Angular overlap treatment of the electronic spectra of the chlorotitanium(III) complexes containing tetrahydrofuran and acetonitrile

G. PLESCH

Institute of Inorganic Chemistry, Centre for Chemical Research,
Slovak Academy of Sciences, CS-842 36 Bratislava

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The electronic spectra of the distorted octahedral complexes $TiCl_3(C_4H_8O)_3$, $TiCl_3(C_4H_8O)_2(CH_3CN)$, and $TiCl_3(CH_3CN)_3$ were interpreted with the aid of the angular overlap model using the transferability assumption for the single ligand parameters. The σ and π bonding parameters e_λ for the Ti(III)—ligand bonds were determined. The following two-dimensional spectrochemical series for Ti(III) complexes was established: e_σ: $Cl < C_4H_8O < CH_3CN$ and e_π: $CH_3CN < C_4H_8O < Cl$.

Электронные спектры искаженных октаэдрических комплексов $TiCl_3$-$(C_4H_8O)_3$, $TiCl_3(C_4H_8O)_2(CH_3CN)$ и $TiCl_3(CH_3CN)_3$ были интерпретированы в рамках модели углового перекрывания предполагая переносность параметров для лигандов. Были вычислены e_λ параметры для σ и π связи Ti(III)—лиганд. Для изученных комплексов Ti(III) был установлен следующий двухразмерный спектрохимический ряд e_σ: $Cl < C_4H_8O < CH_3CN$ и e_π: $CH_3CN < C_4H_8O < Cl$.

The angular overlap model (AOM) has been widely used for the parametrization of ligand fields for the interpretation of *d*—*d* transition energies of complexes with various central atoms [1—3]. However, until now, no AOM parameters have been reported for Ti(III) complexes. This is caused probably by the fact that the Ti(III) complexes are extremely sensitive to oxidation in the air and so only a limited amount of experimental data about these complexes is available. Their spectra, taken at room temperature on mulled solids, or powders, give data of low accuracy only. However, the AOM parameters of complexes with low symmetry can be derived also from such spectra, if not a great accuracy of parameters is required, and if the number of these parameters is reduced by reasonable approximations allowed in AOM [4].

The aim of this work is the determination of the AOM e_λ parameters from the electronic spectral data of complexes with similar structure: $TiCl_3(C_4H_8O)_3$, $TiCl_3(C_4H_8O)_2(CH_3CN)$, and $TiCl_3(CH_3CN)_3$, assuming the transferability of single ligand parameters.

The model

According to the results of the X-ray structural analysis the unit cell of the complex $TiCl_3(C_4H_8O)_3$ contains two independent molecules of $TiCl_3(C_4H_8O)_3$ with meridional arrangement of Cl atoms [5]. The actual symmetry of the coordination polyhedron is near to C_{2v} (Fig. 1*a*). The distances Ti—Cl (in the range 233—236 pm) are nearly equal. The distance Ti—O_{ax} of the tetrahydrofuran located in a *trans* position to the Cl atom is significantly longer (218 pm) than the remaining two distances Ti—O_{eq}, which range between 208 and 211 pm.

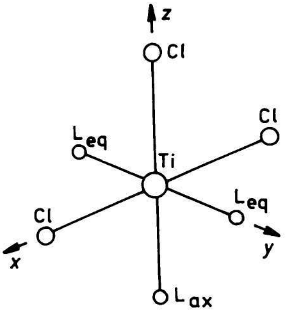

Fig. 1. Scheme of the coordination polyhedron of the complexes $TiCl_3(L_{eq})_2(L_{ax})$.
a) $TiCl_3(C_4H_8O)_3$: $L_{eq} = C_4H_8O$, $L_{ax} = C_4H_8O$; *b*) $TiCl_3(CH_3CN)_3$: $L_{eq} = CH_3CN$, $L_{ax} = CH_3CN$; *c*) $TiCl_3(C_4H_8O)_2(CH_3CN)$: $L_{eq} = C_4H_8O$, $L_{ax} = CH_3CN$.

