Effect of the orientation of coordinated water molecules on the electronic structure of trans halo-aquo complexes: application to $TiCl_2(H_2O)_4^+$ and $VCl_2(H_2O)_4^+$

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The $X\alpha$ method has been utilized to calculate the electronic structure of trans-$TiCl_2(H_2O)_4^+$ and trans $VCl_2(H_2O)_4^+$ ions. Different conformations of coordinated water molecules have been considered. It has been found that the most stable configuration in both cases is the one with the plane of the water molecules parallel to the Cl–metal–Cl axis. The nature of the tetragonally distorted ground state has been found to depend on the orientation of the water molecules in these systems.

Key words: Multiple scattering $X\alpha$—Ligand field theory—Angular overlap model—Trans halo-aquo complexes

Introduction

The trans-$(MX_2(H_2O)_4)^{n+}$ configuration is quite common among the first transition series (1). The crystal structure of a considerable number of compounds belonging to this interesting class have been determined by X-ray diffraction (1-2) and found to have almost perfect D_{4h} symmetry for the chromophore MCl_2O_4. In most cases the location of the hydrogen atoms of the coordinated water molecules was guessed, based on the number and strength of hydrogen bonds which may be formed with the surrounding negative centers. For example

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in the compound $Cs_2CrCl_5 \cdot 4H_2O$ containing the trans-$CrCl_2(H_2O)_4^+$ configuration, the orientation of the water molecules has been assumed to be parallel to the Cl–Cr–Cl axis (1) since in this arrangement hydrogen bonding is possible to eight nearby Cl^- ions.

In D_{4h} the $t_{2g}(O_h)$ representation splits into $e_g + b_{2g}$, while the $e_g(O_h)$ representation splits into $a_{1g} + b_{1g}$, so that the ground state for d^n systems in this environment will depend on the energy order of the split components. There is a controversy from the theoretical point of view regarding the nature of the ground state in D_{4h} symmetry. Figgis et al. [4] were unable to distinguish between a $^4A_{2g}$ and a ^4E_g ground state for trans-$CoCl_2(H_2O)_4$, and for $TiCl_2(H_2O)_4^+$, Schläfer and Fritz [5] proposed a $^2B_{2g}$ ground state while McCarthy and Richardson [6] suggest a ^2E_g ground state. There is now much experimental data favouring the energy order $e_g \ (d_{xz}, d_{yz}) < b_{2g}(d_{xy})$ in the case of $TiCl_2(H_2O)_4^+$ [6], $VCl_2(H_2O)_4^+$ [3], $CrCl_2(H_2O)_4^+$ [1] and $CoCl_2(H_2O)_4$ [7]. In such systems the ordering $e_g < b_{2g} < a_{1g} < b_{1g}$ has been explained in terms of the position of the Cl^- in the spectrochemical series relative to H_2O.

In this work, the effect of the orientation of the coordinated water molecules on the nature of the ground state in the complexes $TiCl_2(H_2O)_4^+$ and $VCl_2(H_2O)_4^+$ will be investigated theoretically using the SCF-MS $X\alpha$ (self-consistent field multiple scattering $X\alpha$) method; this has not been considered before in the ligand field treatment of these systems.

Method of calculations

The updated version of the SCF MS-$X\alpha$ method [8] has been used to calculate the electronic structure of trans-$TiCl_2(H_2O)_4^+$ (spin restricted calculations) and $VCl_2(H_2O)_4^+$ (spin polarized calculations). The exchange alpha parameters invoked around each atomic region were chosen in accordance with the Schwarz values [9], whereas a weighted average of the atomic alpha values was used in outerspherical and interspherical regions. The Norman criteria [10] were used in choosing the atomic radii scaled by a factor of 0.88. Around each of the Cl atomic spheres, an l_{max} of 2 was used, and an l_{max} of 4, 3, 1 and 0 was invoked around the outerspherical region, the metal atom, the oxygen atoms and the hydrogen atoms respectively. The valence shells in this calculation include: Metal center $(3p, 3d, 4s)$; Cl $(3s, 3p, 3d)$; $O(2s, 2p)$ and H $(1s)$.

