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Molecular structures of the sixth period metal pentachlorides, MCl_5 (M = Ta, W or Re), determined by gas electron diffraction; is Jahn–Teller distortion of WCl_5 quenched by spin–orbit coupling?

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The molecular structure of $TaCl_5$ has been optimised under D_{3h} symmetry by density-functional theory calculations. Calculation of the molecular force field and vibrational frequencies showed that the optimised structure corresponds to a minimum on the full potential energy surface. Gas electron diffraction data of MCl_5 (M = Ta, W or Re), recorded with nozzle temperatures ranging from 130 to 210 °C, showed that WCl_5 and $ReCl_5$ are trigonal bipyramidal like $TaCl_5$. Structure refinements based on molecular models of D_{3h} symmetry lead to satisfactory agreement between experimental and calculated intensities for each compound and yield the M−Cl bond distances (ax/eq): Ta 231.3(5)/226.6(4); W 229.1(4)/224.1(5); Re 226.2(12)/223.7(7) pm. Tungsten pentachloride is a d^1 compound and might have exhibited dynamic or static Jahn–Teller distortion from D_{3h} symmetry; it has been suggested that such distortion is quenched by strong spin–orbit coupling.

The global minima on the potential energy surfaces of five-co-ordinate d^0 transition-metal compounds may correspond to trigonal bipyramidal or to square pyramidal equilibrium structures. Thus $TaMe_5$[1,2] and $Ta(NMe_2)_5$[3] are square pyramidal in the gas phase, while the five d^0 pentahalides VF_5, $NbCl_5$, $NbBr_5$, $TaCl_5$ and $TaBr_5$ all are trigonal bipyramidal (*TBPY*).[4] These pentahalides are, however, far from rigid, the barriers to Berry pseudo-rotation over square pyramidal transition states are probably all less than 20 kJ mol^{-1}.

Gas electron diffraction (GED) data for $TaCl_5$ recorded by Ischenko *et al.*[5] were consistent with molecular models of D_{3h} symmetry with axial Ta−Cl bonds 14.2(6) pm longer than the equatorial. The barrier to Berry pseudo-rotation over a C_{4v} transition state was estimated as 5.0(2.5) kJ mol^{-1}. Kang *et al.*[2] have published the results of extensive Hartree–Fock (HF) *ab initio* calculations on $TaCl_5$. A careful search of the potential energy surface yielded only those minima corresponding to D_{3h} equilibrium structures. An optimised C_{4v} model about 7 kJ mol^{-1} above the minimum was found to correspond to a transition state. The mean M−Cl bond distance for the D_{3h} structure was in reasonable agreement with experiment, but the difference between axial and equatorial bonds, 4.3 pm, was less than a third of the experimental estimate.

Two d^1 transition-metal pentahalides have been characterised structurally by GED and high level quantum chemical calculations: experiment and calculations agree that the co-ordination geometries of CrF_5[6,7] and $MoCl_5$[8] are best described as *TBPY*, but both compounds exhibit considerable dynamic Jahn–Teller distortion from ideal D_{3h} symmetry. Tungsten pentachloride does not appear to have been studied by computational methods; the authors of a GED investigation were unable to distinguish between molecular models of D_{3h} or C_{4v} symmetry, and suggested that the equilibrium structure is square pyramidal with a very low barrier to pseudo-rotation over *TBPY* transition states.[9]

Here we report the results of the GED investigation of a d^2 pentahalide, $ReCl_5$, and a reinvestigation of the d^1 compound WCl_5. We have also repeated the GED study of $TaCl_5$, partly in order to shed light on the discrepancy between calculations and experiment regarding the magnitude of the difference between axial and equatorial M−Cl bond distances, and partly to obtain a background against which we could evaluate indications for deviation from D_{3h} symmetry in WCl_5 and $ReCl_5$. The GED investigations were supplemented by density-functional theory (DFT) calculations of the molecular structure, force field, vibrational spectra and vibrational correction terms for $TaCl_5$.

Density-functional Theory Calculations

The calculations were performed by the program system ADF developed by Baerends and co-workers.[10,11] The atomic core orbitals up to and including 2p for Cl and up to and including 5p for Ta were frozen in their atomic shape. The valence shells of both atoms were described by double ζ bases: Basis set II for Ta and Basis set III for Cl.[12] The latter includes a polarisation function.

