Cu–Cl distance in Cu(DAPDH$_2$)Cl$_2$ and the Zn–Cl distances in Zn(DAPDH$_2$)Cl$_2$, which differ by ca. 0.02 Å. For the M–N distances a substantially different situation exists. The Zn–N(py) and Zn–N(oxime) bond distances in Zn(DAPDH$_2$)Cl$_2$ are ca. 0.13 and 0.20 Å longer than their respective Cu–N bond distances in Cu(DAPDH$_2$)Cl$_2$. These unusually long Zn–N bond distances strongly suggest that the angular overlap between the available metal orbitals and the oxime's N donor orbitals is relatively poor in this five-coordinate Zn complex. This remark indicates that it may be possible to enhance the Zn–N bonding interaction by using a tridentate ligand such as (H$_2$NCH$_2$CH$_2$)$_2$NH, which possesses a more flexible chelate backbone than DAPDH$_2$.

The molecular configuration associated with these five-coordinate complexes appears to have a noticeable influence upon the planarity of the coordinated dioxime ligand as well. In both Cu(DAPDH$_2$)Cl$_2$ and [Cu(DAPDH)]$_2^{2+}$ the dioxime ligand is not strictly planar. All of the nonhydrogen atoms of the tridentate ligand are displaced below the plane defined by the three N donor atoms and away from the copper atom which lies 0.289 (1) and ca. 0.19 (1) Å above this plane in Cu(DAPDH$_2$)Cl$_2$ and [Cu(DAPDH)]$_2^{2+}$, respectively. In contrast, for Zn(DAPDH$_2$)Cl$_2$ the corresponding deviations from planarity are significantly smaller and the Zn atom lies in the plane of the oxime ligand.

The bond distances and bond angles within the coordinated oxime ligands in Cu(DAPDH$_2$)Cl$_2$, Zn(DAPDH$_2$)Cl$_2$, and [Cu(DAPDH)]$_2^{2+}$ species are comparable in magnitude despite the observed differences in the mode of oxime coordination. The orbital hybridizations about the N donor atoms and the carbon atoms of the relatively rigid backbone of this chelate ligand are essentially sp^2. The average N–OH distance of 1.376 Å in Cu(DAPDH$_2$)Cl$_2$ and Zn(DAPDH$_2$)Cl$_2$ are comparable to that of 1.39 Å in [Cu(DAPDH)]$_2^{2+}$.[5] Deprotonation of the oxime, however, is accompanied by a significant reduction in the N–O bond distance. The average N–O bond distance is reduced from ca. 1.38 Å for DAPDH$_2$ in M(DAPDH$_2$)Cl$_2$ to ca. 1.33 Å for DAPDH$^-$ in [Cu(DAPDH)]$_2^{2+}$. For the doubly deprotonated DAPD^{2-} chelates of Ni(DAPD)$_2$,[29] a substantially shorter N–O distance of 1.257 (3) Å was determined.

Finally, the N(oxime)–M–N(py) bond angle for the five-membered rings of these dioxime complexes (Table V) is closely related to the magnitude of the M–N(py) bond. As the M–N(py) distance increases from 1.837 (4) Å for Ni(DAPD)$_2$[29] to 1.932 (3) Å for Cu(DAPDH$_2$)Cl$_2$ to 2.063 (2) Å for Zn(DAPDH$_2$)Cl$_2$, the corresponding inner "bite" angle decreases continually from 82.4 (1) to 77.6 (average) to 73.7° (average), respectively. In Ni(DAPD)$_2$ the higher oxidation state and smaller size of the Ni(IV) ion cause the chelating oxime groups to be pulled more strongly toward the nickel. This distortion of the DAPD^{2-} ligand is accompanied by a noticeable increase in the N(oxime)–M–N(py) bond angle. Conversely, the weaker metal–oxime interaction in Zn(DAPDH$_2$)Cl$_2$ is characterized by substantially longer M–N bond distances which distort the coordinated DAPDH$_2$ ligand in the opposite sense as reflected by a reduction of the average N(oxime)–M–N(py) bond angle.

