

사면체 및 사각형 $[M(II)O_2S_2]$ 형태 착물의 쌍극자 모멘트에
대한 π 결합의 영향 $[M(II)=Co(II), Ni(II), Cu(II)$ 및 $Zn]$

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The Effect of π Bonds on the Calculated Dipole Moments for
Tetrahedral and Square Planar $[M(II)O_2S_2]$ Type Complexes
 $[M(II)=Co(II), Ni(II), Cu(II)$ and $Zn(II)]$

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요 약. 두다른 방법을 사용하여 사면체 및 사각형 $[M(II)O_2S_2]$ 형태 착물의 쌍극자모멘트에 대한 π 결합의 영향을 고찰 하였다. 그것째 방법은 금속이온의 원자가 궤도함수와 리간드 궤도함수 사이의 혼성계수 C_M 이 σ 및 π 결합 분자궤도함수에 대하여 모두 같다는 가정에 기초를 둔 근사 분자 궤도함수 법이며 다른 하나는 반경험적인 LCAO-MO 법에 기초를 둔 계산이다. σ 결합만이 형성되었다고 가정한다면 사면체 및 사각형 착물의 계산한 쌍극자 모멘트는 실험치 보다 작다. 계산한 쌍극자 모멘트에 π 결합의 기여분을 모두 고려 해 준다면 사각형 및 사면체 $[M(II)O_2S_2]$ 형태 착물의 계산한 쌍극자모멘트는 실험치 보다크다. 그러나 π 결합이 비편재 되었다고 가정한다면 사면체 $[M(II)O_2S_2]$ 형태 착물의 계산한 쌍극자 모멘트가 실험치 범위안에 들지만 사각형착물의 쌍극자 모멘트는 실험치에서 벗어난다. 이결과는 $[M(II)O_2S_2]$ 형태 착물이 비극성 용매의 용액에서 사면체 구조로 존재함을 암시하며 이 구조는 실험구조와 일치한다. 사면체 $[M(II)O_2S_2]$ 형태착물의 계산한 쌍극자모멘트는 쌍극자모멘트에 π 결합이 참여함을 지적한다.

ABSTRACT. The effect of π bonds on the calculated dipole moments for square planar and tetrahedral $[M(II)O_2S_2]$ type complexes has been investigated by two different approaches. One is the approximate molecular orbital method based on the assumption that the mixing coefficient C_M of the valence basis sets for the central metal ion and the appropriate ligand orbitals is equal for all σ and π bonding molecular orbitals. The other is the more refined calculation based on the semiempirical LCAO-MO method. If σ bonds only are assumed to be formed, the calculated dipole moments for square planar and tetrahedral complexes are lower than those of the experimental values. If the contribution of π bonds to the calculated dipole moments are fully considered, the calculated dipole moments for both square planar and tetrahedral $[M(II)O_2S_2]$ type complexes are higher than the experimental values. However if π bonds are assumed to be delocalized, the calculated dipole moments for tetrahedral $[M(II)O_2S_2]$ type complexes fall in the range of the experimental values, but those for square planar complexes deviate from the experimental values. These results suggest that $[M(II)O_2S_2]$ type complexes may have the tetrahedral structure in inert

solvent solution. This structure is in agreement with the experimental one. The calculated dipole moments for tetrahedral $[M(II)O_2S_2]$ type complexes indicate that the contribution of π bonds to the calculated dipole moments may not be neglected.

1. INTRODUCTION

For a few decades a great deal of interest has been focussed on the measurement of the dipole moments for tetrahedral and square planar complexes in inert solvent solutions¹. The vector method of Wilcox² modified by Gilman was applied to the calculation of the dipole moments for $Cl_nSn(CH_3Cl)_{4-n}$ type complexes⁴ to obtain information in the presence of free rotation. Rigorous evaluation of the complete one, two and three center dipole moment matrices of a multi- ζ basis was carried out for $RC_6H_5Cr(CO)_3$ type complexes as a test of semi-empirical MO models. The computed electric dipole moment matrices (eX , eY and eZ) evaluated using multi- ζ AO basis sets were then transformed into the MO space of several commonly employed semi-empirical LACO-MO methods.⁵ This computation revealed that each of the semi-empirical methods predicts the correct dipole direction but the computed dipole moments were found to deviate markedly from the experimental values.

