

## Bond Lengths and Valences in Tungsten Oxides

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Equations relating bond strength (valence) to bond length have been developed for tungsten-oxygen and phosphorus-oxygen bonds. Bond-valence sums have been carried out for the different tungsten atoms in phosphate tungsten bronzes and other mixed-valence tungsten oxides and for the Mo atoms in  $\text{TeMo}_5\text{O}_{16}$ . Valences intermediate between 5 and 6 are generally found, in agreement with physical measurements that indicate delocalization of *d* electrons in these materials. Evidence is presented that shows that the degree of distortion of  $\text{WO}_6$  octahedra increases with apparent oxidation state of tungsten. © 1985 Academic Press, Inc.

### Introduction

Mixed-valence tungsten oxides ("tungsten bronzes") have been the subject of innumerable investigations over the years because of their fascinating structures and physical properties. Two related topics of perennial interest are the distribution of valences among the crystallographic sites of the crystal and the nature of the conductivity in the material. In this paper we enquire into the information contained in the structural data—specifically bond lengths—using the now well-established method of bond length-bond strength (valence) correlation.

Bart and Ragaini (1), for example, have shown that for molybdenum oxides a universal bond length-bond strength correlation works quite well for the range of oxidation states from Mo(VI) to Mo(II). Le Page and Strobel (2) have used a similar correlation for titanium oxides to determine the individual valences in  $\text{Ti}_6\text{O}_{11}$ . An interesting

result of their work, to which we return, was the observation that bond-strength sums (and hence apparent valences) were not integral but had an intermediate value between 3 and 4. Very recently Trömel (3) has shown that the metal-insulator transition in  $\text{Ti}_4\text{O}_7$  and  $\text{V}_4\text{O}_7$  is mirrored in a transition of valences on the individual atoms in the structure from values close to the average (3.5) to values closer to 3.0 and 4.0.

Valences in mixed tungsten oxides have been investigated extensively. Recent work on the polyanions is that of Sanchez *et al.* (4) and on the reduced tungsten oxides that of Gehlig *et al.* (5). Both these papers give references to earlier work. Gehlig *et al.* studied reduced tungsten oxides with  $\text{O/W} = 2.9$  and  $2.72$  (i.e.,  $\text{W}_{18}\text{O}_{49}$ ) by X-ray-induced photoelectron spectroscopy (XPS). The  $\text{W}(4f)$  spectrum was interpreted as consisting of W(V) and W(VI) components. However, in  $\text{W}_{18}\text{O}_{49}$  in particular, it was observed that the W(V)/W(VI) ratio was much less than expected from the composition

and it was suggested that the remaining electrons were delocalized conduction electrons. A similar conclusion was reached earlier on the basis of structural arguments (6).

The question of the valence of tungsten in these oxides is closely related to that of the conduction mechanism. A well-defined +5 oxidation state corresponds to a localized *d* electron with its surrounding lattice polarization—a so-called small polaron. It implies that around such a site one should find bond lengths characteristic of W(V). On the other hand a more delocalized electron with higher mobility (a large polaron) will “jump” from site to site with frequency greater than those of lattice vibrations so that the observed bond lengths will be intermediate between those expected for oxidation states +5 and +6 (4).

In fact, electrical measurements (7) and electron spin resonance studies (8) on reduced  $\text{WO}_3$  and on  $M_x\text{P}_2\text{W}_8\text{O}_{28}$  (9) tend to support the large polaron picture in these materials so that it might be expected that nonintegral valences should be derived from bond-strength summations just as was found in the case of the titanium oxide. On the other hand structural arguments have been used to assign valences (6) so that it is of considerable interest to do the bond-strength sums for these oxides.

### Bond Strength–Bond Length Correlations for Tungsten Oxides

Bond strength (or valence),  $\nu$ , is usually related to bond length,  $R$ , either by

$$\nu = (R_0/R)^n \quad (1)$$

or by

$$\nu = \exp[(R'_0 - R)/b] \quad (2)$$

where  $R_0$ ,  $R'_0$ ,  $n$ , and  $b$  are empirically determined parameters (10). Several authors have determined the parameters of either Eqs. (1) or (2) for W–O bonds already (11,

