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MOLECULAR STRUCTURES OF MOLYBDENUM AND TUNGSTEN OXIDE TETRACHLORIDES BY GAS ELECTRON DIFFRACTION

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The molecular structures of $MoOCl_4$ and $WOCl_4$ in the gaseous state were determined by electron diffraction. Both molecules were found to have a square-pyramidal structure and the following molecular parameters were obtained by the least-squares method: r_g(Mo-Cl) = 2.278 ± 0.003 Å, r_g(Mo-O) = 1.670 ± 0.012 Å, and ∠OMoCl = 103.0 ± 2.3° for $MoOCl_4$; r_g(W-Cl) = 2.280 ± 0.003 Å, r_g(W-O) = 1.684 ± 0.015 Å, and ∠OWCl = 102.6 ± 1.5° for $WOCl_4$.

The gas-phase structures of oxide halides MOX_4 (M = molybdenum or tungsten and X = halogen) have not yet been determined, although studies of some of MX_5,[1] MX_6,[2] and MO_2X_2[3] were carried out by electron diffraction. On the other hand, the crystal structures of $WOCl_4$,[4] $WOBr_4$,[4] WOF_4,[5] and $MoOF_4$[6] were determined by X-ray diffraction, and the finding is that in the crystals the central metal atoms are surrounded octahedrally by other light atoms and the units are linked by bridging atoms. This is in contrast to the fact that the molecules are monomeric in the vapor.[7] We intended to determine the structures of gas molecules of MOX_4 by electron diffraction in order to elucidate the difference between the gas-phase and solid-phase structures.

The samples were prepared by using the technique described in Refs. 8 and 9 and were purified several times by sublimation in vacuo. The samples were vaporized at about 80°C and photographs were taken with an r^3 sector at the camera length of about 14 cm. The accelerating voltage was about 40 kV. The optical densities of the plates were measured by a digital microphotometer and converted to intensities which covered the range of $q = 17 \sim 102$. The elastic scattering factors calculated by Kimura et al.[10] and the inelastic scattering factors of

Tavard[11] for chlorine and oxygen and those of Bewilogua[12] for molybdenum and tungsten were used in the present analysis.

From the comparisons of the observed molecular intensity curves with the calculated ones based on C_{2v}, C_{3v}, and C_{4v} models and from inspection of the radial distribution curves, it was concluded that $MoOCl_4$ and $WOCl_4$ molecules belong to the C_{4v} point group. The radial distribution curves for $MoOCl_4$ and

