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Trigonal Bipyramid 구조를 갖는 착물의 쌍극자모멘트의 계산

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Calculation of the Dipole Moments for Trigonal Bipyramidal Complexes

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요 약. Trigonal bipyramid 구조를 갖는 착물의 쌍극 자모멘트를 계산하는 새로운 방법을 발전시켰다. 근사분자궤도 함수법 및 원자가 결합법을 사용하여 몇개의 trigonal bipyramid 구조를 갖는 착물의 쌍극 자모멘트를 계산하였으며 근사분자궤도 함수로 계산한 값이 실험치에 보다 가까운 값을 주었다. 이 쌍극자모멘트 계산방법을 trigonal bipyramid 구조를 갖는 착물의 기하학적인 구조를 예측하는 데 도움이 된다.

ABSTRACT. A new method for calculation of the the dipole moments for trigonal bipyramidal complexes has been developed in this work. Illustrative calculations are performed on a few trigonal bipyramidal complexes with the approximate molecular orbital and the valence bond method. The calculated values of the dipole moments by the approximate molecular orbital method are very close to the experimental values. The calculated dipole moments may be used to predict the geometric structure of trigonal bipyramidal complexes.

1. INTRODUCTION

A method for calculation of the dipole moments for octahedral, square planar and tetrahedral complexes has been developed[1]. In this approach, we adopted the approximate molecular orbitals of octahedral, tetrahedral and square planar complexs which are modified by adding a C coefficient to the single basis set orbitals for the substituted ligands when two or three ligands are replaced by the ligands of different nature. The dipole moment calculation by this approach was based on the three assumption[2] that (1) the nuclear part of the dipole moment is completely cancelled, (2) the atoms that bond directly with the metal ion contribute greatly to the dipole moments of the transition metal complexes, and (3) the mixing coefficient C_M of the valence orbitals for the central metal ion with the appropriate ligand orbitals is equal for all σ bonding molecular orbitals. Recently a new calculation method of the dipole moments for octahedral[3], tetrahedral and square planar complexes[4] has been proposed on the basis of two assumptions that (1) the nuclear part of the dipole moment is completely cancelled because of a symmetrical arrangement of ligands around the central metal ion and (2) the atoms that bond directly with the metal ion and are located at the end of the ligands contribute greatly to the dipole moments of the transition metal complexes. In that approach, the valence bond molecular orbitals were adopted.

The purpose of this work is to develop a new calculation method of the dipole moments for trigonal bipyramidal complexes, adopting the molecular orbital appoach and the valence bond approach. The dipole moment mattrix elements were calculated using the transformation method of the dipole moment matrix elements into overlap integrals for Mulliken[5].

2. CALCULATION OF THE DIPOLE MOMENTS BY THE VALENCE BOND METHOD

We chose trigonal bipyramidal [Ni(II)Cl_2N_2O], [Ni(II)Br_3P_2] and [Sn(IV)R_2N_2O] type complexes to calculate the dipole moments.

The dsp^3 hybrid orbitals which point toward the apices of trigonal bipyramid[6] are

$$\begin{aligned}
h_1&=(1/3)^{\frac{1}{2}}n\mathrm{s}+(2/3)^{\frac{1}{2}}n\mathrm{p}_x\\
h_2&=(1/3)^{\frac{1}{2}}n\mathrm{s}-(1/6)^{\frac{1}{2}}n\mathrm{p}_x+(1/2)^{\frac{1}{2}}n\mathrm{p}_y\\
h_3&=(1/3)^{\frac{1}{2}}n\mathrm{s}-(1/6)^{\frac{1}{2}}n\mathrm{p}_x-(1/2)^{\frac{1}{2}}n\mathrm{p}_y\\
h_4&=(1/2)^{\frac{1}{2}}(n-1)\mathrm{d}_{z^2}+(1/2)^{\frac{1}{2}}n\mathrm{p}_z\\
h_5&=(1/2)^{\frac{1}{2}}(n-1)\mathrm{d}_{z^2}+(1/2)^{\frac{1}{2}}n\mathrm{p}_z
\end{aligned}\tag{1}$$

where $n=4$ for Ni(II) and $n=5$ for Sn(IV).

