

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

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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.

Introduction

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

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

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 McGraevy^{3c} extended this and showed that the pseudo contact shift may be expressed in terms of the magnetic susceptibility components, χ_{aa} ,

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

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 Symmetry

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

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

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

$$\mathcal{H} = \sum_{i=1}^n \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} \right\} + \sum_{ij} \frac{e^2}{r_{ij}} + V(r_i) + \mathcal{H}' \quad (2)$$

where

$$\mathcal{H}' = \sum_{i=1}^n \zeta \mathbf{l}_i \cdot \mathbf{s}_i + \sum_{i=1}^n \delta (\mathbf{l}_i^2 - 2) + \sum_{i=1}^n \beta (K \mathbf{l}_i + 2s_i) \quad (3)$$

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$
$-<\phi_2 $	$\zeta/2 + \delta$	$-\zeta/\sqrt{2}$	0
$<\phi_0 $	$-\zeta/\sqrt{2}$	-2δ	0
$<\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 .

$$E_n = e_i + \frac{\langle\phi_i|\beta(KI+2s)H|\phi_i\rangle}{1} + \sum_{i \neq j} \frac{\langle\phi_i|\beta(KI+2s)H|\phi_j\rangle\langle\phi_j|\beta(KI+2s)H|\phi_i\rangle}{e_i - e_j} \quad (5)$$

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

where ϕ_i and e_i are the eigenfunction and eigenvalue for the spin-orbit coupling and distortion interaction ($i=j=1\sim 3$). 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

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

and

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

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

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

where

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

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

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

3. The Magnetic Moments for d^2 Transition Metal 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_{2g}^2) and $(t_{2g}^1 e_g^1)$ (e^1) electron configurations. The mixing coefficients a and b can be obtained by solving the following ligand field-electron repulsion interaction matrix⁶.

	$ \Psi(t_{2g}^2)\rangle$	$ \Psi(e^1, t_{2g}^1)\rangle$
$\langle\Psi(t_{2g}^2) $	$-8D_q - 5B$	$6B$
$\langle\Psi(e^1, t_{2g}^1) $	$6B$	$2D_q + 4B$

The ground state wave function is

$$\Phi({}^3T_1) = a\Psi(t_{2g}^2) - b\Psi(e^1, t_{2g}^1) \quad (8)$$

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 $VCl_3 \cdot 3EtCN^7$, $D_q = 1608$ and $B = 523 \text{ cm}^{-1}$. 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 $|(e^1, t_{2g}^1)\rangle$ to the ground state (3T_1) is negligibly small. We thus neglect the contribution of $|(e^1, t_{2g}^1)\rangle$ 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

$$T=300\text{ K } \delta=500\text{ cm}^{-1} \quad \zeta_p=110\text{ cm}^{-1} \text{ and } K=0.8$$

$\zeta_d(\text{cm}^{-1})$	150	170	190	210	230	250
$\mu_{ }$	1.728	1.727	1.726	1.724	1.723	1.721
μ_{\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

$$\zeta_d=230\text{ cm}^{-1}, \quad \zeta_p=110\text{ cm}^{-1}, \quad \delta=500\text{ cm}^{-1} \text{ and } K=0.8$$

T(K)	200	240	280	300	340	380
$\mu_{ }$	1.722	1.723	1.723	1.723	1.722	1.720
μ_{\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

$$T=300\text{ K}, \quad \zeta_d=230\text{ cm}^{-1}, \quad \zeta_p=110\text{ cm}^{-1} \text{ and } K=0.8$$

$\delta(\text{cm}^{-1})$	250	300	350	400	450	500
$\mu_{ }$	1.679	1.699	1.710	1.716	1.720	1.723
μ_{\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

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

(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,

$$\begin{aligned} e_1 &= \frac{\zeta}{4} + \frac{\delta}{2} - \frac{A}{2}, & \phi_1 &= a_1(\chi_1 + \chi_2) - c_1\chi_5 \\ e_2 &= \frac{\zeta}{4} + \frac{\delta}{2} + \frac{A}{2}, & \phi_2 &= a_2(\chi_1 + \chi_2) + c_2\chi_5 \\ e_3 &= \frac{\zeta}{2} - \delta, & \phi_3 &= \frac{1}{\sqrt{2}}(\chi_1 - \chi_2) \\ e_4 &= \frac{\delta}{2} - \frac{B}{2}, & \phi_4 &= -a_3\chi_6 + b_3\chi_8 \\ & & \phi_5 &= -a_3\chi_9 + b_3\chi_7 \\ e_5 &= \frac{\delta}{2} + \frac{B}{2}, & \phi_6 &= b_3\chi_6 + a_3\chi_8 \end{aligned}$$

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

$$\begin{aligned} \chi_1 &= \frac{1}{\sqrt{2}}|\phi_0^+ \phi_2^+| \\ \chi_2 &= \frac{1}{\sqrt{2}}|\phi_0^- \phi_1^-| \\ \chi_3 &= \frac{1}{\sqrt{2}}|\phi_0^+ \phi_1^+| \\ \chi_4 &= \frac{1}{\sqrt{2}}|\phi_0^- \phi_2^-| \\ \chi_5 &= \frac{1}{2}\{|\phi_1^- \phi_2^+| + |\phi_1^+ \phi_2^-|\} \\ \chi_6 &= \frac{1}{\sqrt{2}}|\phi_1^+ \phi_2^+| \\ \chi_7 &= \frac{1}{2}\{|\phi_0^+ \phi_2^-| + |\phi_0^- \phi_2^+|\} \\ \chi_8 &= \frac{1}{2}\{|\phi_0^+ \phi_1^-| + |\phi_0^- \phi_1^+|\} \\ \chi_9 &= \frac{1}{\sqrt{2}}|\phi_1^- \phi_2^-| \end{aligned}$$

