Conclusions

(i) the potential energy surface model of predicting transition state structure suggests an S_N2 mechanism, where bond-formation is somewhat more important, for the solvolysis of benzoyl chlorides.

(ii) Transition state variation predicted with the quantum mechanical model is consistent with the experimental results whereas the predictions provided by the potential energy surface model is found to be inconsistent in some cases.

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The Effect of Hybridized Atomic Orbitals of Ligands on the Calculated Dipole Moments for Octahedral [M(III)O₃S₃] Type Complexes

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Extended Hückel calculations have been performed to obtain molecular orbital energies and the corresponding eigenvectors for [M(III)O₃S₃] type complexes [M(111) =V(111), Cr(III), Mn(III), Fe(III) and Co(III)] adopting the valence basis set orbital (nP_z) and the hybridized atomic orbital of ligands. The effects of the hybridized atomic orbital of ligands on the calculated dipole moments and $10 D_q$ values are investigated. The calculated $10 D_q$ values and dipole moments are close to the experimental values when the hybridized atomic orbital of ligands is used to obtain the eigenvector for [M(III)O₃S₃] type complexes.

Intoduction

A great deal of interest has been concentrated on physical measurements of infrared, electronic, nmr and esr spectra, magnetic moments and dipole moments of transition metal [M(III)O₃S₃] type complexes to obtain their structual information.[1]

In the previous works, we have reported the calculated dipole moments for octahedral [M (III)O₃S₃] type complexes by using σ-bonding molecular orbitals and valence bond

molecular orbitals. We have investigated the geometric structure of those complexes on the basis of the calculated dipole moments.[2] It is however inevitable to consider the π-bond formation between the central metal ion and ligand orbitals to elucidate electronic, nmr and esr spectra and magnetic properties for such complexes.[1,4] The effect of π bonds on the calculated dipole moments for octahedral [M(III)O₃S₃] type complexes was reported.[3] The calculated dipole moments ($\mu = \mu_\sigma + \mu_\pi$) were closer to the experimental values than those values obtained for the cases where only σ-bonds are assumed to be formed.

In the previous works[5], we adopted the valence basis sets of the central metal ion and the modified linear combinations of only np orbitals to construct σ and π bonding molecular orbitals, and the mixing coefficient, C_M, between the valence basis sets of the central metal ion and the appropriate ligand orbitals was assumed to be equal. A great deal of information has been accumulated on using a hybidized atomic orbital as the ligand σ-bonding orbitals. In this work we thus adopt np orbital of oxygen and sulfur atoms in the case of π-ligand orbitals, but for σ-orbitals the ligand orbitals are assumed to be hybrids of the form

$$\sigma = \sin \theta (ns) + \cos \theta \ (np_z)$$

where $n = 2$ or 3.

We also adopt the two assumptions that (1) the nuclear part of the dipole moments is completely cancelled because of a symmetrical arrangement of ligands around the central metal ion, and (2) the atoms which bond directly with the central metal ion and are located at the end of the ligands are the dominant contribution to the dipole moments of octahedral [M(III)O₃S₃] type complexes. Therefore we use the approximate molecular orbitals which are formed by the linear combinations of the valence basis sets of the central metal ion and the modified linear combination of the valence basis sets, np, and ns and np atomic orbitals, respectively.

The purpose of this work is first to perform the extended Hückel calculation to obtain molecular orbital energies and the corresponding eigenvectors for [M(III)O₃S₃] type complexes, adopting the valence basis sets of the central metal ion and ligands, and secondly to investigate the effect of the hybridized atomic orbital of ligands on the calculated dipole moments for octahedral [M(III)O₃S₃] type complexes.

We adopt SCF basis set functions which have the form

$$\phi_{nlm} = N r^{n-1} \exp(-\tau_{nlm} r) \ Y_{lm}(\theta, \phi) \qquad (1)$$

where n,l and m are usual quantum numbers which have integer values, N a normalization constant, $Y_{lm}(\theta, \phi)$ a spherical harmonic and τ_{nlm} the optimized orbital exponent[6], and then transform them into real forms listed in Table 2.

