

## Composition and Molecular Structure of Gaseous Molybdenum Pentachloride by Electron Diffraction

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At about 115 °C gaseous molybdenum pentachloride exists in two or possibly three configurations. In the most abundant configuration the molybdenum atom is surrounded by five chlorine atoms in a square pyramidal arrangement of  $C_{4v}$  symmetry. A trigonal bipyramidal form of  $D_{3h}$  symmetry is also present. Satisfactory agreement with the data is obtained for a mixture of these two forms if the nonbonded distances of the  $D_{3h}$  configuration exhibit large amplitude motions. However, if the  $D_{3h}$  species vibrates with small harmonic amplitudes, a dimer consisting of two  $C_{4v}$  parts connected by a Mo–Mo bond (assumed  $D_{4d}$  symmetry) may be present. The problem is illustrated by the following least-squares parameters and standard deviations which are based on the assumption that all the three species are present and vibrate with small harmonic amplitudes: 50.7 (4.3)% of  $C_{4v}$  with  $\langle R(\text{Mo}-\text{Cl}) \rangle = 2.227(5)\text{Å}$  and  $\angle(\text{Cl}_a-\text{Mo}-\text{Cl}_b) = 83.6(0.9)^\circ$ , 25.6(5.3)% of  $D_{3h}$  with  $\langle R(\text{Mo}-\text{Cl}) \rangle = 2.300(20)\text{Å}$ , and 23.6(2.6)% of  $D_{4d}$  dimers with  $\langle R(\text{Mo}-\text{Cl}) \rangle = 2.276(24)$ ,  $R(\text{Mo}-\text{Mo}) = 2.600(38)\text{Å}$  and  $\angle(\text{Cl}_a-\text{Mo}-\text{Cl}_b) = 84.4(0.8)^\circ$ .

Monomeric molybdenum pentachloride possesses an odd number of valence electrons. Niobium pentachloride with one electron less, exists in the gas phase as trigonal bipyramidal molecules ( $D_{3h}$  symmetry) pseudorotating over a quite low barrier. The barrier is possibly situated at a square pyramidal form of  $C_{4v}$  symmetry and it is of the magnitude of 6 kJ mol<sup>-1</sup>.<sup>1</sup>

As solids the two compounds consist of dimers where each metal atom is surrounded by six chlorine atoms in a distorted octahedral

arrangement.<sup>2</sup> Monomers of molybdenum pentachloride exist in solutions and in the vapour.

The additional valence electron of the molybdenum compound may lead to degenerate electronic states of a  $D_{3h}$  monomer and the possibility of a Jahn-Teller distortion of this configuration has been discussed.<sup>3</sup>

The results of an electron diffraction investigation of gaseous molybdenum pentachloride at about 115 °C are reported in the following article.

### EXPERIMENTAL AND DATA REDUCTION

Molybdenum pentachloride was synthesized<sup>4</sup> and purified by vacuum sublimation. The compound was analyzed for its content of Mo and Cl which indicated a purity higher than 98 %.

The electron diffraction pattern was recorded using the improved apparatus of Moscow State University.<sup>5</sup> The optical densities of the photographic plates were measured by the Joyce-Loebl digital microphotometer of the University of Oslo. The experimental conditions are summarized in Table 1.

The atomic scattering factor of Cl was computed<sup>6</sup> at 55 kV from an analytical representation of the potential<sup>7</sup> and the scattering factor of Mo was obtained for the same voltage by interpolation of tabulated values.<sup>8</sup>

The data were treated in the usual way<sup>9</sup> and  $sM(s)$  molecular intensities were applied. The background was determined by fitting polyno-

**Table 1.** Experimental parameters for the electron diffraction diagrams of molybdenum pentachloride at about 55 keV.

Camera distance (mm)	362.07	195.23
Wavelength (Å) <sup>a</sup>	0.05075	0.05075
Beam current (μA)	0.10	0.10
Nozzle temp. (°C)	115	115
Exposure time (s)	10–15	30–40
Blackness interval	0.25–0.35	0.09–0.15
Applied <i>s</i> -range (Å <sup>-1</sup> )	4.0–17.5 <sup>b</sup>	10.0–30.0 <sup>c</sup>
Number of plates	4	5