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Registry No. Cu(DAPDH$_2$)Cl$_2$·2H$_2$O, 82310-79-0; Zn(DAPDH$_2$)Cl$_2$·H$_2$O, 82265-78-9.

Supplementary Material Available: Tables of refined thermal parameters, hydrogen-bond distances, specific least-squares planes, and observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Gas-Phase Electron-Diffraction Studies of the Molecular Structures of Tetrachlorosulfidotungsten(VI), WSCl$_4$, and Tetrachloroselenotungsten(VI), WSeCl$_4$

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The molecular structures of WSCl$_4$ and WSeCl$_4$ have been studied by gas-phase electron diffraction at average nozzle temperatures of 200 and 220 °C, respectively. The experimental data for both species are fitted by square-pyramidal models of C_{4v} symmetry in which the tungsten atom is slightly above the plane of the four chlorine atoms. The following principal distances (r_a), angles, and root-mean-square amplitudes of vibration (l) with estimated uncertainties of 2σ were obtained. WSCl$_4$: r(W═S) = 2.086 (6) Å, r(W—Cl) = 2.277 (3) Å, ∠SWCl = 104.2 (5)°, ∠ClWCl = 86.5 (2)°, l(W═S) = 0.031 (6) Å, l(W—Cl) = 0.058 (4) Å, l(S·Cl) = 0.147 (17) Å, l(Cl·Cl) = 0.114 (10) Å, l(Cl··Cl) = 0.120 (25) Å. WSeCl$_4$: r(W═Se) = 2.203 (4) Å, r(W—Cl) = 2.284 (3) Å, ∠SeWCl = 104.4 (3)°, ∠ClWCl = 86.5 (2)°, l(W═Se) = 0.055 (4) Å, l(W—Cl) = 0.060 (3)Å, l(Se·Cl) = 0.147 (9) Å, l(Cl·Cl) = 0.116 (8) Å, l(Cl··Cl) = 0.116 (19) Å. The similarities and differences of these structures, together with that of WOCl$_4$ available in the literature, are interpreted in terms of relative bond orders and nonbond repulsions.

Introduction

The molecular structures in the gas phase of a number of oxo halides of group 6B elements are known from electron-diffraction measurements. Nothing is known about the structures of the analogous sulfido and seleno halides, but it is reasonable to expect the molecules to have C_{4v} symmetry as do the oxygen compounds. Should this be the case, the structural differences resulting from substitution at the axial position in these compounds permit insights into the nature of the bonding operating in them. Accordingly we decided to investigate the structures of WSCl$_4$ and WSeCl$_4$ by electron diffraction. Structural data are already available for WOCl$_4$.[2]

There are apparently no measurements of the vibrational spectra of WSCl$_4$ or WSeCl$_4$ in the literature, but such data do exist for WOCl$_4$.[3,4] Other information includes X-ray