Calculation of the effect of ns orbital for ligands on the calculated dipole moments

In order to investigate the effect of a hybridized atomic orbital of ligands on the calculated dipole moments we have carried out two separate calculations, using σ bonding ligand orbitals obtained from np_z orbitals and those obtained from

a linear combination of ns and np_z orbitals furnished by the ligands as follows

$$\sigma(1) = \sin \theta (ns) \pm \cos \theta (np_z) \qquad (2)$$

The degree of hybridization is estimated after the manner of Ballhausen and Gray,[7] by minimizing the quantity VSIP $(\theta)/S(\theta)$, where $S(\theta)$ is the overlap integral of the $3d_{z^2}$ orbital of the central metal ion with oxygen or sulfur hybrid orbitals of varying values of θ, while VSIP (θ) is the valence state ionization potential of the same oxygen or sulfer hybrid orbital. The angles at which the minimum occurred are listed in Table 1.

As indicated in the previous work, we assume that the cubic symmetry is still maintained for octahedral [M(III)O₃-S₃] type complexes even though three oxygen atoms have been replaced to form *cis* complexes by the sulfer atoms. Therefore we adopt the approximate molecular orbitals of octahedral complex which are modified by adding C coefficients to the valence basis sets for the substituted ligands, and we also adopt the notation of the O point group because the octahedral [M(III)O₃S₃] type complexes have lost the center of symmetry. The orbital transformation scheme for octahedral [M(III)-O₃S₃] type complexes is listed in Table 2.

The molecular orbitals may be approximated as

$$\phi_i(MO) = N_i \{\alpha_i \Gamma_i(M) + \beta_i \Gamma_i(l)\}$$
$$\phi_i^*(MO) = N_i^* \{\alpha_i^* \Gamma_i(M) + \beta_i^* \Gamma_i(l)\} \qquad (3)$$

where N_i and N_i^* are normalization constants for bonding and antibonding molecular orbitals given by

$$N_i = \{\alpha_i^2 + 2\alpha_i \beta_i < \Gamma_i(M) | \Gamma_i(l) > + \beta_i^2 < \Gamma_i(l) | \Gamma_i(l) >\}^{-\frac{1}{2}}$$
$$N_i^* = \{\alpha_i^{*2} + 2\alpha_i^* \beta_i^* < \Gamma_i(M) | \Gamma_i(l) > + \beta_i^{*2} < \Gamma_i(l) | \Gamma_i(l) >)\}^{-\frac{1}{2}}$$
$$\qquad (4)$$

The approximate energies and the corresponding eigen vectors for the molecular orbitals are obtained by solving the usual secular equation[8]

$$(H_{ij} - G_{ij} E) = O \qquad (5)$$

where G_{ij} are group overlap integrals which can be expressed in terms of two center overlap integrals multiplied by suitable coefficients. In equation (5), the diagonal matrix elements for the central metal orbitals, H_{ii}, are estimated as the negative of the valence state ionization potential (VSIP) of atoms[9]

$$H_{ii} = -VSIP \qquad (6)$$

TABLE 1: The Degree of Hybridization for σ Orbitals

Complex	The oxygen wavefunction			The sulfur wavefunction		
	$\sin \theta$	$\cos \theta$	θ	$\sin \theta$	$\cos \theta$	θ
[V(III)O₃S₃]	0.2250	0.9744	13	0.2079	0.9781	12
[Cr(III)O₃S₃]	0.2079	0.9781	12	0.2079	0.9781	12
[Mn(III)O₃S₃]	0.2079	0.9781	12	0.2079	0.9781	12
[Fe(III)O₃S₃]	0.1908	0.9816	11	0.1908	0.9816	11
[Co(III)O₃S₃]	0.1908	0.9816	11	0.1908	0.9816	11