The crystal field analysis of the electronic and e.p.r. spectra of $TiCl_3(CH_3CN)_3$ showed that this complex adopts a meridional arrangement of Cl ligands, the symmetry of coordination polyhedron being C_{2v} [6], and thus it is analogical to $TiCl_3(C_4H_8O)_3$ (Fig. 1*b*).

On the basis of spectral and magnetic properties of $TiCl_3(C_4H_8O)_2(CH_3CN)$ it is assumed that in this complex the acetonitrile molecule is located in a *trans* position to the Cl atom [7, 8] and consequently the symmetry of the coordination polyhedron is C_{2v} (Fig. 1c).

The electronic spectra of the above complexes were reported in the papers [7, 9—11]. The data obtained from the diffuse reflectance spectra are in excellent agreement with those from the nujol mulls.

In the angular overlap approach the parameter of energy, by which a *d* orbital is destabilized upon interaction with a ligand orbital, is proportional to the squared diatomic overlap integral $e_\lambda = K_\lambda S_\lambda^2$. The total energy of *d* orbitals was obtained by summing the σ and π effects over all ligands [12]. The diatomic overlap integrals $\mathrm{Ti^0}(3d)$—$\mathrm{O^0}(2p)$ and $\mathrm{Ti^0}(3d)$—$\mathrm{Cl^0}(3p)$ were computed using the double ζ wave functions given by *Clementi* [13].

The nonzero matrix elements of *d* orbitals for the complexes $\mathrm{TiCl_3(L_{eq})_2(L_{ax})}$ with C_{2v} symmetry of the coordination polyhedron (Fig. 1) are given by

$$\langle z^2|\hat{V}|z^2\rangle = 1.5e_\sigma(\mathrm{Cl}) + 0.5e_\sigma(\mathrm{L_{eq}}) + e_\sigma(\mathrm{L_{ax}})$$
$$\langle x^2-y^2|\hat{V}|x^2-y^2\rangle = 1.5e_\sigma(\mathrm{Cl}) + 1.5e_\sigma(\mathrm{L_{eq}})$$
$$\langle z^2|\hat{V}|x^2-y^2\rangle = \sqrt{3}/2[-e_\sigma(\mathrm{Cl}) + e_\sigma(\mathrm{L_{eq}})]$$
$$\langle yz|\hat{V}|yz\rangle = e_\pi(\mathrm{Cl}) + 2e_\pi(\mathrm{L_{eq}}) + e_\pi(\mathrm{L_{ax}})$$
$$\langle xz|\hat{V}|xz\rangle = 3e_\pi(\mathrm{Cl}) + e_\pi(\mathrm{L_{ax}})$$
$$\langle xy|\hat{V}|xy\rangle = 2e_\pi(\mathrm{Cl}) + 2e_\pi(\mathrm{L_{eq}})$$

In the low symmetry complexes the great number of parameters can be effectively reduced by reasonable approximations within the AOM approach. However this results in lower accuracy of the obtained data.

For linear ligators such as the halogenide ions, the ratio (e_π/e_σ) can be estimated from the squared overlap integral ratio, considering only overlap with ligand *np* orbitals. For the Ti—Cl bonding, $(S_\pi/S_\sigma)^2 = 0.32$. According to recent papers [2] the value of (e_π/e_σ) is always smaller than the ratio $(S_\pi/S_\sigma)^2$. If we assume that $(e_\pi(\mathrm{Cl})/e_\sigma(\mathrm{Cl})) \sim 0.6\cdot(S_\pi/S_\sigma)^2$ as it was found in complexes of Cr(III) and Cu(II) [2], then for our compounds $(e_\pi(\mathrm{Cl})/e_\sigma(\mathrm{Cl}))$ will be 0.19. As the character of our calculations did not allow us to take $(e_\pi(\mathrm{Cl})/e_\sigma(\mathrm{Cl}))$ as a variable parameter, two fitting procedures with the values of $(e_\pi(\mathrm{Cl})/e_\sigma(\mathrm{Cl})) = 0.32$ and 0.19 were carried out. However, there was not a considerable effect on the e_λ parameters obtained from the fitting procedure when the ratio $(e_\pi(\mathrm{Cl})/e_\sigma(\mathrm{Cl}))$ was changed from 0.32 to 0.19. The e_σ parameters were changed not more than by $0.4\times10^3\ \mathrm{cm^{-1}}$ and $e_\pi(\mathrm{O})$ changed by $0.1\times10^3\ \mathrm{cm^{-1}}$, while the ordering of parameters remained the same. Only the results obtained with the ratio $(e_\pi(\mathrm{Cl})/e_\sigma(\mathrm{Cl})) = 0.19$ are further considered.