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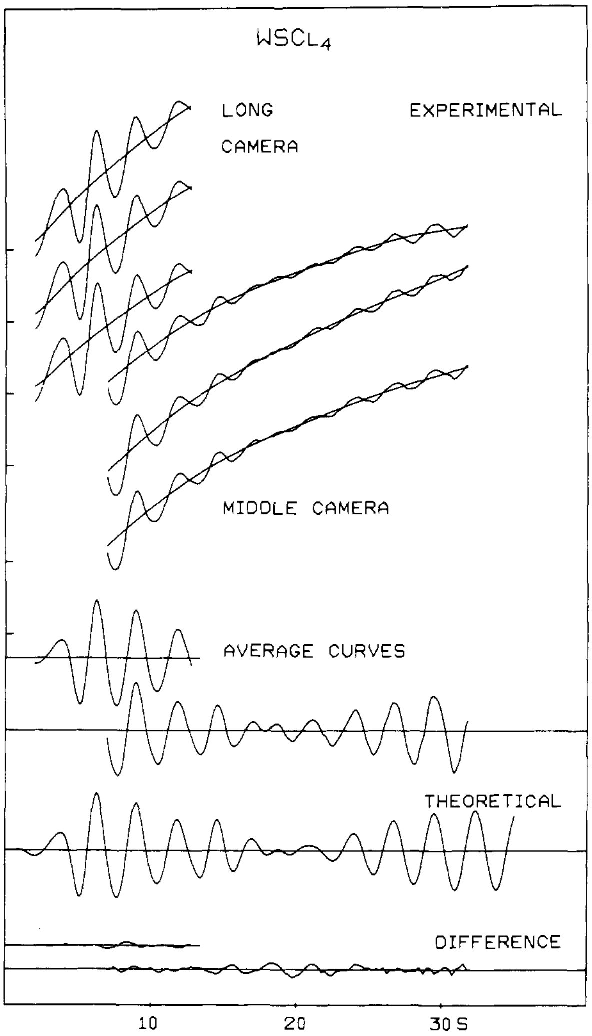

Figure 1. $WSCl_4$ intensity curves. The s^4I_t curves from each plate are shown superposed on the final backgrounds and are magnified 5 times relative to the backgrounds. The sI_m curves are averages from each camera distance. The theoretical curve is for the model of Table I. The differences are experimental minus theoretical.

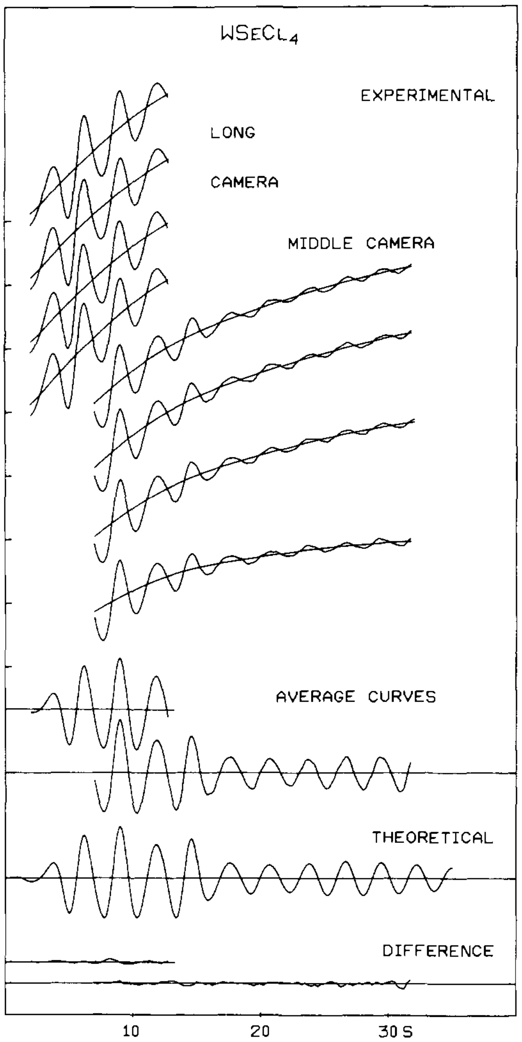

Figure 2. $WSeCl_4$ intensity curves (see legend to Figure 1).

diffraction analyses of the structures of $WOCl_4$[5] and $WSCl_4$[6] in the crystal. The structures are quite different: the former has W—O—W bridges and the latter W═S terminal bonds.

Experimental Section

The compounds $WSCl_4$ and $WSeCl_4$ readily react with oxygen, water, –OH groups on glass surfaces, etc. to yield, among other things, $WOCl_4$. Accordingly, the following preparative and handling techniques[7] were adopted. The WCl_6 needed for the preparation of $WSCl_4$ and $WSeCl_4$ was prepared by the chlorination of the metal (400 °C), and the product was resublimed under an atmosphere of dry chlorine. Analytical grade sulfur was recrystallized from dry toluene. Sb_2Se_3 was prepared from analytical grade samples of the elements. $WSCl_4$ was obtained by heating WCl_6 and sulfur (1:3 molar ratio, 120 °C) in a sealed tube. The product was resublimed under vacuum at 140 °C. $WSeCl_4$ was prepared by the reaction of WCl_6 and Sb_2Se_3 (3:1 molar ratio, 140 °C) in a sealed tube. The product was purified by vacuum sublimation at 150 °C.

