Electron Diffraction Data of Gaseous Molybdenum Pentachloride Agreeing with C_s Symmetric Coordinations Based on a Distorted Prism

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A recent electron diffraction investigation found a trigonal prismatic coordination for gaseous hexamethyltungsten. Removing one ligand from a D_{3h} symmetric prism, distorted prismatic geometries of C_s symmetry seem possible for a pentasubstituted compound. Only five of the seven geometrical parameters of a C_s configuration for molybdenum pentachloride could be determined. Two different distortions of the prismatic configuration both fitted the data equally well and as well as possible. Common to these configurations was the same rectangular and close-to-square arrangement of four chlorine atoms. The results may be described either as distorted prismatic configurations or as distorted C_{4v} geometries; the distortion of the prism is actually toward the C_{4v} square pyramid.

In a joint Soviet–Norwegian gas electron diffraction (GED) cooperation several Group V pentahalides and oligomeric pentafluorides have been investigated.[1] In this connection the structural problem of free molybdenum pentachloride was initiated in 1976, and since then data for this molecule have been analyzed periodically both in Moscow and in Oslo without obtaining simple and convincing results.

Conclusions up to 1983 have been published.[2] In 1984 a GED investigation showed that CrF$_5$ has a rigid C_{2v} symmetric structure somewhat distorted from the D_{3h} configuration of the trigonal bipyramid,[3] and in 1985 a spectroscopic investigation indicated that CrF$_5$ might disproportionate into CrF$_4$ and CrF$_6$.[4]

In view of these results for a related compound, several new models for molybdenum pentachloride were tried during 1987; however, no obviously correct structure was obtained.[5] Ab initio calculations during 1989 suggested that a C_{4v} configuration for molybdenum pentachloride was "highly unlikely".[6]

Following this, a GED investigation found a trigonal prismatic coordination of D_{3h} symmetry in hexamethyltungsten.[7] The possibility of prismatic D_{3h} structures of d^0 ML$_6$ complexes have been confirmed by ab initio calculations.[8]

In view of the prismatic structure of WMe$_6$ it seemed worthwhile to try corresponding configurations of MoCl$_5$. If one ligand at a corner of a prism is removed, distorted trigonal coordinations should be expected. How the detailed distortion should take place is uncertain, but a configuration of C_s symmetry would be expected. In the following, this approach to the structure of free molybdenum pentachloride is described.

Structure investigation

Data. $sM(s)$ molecular intensities from plates recorded at Moscow State University at a nozzle temperature of 115 °C were applied. The experimental conditions and data reduction have been described,[2] and the molecular intensities previously obtained could be applied without further background corrections. Deviations of the intensities from a single plate to the averages of the four and five plates from the long and short camera distances, respectively, gave values of 4.2 and 12.7 % for the agreement parameter R_2.[9]

Initial refinements. In a least-squares fit which was unconstrained by a geometrical model, four distances with the multiplicity of a trigonal bipyramid and their corresponding vibrational amplitudes gave agreement parameters of 3.9 and 12.9 %.[5] The amplitude obtained for the Mo–Cl distance was 0.060(1) Å, a value somewhat larger than that
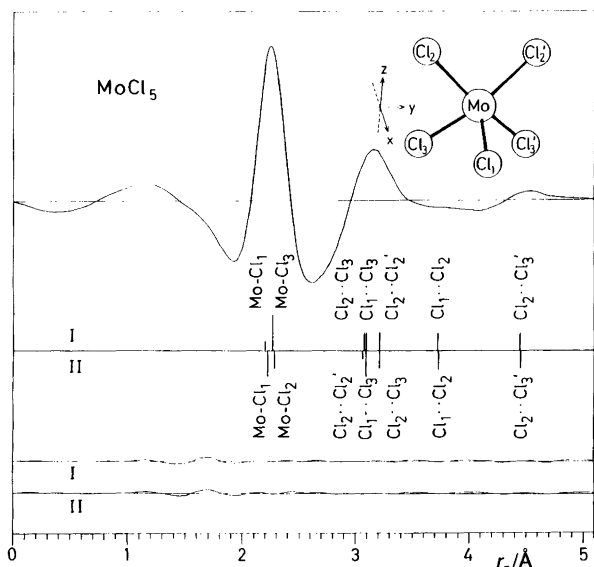
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Fig. 1. Experimental radial distribution function of MoCl₅. The distance spectra and difference curves of the two refinements are included.