TABLE I  
W(VI) OXIDES USED TO DETERMINE BOND  
LENGTH–BOND STRENGTH RELATIONSHIPS

Compound	C.N.	$\nu$ [Eq. (1)]	Ref.
$\text{CaWO}_4$	4	5.63	13
$\text{SrWO}_4$	4	5.80	14
$\text{BaWO}_4$	4	5.76	14
$\text{LiPrW}_2\text{O}_8$	6,6	5.97,5.92	15
$\text{K}_4\text{ZnW}_3\text{O}_{12}$	4,4,4	6.00,5.88,5.90	16
$\text{WO}_3$ (RT)	6,6	6.10,6.26	17
$\text{WO}_3$ (LT)	6,6,6,6	5.94,6.29,6.14,6.32	18
$\text{Na}_2\text{W}_2\text{O}_7$	6,4	6.08,5.73	19
$\text{Al}_2\text{W}_3\text{O}_{12}$	4,4	6.08,6.02	20
$\text{Li}_2\text{WO}_4$	6	6.16	21
$\text{CsLiWO}_4$	4	5.78	22
$\alpha\text{-SnWO}_4$	6	5.75	23
$\beta\text{-SNWO}_4$	4	6.37	24

12); however, as there have subsequently been several new accurate determinations of the structures of tungsten oxides, we have redetermined them. First we took data only from well-defined structures (listed in Table I) containing W(VI). Thirteen structures with a total of 21 independent atoms were used. The parameters in Eqs. (1) and (2) were then determined as those that minimized  $\delta^2 = \Sigma(6 - \Sigma\nu)^2/N$ , where  $\Sigma\nu$  is the valence sum at each of the  $N$  independent W atoms in the set of structures.

The derived parameters for Eq. (1) were

$$R_0 = 1.898 \text{ \AA}, \quad n = 5.75$$

and for Eq. (2):

$$R'_0 = 1.903 \text{ \AA}, \quad b = 0.330.$$

As can be seen from Table I, the fit to the individual data was not spectacular, the value of  $\delta$  being 0.22 for both equations. For this reason, when comparing oxidation states of different atoms within a given compound we used a renormalization procedure described below.

There appear to be only two well-defined structures of compounds containing only W(V), viz.  $\text{AlWO}_4$  (25) and  $\text{CrWO}_4$  (26). For these compounds, the parameters

given above yield bond-strength sums at W of 5.03 and 4.96, respectively. We are encouraged by this result to believe that one set of parameters is therefore valid for both oxidation states of tungsten, as had been shown for Mo (7). However, in view of the relatively large value of  $\delta$ , in applying Eq. (1) to individual crystals, we renormalized by changing  $R$  to make the total of the valence sums at W equal to that expected from the formal oxidation state of tungsten in the crystal. This procedure was justified by the fact that the valence sum at oxygen was then very close to 2 in almost every instance. The exceptions, noted below, appear to be due to errors in the reported structure. As Eqs. (1) and (2) give essentially identical results, only results obtained using Eq. (1) are reported here.

In our analysis of the phosphorus-tungsten bronzes we also calculated the strengths of the phosphorus-oxygen bonds. We found here that the parameters appropriate for Eq. (1) reported by Brown and Shannon (27) ( $R_0 = 1.622 \text{ \AA}$ ,  $n = 4.29$ ) were not suitable, so again the value of  $R_0$  was adjusted to make the valence sum at P equal to 5.0 (keeping the value of  $n = 4.29$ ). The mean of the values thus obtained,  $R_0 = 1.607 \text{ \AA}$ , is also in much better accord with bond lengths in other phosphates such as  $\text{AlPO}_4$  (28), and this value is recommended for general use with phosphates. (As phosphorus is always four-coordinated in oxides, the "best" parameters for Eqs. (1) and (2) are ill-defined in practice and the choice of  $n$  is to this extent arbitrary.)

It is well known that factors other than valence affect bond lengths; for example, it has been shown clearly for alkali metal oxides than nonbonded interactions in cation-rich compounds act to produce longer than normal bonds (29). Possibly more relevant to the present discussion is the observation that bond length configurations  $A-O$  and  $B-O$  in  $A-O-B$  depend to some extent on the angle at oxygen. In the case of  $\text{Si-O}$