Small quantities of the compounds were loaded into glass ampules fitted with a break-seal in a nitrogen-filled drybox. These ampules were evacuated (5×10^{-5} torr) and sealed. For a diffraction experiment an ampule was connected via glass tubing and Swagelok couplings to the apparatus. The whole of the tubing between the apparatus and the break-seal was wrapped with electrical heating tape and kept at approximately 250 °C for about 1.5 h while evacuated to 10^{-6} torr. (If this preheating step was omitted, there was evidence of impurity formation ($WOCl_4$?) in the tubing during the experiment.) The break-seal was then opened and the sample reservoir gradually heated until sufficient vapor for the diffraction experiments was obtained. The tubing connecting the sample reservoir and the apparatus was kept at a temperature between those of the reservoir and the nozzle tip. At the end of the experiment there was no visible sign of sample decomposition or reaction with the glass surfaces, as shown by the lack of "tungsten blue".

The electron-diffraction photographs were taken in the Oregon State apparatus with experimental conditions as follows: Kodak 8 in. × 10 in. projector slide plates (medium contrast), r^3 sector, nominal nozzle-to-plate distances 750 mm (long camera) and 300 mm (intermediate camera), electron wavelengths of about 0.057 Å accurately determined by voltage measurements calibrated against gaseous CO_2 (r_a(C═O) = 1.1646 Å and r_a(O···O) = 2.3244 Å), beam current range 0.34–0.50 μA, nozzle-tip temperature ranges 195–206 °C (sulfide) and 214–232 °C (selenide), pressure range in the apparatus (1–4) $\times 10^{-6}$ torr. The scattered intensity data were obtained from the plates ($WSCl_4$, three long and three intermediate camera distances; $WSeCl_4$, four long and four intermediate camera distances) as previosuly described.[8] Calculated backgrounds[9] containing contributions from theoretical elastic[10] and inelastic[11] atomic scattering were subtracted

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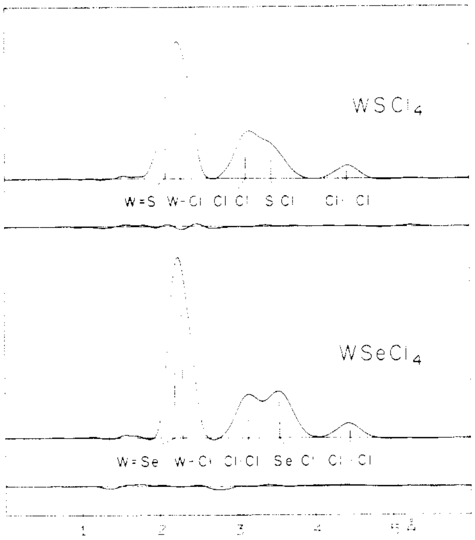

Figure 3. Experimental radial distribution curves. The vertical lines denote interatomic distances and have lengths proportional to $n_{ij}Z_iZ_j/r_{ij}$. The lower curve of each group is the radial distribution difference (experimental minus theoretical).

from the intensity data to yield the experimental molecular intensity distribution in the form $s(I_m(s))$[8] used for analysis at Oregon State.

Data from the long and intermediate camera distances were obtained over the ranges $2.00 \leq s \leq 12.75$ Å^{-1} and $7.00 \leq s \leq 31.75$ Å^{-1}, respectively, at intervals $\Delta s = 0.25$ Å^{-1} ($s = 4\pi\lambda^{-1} \sin \theta$; 2θ is the scattering angle). Curves of the reduced intensity data $[s^4(I_t(s))]$ are shown in Figures 1 and 2; the data themselves and the molecular intensity averages are available as supplementary material.