Since the coordinated acetonitrile behaves like a pure nitrogen σ donor ligand with respect to the coordination with Ti(III) [14, 15], we set $e_\pi(\mathrm{N}) = 0$.

The ratios between the e_λ parameters for chemically equivalent donor atoms with different metal—ligand distances can be estimated from the squared ratios of the corresponding overlap integrals [4]. For the complex $TiCl_3(C_4H_8O)_3$ the following values are obtained: $(e_\sigma(O_{ax})/e_\sigma(O_{eq}))=0.84$ and $(e_\pi(O_{ax})/e_\pi(O_{eq}))=$ $=0.73$. It was found that in all chlorotitanium(III) complexes with solved structure, the symmetry of coordination polyhedron being C_{2v}, as a consequence of the *trans* effect the distances Ti—L_{ax} are greater than the Ti—L_{eq} ones [5, 16]. We assume that this is valid also for the investigated complexes with acetonitrile, and because the overlap integrals for the bonding with oxygen decrease with the distance similarly as those of nitrogen, we set $(e_\sigma(N_{ax})/e_\sigma(N_{eq}))=0.84$.

The oxygen donor atom of the water molecule in aquacomplexes can be reasonably treated as an effective linear ligand [17, 18]. Since the bonding properties of the etheric oxygen from the tetrahydrofuran and those of the O atom of water can be regarded as similar, we assume a linear ligation of the tetrahydrofuran oxygen atom.

The assumption of the transferability of the AOM parameters is a subject of continuing interest [2, 4, 19, 20]. Using e_λ parameters transferable in a series of complexes of Co(II), or Ni(II), or Cr(III) with similar structure, good fit between the calculated and experimental electronic spectral data was found [4, 17, 20]. According to *Vanquickenborne* [21] a reasonable single ligand parameter should perform reasonably well over a series of mixed ligand complexes. Since the Ti(III) complexes under investigation have a similar structure, the transferability of the single ligand e_λ parameters is assumed in this model.

With the above assumptions for the parametrization of the ligand fields of the studied Ti(III) complexes four parameters are necessary: $e_\sigma(Cl)$, $e_\sigma(N)$, $e_\sigma(O)$, and $e_\pi(O)$. The values of $e_\sigma(O)$, $e_\pi(O)$, and $e_\sigma(N)$ are referred to the equatorial ligands. The required bonding parameters were obtained from the experimentally observed *d*—*d* transition energies [11] using the above matrix elements. The "best fit" values were obtained by the mapping routine, where the e_λ parameters were varied over the region of physically reasonable values and the minima of the function $\sigma=\left[\sum^{6}(\bar{\nu}_{exp}-\bar{\nu}_{calc})^2/6\right]^{1/2}$ were determined. Here $\bar{\nu}_{exp}$ are the experimentally obtained *d*—*d* transition bands (from the nujol mull spectra) [11] and $\bar{\nu}_{calc}$ are the calculated wavenumbers of transitions from the ground state to the states $A_1(1)$ and $A_1(2)$ for each complex.

