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## A Mixed-Valence Tungsten Oxide of Divalent Tin: $\text{Sn}_{10}\text{W}_{16}\text{O}_{46}$ . II. Analysis of the Structure and Stereoactivity of the $\text{Sn}^{\text{II}}$ Lone Pair

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### Abstract

The analysis of the structure of the oxide  $\text{Sn}_{10}\text{W}_{16}\text{O}_{46}$  shows that there are two approaches to its description: from the coordination polyhedra and from the anionic packing. In the first description the  $\text{WO}_6$  octahedra form a  $\text{W}_{16}\text{O}_{44}$  framework built up from  $[\text{W}_6\text{O}_{19}]$  and  $[\text{W}_2\text{O}_9]$  units; two supplementary O atoms and ten Sn atoms are inserted in this framework, forming  $\text{SnO}_3E$  tetrahedra and  $\text{SnO}_4E$  bipyramids where  $E$  is the  $5s^2$  lone pair of  $\text{Sn}^{\text{II}}$ . In the second analysis it is shown that the consideration of the lone pair of  $\text{Sn}^{\text{II}}$  allows this structure to be described as an anionic close packed arrangement built up from three sorts of planes with respective compositions  $\text{O}_6E$ ,  $\text{O}_4E_3$  and  $\text{O}_7$ . The sequence of these layers along  $c$  is described. The behaviour of the lone pair of  $\text{Sn}^{\text{II}}$  is discussed using the second description and compared with that previously reported by other authors.

### Introduction

The structural study of  $\text{Sn}_{10}\text{W}_{16}\text{O}_{46}$  (Goreaud, Labbé & Raveau, 1980) has shown that this oxide is characterized by the existence of two kinds of units built up from  $\text{WO}_6$  octahedra: the  $[\text{W}_2\text{O}_9]$  groups and the  $[\text{W}_6\text{O}_{19}]$  blocks forming  $\text{W}_6$  clusters. The behaviour of W in this compound has been considered. The presence of  $\text{Sn}^{\text{II}}$  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  $\text{Sn}_{10}\text{W}_{16}\text{O}_{46}$ . 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  $\text{WO}_6$  octahedra form a three-dimensional framework with the composition  $\text{W}_{16}\text{O}_{44}$ . The structure of this  $\text{W}_{16}\text{O}_{44}$  framework (Fig. 1) can be considered as being built up from two structural units:  $[\text{W}_6\text{O}_{19}]$  formed by six edge-sharing octahedra  $\text{W}(1)\text{O}_6$ , and  $[\text{W}_2\text{O}_9]$  formed by two face-sharing octahedra  $\text{W}(2)\text{O}_6$ . These units have been described in the previous paper.

The  $[\text{W}_6\text{O}_{19}]$  blocks can be considered as 'super-octahedra' whose ternary axes are parallel to  $c$ ; these 'super-octahedra' share their corners with those of the  $[\text{W}_2\text{O}_9]$  units, there being an equal number of these and  $[\text{W}_6\text{O}_{19}]$  blocks. Thus each  $[\text{W}_6\text{O}_{19}]$  block is surrounded by six  $[\text{W}_2\text{O}_9]$  distributed at the corners of a trigonal antiprism, whereas each  $[\text{W}_2\text{O}_9]$  is surrounded by six  $[\text{W}_6\text{O}_{19}]$  whose centres are located at the corners of a trigonal prism. From this arrangement, it follows that the  $[\text{W}_6\text{O}_{19}]$  blocks form rows parallel to  $[001]$ ,

viewed down  $c$  in Fig. 2. In each row, two consecutive octahedral  $[\text{W}_6\text{O}_{19}]$  blocks are rotated by  $60^\circ$  about  $c$  according to the  $6_3$  axis (Fig. 1). An additional O(6) atom is located on the mirror plane between these two consecutive groups, and forms with their O atoms two equivalent corner-sharing tetrahedra which are empty.

