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SEMI-EMPIRICAL MOLECULAR ORBITAL CALCULATIONS ON OCTAHEDRAL COMPLEXES: $[TiCl_6]^{2-}$*

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A. INTRODUCTION

In several previous papers[1-3] we applied the semi-empirical molecular orbital (MO) theory of Pople–Pariser–Parr, which works rather well for unsaturated hydrocarbons, to tetroxo-anions and tetrahalides of the first transition metal series. On the basis of our rather satisfying results, we thought it useful to extend such an investigation to octahedral coordination compounds with the purpose on the one hand, of improving the semi-empirical criteria for evaluation of the integrals and, on the other, of obtaining useful chemical information, such as the order of levels, the charge distribution and the assignment of the observed bands.

First, in a series of studies, we have examined the $TiCl_6^{2-}$ ion as it is a closed shell system (the central metal ion is d^0) and, therefore, easier to treat with the Roothaan SCF procedure[4].

In addition some comparison can be made between the calculated transitions and the spectrum observed for Ti^{IV} in 12 *M* HCl solutions[5].

B. OUTLINE OF THE CALCULATIONS

The calculation procedure is substantially that described in previous papers[1,2]. The MO-LCAO approximation has been used by considering only the 3d, 4s and 4p atomic orbitals (AO) on titanium and 3p AO's on chlorine atoms. The 3s AO's on Cl atoms have been neglected since in our previous calculations[6] carried out on TiCl and $TiCl_4$, we found that this is a sufficiently good approximation.

The geometry of the molecule is that of a regular octahedron with a bond length[7] of 2.35 Å. The coordinate system, the numbering and orientation of the ligand orbitals are shown in Fig. 1. The symmetry orbitals, according to the point symmetry group O_h, are given in Table 1.

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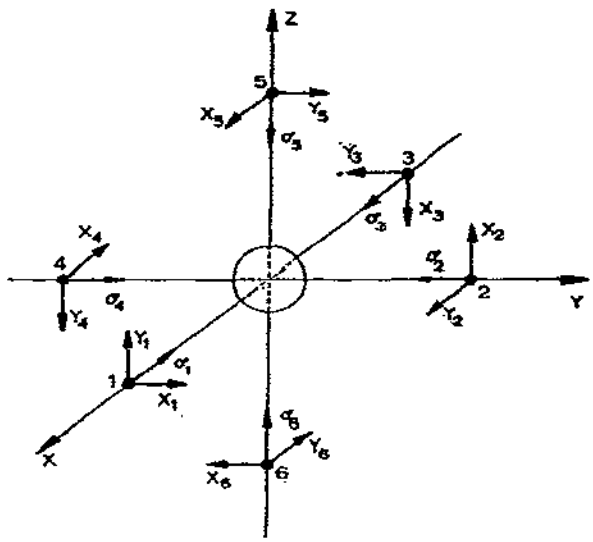

Fig. 1. Coordinate systems, numbering and orientation of the ligand orbitals.

TABLE 1

SYMMETRY ORBITALS FOR O_h MOLECULES

Irreducible representations	*Metal*	*Ligands*	
		p_σ	p_π
A_{1g}	s	$1/\sqrt{6}(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)$	
E_g	d_{z^2}	$\frac{1}{2}\sqrt{3}(-\sigma_1-\sigma_2-\sigma_3-\sigma_4+2\sigma_5+2\sigma_6)$	
	$d_{x^2-y^2}$	$\frac{1}{2}(\sigma_1-\sigma_2+\sigma_3-\sigma_4)$	
T_{1g}			$\frac{1}{2}(y_1+x_3-x_5-y_6)$ $\frac{1}{2}(x_2+y_4-y_5-x_6)$ $\frac{1}{2}(x_1-y_2+y_3-x_4)$
T_{1u}	p_x	$1/\sqrt{2}(\sigma_1-\sigma_3)$	$\frac{1}{2}(y_2-x_4+x_5-y_6)$
	p_y	$1/\sqrt{2}(\sigma_2-\sigma_4)$	$\frac{1}{2}(x_1-y_3+y_5-x_6)$
	p_z	$1/\sqrt{2}(\sigma_5-\sigma_6)$	$\frac{1}{2}(y_1+x_2-x_3-y_4)$
T_{2g}	d_{zx}		$\frac{1}{2}(y_1+x_2+x_5+y_6)$
	d_{zy}		$\frac{1}{2}(x_2+y_4+y_5+x_6)$
	d_{xy}		$\frac{1}{2}(x_1+y_3+y_3+x_4)$
T_{2u}			$\frac{1}{2}(y_2-x_4-x_5+y_6)$ $\frac{1}{2}(x_1-y_3-y_5+x_6)$ $\frac{1}{2}(y_1-x_2-x_3+y_4)$

The ground state has been evaluated by means of an SCF calculation using the "zero differential overlap" approximation between AO's on different centres. Moreover, the energies of the allowed excitations from the ground state ($^1A_{1g}$) to the lowest excited states ($^1T_{1u}$) have been evaluated by means of a configuration interaction calculation (CI) extended to all mono-excited configurations.