Recently a new approach in calculating the dipole moments for transition metal complexes has been proposed.⁶ In this approach, the approximate molecular orbitals of octahedral, tetrahedral and square planar complexes were adopted. The dipole moment calculation by this approach was based on the three assumptions that (1) the nuclear part of the dipole moment is completely cancelled, (2) the atoms bonded directly to 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. In this approach, it was also assumed that the contribution of π bonds to the dipole moments is completely cancelled because of symmetrical arrangement of ligands around the metal ion. The contribution of π bonds to the dipole moments was therefore not considered in the previous works.⁷

However a great deal of interest has been concentrated on π bonds for transition metal complexes.⁸ The electronic, esr spectra and magnetic properties of transition metal complexes could be explained on the basis of π bonds formation between the valence basis sets for the central metal ion and the appropriate ligand orbitals with the same transformation properties.

The purpose of this work is, first, to investigate the effect of π bonds on the dipole moments for tetrahedral and square planar complexes using the assumptions in the previous works,⁶ and secondly to perform the more refined calculation to gain the mixing coefficient of the valence orbitals for the central metal ion with the appropriate ligand orbitals, using VSIP (valence state ionization potential) of the valence basis sets for the central metal ion and ligands, respectively. We also investigate the effect of π bonds on the calculated dipole moments using the approximate molecular orbitals obtained by the more refined calculation.

In this work, we adopt SCF basis orbitals which have integer values of n and the optimized orbital exponents to represent the valence basis sets for central metal ions and ligands instead of fractional values in Slater type 4s and 4p orbitals.⁹ The dipole moment matrix elements are calculated by transforming the

Table 1. Orbital transformation scheme for tetrahedral M(II) (O₂S₂) type complex.

Representation	Metal orbital [F _i (M)]	Ligand orbital [F _i (L)]
e	3d _{z²}	$\frac{1}{2}(2p_z^2 - 2p_x^2 - C3p_y^2 + C3p_z^2)$
	3dx ² -y ²	$\frac{1}{2}(2p_x^2 - 2p_y^2 - C3p_z^2 + C3p_x^2)$
t	4p _x , 3d _{yz}	$\frac{1}{2}(2p_x^2 - 2p_y^2 + C3p_z^2 - C3p_x^2)$
		$\frac{1}{4}((2p_x^2 + 2p_y^2 - C3p_z^2 - C3p_x^2) + \sqrt{3}(-2p_x^2 - 2p_y^2 + C3p_z^2 + C3p_x^2))$
	4p _y , 3d _{xz}	$\frac{1}{2}(2p_y^2 + 2p_x^2 - C3p_z^2 - C3p_y^2)$
		$\frac{1}{4}((2p_y^2 - 2p_x^2 + C3p_z^2 - C3p_y^2) + \sqrt{3}(2p_x^2 - 2p_y^2 + C3p_z^2 - C3p_y^2))$
4p _z , 3d _{xy}	$\frac{1}{2}(2p_z^2 - 2p_x^2 - C3p_y^2 + C3p_z^2), -\frac{1}{2}(2p_x^2 + 2p_y^2 + C3p_z^2 + C3p_x^2)$	
a	4s	$\frac{1}{2}(2p_x^2 + 2p_y^2 + C3p_z^2 + C3p_x^2)$

dipole moment matrix elements into oversap integrals.

2. THE EFFECT OF π BONDS ON THE CALCULATED DIPOLE MOMENTS FOR SQUARE PLANAR AND TETRAHEDRAL COMPLEXES

As for examples, the square planar and tetrahedral [M(II)O₂S₂] type are chosen for calculation of the dipole moments [M(II) = Co(II), Ni(II), Cu(II) and Zn(II)]. For [M(II)O₂S₂] type complexes, it is assumed that the ligand can be treated as a single atom with three p orbitals available for bonding as indicated in the introductory section. The orbital transformation schemes for square planar and tetrahedral [M(II)O₂S₂] type complexes are listed in Table 1 and 2. It should be noted that we choose SFC basis set functions of atoms which have the form

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

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

Table 2. Orbital transformation scheme for square planar [M(II)O₂S₂] type complex¹¹.