The  $\text{W}_{16}\text{O}_{44}$  framework may equally be described as being built up by the stacking along  $c$  of two sorts of layers (Fig. 1): the  $\text{W}_6\text{O}_{16}$  layers formed by the  $[\text{W}_6\text{O}_{19}]$  units, and the  $\text{W}_2\text{O}_6$  layers formed by the  $[\text{W}_2\text{O}_9]$  units. The Sn(1) atoms are located in the  $\text{W}_2\text{O}_6$  layers at the same level as the O(1) atoms and the two additional O(6) atoms which do not belong to the  $\text{W}_{16}\text{O}_{44}$  framework. A perspective view (Fig. 3) shows the position of Sn(1) and its four O atom neighbours making the  $\text{SnO}_4E$  bipyramid, where  $E$  indicates the

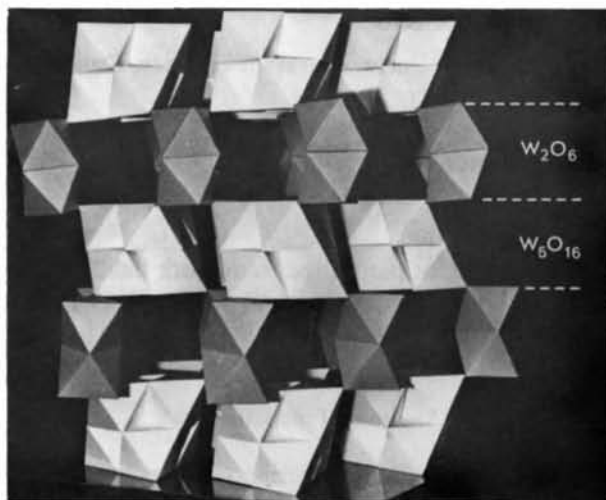


Fig. 1. The  $\text{W}_{16}\text{O}_{44}$  lattice built up from  $[\text{W}_6\text{O}_{19}]$  blocks and  $[\text{W}_2\text{O}_9]$  groups.



Fig. 2. The arrangement of  $[\text{W}_6\text{O}_{19}]$  blocks and  $[\text{W}_2\text{O}_9]$  groups, viewed down  $c$ .

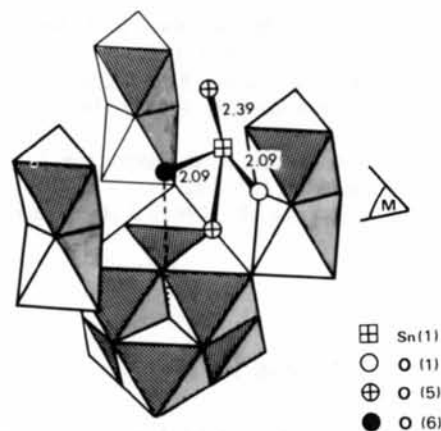


Fig. 3. Surrounding O atoms for Sn(1) lying in the mirror plane  $M$ .

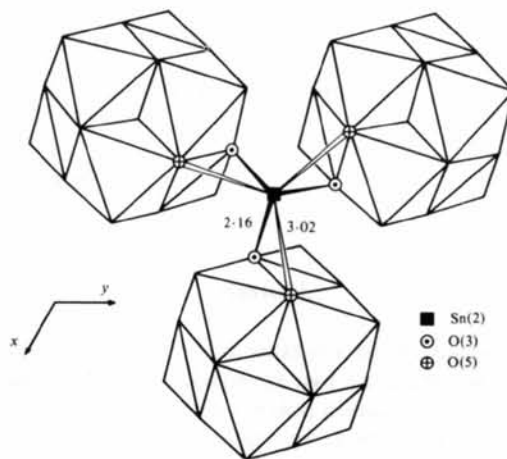


Fig. 4. Surrounding O atoms for Sn(2) lying on the  $\bar{6}$  axis.

lone pair. The Sn(2) atoms are located in the  $\text{W}_6\text{O}_{16}$  layers and each Sn(2) atom is surrounded by three  $[\text{W}_6\text{O}_{19}]$  units (Fig. 4). A perspective view (Fig. 7) shows that Sn(2) is out of the plane formed by the three O(3) atoms belonging to the layer and making the  $\text{SnO}_3E$  tetrahedron.

#### The anionic close packing

The planes of O atoms parallel to (001) are of three types which will be denoted  $\text{O}_6E$ ,  $\text{O}_4E_3$  and  $\text{O}_7$  according to their composition.

