Calculation of the Magnetic Moments and the Dipolar Shifts for d^1 and d^2 Complexes in a Strong Ligand Field of Trigonal Symmetry

Sangwoon Ahn† and Hyuk Choon Suh

Department of Chemistry, Jeonbug National University, Jeonju 520, Korea.

Jeong Soo Ko

Department of Chemistry, Mogpo National College, Mogpo 580, Korea (*Received January 13, 1982*)

A method to calculate the magnetic moments for d^1 and d^2 complexes in a strong crystal field of trigonal symmetry has been developed in this work choosing the trigonal axis (III) as the quantization axis. The calculated magnetic moments using this method for d^1 and d^2 complexes in a strong trigonal ligand field fall in the range of the experimental values. The dipolar shifts for d^1 and d^2 complexes in a strong trigonal ligand field are also calculated using the calculated magnetic susceptibility components. The calculated values of the dipolar shifts also fall in the reasonable range.

Introluction

A great deal of interest has been focussed on the use of the magnetic properties of d-transition metal complexes as a means of determining stereochemistry and ground state electronic properties.[1] It is frequently found in the first series transition metal complexes that the magnetic moments are close to the spin-only magnetic moments. The experimental values of the magnetic moments do not however agree precisely with the magnetic moments calculated from the spin-only formula. Comparing the experimental magnetic moments with the spin-only values for given transition metal complexes, the stereochemistry and ground state electronic properties of those complexes have been inferred[2].

The magnetic moments for d^1 and d^2 transition metal complexes in a strong crystal field of tetragonal symmetry were investigated when the four fold axis was chosen as a quantization axis[3a]. The calculated values of the magnetic moments were reported to be in good agreement with the experimental values if the suitable distortion parameters and the spin-orbit coupling constant are chosen.

The pseudo contact NMR shift was first given by McConnell and Robertson[3b] in the form

$$\frac{\Delta H}{H}=-\mu_B{}^2\frac{S(S+1)}{3kT}\frac{(3\cos^2\theta-1)}{R^3}F(g) \tag{1a}$$

where R is the distance between the paramagnetic center and the NMR nucleus and θ is the angle between the principal axis of the complex and the vector between the paramagnetic center and the NMR nucleus. $F(g)$ is a function of the principal g-values. Kurland and McGravey[3c] extended this and showed that the pseudo contact shift may be expressed in terms of the magnetic susceptibility components, χ_{aa},

$$\frac{\Delta H}{H}=-\frac{1}{3R^3}\left[\left\{\chi_{zz}-\frac{1}{2}(\chi_{xx}+\chi_{yy})\right\}+\frac{3}{2}(\chi_{xx}-\chi_{yy})\sin^2\theta\cos2\phi\right] \tag{1b}$$

The purpose of the present work is first to investigate the magnetic moments for d^1 and d^2 transition metal complexes in a strong crystal field of octahedral and trigonal symmetries when the three fold axis is chosen as a quantization axis, and secondly to examine the dipolar NMR shift for d^1 and d^2 complexes, using the theoretically derived formulas to calculate the magnetic susceptibility.

2. The Magnetic Moments for d^1 Transition Metal Complexes of a Trigonal Symmtry

If the three fold axis is chosen as a quantization axis, the axial wave functions with t_2 symmetry are,[4]

$$\begin{aligned}\phi_0&=|3d_{z^2}\rangle\\ \phi_1&=\sqrt{\tfrac{2}{3}}|2\rangle-\sqrt{\tfrac{1}{3}}|-1\rangle\\ \phi_2&=\sqrt{\tfrac{2}{3}}|-2\rangle+\sqrt{\tfrac{1}{3}}|1\rangle\end{aligned} \tag{1c}$$

For a d^n system in a strong crystal field of trigonal symmetry, the approximate Hamiltonian representing the various interaction is

$$\mathscr{H}=\sum_{i=1}^{n}\left\{-\frac{\hbar^2}{2m}V_i{}^2-\frac{Ze^2}{r_i}\right\}+\sum_{>j}\frac{e^2}{r_{ij}}+V(\boldsymbol{r}_i)+\mathscr{H}' \tag{2}$$

where

$$\mathscr{H}'=\sum_{i=1}^{n}\zeta\boldsymbol{l}_i\cdot s_i+\sum_{i=1}^{n}\delta(\boldsymbol{l}^2{}_{iz}-2)+\sum_{i=1}^{n}\beta(K\boldsymbol{l}_i+2\boldsymbol{s}_i) \tag{3}$$