Representation	Metalorbital [F _i (M)]	Ligand orbital [F _i (L)]
a ₁ (σ)	4s, 3dz ²	$\frac{1}{2}(2p_x^2 + 2p_y^2 + C3p_z^2 + C3p_x^2)$
a ₂ (π)	4p _z	$\frac{1}{2}(2p_x^2 + 2p_y^2 + C3p_z^2 + C3p_x^2)$
b ₁ (σ)	3d _{z²} -y ²	$\frac{1}{2}(2p_x^2 - 2p_y^2 + C3p_z^2 - C3p_x^2)$
b ₂ (π)	3d _{xy}	$\frac{1}{2}(2p_x^2 - 2p_y^2 + C3p_z^2 - C3p_x^2)$
e ₁ (π)	3d _{yz}	$\frac{1}{\sqrt{2}}(2p_x^2 - C3p_x^2)$
	3d _{xz}	$\frac{1}{\sqrt{2}}(2p_x^2 - C3p_x^2)$
e(σ) e ₂ (π)	4p _x	$\frac{1}{\sqrt{2}}(2p_x^2 - C3p_x^2),$
		$\frac{1}{\sqrt{2}}(2p_x^2 - C3p_x^2)$
		$\frac{1}{\sqrt{2}}(2p_x^2 - C3p_x^2)$

Where $C = \frac{\text{Electronegativity of S}}{\text{Electronegativity of O}} = 0.7671$

$\zeta_{n,l,m}$ the optimized orbital exponent⁹, and then we transform them into real forms listed in

Table 1 and 2.

An Approximate Calculation of the Effect of π Bonds on the Dipole Moments. The first two assumptions used in the previous works are applied to calculate the dipole moments for square planar and tetrahedral $[M(II)O_2S_2]$ type complexes. However, we modify the third assumption as follows; the mixing coefficient C_M of the valence basis sets for the central metal ion with the appropriate ligand orbitals is equal for all σ bonding and π bonding molecular orbitals.

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 obtain the approximate molecular orbitals represented, in general, using the group theoretical notation by

$$\phi_i(\text{MO}) = N_i [C_M F_i(M) + (1 - C_M^2)^{\frac{1}{2}} F_i(L)] \quad (2)$$

$$\phi_i^*(\text{MO}) = N_i^* [(1 - C_M^2) F_i(M) + C_M F_i(L)] \quad (3)$$

where N_i and N_i^* are normalization constants

for bonding and anti-bonding molecular orbitals given by

$$N_i = (C_M^2 + 2C_M(1 - C_M^2)^{\frac{1}{2}} \langle F_i(M) | F_i(L) \rangle + (1 - C_M^2) \langle F_i(L) | F_i(L) \rangle)^{-\frac{1}{2}}$$

$$N_i^* = ((1 - C_M^2) - 2C_M(1 - C_M^2)^{\frac{1}{2}} \langle F_i(M) | F_i(L) \rangle + C_M^2 \langle F_i(L) | F_i(L) \rangle)^{-\frac{1}{2}}$$

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

$$\begin{aligned} & \langle \phi_i(\text{MO}) | r | \phi_i(\text{HO}) \rangle \\ &= N_i^2 \{ 2C_M(1 - C_M^2)^{\frac{1}{2}} \langle F_i(M) | r | F_i(L) \rangle \\ & \quad + (1 - C_M^2) \langle F_i(L) | r | F_i(L) \rangle \} \\ & \langle \phi_i^*(\text{MO}) | r | \phi_i^*(\text{MO}) \rangle \\ &= N_i^{*2} \{ -2C_M(1 - C_M^2)^{\frac{1}{2}} \langle F_i(M) | r | F_i(L) \rangle \\ & \quad + C_M^2 \langle F_i(L) | r | F_i(L) \rangle \} \quad (4) \end{aligned}$$