Geometries for $VCl_2(H_2O)_4^+$ and $TiCl_2(H_2O)_4^+$ are based upon X-ray data [3, 6] of the main atoms, with the O–H bond length and H–O–H bond angle being estimated values; a summary of the geometry and sphere radii adopted in this study is given in Table 1. In this calculation different orientations of the water molecules around the M–O bond axis have been considered. We define β (degrees) to be the angle between the plane of any of the coordinated water molecules and the plane containing the metal ion and the four oxygen atoms (MO_4 plane). Different configurations were obtained by changing this angle from $0°$ to $90°$ for all the water molecules at the same time so that the D_4 symmetry of the molecule is preserved; (however only two configurations have the higher D_{4h} symmetry, namely when $\beta = 0°$ and $90°$. Rotating the four water molecules by the same angle

Table 1. Geometry and sphere radii of trans-$TiCl_2(H_2O)_4^+$ and trans-$VCl_2(H_2O)_4^+$. (values are in Ångströms)

Bond lengths and angles

Ti–O 2.04	Ti–Cl 2.40	<Cl–Ti–Cl 180°
<Cl–Ti–O 90°	<O–Ti–O 90°	
V–O 1.969	V–Cl 2.477	<Cl–V–Cl 180°
<Cl–V–O 90°	<O–V–O 90°	
O–H 0.86	<H–O–H 107°	

Sphere radii

$TiCl_2(H_2O)_4^+$	$VCl_2(H_2O)_4^+$
Ti 1.3029	V 1.2536
O 0.8603	O 0.8571
Cl 1.4558	Cl 1.4464
H 0.5269	H 0.5269
Outer sphere	Outer sphere
3.8560	3.8234
Watson sphere	Watson sphere
3.8560	3.8234
−1	−1

is only a matter of convenience, and avoids the other possible configurations which have lower symmetry than D_4. Six different angles have been used in this work: $\beta = 0°$, 22.5°, 34°, 45°, 67.5° and 90° for titanium complex and $\beta = 0°$, 22.5°, 45°, 56°, 67.5° and 90° for the vanadium complex.

Results and discussion

a. $TiCl_2(H_2O)_4^+$

The total energy E_T, the total energy relative to the most stable configuration ΔE_T (for $\beta = 90°$) and the energy gap $(\varepsilon_{b2} - \varepsilon_e)$ are listed in Table 2. There is a change in the nature of the ground state when β is changed from 0° to 90°. In the range 0–34° the d-like MO b_2 has a lower energy than the e MO and so leads to a $^2B_2$ ground state, whereas the reverse situation is found in the range $\beta = 45$–90°, resulting in a ^2E ground state. There is an intermediate point (estimated to be at $\beta = 41.3°$) where the two energy levels (b_2 and e) are accidentally degenerate. This trend is also illustrated in Fig. 1c. The plot of ΔE_T against β in Fig. 1a indicates the presence of two potential energy curves corresponding to the two possible ground states $^2B_2$ and ^2E, with minimum energies at 0° and 90° respectively. The minimum at 0° occurs at 6.1 kJ/mol above the stable configuration with $\beta = 90°$.

Such behaviour can be adequately explained using the angular overlap model (12) for the d-like MOs in this system (e, b_2, a_1 and b_1). An sp^2 hybridization is expected around oxygen in a coordinated water molecule, leaving one p orbital available for π-bonding with the d orbitals (d_{xz}, d_{yz} or d_{xy}) of the metal ion, its orientation being perpendicular to the molecular plane of water. The rotation of H_2O around the M–O bond axis can also be viewed as a rotation of the oxygen

Table 2. Total energy E_T, relative total energy ΔE_T and the energy gap $(\varepsilon_{b2} - \varepsilon_e)^a$ at different β values for $TiCl_2(H_2O)_4^+$

