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Molecular Structure of Tungsten Oxide Tetrachloride by Gas Electron Diffraction

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The molecular structure of tungsten oxide tetrachloride was determined by the sector-microphotometer method of gas electron diffraction. The molecule was found to have a square-pyramidal structure, and the following molecular parameters were obtained by a least-squares method; $r_g(\text{W–Cl})=2.281\pm0.003$ Å, $r_g(\text{W–O})=1.686\pm0.011$ Å, and $r_g(\text{Cl}\cdots\text{Cl(s)})=3.151\pm0.015$ Å. The OWCl angle, 102.4±1.3°, is much larger than the corresponding angles found in other square-pyramidal molecules such as XeOF_4 and IF_5.

The geometrical structures of five-coordinated molecules can be divided into trigonal bipyramid and square pyramid. The former type was reported, for example, for $\text{PCl}_5$¹⁾ and SOF_4,²,³⁾ though SOF_4 was found to be slightly distorted from a regular trigonal bipyramid. The latter type was reported for ClF_5,⁴⁾ BrF_5,⁴⁾ IF_5,⁴⁾ and XeOF_4.⁴,⁵⁾ The possibility of these structures can be explained in terms of the valence-shell electron-pair repulsion theory of Gillespie.⁶⁾ The electron configurations in the outermost shell of neutral tungsten and sulfur atoms are $(5d)^4(6s)^2$ and $(3s)^2(3p)^4$, respectively, and hence, the numbers of valence electrons in WOCl_4 and SOF_4 are equal to each other. Therefore, the structure of WOCl_4 should essentially be the same as that reported for SOF_4. From spectroscopic studies of WOCl_4 in the gas phase,⁷,⁸⁾ where the molecule is monomeric, however, the molecular structure is predicted to be square pyramidal. It is therefore interesting to determine the gas-phase structure of WOCl_4 by means of electron diffraction.* On the other hand, an X-ray diffraction study⁹⁾ has shown that the WOCl_4 molecule has C_{4v} symmetry in the crystal state by formation of –O–W–O– linkages.

Experimental and Analysis

The sample was prepared by the method described in Ref. 10 and was purified by repeated sublimations *in vacuo*. Since the sample was very reactive with moisture, it was loaded in a high-temperature nozzle in a dry box. The sample was vaporized at 65 °C, and electron-diffraction photographs were taken with an r^3-sector at a camera length of 144.08 mm. The accelerating voltage was about 40 kV, the exposure times were 30∼40 sec, and the electron-beam current was 0.6 μA. Diffraction patterns of gold, the lattice constant of which was calibrated by means of X-ray diffraction, were used in order to measure the electron wavelength. Photographs were recorded on Fuji process hard plates, and the photographic densities of two plates were measured with a digital microphotometer at intervals of 0.4 mm. Intensities in a range of $q=17\sim102$ Å^{-1} were obtained and leveled by a theoretical background, which was calculated by using the elastic scattering factors of Kimura *et al.*¹¹⁾ and the inelastic scattering factors of Tavard¹²⁾ for chlorine and oxygen and that of Bewilogua¹³⁾ for tungsten.

The radial distribution function was calculated by the use of the method of Bartell¹⁴⁾ because of the large differences in the atomic numbers. The corresponding correction terms for the radial distribution function are

$$\begin{aligned}\Delta M(q) &= R\sum_{i\neq l}\sum C_{ij}(N_{ij}-\mu_{ij})\cos(\Delta\eta_{ij})\\ &\quad\times\sin[(\pi q/10)\{r_{a_{ij}}-\kappa(\pi q/10)^2\}]\\ &\quad\times\exp\{-l_{ij}{}^2(\pi q/10)^2/2\}/(\pi q/10)r_{a_{ij}},\end{aligned}$$

where R is the index of resolution, and

$$\begin{aligned}C_{ij} &= Z_{ij}/\sum_k(Z_k{}^2+Z_k),\\ \mu_{ij} &= |F_i||F_j|/C_{ij}\sum_k(|F_k|^2+S_k),\\ N_{ij} &= a_{ij}+b_{ij}\exp(-c_{ij}q^2),\\ |F_k| &= h^2(\pi q/10)^2|f_k|/8\pi^2me^2.\end{aligned}$$