TABLE II  
DERIVED VALENCES IN MIXED-VALENCE  
TUNGSTEN OXIDES

(v)	Compound	Ref.	$R_0$	(Atom) and oxidation states
5.333	$\text{P}_2\text{W}_3\text{O}_{13}$	(31)	1.874	(2) 5.10; (1) 5.18; (3) 5.70
5.40	$\text{K}_{0.4}\text{P}_2\text{W}_4\text{O}_{16}$	(32)	1.879	(1) 5.26; (2) 5.53
5.438	$\text{Na}_{0.7}\text{P}_2\text{W}_4\text{O}_{16}$	(33)	1.883	(1) 5.36; (2) 5.51
5.444	$\text{W}_{18}\text{O}_{49}$	(6)	1.876	(9) 4.64; (6) 4.95; (1) 5.17; (2) 5.36; (8) 5.48; (5) 5.53; (4) 5.79; (7) 5.95; (3) 6.12
5.50	$\text{P}_2\text{W}_4\text{O}_{16}$	(34)	1.880	(2) 5.18; (1) 5.82
5.525	$\text{Na}_{0.85}\text{P}_2\text{W}_6\text{O}_{22}$	(33)	1.879	(1) 5.44; (3) 5.50 (2) 5.63
5.591	$\text{Rb}_{0.435}\text{P}_2\text{W}_6\text{O}_{22}$	(35)	1.886	(2) 5.46; (1) 5.65; (3) 5.66
5.614	$\text{K}_{0.7}\text{P}_2\text{W}_7\text{O}_{25}$	(36)	1.883	(1) 5.46; (2) 5.55; (3) 5.58 (4) 5.79
5.629	$\text{K}_{0.37}\text{WO}_3$	(37)	1.895	(2) 5.58; (1) 5.85
5.65	$\text{Rb}_{0.435}\text{P}_2\text{W}_7\text{O}_{25}$	(38)	1.886	(4) 5.41; (3) 5.54; (3') 5.60 (1') 5.73; (2') 5.75; (1) 5.89 (2) 6.09
5.70	$\text{Rb}_{0.42}\text{P}_2\text{W}_8\text{O}_{28}$	(39)	1.885	(4) 5.55; (3b) 5.58; (1b) 5.62 (1a) 5.72; (3a) 5.80; (2a) 5.86 (2b) 5.92

bonds (30) the variation is of the order of  $0.02 \text{ \AA}$  corresponding to about a 5% change in apparent bond valence. For these reasons we do not attach any significance to minor variations of apparent oxidation state of tungsten but focus instead on the major trends observed.

### Apparent Oxidation States in Mixed-Valence Compounds

Table II shows the oxidation states determined for the crystallographically distinct W atoms in a number of compounds in which the average oxidation state is between 5 and 6. The value of  $R_0$  shown is that which makes the average of the individual oxidation states equal to the formal overall oxidation state—it can be seen that only minor variations of  $R_0$  occur. The notation used in the table for the individual atoms is the same as used by the authors cited in the references. With the exception of  $\text{W}_{18}\text{O}_{49}$ , in all the compounds tungsten-oxygen and phosphorus-oxygen polyhedra share only vertices. In  $\text{W}_{18}\text{O}_{49}$  there is also edge-sharing of tungsten-oxygen polyhe-

dra and this compound might be expected to be exceptional on this account (for example, there might be metal-metal bonds). Actually in this instance some of the bond-strength sums at oxygen differed significantly from 2.0. The largest deviation was for O(23) for which  $\Sigma v = 2.83$  as a result of a very short bond to W(7) ( $R = 1.631 \text{ \AA}$ ). As the calculated oxidation state of the other atom [W(9)] bonded to O(23) is clearly too low (corresponding to a W-O bond that is too long), it is possible that the position of O(23) is in error. For this reason we have excluded the calculated oxidation states of these two tungsten atoms from the subsequent analysis.

With the reservations noted in the previous paragraph, we can see that the oxidation states determined here from the reported structure of  $\text{W}_{18}\text{O}_{49}$  are not those proposed by Viswanathan *et al.* (6). Those authors deduced that W(2), W(4), and W(8) were W(VI) whereas we calculate valences of 5.36, 4.95, and 5.48, respectively, for those atoms.

Of the other compounds studied only two,  $\text{P}_2\text{W}_3\text{O}_{13}$  and  $\text{P}_2\text{W}_4\text{O}_{16}$ , showed any indication of containing W(V) and W(VI). In all the other compounds, intermediate oxidation states are the rule. There is an interesting parallel between these results and those of Kihlberg (39) who analyzed the structures of  $\text{Mo}_8\text{O}_{23}$  and orthorhombic  $\text{Mo}_4\text{O}_{11}$  in a similar manner. For the former he found good evidence for mixed valence; for the latter, which belongs to the same structural family as  $\text{P}_2\text{W}_4\text{O}_{16}$ , Mo(V) and Mo(VI) were indicated, although the accuracy with which these structures are known is not very great.