β	Ground state	E_T Rydbergs	ΔE_T kJ/mol	$(\varepsilon_{b2} - \varepsilon_e)$ cm^{-1}
0.0°	$^2B_{2g}$	−4148.8484	6.14	−3043
22.5°	$^2B_2$	−4148.8437	12.471	−1966
34.0°	$^2B_2$	−4148.8395	17.98	−820
45.0°	^2E	−4148.8457	9.845	422
67.5°	^2E	−4148.8523	1.181	2642
90.0°	^2E_g	−4148.8532	0.0	3530

Excited states for $\beta = 90°$ (cm^{-1})

	Calculated^a	Experimental [6]
$^2B_{2g} \leftarrow {}^2E_g$	3530	4250
$^2A_{1g} \leftarrow {}^2E_g$	16240	14970
$^2B_{1g} \leftarrow {}^2E_g$	19500	19220

^{a} Calculated according to the transition state procedure (11)

p_π orbital around the same axis. For any arbitrary angle β the oxygen p_π orbital can be resolved into two directions, one parallel to the Cl–M–Cl axis and the other perpendicular to it, whereupon the angular overlap model in D_4 symmetry yields energies of the d-like MOs (apart from a constant term):

$$e(d_{xz}, d_{yz}): 2e_\pi(O)\cos^2\beta + 2e_\pi(Cl) \tag{1}$$
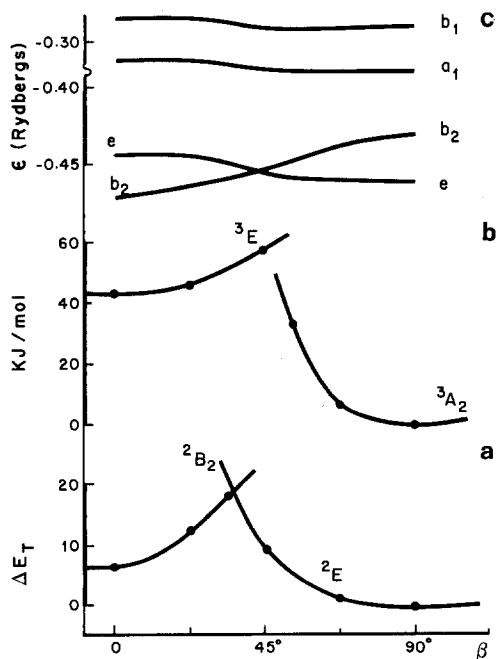
Fig. 1. a Variation of the X_α total energy ΔE_T relative to the configuration with $\beta = 90°$ for $TiCl_2(H_2O)_4^+$; b Variation of the X_α total energy ΔE_T relative to the configuration with $\beta = 90°$ for $VCl_2(H_2O)_4^+$;. c X_α eigenvalues of the d-like MO's of $TiCl_2(H_2O)_4^+$ as function of β

$$b_2(d_{xy}): 4e_\pi(O)\sin^2\beta \tag{2}$$

$$a_1(d_{z2}): e_\sigma(O) + 2e_\sigma(Cl) \tag{3}$$

$$b_1(d_{x2-y2}): 3e_\sigma(O) \tag{4}$$

where $e_\mu (\mu = \sigma, \pi, \ldots)$ is a parameter introduced by the angular overlap model (12–14) and depends only on the radial functions of the metal and ligands and on the bond distance—it is independent of angular quantities.

The relation $10Dq(H_2O) > 10Dq(Cl^-)$ can be deduced from the position of these ligands in the spectrochemical series. Since $10Dq$ is related to the angular overlap parameters by the equation $10Dq(X) = 3e_\sigma(X) - 4e_\pi(X)$, and assuming $e_\sigma(X) > e_\pi(X)$ which is generally true [12]), one expects that $e_\sigma(O) > e_\sigma(Cl)$, and even if $e_\pi(O) \sim e_\pi(Cl)$, the following energy order of the d-like MOs can be obtained from Eqs (1–4):

$\beta = 90°$ $e_g < b_{2g} < a_{1g} < b_{1g}$ with ^2E_g ground state for d^1 system,

$\beta = 0°$ $b_{2g} < e_g < a_{1g} < b_{1g}$ with $^2B_{2g}$ ground state for d^1 system.