The  $\text{O}_6E$  planes are common to the  $\text{W}_2\text{O}_6$  and  $\text{W}_6\text{O}_{16}$  layers and lie at  $z \sim \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$  and  $\frac{7}{8}$ . The O atoms of these planes form an almost ideal packing of spheres, one position out of seven being unoccupied (Fig. 5a). An analysis of the coordination polyhedra shows that this position is in fact occupied by the lone pair  $E(2)$  of Sn(2). These planes can thus be considered as being built up from a close packing of spheres with slight distortions.

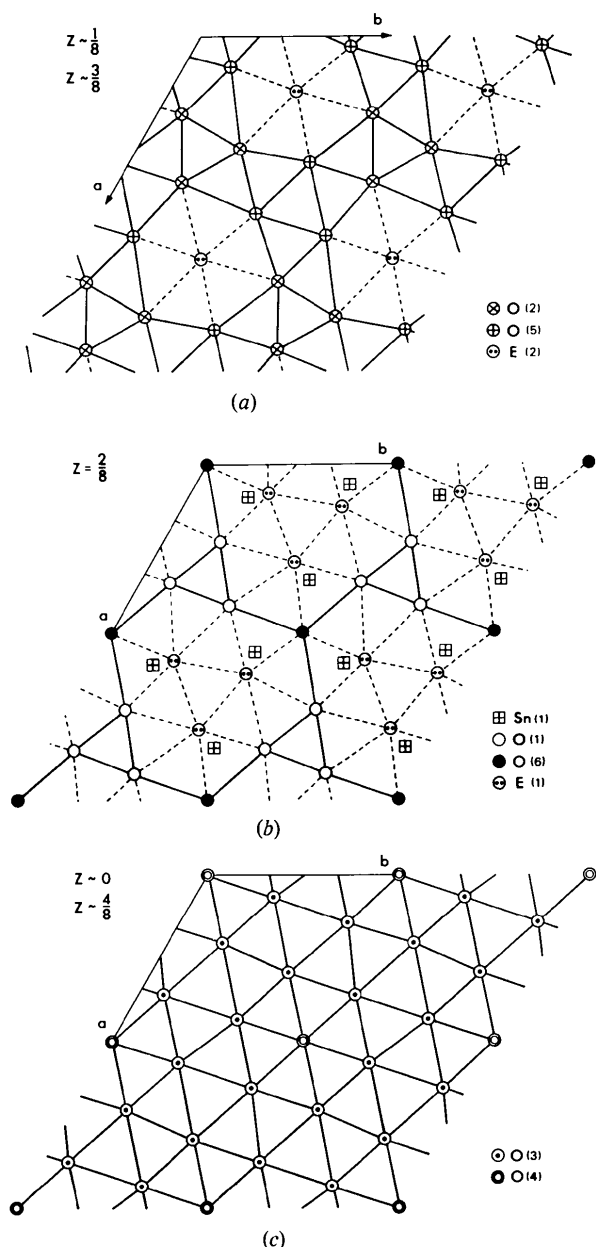


Fig. 5. Anionic planes (001) built up from lone pairs and O atoms; (a)  $O_6E$  planes, (b)  $O_4E_3$  planes, (c)  $O_7$  planes.

The  $O_4E_3$  planes which belong only to the  $W_2O_6$  layers coincide with mirror planes at  $z = \frac{1}{4}$  and  $\frac{3}{4}$ . At first sight they seem to be very deficient in anions (Fig. 5b) since, by drawing the hexagonal diagram passing through the O atoms, one can see that only four positions out of seven are occupied by O atoms. A study of the coordination of the Sn(1) atoms located on these levels shows that each lone pair  $E(1)$  occupies one place in these planes and hence the lone pairs will be located in the three free sites; thus the  $O_4E_3$  planes can also be considered as compact.

The  $O_7$  planes which belong only to the  $W_6O_{16}$  layers, at  $z \sim 0$  and  $\frac{1}{2}$ , are characterized by an almost perfect close packing of O atoms without any vacant sites (Fig. 5c).

