

Gas-Phase Electron-Diffraction Study of Tetrafluorosulfidotungsten(VI)

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The molecular structure of WSF₄ has been studied by gas-phase electron diffraction at an average nozzle temperature of 232 °C. The experimental data are fitted by a square-pyramidal model of C_{4v} symmetry in which the tungsten atom is above the plane of the four fluorine atoms. The distances and angles are r_a(W=S) = 2.104 (7) Å, r_a(W-F) = 1.847 (3) Å, ∠S=W-F = 104.5 (11)°, and ∠F-W-F = 86.6 (5)°. The estimated uncertainties are 2σ.

Introduction

The molecular structures of a number of oxo fluorides of the early transition series have been determined by gas-phase electron diffraction.²⁻⁵ Similar studies of the sulfido fluorides have not been made because, although coordination compounds of WSF₄ have been reported, no pure sulfido fluorides of the transition elements were known until the relatively recent isolation of WSF₄ itself. Since the structural effect of the substitution of sulfur for the more electronegative oxygen atom is of some interest, we decided to investigate the gas-phase structure of WSF₄.

Experimental Section

The pale yellow compound WSF₄ was prepared by allowing WF₆ to react with B₂S₃ at 260 °C. The product was purified by vacuum sublimation at 50 °C. Its infrared spectrum had an intense peak at 577 cm⁻¹ attributable to the stretching mode of a W=S terminal bond.⁶ Small quantities of the compound were sublimed into glass ampules fitted with a vacuum break-seal. 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. The break-seal was then opened and the sample reservoir gradually heated to 140 °C 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 evidence of some sample decomposition as shown by the presence of a "tungsten-blue" deposit on the inside of the tubing. A similar decomposition was noted during the structural investigation of WOF₄.⁴ We attribute the sample decomposition in both cases to reaction with surface O-H groups on the walls of the connecting tube.

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); r³ 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 diffraction experiments of gaseous CO₂ (r_a(C=O) = 1.1646 Å, r_a(O-O) = 2.3244 Å); beam current range 0.34-0.54 μA; nozzle-tip temperature range 229-235 °C; pressure range in the apparatus (1-4) × 10⁻⁶ torr. The scattered intensity data were obtained from the plates (three at the long and one at the intermediate camera distances) as previously described.⁷ Calculated backgrounds⁸ containing contributions from theoretical elastic⁹ and inelastic¹⁰ atomic scattering were subtracted

Table I. Structural Results^d for WSF₄ and Some Similar Molecules

	WSF ₄ ^b	WOF ₄ ^c	WSCl ₄ ^d	WOCl ₄ ^e
Distances				
r(W=Y)	2.104 (7)	1.666 (7)	2.086 (6)	1.685 (11)
r(W-X)	1.847 (3)	1.847 (2)	2.277 (3)	2.280 (3)
r(Y-X)	3.128 (22)	2.786 (12)	3.445 (12)	3.117 (26)
r(X-X)	2.528 (13)	2.525 (8)	3.121 (8)	3.146 (15)
r(X·X)	3.575 (18)	3.570 (11)	4.414 (11)	4.449 (21)
Amplitudes				
I(W=Y)	0.033 ^f	0.036 ^f	0.031 (6)	0.045 (11)
I(W-X)	0.055 (4)	0.041 (3)	0.058 (4)	0.052 (4)
I(Y-X)	0.121 (19)	0.097 (17)	0.147 (17)	0.095 (38)
I(X-X)	0.107 (20)	0.094 (14)	0.114 (10)	0.122 (28)
I(X·X)	0.091 (45)	0.083 (29)	0.120 (25)	0.118 (20)
Bond Angles				
Y-W-X	104.5 (11)	104.5 (6)	104.2 (5)	102.4 (13)
X-W-X	86.6 (5)	86.2 (3)	86.5 (2)	87.3 (5)
R Value ^g				
	0.109		0.112	

^a Distances (r_a) and amplitudes in angstroms; angles in degrees. Parenthesized uncertainties are 2σ. ^b This work. Structure refined with WOF₄ as impurity. Refined percent WOF₄ equals 23.1 (5.8). ^c Reference 4. ^d Reference 16. ^e Reference 15. ^f Constrained. See text. ^g R = [Σw_iΔ_i²/Σw_i(s_iI_i(obsd))²]^{1/2}, where Δ_i = s_iI_i(obsd) - s_iI_i(calcd).

from the intensity data to yield the experimental molecular intensity distribution in the form⁷ sI_m(s) used for analysis at Oregon State.

