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

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A Mixed-Valence Tungsten Oxide of Divalent Tin: $Sn_{10}W_{16}O_{46}$.
I. Structure Determination

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Abstract

$Sn_{10}W_{16}O_{46}$ is hexagonal with $a = 7\cdot667$ (4), $c = 18\cdot640$ (4) Å, space group $P6_3/m$, $Z = 1$. The W atoms are octahedrally coordinated and form two types of units: $[W_6O_{19}]$ and $[W_2O_9]$. The $[W_6O_{19}]$ blocks are built up from six almost-regular edge-sharing octahedra, $W(1)O_6$. The $[W_2O_9]$ groups are built up from two face-sharing octahedra, $W(2)O_6$, 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 $Sn_2W_3O_8$ 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 $Sn_{0.4}WO_3$ to $SnWO_4$, suggested the possibility of synthesizing oxides of intermediate composition. We describe here the structure of the new compound $Sn_{10}W_{16}O_{46}$ in which W presents the two oxidation states W^{IV} and W^V.

Experimental

Red crystals were found next to tetragonal bronze in the system Sn—W—O at 1173 K for a tin composition richer than $Sn_{0.40}WO_3$. An almost pure compound has been prepared in sealed silica ampoules *in vacuo* from a mixture in the ratio 10 SnO_2 + $\frac{26}{3}WO_3$ + $\frac{22}{3}W$ heated at 1073 or 1173 K for 1 week.

Photographs showed the crystals to be hexagonal with the Laue group 6/m. Of the possible space groups (only systematic absences, 00l: l = 2n + 1), the centrosymmetric $P6_3/m$ was found to be correct during the structure determination.

The intensities were collected on an Enraf–Nonius CAD-4 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation from a hexagonal prismatic crystal 80 × 48 × 48 μm up to a maximum Bragg angle of 45°. Lattice constants were refined by least squares from the θ values of 25 reflections. Of the 6293 measured reflections recorded in three equivalent sextants, 966 were independent, had $I \geq 3\sigma(I)$, and were used for structure determination and refinement. The data were corrected for Lorentz and polarization factors. An absorption correction was applied, based on the indexed crystal forms {100} and {001}. Maximum and minimum values of the transmission factors were 0·17 and 0·06 respectively. Table 1 gives crystallographic data for $Sn_{10}W_{16}O_{46}$.

The structure was solved by Patterson and Fourier techniques. The W atom positions were refined and all other atoms located in the subsequent difference synthesis. The coordinates were refined by full-matrix least squares. Scattering factors for W and Sn were from Cromer & Waber (1965), corrected for anomalous dispersion (Cromer, 1965), and for O^{2-} from Suzuki (1960).

A linear weighting scheme was adjusted according to $\langle w|F_o - F_c|\rangle$ in terms of sin θ/λ.

A refinement with anisotropic thermal parameters for non-oxygen atoms and isotropic for O atoms led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.060$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.080$.

During the last cycle, the behaviour of all atoms was satisfactory except for O(4) lying at the centre of symmetry: its isotropic thermal coefficient did not converge and was fixed at an arbitrary value (Table 2).

Table 1. $Sn_{10}W_{16}O_{46}$: crystallographic data

$a = 7.667$ (4) Å	Temperature: 294 K
$c = 18.640$ (4)	Radiation: Mo $K\alpha$ ($\lambda = 0.71069$ Å)
Space group: $P6_3/m$	Scanning mode: ω–2θ
$Z = 1$	
$D_c = 8.51$ Mg m^{-3}	Measured space: $\pm h$, $+k$, $+l$
$D_m = 8.62$ (9)	Number of measured reflections: 6293
$\mu_l = 58.3$ mm^{-1} (Mo $K\alpha$)	Number of reflections used in the refinement: 966