Applying the coordinate transformation schemes for square planar and tetrahedral complexes to the general formulas of the dipole moment matrix elements, first, we evaluate the dipole moment matrix elements and then calculate the dipole moments for square planar and tetra-

Table 3(a). The calculated dipole moments for square planar $[M(II)O_2S_2]$ type complexes. (Unit: Debye)

Complex	R	R'	μ_σ	μ_π	μ	μ_π^*	μ^*	Expl. ¹²
$[\text{CO(II)}O_2S_2]$	1.90	2.20	4.307	6.360	10.667	1.245	5.552	
$[\text{Ni(II)}O_2S_2]$	1.89	2.19	4.777	8.220	12.997	1.746	6.523	2.80-5.84
$[\text{Cu(II)}O_2S_2]$	1.91	2.21	5.486	8.387	13.873	1.803	7.289	4.39-6.02 2.45-6.36
$[\text{Zn(II)}O_2S_2]$	1.99	2.29	6.060	7.946	14.006	1.852	7.911	3.94-4.81 2.16-3.57

Table 3(b). The calculated dipole moments for tetrahedral $[M(II)O_2S_2]$ type complexes. (Unit: Debye)

Complex	R	R'	μ_σ	μ_π	μ	μ_π^*	μ^*	Expl. ¹²
$\text{Co(II)}O_2S_2$	1.90	2.20	2.852	7.935	10.787	1.544	4.393	
$\text{Ni(II)}O_2S_2$	1.89	2.19	2.845	8.359	11.204	1.672	4.517	4.32-6.95 2.80-5.47
$\text{Cu(II)}O_2S_2$	1.91	2.21	2.932	8.949	11.881	1.758	4.690	2.47-4.82
$\text{Zn(II)}O_2S_2$	1.99	2.29	3.156	9.934	13.090	2.184	5.340	3.06-4.80

μ_π^* : The contribution of π bonds to the dipole moment when π bonds are assumed to be delocalized. μ^* : The dipole moment when π bonds are assumed to be delocalized.

Table 4. Group overlap integrals and estimated orbital energies for square planar $M(II)O_2S_2$ type complexes.(a) $[Cu(II)O_2S_2]$ Type Complex

$\Gamma_i(MO)$	G_{ij}	$E_i(eV)$	α_i	β_i	$E_i^*(eV)$	α_i^*	β_i^*
a_1	0.2349	-16.11	0.5991	0.8993	-1.97	0.9606	-0.3774
a_2	0.2719	-17.08	0.6355	0.8222	-1.65	0.9640	-3.3880
b_1	0.0216	-11.62	0.4048	0.9147	-9.72	0.9232	-0.3849
b_2	0.0137	-11.45	0.2983	0.9546	-9.89	0.9586	-0.2852
$e(\sigma)$	0.3133	-18.83	0.6879	0.7972	-1.32	0.7926	-0.4035
$e_1(\pi)$	0.1923	-14.99	0.6607	0.7758	-6.73	-0.6343	0.7975
$e_2(\pi)$	0.0097	-11.32	0.0345	0.9995	-3.80	0.9997	-0.0248
a_1'	0.0306	-5.31	0.9973	-0.0064	—	—	—

a_1' is non bonding orbital with a_1 symmetry.