The molecular integrals have been evaluated semi-empirically. The one-

centre integrals were calculated from the valence state energies[8] and are reported in Tables 2 and 3. The two-centre coulomb repulsion integrals have been evaluated employing the uniformly charged sphere approximation[9].

TABLE 2

SEMI-EMPIRICAL ONE-CENTRE INTEGRALS FOR CHLORINE (eV)

$g_{x,x} = g_{y,y} = g_{z,z}$	11.30
$g_{x,y} = g_{x,z} = g_{y,z}$	9.63
U_p	−53.60
C	−29.63

TABLE 3

SEMI-EMPIRICAL ONE-CENTRE INTEGRALS FOR TITANIUM (eV)

	$q = 0$	$q = +1$
$g_{z^2,z^2} = g_{x^2-y^2,x^2-y^2} = g_{xz,xz} = g_{zy,zy} = g_{xy,xy}$	8.20	12.50
$g_{xz,zy} = g_{xz,xy} = g_{xz,x^2-y^2} = g_{zy,xy} = g_{zy,x^2-y^2}$	7.29	11.10
g_{xy,x^2-y^2}	7.68	11.70
$g_{z^2,xz} = g_{z^2,zy}$	7.55	11.50
$g_{z^2,xy} = g_{z^2,x^2-y^2}$	7.16	10.90
$g_{s,d}$	5.54	7.90
$g_{s,s}$	4.80	5.60
$g_{x,x} = g_{y,y} = g_{z,z}$	4.00	4.83
$g_{x,y} = g_{x,z} = g_{y,z}$	3.48	4.20
$g_{s,p}$	4.20	5.08
g_{z,z^2}	4.85	6.78
$g_{z,xz} = g_{z,zy} = g_{x,xy} = g_{y,xy} = g_{x,zx} = g_{y,zy} = g_{x,x^2-y^2} = g_{y,x^2-y^2}$	4.80	6.66
$g_{z,x^2-y^2} = g_{z,xy} = g_{x,zy} = g_{y,zx}$	4.65	6.40
$g_{x,z^2} = g_{y,z^2}$	4.70	6.43
U_d	−25.74	−36.32
U_s	−22.63	−29.30
U_p	−17.73	−22.80
C	−28.56	−79.05

TABLE 4

OVERLAP INTEGRALS

$S(4s_M, 3p_{\sigma L}) = .2229$	$S(3p_{\sigma L_1}, 3p_{\sigma L_2}) = .0498$
$S(4p_{\sigma M}, 3p_{\sigma L}) = .1852$	$S(3p_{\sigma L_1}, 3p_{\sigma L_4}) = .0171$
$S(4p_{\pi M}, 3p_{\pi L}) = .2218$	$S(3p_{\pi L_1}, 3p_{\pi L_2}) = .0214$
$S(3d_{\sigma M}, 3p_{\sigma L}) = .1599$	$S(3p_{\pi L_1}, 3p_{\pi L_4}) = .0035$
$S(3d_{\pi M}, 3p_{\pi L}) = .1137$	

The β integrals have been calculated by means of the relation:

$$\beta_{ij} = -\tfrac{1}{2}F(I_i + I_j)S_{ij}$$

where $F = 1$. The overlap integrals (Table 4) were evaluated using the following radial functions[10–12]:

$$\text{Ti } R(3d) = 0.4391\ \phi_3(4.55)+0.7397\ \phi_3(1.60)$$
$$R(4s) = -0.02231\ \phi_1(21.40)+0.07751\ \phi_2(8.05)-0.1985\ \phi_3(3.64)+ +1.0164\ \phi_4(1.20)$$
$$R(4p) = 0.00495\ \phi_2(8.80)-0.01823\ \phi_3(3.31)+1.00015\ \phi_4(0.51)$$
$$\text{Cl } R(3p) = -0.01295\ \phi_2(13.79)-0.03983\ \phi_2(8.8355)-0.26254\ \phi_2(5.3987)+ +0.12225\ \phi_3(4.0186)+0.35932\ \phi_3(2.4367)+0.56879\ \phi_3(1.738)+ +0.09941\ \phi_3(0.872)$$

where

$$\phi_n(\mu) = N r^{n-1} \exp(-\mu r)$$

Finally, all the neutral penetration integrals have been neglected considering the rather large bond length. This approximation was also supported by the results of the calculations[6] on TiCl and $TiCl_4$.