Table 2. $Sn_{10}W_{16}O_{46}$: positional parameters and e.s.d.'s

		x	y	z	B (Å^2)
W(1)	12(i)	0·22453 (20)	0·05645 (20)	0·05991 (7)	$B_{eq} = 0.35$ (2)
W(2)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0·67023 (12)	$B_{eq} = 0.32$ (3)
Sn(1)	6(h)	0·1928 (6)	0·3124 (6)	$\frac{1}{4}$	$B_{eq} = 0.81$ (7)
Sn(2)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0·0705 (2)	$B_{eq} = 0.71$ (6)
O(1)	6(h)	0·459 (9)	0·301 (9)	$\frac{1}{4}$	1·0 (6)
O(2)	12(i)	0·462 (6)	0·131 (6)	0·1195 (21)	1·3 (5)
O(3)	12(i)	0·129 (4)	0·412 (4)	0·0060 (14)	0·3 (3)
O(4)	2(b)	0	0	0	3·0
O(5)	12(i)	0·186 (4)	0·245 (4)	0·1243 (12)	0·3 (3)
O(6)	2(a)	0	0	$\frac{1}{4}$	0·3 (7)

Table 3. $Sn_{10}W_{16}O_{46}$: interatomic distances (Å) and angles (°)

W(1) polyhedra

Neighbour N	W(1)	O(2)	O(3)	O(4)	O(5)
W(1)–N	2·687 (2) 2 ×	1·96 (5)	1·97 (3)	1·911 (1)	2·01 (3)
	2·719 (2) 2 ×		2·02 (2)		2·04 (2)
O(2)–W(1)–N			89·3 (16)		84·2 (16)
			86·4 (16)		89·9 (16)
O(3)–W(1)–N			89·4 (12)	92·4 (9)	92·5 (12)
				90·7 (8)	84·5 (12)
O(4)–W(1)–N					94·2 (8)
					93·2 (8)
O(5)–W(1)–N					93·1 (11)

W(2) polyhedra

Neighbour N	W(2)	O(1)	O(2)
W(2)–N	2·974 (3)	3 × 2·10 (3)	3 × 1·82 (5)
O(1)–W(2)–N		3 × 75·4 (18)	3 × 89·3 (19)
			3 × 98·6 (19)
O(2)–W(2)–N			3 × 95·6 (20)

SnO_4E bipyramidal groups

Neighbour N	O(1)	O(5)	O(6)
Sn(1)–N	2·09 (7)	2 × 2·39 (2)	2·093 (4)
O(1)–Sn(1)–N		2 × 84·6 (14)	95·6 (13)
O(5)–Sn(1)–N		156·0 (10)	2 × 79·9 (7)

SnO_3E tetrahedral groups

Neighbour N	O(3)	O(5)
Sn(2)–N	3 × 2·16 (2)	3 × 3·02 (2)
O(3)–Sn(2)–N	3 × 92·0 (11)	
O(5)–Sn(2)–N		3 × 109·5 (8)

This point will be discussed later. An isotropic extinction correction was tested but gave no significant modification of the results.

Final atomic parameters and interatomic distances and angles are given in Tables 2 and 3. A projection of the structure on to (001) is given in Fig. 1.*

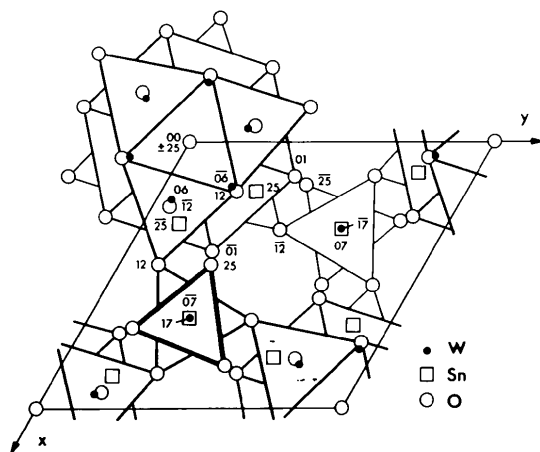
Fig. 1. $Sn_{10}W_{16}O_{46}$: projection of the structure on to (001), drawn from $z = -0.25$ to $z = 0.25$. Atom heights are multiplied by 10^2.