The Vosko–Wilk–Nusair parametrisations[13] with the gradient correction of Becke[14] for exchange and of Perdew[15] for correlation were used for the exchange and correlation energies. The corrections were added self consistently. The accuracy of the integration was adjusted to yield a numerical noise level lower than 0.1 kJ mol^{-1}.[11]

The structure of $TaCl_5$ was optimised under D_{3h} symmetry. Force constants were calculated numerically from analytical

Table 1 Normal modes of gaseous $TaCl_5$ obtained experimentally by IR or Raman (R) spectroscopy or computationally by Hartree–Fock (HF) or DFT calculations

			$\tilde{\nu}$/cm^{-1}			
			Experimental		Calculated	
Mode	Symmetry	Activity	R[a]	IR[b]	HF[c]	DFT
1	A_1'	R	406	—	388	402
2	A_1'	R	324	—	306	324
3	A_2''	IR	—	371	364	344
4	A_2''	IR	—	155	172	153
5	E′	R + IR	—	402	391	395
6	E′	R + IR	127[d]	—	140	124
7	E′	R + IR	54	—	56	57
8	E″	R	181[d]	—	192	194

[a] Ref. 16. [b] Ref. 17. [c] Ref. 2. [d] The assignments of ν_6 and ν_8 have been exchanged.

Table 2 Vibrational correction terms (*D*) and root-mean-square vibrational amplitudes (*l*) of $TaCl_5$ at 131 °C calculated from the DFT force field, and vibrational amplitudes from gas electron diffraction (refinement scheme 3). All values in pm

	D	*l*(DFT)	*l*(GED)
$Ta-Cl_{ax}$	−1.03	5.6	5.9(2)
$Ta-Cl_{eq}$	−1.00	5.3	5.9(2)
$Cl_{ax}\cdots Cl_{eq}$	−1.16	13.9	13.5(2)
$Cl_{eq}\cdots Cl_{eq}$	0.30	19.4	20.3(8)
$Cl_{ax}\cdots Cl_{ax}$	−0.13	7.2	8.6(15)

Table 3 Information on the GED experiment and data processing

	$TaCl_5$		WCl_5		$ReCl_5$	
Nozzle temperature/°C	131 ± 2		207 ± 7		175 ± 5	
Inlet system	Brass/steel		Steel		Brass/steel	
Microdensitometer	Joyce–Loebl		Snoopy		Joyce–Loebl	
Nozzle-to-plate distances/cm	50	25	50	25	50	25
Number of plates	4	4	6	2	4	3
Background polynomials/°	8	12	9	12	7	10
Least-squares weights	1.00	0.25	1.00	0.40	1.00	0.70

Table 4 *R* Factors obtained in least-squares refinements of the molecular structures of $TaCl_5$, WCl_5 and $ReCl_5$ based on GED data *

Compound	$TaCl_5$		WCl_5		$ReCl_5$	
Symmetry	D_{3h}	C_{2v}	D_{3h}	C_{2v}	D_{3h}	C_{2v}
R Factors						
Refinement scheme 1. Without vibrational correction terms	4.6	4.2	4.0	3.9	6.5	6.1
Refinement scheme 2. Vibrational correction terms, $D_{i,j}$, included	4.5	4.3	3.7	3.7	6.0	5.9
Refinement scheme 3. Vibrational correction terms included, phase angles, $\eta_M(s)$, tuned	3.5	3.3	3.7	3.5	5.9	5.9

* $R = [\Sigma w(I_{obs} - I_{calc})^2/\Sigma w(I_{obs})^2]^{\frac{1}{2}}$.

gradients and confirmed that the optimal structure corresponded to a minimum on the potential energy surface. The vibrational frequencies are listed in Table 1. Root-mean-square (r.m.s.) vibrational amplitudes, *l*, and vibrational correction terms, $D = r_\alpha - r_a$, calculated by the program ASYM20[18] are listed in Table 2.

Experimental

Tantalum pentachloride with stated purity better than 99.9% was purchased from Fluka, WCl_5 was prepared and characterised as previously described,[19] $ReCl_5$ was prepared by standard procedures[20] and the purity checked by quantitative analysis for Cl.

Gas electron diffraction

Tungsten pentachloride and $ReCl_5$ are extremely sensitive to oxygen, and volatile oxytetrachlorides, $MOCl_4$, are easily formed.[21] Preliminary GED data yielded radial distribution curves containing distinct peaks corresponding to M=O bond distances below $r = 180$ pm. New GED data were therefore recorded after the samples had been preheated in the inlet system of the diffraction unit under high vacuum at 140 °C for 1 h.

The gas electron diffraction data were recorded on a Balzers Eldigraph KDG-2 instrument.[22] Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. Information about nozzle temperatures, inlet systems, microdensitometers and the number of plates used is given in Table 3. Optical densities were processed with programs written by Strand and coworkers.[23] Atomic scattering factors were taken from ref. 24. Backgrounds were drawn at least-squares adjusted polynomials to the difference between total experimental and calculated molecular intensities.[25] The polynomial degrees are listed in Table 3.

