

## [M(II)O<sub>3</sub>N<sub>3</sub>] 및 [Ni(II)O<sub>2</sub>N<sub>4</sub>] 형태착물의 쌍극자 모멘트에 대한 리간드의 *cis* 및 *trans* 구조의 영향

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## The Effects of the *cis* and *trans* Configurations of Ligands on the Calculated Dipole Moments for [M(II)O<sub>3</sub>N<sub>3</sub>] and [Ni(II)O<sub>2</sub>N<sub>4</sub>] Type Complexes.

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요 약. EHT calculation의 고유함수를 사용하여 [M(II)O<sub>3</sub>N<sub>3</sub>] 및 [Ni(II)O<sub>2</sub>N<sub>4</sub>] 형태착물(M(II) = Co(III), Ni(II) 및 Cu(II))의 쌍극자 모멘트에 대한 *cis* 및 *trans* 구조의 영향을 고찰하였다. *cis* [M(II)O<sub>3</sub>N<sub>3</sub>] 형태착물의 계산한 쌍극자 모멘트가 *trans* 착물의 계산한 쌍극자 모멘트 값보다 큰 값을 가지며 *trans* 착물의 쌍극자 모멘트 값이 실험치 범위안에 들었다. 그러나 [Ni(II)O<sub>2</sub>N<sub>4</sub>] 착물의 경우 *cis* 착물의 쌍극자 모멘트 값이 실험치 범위안에 들었다. 이 결과는 [Co(III)O<sub>3</sub>N<sub>3</sub>] 형태착물이 *trans* 구조, [Ni(II)O<sub>2</sub>N<sub>4</sub>] 형태착물은 *cis* 구조를 가졌음을 암시하며 이는 실험결과와 일치한다([M(II)O<sub>3</sub>N<sub>3</sub>] 형태착물에서 세개의 두자리 (O-N) 리간드가 금속이온에 배위되어 있으며 [Ni(II)O<sub>2</sub>N<sub>4</sub>] 형태 착물에서는 두개의 세자리 (O-N-N) 리간드가 Ni(II) 이온에 배위되어 있음).

**ABSTRACT.** The effects of *cis* and *trans* configurations of ligands for [M(II)O<sub>3</sub>N<sub>3</sub>] and [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes (M(II) = Co(III), Ni(II) and Cu(II)) on the calculated dipole moments have been investigated, adopting the eigenvectors of EHT calculation. The calculated dipole moments for *cis* complexes are higher than those of *trans* complexes. The calculated dipole moments for the octahedral *trans* [Co(III)O<sub>3</sub>N<sub>3</sub>] type complex fall in the range of experimental values. However the calculated dipole moments for *cis* [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes fall in the range of the experimental values. These results predicts the *trans* structure for [Co(III)O<sub>3</sub>N<sub>3</sub>] and [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes. Those structures are in agreement with the experimental one (Three bidentate (O-N) ligands in [M(II)O<sub>3</sub>N<sub>3</sub>] type complexes coordinate to the metal ion and two tridentate (O-N-N) ligands in [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes coordinate to Ni(II) ion).

### 1. INTRODUCTION

The term "trans effect" in metal complexes

was first used to describe the influence of a coordinated group on the substitution reaction of the ligand *trans* to it<sup>1</sup>. The *trans* effect has,

however, been defined to be the tendency of a group coordinated to metal ion to direct an incoming group into the *trans* position to itself.<sup>2</sup> The rate of substitution of an atom or molecule linked to the central atom could be explained by the *trans* effect<sup>3</sup>. The *trans* effect on the reactivities<sup>4</sup>, stabilities<sup>5</sup>, infrared spectra<sup>6</sup> and acid strength of platinum(II) complexes was investigated on the basis of the above definition. They found that, for platinum(II) complexes, the *trans* effect is of dominating importance and ligands of large *trans* effect usually seem to weaken the bond of the ligand *trans* to them. Hartely<sup>6</sup> considered the *cis* and *trans* effects of ligands, depending on the relative positions of the influenced(L) and influencing (A) ligands. He observed that the coordination of a ligand (A) affects the ground state properties, such as bond length, stretching force constant, NMR chemical shift and coupling constant of the *trans* M-L bonds. In his point of view, he defined that this influence of A on the ground state properties of other bond is generally referred to as the *cis* or *trans* effect of A. After his work, considerable interest has been concentrated on the nature of the *trans* and *cis* effects for transition metal complexes<sup>9-12</sup>, Basolo, *et al.* investigated the *trans* effect on the dipole moments for platinum(II) complexes<sup>12a</sup>.

In this work, we shall calculate the effect of the *trans* and *cis* configurations of ligands on the calculated dipole moments for [M(II)O<sub>3</sub>N<sub>3</sub>] (M(II)=Co(III), Ni(II) and Cu(II)) and [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes. Since the purpose of this work is to calculate the effect of the *trans* and *cis* ligands on the calculated dipole moments for octahedral complexes, the former definition of the *cis* and *trans* effects of ligands can not be applied to this report. It is, however, stressed that the effect of *cis* and *trans* ligands must have more or less the same mean-

ing as far as the dipole moment calculation is concerned. To investigate the effects of the *cis* and *trans* configurations of ligands on the calculated dipole moments, we perform EHT calculation on the *cis* and *trans* [M(II)O<sub>3</sub>N<sub>3</sub>] and [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes and calculate the dipole moments for the *cis* and *trans* octahedral [M(II)O<sub>3</sub>N<sub>3</sub>] and [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes, adopting two assumptions in the previous reports<sup>13</sup>. We adopt SCF basis set of functions which have integer values of *n*, *l* and *m* and then transform them into real form as listed in Table 1.<sup>14-15</sup>

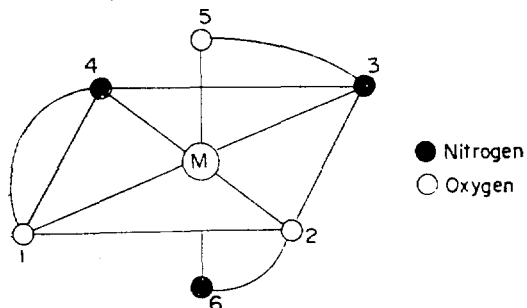
## 2. CALCULATION OF THE EFFECTS OF THE *cis* AND *trans* CONFIGURATIONS OF LIGANDS ON THE CALCULATED DIPOLE MOMENTS

