

centred at 8(c) and the pseudo octahedral site centred at 24(e) ($x \simeq 0.35$) by least-squares refinement. Furthermore, the occupancy of each atomic site of the structure was independently tested, but in all cases this was found to be unity at the 2σ level. If the quantitative chemical analysis is correct, oxygen might possibly form small amounts of oxides in the melt in addition to the $\text{Sc}_{11}\text{Ir}_4$ phase. This hypothesis might be supported by the fact that X-ray powder patterns show weak reflexions which do not belong to the $\text{Sc}_{11}\text{Ir}_4$ phase (this point has been checked on a Gandolfi camera with the same single crystal as for the data collection) but unfortunately these additional lines could not be matched with any known phase containing these elements with or without oxygen.

In this context, it is of interest to note that in the system Zr–Os the $\text{Zr}_{11}\text{Os}_4$ phase competes with the phase having the Ti_2Ni structure type stabilized by N. A phase $\text{Zr}_4\text{Os}_2\text{N}_x$ (Ti_2Ni type with $a = 12.37 \text{ \AA}$) has been reported by Holleck & Thümmeler (1967).

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The Crystal Structure of $\text{K}_4(\beta_1\text{-SiMoW}_{11}\text{O}_{40})\cdot 9\text{H}_2\text{O}$

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Abstract

$\text{K}_4(\beta_1\text{-SiMoW}_{11}\text{O}_{40})\cdot 9\text{H}_2\text{O}$ is orthorhombic, space group $Pnma$, with $a = 20.551$ (15), $b = 15.535$ (12), $c = 12.953$ (9) Å, $Z = 4$. The structure was determined from 2024 diffractometer intensities (Mo $K\alpha$ radiation)

and refined to $R = 0.052$. The structure is isomorphous with that of $\text{K}_4(\beta\text{-SiW}_{12}\text{O}_{40})\cdot 9\text{H}_2\text{O}$. The Mo atom is statistically distributed on three equivalent sites. Results are discussed with regard to both the α - β isomerism of the heteropolyanion and the geometrical isomerism in the β series.

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Introduction

The existence of two isomers, α and β , of the decatungsto- or molybdoheteropolyanions $XM_{12}O_{40}^{n-}$ ($M = \text{W}^{\text{VI}}$ or Mo^{VI}) is known (Marignac, 1864; Copaux, 1908). Recently their syntheses and physicochemical properties have been investigated (Strickland, 1952; Souchay & Contant, 1967; Massart, 1968; Tézé & Hervé, 1977a), with $X = \text{Si}, \text{Ge}, \text{P}$ and As .

Many structural determinations have been performed on the α isomer, known as the Keggin (1934) structure. On the other hand, only one β -isomer structure has been solved (Matsumoto, Kobayashi & Sasaki, 1975), the potassium salt of the β -12-tungstosilicate.

The 12-tungstosilicate ions give by basic hydrolysis 11-tungstosilicate ions $\text{SiW}_{11}\text{O}_{39}^{8-}$ by loss of a WO^{4+} group. There is only one $\alpha\text{-SiW}_{11}\text{O}_{39}^{8-}$ isomer but we have prepared three $\beta\text{-SiW}_{11}\text{O}_{39}^{8-}$ isomers labelled β_1, β_2 and β_3 according to the sequence of isomerization (Tézé & Hervé, 1977a). This is in agreement with Matsumoto's structure: three kinds of metallic sites can be distinguished in the β -12-tungstosilicate. From this observation, and with a simple electrostatic model, we have proposed a correlation between the three possible β structures and the three compounds obtained (Tézé & Hervé, 1977b). An X-ray investigation was necessary to check this interpretation.

The β_1 isomer was chosen for the structural determination because it is obtained by action of tungstate ions on the β -9-tungstosilicate (Hervé & Tézé, 1977), the structure of which is also under investigation. The instability of $\beta_1\text{-SiW}_{11}\text{O}_{39}^{8-}$ in solution precludes the preparation of crystals. Therefore the structure of the $K_4(\beta_1\text{-SiMoW}_{11}\text{O}_{40})\cdot 9\text{H}_2\text{O}$ salt was solved, which is stable in solution (Contant, Fruchart, Hervé & Tézé, 1974). In this compound, the vacant site of $\beta_1\text{-SiW}_{11}\text{O}_{39}^{8-}$ is occupied by Mo^{VI} .