This is what we have found from the $X\alpha$ calculations of $TiCl_2(H_2O)_4^+$. On the basis of this model (Eqs. 3, 4) we can also explain why the a_1 and b_1 orbitals are not affected by altering the angle β, since these orbitals are involved only in a σ type interaction with the surrounding ligands.

In this system we have three possible d–d transitions. If the $X\alpha$ transition energies of the excited states ($^2B_2$ or ^2E), $^2A_1$ and $^2B_1$ are equated to the angular overlap energies (Eqs. 1–4), the following radial parameters can be obtained from a fit at different β values (all in cm^{-1}): $e_\pi(O) = 1089 \pm 19$, $e_\pi(Cl) = 379 \pm 22$ (from $(\varepsilon_{b2} - \varepsilon_e)$ values (Table 2)), $e_\sigma(O) = 6750$ and $e_\sigma(Cl) = 5120$ (from the energies of the $^2A_{1g}$ and $^2B_{1g}$ excited states ($\beta = 90°$), using the average $e_\pi(Cl)$ given above), and $10D_q(H_2O) = 18\,080$, $10Dq(Cl) = 16\,410$.

These parameters are in agreement with the relative positions of H_2O and Cl^- as predicted by the spectrochemical series.

Detailed analysis of the polarized crystal spectrum of $Cs_2TiCl_5 \cdot 4H_2O$ [6] has indicated that the complex has a ^2E_g ground state, and the most stable configuration predicted by the X_α calculation at $\beta = 90°$ agrees well with this. The X_α calculated transition energies for $\beta = 90°$ are also in good agreement with the experimental values (Table 2).

b. $VCl_2(H_2O)_4^+$

Polarised X_α calculations have been performed on trans-$VCl_2(H_2O)_4^+$ (a d^2 system) and the resulting plot of ΔE_T against β shown in Fig. 1b indicates a behaviour similar to that found in titanium complex. Again we have two ground states, $^3A_{2g}(e_g^2)$ at $\beta = 90°$ and ^3E_g (b_{2g}, e_g) at $\beta = 0°$, and two minima separated by 43.7 kJ/mol. An accidental degeneracy of the e and b_2 orbitals is estimated to occur at $\beta = 45.7°$ in $VCl_2(H_2O)_4^+$. In these calculations, the most stable ground state for this complex is found to be of $^3A_{2g}$ symmetry in agreement with

experiment [3], and corresponds to the configuration e_g^2 with $\beta = 90°$. For the d^2 case it seems that a simple approach based on the angular overlap model can explain the stability of the configuration e_g^2 ($\beta = 90°$) over the configuration b_{2g}, e_g ($\beta = 0°$) as indicated in Fig. 1b. For these configurations, using Eqs. (1) and (2) and expressing electron repulsion integrals in terms of Racah parameters we get:

$$E_T(e_g^2) \simeq \text{constant term} + 4e_\pi(\text{Cl}) + A - 5B \tag{5}$$

$$E_T(b_{2g}, e_g) \simeq \text{constant term} + 2e_\pi(\text{O}) + 2e_\pi(\text{Cl}) + A - 5B \tag{6}$$

Within this approximation the results appear to indicate that the configuration $e_g^2(\beta = 90°)$ is more stable than the b_{2g}, $e_g(\beta = 0°)$ configuration for $e_\pi(\text{O}) > e_\pi(\text{Cl})$, a point which is confirmed from the X_α calculations.

The X_α calculated energies of the spin triplet excited states for the configuration with $\beta = 90°$ are compared with available experimental data [3] in Table 3. The comparison shows that the polarised X_α method can provide good estimate for such transitions; note that these transitions (except the first one) are not expected to be affected greatly by the variation in β. The first transition in trans-$\text{VCl}_2(\text{H}_2\text{O})_4^+$, namely $^3E_g(e_g, b_{2g}) \leftarrow {}^3A_{2g}(e_g^2)$, was not observed experimentally, but was estimated to be only 565 cm^{-1} [3]. From the magnetic anisotropy measurements carried out in the range 1.5-20 K on a single crystal of $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$ [15], McCarthy et al. [3] were able to estimate the value 1357 cm^{-1} as an upper limit for the tetragonal splitting of the $^3T_{1g}(O_h)$ in this system. A theoretically calculated value of 3510 cm^{-1} was found in this work for the previously mentioned tetragonal splitting in $\text{VCl}_2(\text{H}_2\text{O})_4^+$ with $\beta = 90°$. Since our calculations have been