While the photographic plates recorded with nozzle-to-plate distances of 25 cm yielded good intensity data for $TaCl_5$ out to $s = 280$ nm^{-1}, the molecular intensities of WCl_5 and $ReCl_5$ were lost in noise beyond $s = 200$ nm^{-1}. Several attempts were made to obtain better data, but without success. The truncated intensity data of WCl_5 yielded *R* factors similar to those obtained for $TaCl_5$, while the *R* factors obtained with the truncated data for $ReCl_5$ were higher, see Table 4. The final modified molecular intensity curves are displayed in Fig. 1.

Structure refinements

Least-squares structures refinements with diagonal weight matrices were carried out with the program KCED26.[26] The weights of the 25 cm data (Table 3) were adjusted for each compound to yield error-square sums for 50 and 25 cm curves proportional to the number of intensity points.

Each of the three molecules was subjected to a series of refinements under both D_{3h} and C_{2v} symmetry. The D_{3h} model is completely characterised by the two bond distances. The vibrational amplitudes of the bond distances were assumed equal.

The symmetry axis of the C_{2v} model coincides with one of the equatorial M–Cl bonds. The Cl atom on the symmetry axis was denoted by Cl_{e1}, the two others by Cl_{e2} and Cl_{e2}'. The angle spanned by the two axial Cl atoms is allowed to deviate from 180°, and the angle spanned by the symmetry-equivalent Cl_{e2} and Cl_{e2}' atoms from 120°. The three equatorial M–Cl bonds were, however, constrained to the same length, and the number of vibrational amplitudes to be refined was kept unaltered by assigning the same amplitude to similar $Cl\cdots Cl$ distances.

The *R* factors obtained under the following refinement schemes are listed in Table 4. Refinement scheme 1: these refinements were carried out without corrections for thermal vibrations. For the D_{3h} models the two bond distances, four vibrational amplitudes and two scale factors were refined simultaneously. For the C_{2v} models the two bond distances, the two valence angles, four vibrational amplitudes and two scale factors were refined simultaneously for $TaCl_5$. Refinement of ten parameters proved impossible for WCl_5 and $ReCl_5$, and one (WCl_5) or two ($ReCl_5$) $Cl\cdots Cl$ amplitudes were constrained as indicated in Table 5.

Refinement scheme 2: these refinements were carried out with the inclusion of thermal correction terms, $D = r_\alpha - r_a$. The vibrational correction terms calculated for the optimised D_{3h} model of $TaCl_5$ are listed in Table 2. We are not aware of any experimental study of the vibrational spectra of gaseous WCl_5

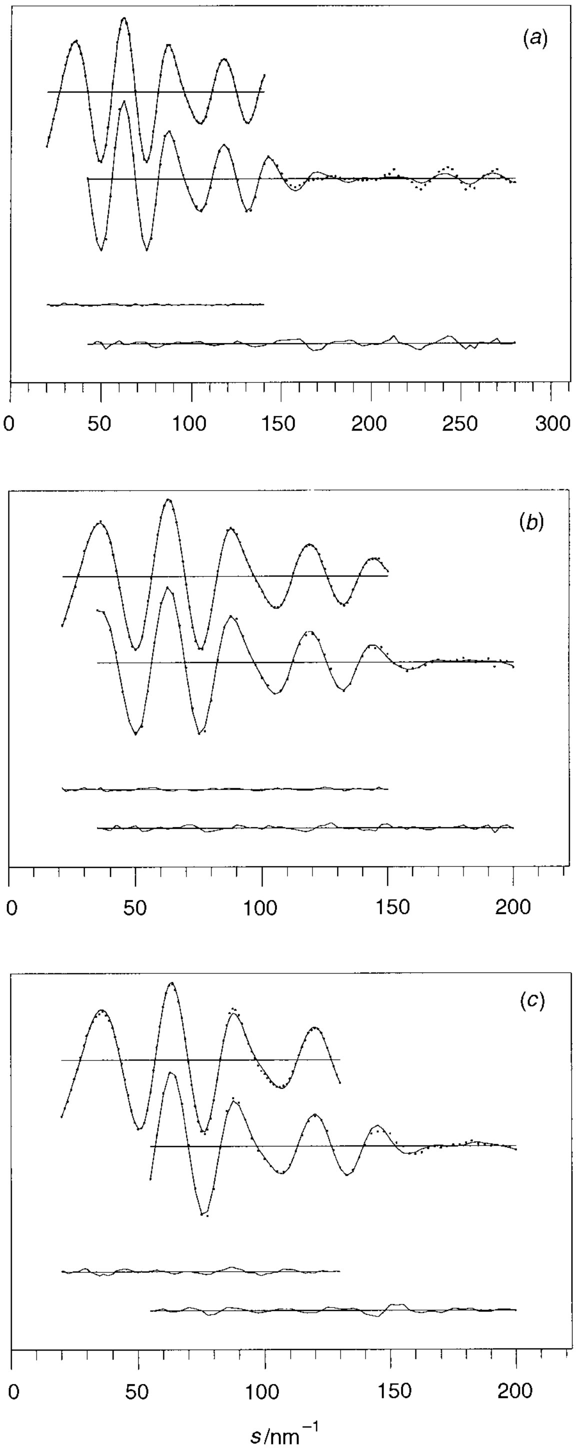
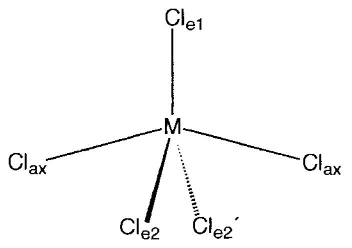