The spin-orbit coupling and distortion interaction are treated as a perturbation acting on the crystal field potential. The spin-orbit coupling and distortion interaction matrices for the axial wave functions of a d^1 system are,

	$-\|\phi_2^-\rangle$	$\|\phi_0^+\rangle$	$\|\phi_1^-\rangle$
$-\langle\phi_2^-\|$	$\zeta/2+\delta$	$-\zeta/\sqrt{2}$	0
$\langle\phi_0^+\|$	$-\zeta/\sqrt{2}$	-2δ	0
$\langle\phi_1^-\|$	0	0	$-\zeta/2+\delta$

(4)

	$\|\phi_1^+\rangle$	$\|\phi_0^-\rangle$	$\|\phi_2^+\rangle$
$\langle\phi_1^+\|$	$\zeta/2+\delta$	$-\zeta/\sqrt{2}$	0
$\langle\phi_0^-\|$	$-\zeta/\sqrt{2}$	-2δ	0
$\langle\phi_2^+\|$	0	0	$-\zeta/2+\delta$

(5)

Solving the above matrices, the $^2T_2$ ground state is separated into three Kramer's doublets. The magnetic field interaction is then added and treated as a perturbation to yield six eigenfunctions $|\phi_n\rangle$ with the corresponding eigenvalues E_n.

$$E_n=e_i+\langle\phi_i|\beta(Kl+2s)H|\phi_i\rangle+\sum_{i\neq j}\frac{\langle\phi_i|\beta(Kl+2s)H|\phi_j\rangle\langle\phi_j|\beta(Kl+2s)H|\phi_i\rangle}{e_i-e_j} \quad (5)$$

$$\phi_n=|\phi_i\rangle+\sum_{i\neq j}\frac{\langle\phi_i|\beta(Kl+2s)H|\phi_j\rangle}{e_i-e_j}|\phi_j\rangle \quad (6)$$

where ϕ_i and e_i are the eigenfunction and eigenvalue for the spin-orbit coupling and distortion interaction ($i=j=1\sim3$). Using the eigenvalues E_n of the magnetic field interactions, we derive general formulas to calculate the magnetic moments for d^1 transition metal complexes of trigonal symmetry. The parallel and perpendicular components of the magnetic moments for this system are

$$\mu_{\parallel}^2=\left\{\frac{\mu_{\parallel}^2(1)\exp(-e_1/kT)+\mu_{\parallel}^2(2)\exp(-e_2/kT)+\mu_{\parallel}^2(3)\exp(-e_3/kT)}{\exp(-e_1/kT)+\exp(-e_2/kT)+\exp(-e_3/kT)}\right\} \quad (7)$$

where

$$\mu_2^{\parallel}(1)=\left\{3\left[\frac{K}{2}-\left(\frac{K}{2}\right)\left(\frac{1}{2}+3x\right)X^{-1}\right]^2+\frac{3(K+2)^2}{X^3}\frac{kT}{\zeta}\right\}$$

$$\mu_2^{\parallel}(2)=\left\{3\left[\frac{K}{2}+\left(\frac{K}{2}\right)\left(\frac{1}{2}+3x\right)X^{-1}\right]^2-\frac{3(K+3)^2}{X^3}\frac{kT}{\zeta}\right\}$$

$$\mu_2^{\parallel}(3)=3(K-1)^2$$

and

$$x=\delta/\zeta,\ X^2=\left(\frac{9}{4}+3x+9x^2\right),\ \zeta^{(5)}=(2K-1)\zeta_d+(1-K)\zeta_p$$

$$e_1=\frac{\zeta}{4}-\frac{\delta}{2}-\frac{A}{2},\ e_2=\frac{\zeta}{4}-\frac{\delta}{2}+\frac{A}{2}\ \text{ and }\ e_3=-\left(\frac{1}{2}\zeta-\delta\right)$$

$$\mu_{\perp}^2=\left\{\frac{\mu_{\perp}^2(1)\exp(-e_1/kT)+\mu_{\perp}^2(2)\exp(-e_2/kT)+\mu_{\perp}^2(3)\ \exp(-e_3/kT)}{\exp(-e_1/kT)+\exp(-e_2|kT)+\exp(-e_3/kT)}\right\} \quad (8)$$