Data from the long and intermediate camera distances were obtained over the ranges 2.00 ≤ s ≤ 12.75 Å⁻¹ and 7.00 ≤ s ≤ 31.75 Å⁻¹, respectively, at intervals Δs = 0.25 Å⁻¹ (s = 4πλ⁻¹ sin θ; 2θ is the scattering angle). Curves of the reduced intensity data (s⁴I_r(s)) are shown in Figure 1; 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 sI_m(s) values by [Z_wZ_F/(A_wA_F)] exp(-0.0025s²); the final one is shown in Figure 2. The early results suggested the presence of an impurity. In view of the known propensity of the sulfido halides to react with oxygenated species to yield oxo halides, the most likely impurity was judged to be WOF₄. This judgment is supported by mass spectrometric studies of WSF₄ where ions derived from WOF₄ were detected.^{6,11} Accordingly, a model for a WSF₄/WOF₄ mixture was formulated in which the structure of WSF₄ was described by the parameters r(W=S), r(W-F), ∠SWF, and the five vibrational amplitudes corresponding to distances in the molecule of assumed C_{4v} symmetry, and the WOF₄ component was assigned the structure and vibrational amplitudes previously determined.⁴

Refinements of the structure were carried out by least squares,¹² adjusting theoretical sI_m(s) curves calculated from models of the

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Table II. Correlation Matrix (X100) for WSF_4

	σ^a	r_1	r_2	r_3	r_4	r_5	l_2	l_3	l_4	l_5	L_1	L_2	%
$r(\text{W}=\text{S})$	0.21	100	-40	<1	8	8	-35	1	-13	-3	-19	8	2
$r(\text{W}-\text{F})$	0.09		100	7	19	19	-4	-9	-6	-2	8	19	-20
$r(\text{S}-\text{F})$	0.78			100	-95	-95	-3	-4	4	-24	98	-95	17
$r(\text{F}-\text{F})$	0.44				100	100	-6	1	-9	22	-96	100	-23
$r(\text{F}=\text{F})$	0.62					100	-6	1	-9	22	-96	100	-23
$l(\text{W}-\text{F})$	0.13						100	3	33	9	5	-6	-26
$l(\text{S}-\text{F})$	0.63							100	-6	-13	-3	1	32
$l(\text{F}-\text{F})$	0.68								100	<1	7	-9	12
$l(\text{F}=\text{F})$	1.57									100	-23	22	-10
$\angle \text{S}-\text{W}-\text{F}$	37.7										100	-96	18
$\angle \text{F}-\text{W}-\text{F}$	18.7											100	-23
% WOF_4	206												100

^a Standard deviations (X100) are from least squares. Distances and amplitude are in angstroms and angles in degrees.

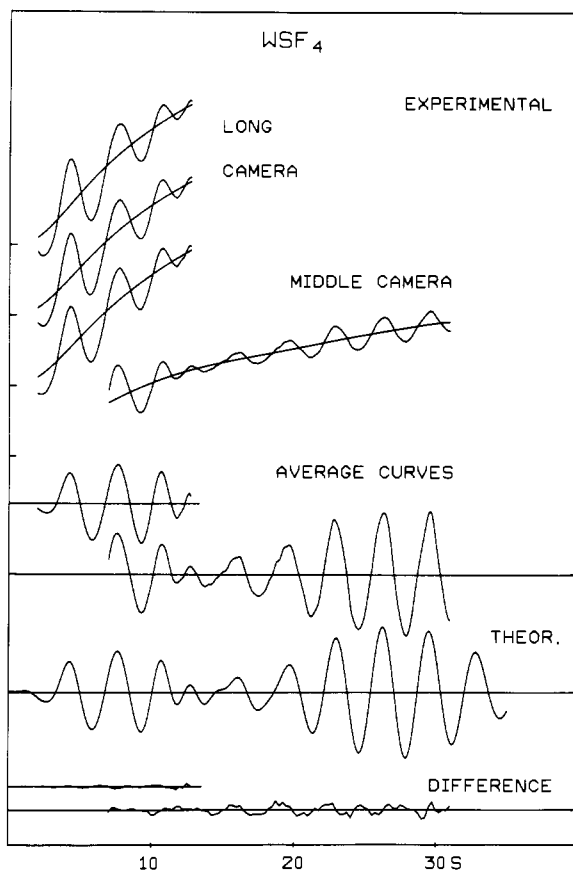


Figure 1. Intensity curves. The $s^4 I_s$ curves from each plate are shown superposed on the final backgrounds and are magnified 7 times relative to the backgrounds. The $s I_m$ curves are averages from each camera distance. The theoretical curve is for the model of Table I. The difference curves are experimental minus theoretical.