Results and discussion

The complexes $TiCl_3(L_{eq})_2(L_{ax})$ have a distorted octahedral structure with the symmetry of a coordination polyhedron C_{2v}. In this symmetry the ^2D term of Ti(III) is splitted into five energy states: $B_1(|xz\rangle)$, $B_2(|yz\rangle)$, $A_2(|xy\rangle)$, $A_1(1)$ $(-\cos\omega|z^2\rangle+\sin\omega|x^2-y^2\rangle)$, and $A_1(2)$ $(\sin\omega|z^2\rangle+\cos\omega|x^2-y^2\rangle)$. The d orbitals belonging to the $A_1(1)$ and $A_1(2)$ representations can form σ bonds with filled ligand orbitals. These orbitals are much more destabilized in the process of interaction with the ligands, than the d orbitals belonging to the B_1, B_2, and A_2 representations, the latter being able to form only π bonds. The energy separations between these "lower" orbitals are too small to be detected in the electronic spectra. Accordingly, in the experimental electronic spectra of the complexes under investigation two d—d bands due to the transitions from the ground to the $A_1(1)$ and $A_1(2)$ states can be observed.

During the fitting procedure in the physically reasonable parameter space two minima of the σ function were found. The first corresponds to the assignment of the antisymmetric combination of d_{z^2} and $d_{x^2-y^2}$ orbitals to the $A_1(2)$ state with the highest energy, while the second one to the assignment of the symmetric combination of d_{z^2} and $d_{x^2-y^2}$ to this state. The experimental and calculated "best fit" wavenumbers of the d—d transitions together with the mixing coefficients of d_{z^2} and $d_{x^2-y^2}$ orbitals for these two assignments are given in Table 1.

Table 1

The "best fit" values of the wavenumbers of the d—d transitions and the mixing coefficients of d_{z^2} and $d_{x^2-y^2}$ orbitals

Complex		Wavenumber of transition/$\mathrm{cm^{-1}}\cdot 10^{-3}$				Mixing coefficients	
		$B_2 \rightarrow A_1(1)$		$B_2 \rightarrow A_1(2)$			
		exp*	calc	exp*	calc	$\sin\omega$	$\cos\omega$
$\mathrm{TiCl_3(C_4H_8O)_3}$	*a*	13.50	13.58	14.70	14.77	0.304	−0.953
	b		13.33		14.88	0.435	0.900
$\mathrm{TiCl_3(C_4H_8O)_2(CH_3CN)}$		14.00	13.67	15.60	15.53	0.189	−0.982
	b		13.96		15.32	0.521	0.854
$\mathrm{TiCl_3(CH_3CN)_3}$	*a*	14.70	14.70	17.10	17.10	0.572	−0.821
	b		14.96		17.12	0.513	0.858

* Obtained from nujol mull spectra [11].

a) The antisymmetric combination of d_{z^2} and $d_{x^2-y^2}$ orbitals belongs to the state with the highest energy.

b) The symmetric combination of d_{z^2} and $d_{x^2-y^2}$ orbitals belongs to the state with the highest energy.

When the antisymmetric combination of d_{z^2} and $d_{x^2-y^2}$ orbitals ($\sin\omega>0$, $\cos\omega<0$) belongs to the $A_1(2)$ state with the highest energy, the following AOM parameters are obtained: $e_\sigma(\mathrm{Cl})=6.5\times10^3\ \mathrm{cm}^{-1}$, $e_\sigma(\mathrm{N})=5.2\times10^3\ \mathrm{cm}^{-1}$, $e_\sigma(\mathrm{O})=6.1\times10^3\ \mathrm{cm}^{-1}$, $e_\pi(\mathrm{O})=1.1\times10^3\ \mathrm{cm}^{-1}$ If these parameters are ordered in a one-dimensional spectrochemical series according to the value $\Delta_0=3e_\sigma-4e_\pi$, we obtain $\Delta(\mathrm{O})<\Delta(\mathrm{Cl})<\Delta(\mathrm{N})$. As this order is not consistent with the well known one-dimensional spectrochemical series, where $\Delta(\mathrm{Cl})<\Delta(\mathrm{O})<\Delta(\mathrm{N})$ [11, 22], these parameters seem to be improbable. On the basis of the above discussion we reject the assignment of the antisymmetric combination of d_{z^2} and $d_{x^2-y^2}$ orbitals to the $A_1(2)$ state with the highest energy.