where

$$\mu_{\perp}^2(1)=\left\{3\left[KX^{-1}-\frac{1}{2}-\frac{1}{2}\left(\frac{1}{2}+3x\right)X^{-1}\right]^2+\frac{3\left[1+K\left(\frac{1}{2}+3x\right)\right]^2}{X^3}\frac{kT}{\zeta}-\frac{6\left\{\left(\frac{K^2}{2}+1\right)+\left(\frac{K^2}{2}-1\right)\left(\frac{1}{2}+3x\right)X^{-1}-2KX^{-1}\right\}}{\left(\frac{3}{2}-3x-X\right)}\cdot\frac{kT}{\zeta}\right\}$$

$$\mu_{\perp}^2(2)=\left\{3\left[KX^{-1}+\frac{1}{2}-\frac{1}{2}\left(\frac{1}{2}+3x\right)X^{-1}\right]^2-\frac{3\left[1+K\left(\frac{1}{2}+3x\right)\right]^2}{X^3}\frac{kT}{\zeta}-\frac{6\left\{\left(\frac{K^2}{2}+1\right)-\left(\frac{K^2}{2}-1\right)\left(\frac{1}{2}+3x\right)X^{-1}+2KX^{-1}\right\}}{\left(\frac{3}{2}-3x+X\right)}\cdot\frac{kT}{\zeta}\right\}$$

$$\mu_{\perp}^2(3)=\left\{\frac{6\left[\left(\frac{K^2}{2}+1\right)+\left(\frac{K^2}{2}-1\right)\left(\frac{1}{2}+3x\right)X^{-1}-2KX^{-1}\right]}{\left(\frac{3}{2}-3x-X\right)}\cdot\frac{kT}{\zeta}+\frac{6\left[\left(\frac{K^2}{2}+1\right)-\left(\frac{K^2}{2}-1\right)\left(\frac{1}{2}+3x\right)X^{-1}+2KX^{-1}\right]}{\left(\frac{3}{2}-3x+X\right)}\cdot\frac{kT}{\zeta}\right\}$$

The calculated magnetic moments using equation (8) are listed in Table 1.

3. The Magnetic Moments for d^2 Transition Metzal Complexes of a Trigonal Symmetry

The ground state for a d^2 system in a strong crystal field of octahedral symmetry is $^3T_1$, which is originated from both (t_2^2) and (t_2^1) (e^1) electron configurations. The mixing coefficients a and b can be obtained by solving the following ligand field-electron repulsion interaction matrix[6].

	$\|\Psi(t_2^2)\rangle$	$\|\Psi(e^1,\ t_2^1)\rangle$
$\langle\Psi(t_2^2)\|$	$-8D_q-5_B$	6B
$\langle\Psi(e^1,\ t_2^1)\|$	6B	$2D_q+4B$

The ground state wave function is

$$\Phi(^3T_1)=a\Psi(t_2^2)-b\Psi(e^1,t_2^1) \quad (8)$$

where

$$a^2=\frac{1}{2}+\frac{1}{2}(10+9x)/A$$

$$b^2=\frac{1}{2}-\frac{1}{2}(10+9x)/A$$

and $ab=-6B/A$

where $A^2=(100+180x+150x^2)$ and $x=B/D_q$.

It was reported that, for VCl_33EtCN[7], $D_q=1608$ and $B=523\ cm^{-1}$. For these values of parameters, the calculated values of mixing coefficients are $a=0.9982$ and $b=0.0600$.

We see that the contribution of $|(e^1,t_2^1)\rangle$ to the ground state ($^3T_1$) is negligbly small. We thus neglect the contribution of $|(e^1,\ t_2^1)\rangle$ to the magnetic moments for d^2 complexes in a strong crystal field of a trigonal symmetry. When the

TABLE 1: The Calculated Magnetic Moments for a d^1 Complexes in a Strong Ligand field of Trigonal Symmetry

(a) Dependence of the Calculated Magnetic Moments on ζ_d
T=300 K δ=500 cm^{-1} ζ_p=110.cm^{-1} and K=0.8

ζ_d(cm^{-1})	150	170	190	210	230	250
$\mu_{\parallel}$	1.728	1.727	1.726	1.724	1.723	1.721
$\mu_{\perp}$	1.805	1.795	1.784	1.774	1.763	1.752
μ	1.780	1.772	1.765	1.757	1.750	1.742

The calculated magnetic moments for a d^1 complex in a strong tetragonal ligand field=1.78~1.86.