Table 1. Root mean-square amplitudes of vibration l and correction terms K and D in Å at 115°C.

	l^a	K^a	l^b	D^c
Mo–Cl₃	0.0541	0.0049		−0.0036
Mo–Cl₁	0.0529	0.0034		−0.0022
Mo–Cl₂	0.0544	0.0047		−0.0034
Cl₂···Cl₂′	0.1189	0.0065		−0.0019
Cl₃···Cl₃′	0.1197	0.0062		−0.0016
Cl₁···Cl₃	0.1261	0.0040		0.0012
Cl₂···Cl₃	0.1195	0.0060		−0.0016
Cl₁···Cl₂	0.1093	0.0031	0.241(0.012)	0.0125
Cl₂···Cl₃′	0.0797	0.0015	0.169(0.007)	0.0049

[a]Estimated from vibrational frequencies. [b]Experimental values. [c]Applied values.

The average electron diffraction distances r_a are related to the distances between the average atomic positions r_α by

$$r_\alpha = r_a + \frac{l^2}{r} - K = r_a + D \tag{1}$$

eqn. (1).[12] For small harmonic vibrations the distances r_α should be consistent with the geometry. In the following refinements the spectroscopic l-values were applied, except for the two distances previously mentioned. The spectroscopic K-values were used for all the distances while the values of D for the latter two distances were based on the electron diffraction vibrational amplitudes.

Geometrical parameters. The geometry was described by the eight parameters defined in Table 2. The parameters θ and φ are spherical polar angles, except for $\theta(Cl_1)$ and $\theta(Cl_3)$, which are angles between the corresponding Mo–Cl bonds and the negative z-axis.

The general C_s symmetric geometry needs seven parameters. In the following refinements either g_5 or g_6 was fixed at zero to anchor the molecule properly in the coordinate system.

estimated from the vibrational frequencies. This indicates the presence of slightly different Mo–Cl distances in the molecule.

The various atoms and their positions in the coordinate system are shown in Fig. 1. The Mo atom is at the origin, with Cl₁ in the symmetry plane, which is the zx plane. Cl₂ and Cl₂′ and Cl₃ and Cl₃′, respectively, are mirror images in the symmetry plane.

A C_s symmetric model with an almost rectangular arrangement of Cl₂···Cl₂′···Cl₃′···Cl₃ and for which the local symmetry of the group Mo–Cl₁···Cl₃···Cl₃′ is close to C_3 was easily fitted to the data with satisfactory agreement. Vibrational amplitudes estimated for other geometries[2] seemed to agree reasonably with the amplitudes of this model, except for the amplitudes of Cl₁···Cl₂ and Cl₂···Cl₃′. The experimental values were 0.241(0.012) and 0.169 (0.007) Å, respectively, which are somewhat larger than previous estimates from the spectra. These initial refinements also showed that the least-squares iterations would not converge if more than five geometrical parameters were refined, and that information from the data seemed exhausted at agreement parameters of about 3.9 and 12.7%.

New vibrational amplitudes and distance correction terms. The root mean-square vibrational amplitudes l and perpendicular amplitude corrections terms K were estimated for the C_s geometry with local C_3 symmetry in the same way as described earlier.[2] The values obtained from the available vibrational frequencies[10,11] are given in Table 1. The Cl₁···Cl₂ and Cl₂′···Cl₃′ l-values from the GED data do not seem to be consistent with the lowest observed frequency of 100 cm⁻¹.

Table 2. Geometrical parameters, scale factors (k) and R-values for the two refinements.

	I	II
g_1 = Mo–Cl₃/Å	2.269(1)	2.234(2)
g_2 = Mo–Cl₃ − Mo–Cl₁/Å	0.062(6)	0
g_3 = Mo–Cl₃ − Mo–Cl₂/Å	0	−0.057(4)
g_4 = θ_3/°	47.2(2)	53.2(2)
g_5 = θ_3 − θ_1/°	−24.3(3)	0
g_6 = θ_3 − θ_2/°	0	10.7(7)
g_7 = φ_3/°	104.8(6)	120
g_8 = φ_3 − φ_2/°	0	37.8(7)
k^a	0.674(4)	0.678(4)
k^b	0.614(20)	0.625(20)
R^a/%	4.0	3.9
R^b/%	12.8	12.7

[a]From data for the long camera distance. [b]From data for short camera distance.