Description of the coordination polyhedra

W(1) and W(2) are characterized by an octahedral coordination, while the Sn atoms present two types of coordination: Sn(1) and Sn(2) are surrounded respectively by four and three O atoms. The centre of the W(1)O_6 octahedron is placed out of the symmetry elements. The interatomic distances W—O, ranging from 1.911 (1) to 2.04 (2) Å, and the bond angles (Table 3) show clearly that the octahedral coordination of W(1) is almost regular: this atom is displaced by only 0.07 (3) Å from the centre of gravity of its octahedron and the O—O distances range from 2.66 to 2.94 Å (σ mean = 0.04 Å). The W(1)—W(1) distances, six of 2.687 (2) and six of 2.719 (2) Å, show that these atoms form an almost-regular octahedral W_6 cluster (Fig. 2a). [W_6O_{19}] blocks are built up from six edge-sharing octahedra (Fig. 2b).

The W(2)O_6 octahedron, centred on the $\bar{6}$ axis, is less regular than W(1)O_6. The reason is that it belongs to a [W_2O_9] group which is built up from two equivalent face-sharing W(2)O_6 octahedra (Fig. 3).

Thus, the three common O—O distances are short, 2.57 (8) Å, the others ranging from 2.70 (6) to 2.98 (5) Å. For the same reason, the W(2) atoms are off-centred by 0.27 (4) Å along c inside their octahedra and for W(2) a 3 + 3 coordination (Table 3) results, the W(2)—W(2) length of 2.974 (3) Å being greater than W(1)—W(1). The units formed, [W_6O_{19}] and [W_2O_9], are corner shared.

The Sn(1) atoms are located in the mirror plane at the same levels, $z = \frac{1}{4}, \frac{3}{4}$, as the O(6) atoms which do not belong to the WO$_6$ polyhedra. O(6) is located at the centre of a triangle, the apices of which are three O(1) atoms of different [W_2O_9] groups (Fig. 4). Sn(1) is close to one O(1) apex of the triangle, forming two short bonds Sn(1)—O(1) = 2.09 (7) Å and Sn(1)—O(6) = 2.093 (4) Å with an angle less than 120° (Table 3). Sn(1) has two other O(5) neighbours at 2.39 (2) Å belonging to W(1)O_6 octahedra which are sited on both sides of the mirror plane. The geometry of the Sn coordination will be discussed later; Sn(1) can, however, already be considered as five-coordinate, its lone pair E being located at the fifth apex of the trigonal bipyramid formed by O(1) and O(6) in the equatorial plane, and two O(5) atoms at larger distances in the axial direction.

Fig. 3. The [W_2O_9] group built up from two face-sharing octahedra. G is the centre of gravity of an O-atom octahedron (distances in Å).
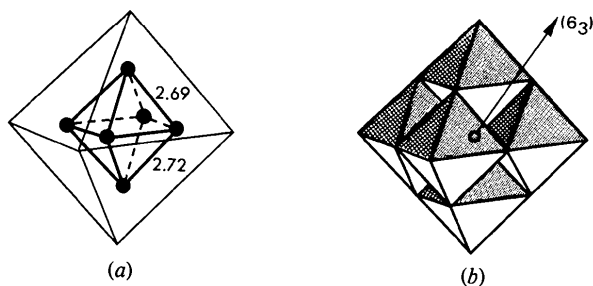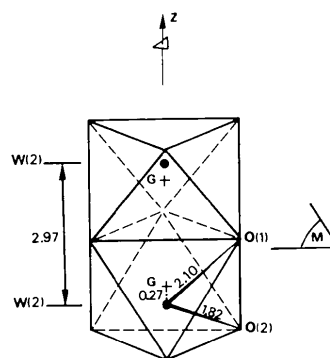

Fig. 2. The [W_6O_{19}] block. (a) The octahedral W_6 cluster. Filled circles represent the W atoms (distances in Å). (b) The six edge-sharing octahedra.
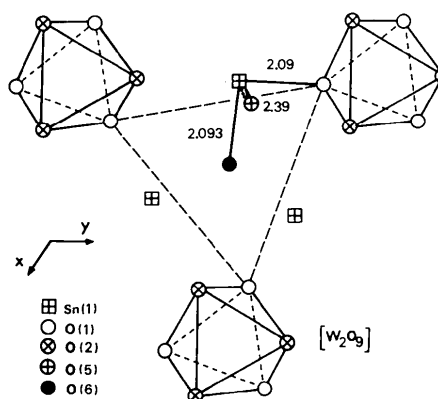

Fig. 4. Arrangement of Sn(1) atoms in relation to the [W_2O_9] groups (distances in Å).