As for examples, we choose octahedral [M(II)O<sub>3</sub>N<sub>3</sub>] and [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes (Fig. 1) to investigate the effects of the *cis* and *trans* configurations of ligands on the calculated dipole moments. The orbital transformation schemes for these complexes are listed in Table 1. Here we assume that the cubic symmetry is still maintained for octahedral [M(II)O<sub>3</sub>N<sub>3</sub>] and [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes although three or two oxygen atoms have been replaced to form *cis* or *trans* complexes by nitrogen atoms. Therefore, we adopt the modified approximate molecular orbitals of octahedral complex<sup>16</sup> and the notation of the O point group. We also adopt the  $\sigma$  bondings as a linear combination of 2s and 2p<sub>z</sub> orbitals of ligands as follows

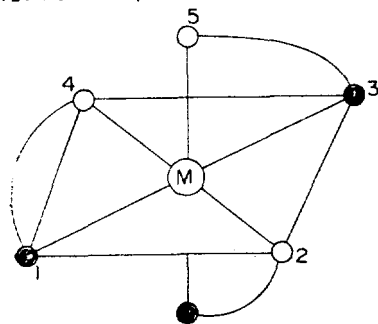
$$\sigma(l) = \sin(2s) \pm \cos(2p_z) \quad (1)$$

The degree of hybridization is estimated after the manner of Ballhausen and Gray<sup>17</sup> by minimizing the quantity VSIP( $\theta$ )/S( $\theta$ ), where S( $\theta$ ) is the overlap integrals of the 3d<sub>z<sup>2</sup></sub> orbital of

(a) cis complex



(b) trans complex



the central metal ion with oxygen or nitrogen hybrid orbital of varying values  $\theta$ , while VSIP ( $\theta$ ) is the valence state ionization potential of the same oxygen or nitrogen hybrid orbital. The angles at which the minimum occurred are listed in Table 2. The molecular orbitals may be approximated as

$$\begin{aligned} \phi_i(MO) &= N_i \{ \alpha_i \Gamma_i(M) + \beta_i \Gamma_{\sigma_i}(L) + \gamma_i \Gamma_{\pi_i}(L) \} \\ \phi_i^*(MO) &= N_i^* \{ \alpha_i^* \Gamma_i(M) + \beta_i^* \Gamma_{\sigma_i}(L) + \gamma_i^* \Gamma_{\pi_i}(L) \} \end{aligned} \quad (2)$$

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

$$\begin{aligned} N_i &= \{ \alpha_i^2 + 2\alpha_i\beta_i \langle \Gamma_i(M) | \Gamma_{\sigma_i}(L) \rangle + 2\alpha_i\gamma_i \langle \Gamma_i(M) | \Gamma_{\pi_i}(L) \rangle + \beta_i^2 \langle \Gamma_{\sigma_i}(L) | \Gamma_{\sigma_i}(L) \rangle + \gamma_i^2 \langle \Gamma_{\pi_i}(L) | \Gamma_{\pi_i}(L) \rangle \}^{1/2} \\ N_i^* &= \{ \alpha_i^{*2} + 2\alpha_i^*\beta_i^* \langle \Gamma_i(M) | \Gamma_{\sigma_i}(L) \rangle + 2\alpha_i^*\gamma_i^* \langle \Gamma_i(M) | \Gamma_{\pi_i}(L) \rangle + \beta_i^{*2} \langle \Gamma_{\sigma_i}(L) | \Gamma_{\sigma_i}(L) \rangle \}^{1/2} \end{aligned}$$

Fig. 1. coordinate system of cis and trans [M(II)-O<sub>3</sub>N<sub>3</sub>] type complexes.

Table 1. Orbital transformation scheme for [M(II)O<sub>3</sub>N<sub>3</sub>] type complex.

(a) cis [M(II)O<sub>3</sub>N<sub>3</sub>] type complex

Representation	Metal ion orbital, $\Gamma_i(M)$	Ligand orbital, $\Gamma_i(L)$
$a_1$	4s	$\frac{1}{\sqrt{6}} (\sigma_1 + \sigma_2 + C\sigma_3 + C\sigma_4 + \sigma_5 + C\sigma_6)$
$e$	$3d_{x^2-y^2}$	$\frac{1}{2} (\sigma_1 - \sigma_2 + C\sigma_3 - C\sigma_4)$
	$3d_{z^2}$	$\frac{1}{\sqrt{12}} (2\sigma_5 + 2C\sigma_6 - \sigma_1 - \sigma_2 - C\sigma_3 - C\sigma_4)$
$t_1$	$4p_x$	$\frac{1}{\sqrt{2}} (\sigma_1 - C\sigma_3), \frac{1}{2} (2p_x^2 - C2p_x^4 + 2p_x^5 - C2p_x^6)$
	$4p_y$	$\frac{1}{\sqrt{2}} (\sigma_2 - C\sigma_4), \frac{1}{2} (2p_y^2 - C2p_y^4 + 2p_y^5 - C2p_y^6)$
	$4p_z$	$\frac{1}{\sqrt{2}} (\sigma_5 - C\sigma_6), \frac{1}{2} (2p_z^2 - C2p_z^4 + 2p_z^5 - C2p_z^6)$
$t_2$	$3d_{xy}$	$\frac{1}{2} (2p_x^2 + C2p_x^4 + 2p_y^2 + C2p_y^4)$
	$3d_{xz}$	$\frac{1}{2} (2p_x^2 + C2p_x^4 + 2p_x^5 + C2p_x^6)$
	$3d_{yz}$	$\frac{1}{2} (2p_y^2 + C2p_y^4 + 2p_x^5 + C2p_x^6)$

where  $C = \frac{\text{Electronegativity of nitrogen}}{\text{Electronegativity of oxygen}}$

