TABLE 6: Optimized Ring Distances of 1-Lithio-2-chlorodifluoro-Cyclopropene

C1–C2	1.29 Å
C1–C3	1.54
C2–C3	1.45

a π-electron donor, he suggested that electron density should be fed into the lowest unoccupied molecular orbital of the ring and showed that this should lead to lengthening of all of the ring C–C bonds. As is seen Table 6, rather dramatic changes occur in the ring distances when one of chlorine atom is replaced by lithium. In 1-lithio-2-chloro-difluorocyclopropene, lithium is a π-electron acceptor, and the removal of electrons from the ring causes a lengthening of the bond adjacent to lithium and shortening of opposite bond. As a result of these considerations, it was concluded that the computed geometries were in accord with the rationalization of Hoffmann's suggestion.

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Calculation of the Dipole Moments for Transition Metal Complexes

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A new approach in calculating the dipole moments for transition metal complexes has been proposed and the calculated results are tabulated with the experimental values. The calculated dipole moments are applied to the theoretical predictiction or confirmation of the geometric structure for the transition metal complexes.

1. Introduction

For a few decades, a great deal of interest has been focussed on the measurement of the dipole moments of transition metal complexes in inert solvent solutions.[1] On the basis of the measured dipole moments, their geometric structures in liquid solutions have been predicted.

Only a few theoretical calculations of the dipole moments for transition metal complexes[2] have been performed, adopting the vector model of Wilcox and Gilmann[3] and a semiempirical method.[4]

A model for theoretical calculation of the dipole moments for transition metal complexes is developed in this work and the calculated results are listed with the experimental values. The calculated dipole moments were applied to the theoretical prediction or confirmation of the geometri structure for the transition metal complexes involved in the dipole moments calculation.

The required dipole moment matrix elements and overlap integrals were evaluated using the general translation method[5].

2. The Theoretical Model For Calculation of the Dipole Moments for Transition Metal Complexes

Since the octahedral, tetrahedral and square planar complexes which are formed by bonding with n equal ligands belong to O_h, T_d and D_{4h} point groups ($n = 6$ or 4), they should not have permanent dipole moments.[6] When three or two ligands in octahedral and tetrahedral or square planar complexes are replaced to form cis complexes by the ligands of different nature, their group theoretical nature is also changed, and these complexes belong to one

of the group theoretical point groups with lower symmetry. We assumed however that the cubic and tetragonal symmetries are still maintained for octahedral or tetrahedral and square planar complexes, unless substitution of a few ligands to the different type ligands causes a large distortion from cubic and tetragonal symmetries to one of lower symmetries. Therefore we adopted the approximated molecular orbitals of octahedral, tetrahedral and square planar complexes which are modified by adding C coefficients to the single basis set orbital for the substituted ligands.

For example, a_{1g} molecular orbital of ligand was modified as follows:

$$a_1 = \frac{1}{\sqrt{6}} (2p_z^1 + 2p_z^2 + C2p_z^3 + C2p_z^4 + 2p_z^5 + C2p_z^6) \quad (1)$$

when third, fourth and sixth ligands are replaced. Here it is also necessary to indicate that we adopted the notation of the O point group because the octahedral complex has lost the centre of symmetry. In the modified ligand orbital, C is a parameter which is used to differentiate the extent of contributions of different ligands to the ligand orbital. We may define the parameter C on a theoretical basis.

Definition of C Coefficient. Following the CNDO/2 formalism, the basic equation for the Fock matrix can be written as[7]

$$F_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) + [(P_{AA} - z_A) - \frac{1}{2}(P_{\mu\mu} - 1)]\gamma_{AA}$$
$$+ \sum_{B \neq A}(P_{AA} - z_B)\gamma_{AB} \quad (2)$$

$$F_{\mu\nu} = \beta_{AB} = \beta_{AB}^0 S_{\mu\nu} - \frac{1}{2}P_{\mu\nu} \quad (3)$$

where $-\frac{1}{2}(I_\mu + A_\mu)$ is the fundamental electronegativity for the atomic orbital μ, closely related to the scale introduced by Mulliken and

$$P_{\mu\nu} = 2\sum_i C_{\mu i} C_{\nu i} \quad (4)$$

$$\gamma_{AB} = \iint \phi_\mu^*(1)\phi_\nu(2)\left(\frac{1}{r_{12}}\right)\phi_\mu(1)\phi_\nu(2)d\zeta_1 d\zeta_2 \quad (5)$$

$$\beta_{AB} = \langle \phi_\nu | -\frac{1}{2}\nabla^2 - V_A - V_B | \phi_\nu \rangle \quad (6)$$

here ϕ_μ is on A and ϕ_ν is on B.

Pople and Beveridge however proposed that initial estimate of the LCAO coefficients may be obtained by a Hückel type theory using matrix elements

$$F_{\mu\mu}^{(0)} = -\frac{1}{2}(I_\mu + A_\mu) \quad (7)$$

$$F_{\mu\nu}^{(0)} = \beta_{AB}^0 S_{\mu\nu} \quad (8)$$

Since SCF or CNDO calculations for transition metal complexes may not be easy at this stage, it seems to be reasonable that the parameter C is approximately defined by

$$C = \frac{\text{Electronegativity of } 2p_z \text{ atomic orbital of } A}{\text{Electronegativity of } 2p_z \text{ atomic orbital of } B} \quad (9)$$

Further approximately

$$C = \frac{\text{Electronegativity of atom } A}{\text{Electronegativity of atom } B} \quad (10)$$

to differentiate the extent of contribution of $2p_z$ atomic orbitals of A and B atoms for the formation of the σ bonding

ligand orbital.