Alternately we may have the d^3sp hybrid orbitals which point toward the apices of trigonal bipyramid,[7]

$$\begin{aligned}
g_1&=(1/3)^{\frac{1}{2}}n\mathrm{s}+(2/3)^{\frac{1}{2}}(n-1)\mathrm{d}_{x^2-y^2}\\
g_2&=(1/3)^{\frac{1}{2}}n\mathrm{s}-(1/6)^{\frac{1}{2}}(n-1)\mathrm{d}_{x^2-y^2}+(1/2)^{\frac{1}{2}}\\
&\quad(n-1)\mathrm{d}_{xy}\\
g_3&=(1/3)^{\frac{1}{2}}n\mathrm{s}-(1/6)^{\frac{1}{2}}(n-1)d_{x^2-y^2}-(1/2)^{\frac{1}{2}}\\
&\quad(n-1)d_{xy}\\
g_4&=(1/2)^{\frac{1}{2}}(n-1)\mathrm{d}_{z^2}+(1/2)^{\frac{1}{2}}n\mathrm{p}_z\\
g_5&=(1/2)^{\frac{1}{2}}(n-1)\mathrm{d}_{z^2}-(1/2)^{\frac{1}{2}}n\mathrm{p}_z
\end{aligned}\tag{2}$$

The valence bond orbitals for trigonal bipyramidal complexes obtained by combining the above hybrid orbitals with the single basis set orbital of ligands are

$$\begin{aligned}
\phi_i(\mathrm{MO})&=N_i\,\{C_M h_i+(1-C_M^2)^{\frac{1}{2}}m\mathrm{p}_z\}\\
\phi_k(\mathrm{MO})&=N_k\{C_M h_k+(1-C_M^2)^{\frac{1}{2}}cm'\mathrm{p}_z\}\\
\phi_j(\mathrm{MO})&=N_j\,\{C_M g_j+(1-C_M^2)^{\frac{1}{2}}m'\mathrm{p}_z\}\\
\phi_l(\mathrm{MO})&=N_l\{C_M g_l+(1-C_M^2)^{\frac{1}{2}}cm'\mathrm{p}_z\}
\end{aligned}\tag{3}$$

where m and m' the principal quantum numbers of ligand atoms which bond directly with the appropriate hybridized orbitals of the central metal ion (here we denote these atoms as A and B, respectively) and C is a coefficient defined by

C= Valence State Ionization Potential of $m'\mathrm{p}_z$ orbital of A/Valence State Ionization Potential of $m\mathrm{p}_z$ orbital of B

to differentiate the extent of contribution of $m\mathrm{p}_z$ and $m'\mathrm{p}_z$ atomic orbitals of A and B atoms for the formation of the valence bond orbitals.

The Coordinate Transformation Scheme for trigonal Bipyramidal Complexes. The coordinate system for a trigonal bipyramidal complex[8] is represented in ***Fig.*** 1.

As shown in ***Fig.*** 1, the coordinate system for the central metal ion is different from those of ligands. It is required to transform the coordinate system for the central metal ion into those of ligands. The coordinate transformation schemes for trigonal bipyramidal complexes are derived, adopting Euler transformation[9] and the resulting transformation matrices are represented in eq. (4).

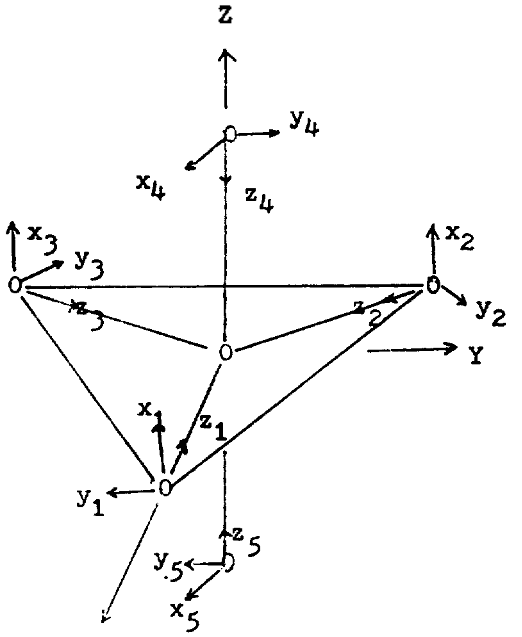

Fig. 1. The coordinate system for trigonal bipyramidal complexes.