(b) Dependence of the Calculated Magnetic Moments on Temperature
ζ_d=230 cm^{-1}, ζ_p=110 cm^{-1}, δ=500 cm^{-1} and K=0.8

T(K)	200	240	280	300	340	380
$\mu_{\parallel}$	1.722	1.723	1.723	1.723	1.722	1.720
$\mu_{\perp}$	1.718	1.736	1.754	1.763	1.780	1.797
μ	1.719	1.732	1.744	1.750	1.761	1.772

The calculated magnetic moments for a d^1 complex in a strong tetragonal ligand field=1.71~1.84.

(c) Dependence of the Calculated Magnetic Moments on δ
T=300 K, ζ_d=230 cm^{-1}, ζ_p=110 cm^{-1} and K=0.8

δ(cm^{-1})	250	300	350	400	450	500
$\mu_{\parallel}$	1.679	1.699	1.710	1.716	1.720	1.723
$\mu_{\perp}$	1.786	1.780	1.775	1.770	1.766	1.763
μ	1.751	1.753	1.753	1.752	1.751	1.750

The calculated magnetic moments for a d^1 complex in a strong tetragonal ligand field=1.80~1.82.
Experimental values 1.68~1.84

three fold axis is taken as the quantization axis, the two electron wave functions for the ground ($^3T_1$) state are,[8]

$$\chi_1=\frac{1}{\sqrt{2}}|\phi_0^+\phi_2^+|$$

$$\chi_2=\frac{1}{\sqrt{2}}|\phi_0^-\phi_1^-|$$

$$\chi_3=\frac{1}{\sqrt{2}}|\phi_0^+\phi_1^+|$$

$$\chi_4=\frac{1}{\sqrt{2}}|\phi_0^-\phi_2^-|$$

$$\chi_5=\frac{1}{2}\{|\phi_1^-\phi_2^+|+|\phi_1^+\phi_2^-|\}$$

$$\chi_6=\frac{1}{\sqrt{2}}|\phi_1^+\phi_2^+|$$

$$\chi_7=\frac{1}{2}\{|\phi_0^+\phi_2^-|+|\phi_0^-\phi_2^+|\}$$

$$\chi_8=\frac{1}{2}\{|\phi_0^+\phi_1^-|+|\phi_0^-\phi_1^+|\}$$

$$\chi_9=\frac{1}{\sqrt{2}}|\phi_1^-\phi_2^-|$$

As described in the previous section, the spin-orbit coupling and distortion interactions are treated as a perturbation acting on the crystal field potential and electron repulsion. The spin-orbit coupling and distortion interaction matrix for the axial wave functions of a d^2 system is represented in the following.

	$\vert\chi_1\rangle$	$\vert\chi_2\rangle$	$\vert\chi_5\rangle$	$\vert\chi_6\rangle$	$\vert\chi_8\rangle$	$\vert\chi_9\rangle$	$\vert\chi_7\rangle$	$\vert\chi_4\rangle$	$\vert\chi_3\rangle$
$\langle\chi_1\vert$	$\frac{\zeta}{2}-\delta$	0	$\zeta/2$						
$\langle\chi_2\vert$	0	$\frac{\zeta}{2}-\delta$	$\zeta/2$						
$\langle\chi_5\vert$	$\zeta/2$	$\zeta/2$	2δ						
$\langle\chi_6\vert$				2δ	$\zeta/2$				
$\langle\chi_8\vert$				$\zeta/2$	$-\delta$				
$\langle\chi_9\vert$						2δ	$\zeta/2$		
$\langle\chi_7\vert$						$\zeta/2$	$-\delta$		
$\langle\chi_4\vert$								$-\zeta/2-\delta$	
$\langle\chi_3\vert$									$-\zeta/2-\delta$

(10a)

Solving the spin-orbit coupling and distortion interaction matrix, the eigenvalues and eigenfunctions for the spin-orbit coupling and distortion matrix for the ground state of a d^2 system are obtained,

$$e_1=\frac{\zeta}{4}+\frac{\delta}{2}-\frac{A}{2}, \qquad \phi_1=a_1(\chi_1+\chi_2)-c_1\chi_5$$

$$e_2=\frac{\zeta}{4}+\frac{\delta}{2}+\frac{A}{2}, \qquad \phi_2=a_2(\chi_1+\chi_2)+c_2\chi_5$$