(b) *trans* [M(II)O<sub>3</sub>N<sub>3</sub>] type complex

Representation	Metal ion orbital, $\Gamma_i(M)$	Ligand orbital, $\Gamma_i(l)$
$a_1$	4s	$\frac{1}{\sqrt{6}}(C\sigma_1 + \sigma_2 + C\sigma_3 + \sigma_4 + \sigma_5 + C\sigma_6)$
$e$	$3d_{x^2-y^2}$	$\frac{1}{2}(C\sigma_1 - \sigma_2 + C\sigma_3 - \sigma_4)$
	$3d_{z^2}$	$\frac{1}{\sqrt{12}}(2\sigma_5 + 2C\sigma_6 - C\sigma_1 - \sigma_2 - C\sigma_3 - \sigma_4)$
$t_1$	$4p_x$	$\frac{1}{\sqrt{2}}(C\sigma_1 - C\sigma_3), \frac{1}{2}(2p_x^2 - 2p_x^4 + 2p_x^5 - C2p_y^6)$
	$4p_y$	$\frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4), \frac{1}{2}(C2p_x^1 - C2p_x^3 + 2p_x^5 - C2p_y^6)$
	$4p_z$	$\frac{1}{\sqrt{2}}(\sigma_5 - C\sigma_6), \frac{1}{2}(C2p_x^1 - C2p_x^3 + 2p_x^2 - 2p_y^4)$
$t_2$	$3d_{xy}$	$\frac{1}{2}(C2p_x^1 + C2p_y^3 + 2p_x^2 + 2p_y^4)$
	$3d_{xz}$	$\frac{1}{2}(2p_x^2 + 2p_x^4 + 2p_x^5 + C2p_y^6)$
	$3d_{yz}$	$\frac{1}{2}(C2p_x^1 + C2p_y^3 + 2p_x^5 + C2p_y^6)$

(c) *cis* [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complex

Representation	Metal ion orbital, $\Gamma_i(M)$	Ligand orbital, $\Gamma_i(l)$
$a_1$	4s	$\frac{1}{\sqrt{6}}(C\sigma_1 + \sigma_2 + C\sigma_3 + C\sigma_4 + C\sigma_5 + \sigma_6)$
$e$	$3d_{x^2-y^2}$	$\frac{1}{2}(C\sigma_1 - \sigma_2 + C\sigma_3 - C\sigma_4)$
	$3d_{z^2}$	$\frac{1}{\sqrt{12}}(2C\sigma_5 + 2\sigma_6 - C\sigma_1 - \sigma_2 - C\sigma_3 - C\sigma_4)$
$t_1$	$4p_x$	$\frac{1}{\sqrt{2}}(C\sigma_1 - C\sigma_3), \frac{1}{2}(2p_x^2 - C2p_x^4 + C2p_x^5 - 2p_y^6)$
	$4p_y$	$\frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4), \frac{1}{2}(C2p_x^1 - C2p_y^3 + C2p_x^5 - 2p_y^6)$
	$4p_z$	$\frac{1}{\sqrt{2}}(C\sigma_5 - \sigma_6), \frac{1}{2}(C2p_x^1 - C2p_x^3 + 2p_x^2 - C2p_y^4)$
$t_2$	$3d_{xy}$	$\frac{1}{2}(C2p_x^1 + C2p_y^2 + 2p_x^2 + C2p_x^4)$
	$3d_{xz}$	$\frac{1}{2}(C2p_x^2 + C2p_x^4 + C2p_x^5 + 2p_x^6)$
	$3d_{yz}$	$\frac{1}{2}(C2p_x^1 + C2p_x^3 + C2p_x^5 + 2p_x^6)$

(d) *trans* [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complex

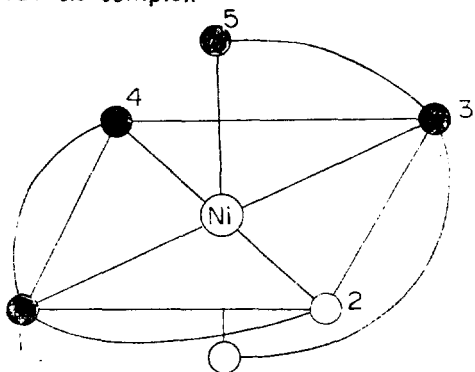
Representation	Metal ion orbital, $\Gamma_i(M)$	Ligand orbital, $\Gamma_i(l)$
$a_1$	4s	$\frac{1}{\sqrt{6}}(C\sigma_1 + \sigma_2 + C\sigma_3 + \sigma_4 + C\sigma_5 + C\sigma_6)$
$e$	$3d_{x^2-y^2}$	$\frac{1}{2}(C\sigma_1 - \sigma_2 + C\sigma_3 - \sigma_4)$
	$3d_{z^2}$	$\frac{1}{\sqrt{12}}(2C\sigma_5 + 2C\sigma_6 - C\sigma_1 - \sigma_2 - C\sigma_3 - \sigma_4)$
$t_1$	$4p_x$	$\frac{1}{\sqrt{2}}(C\sigma_1 - C\sigma_3),$

	4p <sub>y</sub>	$\frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4), \frac{1}{2}(C2p_x^1 - C2p_x^3 + C2p_x^5 - C2p_x^6)$
	4p <sub>z</sub>	$\frac{1}{\sqrt{2}}(C\sigma_5 - C\sigma_6), \frac{1}{2}(C2p_x^1 - C2p_x^3 + 2p_y^2 - 2p_y^4)$
<i>t<sub>2</sub></i>	3d <sub>xy</sub>	$\frac{1}{2}(C2p_x^1 + C2p_x^3 + 2p_y^2 + 2p_y^4)$
	3d <sub>xx</sub>	$\frac{1}{2}(2p_x^2 + 2p_x^4 + C2p_x^5 + C2p_x^6)$
	3d <sub>yz</sub>	$\frac{1}{2}(C2p_y^1 + C2p_y^3 + C2p_x^5 + C2p_y^6)$

Table 2. The degree of hybridization for  $\sigma$  orbitals.