(θ: degree)

TABLE 2: Orbital Transformation Scheme for [M(III)O₃S₃] Type Complexes

Represen-tation	Metal ion orbital, $\Gamma_i(M)$	Ligand orbital, $\Gamma_i(l)$
a_1	4s	$(1/6)^{\frac{1}{2}}(2p_x^1+2p_x^2+C3p_z^3+C3p_z^4+2p_z^5+C3p_z^6)$
		$(1/6)^{\frac{1}{2}}(\sigma_1+\sigma_2+C\sigma_3+C\sigma_4+\sigma_5+C\sigma_6)$
e	$3d_{x^2-y^2}$	$1/2(\sigma_1-\sigma_2+C\sigma_3-C\sigma_4)$,
		$1/2(2p_x^1-2p_x^2+C3p_z^3-C3p_z^4)$
	$3d_{z^2}$	$(1/12)^{\frac{1}{2}}(2\,2p_z^5+2C\,3p_z^6-2p_x^1-2p_x^2$
		$-C3p_z^3-C3p_z^4)$
		$(1/12)^{\frac{1}{2}}(2\sigma_5+2C\sigma_6-\sigma_1-\sigma_2-C\sigma_3-C\sigma_4)$
t_1	$4p_x$	$(1/2)^{\frac{1}{2}}(\sigma_1-C\sigma_3)$, $(1/2)^{\frac{1}{2}}(2p_x^1-C3p_z^3)$
		$1/2(2p_z^2-C3p_z^4+2p_y^5-C3p_y^6)$
	$4p_y$	$(1/2)^{\frac{1}{2}}(\sigma_2-C\sigma_4)$, $(1/2)^{\frac{1}{2}}(2p_z^2-C3p_z^4)$
		$1/2(2p_y^1-C3p_y^3+2p_x^5-C3p_z^6)$
	$4p_z$	$(1/2)^{\frac{1}{2}}(\sigma_5-C\sigma_6)$, $(1/2)^{\frac{1}{2}}(2p_z^5-C3p_z^6)$
		$1/2(2p_x^1-C3p_x^3+2p_y^2-C3p_y^4)$
t_2	$3d_{xy}$	$1/2(2p_y^1+C3p_y^3+2p_x^2+C3p_x^4)$
	$3d_{xz}$	$1/2(2p_x^1+C3p_x^2+2p_y^5+C3p_y^6)$
	$3d_{yz}$	$1/2(2p_y^2+C3p_y^4+2p_z^5+C3p_z^6)$

where $C=\dfrac{\text{Electronegativity of S}}{\text{Electronegativity of O}}$ and $\sigma_i=(\sin\theta\,ns_i\pm\cos\theta np_{zi})$

and the off-diagonal matrix elements are approximated by the following relation,

$$H_{ij}=-\frac{1}{2}K(H_{ii}+H_{jj})G_{ij} \qquad (7)$$

where K is set equal to 1.75, following Wolfsberg-Helmholtz method.[10] Since it is assumed that the ligand σ-bonding orbital can be approximated as a single basis set orbital (np$_z$) or a hybridized atomic orbital, the corresponding diagonal matrix element is then obtained from

$$H_{jj}=-\text{VSIP of } n\text{p}_z \qquad (8)$$

for a single basis set orbital and

$$H_{jj}=-\{\sin^2\theta(\text{VSIP of } n\text{s})+\cos^2\theta(\text{VSIP of } n\text{p}_z)\} \qquad (9)$$

for the hybridized atomic orbitals.[11] Group overlap integrals and estimated energies are listed in Table 3 and 4 when the ligand σ-bonding orbital is approximated as a single basis set orbital (np$_z$) and a hybridized atomic orbital, respectively. Energy level diagrams for [Fe(III)O₃S₃] type complex are represented in Figures 1 and 2 for the cases where the ligand σ-bonding orbital is approximated as a single basis set orbital (np$_z$) and a hybridized atomic orbital, respectively. The calculated values of 10 Dq for octahedral [M(III)O₃S₃] type complexes are also listed in Table 5.

