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Reinvestigation of the molecular structure of gaseous tetrabromooxotungsten(VI), WOBr_4 , by electron diffraction

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bonding MO ($13e'$) (a part from the smaller contributions from the inner t_{2g} -like MOs) is active in the present case, at variance with the isoelectronic cobalt cluster (μ_3 -CY)[Co(CO) $_3$] $_3$.⁴ However, we must remember that the overall cluster stability is ensured by the cluster-C_{apical} interactions.

The agreement between experimental and theoretical IEs is very good, in terms of both absolute and relative energies. We propose to assign band A to the ionizations from $9e''$ (HOMO), $13e'$, and $10a''$ MOs. Band B, showing a smaller relative intensity with respect to band A, is related to the ionization from $12e'$ and $14a'$ MOs. Shoulder S on its higher IE side is associated with the $13a'$ ionization event. Finally, band C is assigned to the ionization from two doubly degenerate MOs ($11e'$ and $8e''$). The stabilization of these two MOs with respect to the other t_{2g} -like MOs is certainly due to bonding interactions with e' and e'' MOs of II, as already proposed for the (μ_3 -CY)[Co(CO) $_3$] $_3$ series.^{2c,4}

Such an assignment is consistent also with the spectral pattern obtained by using the more energetic He II radiation.¹⁶ Actually all the ionizations present in the region below 11 eV come from MOs significantly localized on the metal atoms so that only minor and undetectable variations could be expected on passing from the He I to the He II ionization source.¹⁷

Finally, the present bonding picture suggests that the electronegativity of the apical substituent is of relevance for the stability of the cluster. Actually, the significant localization of the HOMO on the apical substituents (see Table I and Figure 3a) shows that a strong electron-withdrawing substituent (as fluorine) removes charge density from an antibonding Fe-Fe region, enhancing at the same time the cluster-C_{apical} interaction.

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Registry No. (μ_3 -CF) $_2$ [Fe(CO) $_3$] $_3$, 94621-00-8.

- (16) The low-IE region (6.5–8.0 eV) of the He II spectrum suffers from high noise and low resolution because of the photoelectrons originated from the orbitals at ~ 15 eV by operation of a small amount of the He II β radiation (48.40 eV).
 (17) In fact, on the basis of the Gelius model,¹⁸ we expect a marked decrease in the cross-section ratio $\sigma(C_{2p})/\sigma(Fe_{3d})$ on passing from the He I to the He II ionization source.
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Reinvestigation of the Molecular Structure of Gaseous Tetrabromooxotungsten(VI), WOBr $_4$, by Electron Diffraction

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The P=O and P=S bond lengths in the phosphoryl and thiophosphoryl halides, PYX $_3$, have been found to be significantly shorter in the fluorides^{3,4} than in the chlorides^{3,4} or bromides.⁵ As is seen from Table I, a similar situation is found in the oxo

Table I. Bond Lengths (r_a) and Bond Angles in Tungsten Tetrahalides

	$r(W=Y)/$ Å	$r(W-X)/$ Å	$\angle(Y=W-X)/$ deg	ref
WO F_4	1.666 (7)	1.847 (2)	104.8 (6)	6
WO Cl_4	1.684 (11)	2.280 (3)	102.4 (13)	7a
	1.683 (15)	2.279 (3)	102.6 (15)	7b
WO Br_4	1.684 (6)	2.437 (3)	102.8 (11)	this work
WS F_4	2.104 (7)	1.847 (3)	104.5 (11)	9
WSe Cl_4	2.086 (6)	2.277 (3)	104.2 (5)	11
WSe F_4	2.226 (7)	1.853 (5)	105.0 (7)	10
WSe Cl_4	2.203 (4)	2.284 (3)	104.4 (3)	11

tetrahalides of tungsten,⁶⁻⁸ WO X_4 , where the W=O bonds are shortest in the tetrafluoride.⁶ However, in the corresponding sulfo and seleno tetrafluorides^{9,10} and tetrachlorides¹¹ the W=S and W=Se bonds are longer in the fluorides.

One of the unsettled matters in these bond length comparisons is the position of the bromine-containing compounds in the phosphorus and tungsten series. For example, in the phosphoryl compounds the P=O bond length (r_g) in the chloride, 1.449 (5) Å,¹ is the same as that in the bromide, 1.445 (7) Å,⁵ to within the uncertainties of the measurements, and in the sulfonyl compounds the difference between the lengths of the S=O bonds in the bromide (1.894 (4) Å⁵) and in the chloride (1.885 (5) Å⁵) is of marginal significance. In tetrabromooxotungsten(VI) the W=O bond length at 1.695 (25) Å⁸ appears not to be significantly different from that in the chloride (1.684 (11) Å,^{7a} 1.683 (15) Å^{7b}), but the large uncertainties associated with the measurements cloud the issue. Our special interest in compounds of this type has led us to reinvestigate the structure of WOBr $_4$ in an attempt to improve the precision of the measurement of the W=O bond distance and thereby to settle the question of any difference between it and the corresponding distance in the chlorine compound.