The stacking of the anionic layers along  $c$  is shown schematically in Fig. 6. It can be seen that the O atoms and the lone pairs of Sn are close packed: the sequence of successive layers can be described as  $ABA'BACA''C$ . In this scheme, the planes  $A$ ,  $A'$  and  $A''$  are of the same kind: their atoms (or lone pairs) are approximately one above the other, but not exactly, the close packing being not quite perfect. It must, however, be noted that the deviations between the positions in  $A$ ,  $A'$  and  $A''$  do not exceed  $0.34 \text{ \AA}$ . The  $A$  planes contain only O atoms. The  $A'$  and  $A''$  planes, with  $O_4E_3$  composition, are identical and derive from one another by a symmetry-centre operation just like the  $B$  and  $C$  planes which have the composition  $O_6E$ . On the other hand the  $W_6O_{16}$  layers, if considered alone, are characterized by a cubic close-packing arrangement while the  $W_2O_6$  layers show hexagonal packing.

In this framework, the inhomogeneous occupation of interstitial cavities limited by lone pairs and O atoms leads to the different structural features of the  $W_6O_{16}$  and  $W_2O_6$  layers. The occupation by W atoms is preponderant in the former, and that of Sn atoms in the latter.

## Discussion

The analysis of the coordination of  $Sn^{II}$  shows that the  $5s^2$  lone pair of this element is stereoactive and thus can be considered as a ligand (Gillespie & Nyholm, 1957). The calculation of the volume per 'anion' (total number of 'anions' = oxygen anions + lone pairs),  $V = 16.9 \text{ \AA}^3$ , shows, in agreement with the result of Andersson & Aström (1972), that the volume of the lone pair is close to that of the  $O^{2-}$  anion.

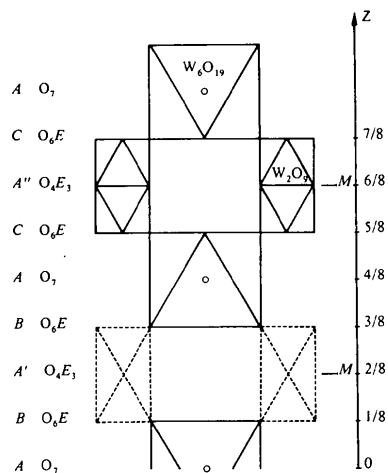


Fig. 6. The stacking of the anionic layers along  $c$ .

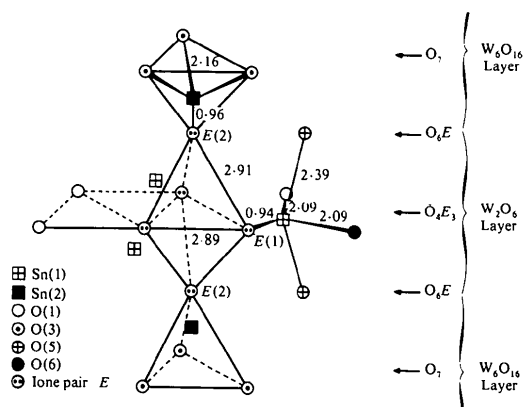


Fig. 7. Arrangement of the lone pairs and coordination of Sn atoms.

The arrangement of Sn atoms with probable positions of the lone pairs and the surrounding O atoms is given in Fig. 7. Two  $E(2)$  pairs belonging to the  $\text{O}_6E$  planes and three  $E(1)$  pairs belonging to the  $\text{O}_4E_3$  plane form a trigonal bipyramid.

In a first approach, an attempt was made to localize the lone pairs with the method developed by Galy, Meunier, Andersson & Aström (1975). The triangular base of the  $\text{Sn}(1)\text{O}_4E(1)$  bipyramid is then considered as equilateral and the  $\text{Sn}(2)\text{O}_3E(2)$  tetrahedron as regular. The calculation of the positions of lone pairs leads to distances between the Sn atoms and their lone pairs,  $\text{Sn}(1)-E(1) = 1.28$  and  $\text{Sn}(2)-E(2) = 1.33$  Å, which are notably greater than the mean distance predicted by the authors (0.95 Å). It can be seen (Table 1) that the coordinates of lone pairs calculated by this method involve very large differences between the  $\text{O}(1)-E(1)$  or  $\text{O}(6)-E(1)$  and  $E(1)-E(1)$  distances in the  $\text{O}_4E_3$  plane. In a similar way, the  $E(2)$  pair would be out of the plane formed by  $\text{O}(2)$  and  $\text{O}(5)$  (Fig. 5a). The Sn-E distances and the position obtained for  $E(2)$ , out of the  $\text{O}_6E$  plane when the cavity offered by this plane is large enough to accept an  $\text{O}^{2-}$  anion, suggest that another model should be considered. There is in fact no reason for having strict equality between the O-E distances and the O-O distance which is the reference for building up the idealized coordination polyhedron of Sn according to Galy, Meunier, Andersson & Aström (1975).