(b) $[Ni(II)O_2S_2]$ Type Complex

$\Gamma_i(MO)$	G_{ij}	$E_i(eV)$	α_i	β_i	$E_i^*(eV)$	α_i^*	β_i^*
a_1	0.2272	-16.77	0.6194	0.8536	-2.14	0.9886	-0.3705
a_2	0.2836	-17.13	0.6336	0.8207	-1.54	0.9589	-0.3944
b_1	0.0261	-11.74	0.4544	0.8917	-9.60	0.9027	-0.4310
b_2	0.0178	-11.67	0.4285	0.9039	-9.67	0.9148	-0.4048
$e(\sigma)$	0.3033	-18.40	0.6761	0.8031	-1.32	0.9704	-0.4002
$e_1(\pi)$	0.2005	-18.70	0.7576	0.6840	-5.29	0.8220	-0.6051
$e_2(\pi)$	0.0126	-11.34	0.0442	0.9991	-3.79	1.0001	-0.0316
a_1'	0.0369	-4.95	0.9959	-0.0025	—	—	—

(c) $[Co(II)O_2S_2]$ Type Complex

$\Gamma(MO)$	G_{ij}	$E_i(eV)$	α_i	β_i	$E_i^*(eV)$	α_i^*	β_i^*
a_1	0.2310	-15.60	0.5727	0.8537	-1.99	0.9636	-0.3626
a_2	0.2846	-12.36	0.5788	0.8637	-3.35	0.9892	-0.3202
b_1	0.0318	-11.76	0.4030	0.9156	-9.01	0.9258	-0.3790
b_2	0.0211	-11.43	0.2311	0.9732	-9.29	0.9778	-0.2106
$e(\sigma)$	0.2738	-17.36	0.6425	0.8174	-1.53	0.9621	-0.3942
$e_1(\pi)$	0.2012	-20.07	0.7837	0.7004	-5.08	0.8719	-0.5869
$e_2(\pi)$	0.0419	-11.35	0.0529	0.9987	-3.79	1.0001	-0.0380
a_1'	0.0449	-4.63	0.9937	-0.0043	—	—	—

hedral $M(II)O_2S_2$ type complexes. The calculated dipole moments are listed in Table 3.

Refined Calculation of the Effect of π Bonds on the Dipole Moments. In this refined calculation, we adopt two assumptions that (1) from symmetry arguments the nuclear part of the dipole moment is completely cancelled, and (2) the atoms bonded directly to the

metal ion are the dominant contribution to the dipole moments of the transition metal complexes.

The approximate energies and the corresponding eigenvectors of the molecular orbitals are obtained by solving the following secular equation for tetrahedral and square planar $[M(II)-O_2S_2]$ type complexes,

$$(H_{ij} - EG_{ij}) = 0 \quad (5)$$

In equation (5), the diagonal matrix elements are chosen as

$$H_{ij} = -VSIP \quad (6)$$

and the off-diagonal matrix elements H_{ij} are calculated using Wolf-berg and Holmholz approximation,¹³

$$H_{ij} = -K((H_{ii} + H_{jj})/2)G_{ij} \quad (7)$$

where $K=2.0$,¹³ and VSIPs are taken from reference (15).

Group overlap integrals and estimated energies are listed in Table 4 and 5. The approximate molecular orbitals for tetrahedral and square planar $[M(II)O_2S_2]$ type complexes may therefore be described, in general, using the group theoretical notation by

$$\phi_i(\text{MO}) = N_i \{ \alpha_i \Gamma_i(M) + \beta_i \Gamma_i(L) \}$$

$$\phi_i^*(\text{MO}) = N_i^* \{ \alpha_i^* \Gamma_i(M) + \beta_i^* \Gamma_i(L) \} \quad (8)$$

where N_i and N_i^* are normalization constants given by

$$N_i = \{ \alpha_i^2 + \beta_i^2 + 2\alpha_i\beta_i \langle \Gamma_i(M) | \Gamma_i(L) \rangle \}^{-\frac{1}{2}}$$

$$N_i^* = \{ \alpha_i^{*2} + \beta_i^{*2} + 2\alpha_i^*\beta_i^* \langle \Gamma_i(M) | \Gamma_i(L) \rangle \}^{-\frac{1}{2}} \quad (9)$$

α_i , β_i , α_i^* and β_i^* are listed in Table 4 and 5.

