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The gas phase structures of tungsten chlorides: density functional theory calculations on WCl_6, WCl_5, WCl_4, WCl_3 and W_2Cl_6 †

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The molecular structures of WCl_6, WCl_5, WCl_4, WCl_3 and the dimer W_2Cl_6 have been optimised by density functional theory calculations at the B3LYP level using the quasi-relativistic electron core potential in combination with basis sets of DZ+P quality. The experimental, octahedral structure and the vibrational frequencies of the hexachloride are well reproduced by the calculations. Calculations on the pentachloride under D_{3h} symmetry indicated an orbitally degenerate ($^2E''$) ground state with bond distances in good agreement with experiment. The Jahn–Teller (J–T) energy of distortion to C_{2v} symmetry was calculated to 1.8 kJ mol^{-1}, an order of magnitude smaller than the estimated spin–orbit (L–S) coupling energy. This is in agreement with an earlier suggestion that J–T distortion is this molecule is quenched by L–S coupling. The ground state of WCl_4 is found to be a tetrahedral (T_d) triplet, that of WCl_3 a trigonal planar (D_{3h}) quartet and that of W_2Cl_6 to be a metal–metal bonded, ethane-shaped singlet. The structures indicated for these molecules are very different from those previously derived from gas electron diffraction data. Investigation by mass spectrometry indicates, however, that the composition of the vapours is much more complex and quite different from what was assumed during the structure analysis. The experimental structures are therefore open to question.

Tungsten and chlorine form solid compounds of composition WCl_2, WCl_3, WCl_4, WCl_5 and WCl_6, and their structures have all been determined by X-ray crystallography. Two crystal modifications of the hexachloride have been found to consist of monomeric, octahedral molecules,[1,2] and an investigation by gas electron diffraction has shown that the octahedral coordination geometry is retained in the gas phase.[3,4]

The pentachloride is dimeric in the solid phase.[5] The coordination geometry of the two W atoms is distorted octahedral; each is surrounded by four terminal and two bridging Cl atoms in *cis* positions, $[WCl_4(\mu\text{-}Cl)]_2$.[5] Mass spectra show that the compound vaporises without decomposition as a monomer,[6] and a gas electron diffraction (GED) study has shown that the coordination geometry is trigonal bipyramidal.[7]

The tetrachloride forms infinite linear polymers in the solid phase.[8] Again the coordination geometry is octahedral; each W atom is surrounded by four bridging and two terminal Cl atoms in *trans* positions, $[WCl_2(\mu\text{-}Cl)_2]_\infty$.[7] This compound suffers partial decomposition on evaporation, mass spectra indicate the presence of significant amounts of WCl_5, WCl_4 and the dimeric trichloride, W_2Cl_6, as well as small amounts of the trimer W_3Cl_9.[6]

The crystal structures of WCl_6, WCl_5 and WCl_4 might, by extrapolation, lead to the expectation that solid WCl_3 consists of a three-dimensional polymeric structure in which each W atom is surrounded by six bridging Cl atoms at the corners of an octahedron; $[W(\mu\text{-}Cl)_3]_\infty$. The real crystal structure of WCl_3 is, however, quite different from those of the higher chlorides: WCl_3 forms hexamers in the solid state, six tungsten atoms being situated at the corners of a perfect octahedron, and each metal atom carries one terminal Cl atom; the remaining twelve bridge the octahedral edges, $W_6Cl_6(\mu\text{-}Cl)_{12}$.[9] Crystalline WCl_2 may be described as a three-dimensional, polymeric array of hexameric units.[10] The W atoms of the hexameric unit again occupy positions at the corners of an octahedron; each of the eight octahedral faces is capped by a triply bridging Cl atom. Two W atoms in *trans* positions carry terminal Cl atoms, and the four equatorial W atoms are linked to other octahedral units through Cl bridges, $\{[W_6Cl_2(\mu_3\text{-}Cl)_8](\mu\text{-}Cl)_2\}_\infty$.