$$e_3=\frac{\zeta}{2}-\delta, \qquad \phi_3=\frac{1}{\sqrt{2}}(\chi_1-\chi_2)$$

$$e_4=\frac{\delta}{2}-\frac{B}{2}, \qquad \phi_4=-a_3\chi_6+b_3\chi_8$$

$$\phi_5=-a_3\chi_9+b_3\chi_7$$

$$e_5=\frac{\delta}{2}+\frac{B}{2}, \qquad \phi_6=b_3\chi_6+a_3\chi_8$$

$$\phi_7=b_3\chi_9+a_3\chi_7$$

$$e_6=-\frac{\zeta}{2}+\delta, \qquad \phi_8=|\chi_4\rangle$$

$$\phi_9=|\chi_3\rangle \tag{11}$$

where $A^2=\left(\frac{9}{4}-3x+9x^2\right)\zeta^2$

$B^2=(1+9x^2)\zeta^2$

where $x=\delta/\zeta$

The magnetic field interaction is then added and treated as a perturbation to yield nine eigenfunctions $|\Psi_n\rangle$ with the corresponding eigenvalues ε_n

$$\varepsilon_n=e_i+\sum_{i=1}^{2}\langle\phi_i\beta(Kl+2s)H\phi_i\rangle$$

$$+\sum_{i=1}^{2}\sum_{i\neq j}\frac{<\phi_i|\beta(Kl+2s)H|\phi_j><\phi_j|\beta(Kl+2s)H|\phi_i>}{e_i-e_j} \quad (12)$$

$$\Psi_n=|\phi_i>+\sum_{i=1}^{2}\sum_{i\neq j}\frac{<\phi_i|\beta(Kl+2s)H|\phi_j>}{e_i-e_j}|\phi_j> \quad (13)$$

Using the eigenvalues ε_n of the magnetic field interactions, the general formulas to calculate the magnetic moments for d^2 transition metal complexes with a trigonal symmetry are derived. The parallel and perpendicular components of the magnetic moments for d^2 transition metal complexes in a strong ligand field of trigonal symmetry are given by

$$\mu^2=\left[\frac{\left\{\begin{matrix}+\mu_{\parallel}^2(4)\exp(-e_4/kT)+\mu_{\parallel}^2(5)\exp(-e_5/kT)+\mu_{\parallel}^2(6)\exp(-e_6/kT)\\ \mu_{\parallel}^2(1)\exp(-e_1/kT)+\mu_{\parallel}^2(2)\exp(-e_2/kT)+\mu_{\parallel}^2(3)\exp(-e_3/kT)\end{matrix}\right\}}{\left\{\begin{matrix}\exp(-e_1/kT)+\exp(-e_2/kT)+\exp(-e_3/kT)+2\exp(-e_4/kT)\\ +2\exp(-e_5/kT)+2\exp(-e_6/kT)\end{matrix}\right\}}\right] \quad (14)$$

where

$$\mu_{\parallel}^2(1)=\frac{24(K+2)^2}{\left(\frac{1}{2}-3x+Y\right)M^2}\ \frac{kT}{\zeta}$$

$$\mu_{\parallel}^2(2)=\frac{24(K+2)^2}{\left(\frac{1}{2}-3x-Y\right)G^2}\ \frac{kT}{\zeta}$$

$$\mu_{\parallel}^2(3)=-\left\{\frac{24(K+2)^2}{\left(\frac{1}{2}-3x+Y\right)M^2}+\frac{24(K+2)}{\left(\frac{1}{2}-3x-Y\right)G^2}\right\}\frac{kT}{\zeta}$$

$$\mu_{\parallel}^2(4)=\left\{6\left[\left(1-\frac{K}{2}\right)-\left(1+\frac{K}{2}\right)3xJ^{-1}\right]^2-\frac{3(K+2)^2}{J^3}\ \frac{kT}{\zeta}\right.$$

$$\mu_{\parallel}^2(5)=\left\{6\left[\left(1-\frac{K}{2}\right)+\left(1+\frac{K}{2}\right)3xJ^{-1}\right]^2+\frac{3(K+2)^2}{J^3}\ \frac{kT}{\zeta}\right\}$$

$$\mu_{\parallel}^2(6)=6(K-2)^2$$

$$\mu_{\perp}^2=\left[\frac{\left\{\begin{matrix}+\mu_{\perp}^2(4)\exp(-e_4/kT)+\mu_{\perp}^2(5)\exp(-e_5/kT)+\mu_{\perp}^2(6)\exp(-e_6/kT)\\ \mu_{\perp}^2(1)\exp(-e_1/kT)+\mu_{\perp}^2(2)\exp(-e_2/kT)+\mu_{\perp}^2(3)\exp(-e_3/kT)\end{matrix}\right\}}{\{\exp(-e_1/kT)+\exp(-e_2/kT)+\exp(-e_3/kT)+2\exp(-e_4/kT)+2\exp(-e_5/kT)+2\exp(-e_6/kT)\}}\right] \quad (15)$$