Radial distribution curves were calculated in the normal manner after multiplication of the $s(I_m(s))$ values by $(s^4 Z_W Z_{Cl}/f_W f_{Cl}) \cdot \exp(-0.0025s^2)$. These are shown in Figure 3. The curves are completely consistent with C_{4v} symmetry for the molecules, as was found for WOCl$_4$[2] and WOF$_4$;[12] accordingly, this symmetry was assumed in refinement of the structures.

Refinements of the structures were carried out by least squares,[13] adjusting theoretical $s(I_m(s))$ values calculated from models of the molecule to the averages of the several sets of observed data obtained at each camera distance. A diagonal weight matrix was used. Models of the molecules assuming C_{4v} symmetry have five different interatomic distances: r(W=Y) (Y = S or Se), r(W—Cl), r(Y·Cl), r(Cl·Cl), and r(Cl··Cl) (one and two dots indicate respectively the cis and trans interactions), which are specified by the three convenient parameters r(W=Y), r(W—Cl), and ∠YWCl. These parameters together with the five amplitudes of vibration corresponding to the five nonequivalent atomic pairs were taken to define the geometrical and dynamical aspects of the structure. "Shrinkage"[14] and anharmonicity effects were expected to be small and were ignored. In accordance with past experience, the phase factors η for osmium were used in place of those for tungsten for all terms involving the latter. The results of the refinements are given in Table I and the correlation matrices in Tables II and III. The theoretical intensity curves for the final models and the differences between these and the observed average curves are shown in Figures 1 and 2.

Discussion

The results of our investigation strongly suggest that the molecules of both WSCl$_4$ and WSeCl$_4$ have structures with C_{4v} symmetry in the gas phase, as was concluded in the cases of WOCl$_4$[2] and WOF$_4$.[12] Of course, we are unable to rule out small equilibrium deviations from this symmetry, but we can confidently exclude the presence of appreciable amounts of C_{3v} structures (i.e., those with a linear Cl-W-Y fragment) or C_{2v} structures (i.e., those with linear Cl-W-Cl and planar Y-W-Cl$_2$ moieties).

Table I. Structure Results for WOCl$_4$, WSCl$_4$, and WSeCl$_4$[a,b]

	WOCl$_4$[c]	WSCl$_4$[d]	WSeCl$_4$[d]
	Distances		
r(W=Y)	1.685 (15)	2.086 (6)	2.203 (4)
r(W-Cl)	2.280 (3)	2.277 (3)	2.284 (3)
r(Y·Cl)	3.117 (35)	3.445 (12)	3.545 (9)
r(Cl·Cl)	3.146 (15)	3.121 (8)	3.129 (6)
r(Cl··Cl)	4.449 (21)	4.414 (11)	4.425 (9)
	Amplitudes		
l(W=Y)	0.045 (11)	0.031 (6)	0.055 (4)
l(W-Cl)	0.052 (4)	0.058 (4)	0.060 (3)
l(Y·Cl)	0.095 (38)	0.147 (17)	0.147 (9)
l(Cl·Cl)	0.122 (28)	0.114 (10)	0.116 (8)
l(Cl··Cl)	0.118 (20)	0.120 (25)	0.116 (19)
	Bond Angles		
Y-W-Cl	102.4 (13)	104.2 (5)	104.4 (3)
Cl-W-Cl	87.3 (5)	86.5 (2)	86.5 (2)
	R Value[e]		
		0.112	0.064

[a] Distances (r_a) and amplitudes in angstroms; angles in degrees. [b] Parenthesized uncertainties are estimated 2σ for WSCl$_4$ and WSeCl$_4$. Uncertainties for WOCl$_4$ were estimated by a slightly different method which gives comparable results. [c] Reference 1. r_g values in this article have been converted to r_a for more direct comparisons. [d] This work. [e] $R = [\Sigma w_i \Delta_i^2 / \Sigma w_i (s_i I_i(\text{obsd}))^2]^{1/2}$, where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