sample mixture to the data obtained at each camera distance. A diagonal weight matrix was used. Shrinkage¹³ 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 the intensity calculations in place of those for tungsten for all terms involving the latter. Initial refinements led to what seemed to be unreasonably large values (>0.044 (8) Å) for the amplitude $l(\text{W}=\text{S})$. In such circumstances the parameter is frequently assigned a more reasonable value and not allowed to refine. We set $l(\text{W}=\text{S}) = 0.033$ Å, which led to $\text{W}=\text{S}$ and $\text{W}-\text{F}$ distances respectively about 0.001 and 0.002 Å shorter than when $l(\text{W}=\text{S})$ was allowed to refine. All other changes were entirely negligible. We also tested the effect of our use of $\eta(\text{Os})$ in place of $\eta(\text{W})$. The $\eta(\text{Os})$ set leads to smaller changes (of opposite sign) than those cited for $l(\text{W}=\text{S})$.

The results of the final refinement, with the uncertainties for $r(\text{W}=\text{S})$ and $r(\text{W}-\text{F})$ expanded slightly to reflect uncertainties in

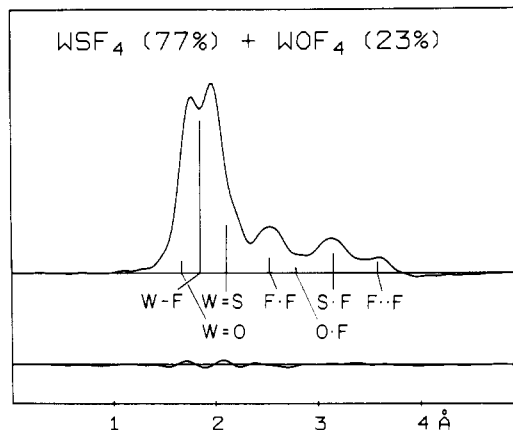


Figure 2. Experimental radial distribution curve. The vertical bars have lengths proportional to the weights of the terms (percent $\times n_{ij} Z_i Z_j / r_{ij}$). The $\text{W}-\text{F}$ and $\text{F}-\text{F}$ distances in the two molecules are essentially the same, and the terms have been combined. The lower curve is the difference experimental minus theoretical.

the value of $l(\text{W}=\text{S})$ and the η 's, are given in Table I. Table II is the correlation matrix. The theoretical intensity curve for the final model, the experimental average curve, and the difference between them are shown in Figure 1.

Discussion

The results of our investigation of WSF_4 are consistent with C_{4v} symmetry for the gas-phase molecule. In this respect WSF_4 is similar to WOCl_4 ,^{14,15} WOB_4 ,¹⁶ WSeCl_4 ,¹⁷ and WSeCl_4 .¹⁷ We emphasize that small deviations of WSF_4 from the assumed C_{4v} symmetry cannot be excluded by our data, but we are confident that appreciable amounts of C_{3v} structures (with a linear $\text{F}-\text{W}=\text{S}$ moiety) or C_{2v} structures (with a linear $\text{F}-\text{W}-\text{F}$ moiety) are not present.

As may be seen from Table I, there are a number of interesting similarities as well as differences in the structures of WSF_4 , WOF_4 , WSeCl_4 , and WOCl_4 . Among the former are the values of the YWX (and XWX) bond angles, which for the first three compounds are essentially identical and for WOCl_4 only marginally different from the others. There are also similarities in bond lengths (the $\text{W}-\text{F}$ bonds in WSF_4 and WOF_4 have the same lengths and the $\text{W}-\text{Cl}$ bonds in WSeCl_4 and WOCl_4 differ only slightly) as well as noteworthy differences such as the lengths of the $\text{W}=\text{S}$ bond in WSF_4 and WSeCl_4 and the $\text{W}=\text{O}$ bond in WOF_4 and WOCl_4 . We turn to these now.

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It is well-known that bonds between a central atom and electronegative ligands tend to shorten as the remaining ligands are substituted by more electronegative ones. For example, the P=S distance in PSF_3 ¹⁸ is less than in PSCl_3 ¹⁹ and the P-Cl distance in POCl_3 ¹⁹ is less than that in PSCl_3 , reflecting the relative electronegativities $F > \text{Cl}$ and $\text{O} > \text{S}$. Operation of the principle in the molecules of Table I is seen in the fact that the W=O bond in WOF_4 is shorter than in WOCl_4 and the W-Cl bonds in WOCl_4 are shorter than in WScCl_4 . In view of the successes, it is surprising to find the principle violated by the length found for the W=S bonds in WSF_4 and WScCl_4 . The reason for this bond length inversion is obscure, but it seems more likely that it reflects abnormality in the structure of WSF_4 rather than in the structure of WScCl_4 . In WSF_4 the W=S distance, for example, is about equal to that in solid WScCl_4 ,²⁰ where there is a weak W-Cl interaction trans to the sulfur atom; moreover it is about equal to W=S distances in a number of other six-coordinate adducts of WScCl_4 .²¹ There remains, of course, the possibility that our results have been significantly affected by the presence of sample impurity. We do not believe this likely because the amount of impurity was not excessive and its effect on the scattered intensity could be easily taken account of.