The Sn(2) atoms placed on the $\bar{6}$ axes have three O(3) atoms as first neighbours at 2·16 (2) Å. These O atoms belong to $W(1)O_6$ octahedra, as do the second neighbours, O(5), which are on the other side with regard to the Sn(2) atoms and at greater distances (Table 3). From the symmetry and from the relative positions of the O atoms and Sn(2), it can be deduced that the lone pair of Sn(2) will be directed along c to form tetrahedral coordination for Sn.

Discussion and conclusion

The study of this oxide brings new information about the problems of composition in the Sn—W—O system and about the coordination polyhedra of W and Sn^{II}. This oxide must be identified with the phase to which the closely related composition $Sn_2W_3O_8$ has been assigned by McColm, Steadman & Dimbylow (1975): a comparison of the X-ray powder data of $Sn_{10}W_{16}O_{46}$ with those given by the same authors for $Sn_2W_3O_8$ confirms this point of view.

The almost-regular octahedral coordination of W(1) in the $[W_6O_{19}]$ blocks is in agreement with its mean oxidation state, 4·5, in this compound. The results obtained for the bronzes In_xWO_3 (Labbé, Goreaud, Raveau & Monier, 1979), in which the octahedra are corner shared, have shown that W tends towards a regular octahedral coordination as its oxidation state decreases, the coordination of W^{VI} in tungstates being more distorted (4 + 2) than in bronzes and intermediate between octahedral and tetrahedral.

The 3 + 3 coordination observed for W in the $[W_2O_9]$ groups is rare and has only been observed, to our knowledge, in Cu_3WO_6 (Gebert & Kihlborg, 1969). The W atom is displaced from the centre of its octahedron, along c towards one face, as in Cu_3WO_6. This configuration is very likely to be connected with the surrounding of this octahedron: it seems reasonable for the W atom to draw nearer to the face which shares its three corners with the $[W_6O_{19}]$ blocks than to the face which is common to the two octahedra of the $[W_2O_9]$ groups, in order to minimize the repulsion between the two W atoms of this unit.

The existence of $[W_6O_{19}]$ blocks is also rare. This type of configuration has been observed in tetrabutyl-ammonium hexatungstate (Henning & Hüllen, 1969), in a sodium hexaniobate (Lindqvist, 1953) and in a potassium hexatantalate (Lindqvist & Aronsson, 1955). In these cases isolated polyanions $[W_6O_{19}]^{2-}$, $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$ were observed, while in $Sn_{10}W_{16}O_{46}$, the $[W_6O_{19}]$ blocks are integrated in the framework. Moreover, the W—W distances in these units are very short (2·687–2·719 Å) compared to those of isolated polyanions: for example, W—W $\geq$ 3·22 Å in $[W_6O_{19}]^{2-}$ (Henning & Hüllen, 1969). This configuration is obtained here for the first time for W

with an oxidation number smaller than six. These observations lead us to believe that the electronic interactions between the W atoms of the blocks $[W_6O_{19}]$ should be strong, and that the W_6 octahedra belonging to these units could be considered as clusters. The behaviour of O(4), which is located at the centre of such a cluster, has been analysed on difference maps: a large delocalization of electron density around the centre of symmetry is observed, in agreement with the anomalous B factor of this atom. However, the absence of an O atom at the centre of the W_6 cluster cannot be totally ruled out; the resulting $[W_6O_{18}]$ block would then be stabilized by a smaller repulsion between the W atoms due to the decrease in the mean oxidation state of W. Nevertheless, this last hypothesis should agree with almost regular $WO_5\square$ octahedra with only five corners occupied by O atoms. Such polyhedra have never been observed and do not seem likely.