The general formulas of the dipole moment matrix elements for the bonding and antibonding molecular orbitals are

$$\langle\phi_i(\text{MO})\,|r|\,\phi_i(\text{MO})\rangle$$
$$=N_i^2\{2\alpha_i\beta_i\langle\Gamma_i(M)\,|r|\Gamma_i(l)\rangle+\beta_i^2\langle\Gamma_i(l)\,|r|\Gamma_i(l)\rangle\}$$
$$\langle\phi_i^*(\text{MO})\,|r|\,\phi_i^*(\text{MO})\rangle$$
$$=N_i^{*2}\{2\alpha_i^*\beta_i^*\langle\Gamma_i(M)\,|r|\Gamma_i(l)\rangle+\beta_i^{*2}\langle\Gamma_i(l)\,|r|\Gamma_i(l)\rangle\}$$
$$\qquad (10)$$

Figure 1. Energy level diagram for [Fe(III)O₃S₃] type complex when the ligand σ-bonding orbital is approximated as a single basis set orbital.

Figure 2. Entergy level diagram for [Fe(III)O₃S₃] type complex when the ligand σ-bonding orbital is approximated as the hybridized orbital.

Applying the coordinate transformation scheme for octahedral complex[12] we evaluate the dipole moment matrix elements for σ-bonding molecular orbitals and then calculate the contribution of σ-bonding molecular orbital to the

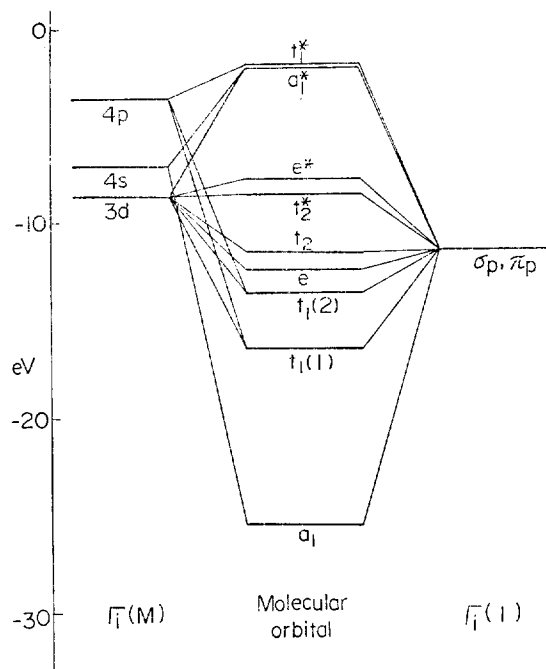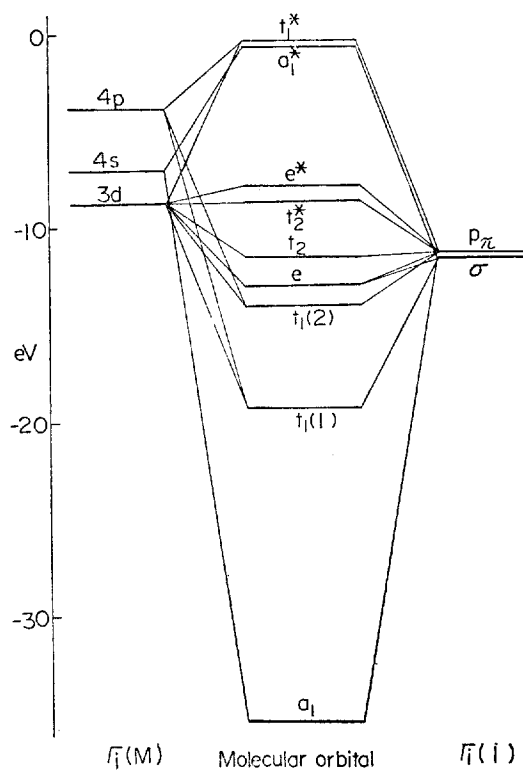**TABLE 3: Group Overlap Integrals and Molecular Orbital Energies for [M(III)O₃S₃] Type Complexes when the Ligand σ-Bonding Orbital is Approximated as a Single Basis set Orbital**