complex	oxygen atom		nitrogen atom			
	sin $\theta$	cos $\theta$	$\theta$	sin $\theta$	cos $\theta$	$\theta$
[Co(III)O <sub>3</sub> N <sub>3</sub> ]	0.2079	0.9781	12	0.1908	0.9816	11
[Ni(II)O <sub>3</sub> N <sub>3</sub> ]	0.2079	0.9781	12	0.1908	0.9816	11
[Cu(II)O <sub>3</sub> N <sub>3</sub> ]	0.2924	0.9536	17	0.2924	0.9536	17
[Ni(II)O <sub>2</sub> N <sub>4</sub> ]	0.2079	0.9781	12	0.1908	0.9816	11

(a) cis complex



(b) trans complex

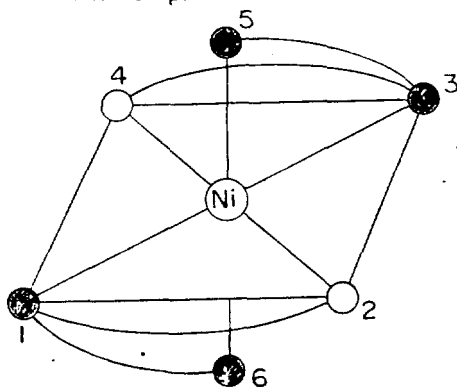


Fig. 2. Coordinate systems for cis and trans (Ni(II)-O<sub>2</sub>N<sub>4</sub>) type complexes.

$$+ r_i^{*1} \langle \Gamma_{\pi_i}(l) | \Gamma_{\pi_i}(l) \rangle^{-1/2} \quad (3)$$

The approximate energies and the corresponding eigenvectors are obtained by solving the following secular equation<sup>18</sup>,

$$(H_{ij} - G_{ij}E) = 0 \quad (4)$$

where  $G_{ij}$  is group overlap integral. In equation(4), the diagonal matrix elements for the central metal orbitals,  $H_{ii}$ , are estimated as the negative of the valence state ionization potential (VSIP) of atom<sup>19</sup>

$$H_{ii} = -VSIP \quad (5)$$

and the off-diagonal matrix elements are calculated by using Wolberg and Helmholtz approximation<sup>20</sup>

$$H_{ij} = +1/2K(H_{ii} + H_{jj})G_{ij} \quad (6)$$

where  $K=1.75$ . Since we choose the  $\sigma$  bonding orbital for ligands as a hybridized atomic orbital of  $2s$  and  $2p_z$ , the corresponding diagonal matrix element is then obtained from

$$H_{jj} = -(\sin^2\theta(\text{VSIP of } 2s) + \cos^2\theta(\text{VSIP of } 2p_z)) \quad (7)$$

Table 3. (a) Group overlap integrals and estimated energies for *cis* [Co(II)O<sub>3</sub>N<sub>3</sub>] type complex

$\Gamma_i(M)$	$G_{ij}$	$G_{ik}$	$E_i(eV)$	$\alpha_i$	$\beta_i$	$\gamma_i$	$E_i(eV)$	$\alpha_i^*$	$\beta_i^*$	$\gamma_i^*$
$a_1$	0.4439		-32.78	0.8834	0.6819		-1.25	1.0031	-0.4890	
$e$	0.0692		-14.17	0.4248	0.9073		-8.55	0.9102	-0.4185	
$t_2$	0.0254		-14.19	0.1817		0.9837	-9.28	0.9881		-0.1562
$t_1(1)$	0.3028	0.2658	-19.63	0.3724	0.6218	-0.7222	-0.71	0.8690	-0.4021	-0.3608
$t_1(2)$	0.3028	0.2658	-16.53	0.3586	0.5098	0.9514				

In the  $t_1$  case subscript  $i$  refers to metal AO  $j$  to  $\sigma$  ligand orbital and  $k$  to  $2p_x$  ligand orbital.

(b) Group overlap integrals and estimated energies for *trans* [Co(III)O<sub>3</sub>N<sub>3</sub>] type complex

$\Gamma_i(M)$	$G_{ij}$	$G_{ik}$	$E_i(eV)$	$\alpha_i$	$\beta_i$	$\gamma_i$	$E_i(eV)$	$\alpha_i^*$	$\beta_i^*$	$\gamma_i^*$
$a_1$	0.4439		-32.78	0.8834	0.6819		-1.25	1.0031	-0.4890	
$e$	0.0692		-14.17	0.4248	0.9073		-8.35	0.9102	-0.4185	
$t_2(xy)$	0.0254		-14.19	0.1815		0.9837	-9.28	0.9880		-0.1654
$t_2(xz)$	0.0226		-14.28	0.1610		0.9872	-9.30	0.9906		-0.1386
$t_2(yz)$	0.0243		-11.14	0.3764		0.9268	-9.15	0.9357		-0.3537
$t_1(x_1)$	0.3081	0.2606	-17.90	-0.1209	-0.3730	1.0623	-0.81	0.9367	-0.3462	-0.2370
$t_1(x_2)$	0.3081	0.2606	-13.99	0.6767	0.7620	0.1225				
$t_1(y_1)$	0.2974	0.2724	-22.92	0.5123	0.8069	-0.3558	-0.68	0.9079	-0.3194	-0.3374
$t_1(y_2)$	0.2974	0.2724	-13.54	0.1855	0.0835	1.1256				
$t_1(z_1)$	0.3028	0.2658	-19.63	0.3724	0.6218	-0.7222	-0.71	0.8690	-0.4021	-0.3608
$t_1(z_2)$	0.3028	0.2658	-10.53	0.3586	0.5098	0.9154				

(c) Group overlap integrals and estimated energies for *cis* [Ni(II)O<sub>3</sub>N<sub>3</sub>] type complex

$\Gamma_i(M)$	$G_{ij}$	$G_{ik}$	$E_i(eV)$	$\alpha_i$	$\beta_i$	$\gamma_i$	$E_i(eV)$	$\alpha_i^*$	$\beta_i^*$	$\gamma_i^*$
$a_1$	0.4686		-34.81	0.9177	0.6627		-1.00	1.0155	-0.5001	
$e$	0.0599		-13.68	0.4662	0.8862		-9.14	0.8890	-0.4609	
$t_2$	0.0213		-14.17	0.1783		0.9482	-9.89	0.9878		-0.1573
$t_1(1)$	0.3116	0.2666	-19.50	0.3695	0.5964	-0.7522	-0.65	0.8648	-0.4145	-0.3680
$t_1(2)$	0.3116	0.2666	-16.39	0.3729	0.5376	0.9305				

In the  $t_1$  case, subscript  $i$  refers to metal AO  $j$  to  $\sigma$  ligand orbital and  $k$  to  $2p_x$  ligand orbital.