It is well-known that the covalent radius of a metal atom increases with increase in its coordination number. It is thus not surprising that the W=S distance in our WSCl$_4$ (Table I) is appreciably shorter than those in a number of WSCl$_4$ adducts having sixfold coordination of the tungsten atom, for example, in the anion [WCl$_5$S]$^-$, where this distance is 2.132 (13) Å.[15] In crystalline WSCl$_4$[6] a long W···Cl interaction exists trans to the sulfur atom; here too, consistent with the coordination-effect principle, the W=S bond length at 2.098 (8) Å is slightly longer than in the free molecule. Although few values for W=Se distances are known, one well-characterized species with sixfold coordination of the tungsten atom is WCl$_3$Se(OCH$_2$CH$_2$OMe) for which the value 2.225 (5) Å for W=Se was obtained.[16] Again, the bond is longer than in our WSeCl$_4$ with its fivefold coordination around the metal atom.

Some ideas about the bonding between the tungsten and axial atoms in the compounds of Table I may be had from the bond lengths. The lengths of normal W=O, W=S, and W=Se double bonds may be estimated by subtracting 0.21 Å from the sums of the covalent single-bond radii;[17] the results are respectively, 1.834, 2.134, and 2.264 Å. (There is uncertainty about the appropriateness of including a correction for electronegativity difference in such calculations when a metal atom is involved, but since the W-Cl distance is predicted to within 0.01 Å without a correction, it seems justified to ignore it for the other bonds as well.) In each case, the measured value is shorter than the predicted one, but the difference for W=O is more than twice as great as for the others. A similar, even greater difference is found for the bond pairs P=O, P=S and As=O, As=S in the compounds PF$_3$Y,[18,19] PCl$_3$Y,[18] P(CH$_3$)$_3$Y,[20] and As(CH$_3$)$_3$Y[20] (Y = O or S). Here it was suggested that partial triple-bond character

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Table II. Correlation Matrix (×100) for $WSCl_4$

	σ^a	r_1	r_2	r_3	r_4	r_5	l_1	l_2	l_3	l_4	l_5	$\angle_1$	$\angle_2$
r(W=S)	0.20	100	−29	12	6	6	23	−71	−5	−16	−6	−21	21
r(W−Cl)	0.09		100	28	28	28	35	6	2	8	4	22	−22
r(S·Cl)	0.42			100	−78	−78	16	−13	17	18	−2	94	−94
r(Cl·Cl)	0.24				100	100	15	−9	−18	−19	3	−88	88
r(Cl··Cl)	0.34					100	15	−9	−18	−19	3	−88	88
l(W=S)	0.23						100	−49	<1	−5	1	2	−2
l(W−Cl)	0.13							100	4	20	6	12	−12
l(S·Cl)	0.56								100	41	6	19	−19
l(Cl·Cl)	0.31									100	8	23	−23
l(Cl··Cl)	0.86										100	−1	1
∠S-W-Cl	17.3											100	−100
∠Cl-W-Cl	8.3												100

[a] Standard deviations (×100) are from least squares. Distances and amplitudes are in angstroms and angles in degrees.

Table III. Correlation Matrix (×100) for $WSeCl_4$

	σ^a	r_1	r_2	r_3	r_4	r_5	l_1	l_2	l_3	l_4	l_5	$\angle_1$	$\angle_2$
r(W=Se)	0.11	100	−56	−2	−13	−13	−30	−24	−6	−14	−2	−21	21
r(W−Cl)	0.08		100	20	42	42	28	21	−2	16	4	16	−16
r(Se·Cl)	0.29			100	−77	−77	−1	<1	18	32	5	97	−97
r(Cl·Cl)	0.19				100	100	14	9	−20	−21	−2	−83	83
r(Cl··Cl)	0.26					100	14	9	−20	−21	−2	−83	83
l(W=Se)	0.12						100	<1	7	7	5	2	−2
l(W−Cl)	0.06							100	6	11	3	3	−3
l(Se·Cl)	0.25								100	2	12	20	−20
l(Cl·Cl)	0.24									100	6	32	−32
l(Cl··Cl)	0.64										100	4	−4
∠Se-W-Cl	12.0											100	−100
∠Cl-W-Cl	5.9												100