Experimental Section

Tungsten(VI) bromide was made by allowing W(CO) $_6$ to react at 0 °C with an excess of dry bromine in an all-glass vacuum line. The mixture was kept at 0 °C and the excess bromine pumped away. The results of tungsten and bromine analyses of the product agreed with theory for WBr $_6$. A sample of WBr $_6$ was placed in an evacuated tube, and a quantity of resublimed Sb $_2$ O $_3$ sufficient to give a W:Sb molar ratio of 3:2 was added under dry nitrogen. The resulting mixture was pumped while being maintained at 0 °C for 3 h, after which the tube was sealed and placed in a furnace at 180 °C, where it remained for 2 days. The tube was opened under an inert atmosphere, and the contents were sublimed twice with use of evacuated sublimation tubes. The first sublimation removed SbBr $_3$ to give the desired WOBr $_4$. The second (resublimation) led to a purified, air-sensitive product that had tungsten and bromine analyses in accord with theory for WOBr $_4$. Small quantities of WOBr $_4$ were loaded under an inert atmosphere into glass ampoules fitted with break-seals. The ampoules were evacuated and sealed. For a diffraction experiment an ampoule was connected via glass tubing and a Swagelok coupling to the apparatus. The whole of the tubing between the break-seal and the apparatus was heated to approximately 250 °C under evacuated conditions for 1.5 h before the break-seal was opened. At the end of the experiment there was no evidence for the formation of any tungsten blue that would have indicated product decomposition or reaction.

The electron-diffraction photographs were made in the Oregon State apparatus at nozzle temperatures of 295–305 °C. Other experimental conditions as well as the various analytical procedures were similar to those described for WSF $_4$.⁶ Data from two plates at the long camera (75

- (1) (a) Reading University. (b) Oregon State University.
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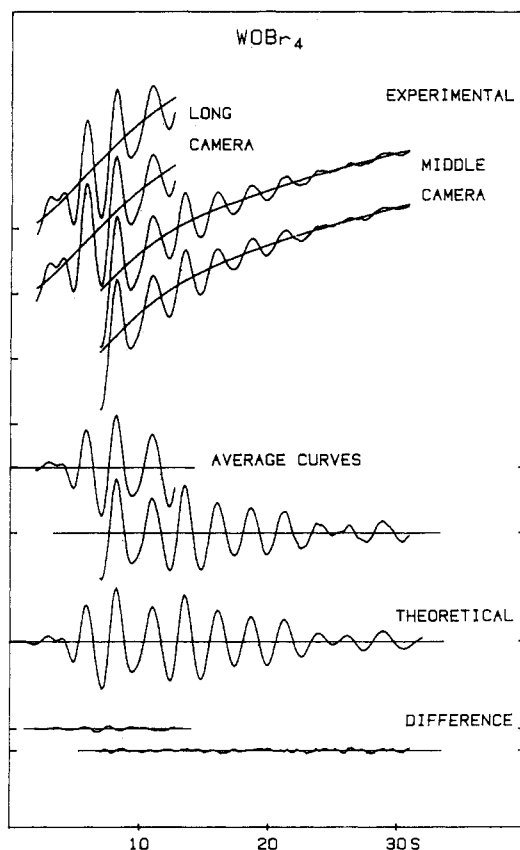


Figure 1. Intensity curves. The $s^4 I_i(s)$ curves from each plate are shown superimposed on the final backgrounds and are magnified 7 times relative to the backgrounds. The average curves are the molecular intensities $s I_m(s)$. The theoretical curve is for our model of Table II. Difference curves are experimental minus theoretical.

Table II. Distances (r), Angles (\angle), and Rms Amplitudes of Vibration for WOBBr_4

parameter	this work		ref 8	
	r_a, \angle	l	r_a, \angle	l
$\text{W}=\text{O}/\text{\AA}$	1.684 (6)	0.039 (5)	1.693 (24)	0.048 (25)
$\text{W}-\text{Br}/\text{\AA}$	2.437 (3)	0.074 (4)	2.452 (4)	0.092 (8)
$\text{O}=\text{W}-\text{Br}/\text{deg}$	102.8 (11)		103.0 (2)	
$\text{Br}-\text{W}-\text{Br}/\text{deg}$	87.2 (5)		87.4 (1)	
$\text{O}-\text{Br}/\text{\AA}$	3.255 (24)	0.137 (34)	3.267 (24)	0.115 (40)
$\text{Br}-\text{Br}/\text{\AA}$	3.361 (14)	0.144 (8)	3.382 (22)	0.125 (42)
$\text{Br}\cdots\text{Br}/\text{\AA}$	4.754 (20)	0.148 (15)	4.780 (4)	0.143 (38)

^a The r_g distances in the original article have been converted to r_a by use of $r_a = r_g - l^2/r$.

cm) and two at the intermediate (30 cm) covered the ranges $2.00 \leq s \leq 12.75 \text{ \AA}^{-1}$ and $7.00 \leq s \leq 31.00 \text{ \AA}^{-1}$, respectively, at intervals $\Delta s = 0.25 \text{ \AA}^{-1}$. Curves of the reduced total intensity data ($s^4 I_i(s)$) are shown in Figure 1. These data and those corresponding to the averaged molecular intensities ($s I_m(s)$) are available as supplementary material.