Table 3. Distances (Å) for the two refinements.

Distance	I	II
Mo–Cl$_3$	2.269(1)	2.234(2)
Mo–Cl$_1$	2.207(5)	2.234(2)
Mo–Cl$_2$	2.269(1)	2.291(3)
Cl$_2$···Cl$_2'$	3.219(4)	3.073(22)
Cl$_3$···Cl$_3'$	3.219(4)	3.101(9)
Cl$_1$···Cl$_3$	3.105(12)	3.101(9)
Cl$_2$···Cl$_3$	3.084(10)	3.219(4)
Cl$_1$···Cl$_2$	3.736(10)	3.742(11)
Cl$_2$···Cl$_3'$	4.457(6)	4.460(5)

Table 5. Atomic coordinates (Å) for the two refinements.

Coordinate	I	II
$x(Cl_1)$	2.0932	1.7903
$z(Cl_1)$	−0.7001	−1.3370
$x(Cl_2)$	−0.4246	0.2092
$y(Cl_2)$	−1.6093	−1.5366
$z(Cl_2)$	1.5419	1.6867
$x(Cl_3)$	−0.4246	−0.8951
$y(Cl_3)$	−1.6093	−1.5504
$z(Cl_3)$	−1.5419	−1.3370

Refinements I and II. The initial refinements showed that only five geometrical parameters could be determined simultaneously in a least-squares refinement. The complete C_s geometry is described by seven parameters. Accordingly the complete determination of a general C_s symmetric structure from the electron diffraction data is impossible. However, if the structure of molybdenum pentachloride is based on a distorted prism, two limiting distortions may be envisaged. (I) The rectangular arrangement of Cl$_2$···Cl$_2'$··· Cl$_3'$···Cl$_3$ remains intact from the original prism, and only the atom Cl$_1$ is distorted. If the molecule is fixed to the coordinate system by $g_6 = 0$, then $g_3 = 0$ and $g_8 = 0$ are consistent with this geometry, and the five parameters left can be determined by the least-squares method. (II) The group Mo–Cl$_1$···Cl$_3$···Cl$_3'$ has kept the local C_3 symmetry of the prism, and the distortion is taken care of by Cl$_2$ (and Cl$_2'$). The molecule is then fixed in the coordinate system by $g_5 = 0$. $g_2 = 0$ and $g_7 = 120°$ are consistent with this geometry and again five geometrical parameters are left to be refined.

The r_α-parameters according to the D-values of Table 1 for these two refinements are given in the Tables 2–5. The numbers in parenthesis are uncorrected standard deviations obtained in the least-squares refinements. Some correlation coefficients are listed in Table 6, and the experimental radial distribution function, the distance spectra and the difference curves of the two refinements are illustrated in Fig. 1.

Table 4. Angles (°) from the two refinements.

Angle	I	II
Cl$_3$–Mo–Cl$_1$	87.8(4)	87.9(3)
Cl$_3$–Mo–Cl$_3'$	90.4(1)	87.9(3)
Cl$_2$–Mo–Cl$_2'$	90.4(1)	84.2(8)
Cl$_2$–Mo–Cl$_3$	85.6(4)	90.7(1)
Cl$_1$–Mo–Cl$_2$	113.1(5)	111.6(5)
Cl$_2$–Mo–Cl$_3'$	158.4(9)	160.5(7)
Cl$_2$···Cl$_3$···Cl$_3'$	90	89.8(3)
Cl$_2'$···Cl$_2$···Cl$_3$	90	90.2(3)

Discussion

The possibility of a distorted prismatic configuration of free molybdenum pentachloride was based on the observed D_{3h} symmetric prism of hexamethyltungsten.[7] The general distorted prismatic configuration of a pentasubstituted compound should have a C_s symmetric geometry determined by seven parameters. From the electron diffraction data a maximum of five geometrical parameters could be determined simultaneously. This is demonstrated by the results of refinements I and II; the two different refinements of five parameters not only fit the data equally well but also as well as possible.