Other notations follow Refs. 14 and 15. N_{ij} was determined as follows so as to fit μ_{ij} in the whole range of the scattering angle:

$$\begin{aligned}N_{\text{W–Cl}} &= 1.200\\ N_{\text{W–O}} &= 1.205+0.289\exp(-0.00040\,q^2)\\ N_{\text{Cl}\cdots\text{Cl}} &= 1.695+0.531\exp(-0.00029\,q^2)\\ N_{\text{Cl}\cdots\text{O}} &= 1.762+1.049\exp(-0.00046\,q^2)\end{aligned}$$

The parameters μ_{ij} and N_{ij} and the radial distribution curve are shown in Figs. 1 and 2, respectively. By inspection of the radial distribution curve and by comparison of the observed molecular intensities with those calculated on the assumption of C_{2v}, C_{3v}, and C_{4v} models, it was concluded that the molecular structure of WOCl_4 is a square pyramid, C_{4v}.

In order to refine the structure parameters, least-squares analyses based on the smooth-background method¹⁶⁾ by use of a polynomial of 7th degree were carried out. When the molecule was assumed to be a trigonal bipyramid like SOF_4, several parameters did not converge even after the 10th cycle of refinement. All the parameters carried large standard deviations, and the equatorial and polar W–Cl distances converged to the same value within the limit of error. The C_{3v} model was not tested in the least-squares calculation. On the other hand, when the molecule was assumed to be a square pyramid, all the parameters converged after several iterations. Thus the above-mentioned conclusion was confirmed by the least-squares analysis.

The index of resolution, $r(\text{W}\cdots\text{Cl})$, $r(\text{W}\cdots\text{O})$, $r(\text{Cl}\cdots\text{Cl(s)})$, and five root-mean-square amplitudes $l(\text{W}\cdots\text{Cl})$, $l(\text{W}\cdots\text{O})$, $l(\text{Cl}\cdots\text{Cl(s)})$, $l(\text{Cl}\cdots\text{Cl(l)})$, and $l(\text{Cl}\cdots\text{O})$ were determined by the least-squares analysis. The asymmetry parameters for bonded distances were estimated by a diatomic-molecule

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* Preliminary results were reported in *Chem. Lett.*, **1972**, 1033. Spiridonov *et al.* have also reported the molecular structure of gaseous WOCl_4 by electron diffraction (V. P. Spiridonov, E. Z. Zasorin, I. M. Zharskii, and G. I. Novikov, *Zh. Strukt. Khim.*, **13**, 511 (1972)). The configuration reported by them is the same as that determined in the present study, but their bond lengths are much larger than those determined in the present study. The origin of the discrepancies, which exceed the limits of error, is unknown.

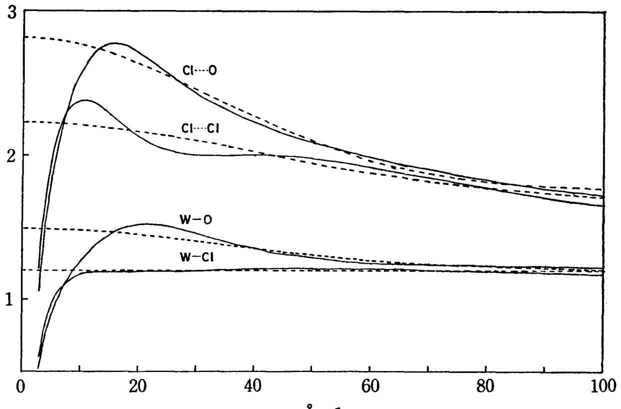

Fig. 1. μ_{ij} (solid lines) and N_{ij} (dashed lines) for $WOCl_4$.

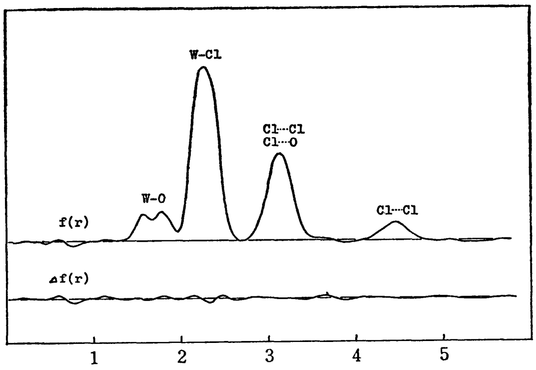

Fig. 2. Radial distribution for $WOCl_4$, $f(r)$, and the difference between observed and theoretical ones, $\Delta f(r)$.