Like the tetrachloride, the tri- and di-chlorides decompose on evaporation; mass spectra show the presence of WCl_5, WCl_4 and W_2Cl_6 species in the gas phase, but *no* detectable amounts of monomeric WCl_3 or WCl_2.[6]

In the present article we report the results of quantum chemical density functional theory calculations on WCl_6, WCl_5, WCl_4, WCl_3 and W_2Cl_6. The optimised structures of the hexachloride and the pentachloride are in good agreement with the experimental structures. The calculated structures of WCl_4, WCl_3 and W_2Cl_6 are, however, very different from the gas-phase electron diffraction structures published by others.[11–14]

Density functional theory calculations

All calculations were carried out with the GAUSSIAN 98 program system[15] using Becke's three parameter functional[16] (B3LYP). For W we used the 14-electron quasi-relativistic (WB) effective core potential (ECP) basis set of Andrae *et al.*[17] augmented by one f function with exponent 0.823,[18] for Cl the 7 electron WB-ECP basis of Dolg *et al.*[19] The basis set is thus of DZ+P quality.

Atomic charges were estimated by Mulliken population analysis. Molecular force fields were calculated analytically, vibrational frequencies and thermal energies at 298.15 K by standard methods.

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† Dedicated to Professor Lev. V. Vilkov, Moscow State University, on occasion of his 70th birthday on June 1, 2001.

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Table 1 Molecular parameters of WCl_6, WCl_5, WCl_4, WCl_3 and W_2Cl_6 obtained by density functional theory calculations

WCl_6:	Symmetry O_h; electronic state $^1A_1$ Energy = −157.398331 au W–Cl 232.1 pm Net charges (au): W, 1.47; Cl, −0.24 ω/cm^{-1}: A_{1g}: 396; E_g: 313; T_{1u}: 360; 164; T_{2g}: 200; T_{2u}: 87
WCl_5:	Symmetry D_{3h}; electronic state $^2E''$ Energy^a = −142.373923 au; ΔE = 1.8 kJ mol^{-1} W–Cl_e 227.3 (3X); W–Cl_a 234.6 pm (2X)
	Symmetry C_{2v} (near D_{3h}); electronic state $^2B_1$ Energy = −142.374613 au; ΔE = 0.0 kJ mol^{-1}. W–Cl_{e1} 227.5 (1X); W–Cl_{e2} = 226.1 (2X); W–Cl_a 234.2 pm (2X) $Cl_{e1}WCl_a$ 89.2 (2X); $Cl_aWCl_{a'}$ 178.4°; $Cl_{e1}WCl_{e2}$ 117.6 (2X); $Cl_{e2}WCl_{e2}$ 124.9° (1X) Net charges (au): W, 1.35; Cl_{e1}, −0.26; Cl_{e2}, −0.25; Cl_a, −0.29 ω/cm^{-1}: A_1: 404; 398; 323; 152; 81: A_2: 183; B_1: 353; 173; 160; B_2: 378; 62; 51*i*
	Symmetry C_{2v} (near D_{3h}; electronic state $^2A_2$ Energy = −142.374602 au; ΔE = 0 W–Cl_{e1} 225.5 (1X); W–Cl_{e2} 227.2 (2X); W–Cl_a 234.1 pm (2X) $Cl_{e1}WCl_a$ 91.2 (2X); $Cl_aWCl_{a'}$ 177.6; $Cl_{e1}WCl_{e2}$ 122.0 (2X); $Cl_{e2}WCl_{e2}$ 116.0° (1X) Net charges (au): W, 1.35; Cl_a, −0.29; Cl_{e1}, −0.26; Cl_{e2}, −0.26 ω/cm^{-1}: A_1: 408; 399; 324; 137; 58; A_2: 169; B_1: 354; 181; 166; B_2: 373; 115; 25
WCl_4:	Symmetry D_{2d} (flattened); electronic state $^1A_1$ Energy = −127.305504 au; ΔE = 81 kJ mol^{-1} W–Cl 226.5 pm, ClWCl −97.7 (4X) and 137.1° (2X) Net charges (au): W, 1.23; Cl, −0.31 ω/cm^1: A_1: 400; 71; B_1: 158; B_2: 370; 109; E: 396; 124
	Symmetry T_d; electronic state $^3A_2$ Energy: −127.336496 au; ΔE = 0 W–Cl 227.7 pm Net charges (au): W, 1.41; Cl, −0.35 ω/cm^{-1}: A_1: 391; E: 79; T_2: 394; 90
WCl_3:	Symmetry D_{3h}; electronic state $^2E''$ Energy^a = −112.226426 au; ΔE = 74 kJ mol^{-1} W–Cl 223.8 pm
	Symmetry C_{2v}; electronic state $^2A_2$ Energy = −112.228823 au; ΔE = 68 kJ mol^{-1} W–Cl 224.6 (2X), 222.4 pm (1X); ClWCl 108.3 (1X), 125.9° (2X) Net charges (au): W, 1.15; Cl, −0.37 (2X) and −0.40 (1X) ω/cm^{-1}: A_1: 430; 394; 101; B_1: 93; B_2: 381; 60
	Symmetry D_{3h}; electronic state $^4A_1'$ Energy = −112.254549 au; ΔE = 0 W–Cl 227.7 pm Net charges (au): W, 1.17; Cl, −0.39 ω/cm^{-1}: A_1': 385; A_2'': 76; E': 406; 96
W_2Cl_6:	Symmetry D_{2h} (diborane shape); electronic state $^1A_{1g}$ Energy = −224.460942 au; ΔE = 443 kJ mol^{-1} W–Cl_t 226.9; W–Cl_b = 239.1 pm Cl_tWCl_t 113.6; WCl_bW 100.4° Net charges: W, 1.03; Cl_t, −0.41 Cl_b, −0.22 ω/cm^{-1}: A_g: 397; 332; 142; 71; A_u: 35; B_{1g}: 398; 63; B_{2g}: 298; 93; B_{3g}: 101; B_{1u}: 290; 64; B_{2u}: 398; 143; 18; B_{3u}: 377; 311; 79
	Symmetry D_{3d} (ethane shape); electronic state $^1A_{1g}$ Energy = −224.629625 au; ΔE = 0 W–W 230.5; W–Cl 227.9 pm, WWCl 103.3° Net charges (au): W, 1.20; C, −0.40 ω/cm^{-1}: A_{1g}: 395; 294; 109; A_{1u}: 24; A_{2u}: 375; 116; E_g: 398; 139; 100; E_u: 402; 94; 84