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

$$\begin{aligned} & \langle \phi_i(\text{MO}) | r | \phi_i(\text{MO}) \rangle \\ &= N_i^2 \{ 2\alpha_i\beta_i \langle \Gamma_i(M) | r | \Gamma_i(L) \rangle \\ & \quad + \beta_i^2 \langle \Gamma_i(L) | r | \Gamma_i(L) \rangle \} \\ & \langle \phi_i^*(\text{MO}) | r | \phi_i^*(\text{MO}) \rangle \\ &= N_i^{*2} \{ 2\alpha_i^*\beta_i^* \langle \Gamma_i(M) | r | \Gamma_i(L) \rangle \\ & \quad + \beta_i^{*2} \langle \Gamma_i(L) | r | \Gamma_i(L) \rangle \} \quad (10) \end{aligned}$$

As mentioned in the previous section, first, we evaluate the dipole moment matrix elements

Table 5. Group overlap integrals and estimated orbital energies for tetrahedral $[M(II)O_2S_2]$ type complex.

(a) $[Co(II)O_2S_2]$ Type Complex

$\Gamma_i(\text{MO})$	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
<i>a</i>	0.3268	-23.07	0.7945	0.6988	-2.21	0.2901	-0.5226
<i>t</i> (σ)	0.2396	-15.87	0.5907	0.8438	-1.99	0.9607	-0.3713
<i>t</i> (π)	0.0099	-11.35	0.1338	0.9911	-9.37	0.9923	-0.1240
<i>e</i>	0.0173	-11.46	0.2626	0.9651	-9.27	0.9644	-0.2458

(b) $[Ni(II)O_2S_2]$ Type Complex

$\Gamma_i(\text{MO})$	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
<i>a</i>	0.3367	-24.09	0.8101	0.6873	-2.12	0.9204	-0.5305
<i>t</i> (σ)	0.2477	-18.10	0.6284	0.8188	-1.81	0.9489	-0.4060
<i>t</i> (π)	0.0080	-11.35	0.1631	0.9866	-9.97	0.9880	-0.1548
<i>e</i>	0.0145	-11.46	0.3105	0.9507	-9.86	0.9551	-0.2967

(c) $[Cu(II)O_2S_2]$ Type Complex

$\Gamma_i(\text{MO})$	G_{ij}	$E_i(\text{eV})$	α_i	β_i	$E_i^*(\text{eV})$	α_i^*	β_i^*
<i>a</i>	0.3449	-24.69	0.8185	0.6819	-2.03	0.9224	-0.5331
<i>t</i> (σ)	0.2558	-16.59	0.6200	0.8281	-1.89	0.9591	-0.3875
<i>t</i> (π)	0.0064	-11.36	0.2537	0.9673	-10.66	0.9689	-0.2475
<i>e</i>	0.0112	-11.49	0.4336	0.9012	-10.53	0.9060	-0.4235

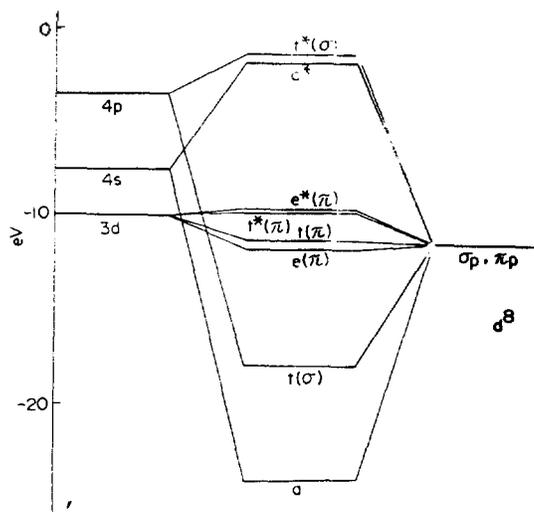


Fig. 1. The energy level scheme for tetrahedral [Ni(II)O₂S₂] type complex.