Fig. 1 Experimental modified molecular intensity curves (●) for MCl_5 [M = Ta (*a*), W (*b*) or Re (*c*)] obtained with nozzle-to-plate distances of 50 and 25 cm and modified molecular intensity curves (—) calculated for structure parameters obtained by least-squares refinements of molecular models of D_{3h} symmetry (refinement scheme 3), see Table 5

or $ReCl_5$, and DFT calculations of molecular force fields were beyond our computational resources. The close similarities of the molecular structures and of the r.m.s. vibrational amplitudes obtained from the GED data suggest, however, that the force fields of WCl_5 and $ReCl_5$ are similar to that of $TaCl_5$. The correction terms listed in Table 2 were therefore used for the D_{3h} model of each compound. As indicated in Table 4, introduction of the vibrational correction terms led to slight improvement of the fit.

The structure parameters obtained for C_{2v} models under refinement scheme 1 indicated only small deviations from D_{3h} symmetry. We decided, therefore, to repeat the refinements with inclusion of the D_{3h} correction terms. This led to a marginally poorer fit for $TaCl_5$ and a marginally better fit for WCl_5 and $ReCl_5$, see Table 4.



Refinement scheme 3: in the past GED studies of compounds containing Sixth Period elements we have often found disagreement between calculated and experimental intensity curves in the region of the 'beat-out', *i.e.* the region where the factor depending on the phase angles of the atomic scattering factors, $\cos[\eta_M(s) - \eta_{Cl}(s)]$, is equal to zero. Experience has shown that the disagreement may be partly removed by tuning the phase angle of the metal atom, $\eta_M(s)$, through multiplication with an adjustable constant. In the present study the optimal value of the constant was 1.035 for Ta, 1.048 for W and 1.045 for Re. The refinements under scheme 3 were carried out with tuned phase angles and inclusion of thermal correction terms. Tuning of the phase angle led to a significant improvement of the fit for $TaCl_5$, but left the fit obtained for WCl_5 and $ReCl_5$ largely unaffected.

Structure refinements under each scheme were carried out for starting models with axial bonds longer or shorter than the equatorial ones. In each case these refinements converged to models in which the axial bonds were longer. Comparison of the results showed that the structural parameters obtained were insensitive to the refinement scheme. The structure parameters obtained under scheme 3 are listed in Table 5.

Refinements were also carried out with inclusion of three-atom scattering calculated with a program developed by Miller and Bartell[27] and modified by Mawhorter and coworkers.[28] For $TaCl_5$ the agreement thus obtained was as good as that obtained by tuning of the phase angle $\eta_M(s)$, for WCl_5 and $ReCl_5$ the agreement was poorer. The structure parameters obtained by inclusion of three-atom scattering were not significantly different from those obtained under scheme 3.

Results and Discussion

Our DFT calculations on $TaCl_5$, as well as the HF calculations published by Kang *et al.*,[2] indicate that the D_{3h} model corresponds to a minimum on the potential energy surface and the calculated vibrational frequencies are in good agreement with experimental IR[17] and Raman[16] spectra, see Table 1. The low barrier to Berry pseudo-rotation over C_{4v} transition states obtained by the HF calculations, 7 kJ mol^{-1},[2] the low frequency of the degenerate deformation mode $\nu_7 = 57$ cm^{-1} and the large r.m.s. vibrational amplitudes, in particular the amplitude $l(Cl_{eq} \cdots Cl_{eq}) = 19.4$ pm, all indicate that the molecule undergoes large-amplitude deformation vibrations.