Crystal preparation

Potassium β_1 -11-tungstosilicate was prepared according to Tézé & Hervé (1977a). 32 g of this salt were added to 50 ml of 1 M sodium molybdate and 2 M hydrochloric acid solution. The salt was precipitated by potassium chloride, separated and recrystallized twice from water.

Experimental

The cell dimensions were determined from Laue and precession photographs. The space group corresponding to the systematic absences is $Pnma$, which indicates that this structure may be isomorphous with $K_4(\beta_1\text{-$

$\text{SiW}_{12}\text{O}_{40})\cdot 9\text{H}_2\text{O}$ (Matsumoto, Kobayashi & Sasaki, 1975). Our crystal parameters were $a = 20.551$ (15), $b = 15.535$ (12), $c = 12.953$ (9) Å, $V = 4135$ Å³. The calculated density agreed with the measured one ($d_c = 4.98$, $d_m = 5.21$ Mg m⁻³) for $Z = 4$. For Mo $K\alpha$ radiation $\mu = 33.396$ mm⁻¹. 2024 independent reflexions were collected with Mo $K\alpha$ ($\lambda = 0.7107$ Å) Zr-filtered radiation on an automatic diffractometer in the θ - 2θ scan mode up to $2\theta = 40^\circ$ at room temperature. 1320 reflexions with $I > 3\sigma(I)$ were considered as observed and kept for further calculations. The standard deviations $\sigma(I)$ were calculated from counting statistics. The scan range was $\Delta\theta = 0.80^\circ + 0.34^\circ \text{tg}\theta$. Three standard reflexions were monitored every 50 reflexions and remained constant. The intensities were corrected for Lorentz and polarization factors.

Solution and refinement

The successful refinement of the coordinates of the seven independent W atoms of $K_4(\beta\text{-SiW}_{12}\text{O}_{40})$ confirmed that the two structures are isomorphous.

Two of these atoms, $M(6)$ and $M(7)$, had too large B values. With $M(7)$ being located in the symmetry plane, $M(6)$ and $M(7)$ define three sites of the polyanionic structure. Thus we thought that the Mo atom was statistically distributed on these three sites. This assumption has been checked as follows: (i) W and Mo were placed on the same sites and their multiplicity factors only were refined; values of $\frac{2}{3}$ and $\frac{1}{3}$ were found; (ii) with the multiplicity factors kept constant, coordinates only were varied in order to check that Mo and W had the same coordinates, as has actually been found; (iii) for further calculations a weighted scattering factor was used, $f_M = (f_{\text{Mo}} + 2f_{\text{W}})/3$.

Then we introduced the Si, K and polyanionic O atoms. R dropped to 0.10. The water molecules were located on a difference synthesis. At this stage a weighting scheme of the form $w = (5.0 - 0.17855F_o + 0.00581F_o^2)^{-1}$ was used (Cruickshank, 1965); R was 0.087. The usual absorption correction (Wehe, Busing & Levy, 1962) was unsuccessful. However, it was found that thermal-ellipsoid axes had nearly the same direction and were anomalously long, although the overall temperature factor was only about 1 Å². We ascribe this anomaly to absorption. The structure factors were multiplied by an empirical factor $\exp[-(A_1 h^2 + A_2 k^2 + A_3 l^2 + A_4 hk + A_5 hl + A_6 kl)]$ and the six parameters A_i were refined by least squares. Thus we obtained more consistent anisotropic thermal parameters. Nevertheless, Table 1 shows some scatter for the B values of the O atoms. No systematic features relating to the O-atom surroundings can be found, so we attribute the scatter to imperfect absorption corrections and to the fact that this compound contains heavy atoms bound to light atoms. The final $R =$

$\sum |F_o| - |F_c| / \sum |F_o| = 0.052$ and $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.068$. The final atomic coordinates and thermal parameters are listed in Table 1.* Fig. 1. depicts the polyanion.