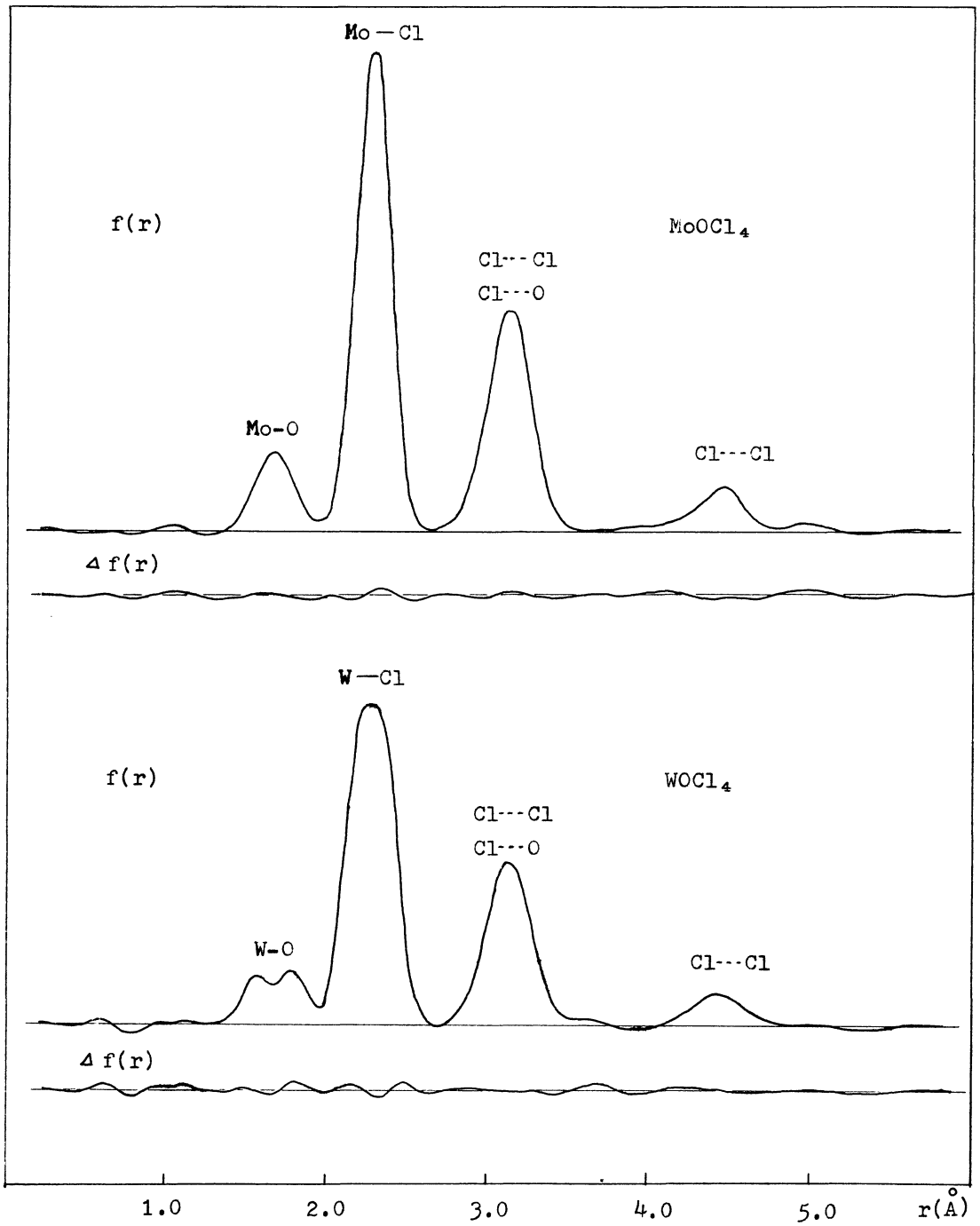

Fig. 1. Experimental radial distribution, f(r), and the difference between experimental and calculated radial distributions, Δf(r).

Table 1. Structural parameters for $MoOCl_4$ and $WOCl_4$ (in Å)

	$MoOCl_4$		$WOCl_4$	
	r_g	l	r_g	l
M—Cl	2.278 ± 0.003	0.064 ± 0.005	2.280 ± 0.003	0.052 ± 0.005
M—O	1.670 ± 0.012	0.063 ± 0.019	1.684 ± 0.015	0.044 ± 0.015
Cl---Cl (short)	3.143 ± 0.016	0.118 ± 0.016	3.159 ± 0.020	0.121 ± 0.030
Cl---Cl (long)	4.439 ± 0.016	0.124 ± 0.020	4.457 ± 0.028	0.120 ± 0.028
Cl---O	3.112 ± 0.030	0.108 ± 0.016	3.116 ± 0.035	0.092 ± 0.040
∠OMCl	103.0 ± 2.3°		102.6 ± 1.5°	

$WOCl_4$ are shown in Fig. 1. The least-squares analysis[13] refined the interatomic distances and the root-mean-square amplitudes. The results are shown in Table 1. The experimental errors tabulated include the systematic errors and correspond to 99 % confidence intervals.

The most interesting result is that the structures of gaseous $MoOCl_4$ and $WOCl_4$ are square pyramids rather than trigonal bipyramids whereas five-coordinated compounds generally prefer the latter to the former as found in $MoCl_5$.[1] The molecular structures of $MoOCl_4$ and $WOCl_4$ in the vapor were found to be in agreement with each other within experimental errors. The OMCl angles in the gaseous $MoOCl_4$ and $WOCl_4$ molecules are about 103° and are much larger than the corresponding angles in other square-pyramidal compounds such as ClF_5, BrF_5, IF_5,[14] and $XeOF_4$,[15] in which the angles were estimated to be about 90° or less. In each of $MoOCl_4$ and $WOCl_4$, the metal atom lies significantly (about 0.5 Å) out of the chlorine plane. This can readily be accounted for by the electron-pair repulsion model.[16] The W-Cl distance in the gas molecule is equal to that in the crystal, whereas the W-O distance in the gas molecule is considerably shorter than the W-O distances (1.8 and 2.2 Å) in the cryatal. The lengthening of the W-O distances in the solid state is apparently due to the decrease in double bond character by forming -W-O-W- linkage.

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