

## Gas-phase Electron Diffraction Study of Tetrafluoro(seleno)tungsten(vi), $WSeF_4$ \*

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The molecular structure of  $WSeF_4$  has been determined by gas-phase electron diffraction with a nozzle temperature of 130 °C. The experimental data are in agreement with a  $C_{4v}$  square-pyramidal model being present in the gas phase in which the tungsten atom is above the plane of the four fluorine atoms. The distances and angles are  $r_s(W=Se) = 2.226(7)$ ,  $r_s(W-F) = 1.853(5)$  Å,  $\angle Se-W-F = 105.0(7)$ ,  $\angle F-W-F = 86.1(4)^\circ$ . The errors are  $2\sigma$ , plus estimates of correlation in the experimental data and uncertainties in the electron wavelength.

There have been a number of gas-phase electron diffraction studies of Group 6A oxohalides of formula  $MOX_4$  ( $M = Mo$  or  $W$ ;  $X = F, Cl$ , or  $Br$ )<sup>1-5</sup> and all the data have been shown to be consistent with the molecular species having  $C_{4v}$  symmetry. The  $M-O$  distances were found to be shorter for the fluorides than for the bromides or chlorides of the same element and this was ascribed to the electronegativity of the fluorine atoms, causing a reduction (compared to that for the chloride or bromide) in the covalent radius of the metal atom, which in turn gives rise to a short metal-oxygen distance. For the tungsten species the  $O-W-F$  angle was found to be larger than  $O-W-Cl$ .

A similar situation was observed with the phosphorus compounds  $POCl_3$ <sup>6</sup> and  $POF_3$ .<sup>6</sup> Indeed, it was found to extend to the thio species  $PSF_3$ <sup>7</sup> and  $PSCl_3$ <sup>6</sup> with the shorter  $P-S$  distance and larger  $S-P-X$  angle being observed in the fluoride. There have only been three studies on thio- and seleno-halides of Group 6A [ $WSeCl_4$ ,<sup>8</sup>  $WSeCl_4$ ,<sup>8</sup> and  $WSF_4$ ].<sup>9</sup> Comparison of the two  $W-S$  distances reveals that, in contrast to the situation with the oxohalides, the shorter  $W-S$  distance is found with the chloride while the  $S-W-F$  angle in  $WSF_4$  is equivalent to  $W-O-F$  in  $WOF_4$ .

In view of these somewhat surprising results it was decided to investigate the structure of  $WSeF_4$  by gas-phase electron diffraction and the results of the study are now reported.

### Experimental

The sample of  $WSeF_4$  was prepared by allowing stoichiometric amounts of tungsten(vi) fluoride and antimony(III) selenide to react at 350 °C for 6 h in a stainless-steel reactor.<sup>10</sup> The purity of the product was determined by X-ray powder diffraction and i.r. spectroscopy. Small quantities of amber crystals of pure material, obtained by sublimation at 120 °C, were introduced into Pyrex glass ampoules. Electron diffraction photographs were obtained using the Balzers' Eldigraph KDG-2 at the University of Oslo and the data were handled as previously described.<sup>11</sup>

Data were obtained at nozzle-to-plate distances of 50.012 and

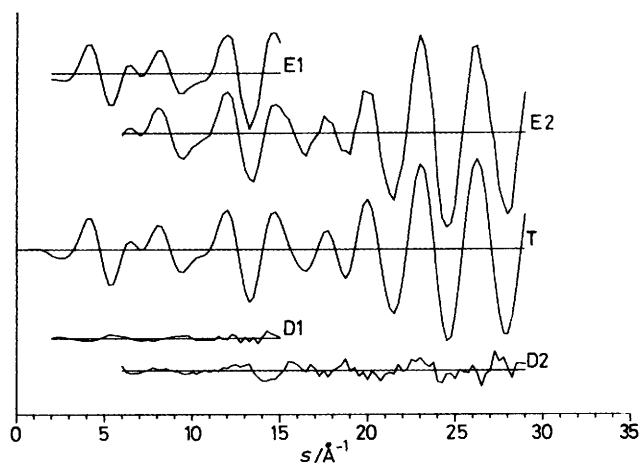


Figure 1. Intensity curves  $sI_m(s)$  for  $WSeF_4$ . Experimental curves (E1, E2) are averages of all plates for the two camera distances. Theoretical curve (T) was calculated from the structural parameters in Table 1. Difference curves (D1, D2) are  $E - T$ .

