of packing as well as of molecular structure due to the differences of coordination of the metals as well as to the substituent group *R* present in the molecule.

Frasson, Bardi & Bezzi (1959) have recently described the structure of Cu-dimethyl–glyoxime showing the differences between it and the Ni–dimethyl–glyoxime studied by Godycki & Rundle (1953). The two structures are mainly differentiated by the pyramidal five-fold coordination of the copper, the lack of planarity of the molecule, the formation of a dimer through Cu–O bonds between atoms of different molecules on the one hand and the regular octahedral coordination of the Ni, the planarity of the molecule