

The Molecular Structure of Tungsten Hexachloride by Gas Electron Diffraction

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Molecular structures of gaseous main group and transition metal halides determined before 1986 have been reviewed by M. Hargattai.¹ Since the appearance of this review we have published the gas-phase structures of BiCl₃,² CdCl₂,³ monomeric GaCl₃ and InCl₃,⁴ and PbCl₄.⁴ In this communication we report the structure of gaseous WCl₆.

It has recently been found that the coordination polyhedron in gaseous hexamethyltungsten is trigonal prismatic rather than octahedral as expected for a *d*⁰ ML₆ compound.⁵ The coordination polyhedra of WF₆,⁶ W(OCH₃)₆,⁷ and W(N(CH₃)₂)₆⁸ are all octahedral in the gas phase, and WCl₆ has been found to be octahedral in two different crystal modifications.^{9,10} We felt, however, that even the slightest possibility that WCl₆ might prove to be trigonal prismatic in the gas phase justified the effort of an investigation by gas electron diffraction (GED). Moreover, we wished to determine the molecular structure of the hexachloride for comparison with the structures of lower tungsten chlorides.

WCl₆ with a stated purity of >99.9% was purchased from Aldrich. Both GED data and mass spectra recorded with this sample without further purification showed, however, the presence of significant amounts of volatile tungsten oxychlorides, predominantly if not exclusively WOCl₄.¹¹ The impurities were removed by heating the sample in high vacuum at temperatures rising from 120 to 160 °C in the course of an hour. The gas electron diffraction data of WCl₆ were recorded on a Baltzers Eldigraph KDG-2 instrument¹² with an inlet system of stainless steel and reservoir and nozzle temperatures of 168 ± 4 °C, corresponding to a vapor pressure of about 4.0 Torr.¹³ Structure refinements were based on six plates obtained with a nozzle-to-plate distance of 50 cm (*s* from 15.00 to 150.00 nm⁻¹ with increment Δ*s* = 1.25 nm⁻¹) and six plates obtained with a nozzle-to-plate distance of 25 cm (*s* from 35.00 to 280.00 nm⁻¹ with increment Δ*s* = 2.50 nm⁻¹). Optical densities were recorded on the Snoopy densitometer and

processed by standard procedures.¹⁴ Atomic scattering factors were taken from Ref. 15. Backgrounds were drawn as fifth- (50 cm) or sixth-degree (25 cm) polynomials to the difference between total and calculated molecular intensities. The resulting modified molecular intensity curves are displayed in Fig. 1.

An experimental radial distribution curve obtained by Fourier inversion of the modified molecular intensity curves is shown in Fig. 2. This curve contains a peak representing the W–Cl bond distances at 228 pm, and two peaks representing nonbonded Cl–Cl distances at 322 and 456 pm. Both the positions and relative areas under the peaks correspond to an octahedral model.

Exploratory least-squares refinements of a sterically consistent octahedral model and three root-mean-square vibrational amplitudes, plus the mole fraction of WOCl₄ with known structure¹¹ as a possible contaminant, yielded χ(WOCl₄) = 3.4(1.4)% for the 50 cm plates and –2.4(3.0)% for the 25 cm plates. Inclusion of the possible impurity changes the W–Cl bond distance in WCl₆ by less

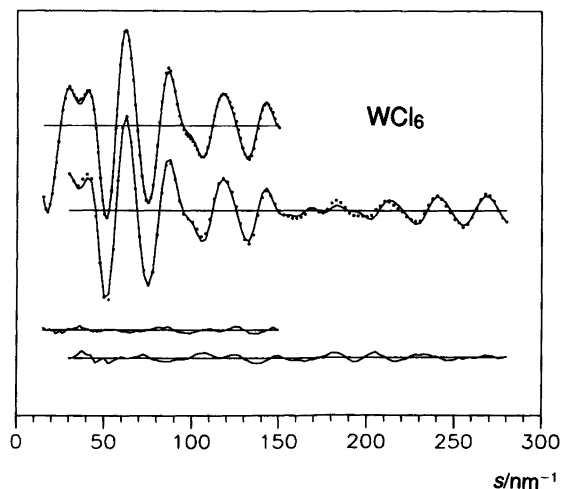


Fig. 1. Calculated (full line) and experimental (dots) modified molecular intensity curves of WCl₆ with difference curves below.