(d) Group overlap integrals and estimated energies for *trans* [Ni(II)O<sub>3</sub>N<sub>3</sub>] type complex

$\Gamma_i(M)$	$G_{ij}$	$G_{ik}$	$E_i(eV)$	$\alpha_i$	$\beta_i$	$\gamma_i$	$E_i(eV)$	$\alpha_i^*$	$\beta_i^*$	$\gamma_i^*$
$a_1$	0.4686		-34.81	0.9177	0.6627		-1.00	1.0155	-0.5001	
$e$	0.0599		-13.68	0.4662	0.8862		-9.14	0.8890	-0.4609	

$t_2(xy)$	0.0213		-14.17	0.1783		0.9842	-9.89	0.9878		-0.1573
$t_2(xz)$	0.0189		-14.26	0.1560		0.9879	-9.92	0.9907		-0.1372
$t_2(yz)$	0.0204		-11.17	0.4601		0.8881	-9.72	0.8973		-0.4418
$t_1(x_1)$	0.3205	0.2611	-17.93	-0.1633	-0.4186	1.0388	-7.02	0.9445	-0.3492	-0.2271
$t_1(x_2)$	0.3205	0.2611	-14.36	0.6955	0.7427	0.1738				
$t_1(y_1)$	0.3104	0.2721	-23.61	0.5311	0.8018	-0.3573	-0.57	0.9116	-0.3254	-0.3402
$t_1(y_2)$	0.3104	0.2721	-13.47	0.1775	0.0769	1.1260				
$t_1(z_1)$	0.3116	0.2666	-19.50	0.3695	0.5964	-0.7522	-0.65	0.8648	-0.4145	-0.3681
$t_1(z_2)$	0.3116	0.2666	-16.39	0.3729	0.5376	0.9305				

(e) Group overlap integrals and estimated energies for (Cu(II)O<sub>3</sub>N<sub>3</sub>) type complex

$\Gamma_i(M)$	$G_{ij}$	$G_{ik}$	$E_i(eV)$	$\alpha_i$	$\beta_i$	$\gamma_i$	$E_i^*(eV)$	$\alpha_i^*$	$\beta_i^*$	$\gamma_i^*$
$a_1$	0.4780		-35.93	0.9293	0.6578		-0.90	1.022	-0.5017	
$e$	0.0508		-13.62	0.5222	0.8544		-9.84	0.8798	-0.5781	
$t_2$	0.0163		-14.13	0.1675		0.9867	-10.62	0.9886		-0.1514
$t_1(1)$	0.3353	0.2777	-20.48	0.4425	0.6445	-0.6826	-0.48	0.8720	-0.4131	-0.3821
$t_1(2)$	0.3353	0.2777	-16.70	0.3363	0.4237	1.0105				

In the  $t_1$  case, subscript  $i$  refers to metal AO  $j$  so  $\sigma$  ligand orbital and  $k$  to  $2p_z$  ligand orbital.

(f) Group overlap integrals and estimated energies for *trans* [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complex.

$\Gamma_i(M)$	$G_{ij}$	$G_{ik}$	$E_i(eV)$	$\alpha_i$	$\beta_i$	$\gamma_i$	$E_i^*(eV)$	$\alpha_i^*$	$\beta_i^*$	$\gamma_i^*$
$a_1$	0.4780		-35.95	0.9293	0.6578		-0.90	1.022	-0.5017	
$e$	0.0508		-13.62	0.5222	0.8544		-9.84	0.8798	-0.4718	
$t_2(xy)$	0.0163		-14.13	0.1678		0.9860	-10.62	0.9886		-0.1514
$t_2(xz)$	0.0189		-14.28	0.1874		0.9825	-10.60	0.9859		-0.1688
$t_2(xz)$	0.0204		-11.41	0.6674		0.7450	-10.18	0.7585		-0.6520
$t_1(x_1)$	0.3210	0.2611	-20.15	0.4384	0.6592	0.6628	-0.68	0.8784	-0.4042	-0.3621
$t_1(x_2)$	0.3210	0.2611	-16.61	0.3264	0.4178	1.00001				
$t_1(y_1)$	0.4726	0.2721	21.78	0.7615	0.7230	-0.4140	0.60			
$t_1(y_2)$	0.4726	0.2721	-12.80	0.0956	0.0419			0.9831	-0.3926	-0.3915
$t_1(z_1)$	0.3353	0.2777	-20.48	0.4425	0.6445	-0.6826	-0.48	0.8720	-0.4131	-0.3820
$t_1(z_2)$	0.3353	0.2777	-16.70	0.3363	0.4237	1.0105				

Group overlap integrals and estimated energies for *cis* and *trans* M(II)O<sub>3</sub>N<sub>3</sub> and [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes are listed in Table 3 and 4, respectively. Energy level diagrams for *cis* and

*trans* [Ni(II)O<sub>3</sub>N<sub>3</sub>] and [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes are listed in Table 3 and 4, respectively.