where

$$\mu_{\perp}^2(1)=12\left\{-\frac{(1+L^2)\left(2+\frac{K^2}{2}-2KJ^{-1}\right)+(1-L^2)\left(2-\frac{K^2}{2}\right)3xJ^{-1}-2L\left[\left(2+\frac{K^2}{2}\right)J^{-1}-2K\right]}{\left(\frac{1}{2}-Y+J\right)M^2}\right.$$
$$\left.-\frac{(1+L^2)\left(2+\frac{K^2}{2}+2KJ^{-1}\right)-(1-L^2)\left(2-\frac{K^2}{2}\right)3xJ^{-1}+2L\left[\left(2+\frac{K^2}{2}\right)J^{-1}+2K\right]}{\left(\frac{1}{2}-Y-J\right)M^2}\right\}\frac{kT}{\zeta}$$

$$\mu_{\perp}^2(2)=12\left\{-\frac{(1+F^2)\left(2+\frac{K^2}{2}-2KJ^{-1}\right)+(1-F^2)\left(2-\frac{K^2}{2}\right)3xJ^{-1}+2F\left[\left(2+\frac{K^2}{2}\right)J^{-1}-2K\right]}{\left(\frac{1}{2}+Y+J\right)G^2}\right.$$
$$\left.-\frac{(1+F^2)\left(2+\frac{K^2}{2}+2KJ^{-1}\right)-(1-F^2)\left(2-\frac{K^2}{2}\right)3xJ^{-1}+2F\left[\left(2+\frac{K^2}{2}\right)J^{-1}-2K\right]}{\left(\frac{1}{2}+Y-J\right)G^2}\right\}\frac{kT}{\zeta}$$

$$\mu_{\perp}^2(3)=3\left\{-\frac{\left[\left(2+\frac{K^2}{2}\right)+\left(2-\frac{K^2}{2}\right)3xJ^{-1}+2KJ^{-1}\right]}{(1-3x+J)}-\frac{\left[\left(2+\frac{K^2}{2}\right)-\left(2-\frac{K^2}{2}\right)3xJ^{-1}-2KJ^{-1}\right]}{(1-3x-J)}\right\}\frac{kT}{\zeta}$$

$$\mu_{\perp}^2(4)=12\left\{\frac{(1+L^2)\left(2+\frac{K^2}{2}-2KJ^{-1}\right)+(1-L^2)\left(2-\frac{K^2}{2}\right)3xJ^{-1}-2L\left[\left(2+\frac{K^2}{2}\right)J^{-1}-2K\right]}{\left(\frac{1}{2}-Y+J\right)M^2}\right.$$
$$+\frac{(1+F^2)\left(2+\frac{K^2}{2}-2KJ^{-1}\right)+(1-F^2)\left(2-\frac{K^2}{2}\right)3xJ^{-1}+2F\left[\left(2+\frac{K^2}{2}\right)J^{-1}-2K\right]}{\left(\frac{1}{2}+Y+J\right)G^2}$$
$$+\frac{\left[\left(2+\frac{K^2}{2}\right)+\left(2-\frac{K^2}{2}\right)3xJ^{-1}+2KJ^{-1}\right]}{4(1-3x+J)}-\frac{\left[\left(2+\frac{K^2}{2}\right)+\left(2-\frac{K^2}{2}\right)3xJ^{-1}-2KJ^{-1}\right]}{(1+3x-J)}\cdot\frac{kT}{\zeta}$$

$$\mu_{\perp}^2(5)=21\left\{\frac{(1+L^2)\left(2+\frac{K^2}{2}+2KJ^{-1}\right)-(1-L^2)\left(2-\frac{K^2}{2}\right)3xJ^{-1}+2L\left[\left(2+\frac{K^2}{2}\right)J^{-1}+2K\right]}{\left(\frac{1}{2}-Y-J\right)M^2}\right.$$

$$+\frac{(1+F^2)\left(2+\frac{K^2}{2}+2KJ^{-1}\right)-(1-F^2)\left(2-\frac{K^2}{2}\right)3xJ^{-1}+2F\left[\left(2+\frac{K^2}{2}J^{-1}-2K\right]}{\left(\frac{1}{2}+Y-J\right)G^2}$$