Assumptions. In order to calculated theoretically the dipole moments for transition metal complexes, it is convenient to split the dipole moment into the nuclear part and the electronic part of the dipole moment[8]

$$\mu = \mu_e + \mu_N \quad (11)$$

where

$$\mu_e = -e\sum_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} \langle \phi_\mu | r | \phi_\nu \rangle \quad (12)$$

$$\mu_N = e\sum_K n_K R_K \quad (13)$$

For most transition metal complexes, the ligands or a group of atoms (nuclear charge) are arranged symmetrically around the central metal ion, though a small distortion would be expected because the cis sites are occupied by different atoms. Therefore

(1) From symmetry arguments the nuclear part of the dipole moment is assumed to be completely cancelled.

(2) The atoms (co-ordination unit) that bond directly with the metal ions and are located at the end of the ligands are assumed to be the dominant contribution to the dipole moments of the transition metal complexes. Therefore the approximate molecular orbitals which are formed by a linear combination of the valence basis sets of the transition metal ion and the modified linear combinations of the single basis set orbital (np_z) for ligand atoms are used to calculate the dipole moments for transition metal complexes.

(3) The mixing coefficient C_M of the valence orbitals for the central metal ion with the appropriate ligand orbitals is assumed to be the same for all σ bonding molecular orbitals.

The Co-Ordinate Transformation. The co-ordinate systems adopted for calculation of the dipole moments for octahedral, square planar and tetrahedral complexes are represented in Figure 1.

Since the coordinate system of the metal ion is different from those of the ligands as shown in Figure 1, the coordinate systems for ligands were transformed into that of the central metal ion to calculate the dipole moments for transition metal complexes, using the following coordinate transformation scheme.

For tetrahedral complexes, the co-ordinate transformation

TABLE 1: **The Co-Ordinate Transformation Scheme of Ligands into the Co-Ordinate System of the Central Metal Ion**

$1 \to M$	$2 \to M$	$3 \to M$	$4 \to M$	$5 \to M$	$6 \to M$
$z^2 \to x^2$	$z^2 \to y^2$	$z^2 \to x^2$	$z^2 \to y^2$	$z^2 \to z^2$	$z^2 \to z^2$
$x^2 \to y^2$	$x^2 \to z^2$	$x^2 \to z^2$	$x^2 \to x^2$	$x^2 \to x^2$	$x^2 \to y^2$
$y^2 \to z^2$	$y^2 \to x^2$	$y^2 \to y^2$	$y^2 \to z^2$	$y^2 \to y^2$	$y^2 \to x^2$

TABLE 2: **Tht Polar and Azimuthal Angles of the Ligands**

Ligand	Apex			θ	ϕ
1	(1,	1,	1)	54.73°	45°
2	(−1,	1,	−1)	125.27°	225°
3	(1,	−1,	−1)	125.27°	135°
4	(−1,	−1,	1)	54.73°	315°

Substituting the Euler angles into the Euler transformation matrix leads to the transformation matrix for ligand 1.

$$\pm \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}_{new} = \begin{pmatrix} -\dfrac{1}{\sqrt{6}} & -\dfrac{1}{\sqrt{6}} & \dfrac{\sqrt{6}}{3} \\ \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 \\ \dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}_{old} \qquad (14)$$

Using the polar and azimuthal angles listed in Table 2, the transformation matrix for other ligands were also derived

$$\pm \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix}_{new} = \begin{pmatrix} \dfrac{1}{\sqrt{6}} & -\dfrac{1}{\sqrt{6}} & \dfrac{\sqrt{6}}{3} \\ -\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 \\ -\dfrac{1}{\sqrt{3}} & -\dfrac{1}{\sqrt{3}} & -\dfrac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix}_{old} \qquad (15)$$

$$\pm \begin{pmatrix} x_3 \\ y_3 \\ z_3 \end{pmatrix}_{new} = \begin{pmatrix} -\dfrac{1}{\sqrt{6}} & -\dfrac{1}{\sqrt{6}} & \dfrac{\sqrt{6}}{3} \\ -\dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 \\ -\dfrac{1}{\sqrt{3}} & -\dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} x_3 \\ y_3 \\ z_3 \end{pmatrix}_{old} \qquad (16)$$

$$\pm \begin{pmatrix} x_4 \\ y_4 \\ z_4 \end{pmatrix}_{new} = \begin{pmatrix} \dfrac{1}{\sqrt{6}} & \dfrac{1}{\sqrt{6}} & -\dfrac{\sqrt{6}}{3} \\ -\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 \\ -\dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} x_4 \\ y_4 \\ z_4 \end{pmatrix}_{old} \qquad (17)$$

Using the above two transformation schemes the dipole moments for octahedral, square planar and tetrahedral complexes were calculated.

3. Calculation of the Dipole Moments for Transition Metal Complexes by the Approximate Molecular Orbital Method

There are two ways of obtaining the molecular orbitals for transition metal complexes. One is to combine the valence basis sets of the central metal ion into the hybrid orbitals localized to the specific directions, and again to combine the hybrid orbitals with the single basis set of ligand atoms into the valence bond orbitals for transition metal complexes. This approach has been developed by Pauling[10] and has been applied to transition metal complexes by Kimball.[11] The other is to combine the valence basis sets of ligands into ligand orbital sets using the group theoretical method and then to combine the ligand orbitals with the valence basis sets of the central metal ion into the approximate molecular orbitals for transition metal complexes.[9,12]

First we shall use the approximate molecular orbital approach for calculation of the dipole moments for transition metal complexes.