<sup>a</sup> From zinc oxide diffraction patterns. <sup>b</sup> In intervals of  $\Delta s=0.125 \text{ \AA}^{-1}$ . <sup>c</sup> In intervals of  $s=0.25 \text{ \AA}^{-1}$ .

mials to the intensities from each plate and it was adjusted several times according to the different theoretical molecular intensities.<sup>10</sup> The agreement between the molecular intensities from each plate of the same camera distance was satisfactory. The standard deviations at each point of the average intensities and the weighted agreement factor  $R_2$  according to eqn. (16) of Ref. 11 were estimated. In this way values of  $R_2$  of 4.2 and 12.7 % were obtained for the average intensities of the data from the long and the short camera distances, respectively.

Least-squares refinements were carried out on the average molecular intensities keeping the data from each camera distance separated. The diagonal part of the weight matrix was estimated from the standard deviations of the average

intensities. In the final refinements nondiagonal elements typical for data from the Oslo apparatus were included in the weight matrix.<sup>11</sup>

#### ESTIMATES OF *u*- AND *D*-VALUES

The root mean-square amplitudes of vibrations *u* and the correction terms between the electron diffraction distances and the distances between the thermal average atomic positions, the *D*-values, were estimated from simple valence force fields. From the valence force field the symmetry force field and the transformation matrix (*L* matrix) between the symmetry and the normal coordinates were obtained.<sup>12</sup> The valence force constants were then adjusted to agree with the

**Table 2.** Estimated *u*- and *D*-values (Å) for molybdenum pentachloride at 115 °C. For naming of configurations and atoms, see Fig. 1.

Con-figuration	Distance	A <sup>a</sup>		B <sup>b</sup>	
		<i>u</i>	<i>D</i>	<i>u</i>	<i>D</i>
<i>C</i> <sub>4v</sub>	Mo–Cl <sub>a</sub>	0.0532	–0.0022	0.0568	–0.0015
	Mo–Cl <sub>b</sub>	0.0540	–0.0035	0.0547	–0.0036
	Cl <sub>a</sub> ···Cl <sub>b</sub>	0.1283	0.0013	0.1199	0.0009
	Cl <sub>b</sub> ···Cl <sub>b'</sub>	0.1165	–0.0018	0.1159	–0.0019
	Cl <sub>b</sub> ···Cl <sub>b''</sub>	0.0734	–0.0002	0.0863	0.0002
<i>D</i> <sub>3h</sub>	Mo–Cl <sub>eq</sub>	0.0533	–0.0054	0.0499	–0.0034
	Mo–Cl <sub>ax</sub>	0.0533	–0.0017	0.0542	–0.0056
	Cl <sub>ax</sub> ···Cl <sub>eq</sub>	0.1158	–0.0013	0.1047	0.0001
	Cl <sub>eq</sub> ···Cl <sub>eq</sub>	0.1402	0.0016	0.1347	–0.0016
	Cl <sub>ax</sub> ···Cl <sub>ax</sub>	0.0654	–0.0007	0.0754	–0.0006
<i>D</i> <sub>4d</sub>	Mo–Cl <sub>a</sub>	0.0528	–0.0163		
	Mo–Cl <sub>b</sub>	0.0541	–0.0160		
	Mo–Mo	0.0746	–0.0015		

<sup>a</sup> Estimated by J.B. and used in the following electron diffraction investigation. <sup>b</sup> Estimated by A.A.I. and V.P.S.

Table 3. Least-squares results and standard deviations for the composition and parameters of the thermal average atomic positions of the different configurations of gaseous molybdenum pentachloride at about 115 °C. For naming of configuration and chlorine atoms, see Fig. 1. The best estimate of the composition and structures is assumed to be limited by the two refinements C and D.