[a] See comment in text.

Results and discussion

Tungsten hexachloride

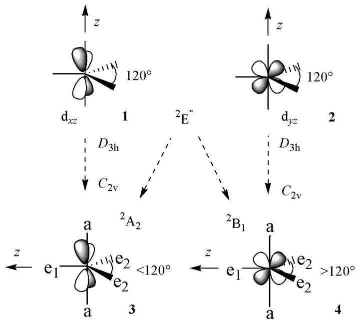
Two different crystal modifications of WCl_6 have been found to consist of monomeric, octahedral molecules,[1,2] and gas-phase electron diffraction (GED) data are in excellent agreement with O_h symmetry and a W–Cl bond distance of 228.1(3) pm.[3,4]

Structure optimisation by DFT calculations shows that an octahedral model with W–Cl 232.1 pm (about 4 pm longer than the experimental value) corresponds to a minimum on the potential energy surface. See Table 1 for a more complete description of the molecule. The six calculated normal modes reproduce the experimental values with an average deviation of less than 10 cm^{-1}.[20]

Tungsten pentachloride

WCl_5 is dimeric in the crystal phase,[5] but evaporates (without decomposition) as a monomer.[6] $TaCl_5$ and other d^0 pentahalides of the Group 5 metals adopt trigonal bipyramidal structures of D_{3h} symmetry in the gas phase.[7,21] WCl_5 and other pentahalides of the Group 6 metals contain one unpaired electron however, and may be subject to Jahn–Teller distortion. If the molecular symmetry is D_{3h}, and in the absence of significant spin–orbit (L–S) coupling, the unpaired electron is expected to reside in an e″ (d_{xz} or d_{yz}) atomic orbital on the metal atom (**1** or **2**). The molecule would then be orbitally degenerate and deformation to C_{2v} symmetry would split the doubly degenerate $^2E''$ state into the non-degenerate states $^2A_2$ (**3**) and $^2B_1$ (**4**).[22]