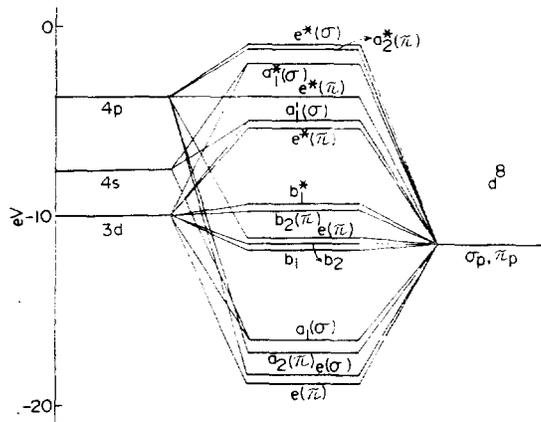


Fig. 2. The energy level scheme for square planar [Ni(II)O₂S₂] type complex.

applying the coordinate transformation schemes for tetrahedral and square planar complexes to the general formulas of the dipole moment matrix elements and then calculate the dipole moments for square planar and tetrahedral [M(II)-O₂S₂] type complexes. The calculated dipole moments are listed in Table 6.

Molecular orbital energy level diagrams for the tetrahedral and square planar [M(II)O₂S₂] type complexes are shown in Fig. 1 and 2.

Calculation of the Dipole Moments for Delocalized π Bonding Orbitals. In order to consider delocalization of π bonds in [M(II)-O₂S₂] type complexes, we modify the π bonding molecular orbitals as

$$\begin{aligned}\phi_{e_i}(\text{MO}) &= N_i \{ C_M F_i(M) + (1 - C_M^2)^{\frac{1}{2}} \\ &\quad [\gamma F_i(L) + (1 - \gamma^2)^{\frac{1}{2}} F_i(\text{del})] \} \\ \phi_{e_i}^*(\text{MO}) &= N_i^* \{ (1 - C_M^2)^{\frac{1}{2}} F_i(M) \\ &\quad - C_M [\gamma F_i(L) + (1 - \gamma^2)^{\frac{1}{2}} F_i(\text{del})] \}\end{aligned}$$

for the approximate molecular orbitals described in section (a), and

$$\begin{aligned}\phi_{e_j}(\text{MO}) &= N_j \{ \alpha_j F_j(\text{MO}) \\ &\quad + \beta_j [\gamma F_j(L) + (1 - \gamma^2)^{\frac{1}{2}} F_j(\text{del})] \} \\ \phi_{e_j}^*(\text{MO}) &= N_j^* \{ \alpha_j^* F_j(\text{MO}) \\ &\quad + \beta_j^* [\gamma F_j(L) + (1 - \gamma^2)^{\frac{1}{2}} F_j(\text{del})] \}\end{aligned} \quad (11)$$

for the refined approximate orbitals described in section (b).

The general formulas of the dipole moments matrix elements for the above modified molecular orbitals are,

$$\begin{aligned}\langle \phi_{e_i}(\text{MO}) | r | \phi_{e_i}(\text{MO}) \rangle &= N_i^2 \{ 2C_M (1 - C_M^2)^{\frac{1}{2}} \gamma \langle F_i(M) | r | F_i(L) \rangle \\ &\quad + (1 - C_M^2) \gamma^2 \langle F_i(L) | r | F_i(L) \rangle \} \\ \langle \phi_{e_i}^*(\text{MO}) | r | \phi_{e_i}^*(\text{MO}) \rangle &= N_i^{*2} \{ -2C_M (1 - C_M^2)^{\frac{1}{2}} \gamma \langle F_i(M) | r | F_i(L) \rangle \\ &\quad + C_M^2 \gamma^2 \langle F_i(L) | r | F_i(L) \rangle \} \\ \langle \phi_{e_j}(\text{MO}) | r | \phi_{e_j}(\text{MO}) \rangle &= N_j^2 \{ 2\alpha_j \beta_j \gamma \langle F_j(M) | r | F_j(L) \rangle \\ &\quad + \beta_j^2 \gamma^2 \langle F_j(L) | r | F_j(L) \rangle \} \\ \langle \phi_{e_j}^*(\text{MO}) | r | \phi_{e_j}^*(\text{MO}) \rangle &= N_j^{*2} \{ \alpha_j^* \beta_j^* \gamma \langle F_j(M) | r | F_j(L) \rangle \\ &\quad + \beta_j^{*2} \gamma^2 \langle F_j(L) | r | F_j(L) \rangle \}\end{aligned} \quad (12)$$

where $\gamma^2 = 1/n$ and n is the number of atoms in chelate ring.