Octahedral Complexes. The octahedral $[Co(III)O_3N_3]$[13] type and $[M(II)Cl_2O_2N_2]$[14] type complexes were chosen as examples to calculate the dipole moments ($M(II)=Ni(II)$ or $Co(II)$). As indicated in the introduction, these complexes are assumed to belong to O point group which is a subgroup
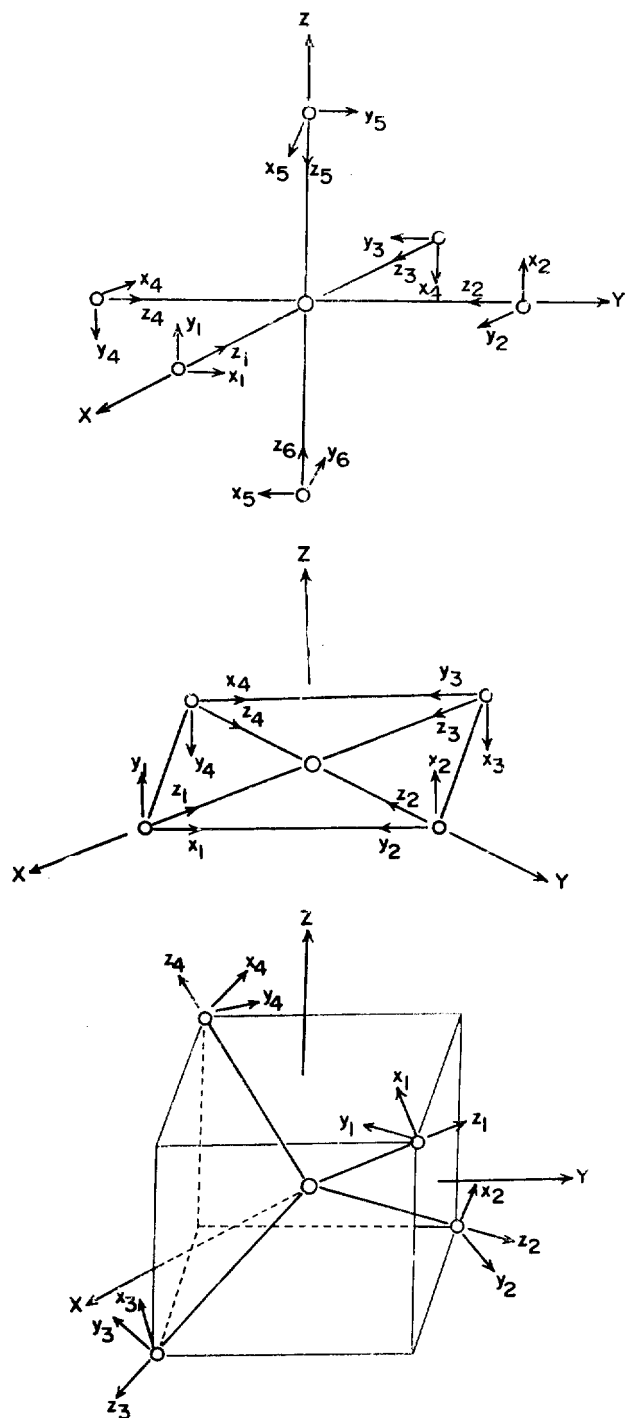
Figure 1. (a) The co–ordinate system for octahedral complex. (b) The co–ordinate system for square planar complex. (c) The co–ordinate system for tetrahedral complex.

scheme is more complicated than that for the octahedral complexes.

The four ligands located at the apices of the tetrahedron in Figure 1(c) can be described by the polar and azimuthal angles listed in Table 2.

The co–ordinate system of ligand 1 is related to that of the central metal ion by the following Euler angle[9]

$$\phi = -\frac{\pi}{4} \qquad \theta = -\left(\frac{\pi}{2}-b\right)$$

where

$$\tan b = \frac{1}{\sqrt{2}}, \quad \sin b = \frac{1}{\sqrt{3}}, \quad \cos b = \frac{\sqrt{2}}{\sqrt{3}} \text{ and } \alpha = -\frac{\pi}{2}$$

TABLE 3(a): Orbital Transformation Scheme for Octahedral [Co(III)O₃N₃] type Complexes

Representation	M(III) orbitals $\Gamma_i(M)$	Ligand orbitals [$\Gamma_i(l)$]
a_1	4s	$-\dfrac{1}{\sqrt{6}}(2p_z{}^1+2p_z{}^2+C2p_z{}^3+C2p_z{}^4+2p_z{}^5+C2p_z{}^6)$
e	$3d_{z^2}$	$-\dfrac{1}{\sqrt{12}}(22p_z{}^5+2C2p_z{}^6-2p_z{}^1-C2p_z{}^3-2p_z{}^2-C2p_z{}^4)$
	$3d_{x^2-y^2}$	$\dfrac{1}{4}(2p_z{}^1-2p_z{}^2+C2p_z{}^3-C2p_z{}^4)$
t	$4p_x$	$-\dfrac{1}{\sqrt{2}}(2p_z{}^1-C2p_z{}^3)$
	$4p_y$	$\dfrac{1}{2}(2p_z{}^2-C2p_z{}^4)$
	$4p_z$	$\dfrac{1}{2}(2p_z{}^5-C2p_z{}^6)$

where $C = \dfrac{\text{Electronegativity of N atom}}{\text{Electronegativity of O atom}}$

TABLE 3(b): Orbital Transformation Scheme for Octahedral [M(II)Cl₂N₂O₂] Type Complex