TABLE 1. RESULTS OF THE LEAST-SQUARES ANALYSIS (IN Å UNITS)

	Plate 1	Plate 2	Average	σ_l
r_a(W–Cl)	2.2793	2.2800	2.2797	0.0007
r_a(W–O)	1.6847	1.6841	1.6844	0.0043
r_a(Cl···Cl(s))	3.1427	3.1493	3.1460	0.0057
l(W–Cl)	0.0523	0.0520	0.0522	0.0015
l(W–O)	0.0456	0.0439	0.0448	0.0043
l(Cl···Cl(s))	0.1220	0.1214	0.1217	0.0102
l(Cl···Cl(l))	0.1160	0.1202	0.1181	0.0078
l(Cl···O)	0.1002	0.0903	0.0953	0.0148
R	0.9232	0.9226	0.9229	0.0071

TABLE 2. DISTANCES AND MEAN AMPLITUDES

r_g(W–Cl)	2.281±0.003 Å
r_g(W–O)	1.686±0.011
r_g(Cl···Cl(s))	3.151±0.015
r_g(Cl···Cl(l))	4.452±0.021
r_g(Cl···O)	3.120±0.026
l(W–Cl)	0.052±0.004
l(W–O)	0.045±0.011
l(Cl···Cl(s))	0.122±0.028
l(Cl···Cl(l))	0.118±0.020
l(Cl···O)	0.095±0.038
∠OWCl	102.4±1.3°
∠ClWCl	87.3±0.5°

approximation.[17] The parameter in the Morse function, a, was assumed to be 2.0 Å^{-1}, and the frequencies of ν_{W-O} and ν_{W-Cl} were taken to be 1027 and 402 cm^{-1}, respectively.[8] The assymmetry parameters thus obtained were 0.5×10^{-6} Å^3 for W–O and 4.0×10^{-6} Å^3 for W–Cl, and those for non-bonded distances were assumed to be zero. These asymmetry parameters were fixed throughout the least-squares analysis.

In the first stage, it was discovered that the correlation between the Cl···Cl(s) and Cl···O amplitudes was very large. This is probably because of the small difference between the distances, as observed by Jacob *et al.* in the analysis of $XeOF_4$.[5] In the analyses, where no constraint was set on the l(Cl···Cl(s)) and l(Cl···O), the difference between them was estimated to be about 0.03 Å, as listed in Table 1.

Since the results obtained from two independent intensity data are in good agreement with each other, as shown in Table 1, random errors were estimated as 2.5 σ_l from the standard errors in least-squares calculations.[18] Systematic errors were estimated as follows. The error associated with the calibration of the lattice constant of gold was 0.06%, and the errors in the measurements of the diffraction patterns of the gold foil and the camera length were 0.08 and 0.04%, respectively. Then the total error of the wavelength was estimated to be 0.11% from the square root of the squared sum of the individual errors. The error in the q values was estimated from those in the electron wavelength and the camera length. The total errors in the bond distances were evaluated from the systematic errors (0.12%) and the random errors. The uncertainties in the atomic scatterign factor, f, and the phase angle, η, of tungsten were estimated** to have negligible effect on the systematic error in the atomic distances, but the systematic errors from this origin were found to be about 0.01 Å for l(Cl···Cl(s)) and l(Cl···O).

The final results of the analysis are given in Table 2, where r_g parameters were calculated from r_a parameters by $r_g = r_a + l^2/r_a$. The correlation matrix[19] is given in Table 3, and the best-fit theoretical intensity curve is shown in Fig. 3.*** The least-squares computations were carried out by the use of a FACOM 230—60 at Nagoya University Computing Center.