Con-figuration	No.	Parameter <sup>a</sup>	A	B	C	D	E
C <sub>4v</sub>	1	%	56.0(3.6)	69.4(2.2)	50.7(4.3)	55.7(3.1)	52.0(6.7)
	2	$\langle R(\text{Mo}-\text{Cl}) \rangle$	2.249(5)	2.237(3)	2.227(5)	2.230(7)	2.244(22)
	3	$\angle(\text{Cl}_a-\text{Mo}-\text{Cl}_b)$	83.3(0.8)	83.5(0.4)	83.6(0.9)	88.1(0.9)	86.8(2.1)
	4	%	44.0(3.6)	0.0	25.6(5.3)	44.3(3.1)	29.6(16.1)
D <sub>3h</sub>	5	$\Delta \equiv R(\text{Mo}-\text{Cl}_{\text{ax}}) - R(\text{Mo}-\text{Cl}_{\text{eq}})$	0.119(21)			0.064(31)	
	6	$R(\text{Mo}-\text{Cl}_{\text{eq}})$	2.227(13)			2.271(16)	
	7	$\langle R(\text{Mo}-\text{Cl}) \rangle$	2.275(13)		2.300(20)	2.297(16)	2.315(25)
	8	$\nu(\text{Cl}_{\text{ax}} \cdots \text{Cl}_{\text{eq}})$				0.358(82)	0.191(97)
	9	$\nu(\text{Cl}_{\text{eq}} \cdots \text{Cl}_{\text{eq}})$				0.245(58)	0.168(77)
D <sub>4d</sub>	10	%	0.0	30.6(2.2)	23.6(2.6)	0.0	18.4(10.7)
	11	$\langle R(\text{Mo}-\text{Cl}) \rangle$		2.313(9)	2.276(24)		2.204(21)
	12	$R(\text{Mo}-\text{Mo})$		2.637(23)	2.600(38)		2.607(46)
	13	$\angle(\text{Cl}_a-\text{Mo}-\text{Cl}_b)$		85.8(0.5)	84.4(0.8)		81.2(1.4)
	14	K <sub>1</sub>	0.713(16)	0.734(16)	0.725(15)	0.725(13)	0.731(20)
	15	K <sub>2</sub>	0.678(47)	0.693(47)	0.672(43)	0.688(40)	0.688(46)
		R <sub>long</sub>	8.2	6.4	4.4	3.9	3.6
		R <sub>short</sub>	19.4	13.2	14.5	12.9	11.9
		R <sub>tot</sub>	8.4	6.5	4.6	4.1	3.8

<sup>a</sup> R<sub>o</sub> distances (Å) and angles (°). K<sub>1</sub> and K<sub>2</sub> are scale factors for the data of the long and short camera distance, respectively. R<sub>long</sub>, R<sub>short</sub> and R<sub>tot</sub> (%) are weighted agreement factors (eqn. 16 of Ref. 11) for the long and short camera distance data and the total data, respectively.

infrared spectrum in carbon tetrachloride<sup>3b</sup> and the gas phase Raman spectrum.<sup>13</sup>

The values obtained for the different species of interest to the electron diffraction investigation are listed in Table 2. The force field of the  $D_{4d}$  dimer were uncertain and only values of the bonded distances are included in the table for this species.

For the  $D_{3h}$  and  $C_{4v}$  forms two sets of  $u$ - and  $D$ -values are given. Set A was estimated by one of us (J.B.) and used in the following electron diffraction investigation. The values of set B were computed by A.A.I. and V.P.S. and are based on an improved force field.

## THE STRUCTURE INVESTIGATION

Satisfactory agreement could not be obtained for only a  $D_{3h}$  configuration even when pseudo-rotation and/or vibronic interaction were included. The same was the case for the  $C_{4v}$  form. The agreement was greatly improved when these two forms were allowed to be present together. The difference curves of some refinements indicated that also the presence of a  $D_{4d}$  dimer should be investigated.

The problem is demonstrated by the results of the five least-squares refinements given in Table 3. The corresponding radial distribution representations are illustrated in Fig. 1.