The general formulas of the dipole moment matrix elements for the bonding and antibon-

Table 4. (a) Group overlap integrals and estimated energies for *cis* [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complex

$\Gamma_i(M)$	$G_{ij}$	$G_{ik}$	$E_i(eV)$	$\alpha_i$	$\beta_i$	$\gamma_i$	$E_i^*(eV)$	$\alpha_i^*$	$\beta_i^*$	$\gamma_i^*$	
$a_1$	0.5468		-43.25	1.0105	0.6368		-0.11	1.0857	-0.4978		
$e$	$(z^2)$	0.0607	-13.76	0.4866	0.8757		-9.14	0.9036	-0.4326		
	$(x^2-y^2)$	0.0607	-13.50	0.5075	0.8638		-9.04	0.8930	-0.4541		
$t_2$	$(xy)$	0.0204	-11.16	0.4564		0.8900	-0.72	0.8992		-0.4381	
	$(xz)$	0.0197	-12.66	0.2313		0.9731	-9.87	0.9774		-0.2121	
$t_1$	$(x_1)$	0.3474	0.2721	-26.10	0.5718	0.8208	-0.3018	0.52	0.9082	-0.3021	-0.4191
	$(x_2)$	0.3474	0.2721	-13.87	0.1998	0.0573	1.1212				
$t_1$	$(y_1)$	0.3660	0.2666	-16.87	0.5688	0.7585	-0.4644	0.19	0.8912	-0.3691	-0.4289
	$(y_2)$	0.3660	0.2666	-15.57	0.2614	0.1093	1.0984				
$t_1$	$(z_1)$	0.3567	0.2721	-21.52	0.5966	0.8079	-0.3060	0.37	0.9064	-0.3195	-0.4227
	$(z_2)$	0.3567	0.2721	-13.83	0.1949	-0.0626	1.1213				

(b) Group overlap integrals and estimated energies for *trans* [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complex

$\Gamma_i(M)$	$G_{ij}$	$G_{ik}$	$E_i(eV)$	$\alpha_i$	$\beta_i$	$\gamma_i$	$E_i^*(eV)$	$\alpha_i^*$	$\beta_i^*$	$\gamma_i^*$	
$a_1$	0.5468		-43.25	1.0105	0.6368		-0.11	1.0857	-0.4978		
$e$	$(z^2)$	0.0607	-12.41	0.4475	0.8943		-9.45	0.8943	-0.4475		
	$(x^2-y^2)$	0.0607	-14.13	0.3483	0.9384		-9.57	0.9528	-0.3067		
$t_2$	$(xz)$	0.0204	-11.16	0.4564		0.8900	-9.72	0.8992		-0.4381	
	$(yz)$	0.0217	-10.47	0.7831		0.6216	-9.71	-0.6528		0.7970	
$t_1$	$(x_1)$	0.3567	0.2721	-21.52	0.5966	0.8079	-0.3060	0.37	0.9064	-0.3195	-0.4227
	$(x_2)$	0.3660	0.2721	-13.83	0.1949	-0.0626	1.1213				
$t_1$	$(y_1)$	0.3104	0.2648	-23.63	0.5411	0.8076	-0.3310	-0.64	0.9144	-0.3243	-0.3367
	$(y_2)$	0.3104	0.2648	-12.31	0.1678	0.0497	1.1224				
$t_1$	$(z_1)$	0.3567	0.2721	-21.52	0.5966	0.8079	-0.3060	0.37	0.9064	-0.3195	-0.4227
	$(z_2)$	0.3567	0.2721	-13.83	0.1949	-0.0626	1.1213				

ding molecular orbitals are

$$\begin{aligned}
 & \langle \phi_i(MO) | r | \phi_i(MO) \rangle \\
 &= N_i^2 \{ 2\alpha_i \beta_i \langle \Gamma_i(M) | r | \Gamma_{\sigma_i}(L) \rangle + 2\alpha_i \gamma_i \langle \Gamma_i(M) | r | \Gamma_{\pi_i}(L) \rangle + \beta_i^2 \langle \Gamma_{\sigma_i}(L) | r | \Gamma_{\sigma_i}(L) \rangle \\
 & \quad + \gamma_i^2 \langle \Gamma_{\pi_i}(L) | r | \Gamma_{\pi_i}(L) \rangle \} \\
 & \langle \phi_i^*(MO) | r | \phi_i^*(MO) \rangle \\
 &= N_i^{*2} \{ 2\alpha_i^* \beta_i^* \langle \Gamma_i(M) | r | \Gamma_{\sigma_i}(L) \rangle + 2\alpha_i^* \gamma_i^* \langle \Gamma_i(M) | r | \Gamma_{\pi_i}(L) \rangle + \beta_i^{*2} \langle \Gamma_{\sigma_i}(L) | r | \Gamma_{\sigma_i}(L) \rangle \\
 & \quad + \gamma_i^{*2} \langle \Gamma_{\pi_i}(L) | r | \Gamma_{\pi_i}(L) \rangle \} \quad (8)
 \end{aligned}$$

Applying the coordinate transformation sch-

eme for octahedral<sup>16</sup> complex to the approximate molecular orbitals, we evaluate the dipole moment matrix elements and then calculate the contributions of  $\sigma$  and  $\pi$  bonds to the dipole moments for octahedral [M(II)O<sub>3</sub>N<sub>3</sub>] and [Ni(II)-O<sub>2</sub>N<sub>4</sub>] type complexes. The calculated contribution of  $\sigma$  and  $\pi$  bonds are listed in Table 5.

For monothio- $\beta$ -diketonate chelates, a considerable delocalization of  $\pi$ -bonds over the ligands was reported<sup>21</sup>. Thus, we assume that  $\pi$ -bonds of [M(II)O<sub>3</sub>N<sub>3</sub>]<sup>22</sup> type complexes are con-



siderably delocalized over the ligands. In order to consider delocalization of  $\pi$ -bonds in octahedral {M(II)O<sub>3</sub>N<sub>3</sub>} type complexes, we modify the approximate orbitals as

$$\phi_i^*(MO) = N_i^* \{ \alpha_i^* \Gamma_i(M) + \beta_i^* \Gamma_{\sigma_i}(L) + \gamma_i^* \{ (L) + (1 - \delta^2)^{1/2} \Gamma_{\pi_i}(del) \} \}$$

$$[\delta_i \Gamma_{\pi_i}(L) + (1 - \delta^2)^{1/2} \Gamma_{\pi_i}(del)] \quad (4)$$

$\phi_i(MO) = N_i \{ \alpha_i \Gamma_i(M) + \beta_i \Gamma_{\sigma_i}(L) + \gamma_i \delta \Gamma_{\pi_i}$  where  $\delta$  is the measure of delocalization of

Table 5. The calculated dipole moments for {M(II)O<sub>3</sub>N<sub>3</sub>} and {Ni(II)O<sub>2</sub>N<sub>4</sub>} type complexes.