Table 3. Total energy E_T, relative total energy ΔE_T and the energy gap $(\varepsilon_{b2}\uparrow - \varepsilon_e\uparrow)^a$ at different β values for $\text{VCl}_2(\text{H}_2\text{O})_4^+$

β	Ground state	E_T Rydbergs	ΔE_T kJ/mol	$(\varepsilon_{b2}\uparrow - \varepsilon_e\uparrow)$ cm^{-1}
0.0°	^3E_g	−4337.6243	43.68	−5046
22.5°	^3E	−4337.6223	45.55	−3499
45.0°	^3E	−4337.6135	57.10	173
56.0°	$^3A_2$	−4337.6381	24.80	1290
67.5°	$^3A_2$	−4337.6524	6.17	2522
90.0°	$^3A_{2g}$	−4337.6570	0.0	3510

Excited states for $\beta = 90°$ (cm^{-1})

	Excited config.	Calculated[a]	Experimental [3]
$^3E_g \leftarrow {}^3A_{2g}$	$e_g b_{2g}$	3510	—
$^3E_g \leftarrow {}^3A_{2g}$	$e_g a_{1g}$	15208	16430
$^3B_{2g} \leftarrow {}^3A_{2g}$	$b_{2g} a_{1g}$	17953	
$^3E_g \leftarrow {}^3A_{2g}$	$e_g b_{1g}$	18311	23240
$^3A_{2g} \leftarrow {}^3A_{2g}$	$b_{2g} b_{1g}$	21157	25000
$^3B_{1g} \leftarrow {}^3A_{2g}$	$a_{1g} b_{1g}$	36264	32820

[a] Calculated according to the transition state procedure [11]

Table 4. Different energy terms contributing to ΔE_T at $\beta = 0°$ (all in kJ/mol)

	$TiCl_2(H_2O)_4^+$	$VCl_2(H_2O)_4^+$	$TiCl(H_2O)_4^{2+}$
Nuclear–nuclear repulsion	−1148.04	−1232.83	−1148.04
Nuclear–electron attraction	+2037.22	+1630.30	+2520.28
Electron–electron repulsion	−886.56	−505.89	−1388.38
Electron exchange	−7.11	−49.13	−8.05
Kinetic energy	+10.63	+201.23	+55.13
ΔE_T	+6.14	+43.68	+30.94

performed for the isolated complex ion, the results of such calculations are not always expected to resemble the situation in the solid state, especially when the results are sensitive to the orientation of the coordinated water molecules. Thus the most stable configuration should also depend on the arrangements of the surrounding ions and the possible intramolecular hydrogen bonds that may be formed within the lattice. Good agreement between theory and experiment can be obtained for the tetragonal splitting of the $^3T_{1g}(O_h)$ term in $VCl_2(H_2O)_4^+$ if we assume that $50° < \beta < 67.5°$ for the stable configuration of this complex ion in the solid state (see Table 3).

In Table 4 the decomposition of ΔE_T ($\beta = 0°$) into its different interaction energy terms is given for $TiCl_2(H_2O)_4^+$, $VCl_2(H_2O)_4^+$ and the hypothetical complex $TiCl_2(H_2O)_4^{2+}$. The calculations for the latter complex (a d^0 system) have been performed to show that the stability of these systems for $\beta = 90°$ is not due primarily to the electrons occupying the d-like MOs, but is due to an overall electronic effect. An inspection of Table 4 reveals that the stability arises mainly from the contribution of the nuclear–electron attraction term, with most of the other terms destabilizing this particular configuration ($\beta = 90°$) relative to that with $\beta = 0°$.

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