All calculations were performed on an IBM 370-168 computer with local versions of *ORFLS* (Busing, Martin & Levy, 1962) for full-matrix least-squares calculations, *GEST* (De Rango, Tsoucaris, Zelwer & Baudour, 1964) for the Fourier syntheses, and NRC programs (Ahmed, Hall, Pippy & Huber, 1966) for the geometrical calculations. Scattering factors were taken

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34699 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^5$ for W and M atoms and $\times 10^4$ for other atoms)

The e.s.d.'s in parentheses refer to last decimal places.

	x	y	z	B (\AA^2)
W(1)	27796 (11)	75000	32426 (17)	0.67 (10)
W(2)	16179 (8)	64225 (12)	45105 (12)	0.49 (7)
W(3)	16047 (7)	63029 (10)	73196 (12)	0.32 (7)
W(4)	27624 (7)	52248 (10)	61105 (12)	0.31 (7)
W(5)	40695 (7)	64286 (11)	47081 (12)	0.43 (7)
M(6)	31209 (9)	63059 (12)	82742 (13)	0.31 (8)
M(7)	44126 (13)	75000	68998 (20)	0.44 (11)
Si	2788 (7)	7500	6989 (13)	0.8 (7)
O _a (346)	2608 (11)	6646 (17)	6694 (19)	0.7 (5)
O _a (22'1)	2341 (16)	7500	4969 (26)	0.1 (6)
O _a (55'7)	3566 (16)	7500	5638 (25)	0.1 (6)
O _b (15)	3375 (11)	6631 (16)	3764 (18)	0.3 (5)
O _b (23)	1350 (15)	6563 (20)	5940 (24)	2.4 (6)
O _b (24)	2277 (11)	5656 (15)	4936 (18)	0.1 (6)
O _b (45)	3536 (12)	5671 (16)	5478 (19)	0.6 (5)
O _b (67)	3905 (12)	6664 (17)	7609 (20)	0.8 (5)
O _b (33')	1551 (18)	7500	7640 (28)	0.9 (7)
O _b (66')	2996 (17)	7500	8598 (29)	0.9 (7)
O _b (12)	2097 (11)	6626 (17)	3307 (19)	0.4 (5)
O _c (34)	1969 (11)	5229 (16)	6828 (19)	0.4 (5)
O _c (36)	2205 (11)	6122 (15)	8449 (18)	0.1 (4)
O _c (46)	3194 (13)	5300 (18)	7460 (22)	1.2 (5)
O _c (57)	4641 (11)	6589 (18)	5873 (18)	0.5 (5)
O _c (22')	1172 (15)	7500	4259 (25)	0.1 (6)
O _c (55')	4428 (17)	7500	4190 (26)	0.5 (7)
O _d (1)	2942 (20)	7500	1924 (32)	1.6 (8)
O _d (2)	1040 (14)	5724 (19)	4055 (22)	1.9 (6)
O _d (3)	904 (12)	5937 (17)	7857 (19)	0.8 (5)
O _d (4)	2835 (13)	4169 (17)	5856 (20)	1.1 (5)
O _d (5)	4542 (15)	5706 (20)	4059 (23)	2.2 (6)
O _d (6)	3435 (12)	5941 (18)	9434 (21)	1.3 (5)
O _d (7)	5090 (16)	7500	7595 (25)	0.1 (6)
K(1)	43 (8)	2500	7022 (12)	2.6 (8)
K(2)	7031 (7)	7500	4857 (12)	2.0 (7)
K(3)	287 (5)	4908 (7)	2465 (8)	2.1 (5)
O _w (1)	9093 (15)	1435 (20)	45 (24)	2.2 (6)
O _w (2)	5043 (21)	893 (30)	684 (33)	5.5 (10)
O _w (3)	830 (16)	6426 (22)	2002 (26)	3.0 (7)
O _w (4)	4182 (19)	5977 (27)	1614 (31)	4.4 (9)
O _w (5)	5594 (38)	2500	-59 (61)	7.5 (19)