$$+\frac{\left[\left(2+\frac{K^2}{2}\right)-\left(2-\frac{K^2}{2}\right)3xJ^{-1}-2KJ^{-1}\right]}{4(1-3x-J)}-\frac{\left[\left(2+\frac{K^2}{2}\right)-\left(2-\frac{K^2}{2}\right)3xJ^{-1}+2KJ^{-1}\right]}{(1+3x+J)}\Bigg\}\frac{kT}{\zeta}$$

$$\mu_\perp^2(6)=12\left\{\frac{\left[\left(2+\frac{K^2}{2}\right)+\left(2-\frac{K^2}{2}\right)3xJ^{-1}-2KJ^{-1}\right]}{(1+3x-J)}+\frac{\left[\left(2+\frac{K^2}{2}\right)-\left(2-\frac{K^2}{2}\right)3xJ^{-1}+2KJ^{-1}\right]}{(1+3x+J)}\right\}\frac{kT}{\zeta}$$

where

$$e_1=\frac{1}{2}\left(\frac{1}{2}+x-Y\right)\zeta$$
$$e_2=\frac{1}{2}\left(\frac{1}{2}+x+Y\right)\zeta$$
$$e_3=\left(\frac{1}{2}-x\right)\zeta$$
$$e_4=\frac{1}{2}(x-J)\zeta$$
$$e_5=\frac{1}{2}(x+J)\zeta$$
$$e_6=-\left(\frac{1}{2}+x\right)\zeta$$
$$J^2=(1+9x^2)$$
$$Y^2=\left(\frac{9}{4}-3x+9x^2\right)$$
$$L=\left(\frac{1}{2}-3x+Y\right)$$
$$M^2=(L^2+2)$$
$$F=\left(\frac{1}{2}-3x-Y\right)$$
$$G^2=(F^2+2)$$

The average magnetic moments for trigonally distorted d^2 transition metal complexes can be calculated from the following equation.

$$\mu=\{\mu_\parallel^2+2\mu_\perp^2\}^{\frac{1}{2}} \tag{16}$$

The calculated magnetic moments are listed in Table 2.

If d^2 transition metal complexes are in a strong ligand field of octahedral symmetry, the distortion parameter, δ, in equation (3) is zero. The expressions for the parallel and perpendicular components of the magnetic moments for d^2 transition metal complexes are found to be reduced to the form,

$$\mu^2=\left\{\frac{\mu^2(1)\exp\left(\frac{\zeta}{2kT}\right)+\mu^2(2)\exp\left(-\frac{\zeta}{2kT}\right)+\mu^2(3)\exp\left(-\frac{\zeta}{kT}\right)}{5\exp\left(\frac{\zeta}{2kT}\right)+3\exp\left(-\frac{\zeta}{2kT}\right)+\exp\left(-\frac{\zeta}{kT}\right)}\right\} \tag{17}$$

where

$$\mu^2(1)=\left\{\frac{15(K-2)^2}{2}+5(K+2)^2\right\}$$
$$\mu^2(2)=\left\{\frac{3(K-2)^2}{2}+3(K+2)^2\frac{kT}{\zeta}\right\}$$
$$\mu^2(3)=-8(K+2)^2$$

It is found that when the four fold axis is taken as a quantization axis the exactly same form as equation (17) can be derived for d^2 transition metal complexes in a strong ligand field of octahedral symmetry.[9]

4. Calculation of the Dipolar Shift for d^1 and d^2 Complexes

The paramagnetic susceptibility, $\chi_\parallel$ of the system when the magnetic field is parallel to the z axis may be calculated from the parallel component of the magentic moment as

$$\chi_\parallel=\frac{N\beta^2}{3kT}\mu_\parallel^2 \tag{18}$$

where $\mu_\parallel$ is the parallel component of the magnetic moment. The magnetic susceptibility when the magentic field is perpendicular to the z axis may also calculated from the perpendicular component of the magentic moment as

$$\chi_\perp=\frac{N\beta^2}{3kT}\mu_\perp^2 \tag{19}$$

TABLE 2: The Calculated Magnetic Moments for d^2 Complexes in a Strong Ligand field of Trigonal Symmetry

(a) Dependence of the Calculated Magnetic Moments on ζ_d
T=300 K, δ=500 cm^{-1}, ζ_p=110 cm^{-1} and K=0.8

ζ_d(cm^{-1})	210	230	250	270	290	310	330
$\mu_\parallel$	2.786	2.748	2.710	2.674	2.639	2.604	2.571
$\mu_\perp$	2.674	2.669	2.664	2.657	2.650	2.643	2.634
μ	2.712	2.696	2.679	2.663	2.646	2.630	2.613

The calcuated magnetic moments for a d^2 complex in a strong tetragonal ligand field=2.93 (ζ_d=210 cm^{-1}).