The relative bond orders of the bonds W=S and W=O in, respectively, WSF_4 and WOF_4 are of some interest. We believe that the latter is greater than the former. There are two pieces of evidence that support this view. The first concerns

the stretching wavenumbers of these bonds, $\nu(\text{W}=\text{S}) = 577 \text{ cm}^{-1}$ ²³ and $\nu(\text{W}=\text{O}) = 1055 \text{ cm}^{-1}$.²⁴ A rough comparison of the corresponding force constants is obtained from $k_{\text{W}=\text{O}}/k_{\text{W}=\text{S}} = (\nu^2\mu)_{\text{W}=\text{O}}/(\nu^2\mu)_{\text{W}=\text{S}} = 1.77$, a value similar to the value 1.86 obtained for these bonds in WScCl_4 and WOCl_4 . The second piece of evidence involves a consideration of the sums of the covalent radii. For both W=O and W=S the observed bond lengths are less than the nominal double-bond values (1.834 and 2.134 Å) obtained by subtracting 0.21 Å from the sums of the covalent single bond radii. However, the difference for W=O (0.17 Å) is much greater than that for W=S (0.03 Å), suggesting much higher bond multiplicity. We note in passing that these differences themselves differ by about the same amount as do the lengths of a triple bond and double bond and that the ratio of the force constants for such bonds is very close to the ratio 1.77 we calculate for $k(\text{W}=\text{O})/k(\text{W}=\text{S})$.

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Supplementary Material Available: Total scattered intensities $s^4I_i(s)$ from each plate (Table III), calculated backgrounds for each plate (Table IV), and average molecular intensities $sI_m(s)$ from each camera distance (Table V) (6 pages). Ordering information is given on any current masthead page.

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Low-Temperature Neutron Diffraction Analysis of $[\text{Rh}_4(\eta^5\text{-C}_5\text{Me}_5)_4\text{H}_4][\text{BF}_4]_2$ ¹

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A low-temperature (12 K) neutron diffraction study of $[\text{Rh}_4(\eta^5\text{-C}_5\text{Me}_5)_4\text{H}_4][\text{BF}_4]_2$ has been undertaken in order to determine whether the hydride ligands bridge the edges or faces of the tetranuclear rhodium cluster. Both anions and cations lie on sites of 4-S₄ symmetry. The cation is a stable, 58-electron, diamagnetic complex consisting of a tetrahedral cluster with a C₅Me₅ ligand attached to each metal. The Rh₄ core shows substantial distortion from a regular tetrahedron, resulting in four long and two short Rh-Rh distances. The hydrides were found to bridge the faces of the tetrahedral cluster at a distance of 0.96 Å above the planes formed by three Rh atoms. The Rh-Rh distances are 2.610 (5) and 2.829 (5) Å, and the Rh atoms are 1.84 Å from the C₅-ring planes. A detailed ¹H and ¹³C NMR analysis establishes that the hydride ligands also are face bridging in solution. Calculations based on idealized tetrahedral geometry for the molecular framework show no abnormally short nonbonded contacts, and thus distortion from T_d symmetry appears to be electronic rather than steric in origin. Crystallographic data for $[\text{C}_{40}\text{H}_{64}\text{Rh}_4][\text{BF}_4]_2$: tetragonal, space group I $\bar{4}$, Z = 2, a = 11.459 (3) Å, c = 15.481 (8) Å, R(F²) = 0.069 for 1371 reflections with (sin θ)/λ < 0.83 Å⁻¹.

Introduction

The X-ray crystal structure of the polynuclear transition-metal hydride $[\text{Rh}_4(\eta^5\text{-C}_5\text{Me}_5)_4\text{H}_4][\text{BF}_4]_2$ was reported recently.⁶ The cation contains four rhodium atoms clustered

in a distorted tetrahedral array with four long and two short Rh-Rh bonds. Each rhodium atom is symmetrically η⁵ bonded to a C₅Me₅ ligand. Attempts to locate the hydride ligands were unsuccessful, and it was predicted on the basis of earlier structural work on metal hydride clusters that the four hydrogens would bridge the longer Rh-Rh bonds. ¹H NMR measurements showed that the four hydrides were chemically equivalent as were the rhodium nuclei but that the hydride ligands were not free to move over the molecular framework.⁶

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