$$\pm\begin{pmatrix}x_1\\y_1\\z_1\end{pmatrix}_{\text{new}}=\begin{pmatrix}0&0&1\\0&1&0\\-1&0&0\end{pmatrix}\begin{pmatrix}x_1\\y_1\\z_1\end{pmatrix}_{\text{old}}$$

$$\pm\begin{pmatrix}x_2\\y_2\\z_2\end{pmatrix}_{\text{new}}=\begin{pmatrix}0&-(3/4)^{\frac{1}{2}}&-1/2\\0&-1/2&(3/4)^{\frac{1}{2}}\\-1&0&0\end{pmatrix}\begin{pmatrix}x_2\\y_2\\z_2\end{pmatrix}_{\text{old}}$$

$$\pm\begin{pmatrix}x_3\\y_3\\z_3\end{pmatrix}_{\text{new}}=\begin{pmatrix}0&(3/4)^{\frac{1}{2}}&-1/2\\0&-1/2&-(3/4)^{\frac{1}{2}}\\-1&0&0\end{pmatrix}\begin{pmatrix}x_3\\y_3\\z_3\end{pmatrix}_{\text{old}}$$

$$\pm\begin{pmatrix}x_4\\y_4\\z_4\end{pmatrix}_{\text{new}}=\begin{pmatrix}1&0&0\\0&1&0\\0&0&-1\end{pmatrix}\begin{pmatrix}x_4\\y_4\\z_4\end{pmatrix}_{\text{old}}$$

$$\pm\begin{pmatrix}x_5\\y_5\\z_5\end{pmatrix}_{\text{new}}=\begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\begin{pmatrix}x_5\\y_5\\z_5\end{pmatrix}_{\text{old}}\qquad(4)$$

Calculation of the Dipole Moments for Trigonal Bipyramidal Complexes. For the valence bond molecular orbitals given by equation (3), the general formulas of the dipole moments matrix elements are

$$\begin{aligned}
&\langle\phi_i(\text{MO})|r|\phi_i(\text{MO})\rangle\\
&\quad=N_i^2\{2C_M(1-C_M^2)^{\frac{1}{2}}\ \langle h_i|r|m\text{p}_z\rangle\\
&\qquad+(1-C_M^2)\langle m\text{p}_z|r|m\text{p}_z\rangle\}\\
&\langle\phi_k(\text{MO})|r|\phi_k(\text{MO})\rangle\\
&\quad=N_k^2\{2C_M(1-C_M^2)^{\frac{1}{2}}C\langle h_k|r|m'\text{p}_z\rangle\\
&\qquad+(1-C_M^2)C^2\langle m'\text{p}_z|r|m'\text{p}_z\rangle\}\\
&\langle\phi_j(\text{MO})|r|\phi_j(\text{MO})\rangle\\
&\quad=N_j^2\{2C_M(1-C_M^2)^{\frac{1}{2}}\langle g_j|r|m\text{p}_z\rangle\\
&\qquad+(1-C_M^2)\langle m\text{p}_z|r|m\text{p}_z\rangle\}\\
&\langle\phi_l(\text{MO})|r|\phi_l(\text{MO})\rangle\\
&\quad=N_l^2\{2C_M(1-C_M^2)^{\frac{1}{2}}C\langle g_l|r|m\text{p}_z\rangle\\
&\qquad+(1-C_M^2)C^2\langle m'\text{p}_z|r|m'\text{p}_z\rangle\}
\end{aligned}\qquad(5)$$

where N_i, N_j, N_k, and N_l are normalization constants given by

$$\begin{aligned}
&N_i=\{C_M^2+2C_M(1-C_M^2)^{\frac{1}{2}}\langle h_i|m\text{p}_z\rangle\\
&\qquad+(1-C_M^2)\}^{-\frac{1}{2}}\\
&N_k=\{C_M^2+2C_M(1-C_M^2)^{\frac{1}{2}}\langle h_k|m'\text{p}_z\rangle\\
&\qquad+C^2(1-C_M^2)\}^{-\frac{1}{2}}\\
&N_j=\{C_M^2+2C_M(1-C_M^2)^{\frac{1}{2}}\langle g_j|m\text{p}_z\rangle\\
&\qquad+(1-C_M^2)\}^{-\frac{1}{2}}\\
&N_l=\{C_M^2+2C_M(1-C_M^2)^{\frac{1}{2}}\\
&\qquad\langle g_l|m'\text{p}_z\rangle+C^2(1-C_M^2)\}^{-\frac{1}{2}}
\end{aligned}\qquad(6)$$

Applying the coordinate transformation scheme for trigonal bipyramidal complexes to the dipole moment matrix elements, we evaluated the dipole moment matrix elements for the valence bond molecular orbitals of trigonal bipyramidal complexes and then calculated the dipole moments. The calculated dipole moments for trigonal bipyramidal [Ni(II)Cl_2N_2O], [Ni(II)-Br_3P_2] and [Sn(IV)R_2N_2O] type complexes are listed in *Table* 2.