All the calculations (SCF for the ground state and CI for the excited states) were carried out twice: the first time using semi-empirical integrals corresponding to a zero oxidation state of titanium ($q = 0$), and the second, using the semi-empirical integrals which correspond to an oxidation state of $+1$ ($q = +1$).

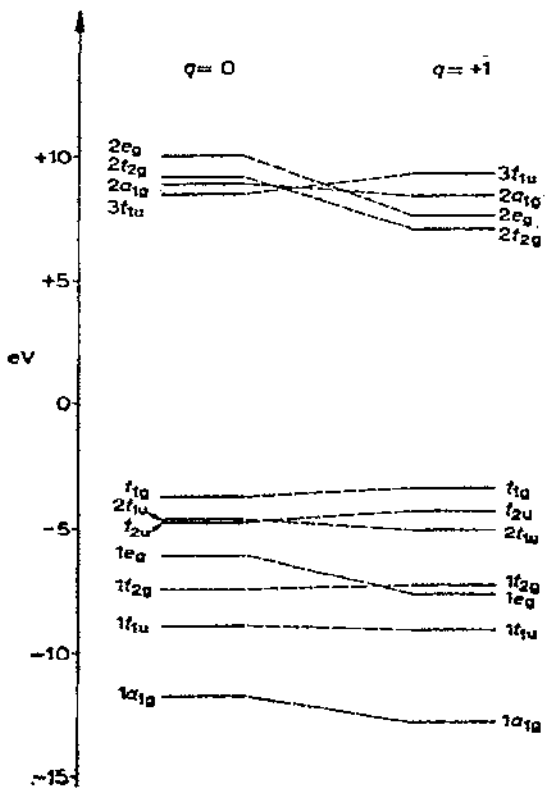

Fig. 2. MO energy levels.

C. RESULTS AND DISCUSSION

For each calculation the following data are reported:
(a) MO energy levels (Fig. 2)
(b) SCF eigenvectors (Table 5)
(c) Total gross population analysis (Table 6)
(d) CI eigenvectors and excitation energies (Table 7)

In Fig. 2 the levels scheme, obtained on the basis of the SCF eigenvalues, is shown. The order for $q = +1$ is substantially in agreement with that of other authors and is supported by the experimental data[13,14]. In particular the first empty MO's are of T_{2g} and E_g symmetry, precisely as required by the Crystal Field Theory. The order for $q = 0$ is rather incongruous, because the $3t_{2u}$ and $2a_{1g}$ MO energies are slightly lower than those of $2t_{2g}$ and $2e_g$. Probably this arises through insufficient accuracy in the Ti one centre integrals.

With regard to the filled MO's, in both cases the $1a_{1g}$, $1t_{1u}$, $1e_g$ and $1t_{2g}$ MO's give a positive contribution to the bonding, whereas the $2t_{1u}$ MO's have a

TABLE 5

EIGENVALUES E (eV) AND EIGENVECTORS

MO	E(eV)	$q = 0$					E(eV)	$q = +1$				
		d	s	p	p_σ	p_π		d	s	p	p_σ	p_π
$1a_{1g}$	−11.79		.389		.922		−12.86		.392		.920	
$1t_{1u}$	−9.00			.375	.559	.739	−9.20			.358	.669	.651
$1e_g$	−6.14	.331			.944		−7.62	.416			.909	
$1t_{2g}$	−7.49	.236				.972	−7.33	.299				.954
$2t_{1u}$	−4.75			.045	−.808	.588	−5.10			.111	−.723	.682
t_{2u}	−4.79					1	−4.40					1
t_{1g}	−3.82					1	−3.46					1
$2t_{2g}$	9.17	.972				−.236	7.07	.954				−2.99
$2e_g$	10.00	.944			−.331		7.60	.909			−.416	
$2a_{1g}$	8.84		.922		−.389		8.38		.920		−.392	
$3t_{1u}$	8.49			.926	−.187	−.328	9.26			.927	−.172	−.332