Starting from the hypothesis that the lone pairs and the O atoms tend to make the closest packing, the lone pair  $E(2)$  of the  $\text{Sn}(2)\text{O}_3E(2)$  tetrahedron has thus been placed in the  $\text{O}_6E$  plane, at the barycentre of the hexagon formed by  $\text{O}(2)$  and  $\text{O}(5)$  (Fig. 5a). The  $\text{Sn}(2)-E(2)$  distance obtained from this hypothesis, 0.96 Å, agrees with that predicted by Galy *et al.* (1975), and the  $\text{O}(3)-E(2)$  distances, 2.81 Å, are close to those generally observed. As a second stage, we have assumed that the distances  $\text{O}(1)-E(1)$  and  $\text{O}(6)-E(1)$  in the  $\text{Sn}(1)\text{O}_4E(1)$  bipyramid have the same value. For the bipyramid a distance  $\text{Sn}(1)-E(1) = 0.94$  Å results.

Table 1.  $\text{Sn}_{10}\text{W}_{16}\text{O}_{46}$ : positions of the lone pair of  $\text{Sn}^{\text{II}}$  and related distances (Å)

	(a)	(b)
$E(1)$ position	$\begin{cases} x & 0.1583 \\ y & 0.4591 \\ z & \frac{1}{4} \end{cases}$	$\begin{cases} 0.1673 \\ 0.4200 \\ \frac{1}{4} \end{cases}$
$\text{Sn}(1)-E(1)$	1.28	0.94
$E(1)-E(1)$	2.57	2.89
$\text{O}(1)-E(1)$	3.10	2.81
$\text{O}(6)-E(1)$		
$E(2)$ position	$\begin{cases} x & \frac{1}{4} \\ y & \frac{1}{4} \\ z & 0.1420 \end{cases}$	$\begin{cases} \frac{1}{4} \\ \frac{1}{4} \\ 0.1219 \end{cases}$
$\text{Sn}(2)-E(2)$	1.33	0.96
$E(1)-E(2)$	2.50	2.91
$\text{O}(3)-E(2)$	3.11	2.81

(a) Calculated from the method of Galy *et al.* (1975). (b) Calculated from our hypothesis.

Moreover, the  $E(1)-E(2)$  distances in the trigonal bipyramid  $E_5$  (Fig. 7, Table 1) are then homogeneous and close to 2.9 Å whereas they were too short in the preceding model.

### Conclusion

The structure analysis of  $\text{Sn}_{10}\text{W}_{16}\text{O}_{46}$  led to an obvious stereoactivity of the  $\text{Sn}^{\text{II}}$  atom lone pair and to its fundamental role in the building of an anionic framework. The description of the structure, when regarded as an almost close-packed arrangement of layers formed by O atoms and lone pairs, shows that no site is empty. The observed succession along  $c$  is in fact produced by alternating cubic and hexagonal close packed slices. The octahedral interstitial sites of this framework are not occupied in an homogeneous manner by heavy atoms: W atoms form either  $W_6$  clusters or  $W_2$  groups.

On the other hand, the results concerning the Sn atom and its lone pair are not satisfactory if we consider a regular Sn coordination polyhedron. On the contrary, if we suppose that the  $5s^2$  lone pair of the Sn atom behaves as an anion and realizes, as far as possible, the most compact layer with surrounding O atoms, the model found is correct and the calculated distances agree with previous work.

Structures of this type should thus be particularly suitable for a study of lone-pair stereoactivity.

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