3. CALCULATION OF THE DIPOLE MOMENTS BY THE APPROXIMATE MOLECULAR ORBITAL METHOD

We assumed that the ligand could be treated

Table 1a. Orbital transformation scheme for $[Ni(II)Cl_2N_2O]$ type complex.[11]

Irred. repr.	Metal orbitals $\Gamma_i(M)$	Ligand orbitals, $\Gamma_i(l)$
a'_1	4s	$(1/3)^{\frac{1}{2}}(2p_z^1+C3p_z^2+C3p_z^3)$
	$3d_{z^2}$	$(1/2)^{\frac{1}{2}}(2p_z^4+2p_z^5)$
	$3d_{xy}$	$(1/2)^{\frac{1}{2}}(3p_z^2+3p_z^3)$
e'	$3d_{x^2-y^2}$	$(1/6)^{\frac{1}{2}}(2\,2p_z^1-C3p_z^2-C3p_z^3)$
a''_2	$4p_z$	$(1/2)^{\frac{1}{2}}(2p_z^4-2p_z^5)$

Where $C=\dfrac{\text{VSIP of }3p_z\text{ orbital of Cl atom}}{\text{VSIP of }2p_z\text{ orbital of O atom}}=0.8671$

Table 1b. Orbital transformation scheme for $[Ni(II)Br_3P_2]$ type complex.[11]

Irred. repr.	Metal orbital $\Gamma_i(M)$	Ligand orbitals $\Gamma_i(l)$
a'_1	4s	$(1/3)^{\frac{1}{2}}(C3p_z^1+4p_z^2+4p_z^3)$
	$3d_{z^2}$	$(1/2)^{\frac{1}{2}}(C3p_z^4+4p_z^5)$
e'	$3d_{xy}$	$(1/2)^{\frac{1}{2}}(4p_z^2+4p_z^3)$
	$3d_{x^2-y^2}$	$(1/6)^{\frac{1}{2}}(2C3p_z^1-4p_z^2-4p_z^3)$
a'_2	$4p_z$	$(1/2)^{\frac{1}{2}}(C3p_z^4-4p_z^5)$

where $C=\dfrac{\text{VSIP of }3p_z\text{ atomic orbital of P}}{\text{VSIP of }4p_z\text{ atomic orbital of Br}}=0.8080$

Table 1c. Orbital transformation scheme for $[Sn(IV)R_2N_2O]$ type complex.[12]

Irred. repr.	Metal orbitals $\Gamma_i(M)$	Ligand orbitals $\Gamma_i(l)$
a'_1	5s	$(1/3)^{\frac{1}{2}}(2p_z^1+C2p_z^2+C2p_z^3)$
	$4dz^2$	$(1/2)^{\frac{1}{2}}(2p_z^4+C'2p_z^5)$
e'	$4d_{xy}$	$(1/2)^{\frac{1}{2}}(2p_z^2-2p_z^3)$
	$4d_{x^2-y^2}$	$(1/6)^{\frac{1}{2}}(22p_z^1-C2p_z^2-C2p_z^3)$
a''_2	$5p_z$	$(1/2)^{\frac{1}{2}}(2p_z^4-C'2p_z^5)$

where $C=\dfrac{\text{VSIP of }2p_z\text{ atomic orbital of C}}{\text{VSIP of }2p_z\text{ atomic orbital of N}}=0.8030$

$C'=\dfrac{\text{VSIP of }2p_z\text{ atomic orbital of N}}{\text{VSIP of }2p_z\text{ atomic orbital of O}}=0.8354$

as single atom with only one p_z orbital available for bonding. Orbital transformation scheme for trigonal bipyramidal $[Ni(II)Cl_2N_{20}]$, $[Ni(II)Br_3\text{-}P_2]$, and $[Sn(IV)R_2N_2O]$ type complexes are listed in *Table* 1.[10]

It should be noted that σ bonds are only assumed to be formed and the ligand orbitals of trigonal bipyramidal complexes are modified by adding a C coefficient to the single basis set orbitals for the substituted ligands as shown in

Table 2. The calculated dipole moments for trigonal bipyramidal complexes.

Complex	R	R′	VB		MO	Expl.
			dsp^3	d^3sp		
$[Ni(II)OCl_2N_2]$	1.59	2.25	3.06	2.63	5.66	
$[Sn(IV)R_2N_2O]$*	2.14	2.16	1.18		3.19	6.20[12]
$[Sn(IV)R_2N_2O]$**	2.14	2.18	2.39		6.30	7.80[12]
$[Sn(IV)R_2N_2O]$†	2.14	2.18	2.17		5.96	
cis$[Ni(II)Br_3P_2]$	2.29	2.21	3.71	3.87	6.27	7.10[11]
trans$[Ni(II)Br_3P_2]$	2.29	2.21	0	0	0	0