(a) [V(III)O₃S₃] Type Complex

$\Gamma_i(M)$	G_{ij}	G_{ik}	E(eV)	α	β	γ	E^*(eV)	α^*	β^*	γ^*
a_1	0.3315		−21.20	0.7686	0.7299		−2.39	0.9434	−0.4133	
e	0.1175		−12.97	0.4694	0.8909		−5.31	0.9398	−0.3615	
t_2	0.0505		−11.68	0.2567	0.9678		−6.06	0.9795	−0.2075	
$t_1(1)$	0.2183	0.2856	−16.22	0.4899	−0.4786	0.7588	−1.10	0.9046	−0.3026	−0.3673
$t_1(2)$	0.2183	0.2856	−13.01	0.2390	1.0426	0.2509				

Where $(R-C^2R')=1.1940$ a.u.

(b) [Cr(III)O₃S₃] Type Complex

$\Gamma_i(M)$	G_{ij}	G_{ik}	E(eV)	α	β	γ	E^*(eV)	α^*	β^*	γ^*
a_1	0.3498		−22.52	0.7939	0.7135		−2.26	0.9462	−0.4942	
e	0.1019		−12.86	0.4842	0.8809		−6.19	0.9257	−0.3920	
t_2	0.0439		−11.65	0.2678	0.9645		−6.96	0.9753	−0.2253	
$t_1(1)$	0.2295	0.2947	−16.51	0.4941	−0.4922	0.7505	−0.99	0.9044	−0.3152	−0.3710
$t_1(2)$	0.2295	0.2947	−13.14	0.2444	1.0490	0.2544				

where $(R-C^2R')=1.1631$ a.u.

(c) [Mn(III)O₃S₃] Type Complex

$\Gamma_i(M)$	G_{ij}	G_{ik}	E(eV)	α	β	γ	E^*(eV)	α^*	β^*	γ^*
a_1	0.3572		−23.17	0.8056	0.7052		−2.22	0.9464	−0.5006	
e	0.0812		−12.53	0.4726	0.8850		−7.03	0.9205	−0.3992	
t_2	0.0331		−11.55	0.2518	0.9683		−7.72	0.9761	−0.2196	
$t_1(1)$	0.2445	0.2946	−16.54	0.4763	−0.5275	0.7350	−0.98	0.8897	−0.3333	−0.3776
$t_1(2)$	0.2445	0.2946	−13.38	0.2709	1.0484	0.2836				

Where $(R-C^2R')=1.1552$ a.u.

(d) [Fe(III)O₃S₃] Type Complex

$\Gamma_i(M)$	G_{ij}	G_{ik}	E(eV)	α	β	γ	E^*(eV)	α^*	β^*	γ^*
a_1	0.3860		−25.49	0.8421	0.6861		−1.93	0.9594	−0.5095	
e	0.0673		−12.41	0.4917	0.8733		−7.86	0.9044	−0.4319	
t_2	0.0265		−11.33	0.2640	0.9649		−8.72	0.9715	−0.2383	
$t_1(1)$	0.2602	0.2907	−16.43	0.4383	−0.5857	0.7083	−0.93	0.8755	−0.3511	−0.3837
$t_1(2)$	0.2602	0.2907	−13.63	0.3093	1.0341	0.3469				

Woere $(R-C^2R')=1.1552$ a.u.