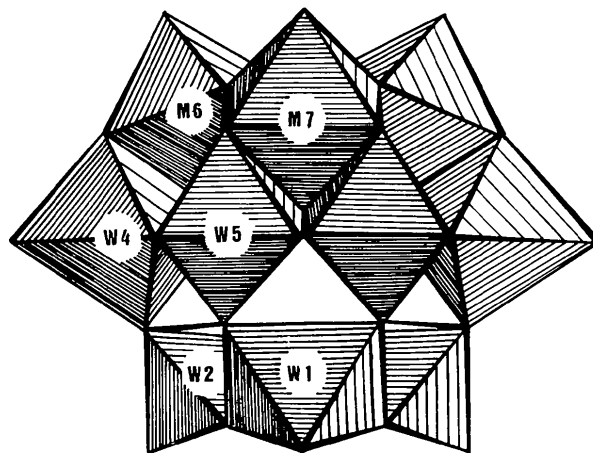


Fig. 1. The β_1 -SiMoW₁₁O₄₀⁸⁻ anion.

from *International Tables for X-ray Crystallography* (1974). Real and imaginary parts of the anomalous dispersion were introduced for W, Mo and Si.

Discussion

The β isomer results from a 60° rotation about the threefold axis of one trigonal edge-sharing W₃O₁₃ unit of the Keggin (1934) structure.

The β -12-tungstosilicate ion has three kinds of W atoms (Tézé & Hervé, 1977b): the three on the side opposite the rotated group (sites designated by I), the six in octahedra adjacent to the preceding ones (sites designated by II), and the three in the rotated group (sites designated by III). In the following discussion, four types of O atoms will be distinguished: O_a shared between three WO₆ octahedra and the central SiO₄ tetrahedron, O_b shared between adjacent W₃O₁₃ units, O_c shared between two WO₆ octahedra in the same W₃O₁₃ unit, and O_d linked only to one W atom.

Location of Mo in the polyanionic structure

This study shows that the Mo atom in the β_1 -molybdo-11-tungstosilicate is statistically distributed on three metallic sites; these three sites are unambiguously of type I. This is in agreement with the structure proposed for the β_1 -SiW₁₁O₃₉⁸⁻ ion where the vacant site was supposed to be of type I (Tézé & Hervé, 1977b). The polyanionic O atoms build such a rigid framework that it is only slightly disturbed by the substitution of W by Mo. Thus, in the crystal, the polyanion is statistically oriented around its threefold axis. Nevertheless, since the polyanion has C_{3v} symmetry, it has been possible to determine the type of site occupied by Mo, while the location of V in V₂W₄O₁₉⁸⁻ was unsuccessful because of the higher O_h symmetry of

its O atom framework (Nishikawa, Kobayashi & Sasaki, 1975).

SiO₄ tetrahedral geometry

This tetrahedron formed by four O_a atoms around the Si is regular: the O_a-Si-O_a angles (109–112°) and Si-O_a lengths (1.61–1.66 Å) do not differ significantly. This result is in agreement with the geometry of the Keggin polyanionic structure (α isomer) and the rigid framework pointed out above. On the other hand, Matsumoto *et al.* (1975) have observed that a large distortion occurs on passing from an α (T_d symmetry) to a β isomer (C_{3v} symmetry) by rotating a W₃O₁₃ unit. The differences between our results on $\beta_1\text{-SiMoW}_{11}\text{O}_{40}^{4-}$ and those of Matsumoto *et al.* (1975) on $\beta\text{-SiW}_{12}\text{O}_{40}^{4-}$ are probably due to their less well refined structure ($R = 0.138$).

WO₆ octahedral geometry

The geometries of the WO₆ octahedra do not depend on their location in sites I, II or III in the polyanion. The mean values of bond lengths are: W-O_a 2.35 (4), W-O_b 1.92 (2), W-O_c 1.93 (4), W-O_d 1.71 (3) Å (Table 2). The corresponding mean values obtained by Matsumoto *et al.* (1975) do not differ significantly from ours, but their spread is larger. As for all the polyanion structures, the W atom is displaced towards the outside of the polyanion from the centre of its octahedron.