Experimental radial distribution curves of $TaCl_5$, WCl_5 and $ReCl_5$ are shown in Fig. 2. Each curve contains an unresolved peak representing five M–Cl bond distances between 225 and 230 pm, followed by three distinct peaks at positions corresponding to non-bonded $Cl \cdots Cl$ distances spanning Cl–M–Cl angles of 90, 120 and 180°, and relative areas consistent with multiplicities of 6 : 3 : 1. The close similarity of the curves shows that WCl_5 and $ReCl_5$ must be trigonal bipyramidal like their Ta analogue. Rhenium pentachloride is a d^2 compound and a D_{3h} structure is not expected to be orbitally degenerate or

Table 5 Structure parameters of $TaCl_5$, WCl_5 and $ReCl_5$ obtained under refinement scheme 3. Distances and vibrational amplitudes in pm, angles in °, e.s.d.s in parentheses and non-refined parameters in square brackets

Compound	$TaCl_5$		WCl_5		$ReCl_5$	
Symmetry	D_{3h}	C_{2v}	D_{3h}	C_{2v}	D_{3h}	C_{2v}
Bond distances (r_a)						
$M{-}Cl_{ax}$	231.3(5)	230.9(6)	229.1(4)	229.8(6)	226.2(12)	226.3
$M{-}Cl_{eq}$	226.6(4)	227.0(4)	224.1(5)	223.7(4)	223.7(7)	223.6
M−Cl(mean)	228.5(2)		226.1(2)		224.8(3)	
Δ(M−Cl)[a]	4.7(7)		5.1(8)		2.6(7)	
Valence angles (α)						
$Cl_{ax}{-}M{-}Cl_{ax}$	[180]	180(3)	[180]	173(2)[b]	[180]	177(2)
$Cl_{e2}{-}M{-}Cl_{e2}'$	[120]	128.8(13)[b]	[120]	118(4)	[120]	116(5)
Vibrational amplitudes						
$l(M{-}Cl_{ax})$	5.9(2)	6.1(2)	5.9(3)	5.7(3)	5.2(6)	5.5(5)
$l(Cl_{ax}\cdots Cl_{eq})$	13.5(2)	13.5(2)	13.8(3)	11.9(9)	11.4(2)	[11.4]
$l(Cl_{eq}\cdots Cl_{eq})$	20.3(8)	16(2)	19.1(9)	[19.1]	20(2)	[20]
$l(Cl_{ax}\cdots Cl_{ax})$	8.6(15)	8.4(15)	9(2)	9(2)	10(3)	11(3)

[a] $\Delta(M{-}Cl) = r(M{-}Cl_{ax}) - r(M{-}Cl_{eq})$. [b] See text.

Jahn–Teller active. Tungsten pentachloride, however, is d^1 and might show static or dynamic distortions from D_{3h} symmetry: evidence for such distortions has been found in GED studies of the d^1 compounds CrF_5 and $MoCl_5$.[6,8]

Under the circumstances, we could have chosen to refine the molecular structures of the Ta and Re pentachlorides under D_{3h} symmetry only, while the structure of WCl_5 was refined under C_{2v} symmetry. All workers in the field know, however, that it is often difficult to decide whether a small deviation from ideal symmetry is real or not: reducing the molecular symmetry from D_{3h} to C_{2v} increases the number of independent structure parameters, and the refinement of the greater number of parameters is bound to improve the fit, but is the improvement significant? An answer to this question might be sought by examining the estimated standard deviations (e.s.d.s) of the parameters obtained in the lower symmetry refinements. Such a procedure does, however, depend on the absence of systematic errors which might be compensated by the increased number of adjustable parameters.

Gas electron diffraction provides direct information on the thermal average rather than the equilibrium structure of the molecule. Even if the equilibrium structure is highly symmetrical, say D_{3h}, a model of lower symmetry, say C_{2v}, will give a significantly better description of the thermal average structure. Vibrational effects should be eliminated through introduction of thermal correction terms, but these terms are calculated under the assumption of infinitesimal vibrations in a harmonic force field. It is not obvious that such correction terms will prove adequate for molecules that undergo large-amplitude motion on anharmonic potential energy surfaces.

We decided, therefore, to subject each pentachloride to a series of structure refinements under both D_{3h} and C_{2v} symmetry. The parameters thus obtained proved insensitive to the refinement scheme, and since the best agreement was obtained when vibrational correction terms were included and the phase angle of the metal atom, $\eta_M(s)$, was tuned through multiplication with an adjustable constant, we base our discussion on the results of refinements under scheme 3, see Table 5. The table also contains the mean M−Cl bond distances and the difference between axial and equatorial bond distances for the D_{3h} models.