25.012 cm and at a nozzle temperature of 130 °C. The electron wavelength (0.05876 Å) was calibrated against benzene.<sup>12</sup> Three plates from the short camera distance and three from the long camera distance that were suitable for densitometry were obtained. Data from the long and short camera distances were obtained over the  $s$  ranges of 2.00–15.00 and 6.00–29.00 Å<sup>-1</sup> respectively, at intervals of 0.25s (where  $s = 4\pi\lambda^{-1} \sin\theta$  and  $2\theta$  is the scattering angle). The averages of the molecular intensities are shown in Figure 1 and the data for the total intensity and the background curves are available as SUP No. 56556.

The radial distribution curve was calculated<sup>11</sup> and the resulting curve is depicted in Figure 2.

A model with  $C_{4v}$  symmetry was found to be consistent with the experimental data. In such a model there are five types of interatomic distance [ $r(W=Se)$ ,  $r(W-F)$ ,  $r(F \cdots Se)$ ,  $r(F \cdots F)$  (*cis*), and  $r(F \cdots F)$  (*trans*)] and these can all be defined by three parameters, namely,  $r(W=Se)$ ,  $r(W-F)$ , and the  $Se-W-F$  angle.

The differences between the theoretical and experimental radial distribution curves can be seen to be small (see Figure 2),

\* Supplementary data available (No. SUP 56556, 5 pp.): total scattered intensities for each of six plates, calculated background curves. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx.

**Table 1.** Structural results<sup>a</sup> for WSeF<sub>4</sub> and some similar molecules

	WSeF <sub>4</sub> <sup>b</sup>	WSF <sub>4</sub> <sup>c</sup>	WOF <sub>4</sub> <sup>d</sup>	WSeCl <sub>4</sub> <sup>e</sup>	WSeCl <sub>4</sub> <sup>e</sup>
<i>r</i> (W=Se)	2.226(7)	2.104(7)	1.666(7)	2.086(6)	2.203(4)
<i>r</i> (W-X)	1.853(5)	1.847(3)	1.847(2)	2.277(3)	2.284(3)
<i>r</i> (Y...X)	3.239(11)	3.128(22)	2.786(12)	3.445(12)	3.545(9)
<i>r</i> (X...X)( <i>cis</i> )	2.526(10)	2.528(13)	2.525(8)	3.121(8)	3.129(6)
<i>r</i> (X...X)( <i>trans</i> )	3.572(11)	3.575(18)	3.570(11)	4.414(11)	4.425(9)
<i>l</i> (W=Se)	0.050(8)	0.033 <sup>f</sup>	0.036 <sup>f</sup>	0.031(6)	0.055(4)
<i>l</i> (W-X)	0.037(6)	0.055(4)	0.041(4)	0.058(4)	0.060(3)
<i>l</i> (Y...X)	0.109(9)	0.121(19)	0.097(17)	0.147(17)	0.147(9)
<i>l</i> (X...X)( <i>cis</i> )	0.107(24)	0.107(20)	0.094(14)	0.114(10)	0.116(8)
<i>l</i> (X...X)( <i>trans</i> )	0.064(27)	0.091(45)	0.083(29)	0.120(25)	0.116(19)
Y-W-X	105.0(7)	104.5(11)	104.5(6)	104.2(5)	104.4(3)
X-W-X	86.1(4)	86.5(5)	86.2(3)	86.5(2)	86.5(2)

<sup>a</sup> Distances (*r*<sub>a</sub>) and amplitudes (*l*) are in Å; angles in degrees. Parenthesized values are 2σ, plus estimates for the uncertainties in electron wavelength etc. and correlation of the data. X = F or Cl, Y = Se, S, or O. <sup>b</sup> This study. <sup>c</sup> Ref. 9. <sup>d</sup> Ref. 3 with error 2σ. <sup>e</sup> Ref. 8. <sup>f</sup> Constrained.