Moreover, a comparison can be made with the Mo_6 octahedral cluster observed in Mo_6Cl_{12} (Schäfer, von Schnering, Tillack, Kuhnen, Wöhrle & Baumann, 1967). The Mo_6 octahedron is perfect and each Mo has five Cl neighbours forming a tetragonal pyramid. The corresponding block $\{[Mo_6Cl_8]Cl_2\}Cl_4$ could equally be described by six face-sharing octahedra $MoCl_5\square$. We note that in this kind of cluster, in contrast to W_6 in $[W_6O_{19}]$, the distance between Mo and the centre of the cluster, ~1·85 Å, is very small compared with the mean Mo—Cl distance (2·465 Å). Therefore the Mo_6 cluster cannot contain an anion and the $MoCl_5\square$ octahedra are not regular. This is not the case in the title compound.

The lone pair of Sn^{II} possesses important stereo-activity and can be considered as a ligand in order to form tetrahedral and bipyramidal coordination for the two kinds of Sn atoms present in this structure, according to the model described by Gillespie & Nyholm (1957). The consequences of this stereo-activity on the framework constitution merit a special study which forms the subject of the following paper.

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A Mixed-Valence Tungsten Oxide of Divalent Tin: $Sn_{10}W_{16}O_{46}$.
II. Analysis of the Structure and Stereoactivity of the Sn^{II} Lone Pair

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Abstract

The analysis of the structure of the oxide $Sn_{10}W_{16}O_{46}$ shows that there are two approaches to its description: from the coordination polyhedra and from the anionic packing. In the first description the WO_6 octahedra form a $W_{16}O_{44}$ framework built up from $[W_6O_{19}]$ and $[W_2O_9]$ units; two supplementary O atoms and ten Sn atoms are inserted in this framework, forming SnO_3E tetrahedra and SnO_4E bipyramids where E is the $5s^2$ lone pair of Sn^{II}. In the second analysis it is shown that the consideration of the lone pair of Sn^{II} allows this structure to be described as an anionic close packed arrangement built up from three sorts of planes with respective compositions O_6E, O_4E_3 and O_7. The sequence of these layers along c is described. The behaviour of the lone pair of Sn^{II} is discussed using the second description and compared with that previously reported by other authors.

Introduction

The structural study of $Sn_{10}W_{16}O_{46}$ (Goreaud, Labbé & Raveau, 1980) has shown that this oxide is characterized by the existence of two kinds of units built up from WO_6 octahedra: the $[W_2O_9]$ groups and the $[W_6O_{19}]$ blocks forming W_6 clusters. The behaviour of W in this compound has been considered. The presence of Sn^{II} should give information about the stereoactivity of the lone pair $E(5s^2)$; the Sn should

play an important part in the framework building, due to its relatively high proportion in $Sn_{10}W_{16}O_{46}$. An analysis of this structure is given here.

Analysis of the structure

There are two ways to describe the structure of this oxide: from the coordination polyhedra and from the anionic packing.

The coordination polyhedra

The WO_6 octahedra form a three-dimensional framework with the composition $W_{16}O_{44}$. The structure of this $W_{16}O_{44}$ framework (Fig. 1) can be considered as being built up from two structural units: $[W_6O_{19}]$ formed by six edge-sharing octahedra $W(1)O_6$, and $[W_2O_9]$ formed by two face-sharing octahedra $W(2)O_6$. These units have been described in the previous paper.

The $[W_6O_{19}]$ blocks can be considered as 'super-octahedra' whose ternary axes are parallel to c; these 'super-octahedra' share their corners with those of the $[W_2O_9]$ units, there being an equal number of these and $[W_6O_{19}]$ blocks. Thus each $[W_6O_{19}]$ block is surrounded by six $[W_2O_9]$ distributed at the corners of a trigonal antiprism, whereas each $[W_2O_9]$ is surrounded by six $[W_6O_{19}]$ whose centres are located at the corners of a trigonal prism. From this arrangement, it follows that the $[W_6O_{19}]$ blocks form rows parallel to [001],