Complex	Type	$\mu_{ox}$	$\mu_{oy}$	$\mu_{oz}$	$\mu_o$	$\mu_{xx}$	$\mu_{xy}$	$\mu_{xz}$	$\mu_x$	$\mu_{dx}$	$\mu_{dy}$	$\mu_{dz}$	$\mu_{xd}$	$\mu$	$\mu_d$	Expl.
{Co(III)O <sub>3</sub> N <sub>3</sub> }	<i>cis</i>	2.926	2.926	2.926	5.068	5.426	5.426	5.426	9.398	1.102	1.102	1.102	1.908	14.484	6.994	3.70
	<i>trans</i>	0	0	2.274	2.274	0	0	7.474	7.474	0	0	1.443	1.443	9.948	3.717	~6.27 <sup>22</sup>
{Ni(II)O <sub>3</sub> N <sub>3</sub> }	<i>cis</i>	3.036	3.036	3.036	5.259	5.322	5.322		9.219	1.007	1.007	1.007	1.745	14.478	7.274	24
	<i>trans</i>	0	0	2.726	4.158	0	0	7.682	7.68	0	0	1.449	1.449	10.354	4.225	
{Cu(II)O <sub>3</sub> N <sub>3</sub> }	<i>cis</i>	2.768	2.768	2.768	4.795	5.457	5.457	5.457	9.449	1.094	1.094	1.094	1.868	14.224	6.663	
	<i>trans</i>	0	0	2.402	2.402	0	0	5.344	5.344	0	0	1.074	1.074	7.746	3.476	
{Ni(II)O <sub>2</sub> N <sub>4</sub> }	<i>cis</i>	0	1.714	2.577	3.095	0	5.302	4.084	6.693					9.788		8.09
	<i>trans</i>	0	0	0	0	0	0	0	0					0		~10.0 <sup>22</sup>

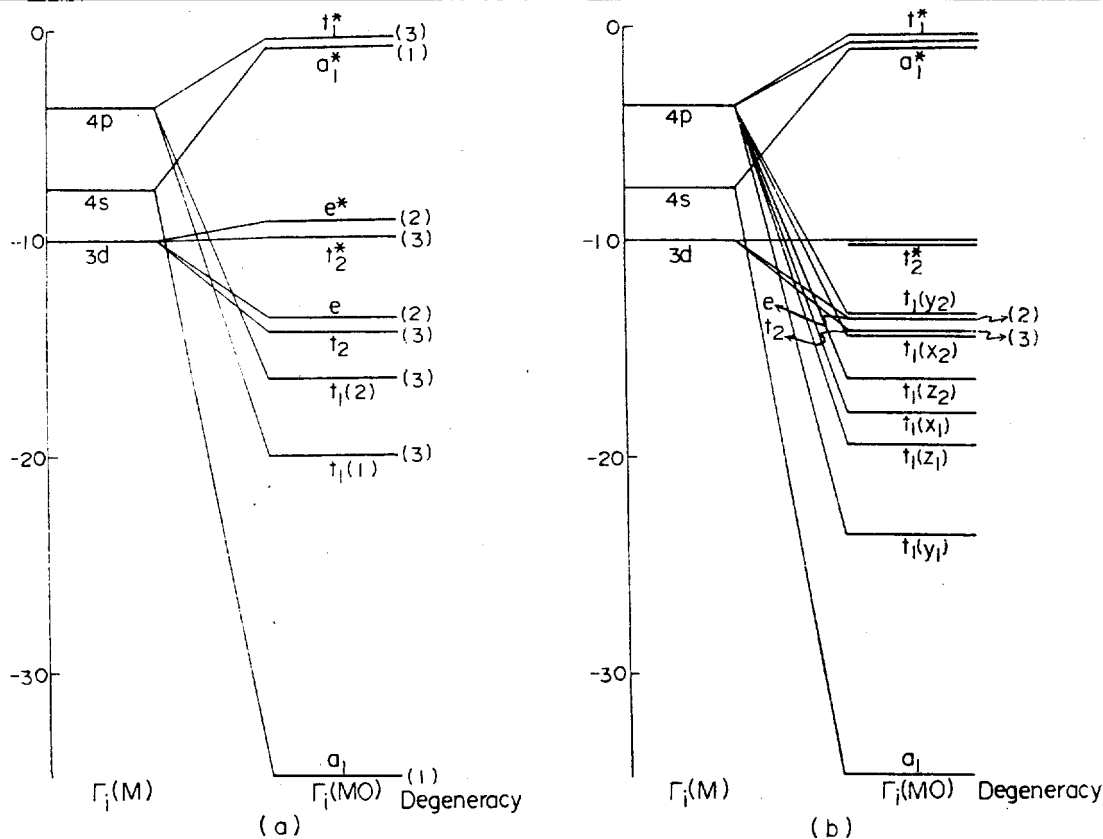
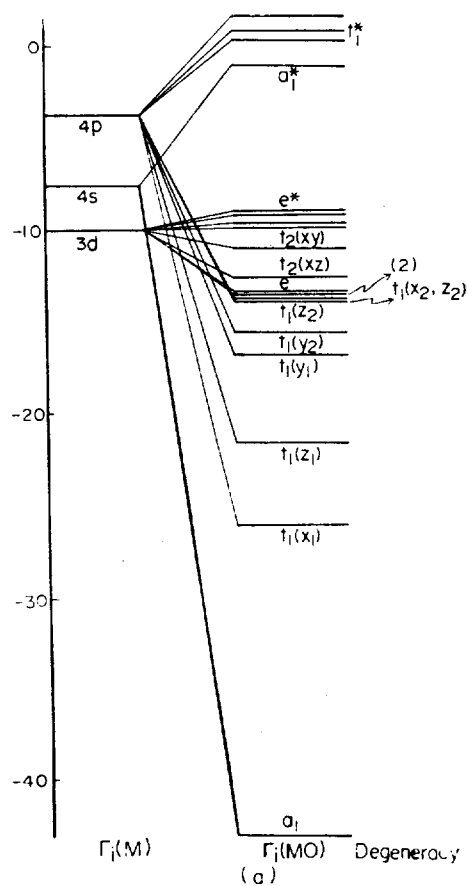


Fig. 3. (a) Energy level diagram for *cis* {Ni(II)O<sub>3</sub>N<sub>3</sub>} type complex; (b) Energy level diagram for *trans* {Ni(II)O<sub>3</sub>N<sub>3</sub>} type complex.