Representation	M(II) orbitals $\Gamma_i(M)$	Ligand orbitals Γ_i (l)
a_1	4s	$-\dfrac{1}{\sqrt{6}}(C'2p_z{}^1+C3p_z{}^2+C'2p_z{}^3+2p_z{}^4+2p_z{}^5+C3p_z{}^6)$
e	$3d_{x^2-y^2}$	$\dfrac{1}{2}(C'2p_z{}^1-C3p_z{}^2+C'2p_z{}^3-2p_z{}^4)$
	$3d_{z^2}$	$-\dfrac{1}{\sqrt{12}}(22p_z{}^5+2C3p_z{}^6-C'2p_z{}^1-C3p_z{}^2-C'2p_z{}^3-2p_z{}^4)$
	$4p_x$	$-\dfrac{1}{\sqrt{2}}(C'2p_z{}^1-C'2p_z{}^3)$
t_1	$4p_y$	$-\dfrac{1}{\sqrt{2}}(C3p_z{}^2-2p_z{}^4)$
	$4p_z$	$-\dfrac{1}{\sqrt{2}}(C3p_z{}^6-2p_z{}^5)$

$C = \dfrac{\text{Electronegativity off Cl atom}}{\text{Electronegativity of O atom}}$, $C' = \dfrac{\text{Electronegativity of N atom}}{\text{Electronegativity of O atom}}$

of O_h point group. The orbital transformation scheme for the octahedral [Co(III) O₃N₃] and [M(II)Cl₂O₂N₂] type complexes are listed in Table 3.

The valence basis sets of the metal ions were combined with the appropriate ligand orbitals having the same transformation property into the approximate molecular orbitals,

$$\phi_i(MO)=N_i\{C_M\Gamma_i(M)+(1-C_M{}^2)^{1/2}\,\Gamma_i(l)\}$$
$$\phi_i(MO)=N_i{}^*\{(1-C_M{}^2)^{1/2}\,\Gamma_i(M)-C_M\Gamma_i(l)\} \qquad (18)$$

where N_i is the normalization constant given by

$$N_i=\{C_M{}^2+(1-C_M{}^2)<\Gamma_i(l)\,|\,\Gamma_i(l)>+2C_M(1-C_M{}^2)^{1/2}$$
$$<\Gamma_i(M)\,|\,\Gamma_i(l)>\}^{-1/2}$$
$$N_i{}^*=\{C_M{}^2+(1-C_M{}^2)<\Gamma_i(l)\,|\,\Gamma_i\ >-2C_M(1-C_M{}^2)^{1/2}$$
$$<\Gamma_i(M)\,|\,\Gamma_i(l)>\}^{-1/2} \qquad (19)$$

and C_M is the mixing coefficient of the valence orbitals for the central metal ion with the appropriate ligand orbitals. We chose the mixing coefficient as $C_M = 0.75$. This value corresponds to orbital reduction factor $K=0.74$ if we define the orbital reduction factor as

$$K=1-\frac{C_M{}^2}{4}(1+C^2)N^2 \qquad (20)$$

following the Ballhausen formalism.[9]

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

$$<\phi_i(MO)\,|\,r\,|\,\phi_i(MO)>=N_i{}^2\ [2C_M(1-C_M{}^2)^{1/2}$$

$$<\Gamma_i(M)\,|\,r\,|\,\Gamma_i(l)>+(1-C_M{}^2)<\Gamma_i(l)\,|\,r\,|\,\Gamma_i\ (l)>\} \qquad (21)$$
$$<\phi_i{}^*(MO)\,|\,r\,|\,\phi_i{}^*(MO)>=N_i{}^{*2}\{-2C_M(1-C_M{}^2)^{1/2}<$$
$$\Gamma_i(M)\,|\,r\,|\,\Gamma_i(l)>+C_M{}^2<\Gamma_i(l)\,|\,r\,|\,\Gamma_i(l)>\} \qquad (22)$$

First we evaluated the dipole moment matrix elements for the octahedral [Co(III)N₃O₃] and [M(II)Cl₂N₂O₃] type complexes applying the coordinate transformation scheme for the octahedral complex to the general formulas of the dipole moment matrix elements given by equation (21)-(22), and then calculated their dipole moments. The calculated dipole moments are listed in Table 4.

As shown in Table 4, the calculated dipole moment for the cis octahedral complex is bigger than for the trans complex and also falls in the range of the experimental values. The calculated results in Table 4 suggest that the cis configuration for the octahedral [Co(III)N₃O₃] type com. plexes is more favorable than the trans structure. In Table 4(b), the calculated dipole moments of [M(II) Cl₂N₂O₂] type complexes for different C values are listed. This result indicates that the calculated values of the dipole moments are heavily dependent on the C value chosen, but the dipole moments calculated using both C values fall in the range of the experimental values.

Square Planar and Tetrahedral Complexes. The square planar, tetrahedral [M(II)=N₂O₂],[15] [M(II)N₂S₂][16] and [Pd(II)N₂X₂][17] type complexes were chosen for the cal-

TABLE 4(a): The Calculated Dipole Moments for the *cis* and *trans* [Co(III)–N$_3$O$_3$] Type Complex.