Since the least-squares calculations were carried out with diagonal weight matrices, the estimated standard deviations listed in the table have been obtained from those calculated by the program (σ_{LS}) through multiplication with a factor of 2 to include the uncertainty due to data correlation[29] and further expanded to include a scale uncertainty of 0.1%. The estimated standard deviations given for the $M{-}Cl_{ax}$ and $M{-}Cl_{eq}$ bond distances and for their average are largely determined by the scale uncertainty, while the standard deviation of the relatively small difference between axial and equatorial bond distances is largely determined by σ_{LS}.

Refinement of a molecular model of D_{3h} symmetry to the GED data of $TaCl_5$ yields good agreement between experimental and calculated intensities. Vibrational amplitudes are in excellent agreement with those calculated from the DFT force field (see Table 2) and bond distances are in reasonable agreement with DFT and HF calculations: $Ta{-}Cl_{ax}/Ta{-}Cl_{eq}$ = 231.5(5)/226.6(4) pm by GED; 236.9/232.6 pm by HF; 235.4/227.7 pm by DFT. The mean Ta−Cl bond distance obtained by GED is a few pm shorter than the computed value, the difference between axial and equatorial bond distances is 4.7(6) pm by GED, 4.3 pm by HF and 7.7 by DFT.

Refinement of a C_{2v} model of $TaCl_5$ yields marginally better fit to the GED data; the R factor decreases from 3.5 to 3.3%. The value obtained for the valence angle $Cl_{ax}{-}Ta{-}Cl_{ax}$ [180(3)°] is consistent with D_{3h} symmetry, but if the estimated standard deviations are taken at their face value, the angle $Cl_{e2}{-}Ta{-}Cl_{e2}'$ [128.8(13)°] is not.

Tantalum pentachloride is a d^0 compound and no Jahn–Teller distortion is expected. Hartree–Fock and DFT calculations that yield vibrational frequencies and bond distances in good agreement with experiment indicate that the equilibrium structure has D_{3h} symmetry. We believe, therefore, that the value obtained for the angle $Cl_{e2}{-}Ta{-}Cl_{e2}'$ reflects inadequate corrections for vibrational motion in a molecule undergoing large-amplitude motion on an anharmonic potential energy surface.

Rhenium pentachloride is a d^2 compound. The two electrons presumably have parallel spins and occupy the non-bonding d_{xz} and d_{yz} atomic orbitals. The electronic ground state is then orbitally non-degenerate, and no Jahn–Teller distortion is expected. The D_{3h} and C_{2v} models are in fact in equally good agreement with the GED data. Symmetry cannot be proven, but in the absence of evidence to the contrary we conclude that the equilibrium symmetry is D_{3h}.

The unpaired electron in the d^1 compounds CrF_5 or $MoCl_5$ resides in one of the degenerate, non-bonding, d_{xz} or d_{yz} orbitals.[7,8] The degeneracy of these orbitals is lifted if the molecule is deformed to C_{2v} symmetry, and GED data for CrF_5[6] and $MoCl_5$[8] contain manifest evidence for Jahn–Teller distortion. Structure refinement of a C_{2v} model of $MoCl_5$ leads to an R factor of 3.8% as compared to 7.7% for a D_{3h} model, and yields the valence angles $Cl_{ax}{-}Mo{-}Cl_{ax}$ 167.6(2) and $Cl_{e2}{-}Mo{-}Cl_{e2}'$ 132.4(6)°.

The GED data for WCl_5, on the other hand, appear to be consistent with a D_{3h} model: refinement yields an R factor of 3.7%, essentially equal to that obtained by similar refinements