W-W distances and angles

In a W₃O₁₃ unit, the distances between W atoms (mean 3.34 Å), and the W-O_c-W (120°) and W-

Table 3. W-O-W angles (°) and corresponding W-W distances (Å)

	Angle	Distance
W(3)-O _a (346)-W(4)	91.0 (9)	3.304 (2)
W(3)-O _a (346)-M(6)	92.5 (9)	3.352 (2)
W(4)-O _a (346)-M(6)	90.5 (9)	3.349 (2)
W(1)-O _a (22'1)-W(2)	90.1 (9)	3.347 (3)
W(2)-O _a (22'1)-W(2')	92.6 (10)	3.348 (2)
W(5)-O _a (55'7)-M(7)	91.8 (9)	3.366 (3)
W(5)-O _a (55'7)-W(5')	92.7 (10)	3.329 (2)
W(1)-O _b (15)-W(5)	144.0 (14)	3.661 (3)
W(2)-O _b (23)-W(3)	142.3 (17)	3.644 (2)
W(2)-O _b (24)-W(4)	144.8 (13)	3.645 (2)
W(4)-O _b (45)-W(5)	158.4 (15)	3.743 (2)
M(6)-O _b (67)-M(7)	151.6 (15)	3.696 (3)
W(3)-O _b (33')-W(3')	154.0 (18)	3.719 (2)
M(6)-O _b (66')-M(6')	150.3 (17)	3.710 (3)
W(1)-O _c (12)-W(2)	122.1 (13)	3.347 (3)
W(3)-O _c (34)-W(4)	120.1 (13)	3.304 (2)
W(3)-O _c (36)-M(6)	121.0 (12)	3.352 (2)
W(4)-O _c (46)-M(6)	120.6 (14)	3.349 (2)
W(5)-O _c (57)-M(7)	118.0 (12)	3.366 (3)
W(2)-O _c (22')-W(2')	119.7 (13)	3.348 (2)
W(5)-O _c (55')-W(5')	118.2 (14)	3.329 (2)

O_a-W (92°) angles are approximately constant (Table 3). On the other hand, the distance between two W atoms linked by an O_b atom and belonging to different W₃O₁₃ units depends on the relationship between these units. This distance is shorter if one W atom is in site III, *i.e.* in the rotated W₃O₁₃ unit (3.64 instead of 3.71 Å). In the same way, the angles of the W-O_c-W bridges are smaller if one of the W atoms is in site III (144 instead of 154°). We have already used these facts to explain why the β is less stable than the α structure (Tézé & Hervé, 1977b).

Table 2. Selected bond lengths (Å)

W(1)-O _b (15)	1.94 (2)	W(4)-O _c (34)	1.88 (2)
W(1)-O _c (12)	1.95 (2)	W(4)-O _c (46)	1.96 (3)
W(1)-O _a (22'1)	2.41 (3)	W(4)-O _a (4)	1.68 (3)
W(1)-O _d (1)	1.74 (4)		
W(2)-O _b (23)	1.94 (3)	W(5)-O _b (15)	1.91 (2)
W(2)-O _b (24)	1.89 (2)	W(5)-O _b (45)	1.89 (2)
W(2)-O _c (12)	1.87 (2)	W(5)-O _c (57)	1.93 (2)
W(2)-O _a (2)	1.71 (3)	W(5)-O _a (5)	1.71 (3)
W(2)-O _c (22')	1.94 (2)	W(5)-O _a (55'7)	2.30 (2)
W(2)-O _a (22'1)	2.32 (2)	W(5)-O _c (55')	1.94 (2)
W(3)-O _a (346)	2.28 (2)	M(6)-O _a (346)	2.36 (2)
W(3)-O _b (23)	1.91 (3)	M(6)-O _b (67)	1.91 (3)
W(3)-O _c (34)	1.94 (2)	M(6)-O _c (36)	1.92 (2)
W(3)-O _c (36)	1.93 (2)	M(6)-O _c (46)	1.89 (3)
W(3)-O _a (3)	1.70 (3)	M(6)-O _a (6)	1.73 (3)
W(3)-O _b (33')	1.91 (1)	M(6)-O _b (66')	1.92 (1)
W(4)-O _a (346)	2.36 (3)	M(7)-O _b (67)	1.90 (3)
W(4)-O _b (24)	1.94 (2)	M(7)-O _c (57)	2.00 (2)
W(4)-O _b (45)	1.92 (2)	M(7)-O _a (55'7)	2.39 (3)
		M(7)-O _d (7)	1.66 (3)