TABLE 6

TOTAL GROSS POPULATION AND OXIDATION STATE

		$q = 0$	$q = +1$
$N(4s_M)$		.299	.306
$N(4p_M)$		.285	.282
$N(3d_{z^2,M}) = N(3d_{x^2-y^2,M})$		.217	.342
$N(3d_{xz,M}) = N(3d_{xy,M}) = N(3d_{xy,M})$		.112	.178
$N(3p_{\sigma,L})$		1.844	1.806
$N(3p_{\pi,L})$		1.918	1.900
Oxidation	a	2.076	1.630
State	b	−.056	−.644

TABLE 7

RESULTS OF THE CONFIGURATIONAL INTERACTION CALCULATIONS

	$q = 0$					$q = +1$				
	A	*CI eigenvectors*				A	*CI eigenvectors*			
$1a_{1g} \rightarrow 3t_{1u}$	16.16	−.013	−.012	.007	−.005	17.33	−.007	.003	.002	.010
$1t_{1u} \rightarrow 2a_{1g}$	13.14	−.004	−.027	.016	−.009	12.38	−.020	−.003	−.009	.026
$2t_{1u} \rightarrow 2a_{1g}$	8.87	.067	−.017	−.460	.675	8.26	.043	−.002	−.080	−.109
$1e_g \rightarrow 3t_{1u}$	10.31	−.003	−0.47	.009	−.049	11.63	−.012	−.006	.006	.024
$1t_{1u} \rightarrow 2e_g$	13.52	−.026	−.070	−.078	+.007	10.75	−.114	−.019	.002	−.103
$2t_{1u} \rightarrow 2e_g$	8.84	.119	.469	.592	−.103	6.69	.519	.111	.167	.777
$t_{2u} \rightarrow 2e_g$	9.02	.018	−.121	−.031	.097	6.37	−.096	−.070	−.945	.294
$t_{1g} \rightarrow 3t_{1u}$	8.42	.186	−.857	.297	−.118	8.20	−.021	−.020	−.130	−.245
$1t_{1u} \rightarrow 2t_{2g}$	12.68	−.061	−.016	.088	.088	10.25	.013	.034	.000	.022
$2t_{1u} \rightarrow 2t_{2g}$	8.01	.898	.115	−.303	−.275	6.22	.395	−.909	−.006	−.118
$1t_{2g} \rightarrow 3t_{1u}$	12.06	.008	−.094	.042	−.004	11.89	−.006	−.001	−.023	.034
$t_{2u} \rightarrow 2t_{2g}$	8.50	−.367	−.002	−.491	−.651	6.31	−.741	−.393	.236	.459
B CI eigenvalues		7.87	8.11	8.54	8.64		6.02	6.23	6.33	6.66

slight antibonding character and the t_{2u} and t_{1g} MO's have a non-bonding character, being completely localized on the chlorine atoms.

The excitation energies obtained by a CI calculation are reported in Table 7. The data of columns A are the diagonal elements of the CI secular equation (*i.e.*, the excitation energies of each single configuration) and the data of row B are the calculated excitation energies.

The results for $q = +1$ agree better with the observed spectrum of $TiCl_6^{2-}$ in 12 *M* HCl solutions, in which the first observed band appears at 45,00 cm^{-1} (5.58 eV). The results for $q = 0$ give high transition energies.

The results can be interpolated in such a way that the oxidation state of Ti obtained from the calculations is equal to that to which the semi-empirical molecular integrals correspond. However, evaluating the oxidation state of Ti by relation[1]:

$$q_k = Z_k - \sum_{r_k} n_{r_k}$$

(where n_{r_k} is the occupation number of the χ_{r_k} AO on atom k), different results are obtained according to whether n_{r_k} is considered equal to the diagonal density matrix $D_{r_k r_k}$ (row a in Table VI) or as given by the expression (row b in Table 6)[1]:

$$n_{r_k} = D_{r_k r_k} + \sum_{h \neq k} \sum_{s_h} D_{r_k s_h} S_{r_k s_h}$$

Using the graphical procedure described in a previous paper[1], the following values, corresponding to the two different criteria, are obtained: $q = +1.44$ and $q = -0.03$.

With $q = 1.44$ we obtain a good agreement with the first experimentally observed band to which we can assign three different one-electron transitions:

$$t_{2u} \rightarrow 2t_{2g} \qquad 2t_{1u} \rightarrow 2t_{2g} \qquad t_{2u} \rightarrow 2e_g$$

With the second criterion, $q = -0.03$, we have a discrepancy with the observed band but a better agreement with the Pauling electroneutrality principle.

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