(b) Dependence of the Calculated Magnetic Moments on Temperature
δ=300 cm^{-1}, ζ_d=310 cm^{-1}, ζ_p=110 cm^{-1} and K=0.8

T(K)	200	240	280	300	340	380	400
$\mu_\parallel$	2.604	2.683	2.742	2.767	2.808	2.841	2.854
$\mu_\perp$	2.643	2.664	2.679	2.685	2.696	2.706	2.701
μ	2.630	2.670	2.700	2.713	2.734	2.752	2.759

The calculated magnetic moments for a d^2 complex in a strong tetagonal ligand field=2.89~2.97.

(c) Dependence of the Calculated Magnetic Moments on δ
ζ_d=310 cm^{-1}, ζ_p=110 cm^{-1}, T=300 and K=0.8

δ(cm^{-1})	400	450	500	550	600	650	700
$\mu_\parallel$	2.764	2.765	2.757	2.768	2.768	2.769	2.769
$\mu_\perp$	2.696	2.290	2.685	2.681	2.678	2.675	2.673
μ	2.718	2.715	2.713	2.710	2.709	2.707	2.706

The calcuated magnetc moments for a d^2 complex in a strong tetragonal ligand field=2.93~2.96 (δ=400~500 cm^{-1}). Experimental values=2.63~2.82.

TABLE 3: The Calculated dipolar Shift for a d^1 Complex in a Strong Ligand Field of Trigonal Symmetry
(T=300 K, ζ_d=154, and δ=500 cm^{-1})

R(nm)	$\Delta H/H(z)$	$\Delta H/H(x)$
0.05	739.56	−369.78
0.09	126.811	− 63.405
0.15	27.391	− 13.696
0.19	13.48	− 6.739
0.25	5.916	− 2.958
0.29	3.790	− 1.195
0.35	2.156	− 1.078
0.39	1.558	− 0.779
0.45	1.014	− 0.507
0.49	0.786	− 0.393

TABLE 4: The Calculated Dipolar Shift for a d^2 Complex in a Strong Ligand Field of Trigonal Symmetry
(T=300 K, ζ_d=320, and δ=500 cm^{-1})

R(nm)	$\Delta H/H(z)$	$\Delta H/H(x)$
0.05	−14839.7	7419.87
0.09	−2544.54	1272.27
0.15	− 549.619	274.810
0.19	− 270.443	135.221
0.25	− 118.718	59.359
0.29	− 76.058	38.028
0.35	− 43.265	21.632
0.39	− 31.271	15.636
0.45	− 20.356	10.178
0.49	− 13.984	7.883

where $\mu_\perp$ is the perpendicular component of the magnetic moment.

Substituting the calculated values of the magnetic susceptibility using equation (18) and (19) into equation (1b), we can evaluate the dipolar shift for d^1 and d^2 complexes in a strong crystal field of trigonal symmetry and the calculated dipolar shifts are listed in Table 3.

5. Results and Discussion

As shown in Table 1, the calculated magnetic moments for d^1 complexes fall in the range of the experimental values[11]. The calculated magnetic moments for a d^1 complex in a strong trigonal ligand field decrease slightly as the values of the spin–orbit coupling constant are increased. The calculated magnetic moments for a d^1 complex however increase slightly as the temperature is increased.

The calculated magnetic moments for a d^1 complex in a strong trigonal ligand field are almost independent of the distortion parameter, δ as shown in Table 1. Such a trend may be also observed in a strong ligand field of trigonal symmetry as shown in Table 2. The calculated magnetic moments for d^2 complexes in s trong trigonal ligand field fall in the range of the experimental values.[12]

As shown in Table 1 and 2, the caculated magentic moments for d^1 and d^2 complexes[9] in a strong tetragonal ligand field are slightly higher than those for d^1 and d^2 complexes[9] in strong trigonal ligand field.

The calculated dipolar shift for d^1 and d^2 complexes in a strong crystal field of trigonal šymmetry decrease as the distance from the NMR nucleus to the paramagnetic center is increased as expected from the previous works[13]. The calculated values of the dipolar shifts for a d^1 complex in a strong trigonal field are in reasonable agreement with the previous reports[14]. No theoretical value of the dipolar shift for a d^2 complex has been reported so far.

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