(e) [Co(III)O₃S₃] Type Complex

$\Gamma_i(M)$	G_{ij}	G_{ik}	E(eV)	α	β	γ	E^*(eV)	α^*	β^*	γ^*
a_1	0.3916		−25.98	0.8483	0.6794		−1.90	0.9573	−0.5146	
e	0.0569		−12.16	0.4974	0.8694		−8.71	0.8963	−0.4471	
t_2	0.0221		−11.53	0.3093	0.9512		−9.21	0.9578	−0.2882	
$t_1(1)$	0.2722	0.2898	−16.44	0.4132	−0.6253	0.6965	−0.91	0.8645	−0.3651	−0.3903
$t_1(2)$	0.2722	0.2898	−13.83	0.3376	1.0220	0.3885				

Where $(R-C^2R')=1.1473$ a.u.

In the t_1 case, subscript i refers to $4p_z$, j to σ and k to $2p_\pi$

dipole moments for octahedral[M (III)O₃S₃] type complexes.

The chemistry of monothio-β-diketionate chelates has been investigated extensively during the last decade.[1,13] From the bonding parameters obtained from the esr spectra, a considerable delocalization of π-bonds over the ligands was suggested.[14] In order to consider delocalization of π-bonds in octahedral [M(III)O₃S₃] type complexes, we modify the π-bonding molecular orbitals as

$$\phi_{\pi j}(MO) = N_j\{\alpha_j\Gamma_j(MO) + \beta_j[\gamma\Gamma_j(l) + (1-\gamma^2)^{\frac{1}{2}}\Gamma_j(\text{del.})]\}$$

$$\phi_{\pi j}^*(MO) = N_j^*\{\alpha_j^*\Gamma_j(MO) + \beta_j^*[\gamma\Gamma_j(l) + (1-\gamma^2)^{\frac{1}{2}}\Gamma_j(\text{del.})]\} \tag{11}$$

where $\gamma^2 = 1/n$ and n is equal to the number of atoms in chelate ring for the delocalized π-bonding molecular orbitals and is equal to l for the π-bonding molecular orbitals.

The general formulas of the dipole moment matrix elements for the modified orbitals are

$$\langle\phi_{\pi j}(MO)|r|\phi_{\pi j}(MO)\rangle$$
$$= N_j^2\{2\alpha_j\beta_j\gamma\langle\Gamma_j(M)|r|\Gamma_j(l)\rangle + \beta_j^2\gamma^2\langle\Gamma_j(l)|r|\Gamma_j(l)\rangle\}$$

TABLE 4: Group Overlap Integrals and Molecular Orbital Energies for [M(III)O$_3$S$_3$] Type Complexes When the Ligand σ-Bonding Orbital is Approximated as the Hybridized Orbital

(a) [V(III)O$_3$S$_3$] Type Complex

Γ_i(M)	G_{ij}	G_{ik}	E(eV)	α	β	γ	E^*(eV)	α^*	β^*	γ^*
a_1	0.4601		−30.56	0.8957	0.6828		−0.88	1.0183	−0.4812	
e	0.1313		−13.81	0.4875	0.8829		−5.15	0.9394	−0.3670	
t_2	0.0505		−11.68	0.2567	0.9678		−6.06	0.9795	−0.2075	
$t_1(1)$	0.3260	0.2856	−18.12	0.4941	0.7287	−0.5387	−0.37	0.8845	−0.3745	−0.3779
$t_1(2)$	0.3260	0.2856	−14.00	0.2717	0.2554	1.0923				

(b) [Cr(III)O$_3$S$_3$] Type Complex

Γ_i(M)	G_{ij}	G_{ik}	E(eV)	α	β	γ	E^*(eV)	α^*	β^*	γ^*
a_1	0.4754		−32.30	0.9179	0.6705		−0.77	1.0262	−0.4888	
e	0.1110		−13.51	0.4910	0.8783		−6.08	0.9274	−0.3904	
t_2	0.0439		−11.65	0.2678	0.9645		−6.96	0.9753	−0.2253	
$t_1(1)$	0.3293	0.2947	−18.28	0.4838	0.7124	−0.5701	−0.36	0.8805	−0.3806	−0.3829
$t_1(2)$	0.3293	0.2947	−14.05	0.2831	0.2895	1.0901				