Two d^1 transition metal pentahalides had been studied by gas electron diffraction prior to our own study of WCl_5. The GED data of CrF_5 and $MoCl_5$ were found to be incompatible with D_{3h} symmetry.[23,24] In a D_{3h} model all valence angles are fixed by symmetry at 90 or 120°, while a C_{2v} model is characterised by two independent valence angles, *e.g.* e_1–M–e_2 and e_1–M–a. See Scheme 1. Least-squares refinements of these angles led to good agreement between calculated and observed intensities: for CrF_5 the *R* factor decreased from 6.3 to 4.9% when the symmetry was reduced from D_{3h} to C_{2v} symmetry; for $MoCl_5$ from 7.7 to 3.8%.[23,24] Subsequent structure optimisation of the $^2A_2$ and $^2B_1$ states of CrF_5 by DFT calculations[25] yielded bond distances which differed from the optimised D_{3h} values by 1.0 pm or less and valence angles that deviated from the D_{3h} values of 90 or 120° by up to 5°. The greatest deformation was suffered by the angle e_2–Cr–e_2 which was calculated to be 116° in the $^2A_2$ and 125° in the $^2B_1$ state. These angles may be rationalised as a result of repulsion between the unpaired electron and CrF bonding electron pairs. The relative energies of the two states was found to depend on the functional, but it was concluded that the energy difference probably is smaller than 4 kJ mol^{-1}. Normal vibrational modes could not calculated due to convergence problems. Similar results have also been obtained by restricted Hartree–Fock calculations on $MoCl_5$.[24] Taken



Scheme 1

together the GED and computational studies indicate that CrF_5 and $MoCl_5$ undergo dynamic Jahn–Teller distortions from D_{3h} symmetry.

We were therefore surprised when we found the GED pattern of WCl_5 to be in very good agreement with a model of D_{3h} symmetry. Structure refinement under C_{2v} symmetry did not improve the fit between calculated and observed intensities (the *R* factor remained unaltered at 3.7%) and yielded valence angles that differed from the D_{3h} values by less than one estimated standard deviation.[7] We suggested, therefore, that Jahn–Teller distortion of this molecule is quenched by spin–orbit coupling.[22] Such 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. Each new spinor corresponds to a cylindrical electron density, and the degeneracy of the lower doublet is not lifted by molecular distortion to C_{2v} symmetry.

The DFT calculations reported in this article, like the DFT calculations on CrF_5[25] or the HF calculations reported for $MoCl_5$,[24] do *not* include L–S coupling. As expected, structure optimisation of WCl_5 under D_{3h} symmetry failed to converge, but confirmed that the unpaired electron resides in an e″ (d_{xz} or d_{yz}) atomic orbital. The lowest energy obtained and the corresponding bond distances are listed in Table 1. These bond distances are, as for the hexachloride, about 4 pm longer than the experimental.

Structure optimisation of the $^2A_2$ state under C_{2v} symmetry yielded an energy about 1.8 kJ mol^{-1} below the best D_{3h} model. See Table 1. All vibrational frequencies were calculated to be real indicating that the structure corresponds to a minimum on the potential energy surface. Optimisation of the $^2B_1$ state under C_{2v} symmetry yielded a structure characterised by one imaginary frequency of B_2 symmetry, indicating that this structure represents the transition states for conversion between the three symmetry equivalent $^2A_2$ minima. The energy calculated for the $^2B_1$ state was 0.03 kJ mol^{-1} below that of the $^2A_2$ state; this energy difference is probably smaller than the numerical noise level. In order to confirm that the $^2A_2$ state is the equilibrium structure (at this computational level) we reoptimised the structure without imposition of symmetry and found that with a start model close to the optimal $^2B_1$ the calculations yielded a structure very close to that of the $^2A_2$. We conclude therefore that the energy difference between the two states is very small (perhaps less than 1 kJ mol^{-1}), and that the equilibrium state probably is $^2A_2$, at least at the present computational level.

The DFT calculations thus indicate that the D_{3h} to C_{2v} Jahn–Teller distortion energy is about 1.8 kJ mol^{-1}, an order of magnitude smaller than the estimated spin–orbit coupling energy in a trigonal bipyramidal tungsten pentahalide, 17 kJ mol^{-1}.[26] We conclude, therefore, that Jahn–Teller distortion is indeed quenched by spin-orbit coupling and that the molecular symmetry remains D_{3h} as indicated by the GED study.

Tungsten trichloride

Two d^0 transition metal trichlorides, $ScCl_3$ and YCl_3, have recently been found to be trigonal planar (D_{3h}) by GED and quantum chemical calculations.[27,28]

If the trigonal planar structure is retained in a high-spin trihalide of a Group 6 metal the three unpaired electrons are expected to reside in the a_1' (d_{z^2}) and e″ (d_{xz} and d_{yz}) orbitals on the metal atom. The resulting $^4A_{1'}$ state would be orbitally non-degenerate and no Jahn–Teller distortion is expected. Recent quantum chemical calculations on CrF_3 at the SOCI/CASSCF level show that the molecule indeed has a high-spin $^4A_1'$ ground state of D_{3h} symmetry. The trigonal planar equilibrium geometry is supported by spectroscopic (ESR, IR and Raman) evidence.[21] Similar results have been obtained by DFT (B3LYP) calculations on WF_3.[26]

Our DFT calculations on WCl_3 likewise yield a quartet ground state $^4A_{1'}$ with trigonal planar (D_{3h}) geometry. See Table 1.