The two refinements are both based on distorted prismatic configurations in which one atom at a time takes care of the whole possible distortion, thereby reducing the structure problem to five geometrical parameters. In refinement I the rectangular arrangement of Cl$_2$···Cl$_2'$···Cl$_3'$···Cl$_3$ is conserved, and the Cl$_1$ atom is free to move in the symmetry plane. The local C_3 symmetry of the Mo–Cl$_3$···Cl$_3'$···Cl$_1$ group is maintained in refinement II. Here Cl$_2$ (and Cl$_2'$) takes care of the distortion.

The Cl$_2$···Cl$_2'$···Cl$_3'$···Cl$_3$ arrangements obtained in the two refinements are compared in Fig. 2. Within 0.02 Å and 0.2°, the two arrangements are rectangular and identical. The main difference between the two refinements is the relative orientation of the symmetry plane, including the Cl$_1$ atom and the long and short sides of the rectangle.
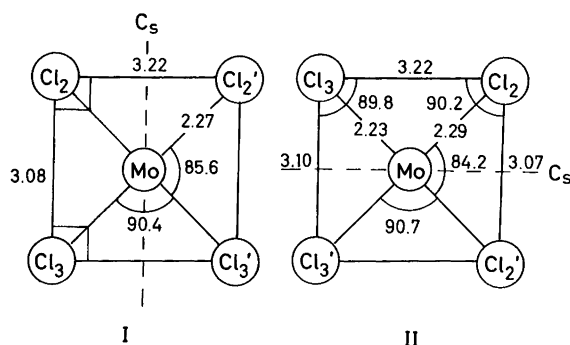

Fig. 2. Comparison of Cl$_2$···Cl$_2'$···Cl$_3'$···Cl$_3$ arrangements of refinements I and II. Note the relative rotation of the arrangements.

Table 6. Correlation coefficients with absolute values greater than 0.70 for the two refinements. The parameters are defined in Table 2.

Refinement I:

$0.94(g_1, g_2)$	$0.91(g_4, g_7)$	$0.75(k,^a g_1)$	$0.79(k,^a g_2)$

Refinement II:

$0.97(g_1, g_3)$	$0.97(g_4, g_6)$	$-0.77(k,^a g_1)$	$-0.79(k,^a g_3)$
$-0.76(g_4, g_8)$	$-0.83(g_6, g_8)$		

In WMe_6 the angle between the W–C bond and the threefold symmetry axis is 52.0°. The corresponding angle of $Mo–Cl_5$ obtained in refinement II is 53.2°. The two smallest C–W–C bond angles of WMe_6 are 76.1 and 86.0°, respectively, with the largest angle between any two of the three bonds to the same equilateral triangle. The corresponding Cl–Mo–Cl angles of the two refinements span the range 84.2–90.7°. The sides of the equilateral triangles of WMe_6 are 0.3 Å longer than the edges of the prism. The ratio of the long and short sides of the rectangles of WMe_6 is 1.11, which should be compared with the ratio of 1.05 in $MoCl_5$. The rectangular arrangement is closer to a square, and the bond angles are larger, in $MoCl_5$ than in WMe_6. The increased bond angles in the pentasubstituted compound seem reasonable in view of the increased space on the coordination sphere.

The two sides of the $Cl_2 \cdots Cl_2' \cdots Cl_3' \cdots Cl_3$ rectangle of $MoCl_5$ differ by only about 5 %, and the angles between the $Mo–Cl_1$ bond and the normal of the rectangle are 18.5 and 16.7° from refinements I and II, respectively. This angle is 38.0° in WMe_6. Accordingly, the results of the two refinements may be characterized by a distortion from the regular trigonal prism towards a C_{4v} square pyramid.

The conclusions from refinements I and II and from this discussion are that C_s symmetric models fit the data for $MoCl_5$, that all the parameters of the C_s geometry cannot be determined, and that four of the chlorine atoms are in a close-to-rectangular arrangement, with small deviations from a square. Comparing the results with the prismatic WMe_6, the conformation of $MoCl_5$ may be described as a distortion of a trigonal prism toward a square pyramid.

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