**Table 2.** Correlation matrix (× 100) for WSeF<sub>4</sub>

	σ*	<i>r</i> <sub>1</sub>	<i>r</i> <sub>2</sub>	Se-W-F	<i>l</i> <sub>1</sub>	<i>l</i> <sub>2</sub>	<i>l</i> <sub>3</sub>	<i>l</i> <sub>4</sub>	<i>l</i> <sub>5</sub>
<i>r</i> (W=Se)	0.16	100	-12	-35	-27	-14	-4	-30	-2
<i>r</i> (W-F)	0.08		100	5	7	11	11	4	6
Se-W-F	22.9			100	4	13	-14	0	-23
<i>l</i> (W=Se)	0.26				100	41	29	13	1
<i>l</i> (W-F)	0.15					100	30	-9	4
<i>l</i> (Se...F)	0.47						100	10	19
<i>l</i> (F...F)	0.79							100	3
( <i>cis</i> )									100
<i>l</i> (F...F)	1.33								
( <i>trans</i> )									

\* Standard deviations (× 100) from least squares. Distances and amplitudes are in Å and angles in degrees.

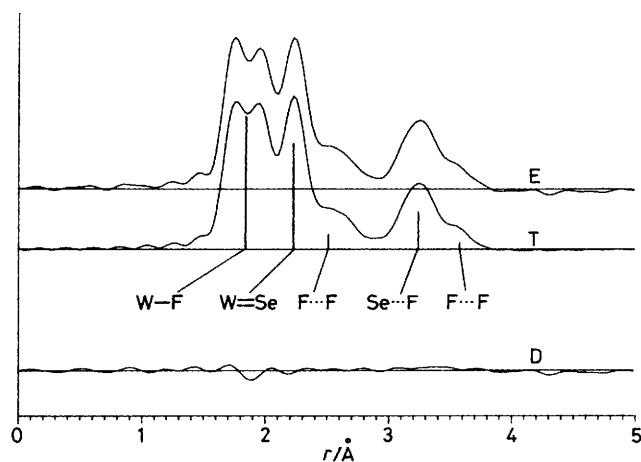
the major discrepancy being in the W-F region. Part of this error may come from three-atom scattering or errors in the phase shift factors. The molecular parameters are given in Table 1 and the correlation matrix in Table 2.

## Results and Discussion

The data obtained for WSeF<sub>4</sub> are consistent with a model of C<sub>4v</sub> symmetry being present in the gas phase. Refinements of models with either C<sub>3v</sub> or C<sub>2v</sub> symmetry were unsatisfactory. Although the crystal structure of WSF<sub>4</sub> has been determined<sup>13</sup> and WSeF<sub>4</sub> in the solid state is known to be isostructural,<sup>10</sup> attempts to obtain the crystal structure of WSeF<sub>4</sub> have so far proved abortive and so the data presented here (Table 1) are the only definitive structural information on this ternary compound. Also given in Table 1 are data for related studies and these enable a ready comparison of the similarities and differences between WSeF<sub>4</sub>, WSeCl<sub>4</sub>,<sup>8</sup> WSeCl<sub>4</sub>,<sup>8</sup> WOF<sub>4</sub>,<sup>3</sup> and WSF<sub>4</sub>.<sup>9</sup>

The W=Se distance in WSeF<sub>4</sub> [2.226(7) Å] is longer than the comparable distance in WSeCl<sub>4</sub> [2.203(4) Å].<sup>8</sup> A similar difference is found in the tungsten-sulphur distances in WSF<sub>4</sub> [2.104(7) Å]<sup>9</sup> and WSeCl<sub>4</sub> [2.086(6) Å].<sup>8</sup> The W-F distances in WSeF<sub>4</sub>, WSF<sub>4</sub>, and WOF<sub>4</sub> are all equivalent and longer than those observed in WF<sub>6</sub> [1.833(8),<sup>14</sup> 1.831(30) Å<sup>15</sup>].

An explanation for the longer W=Se bond in the fluoride than the chloride cannot lie in simple electronegativity arguments as these would predict the reverse situation. However a number of alternatives to electronegativity arguments can be suggested, two of which are (i) the influence of *p*<sub>π</sub>-*d*<sub>π</sub> bonding and (ii) the effect of repulsions between non-bonded atoms. The influence



**Figure 2.** Radial distribution curves for WSeF<sub>4</sub> showing experimental (E), theoretical (T), and difference (D) curves. The curves were calculated from the curves of Figure 1 after multiplication by  $Z_W Z_F / f_W f_F \exp(-0.0025s^2)$  and using theoretical data for the unobserved area  $s < 2.0 \text{ \AA}^{-1}$ . The vertical lines indicate the position of the interatomic distances, height being proportional to weight of distance

of *p*<sub>π</sub>-*d*<sub>π</sub> bonding arises from a consideration of the effect of the lone pairs of the halogen atoms in WSeF<sub>4</sub> and WSeCl<sub>4</sub>. The lone pairs on fluorine are more likely than those on chlorine to impart some partial multiple bonding to the tungsten-halogen bond (as suggested to be the case in BF<sub>3</sub>) thus causing a build up of electron density on the tungsten atom. Additionally, on going from the WCl<sub>4</sub> moiety to WF<sub>4</sub>, a reduction in the size of the tungsten *d* orbitals that take part in (*p*-*d*)π bonding to selenium may take place thus leading to less efficient overlap. Both effects would cause a weakening and lengthening of the W=Se bond.