A mixed-valence compound whose structure has been well defined is  $\text{TeMo}_5\text{O}_{16}$  (40). We have analyzed this structure using the recommended (1, 10) value of  $n = 6.0$  and determine  $R_0 = 1.879 \text{ \AA}$  (to make the average oxidation state equal to 5.6). We then calculate the individual oxidation

states of Mo(1)–Mo(5) to be 5.90, 5.60, 5.51, 5.39, and 5.60 respectively, suggesting that here also the  $d$  electrons are delocalized [i.e., there is no Mo(V)].

Thus it may be concluded that in most of the mixed-valence oxides of tungsten and molybdenum the electrons are delocalized, rather than there being well-defined  $M(\text{V})$ , in agreement with the interpretation of both electrical and magnetic measurements (9). Even in  $\text{P}_2\text{W}_4\text{O}_{16}$  where the structure suggests that there may be W(V) and W(VI), the physical properties again suggest delocalized  $d$  electrons (41). It may be here that there is still some degree of localization such that different oxidation states can be observed in the structure. Certainly the apparent oxidation states of the different atoms in a given structure are not identical, suggesting in turn that the  $d$  electron density is not uniform, but greater at some sites than others—this may explain the XPS results.

The origin of this ambiguity concerning electron localization may be found by examining the order of magnitude of the mobility deduced from the measured conductivities which are about  $10^5 \text{ S m}^{-1}$  in every case (6, 9, 41). The carrier concentration, either measured (6), or deduced from the formal concentration of W(V) is likewise reasonably constant and about  $10^{28} \text{ m}^{-3}$ . The mobility is then calculated to be about  $6 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ . This value is both too small to be unambiguously attributed to band conduction and rather larger for it to be normally associated with hopping conduction (42).

### Oxidation States and Local Geometry

It is a striking feature of the crystal chemistry of the oxides of tungsten in particular (and of the early transition metals in general) that bond lengths in octahedral coordination are unequal. This variability of bond length is, of course, accompanied by a flexi-

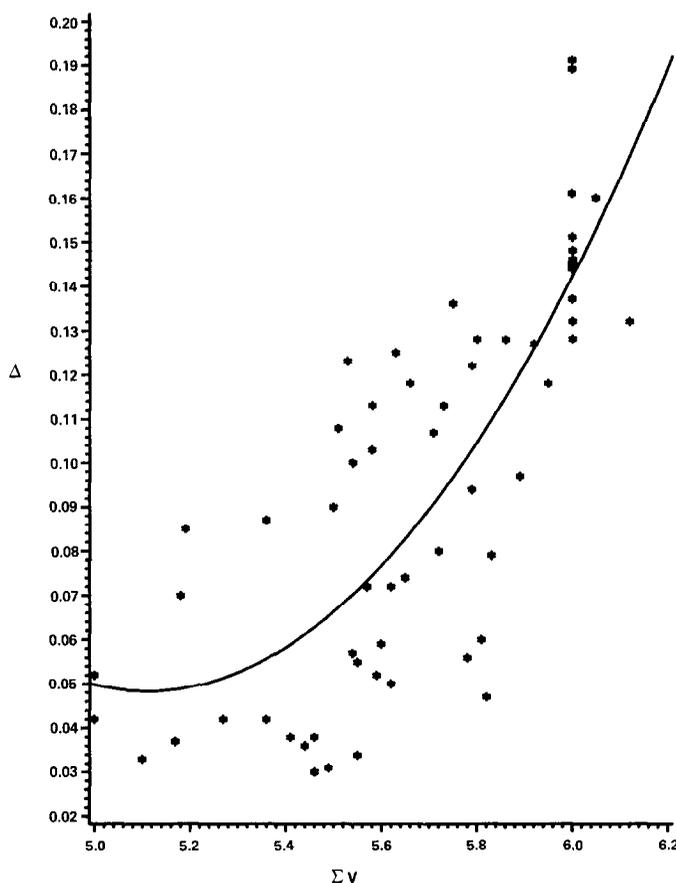


FIG. 1. The distortion  $\Delta = \langle |R - \langle R \rangle| \rangle$  of  $W_6$  polyhedra as a function of apparent oxidation state  $v$  of the tungsten atoms.