(c) [Mn(III)O$_3$S$_3$] Type Complex

Γ_i(M)	G_{ij}	G_{ik}	E(eV)	α	β	γ	E^*(eV)	α^*	β^*	γ^*
a_1	0.4817		−33.30	0.9290	0.6639		−0.73	1.0299	−0.4931	
e	0.0897		−13.15	0.4778	0.8831		−6.93	0.9223	−0.3967	
t_2	0.0331		−11.55	0.2518	0.9683		−7.72	0.9761	−0.2196	
$t_1(1)$	0.3437	0.2946	−18.96	0.5217	0.7207	−0.5395	−0.31	0.8871	−0.3837	−0.3853
$t_1(2)$	0.3437	0.2946	−14.03	0.2590	0.2402	1.1070				

(d) [Fe(III)O$_3$S$_3$] Type Complex

Γ_i(M)	G_{ij}	G_{ik}	E(eV)	α	β	γ	E^*(eV)	α^*	β^*	γ^*
a_1	0.4999		−35.38	0.9531	0.6517		−0.58	1.0409	−0.4997	
e	0.0736		−12.89	0.4905	0.8743		−7.78	0.9082	−0.4244	
t_2	0.0265		−11.33	0.2640	0.9649		−8.72	0.9715	−0.2383	
$t_1(1)$	0.3503	0.2907	−19.23	0.5444	0.7250	−0.5185	−5.31	0.8911	−0.4867	−0.3838
$t_1(2)$	0.3503	0.2907	−14.12	0.2447	0.2110	1.1119				

(c) [Co(III)O$_3$S$_3$] Type Complex

Γ_i(M)	G_{ij}	G_{ik}	E(eV)	α	β	γ	E^*(eV)	α^*	β^*	γ^*
a_1	0.5142		−37.28	0.9723	0.6436		−0.45	1.0519	−0.5029	
e	0.0621		−12.78	0.5107	0.8620		−8.52	0.9579	−0.2871	
t_2	0.0221		−11.53	0.3093	0.9512		−9.21	0.9578	−0.2882	
$t_1(1)$	0.3617	0.2898	−19.86	0.5721	0.7269	−0.4989	−0.27	0.8965	−0.3904	−0.3854
$t_1(2)$	0.3617	0.2898	−13.94	0.2272	0.1797	1.1197				

In the t_1 case, subscript i refers to $4p_z$, j to σ and k to $2p_\pi$

TABLE 5: Effect of Hybridization of σ-bonding Ligand Orbitlas on the Calculated 10 Dq Values for Octahedral [M(III)O$_3$S$_3$] Type Complexes (Unit: cm^{-1})

Complex	Single basis orbital	Hybridized orbital	Observed
[V(III)O$_3$S$_3$]	6049	7340	
[Cr(III)O$_3$S$_3$]	6210	7098	
[Mn(III)O$_3$S$_3$]	5565	6372	
[Fe(III)O$_3$S$_3$]	6936	7582	10500[1]
[Co(III)O$_3$S$_3$]	4032	5565	7300[1]

$$<\phi_{\pi i}^*(\mathrm{MO})\,|r|\phi_{\pi i}^*(\mathrm{MO})>$$
$$=N_i^{*2}\{2\alpha_j^*\beta_j^*\gamma<\Gamma_j(M)\,|r|\Gamma_j(l)>+\beta_j^{*2}\gamma^2<\Gamma_j(l)\,|r|\Gamma_j(l)>\}$$

(12)

Applying the coordinate transformation scheme for octahedral

complex, we evaluate the dipole moment matrix elements for π-bonding and delocalized π-bonding molecular orbitals and then calculate the contributions of π-bonds and delocalized π-bonds to the dipole moments for octahedral [M(III)O$_3$S$_3$] type complexes. The calculated dipole moments are listed in Table 6 and 7.