In the case, where the symmetric combination of the d_{z^2} and $d_{x^2-y^2}$ orbitals ($\sin\omega>0$, $\cos\omega>0$) is assigned to the $A_1(2)$ state with the highest energy, we obtain

$$\begin{aligned} e_\sigma(\mathrm{Cl}) &= 5.3\times10^3\ \mathrm{cm}^{-1}\\ e_\sigma(\mathrm{N}) &= 6.4\times10^3\ \mathrm{cm}^{-1}\\ e_\sigma(\mathrm{O}) &= 6.0\times10^3\ \mathrm{cm}^{-1}\\ e_\pi(\mathrm{O}) &= 0.5\times10^3\ \mathrm{cm}^{-1}\end{aligned}$$

(From the above assumptions $e_\pi(\mathrm{Cl})=1.0\times10^3\ \mathrm{cm}^{-1}$, $e_\pi(\mathrm{N})=0$.) For these parameters the one-dimensional spectrochemical series is $\Delta(\mathrm{Cl})<\Delta(\mathrm{O})<\Delta(\mathrm{N})$ in accordance with [11, 22]. The values of the e_λ parameters are similar to those published for Cu(II) and Cr(III) complexes [1, 21]. For Ti(III) complexes under investigation the following two-dimensional spectrochemical series can be established

$$\begin{aligned} e_\sigma&: \mathrm{Cl}<\mathrm{C_4H_8O}<\mathrm{CH_3CN}\\ e_\pi&: \mathrm{CH_3CN}<\mathrm{C_4H_8O}<\mathrm{Cl}\end{aligned}$$

The position of a given ligand in such a series reflects the energetic effect of its σ and π bonding on the d-shell of the central atom. The relative position of acetonitrile is similar to that of aliphatic amines in such a series established for Cr(III) complexes [21]. While in the e_σ series the oxygen ligator tetrahydrofuran stands higher than the Cl^- ion, similarly as water in Cr(III) complexes [21], in the e_π series this order is inverted. This suggests that tetrahydrofuran is a weaker π donor than water.

Using the above e_λ parameters the order of energy levels in the Ti(III) complexes under investigation is $B_2<A_2<B_1<A_1(1)<A_1(2)$, with the exception of the complex $\mathrm{TiCl_3(C_4H_8O)_2(CH_3CN)}$, in which an accidental degeneration of the A_2 and B_1 states takes place. While the energetic separations of the ground state B_2 and the states $A_1(1)$ and $A_1(2)$ are in the visible region of electronic spectra, the separations between the "lower" states B_2, A_2, and B_1 are in the range 600—2000 cm^{-1} This is in agreement with the e.p.r. spectra of polycrystalline

solids, the experimental spectra of which with $g_{\perp} > g_{\parallel}$ for $TiCl_3(C_4H_8O)_3$ and $TiCl_3(CH_3CN)_3$ require an order of "lower" energy states $B_2 < A_2 < B_1$ [6, 23]. The isotropic spectrum of the complex $TiCl_3(C_4H_8O)_2(CH_3CN)$ can be explairied by the order of energy levels $B_2 < A_2 \sim B_1$ [8, 23].

Summing up we can state that on the basis of electronic spectral data, using a single angular overlap model the σ and π bonding parameters can be obtained for the chlorotitanium(III) complexes with various ligands. Their values are similar to those published for Cu(II) and Cr(III) complexes. The application of approximations results in a lower accuracy of the obtained parameters. The usefulness of such parameters lies in the possibility of a semiquantitative description of spectrochemical behaviour of some Ti(III) complexes. It will be possible to obtain more accurate values, if more accurate experimental data (e.g. single crystal electronic and e.p.r. spectra) for a number of Ti(III) complexes with solved structure will be available.

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