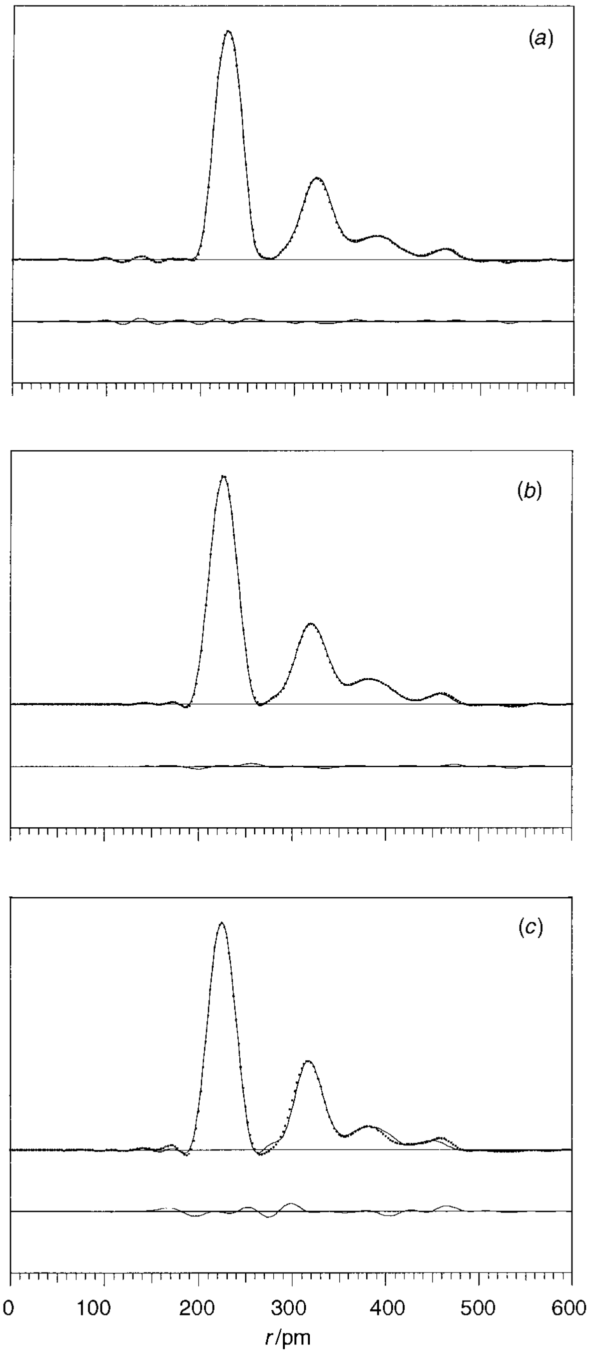


Fig. 2 Experimental radial distribution curves (●) for MCl_5 [M = Ta (*a*), W (*b*) or Re (*c*)] and radial distribution curves (—) calculated for molecular models of D_{3h} symmetry (refinement scheme 3), see Table 5. Artificial damping constant, $k = 25$ pm^2

of $TaCl_5$ (3.5%) and the vibrational amplitudes obtained for the two molecules are indistinguishable. Reduction of the symmetry of WCl_5 to C_{2v} leads to a reduction of the R factor by 0.2%, a similar reduction was observed for refinements of $TaCl_5$. The valence angle Cl_{ax}–W–Cl_{ax} thus obtained is equal to 173(2)° as compared to the D_{3h} value of 180°. Measured in multiples of the e.s.d. the deviation is, however, smaller than that obtained in the C_{2v} refinements of $TaCl_5$. Since we chose to interpret the deviation from D_{3h} symmetry in $TaCl_5$ as an artifact, we cannot interpret a smaller deviation from D_{3h} symmetry in WCl_5 as physically significant.

We conclude, therefore, that the GED data of WCl_5 are consistent with D_{3h} symmetry, and suggest that Jahn–Teller distortion is quenched by strong spin–orbit coupling.[30] The strength of such coupling increases down the triad Cr < Mo < W. The splitting between the $j = 0$ and $j = 1$ levels of the ground state ^{5}D manifold of atomic W, 20 kJ mol^{-1}, is ten times larger than the splitting between the two corresponding states of atomic Mo.[31] Hartree–Fock calculations on $MoCl_5$ indicate a Jahn–Teller stabilisation energy of 1.5 kJ mol^{-1}.[8]

Spin–orbit coupling splits the four degenerate spin orbitals, $d_{xz}\alpha$, $d_{yz}\alpha$, $d_{xz}\beta$ and $d_{yz}\beta$, into a Kramer doublet of spin orbitals, $d_{+1}\alpha$ and $d_{-1}\beta$ at higher energy and $d_{+1}\beta$ and $d_{-1}\alpha$ at lower energy. Each of the new spin orbitals corresponds to cylindrical electron density, and the degeneracy of the lower doublet is not lifted by molecular distortion to C_{2v} symmetry.