In refinement A it is assumed that both a square pyramidal configuration ( $C_{4v}$  symmetry) and a trigonal bipyramidal form of  $D_{3h}$  symmetry are present. In refinement B the  $D_{3h}$  species is substituted by a dimer consisting of two  $C_{4v}$  parts connected by a Mo–Mo bond to a configuration of assumed  $D_{4d}$  symmetry, and in refinement C all the three species are assumed to be present.

In these three refinements the molecules are vibrating according to the  $u$ -values estimated from the spectroscopic data (Table 2). Attempts to refine the difference between the Mo–Cl<sub>a</sub>(apical) and the Mo–Cl<sub>b</sub>(basal) distances of the  $C_{4v}$  species and the  $D_{4d}$  dimer resulted in values smaller than the corresponding standard deviations. Consequently only the average value of the Mo–Cl bonds were determined for these configurations in the final refinements.

The difference between the Mo–Cl<sub>ax</sub>(axial) and the Mo–Cl<sub>eq</sub>(equatorial) distances of the  $D_{3h}$  spe-

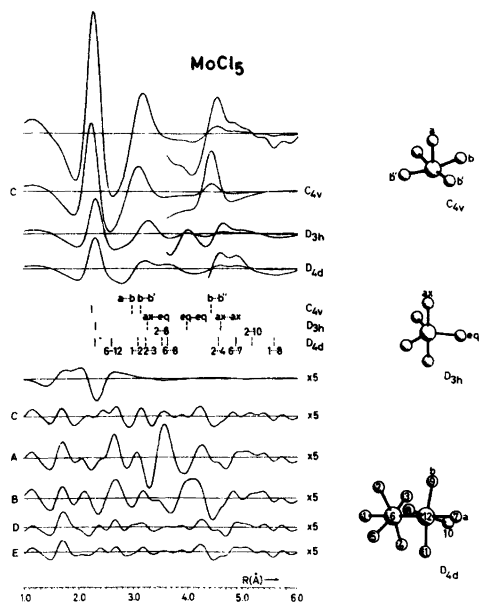


Fig. 1. The upper curve is the experimental radial distribution function of molybdenum pentachloride from the experimental  $s$ -range of 4.0–30.0  $\text{\AA}^{-1}$  and for a damping function of  $\exp(-0.005s^2)$ . Then follow corresponding theoretical functions of the three configurations according to the composition and structures of refinement C of Table 3. The distance spectra and corresponding transform of only the three atomic scattered intensities for refinement C are illustrated. The five bottom curves are the differences between the experimental and theoretical functions of the refinement C, A, B, D and E multiplied by a factor of five. The outer part of the radial distribution functions multiplied by a factor of five is also illustrated.

cies was refined when only the  $C_{4v}$  and the  $D_{3h}$  forms were assumed to be present. In the more complex problem with all three configurations present, the number of independent parameters was reduced by refining only the average Mo–Cl distance of also the  $D_{3h}$  species.

When the possible presence of a dimeric form arose in the initial refinements, also the  $D_{2h}$  symmetric dimer of solid molybdenum pentachloride was tested. This did not improve the agreement very much and resulted in unreasonable structure parameters for this configuration.

Neither refinement A nor refinement B agree satisfactorily with the experimental data. Com-

Table 4. Correlation coefficients with absolute values greater than 0.70 for the least-squares refinements A–E of Table 3. The numbering of the parameters is defined in Table 3.

A	-0.88(2,6)	-0.79(5,6)			
C	-0.87(1,4)	-0.70(3,7)	-0.73(7,11)	0.71(7,12)	
D	-0.79(2,3)	0.82(2,5)	-0.88(2,6)	0.75(3,6)	-0.93(5,6)
E	0.84(1,2)	-0.87(1,4)	0.81(1,7)	-0.74(1,9)	-0.70(1,11)
	-0.89(2,3)	-0.95(2,4)	0.85(2,7)	-0.75(2,8)	-0.78(2,9)
	-0.76(2,11)	0.85(3,4)	-0.77(3,7)	0.92(3,8)	-0.93(4,7)
	0.76(4,8)	0.84(4,9)	-0.71(7,8)	-0.81(7,9)	0.70(7,14)
	0.72(12,13)				

paring the difference curve of refinement A to the distance spectrum of the  $D_{4d}$  dimer (Fig. 1) there are indications that contributions from the Mo–Mo and the Mo(6)⋯Cl(8) distances of this dimer are missing. In the same way the difference curve of refinement B indicates the absence of contributions from the Cl<sub>eq</sub>⋯Cl<sub>eq</sub> distances of the  $D_{3h}$  configuration. Then combining these two refinements in C, the agreement is improved and it is now satisfactory in relation to the data.