Results and Discussion

The results in Table 1 suggest that the σ-bonding molecular orbitals have only about 4–5 % s-character. The calculated results in Table 3 and 4 show that this s-character significantly affects the values of the group overlap integrals, orbital energies and eigenvectors for octahedral [M(III)O$_3$S$_3$] type complexes. The calculated values of 10 Dq are markedly

TABLE 6: The Calculated Dipole Moments for [M(III)O₃S₃] Type Complexes When the Ligand σ-Bonding Orbital is Approximated as a Single Basis set Orbital

Complex	R	R′	μ_σ	μ_π	μ	$\mu_{\pi\sigma}$	μ_σ	Expl.
[V(III)O₃S₃]	1.95	2.24	8.529	11.533	20.062	2.859	11.388	
[Cr(III)O₃S₃]	1.91	2.20	7.660	11.052	18.712	2.771	10.431	
[Mn(III)O₃S₃]	1.90	2.19	8.588	11.429	20.350	2.849	11.770	
[Fe(III)O₃S₃]	1.90	2.19	8.858	11.582	20.440	2.889	11.747	3.52−7.00[18]
[Co(III)O₃S₃]	1.89	2.18	8.911	11.663	20.574	2.884	11.795	6.54−8.57[18]

TABLE 7: The Calculated Dipole Moments for [M(III)O₃S₃] Type Complexes when the Ligand σ-bonding Orbital is Approximated as the Hybridized Orbital

Complex	R	R′	μ_σ	μ_π	μ	$\mu_{\pi\sigma}$	μ_σ	Expl.
[V(III)O₃S₃]	1.95	2.24	3.497	12.623	16.120	2.490	5.987	
[Cr(III)O₃S₃]	1.91	2.20	3.407	11.876	15.283	2.315	5.722	3.93−7.07[17]
[Mn(III)O₃S₃]	1.90	·· 2.19	3.664	11.998	15.662	2.324	5.988	
[Fe(III)O₃S₃]	1.90	2.19	3.729	11.958	15.687	2.316	6.045	3.59−7.00[18]
[Co(III)O₃S₃]	1.89	2.18	3.127	10.689	13.816	1.770	4.897	3.27−7.36[16]

lower than the observed for octahedral [M(III)O₃S₃] type complexes, but the improved values can be obtained, using a hybridized atomic orbital as the ligand σ-bonding orbital as shown in Table 5.

The calculated contribution of σ bonds to the dipole moments for [M (III) O₃S₃] type complexes are markedly higher than the experimental values if we adopt a single basis set orbital (np_z) as the ligand σ-bonding orbital as shown in Table 6. The calculated dipole moments are also significantly higher than the experimental values even though π-bonds are assumed to be delocalized over the ligands. This is because the contribution of $t_1(2)$ molecular orbital to the calculated μ_σ is very high compared to that for the case where a hybridized atomic orbital is adopted as the ligand σ-bonding orbital. The calculated contribution of σ-bonds to the dipole moments for octahedral [M(III)O₃S₃] type complexes falls in the resonable range, if we adopt the hybridized atomic orbital as the ligand σ-bonding orbital. The contribution of π-bonds to the dipole moments is still so high that the calculated dipole moments are significantly higher than the experimental values. The calculated contribution of π-bonds to the dipole moments however falls in the resonable range of values if π-bonds are assumed to be delocalized. The calculated dipole moments thus fall in the range of the experimental values as shown in Table 7.

These results indicate that the hybridized atomic orbital should be adopted as the ligand σ-bonding orbital in the dipole moment calculation of octahedral [M(III)O₃S₃] type complexes.

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