Type	C	C_M	R [Co(111)–O]	R' [Co(III)–N	μ_x	μ_z	μ	Expl Values
cis	0.8571	0.50	1.89	1.91	2.964	2.168	4.264	3.70–6.27[a]
trans	0.8571	0.50	1.89	1.91	O	2.163	2.163	

X	R	μ	X	R	μ
H	CH$_3$	4.99	H	n–C$_5$H$_{11}$	4.78
H	C$_2$H$_5$	4.69	H	C$_6$H$_5$	3.70
H	n–C$_3$H$_7$	4.59	3-Cl	n–C$_3$H$_7$	6.27
H	n–C$_4$H$_9$	4.83	5-Cl	n–C$_3$H$_7$	4.98

TABLE 4(b): The Calculated Dipole Moments for Octahedral [M(II)Cl$_2$N$_2$O$_2$] Type Complexes (Debye)

Complexes	M(II)–O	M(II)Cl	C	μ_x	μ_z	μ	Expl. Values
[Co(11)Cl$_2$N$_2$O$_2$]	1.82	2.15	0.8571	2.134	1.655	2.701	1.60–2.70[a]
[Co(11)Cl$_2$N$_2$O$_2$]	1.82	2.15	0.8762	1.623	1.256	2.058	
[Ni(11)Cl$_2$N$_2$O$_2$]	1.88	2.14	0.8571	1.983	1.401	2.428	1.18–2.04[b]
[Ni(11)Cl$_2$N$_2$O$_2$]	1.88	2.15	0.8762	1.786	1.158	2.128	

[a] *bis*-[3–(3'–Fluoroanilion)–l–phenyl–2–hydroxy propanato]cobalt (II) (2.09), *bis*-[3–(4'–fluoroanilion)–l–phenyl–2–hydroxy propanato]cobalt (II) (1.60), *bis*-[3(2',6'–dichloroanilino)–l–phenyl–2–hydroxy propanato] Cobalt(II) (2.70). [b] *bis*-[3–(2',6'–Dichloroanilino)–1–phenyl–2–hydroxypro panato] Nickel (11) (2.04), *bis*-[3–(2'–chloro–4',6'–dibromoanilino)–1–phenyl–2–hydroxy propnato]nickel (II) (1.71), *bis*-[3–(2',4'6–tribromoanilino)–1–phenyl–2–hydroxypropanato]nickel (II) (1.18).

TABLE 5(a): Orbital Transformation Scheme for Square Planar [M(II)N$_2$O$_2$] Type Complexes [M(II)=Ni(II) or Cu(II)]

Representation	M(II) orbitals $\Gamma_i(M)$	Ligand orbitals, $\Gamma_i(l)$
a_1	4s *and* 3d$_{z^2}$	$\frac{1}{2}(2p_z{}^1+2p_x{}^2+C2p_z{}^3+C2_z{}^4)$
b_1	3d$_{x^2-y^2}$	$\frac{1}{2}(2p_z{}^1-2p_x{}^2+C2p_z{}^3-C2_z{}^4)$
e	4p$_x$	$\frac{1}{\sqrt{2}}(2p_z{}^1-C2p_z{}^3)$
	4p$_y$	$\frac{1}{\sqrt{2}}(2p_z{}^2-C2p_z{}^4$

where C=Electronegativity of N/Electronegative of 0.

TABLE 5(b): Orbital Transformation Scheme for Square Planar [M(II)N$_2$S$_2$] Type Complexes [M(II)=Ni(II), Co(II),Cu(II) or Zn (II)]

Representation*	Pd(II) orbitals $\Gamma_i(M)$	Ligands, $\Gamma_i(l)$
a_1	4s *and* 3d$_z{}^2$	$\frac{1}{2}(2p_z{}^1+2p_x{}^2+C3_z{}^3+C3_z{}^4)$
b_1	3d$_{x^2-y^2}$	$\frac{1}{2}(2p_z{}^1-2p_x{}^2+C3p_z{}^3-C3p_z{}^4)$
e	4p$_z$	$\frac{1}{\sqrt{2}}(2p_z{}^1-C3pz^3)$
	4p$_y$	$\frac{1}{\sqrt{2}}(2p_z{}^2-C3p_z{}^4)$

where $C = \dfrac{\text{Electronegativity of S atom}}{\text{Electronegativity of O atom}}$

culation of the dipole moments [M(II) Ni(II), Cu(II), Co(II) or Zn(II) and X=O or S] as examples in such a system. The orbital transformation schemes for square planar and tetrahedral complexes are listed in Tables 5 and 6.

As the transformation properties of the central metal ion and ligand orbitals are known, the valence basis sets of the metal ion can be combined with the ligand orbitals having the same transformation properties. The approximate orbitals gained may be represented, in general, using the

TABLE 5(c): Orbital Transformation Scheme for Square Planar [Pb(II)N$_2$O$_2$] or [Pb(II)O$_2$S$_2$] Type Complexes

Representation*	Pd(II) orbitals $\Gamma_i(M)$	Ligand orbitals, $\Gamma_i(l)$
a_1	5s	$\frac{1}{2}(2_z{}^1+2p_x{}^2+C2p_z{}^3+C2p_z{}^4)or$
	4d$_{z^2}$	$\frac{1}{2}(2p_z{}^1+2p_z{}^2+C'3p_z{}^3+C'3p_z{}^4)$
b_1	4d$_{x^2-y^2}$	$\frac{1}{2}(2p_z{}^1-2p_z{}^2+C2p_z{}^3-C2p_z{}^4)or$
		$\frac{1}{2}(2p_z{}^1-2p_z{}^2+C'3p_z{}^3-C'3p_z{}^4)$
e_z	4p$_z$	$\frac{1}{\sqrt{2}}(2p_z{}^1-C2p_z{}^3)\ or\ \frac{1}{2}(2p_z{}^1-C'3p_z{}^3)$
e_y	4p$_y$	$\frac{1}{\sqrt{2}}(2p_z{}^2-C2p_z{}^4)\ or\ \frac{1}{2}(2p_z{}^2-C'3p_z{}^4)$

$C = \dfrac{\text{Electronegativity of N atom}}{\text{Electronegativity of O atom}}$, $C' = \dfrac{\text{Electronegativity of S atom}}{\text{Electronegativity of O atom}}$

* irreducible representation of C_{4v} point group.