Discussion

The square-pyramidal structure of $WOCl_4$ in the gas phase is in accord with that derived from infrared and Raman spectroscopy.[7,8] Although the structure of $WOCl_4$ in the gas phase is essentially the same as those of IF_5, ICl_5, IBr_5, and $XeOF_4$, the XMY angle in an MXY_4 molecule of C_{4v} symmetry is found to be remarkably different. The OWCl angle is 102.4± 1.3°, whereas the corresponding angles in IF_5, ICl_5, IBr_5, and $XeOF_4$ are about 90° or less. Moreover,

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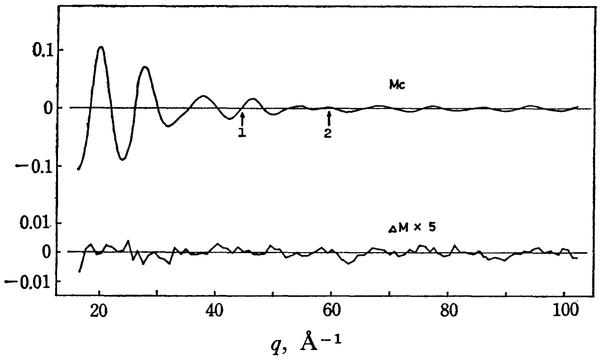
** A least-squares calculation, where the f and η values for platinum were used in place of those for tungsten, was carried out, and the changes in the parameter values were used for the estimation of their errors. The choice of platinum was inferred from a comparison of the observed cut-off point with the calculated ones.

*** Numerical experimental data of the leveled total intensity and the background have been deposited with the Chemical Society of Japan (Document No. 7411).

Table 3. Correlation matrix for molecular parameters of $WOCl_4$[a]

	r_{W-Cl}	r_{W-O}	$r_{Cl\cdots Cl(s)}$	l_{W-Cl}	l_{W-O}	$l_{Cl\cdots Cl(s)}$	$l_{Cl\cdots Cl(l)}$	$l_{Cl\cdots O}$	R
r_{W-Cl}	1.0	−0.235	0.053	−0.006	0.191	0.210	0.043	−0.223	−0.027
r_{W-O}		1.0	0.097	−0.106	−0.085	0.288	0.065	−0.287	0.171
$r_{Cl\cdots Cl(s)}$			1.0	−0.003	−0.009	−0.286	−0.007	0.201	0.003
l_{W-Cl}				1.0	−0.013	0.095	0.087	−0.015	0.608
l_{W-O}					1.0	0.046	0.032	−0.037	0.001
$l_{Cl\cdots Cl(s)}$						1.0	0.094	−0.955	0.312
$l_{Cl\cdots Cl(l)}$							1.0	−0.056	0.166
$l_{Cl\cdots O}$								1.0	−0.167
R									1.0

a) The elements are defined as $\rho_{ij}=B^{-1}_{ij}/(B^{-1}_{ii}\times B^{-1}_{jj})^{1/2}$.



Fig, 3. Calculated molecular intensities, M_c, and the difference between observed and calculated ones, ΔM. The arrows 1 and 2 indicate the theoretical cut-off points due to the atomic pairs of W–O and W–Cl, respectively.

the OWCl angle in $WOCl_4$ is nearly equal to the OTiCl angle in $TiOCl_4^{2-}$ (102°) in crystalline $[N(C_2H_5)_4]_2$-$TiOCl_4$.[20] $TiOCl_4^{2-}$ has approximate C_{4v} symmetry in the crystalline state, and the Ti–O distance is 1.79 Å and the Ti–Cl distances are 2.32 and 2.34 Å. The shortening of the W–Cl distances of $WOCl_4$ in comparison with the Ti–Cl distance of $TiOCl_4^{2-}$ is consistent with the fact that the ionic radius of W^{6+} is about 0.06 Å shorter than that of Ti^{4+}.

The W–Cl distance found in the gaseous $WOCl_4$ molecule is equal to that in the crystal (2.28 Å), whereas the W–O distance in the vapor is considerably shorter than those in the crystal (1.8 and 2.2 Å).[9] The lengthening of the W–O distance in the crystal is apparently due to the decrease in the double bond character by the formation of –O–W–O– linkage.

Available data of infrared and Raman spectra are not sufficient to calculate the mean amplitudes of vibration of the atomic pairs in $WOCl_4$. However, if fundamental frequencies, ν_{W-O} and ν_{W-Cl}, are estimated to be 1027 and 402 cm^{-1}, respectively,[8] l(W–O) and l(W–Cl) can be estimated by a diatomic-molecule approximation to be 0.034 and 0.049 Å, respectively, in essential agreement with the results from the electron diffraction analysis.

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