Conclusion

The location of the Mo atom in the title compound shows that the vacant coordination site is in site I of the polyanionic structure for the β_1 isomer. This agrees with the mode of formation of $\beta_1\text{-SiW}_{11}\text{O}_{39}^{8-}$ from $\beta\text{-SiW}_9\text{O}_{34}\text{H}^{9-}$. In the latter, the three coordination sites I are vacant; two of them are occupied by W atoms in $\beta_1\text{-SiW}_{11}\text{O}_{39}^{8-}$ (no intermediate step involving one W atom has yet been observed). As suggested by Tézé & Hervé (1977b), the formation of the α isomer occurs through the apparent migration of the vacant coordination site following the sequence site I, site II, site III.

Thus this work establishes the mode of formation of stable Keggin structures of α -12-tungstosilicates *via* unstable β structures and isomerization reactions. This result can be considered as general for tetra-coordinated heteroelements X having tetrahedral symmetry, since analogous $\beta\text{-XW}_9\text{O}_{34}\text{H}^{9-}$ and $\beta\text{-XW}_{11}\text{O}_{39}^{8-}$

intermediates have been obtained with $X = \text{Ge}^{\text{IV}}$, P^{V} and As^{V} (Contant, Fruchart, Hervé & Tézé, 1974).

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A Mixed-Valence Tungsten Oxide of Divalent Tin: $\text{Sn}_{10}\text{W}_{16}\text{O}_{46}$

I. Structure Determination

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Abstract

$\text{Sn}_{10}\text{W}_{16}\text{O}_{46}$ is hexagonal with $a = 7.667(4)$, $c = 18.640(4)$ Å, space group $P6_3/m$, $Z = 1$. The W atoms are octahedrally coordinated and form two types of units: $[\text{W}_6\text{O}_{19}]$ and $[\text{W}_2\text{O}_9]$. The $[\text{W}_6\text{O}_{19}]$ blocks are built up from six almost-regular edge-sharing octahedra, $\text{W}(1)\text{O}_6$. The $[\text{W}_2\text{O}_9]$ groups are built up from two face-sharing octahedra, $\text{W}(2)\text{O}_6$, the W(2) atoms being off-centred inside their octahedra along c . Sn(1) and Sn(2) are respectively surrounded by four and three O atoms. A consideration of their lone-pair $5s^2$ electrons suggests a bipyramidal coordination for Sn(1) and a tetrahedral coordination for Sn(2).

Introduction

Of the cations which are characterized by a lone pair, Sn^{II} has, to our knowledge, been little studied as its oxides. In contrast to its halides, for which much work

has been carried out (Donaldson, 1967; Dénès, 1978), only a few Sn^{II} oxides are known at the present time: we can cite SnO (Moore & Pauling, 1941; Serebrjanaja, Kabalkina & Verescagin, 1969), α - and β - SnWO_4 (Jeitschko & Sleight, 1972, 1974). In a recent study, McColm, Steadman & Dimbylow (1975) have shown the existence of Sn^{II} pseudo-hexagonal and tetragonal tungsten bronzes Sn_xWO_3 and of a $\text{Sn}_2\text{W}_3\text{O}_8$ phase. However, Steadman, Tilley & McColm (1972) have described the new Sn_xWO_3 oxides as intergrowths of WO_3 and hexagonal-tungsten-bronze structures.

In the course of our structural studies of oxides containing a lone-pair cation, we have tried a new investigation of the Sn–W–O system. The existence of Sn^{II} compounds in this system, ranging from $\text{Sn}_{0.4}\text{WO}_3$ to SnWO_4 , suggested the possibility of synthesizing oxides of intermediate composition. We describe here the structure of the new compound $\text{Sn}_{10}\text{W}_{16}\text{O}_{46}$ in which W presents the two oxidation states W^{IV} and W^{V} .