DFT structure optimisation of a D_{3h} molecular model with a doublet $(a_1')^2(e'')^1$ electronic state yielded energies more than 74 kJ mol^{-1} above the ground state but failed to converge. This $^2E''$ state is, like the corresponding state of the pentachloride, orbitally degenerate and may thus be subject to Jahn–Teller (J–T) distortion. Optimisation of the $^2A_2$ state under C_{2v} symmetry proceeded without difficulties to yield an energy about 6 kJ mol^{-1} below the undistorted D_{3h} structure and the structure parameters and vibrational frequencies listed in Table 1. Attempts to optimise the $^2B_1$ state under C_{2v} symmetry yielded energies similar to those obtained for the undistorted structure and also failed to converge. Since the D_{3h} to C_{2v} distortion energy is calculated to be less than half the spin–orbit coupling energy, and J–T distortion therefore will be prevented by L–S coupling, we did not pursue this matter further.

Ezhov and Komarov (hereafter referred to as EK) have recorded electron diffraction from molecular beams generated by evaporating solid samples of composition $WCl_{2.8}$ or $WCl_{3.4}$ at about 350 °C and superheating the vapour to about 530 °C.[11] The data were found to be consistent with a beam consisting exclusively of T-shaped WCl_3 molecules of C_{2v} symmetry.[13] Least-squares refinement yielded an average bond distance of W–Cl 226.9(3) pm and an angle between the pseudo-axial ligands of about 180°.[12] These results are clearly in disagreement with those of our calculations.

We note, however, that the mass spectra of vapours obtained by evaporating solid samples of WCl_2, WCl_3 and WCl_4 at 300 °C show the presence of comparable amounts of WCl_5, WCl_4 and W_2Cl_6 molecules in the gas phase, but offer *no evidence* for the existence of WCl_3 molecules. It therefore appears unlikely that the molecular beam generated by EK should have contained significant amounts of WCl_3, let alone that this species should be predominant.

Ditungsten hexachloride

EK also recorded GED data after evaporating solid samples of composition $WCl_{2.8}$ or $WCl_{3.4}$ at 320 °C and superheating the vapour to about 390 °C (*i.e.* 140 °C lower than in the experiments performed in order to record data for monomeric WCl_3).[13] In the analysis of their data published in 1990 they found them to be in satisfactory agreement with a gas consisting of 60% monomeric T-shaped WCl_3 and 40% of a dimer, W_2Cl_6. The dimer was found to have a diborane-like structure of D_{2h} symmetry, $[WCl_2(\mu\text{-}Cl)]_2$.[12]

Our DFT calculations on singlet electronic states led to the identification of two stationary points on the potential energy surface of W_2Cl_6, one corresponding to a diborane-like structure similar to that suggested by EK, the other corresponding to an ethane-like, metal–metal bonded structure of D_{3d} symmetry. See Table 1. The energy of the metal–metal bonded structure was calculated to be 443 kJ mol^{-1} below that of the di-bridged. Similar metal–metal bonded structures have been found for several solid ditungsten hexaamides or hexaalkoxides.[29] The WW bond distances in these compounds range from 229 to 234 pm, the optimal bond distance in ethane-like W_2Cl_6 is 229.9 pm.

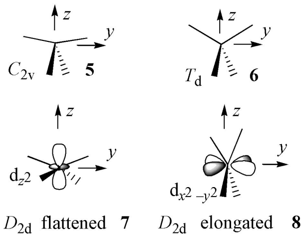
Inspection of the occupied molecular orbitals shows that the tungsten atoms are joined by a triple (one σ and two π) bond. The barriers restricting internal rotation about such a bond are expected to be very small. Indeed, optimisation of a metal–metal bonded dimer with eclipsing W–Cl bonds (symmetry D_{3h}) yields an energy less than 3 kJ mol^{-1} above that of the staggered model.