$\pi$ -bonds. Here, we assume that  $\delta^2$  is equal to  $1/n$  and  $n$  is the numbers of atoms in chelate ring for delocalized  $\pi$ -bonding molecular orbitals. The general formulas of the dipole moment matrix elements for the modified orbitals are

$$\begin{aligned} &\langle \phi_i(MO) | r | \phi_i(MO) \rangle \\ &= N_i^2 \{ 2\alpha_i \beta_i \langle \Gamma_i(M) | r | \Gamma_{\sigma_i}(L) \rangle \\ &\quad + 2\alpha_i \gamma_i \delta \langle \Gamma_i(M) | r | \Gamma_{\pi_i}(L) \rangle \\ &\quad + \beta_i^2 \langle \Gamma_{\sigma_i}(L) | r | \Gamma_{\sigma_i}(L) \rangle \\ &\quad + \gamma_i^2 \delta^2 \langle \Gamma_{\pi_i}(L) | r | \Gamma_{\pi_i}(L) \rangle \} \end{aligned}$$

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



$+ \gamma_i^{*2} \delta^2 \langle \Gamma_{\pi_i}(L) | r | \Gamma_{\pi_i}(L) \rangle$

Applying again the coordinate transformation scheme for octahedral complex to the modified molecular orbitals, we evaluate the dipole moment matrix elements for the modified molecular orbital and then calculate the contribution of delocalized  $\pi$ -bonds to the dipole moments for octahedral  $[M(II)O_2N_4]$  type complexes. The calculated contributions are listed in Table 5.

### 3. RESULTS AND DISCUSSION

As shown in Table 2, the hybrid orbitals of ligands are appeared to approximately 4 %  $s$ -character and 96 %  $p$ -character for Co(III) and Ni(II) complexes and 9 %  $s$ - and 91 %  $p$ -character for Cu(II) complex. No experimental re-

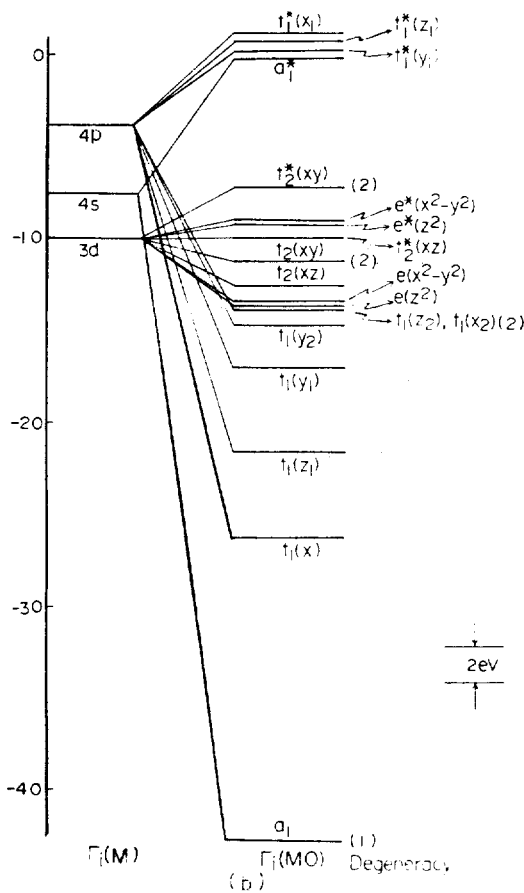


Fig. 4. (a) Energy level diagram for *cis*  $[Ni(II)O_2N_4]$  type complex; (b) Energy level diagram for *trans*  $[Ni(II)O_2N_4]$  type complex.

sults have been reported for bond character of [M(II)O<sub>3</sub>N<sub>3</sub>] and [Ni(II)O<sub>2</sub>N<sub>4</sub>] type complexes.

As shown in Table 3 and Fig. 3, the degeneracy of *cis* complexes is removed in *trans* complexes. This is the effect of the *trans* configuration of ligands on the degenerate energy levels of *cis* complexes. We can find such the effect of *trans* configuration of ligands on the degenerate energy levels for all the *cis* complexes involved in this work.

The calculated dipole moments for *cis*[M(II)-O<sub>3</sub>N<sub>3</sub>] type complexes are higher than those of *trans* [M(II)O<sub>3</sub>N<sub>3</sub>] type complexes as shown in Table 5. These results mean that the calculated dipole moments for [M(II)O<sub>3</sub>N<sub>3</sub>] type complexes decrease significantly when three ligands in *cis* position has been replaced to those in *trans* position. Such a phenomenon results from the effect of *trans* configuration on the calculated dipole moments for [M(II)O<sub>3</sub>N<sub>3</sub>] type complexes. The previous calculation of the dipole moments<sup>16</sup> was based upon the assumptions that  $\sigma$  bonds are only formed and the mixing coefficient  $C_M$  of the valence orbitals is the same for all  $\sigma$  bonding molecular orbitals. The calculated dipole moment for *cis* [Co(III)O<sub>3</sub>N<sub>3</sub>] type complexes was closer to the experimental values than that of *trans* complexes. In this work, the two assumptions are eliminated by performing EHT calculation, including  $\pi$  bonds and the calculated dipole moment for *trans* [Co(III)O<sub>3</sub>N<sub>3</sub>] type complexes is closer to the experimental values than that of *cis* complexes. This result indicates that the contribution of  $\sigma$  bonds and  $\pi$  bonds to the dipole moments should be considered. The calculated dipole moment for *cis* (Ni(II)O<sub>2</sub>O<sub>4</sub>) complexes falls in the range of experimental values. Such a result suggests that (Ni(II)O<sub>2</sub>N<sub>4</sub>) type complexes may have *cis* figuation.

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