[a] Standard deviations (×100) are from least squares. Distances and amplitudes are in angstroms and angles in degrees.

results for the oxo compounds by donation from the two filled oxygen p_π orbitals to empty d_π orbitals on the central atom, a process less likely in the sulfur compounds because the bonds are less polar. It seems reasonable that the same effect, less pronounced, operates in the tungsten compounds. With the assumption that $WSeCl_4$ has terminal W=Y bonds in the solid, as does $WSCl_4$,[6] there is spectroscopic evidence to support this view.[21] Infrared bands assigned to the W=Y stretching vibration have been measured at 1030 cm^{-1} ($WOCl_4$[3,4] in the gas), 555 cm^{-1} ($WSCl_4$[21] in the solid), and 388 cm^{-1} ($WSeCl_4$[21] in the solid). The ratios of the force constants for these bonds, estimated from the formula $k_A/k_B = \nu_A^2\mu_A/\nu_B^2\mu_B$ are 1.01 for k(W=S)/k(W=Se) and 1.86 for k(W=O)/k(W=S). Clearly the W=O force constant is much larger than those for the other bonds and is consistent with the higher bond order deduced from the bond lengths. Rough values for the force constants themselves are 9.2, 5.0, and 4.9 aJ/Å^2 for W=O, W=S, and W=Se, respectively; many force constants for single bonds to metals are found in the range 2.2–3.2 aJ/Å^2.

It is somewhat surprising that the bond angles in the $WYCl_4$ molecules are so similar in view of the rather different properties of the Y atoms—their sizes, distances from the tungsten atom, and in the case of the oxide, different bonding. We presume that nonbond repulsions play an important role in determining the magnitudes of the bond angles because the measured values of the nonbond distances are all less than the sum of the van der Waals radii: 0.08 Å for O·Cl, 0.20 Å for S·Cl and Se·Cl, and about 0.50 Å for Cl·Cl. These values differ substantially, but because the "hardness" of a peripheral atom is expected to increase with increasing multiplicity of its bond, it is likely that the nonbond repulsions are quite similar.

Another matter is the length of the W–Cl bonds in these compounds. They are quite similar whereas, for example, in $POCl_3$ the halogen bond is about 0.03 Å shorter than in $PSCl_3$. The bond shortening that follows increased substitution with electronegative ligands is also well-known in carbon compounds. Such electronegativity effects are apparently less important in compounds of heavy metals, as we have implied in our earlier discussion of the W–Y bond lengths.

Finally, we note that three-atom (multiple) scattering[22] has been an important factor in diffraction from the hexafluorides of heavy atoms. It seems not to be so in our compounds, where good agreement between experimental and theoretical radial distribution curves is seen without allowing for the effect. In any case, other work suggests multiple scattering to have only a small effect on the derived distance values (0.001–0.002 Å) but perhaps a considerably greater one on amplitude values.

Acknowledgment. We are grateful to the National Science Foundation for support of this work under Grant CHE78-04258 and to the Royal Society and the University of Reading Research Board for travel grants (D.A.R.).

Registry No. $WSCl_4$, 25127-53-1; $WSeCl_4$, 41549-02-4.

Supplementary Material Available: Total scattered intensities $s^4(I_t(s))$ from each plate (Tables IV and VII), calculated backgrounds for each plate (Tables V and VIII), and average molecular intensities $s(I_m(s))$ from each camera distance (Tables VI and IX) (16 pages). Ordering information is given on any current masthead page.

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