The strength of the triple bond may be assessed by calculating the enthalpy of the reaction $W_2Cl_6(g) \longrightarrow 2WCl_3(g)$ at 298 K; $\Delta H° = 311$ kJ mol^{-1}. The high bond energy explains why the monomer has not been detected in the mass spectra of vapours over the solid trichloride. (If W_2Cl_6 is assumed to have a diborane-like structure the dissociation reaction is calculated to be *exothermic* with $\Delta H° = -131$ kJ mol^{-1}. Under these circumstances no dimer should be detectable in the mass spectrum.)

Since our calculations indicate that the energy of the ethane-like structure is more than 400 kJ mol^{-1} below that of the diborane-like, and since mass spectroscopic investigations indicate that the gas would consist of WCl_5, WCl_4 and W_2Cl_6 rather than of W_2Cl_6 and WCl_3,[6] we feel that the calculated structure is more reliable than the experimental.

Tungsten tetrachloride

Finally EK have recorded the electron diffraction data from a molecular beam generated by evaporating a solid sample of WCl_4 at about 115 °C and superheating the vapour slightly to about 130 °C.[14] The data were found to be consistent with a beam consisting exclusively of WCl_4 molecules of C_{2v} symmetry (**5**, Scheme 2). The coordination polyhedron might be described as a distorted trigonal bipyramid with one equatorial ligand missing. The mean W–Cl bond distance was found to be 224.7(3) pm, the angle spanned by the pseudo-axial ligands was about 150°, and the angle spanned by the pseudo-equatorial ligands about 90°.[12] This structure is surprising. All monomeric tetrahalides of the Group 4 metals as well as the d^2 tetrafluorides CrF_4 and MoF_4 have been found to be tetrahedral in the gas phase.[21,30,31] *Ab initio* (SCF-CI) calculations show that the ground state of CrF_4 is a tetrahedral (T_d) triplet $^3A_2$ where the two unpaired electrons occupy atomic orbitals of e symmetry (d_{z^2} and $d_{x^2-y^2}$) on the metal atom.[32] The ground state is thus orbitally non-degenerate and no Jahn–Teller distortion is expected.



Scheme 2

We have been unable to locate any minimum on the DFT potential energy surface of WCl_4 corresponding to a structure of C_{2v} symmetry. Structure optimisation of a triplet electronic state starting from the C_{2v} configuration suggested by EK converged to a model of T_d symmetry (**6**). Calculation of the molecular force field confirmed that this structure corresponds to a minimum on the potential energy surface.

Structure optimisation of a singlet state yielded a potential energy minimum corresponding to an compressed tetrahedron of D_{2d} symmetry, the non-bonding electron pair residing in the d_{z^2} orbital (**7**). For structure parameters see Table 1. The energy of this ($^1A_1$) state is, however, calculated to be 79 kJ mol^{-1} above the tetrahedral $^3A_2$ state.[33]

Several attempts were made to locate a second minimum on the potential energy surface of the singlet state with the electron pair occupying the $d_{x^2-y^2}$ atomic orbital on W (**8**), but the only minimum found corresponding to an elongated tetrahedral geometry had an energy 1600 kJ mol^{-1} above the $^3A_2$ state. Inspection of the geometry showed the structure to correspond to two Cl_2 molecules (Cl–Cl 206 pm) absorbed on a W atom (W–Cl 260 pm).

Mass spectra of the vapour from a solid sample of WCl_4 recorded at about 300 °C (*i.e.* at a temperature about 170 °C above that used for the registration of gas electron diffraction data) indicate that the gas consists of comparable amounts of WCl_5, WCl_4 and W_2Cl_6. The entropy of the reaction $4WCl_4(g) \longrightarrow 2WCl_5(g) + W_2Cl_6(g)$ is expected to be negative since the number of gas phase molecules decreases. Indeed the standard entropy of the reaction at 298 K, calculated from the standard entropies listed in Table 2, is $\Delta S° = -182.8$ J K^{-1} mol^{-1}. This means that the equilibrium will shift to the right and the amount of tetrachloride decrease with decreasing temperature. It appears unlikely, therefore, that the molecular beam generated by EK has consisted exclusively of tetrachloride as assumed in their analysis. Except for the structure of $MoBr_4$,[35] also published by EK, the molecular structure obtained is, as far as we are aware, unprecedented for a transition metal tetrahalide. Our calculations indicate that the energy of a tetrahedral $^3A_2$ state is at least 75 kJ mol^{-1} below the first excited state. Since a T_d coordination geometry is in good agreement with what we know about the structures of related metal tetrahalides, we again believe that the the calculated structure is more reliable than the experimental.