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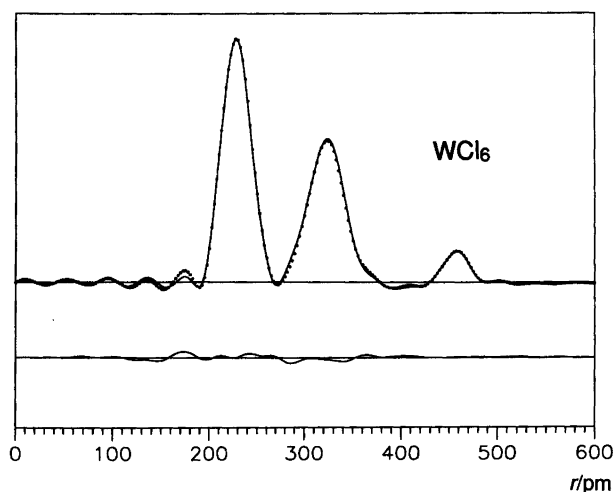


Fig. 2. Experimental (·) and calculated (—) radial distribution curves for WCl_6 . Below: Difference curve. Artificial damping constant, $k = 25 \text{ pm}^2$.

than 0.1 pm, and in subsequent refinements it was disregarded.

As in our study of PbCl_4 ,⁴ we found that the tabulated scattering factors failed to reproduce the experimental intensity curves in the region of the W–Cl beatout. The discrepancy was at least partly removed by multiplying the phase angle of η of W with a constant, 1.0675.

Least-squares refinements of the three interatomic distances as *independent* parameters and the three vibrational amplitudes yielded the best values listed in Table 1. All correlation coefficients were less than 0.6. Since our refinements were carried out with diagonal weight matrix, the estimated standard deviations quoted in the table have been multiplied with a factor of 2.0 to include uncertainty due to data correlation,¹⁶ and expanded to include an estimated scale uncertainty of 0.1 %.

Owing to the effect of intramolecular motion, the thermal average Cl---Cl distances (r_a) are found to be slightly shorter than $\sqrt{2}$ and 2 times the thermal average (r_a) W–Cl bond distance. These discrepancies are often referred to as shrinkages [eqns. (1) and (2)]. Using the six normal modes

$$\delta_{90^\circ} = \sqrt{2} \times r_a(\text{W-Cl}) - r_a(\text{Cl---Cl})_{90^\circ} \quad (1)$$

$$\delta_{180^\circ} = 2 \times r_a(\text{W-Cl}) - r_a(\text{Cl---Cl})_{180^\circ} \quad (2)$$

of octahedral WCl_6 as assigned by Konigs and Booij¹⁷ and the program Asym 20,¹⁸ we have constructed a diagonal symmetry force field which in turn was used to calculate vibrational amplitudes and shrinkages with the Kuchitsu algorithm.¹⁹ The results are listed in Table 1; both amplitudes and shrinkages are in good agreement with the electron diffraction counterparts, and we conclude that *the GED data are in excellent agreement with octahedral symmetry*.

The mean W–Cl bond distance found in the crystalline phase, 226(2) pm,¹⁰ although less accurate, is in good agreement with the gas-phase value. The bond distance in

Table 1. Interatomic distances (r_a), root mean-square vibrational amplitudes (l) and shrinkages (δ) (all in pm) obtained by least-squares calculations on the gas electron diffraction intensities (GED) and from molecular force field (FF) calculations.^a

	GED	FF
$r_a(\text{W-Cl})$	228.1(3)	—
$l(\text{W-Cl})$	5.8(3)	5.6
$r_a(\text{Cl---Cl})_{90^\circ}$	322.3(4)	—
$l(\text{Cl---Cl})$	14.3(4)	14.0
$\delta(\text{Cl---Cl})$	0.3(4)	0.5
$r_a(\text{Cl---Cl})_{180^\circ}$	456.2(9)	—
$l(\text{Cl---Cl})$	8.0(10)	7.4
$\delta(\text{Cl---Cl})$	0.1(9)	0.8
R-factor ^b	0.058	

^aEstimated standard deviations in parentheses in units of the last digit. ^b $R = \{[\sum w(l_{\text{obs}} - l_{\text{calc}})^2] / [\sum w l_{\text{obs}}^2]\}^{1/2}$.

WCl_6 obtained in this study, 228.1(3) pm, appears to be significantly longer than the mean bond distances in WCl_4 and WCl_5 , 224.8(2) and 226.0(3) pm, respectively.^{20,21}

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