In a consideration of the influence of repulsions between non-bonded atoms the important interaction is that between the fluorine and the selenium atoms. The observed Se...F distance [3.239(11) Å] is smaller than the sum of the relevant van der Waals radii (3.35 Å)<sup>16</sup> and, if the W=Se distance were reduced to that observed in WSeCl<sub>4</sub>, the Se...F distance would become even smaller thus causing an even greater Se...F repulsion. With WOF<sub>4</sub> the situation is different as the O...F distance [2.786(12) Å]<sup>3</sup> is longer than the sum of the van der Waals radii (2.75 Å).<sup>16</sup> Noticeably, the geometry of the WF<sub>4</sub> moiety is the same in WOF<sub>4</sub>,<sup>3</sup> WSF<sub>4</sub>,<sup>9</sup> and WSeF<sub>4</sub> with the F...F(*cis*)

distances [2.525(8),<sup>3</sup> 2.528(13),<sup>9</sup> and 2.526(10) Å respectively] being substantially less than twice the van der Waals radius of fluorine (2.70 Å).<sup>16</sup> Therefore, it is unlikely that the increase in strain upon going from WOF<sub>4</sub> to WSeF<sub>4</sub> would be reduced by an increase in the Se...F distance facilitated by a further compression of the F...F(*cis*) distances and consequent increase of the Se-W-F angle.

The effect of interactions between non-bonded atoms is different in the three chloro-species WOCl<sub>4</sub>,<sup>4</sup> WSeCl<sub>4</sub>,<sup>8</sup> and WSeCl<sub>4</sub>.<sup>8</sup> The geometry of the WCl<sub>4</sub> moiety is not the same in all three compounds. The length of the tungsten-chlorine bonds [2.280(3) (WOCl<sub>4</sub>), 2.277(3) (WSeCl<sub>4</sub>), and 2.284(3) Å (WSeCl<sub>4</sub>)] is constant but the Cl-W-Cl angle is larger for WOCl<sub>4</sub> [87.3(5)°] than for WSeCl<sub>4</sub> or WSeCl<sub>4</sub> [86.5(2)°]. Considering the Y...Cl distance [Y = O, S, or Se] the value for Y = O [3.117(35) Å]<sup>4</sup> is smaller than, but close to, the sum of the van der Waals radii (3.20 Å)<sup>16</sup> while for Y = S [3.445(12) Å]<sup>8</sup> and Y = Se [3.545(9) Å]<sup>8</sup> the values are much smaller than sums of the van der Waals radii which are respectively 3.65 and 3.80 Å.<sup>16</sup> Thus on going from WOCl<sub>4</sub> to WSeCl<sub>4</sub> or WSeCl<sub>4</sub>, it can be envisaged that an increase in the Y-W-Cl angle takes place from 102.4(13) [Y = O]<sup>4</sup> to 104.2(5) [Y = S]<sup>8</sup> or 104.4(3)° [Y = Se]<sup>8</sup> to accommodate some of the increase in Y...Cl repulsions. Naturally, these latter changes cause a noticeable difference in the Cl...Cl(*cis*) distances [3.146(15) (WOCl<sub>4</sub>), 3.121(8) (WSeCl<sub>4</sub>), and 3.129(6) Å (WSeCl<sub>4</sub>)]. Twice the value of the chlorine van der Waals radius is 3.60 Å<sup>16</sup> and so in all three compounds the difference between the Cl...Cl(*cis*) distance and twice the chlorine covalent radii is much greater than the comparable difference in the fluoro-compounds thus confirming that it is easier to compress covalently-bound chlorine atoms than fluorine atoms.

### Conclusions

The results of the study presented here indicate that, while electronegativity considerations can be used to rationalise

trends in the bond lengths and angles for main group chalcogenide halides, for the chalcogenide halides of molybdenum and tungsten other factors, and in particular  $\pi$  bonding and repulsions between non-bonded atoms, have to be considered.

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