TABLE 6(a): Orbital Transformation Scheme for the Tetrahdral [M(II)O$_2$N$_2$] Type Complexes [M(II) Ni, Cu(II) or Pb(II)]

Representation*	M(II)orbitals $\Gamma_i(M)$	Ligand orbitals, $\Gamma_i(l)$
a	ns	$\frac{1}{2}(2p_z{}^1+2p_z{}^2+C2p_z{}^3+C2_z{}^4)$
$t(x)$	np$_z$	$\frac{1}{2}(2p_z{}^1-2p_x{}^2+C2p_z{}^3-C2p_z{}^4)$
$t(y)$	np$_y$	$\frac{1}{2}(2p_z{}^1+2p_z{}^2-C2p_z{}^3-C2p_z{}^4)$
$t(z)$	np$_z$	$\frac{1}{2}(2p_z{}^1-sp_z{}^2-C2p_z{}^3+C2p_z{}^4)$

*Irreducible representation of cubic group (T) where $n=4$ for Ni (II) and Cu(II) and $n=5$ for Pd(II).

group theoretical notation by

$$\phi_i(MO)=N_i\{C_M\Gamma_i(M)+(1-C_M{}^2)^{1/2}\Gamma_i(l)\}$$
$$\phi_i^*(MO)=N_i^*\{(1-C_M{}^2)^{1/2}\Gamma_i(M)-C_M\Gamma_i(l)\} \qquad (24)$$

TABLE 6(b): Orbital Transformation Sheeme for the Tetrahedral [M(II)O$_2$S$_2$] Type Complexes [M(II)=Ni(II), Co(II), Cu(II), Zn(II) Zn(II) or Pd(II)]

Representation	M(II) orbitals $\Gamma_i(M)$	Ligand orbitals, $\Gamma_i(l)$
a	ns	$\frac{1}{2}(2p_z{}^1+2p_z{}^2+C3p_z{}^3+C3p_z{}^4)$
$t(x)$	np_x	$\frac{1}{2}(2p_z{}^1-2p_z{}^2+C3p_z{}^3-C3p_z{}^4)$
$t(y)$	np_y	$\frac{1}{2}(2p_z{}^1+2p_z{}^2-C3p_z{}^3-C3p_z{}^4)$
$t(z)$	np_z	$\frac{1}{2}(2p_z{}^1-2p_z{}^2-C3p_z{}^3+C3p_z{}^4)$

where $C=\dfrac{\text{Electronegativity of S atom}}{\text{Electronegativity of O atom}}$ and $n=4$ for Ni(II), Co(II), Zn(II) and Cu(II) $n=5$ for Pd(II)

where C_M is the mixing coefficient chosen as $C_M=0.50$

The dipole moments for the square planar and tetrahedral complexes were calculated using the numerical values of the dipole moment matrix elements which were evaluated applying the co-ordinate transformation schemes to the general formulae of the dipole moment matrix elements for the square planar and tetrahedral complexes.

$$<\phi_i(MO)|r|\phi_i(MO)>$$
$$=N_i{}^2\{2C_M(1-C_M{}^2)^{1/2}<\Gamma_i(M)|r|\Gamma_i(l)>$$
$$+(1-C_M{}^2<\Gamma_i(l)|r|\Gamma_i(l)>\}$$
$$<\phi_i^*(MO)|r|\phi_i(MO)>=N_i^{*2}\{-2C_M(1-C_M{}^2)^{1/2}$$
$$<\Gamma_i(M)|r|\Gamma_i(l)>C_M{}^2<+\Gamma_i(l)|r|\Gamma_i(l)>\} \tag{25}$$

TABLE 7(a) The Calculated Dipole Moments for the Tetrahedral an d Square Planar [Ni(II)–O$_2$N$_2$] Type Complexes,[15] Choosing C$_M$=0.50 and C=0.8771

R[Ni(II)–O]	R′[Cu(II)–N]	Square planar μ_z	Square planar μ	Tetrahedral	Expl. value	ΔR
1.851	1.922	3.122	4.415	3.66	4.43–4.23	0.071
1.894	1.990	3.161	4.470	3.64	2.68	0.096
1.893	1.950	3.381	4.872	3.89	2.44	0.052
1.837	1.920	3.146	4.45	3.59	2.70	0.083
1.841	1.851	3.284	4.644	3.93	2.04	0.010
1.80	1.90	3.150	4.455	3.39	1.92	0.10
1.83	1.86	3.018	4.268	3.80	1.94	0.03
1.84	1.86	3.246	4.591	3.87	3.33–3.77	0.02
1.80	1.84	3.304	4.673			0.04

TABLE 7(b): The Calculated Dipole Moments for [Cu(II)–N$_2$O$_2$] Type Complexes[15]

R[Cu(II)–O]	R′[Cu(II)–N]	Square Planar μ	Square Planar μ_z	Tetrahedral	Expl. value	ΔR
1.878	1.993	2.823	3.992	3.55	3.06–4.72	0.115
1.901	1.989	2.869	4.057	3.72	2.34–2.63	0.088
1.92	1.94	3.149	4.453	4.225	2.91	0.02
1.908	1.957	2.966	4.194	3.998	3.73	0.049

TABLE 7(c): The Calculated Dipole Moments for Tetrahedral and Square Planar [Pd(II)O$_2$N$_2$] Type Complexes[17]