Table 2 Calculated standard enthalpies of formation ($\Delta H°_f$) and standard entropies ($S°$) at 298 K and mean W–Cl bond energies (MBE) in gaseous tungsten chlorides

	$\Delta H°_f$/kJ mol^{-1}	$S°$/J K^{-1} mol^{-1}	MBE/kJ mol^{-1}
WCl_6	[−493.7][a]	422.5	345
WCl_5	[−412.5][a]	433.7	374
WCl_4	−294	390.0	408
WCl_3	−60	355.8	425
W_2Cl_6	−430	509.8	

[a] Ref. 36.

Standard enthalpies of formation, standard entropies and mean bond energies

The standard enthalpies of formation of $WCl_6(g)$, $WCl_5(g)$ and $WCl_4(g)$ at 298 K are listed in the NIST-JANAF Tables.[36] No data are listed for gaseous WCl_3 or W_2Cl_6. In view of the complex composition of the gas obtained by evaporation of solid WCl_4, the reliability of the enthalpy of formation of the gaseous molecule appears uncertain. We have therefore used the sum of the calculated electronic and thermal energies of the hexa, penta- and tetra-chlorides at 298 K to calculate the enthalpy of the reaction $2\ WCl_5(g) \longrightarrow WCl_6(g) + WCl_4(g)$; $\Delta H°_{298} = 38$ kJ. This enthalpy, in conjunction with the NIST-JANAF standard enthalpies of formation of $WCl_6(g)$ and $WCl_5(g)$, allows us to estimate the standard enthalpy of formation of gaseous WCl_4, see Table 2. Similarly we have combined the calculated enthalpy of the reaction $2\ WCl_4(g) \longrightarrow WCl_5(g) + WCl_3(g)$, $\Delta H°_{298} = 115$ kJ, with the standard enthalpies of formation of $WCl_5(g)$ and $WCl_4(g)$ to estimate $\Delta H_f°$ for gaseous WCl_3.

Finally, we have used the standard enthalpies of formation listed in Table 2 to calculate the mean bond energies of the gaseous chlorides at 298 K. These are found to decrease monotonically from 425 kJ mol^{-1} for the trichloride to 345 kJ mol^{-1} for the hexachloride.

Concluding remarks

The DFT calculations reported here reproduce the octahedral symmetry of gaseous WCl_6 and the experimentally determined bond distance and vibrational frequencies with good accuracy. Structure optimisation of WCl_5 confirmed the trigonal bipyramidal coordination geometry and yielded bond distances in good agreement with the experimental. Calculations under D_{3h} symmetry yielded an orbitally degenerate ground state. The calculated energy gain by Jahn–Teller distortion to C_{2v} symmetry was, however, one order of magnitude smaller than the estimated spin–orbit coupling energy. This is in agreement with our earlier suggestion that J–T distortion in this molecule is prevented by L–S coupling.

However, the calculated equilibrium structures of WCl_4, WCl_3 and W_2Cl_6 are entirely different from those suggested by Ezhov and Komarov on the basis of gas electron diffraction data: for the tetra- and tri-chlorides EK suggested structures obtained by extraction of one or two Cl equatorial atoms from the trigonal bipyramidal pentachloride; such structures are consistent with the VSEPR model if the non-bonding electrons in these species are assumed to be stereochemically active. Our calculations indicate that these molecules are *high spin*, and that the unpaired electrons have no effect on the molecular structures; WCl_4 is calculated to be tetrahedral and WCl_3 to be trigonal planar as suggested by a model considering repulsion between the ligands only.

EK have interpreted their GED data for W_2Cl_6 in terms of a di-bridged diborane-like structure similar to that adopted by Al_2Cl_6 or Fe_2Cl_6.[37,38] The calculated equilibrium structure of W_2Cl_6, on the other hand, is similar to the ethane-like metal–metal bonded structures adopted by several dimeric tungsten(III) amides or alkoxides in the solid phase.[29]

Since the mass spectra of vapours derived from solid samples of the tetra- and tri-chlorides indicate the presence of WCl_5, WCl_4 and W_2Cl_6 molecules, but provide no evidence for the presence of monomeric WCl_3, the real vapor compositions were probably more complex than suspected by EK. We believe, therefore, that the calculated structures of WCl_4, WCl_3 and W_2Cl_6 are more reliable than the experimental.

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