However, large amplitude motions due to pseudorotation and/or vibronic interaction are possible for the monomers. In refinement D the dimer is excluded and the  $u$ -values of the Cl<sub>ax</sub>⋯Cl<sub>eq</sub> and the Cl<sub>eq</sub>⋯Cl<sub>eq</sub> distances of the  $D_{3h}$  configuration are determined. Attempts to determine the vibrational amplitude of also the Cl<sub>ax</sub>⋯Cl<sub>ax</sub> distance resulted in a very large standard deviation for this parameter and the agreement was not significantly improved.

In refinements corresponding to D the non-bonded  $u$ -values of the  $C_{4v}$  species were varied in addition to the other parameters. These non-bonded amplitudes of the  $C_{4v}$  configuration converged to values very close to the values estimated from the spectroscopic data and the results of these refinements differ very little from the results of refinement D. The two models from refinement C and D were then combined in refinement E.

The theoretical intensities of the least-squares refinements of Table 3 all include contributions from three atomic scattering according to the ITP<sub>2</sub> approximation.<sup>14</sup> The Fourier sine transform of only these intensities for the parameters of refinement C is included in Fig. 1. Leaving these intensities out without changing the parameters,  $R_{\text{tot}}$  increased to 5.8 % for this refinement.

The correlation coefficients of the least-squares parameters with absolute value larger than 0.70 are listed in Table 4.

## RESULTS AND DISCUSSION

Both the presence of the three configurations of refinement C and the combination in refinement D of the  $C_{4v}$  configuration and a  $D_{3h}$  species exhibiting a large amplitude motion agree satisfactorily with the data. Combining these two models in refinement E, several of the parameters are strongly correlated, some of the standard deviations are large and the agreement factors are probably too small compared to the values 4.2 and 12.7 % estimated for the average intensities from the reproducibility of the experiment. No significant additional information is obtained by this refinement, and the data are not sufficiently accurate to discriminate between the two models of refinements C and D.

Then the best estimate is that the composition and molecular structures are somewhere in between the limits set by refinement C and refinement D with both of these limits included. Accordingly the different standard deviations of Table 3 are meaningful only in connection with the different assumptions of the specific refinement. For example refinement C results in 23.6 % of the  $D_{4d}$  dimer with a standard deviation of 2.6 % while according to refinement D this dimer is not present at all.

The most abundant configuration is the square pyramidal  $C_{4v}$  species with an average Mo–Cl distance of 2.23 Å or 0.05 Å shorter than the average Nb–Cl distance of NbCl<sub>5</sub>.<sup>1</sup> The single bond radius of molybdenum is, according to Pauling, 1.296 Å with the niobium value 0.046 Å longer.<sup>15</sup>

The less abundant  $D_{3h}$  species has an average Mo–Cl bond about 0.07 Å longer than the  $C_{4v}$  form. The possible large amplitude motion of the  $D_{3h}$  configuration according to refinement D could be explained by a pseudoration against a quite low barrier and/or by vibronic interactions.<sup>3</sup> Since the vibrational amplitudes of the  $C_{4v}$  species seem to agree with the amplitudes estimated for small harmonic vibrations, the energy barrier between the  $C_{4v}$  and the  $D_{3h}$  forms should be relatively high and the possible large amplitude motion of the  $D_{3h}$  configuration does not seem to involve the  $C_{4v}$  species.

The Mo–Mo bondlength obtained for the  $D_{4d}$  dimer of about 2.60 Å is not inconsistent with the single bond radius of the element, and the presence of this species cannot be excluded because of an unreasonable structure.

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