R Pd(II)–O	R′ Pd(II)–N	Square Planar μ_x	Square Planar μ	Tetrahedral	C	Expl. value	ΔR*
1.94	1.86	3.379	4.779	4.69	0.8771	4.72	0.08
2.00	2.01	3.618	5.117	4.496	0.8771		—0.01
1.99	1.94	4.084	5.776	4.617	0.8771		0.05
2.02	1.99	4.052	5.731	4.565	0.8771		0.03

*ΔR=R–R′

TABLE 8: The Calculated Dipole Moments for Square Planar and Tetrahedral [M(II)N$_2$S$_2$] Type Complexes[16]

Complex	R	R′	Square planar μ_x	Square planar μ	Tetrahedral μ	C	Expl. value
[Cu(II)N$_2$S$_2$]	1.91	2.18	3.316	4.689	5.361	0.7948	3.93–6.82
				5.225	5.895	0.7948	
[Ni(II)N$_2$S$_2$]	1.90	2.17	2.240	3.168	4.444	0.8333	3.27–5.11
[Cu(II)N$_2$S$_2$]	1.92	2.19	—	—	4.506	0.8333	3.42–5.07
							3.42–6.05
[Zn(II)N$_2$S$_2$]	1.99	2.27	4.332	6.126	5.941	0.7948	5.93–6.81
							3.42–7.83
							4.50

The calculated dipole moments are listed in Tables 7 and 8.

As shown in Tables 7 and 8, the calculated dipole moments for the tetrahedral and square planar complexes fall in the range of the experimental values. Comparing the calculated values of the dipole moments with the experimental values we may predict the geometric structure of the transition metal complexes. We found that the results are in agreement with the experimental structures. For example, the calculated dipole moments for the square planar [Ni(II)O₂N₂] type complexes are closer to the experimental values than those of the tetrahedral complexes. This results predict that [Ni(II)O₂N₂] type complexes have the square planar structure in inert solvent solutions.   This prediction is in agreement with the experimental structure of McCarty and Martell.[15]

4. Calculation of the Dipole Moments for Transition Metal Complexes by the Valence Bond Method

In order to calculate the dipole moments for transition metal complexes by the valence bond method, it is also necessary to assume that (1) the nuclear part of the dipole moment is completely cancelled because the central metal ion is symmetrically surrounded by ligand, and (2) the atoms that bond directly with the metal ions and are located at the end of the ligands contribute greatly to the dipole moments of the transition metal complexes. Since the hybrid orbitals localized at the specific directions are all equal, the mixing coefficient is automatically equalized.

The octahedral[M(III)O₃S₃][18] type complexes were chosen for calculation of the dipole moments by the valence bond method [M(III) = V(III), Cr(III), Mn(III), Fe(III), Co(III), Ru(III), Rh(III) or Os(III)]. Since the representation which is formed by six σ orbitals on the central metal ion reduces to[19]

$$\Gamma_\sigma = A_1 + E + T_1 \tag{16}$$

the valence orbitals of the central metal ions which correspond to the irreducible representations A, E and T_1 may be combined into six hybrid orbitals which orient toward the apices of octahedron.

$$h_1 = \frac{1}{\sqrt{6}}ns + \frac{1}{\sqrt{2}}np_x - \frac{1}{\sqrt{2}}(n-1)d_{z^2} + \frac{1}{2}(n-1)d_{x^2-y^2}$$

$$h_2 = \frac{1}{\sqrt{6}}ns + \frac{1}{\sqrt{2}}np_y - \frac{1}{\sqrt{6}}(n-1d)_{z^2} - \frac{1}{2}(n-1)d_{x^2-y^2}$$

$$h_3 = \frac{1}{\sqrt{6}}ns - \frac{1}{\sqrt{6}}np_x - \frac{1}{\sqrt{12}}(n-1)d_{z^2} + \frac{1}{2}(n-1)d_{x^2-y^2}$$

$$h_4 = \frac{1}{\sqrt{6}}ns - \frac{1}{\sqrt{2}}np_y - \frac{1}{\sqrt{12}}(n-1)d_{z^2} - \frac{1}{2}(n-1)d_{x^2-y^2}$$

$$h_5 = \frac{1}{\sqrt{6}}ns + \frac{1}{\sqrt{6}}np_z + \frac{1}{\sqrt{3}}(n-1)d_{z^2}$$

$$h_6 = \frac{1}{\sqrt{6}}ns - \frac{1}{\sqrt{2}}np_z + \frac{1}{\sqrt{3}}(n-1)d_{z^2} \tag{27}$$

where $n=4$ for V(III), Cr(III), Nn(III), Fe(III) and Co(III),

$n=5$ for Ru(III), Rh(III) and $n=6$ for O(III). Combining these hybrid orbitals with the single basis set of ligands gives the valence bond orbitals for octahedral complexes.

$$\phi_1 = N_1\{C_M h_1 + (1-C_M^2)^{1/2}C3p_z\}$$
$$\phi_2 = N_1\{C_M h_2 + (1-C_M^2)^{1/2}C3p_z\}$$
$$\phi_3 = N_2\{C_M h_3 + (1-C_M^2)^{1/2}2p_z\}$$
$$\phi_4 = N_2\{C_M h_4 + (1-C_M^2)^{1/2}2p_z\}$$
$$\phi_5 = N_1\{C_M h_5 + (1-C_M^2)^{1/2}C3p_z\}$$
$$\phi_6 = N_2\{C_M h_6 + (1-C_M^2)^{1/2}2p_z\}$$

where N_1 and N_2 are normalization constants represented by

$$N_1 = \{C_M^2 + 2C_M(1-C_M^1)^{1/2}C\left[\frac{1}{\sqrt{6}}<ns\,|\,3p_z>\right.$$
$$\left. + \frac{1}{\sqrt{2}}<np_x|3p_z> \frac{1}{2\sqrt{3}}<(n-1)d_{z^2}|3p_z>\right]$$
$$+ (1-C_M^2)C^2\}^{-1/2}$$

$$N_2 = \{C_M^2 + 2C_M(1-C_M^2)^{1/2}$$
$$\left[\frac{1}{\sqrt{6}}<ns\,2p_z> + \frac{1}{\sqrt{2}}<np_x|2p_z>\right.$$