Radial distribution curves were consistent with a molecule of C_{4v} symmetry with an $\text{O}=\text{W}-\text{Br}$ bond angle of about 103° ; the final curve calculated with the convergence factor $\exp[-0.0025s^2]$ is seen in Figure 2. Parameters for the least-squares refinements were chosen to be the two bond lengths, the $\text{O}=\text{W}-\text{Br}$ bond angle, and the root-mean-square amplitudes of vibration corresponding to the five interatomic distances. The model was defined in terms of the r_a type of distance with the assumption that the effect on them of vibrational averaging would be negligible. The refinements converged quickly to the results given in the second column of Table II. The correlation matrix (available in the supplementary material) for the parameters of this model has only one element larger than 0.25—that for $\angle \text{O}=\text{W}-\text{Br}/l(\text{O}-\text{Br})$ equal to 0.83.

Discussion

In addition to the results from our present work, Table II contains results from the earlier electron-diffraction investigation

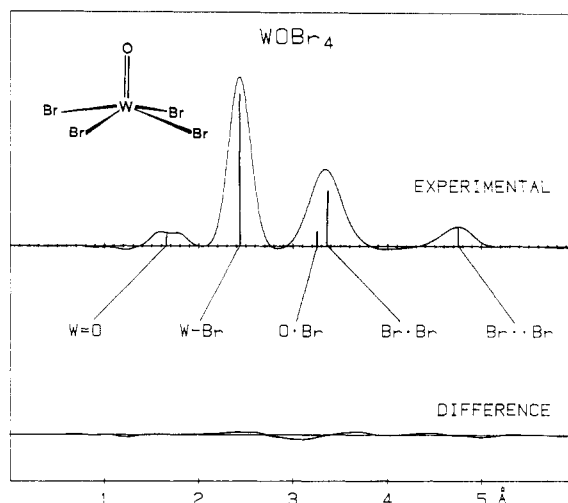


Figure 2. Experimental radial distribution curve. The lines denoting the interatomic distances have lengths proportional to the weights of the terms. The difference curve is experimental minus theoretical. The convergence coefficient B was given the value 0.0025 \AA^2 .

of WOBBr_4 .⁸ The agreement between the present and earlier work is not entirely satisfactory. At first glance, the results appear to differ mainly in the $\text{W}-\text{Br}$ bond lengths, which have values differing by more than the sum of the attached uncertainties. Closer examination reveals that all of our measurements are slightly smaller (although within the range defined by the uncertainty sum) than those from the other study and suggests the problem is really one of overall molecular size. Confirmation of the idea is found in the very good agreement between the two sets of bond angle values. The magnitude of the scale differential is about 0.5% and is rather more than would be expected. Although we have no proof that our scale is the more accurate, we believe it to be likely because our results are based on roughly twice as much intensity data that extend to a higher scattering angle ($s = 31.0 \text{ \AA}^{-1}$ vs. $s = 25.2 \text{ \AA}^{-1}$) than do those of the other investigators. An error in our electron wavelength, which could account for the scale difference, seems to be ruled out: Our wavelength (calibrated with CO_2 in separate experiments) is closely similar to others done about the same time.

Apart from the scale problem, there is no doubt that in the tungsten oxo tetrahalides the $\text{W}=\text{O}$ bond is shortened by a greater amount from replacement of the chlorine atoms by fluorines than by replacement of bromines by chlorines. A similar statement applies to the phosphoryl halides and, with a bit less certainty, to the thiophosphoryl halides. Interestingly, the effect is not observed for the $\text{W}=\text{S}$ and $\text{W}=\text{Se}$ bonds in the compounds WYF_4 and WYCl_4 ($\text{Y} = \text{O}, \text{S}, \text{Se}$). These observations suggest that the properties of WOF_4 are special among the five-coordinate tungsten molecules, perhaps because all of the ligands are very electronegative. Steric effects appear to be similar for all the molecules: the geminal $\text{Y}\cdots\text{X}$ distances are uniformly about $0.2\text{--}0.3 \text{ \AA}$ less than the van der Waals radius sums, the geminal $\text{X}\cdots\text{X}$ distances are less by about $0.4\text{--}0.5 \text{ \AA}$, and the $\text{Y}=\text{W}-\text{X}$ bond angles all have values in the range $102\text{--}105^\circ$.

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Supplementary Material Available: Correlation matrix for the final model (Table III), total scattered intensities $s^4 I_i(s)$ from each plate (Table IV), calculated backgrounds for each plate (Table V), and averaged molecular intensities $s I_m(s)$ from each camera distance (Table VI) (8 pages). Ordering information is given on any current masthead page.