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References

1 C. Pulham, A. Haaland, A. Hammel, K. Rypdal, H. P. Verne and H. V. Volden, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1464.
2 S. K. Kang, H. Tang and T. A. Albright, *J. Am. Chem. Soc.*, 1993, **115**, 1971.
3 K. Hagen, C. J. Holwill, D. A. Rice and J. D. Runnacles, *Inorg. Chem.*, 1992, **31**, 4733.
4 M. Hargittai, in *Stereochemical Applications of Gas-Phase Electron Diffraction. Part B. Structural Information on Selected Classes of Compounds*, eds. I. Hargittai and M. Hargittai, VCH, Weinheim, 1988, p. 383.
5 A. A. Ischenko, T. G. Strand, A. V. Demidov and V. P. Spiridonov, *J. Mol. Struct.*, 1978, **43**, 227.
6 E. J. Jacob, L. Hedberg, K. Hedberg, H. Davis and G. L. Gard, *J. Phys. Chem.*, 1984, **88**, 1935.
7 L. G. Vanquickenborne, A. E. Vinckier and K. Pierloot, *Inorg. Chem.*, 1996, **35**, 1305.
8 K. Fægri, K.-G. Martinsen, T. G. Strand and H. V. Volden, *Acta Chem. Scand.*, 1993, **47**, 547.
9 Yu. S. Ezhov and A. P. Sarvin, *Zh. Strukt. Khim.*, 1983, **24**, 149.
10 Amsterdam Density Functional (ADF) Release 1.1.3, Vrije Universiteit, Amsterdam, 1994; E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41; E. J. Baerends, Ph.D. Thesis, Vrije Universiteit, Amsterdam, 1975; W. Ravenek, in *Algorithms and Applications of Vector and Parallel Computers*, eds. H. J. J. te Riele, Th. J. Dekker and H. A. van de Vorst, Elsevier, Amsterdam, 1987; P. M. Boerrigter, G. te Velde and E. J. Baerends, *Int. J. Quantum Chem.*, 1988, **33**, 87.
11 G. te Velde and E. J. Baerends, *J. Comput. Phys.*, 1992, **99**, 84.
12 J. G. Snijders, E. J. Baerends and P. Vernooijs, *At. Data Nucl. Data Tables*, 1982, **26**, 483; P. Vernooijs, J. G. Snijders and E. J. Baerends, *Slater Type Basis Functions for the Whole Periodic System*, Internal Report, Vrije Universiteit, Amsterdam, 1981; J. Krijn and E. J. Baerends, *Fit Functions for the HFS-method*, Internal Report (in Dutch), Vrije Universiteit, Amsterdam, 1984.
13 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
14 A. D. Becke, *Phys. Rev. A.*, 1988, **38**, 3098; *ACS Symp. Ser.*, 1989, **394**, 165; *Int. J. Quantum Chem.*, 1989, **S23**, 599.
15 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822; 1986, **34**, 7406.
16 N. Zavalishin, Candidate Dissertation, University of Moscow, 1975; quoted in ref. 5.
17 I. R. Beattie and G. A. Ozin, *J. Chem. Soc. A*, 1969, 1691.
18 L. Hedberg and I. M. Mills, *J. Mol Spectrosc.*, 1993, **160**, 117.
19 C. Persson and C. Andersson, *Inorg. Chim. Acta*, 1993, **203**, 235.
20 G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Enke Verlag, Stuttgart, 1978.
21 J. R. Canterford and R. Colton, *Halides of Second and Third Row Transition Metals*, Wiley, New York, 1968; F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988.
22 W. Zeil, J. Haase and L. Wegmann, *Z. Instrumentenkd.*, 1966, **74**, 84; O. Bastiansen, R. Graber and L. Wegmann, *Balzers High Vacuum Report*, 1969, **25**, 1.
23 S. Gundersen, T. G. Strand and H. V. Volden, *J. Appl. Crystallogr.*, 1992, **25**, 409; *J. Mol. Struct.*, 1995, **346**, 121.
24 A. W. Ross and M. Fink, *J. Chem. Phys.*, 1986, **86**, 6810; A. W. Ross, M. Fink and R. Hilderbrandt, in *International Tables for X-Ray*

Crystallography, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, vol. C, p. 245.
25 G. Gundersen and S. Samdal, KCED12, Internal Report, University of Oslo, 1980.
26 G. Gundersen, S. Samdal and H. M. Seip, KCED26, Internal Report, University of Oslo, 1980.
27 B. R. Miller and L. S. Bartell, *J. Chem. Phys.*, 1980, **72**, 800.
28 R. P. Dicky, D. Maurice, R. J. Cave and R. J. Mawhorter, *J. Chem. Phys.*, 1993, **98**, 2182.
29 H. M. Seip, T. G. Strand and R. Stølevik, *Chem. Phys. Lett.*, 1969, **3**, 617.
30 R. F. W. Bader and A. D. Westland, *Can. J. Chem.*, 1961, **39**, 2306.
31 C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards, Washington, 1958, vol. 3.

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