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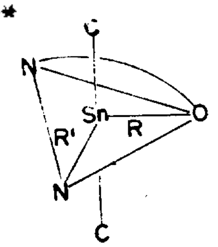

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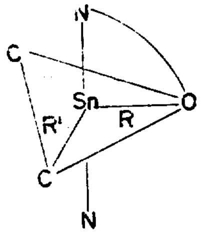

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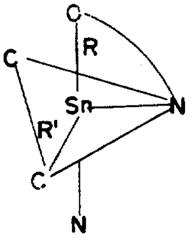

Table 1. We also chose SCF basis set functions of the valence basis sets for the central metal ion and a single basis set for ligands which have the form,

$$\phi_{nlm}=Nr^{n-1}\exp\ (-\zeta_{n,l,m}r)\ \ Y_{lm}(\theta,\phi) \qquad (7)$$

where $n, l,$ and m are usual quantum numbers which have integer values, N a normalization constant, $Y_{lm}(\theta,\phi)$ spherical harmonics and $\zeta_{n,l,n}$ the optimized orbital exponent[13,14].

As the transformation properties of the valence orbitals for the central metal ion and ligand orbitals are known, the valence basis sets of the metal ion can be combined with the appropriate ligand orbitals to gain the approximate molecular orbitals represented, using the group theoretical notation, by

$$\begin{aligned}\phi_i(\mathrm{MO})&=N_i\{C_M\Gamma_i(M)+1-C_M^2)^{\frac{1}{2}}\Gamma_i(l)\}\\ \phi_i^*(\mathrm{MO})&=N_i^*\{(1-C_M^2)^{\frac{1}{2}}\Gamma_i(M)-C_M\Gamma_i(l)\} \qquad (8)\end{aligned}$$

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

$$\begin{aligned}N_i=&\{C_M^2+2C_M(1-C_M^2)^{\frac{1}{2}}<\Gamma_i(M)\,|\,\Gamma_i(l)>\\ &+(1-C_M^2)<\Gamma_i(l)\,|\,\Gamma_i(l)>\}^{-\frac{1}{2}}\\ N_i^*=&\{(1-C_M^2)-2C_M(1-C_M^2)^{\frac{1}{2}}<\Gamma_i(M)\,|\,\Gamma_i(l)>\\ &+C_M^2<\Gamma_i(l)\,|\,\Gamma_i(l)>\}^{-\frac{1}{2}}\end{aligned}$$

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

$$\begin{aligned}&<\phi_i(\mathrm{MO})\,|r|\,\phi_i(\mathrm{MO})>\\ &=N_i^2\{2C_M(1-C_M^2)^{\frac{1}{2}}<\Gamma_i(M)\,|r|\,\Gamma_i(l)>\\ &\quad+(1-C_M^2)<\Gamma_i(l)\,|r|\,\Gamma_i(l)>\}\\ &<\phi_i^*(\mathrm{MO})\,|r|\,\phi_i^*(\mathrm{MO})>\\ &=N_i^{*2}\{-2C_M(1-C_M^2)^{\frac{1}{2}}<\Gamma_i(\mathrm{MO})\,|r|\,\Gamma_i(l)>\\ &\quad+C_M^2<\Gamma_i(l)\,|r|\,\Gamma_i(l)>\} \qquad (9)\end{aligned}$$

Applying the coordinate transformation scheme for trigonal bipyramidal complex to the general formulas of the dipole moment matrix elements we calculated the dipole moments for trigonal bipyramidal [Ni(II)Cl_2N_2O], [Ni(II)-Br_3P_2] and [Sn(IV)R_2N_2O] type complexes. The calculated dipole moments are listed in *Table* 2.

4. RESULTS AND DISCUSSION

As shown in *Table* 2, the calculated dipole moments by the approximate molecular orbital method are higher than those by the valence bond method and are also closer to the experimental values. The calculated values of the dipole moments obtained from the dsp^3 hybrid orbitals of central metal ion are almost same as those gained from the d^3sp hybrid orbitals. This indicates that the approximate molecular orbital method is superior than the valence bond method as far as the dipole moment calculation for trigonal bipyramidal complexes is concerned. The calculated dipole moments for *cis* [Ni(II)Br_3P_2] type complex by both the approximate molecular orbital method and the valence bond method is higher than that for trans complex as shown in *Table* 2. Such a result suggests that the valence bond method for calculation of the dipole moments may also be used to predict the geometric structure of trigonal bipyramidal complexes.

The calculation method of the dipole moments developed in this work may be used to predict the geometric structure for trigonal bipyramidal complexes even though the dipole moment calculation is based on the two and three assumptions.

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