TABLE 9: The Calculated Dipole Moments for Octahedral [M(III)O₃S₃] Type Complexes ($C_M = 0.7071$, $C = 0.7671$)

Complex	M(III)-O	M(III)-S	VB μ(D)	MO μ(D)*	Expl. values
[Fe(III)O₃S₃] facial	1.90	2.19	3,401	4,434	2.46–7.00
[Fe(III)O₃S₃] meridional	1.90	2.19	1,936	2.56	3.52–7.00
[Mn(III)O₃S₃] facial	1.90	2.19	3,144	4,503	
[Mn(III)O₃S₃] meridional	1.90	2.19	1,815	2.60	
[Cr(III)O₃S₃] facial	1.91	2.20	2,668	4,339	3.93–7.07
[Cr(III)O₃S₃] meridional	1.91	2.20	1,540	2,506	
[V(III)O₃S₃] facial	1.95	2.24	2,490	4,479	
[V(III)O₃S₃] meridional	1.95	2.24	1,437	2,657	
[Ci(III)O₃S₃] facial	1.89	2.18	3,549	4,533	3.29–7.36
[Co(III)O₃S₃] meridional	1.89	2.18	2,049	2,617	2.88–7.14
					6.54–8.57
[Ru(III)O₃S₃] facial	1.98	2.27	4,099	4,201	4.55–6.91
[Ru(III)O₃S₃] meridional	1.98	2.27	3,347	3,430	
[Rh(III)O₃S₃] facial	1.98	2.27	3,182	4,495	6.52–8.14
[Rh(III)O₃S₃] meridional	1.98	2.27	2,598	3,670	4.13–7.19
[Os(III)O₃S₃] facial	1.99	2.28	3,335	4,274	
[Os(III)O₃S₃] meridional	1.99	2.28	2,723	3,490	

*The dipole moments calculated by the approximate molecular orbital method.

$$+\frac{1}{2\sqrt{3}}<(n-1)d_{z^2}|2pz>\Big]+(1-C_M^2)^{-1/2} \qquad (29)$$

where $C=\dfrac{\text{Electronegativity of sulphur atom}}{\text{Electronegativity of oxygen atom}}=0.7671$

Applying the co-ordinate transformation scheme for octahedral complexes to the valence bond orbitals, the dipole moment matrix elements for the octahedral $[M(III)O_3S_3]$ type complexes were derived.

$$<\phi_1|x|\phi_1>=N_1^2\{C_M^2<h_1|x|h_1>+2C_M(1-C_M^2)^{1/2}$$
$$C<h_1|x|3p_x>+C^2(1-C_M^2)<3p_x|x|3p_x>\}$$

$$<\phi_2|y|\phi_2>=N_1^2\{C_M^2<h_2|y|h_2>+2C_M(1-C_M^2)^{1/2}$$
$$C<h_2|y|3p_y>+(1-C_M^2)<3p_y|y|3p_y>\}$$

$$<\phi_3|x|\phi_3>=-N_2^2\{C_M^2<h_3|x|h_3>+2C_M(1-M^2)^{1/2}$$
$$<h_3|x|2p_x>+(1-C_M^2)<2p_x|x|2p_x>\}$$

$$<\phi_4|y|\phi_4>=-N_2^2\{C_M^2<h_4|y|h_4>+2C_M(1-C_M^2)^{1/2}$$
$$<h_4|y|2p_y>+(1-C_M^2)<2p_y|y|2p_y>\}$$

$$<\phi_5|z|\phi_5>=N_1^2\{C_M^2<h_5|z|h_5>+2C_M(1-C_M^2)^{1/2}$$
$$C<h_5|z|3p_z>+C^2(1-C_M^2)<3p_z|z|3p_z>\}$$

$$<\phi_6|z|\phi_6>=-N_2^2\{C_M^2<h_6|z|h_6>+2C_M(1-C_M^2)^{1/2}$$
$$<h_6|z|2p_z>+(1-C_M^2)<2p_z|z|2p_z>\} \qquad (30)$$

The calculated dipole moments using the dipole moment matrix elements of equation (30) are listed in Table 9.

As shown in Table 9, the calculated dipole moments for the facial $(M(III)O_3S_3)$ type complexes are bigger and closer than those of the meridional complexes to the experimental values. Such results suggest that $(M(III)O_3S_3)$ type complexes have the meridional structure in inert solvent solutions.

The dipole moment calculation by the valence bond method does not assume the value of the mixing coefficient, C_M, for the hybrid orbitals with the single basis set orbital for the ligands to be equal which is different from the approximate molecular orbital method. The calculation of the dipole moment by the valence bond method is much easier than using the approximate molecular orbital method because the six dipole moment matrix elements for the valence bond molecular orbitals for octahedral complexes need to be calculated.

The numerical values of the dipole moments calculated by the valence bond method are smaller than those of the approximate molecular orbital method.

As shown in Table 9, the calculated values of the dipole mements for octahedral complexes also fall in the range of the experimental values. Hence we can use the dipole moment calculation by the valence bond method to predict the geometrical structures of transition metal complexes in inert solvent solutions.

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