bility of bond strength; this in turn allows the formation of a great number of compounds (including "shear structures") that might not be expected on the basis of Pauling's electrostatic valence sum rule (43). It is of considerable interest to see if this phenomenon correlates in any way with oxidation state. Accordingly we have calculated, as a measure of distortion, the mean absolute deviation of the bond lengths of each polyhedron  $\langle |R - \langle R \rangle| \rangle$ . This has then been plotted in Fig. 1 as a function of oxidation state for 58 polyhedra. The two "bad" W atoms in  $W_{18}O_{49}$  and the data for  $K_{0.37}WO_3$ —which has unusually regular polyhedra—were omitted. Although there

is considerable scatter in the data, a definite trend of increasing distortion with increasing oxidation state is established. The curve shown in the figure is a quadratic regression for which the squared correlation coefficient is  $r^2 = 0.62$ . However, no special significance is attached to this curve other than as a guide to the eye.

Most of the compounds studied were the various phosphate tungsten bronzes. In these compounds,  $WO_6$  octahedra share corners with either three, two, one, or no  $PO_4$  tetrahedra. It is of interest to see whether this feature also correlates with oxidation state. Pauling's rule predicts that corner-sharing between  $WO_6$  octahedra and

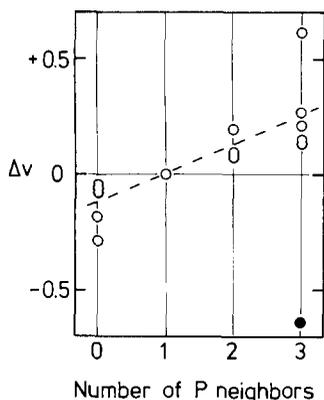


FIG. 2. The difference  $\Delta v$  between the valence of tungsten atoms in  $\text{WO}_6$  octahedra having various numbers of neighboring phosphate groups and the valence of tungsten atoms in octahedra having just one such neighbor in phosphate tungsten bronzes. The filled circle is the point for  $\text{P}_2\text{W}_4\text{O}_{16}$ .

$\text{PO}_4$  tetrahedra would be favored for W(V) (in which case  $\Sigma v$  at oxygen is 2.08) rather than for W(VI) (with  $\Sigma v = 2.25$ ). However, if we adopt the Zachariassen (44) point of view, it can be seen that at an oxygen atom bridging P and W, the P–O bond strength of  $5/4$  would require a W–O bond strength of  $3/4$ . In order to make the total bond-strength sum at W equal to its valence, some of the other W–O bonds must be correspondingly stronger (shorter). In other words  $\text{WO}_6$  octahedra that share corners with  $\text{PO}_4$  tetrahedra will of necessity be distorted. In the light of the results of the last paragraph, these octahedra will contain W in a higher oxidation state as it is these that are the more prone to distortion. That this is the case is shown in Fig. 2 where we have plotted the *relative* oxidation state of the tungsten atoms as a function of the number of phosphorus neighbors. For each compound what is plotted is the difference in the mean oxidation state of atoms with a given number of phosphorus neighbors and the mean oxidation state of those atoms with just one phosphorus neighbor. This procedure was adopted because the overall

oxidation state varies considerably for the various phosphate tungsten bronzes.

Reference to Fig. 2 and Table II shows that  $\text{P}_2\text{W}_4\text{O}_{16}$  is exceptional. W(1), which has an apparent valence of 5.82, has one P neighbor; W(2), with a valence of 5.18, has three P neighbors. We have no explanation for this.

## Conclusions

We have shown that in mixed-valence tungsten (and molybdenum) oxides, bond-valence sums give results intermediate between 5 and 6. This is in accord with the results of physical measurements which indicate that the *d* electrons are largely delocalized in these materials. In the classification of Robin and Day (45), these are class IIIB materials.  $\text{P}_2\text{W}_4\text{O}_{16}$  and  $\text{P}_2\text{W}_3\text{O}_{13}$  are to some extent anomalous in that the valence at different sites are more different (indeed approach 5 and 6) so that these may be class II (small polaron) oxides, although the physical properties suggest otherwise.

In the tungsten oxides,  $\text{WO}_6$  octahedra always show a broad range of bond lengths, and hence bond strengths, the effect being more pronounced for higher oxidation states. This adaptability of metal–oxygen bonds permits the formation of a wide range of bronzes and related compounds by tungsten (and other early-transition metals).

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