The dipole moment matrix elements are evaluated applying the coordinate transformation schemes for tetrahedral and square planar complexes to the above formulas and then the contributions of delocalized π bonds to the dipole

Table 6(a). The calculated dipole moments for square planar $[M(II)O_2S_2]$ type complexes.

Complex	R	R'	μ_σ	μ_π	μ	μ_{rd}	μ_d	Expl. ¹²
$[\text{Co(II)}O_2S_2]$	1.90	2.20	5.89	7.25	13.14	1.77	7.76	
$[\text{Ni(II)}O_2S_2]$	1.89	2.19	5.73	7.47	13.20	1.61	7.34	2.80~5.84
$[\text{Cu(II)}O_2S_2]$	1.91	2.21	5.84	9.31	15.12	1.98	7.82	2.45~6.36

Table 6(b). Calculated dipole moment for tetrahedral $[M(II)O_2S_2]$ type complexes.

Complex	R	R'	μ_σ	μ_π	μ	μ_{rd}	μ_d	Expl. ¹²
$[\text{Co(II)}O_2S_2]$	1.90	2.20	3.68	9.884	13.564	1.771	5.451	
$[\text{Ni(II)}O_2S_2]$	1.89	2.19	3.42	9.748	13.168	1.948	5.368	4.32~5.84
$[\text{Cu(II)}O_2S_2]$	1.91	2.21	3.56	10.006	13.566	1.924	5.484	4.39~6.36

moments are evaluated. The calculated contributions are listed in Table 6.

3. RESULTS AND DISCUSSION.

The first approximate calculation which neglects the contribution of π bonds to the dipole moments shows that the calculated dipole moments for tetrahedral $[M(II)O_2S_2]$ type complexes are markedly lower than the experimental values, but those for square planar complexes are closer to the experimental values.¹² If the contribution of π bonds to the calculated dipole moments is fully considered, the calculated results are markedly higher than the experimental values. The calculated dipole moments for tetrahedral complexes however fall in the range of the experimental values if π bonds are assumed to be localized. Such a trend also appears in the refined calculation. The contributions of both σ and π bonds to the calculated dipole moments obtained by the refined calculation are significantly higher than those obtained by the first approximate calculation. Such results suggest that care needs to be exercised in choosing the C_M value.

The contributions of delocalized π bonds to the calculated dipole moments in both calculations are almost same. These results indicate

that the contribution of π bonds to the dipole moments is small compared to that of σ bonds. The calculated dipole moments listed in Table 3 and 4 also indicate that the contribution of π bonds should be included in the dipole moment calculation. The calculated dipole moments for tetrahedral complexes fall in the range of experimental values if π bonds are assumed to be delocalized. We may thus suggest that $[M(II)O_2S_2]$ type complexes may have the tetrahedral structure in inert solvent solution. This structure is in agreement with the experimental one.

The vector method of Wilcox² and Gilman³ can be applied only to the calculation of dipole moments for the molecules with both fixed and rotating polar groups. The method of rigorous evaluation of the complete one, two and three center dipole moment matrices using multi- ζ basis can be used to calculate the dipole moments for metal carbonyl complexes such as $\pi\text{-RC}_6\text{H}_5\text{-Cr(CO)}_3$ whose geometric structure is known, but this method requires too much computing time and the computed values of the dipole moments were reported to deviate markedly from the experimental ones. For example, the computed dipole moments for $\text{C}_6\text{H}_5\text{Cr(CO)}_3$ using the methods of Mulliken and Lowdin charge convergence are 7.13 and 10.2 D respectively. Both

of them are too much higher than the experimental value, 4.95 D.

We may predict the geometric structure of any $[M(II)A_2B_2]$ type complexes using the method shown in the present work even though the dipole moment calculation is based on the two or three assumptions.

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