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.

$$\begin{aligned} e_6 &= -\frac{\zeta}{2} + \delta, & \phi_7 &= b_3\chi_9 + a_3\chi_7 \\ & & \phi_8 &= |\chi_4\rangle \\ & & \phi_9 &= |\chi_3\rangle \end{aligned} \quad (11)$$

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

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

$$\text{where } x = \delta/\zeta$$

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

$$\epsilon_n = e_i + \sum_{j=1}^2 \langle\phi_i|\beta(KL + 2s)H\phi_j\rangle$$

$$+ \sum_{i=1}^2 \sum_{j=1}^2 \frac{\langle \phi_i | \beta(KL+2s)H | \phi_j \rangle \langle \phi_j | \beta(KL+2s)H | \phi_i \rangle}{e_i - e_j} \quad (12)$$

$$\Psi_n = |\phi_i\rangle + \sum_{i=1}^2 \sum_{j=1}^2 \frac{\langle \phi_i | \beta(KL+2s)H | \phi_j \rangle}{e_i - e_j} |\phi_j\rangle \quad (13)$$

Using the eigenvalues ε_n of the magnetic field interactions,

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

where

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

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

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

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

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

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

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

where

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

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

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

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

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

$$\mu_{\perp}^2(6) = 12 \left\{ \frac{\left(2 + \frac{K^2}{2} + 2KJ^{-1}\right) - (1-F^2)\left(2 - \frac{K^2}{2}\right)3xJ^{-1} + 2F\left[\left(2 + \frac{K^2}{2}J^{-1} - 2K\right)\right]}{\left(\frac{1}{2} + Y - J\right)G^2} + \frac{\left[\left(2 + \frac{K^2}{2}\right) - \left(2 - \frac{K^2}{2}\right)3xJ^{-1} - 2KJ^{-1}\right]}{4(1-3x-J)} - \frac{\left[\left(2 + \frac{K^2}{2}\right) - \left(2 - \frac{K^2}{2}\right)3xJ^{-1} + 2KJ^{-1}\right]}{(1+3x+J)} \right\} \frac{kT}{\zeta}$$

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

where

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

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

$$\mu = \{ \mu_{\parallel}^2 + 2\mu_{\perp}^2 \}^{\frac{1}{2}} \quad (16)$$

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,

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

where

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

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, χ_{\parallel} of the system when the magnetic field is parallel to the z axis may be calculated from the parallel component of the magnetic moment as

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

where μ_{\parallel} is the parallel component of the magnetic moment. The magnetic susceptibility when the magnetic field is perpendicular to the z axis may also be calculated from the perpendicular component of the magnetic moment as

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

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, $\delta=500$ cm^{-1} , $\zeta_p=110$ cm^{-1} and $K=0.8$

$\zeta_d(\text{cm}^{-1})$	210	230	250	270	290	310	330
μ_{\parallel}	2.786	2.748	2.710	2.674	2.639	2.604	2.571
μ_{\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 calculated magnetic moments for a d^2 complex in a strong tetragonal ligand field = 2.93 ($\zeta_d=210$ cm^{-1}).

(b) Dependence of the Calculated Magnetic Moments on Temperature
 $\delta=300$ cm^{-1} , $\zeta_d=310$ cm^{-1} , $\zeta_p=110$ cm^{-1} and $K=0.8$

$T(\text{K})$	200	240	280	300	340	380	400
μ_{\parallel}	2.604	2.683	2.742	2.767	2.808	2.841	2.854
μ_{\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 tetragonal ligand field = 2.89 ~ 2.97.

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

$\delta(\text{cm}^{-1})$	400	450	500	550	600	650	700
μ_{\parallel}	2.764	2.765	2.757	2.768	2.768	2.769	2.769
μ_{\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 calculated magnetic moments for a d^2 complex in a strong tetragonal ligand field = 2.93 ~ 2.96 ($\delta=400$ ~ 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 $(T=300\text{ K}, \zeta_d=154, \text{ and } \delta=500\text{ cm}^{-1})$

$R(\text{nm})$	$\Delta H/H(z)$	$\Delta H/H(x)$
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 $(T=300\text{ K}, \zeta_d=320, \text{ and } \delta=500\text{ cm}^{-1})$

$R(\text{nm})$	$\Delta H/H(z)$	$\Delta H/H(x)$
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 μ_{\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 values¹¹. 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^2 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 a strong trigonal ligand field fall in the range of the experimental values.¹²

As shown in Table 1 and 2, the calculated magnetic moments for d^1 and d^2 complexes⁹ in a strong tetragonal ligand field are slightly higher than those for d^1 and d^2 complexes⁹ in strong trigonal ligand field.

The calculated dipolar shift for d^1 and d^2 complexes in a strong crystal field of trigonal symmetry decrease as the distance from the NMR nucleus to the paramagnetic center is increased as expected from the previous works¹³. The calculated values of the dipolar shifts for a d^1 complex in a strong trigonal field are in reasonable agreement with the previous reports¹⁴. No theoretical value of the dipolar shift for a d^2 complex has been reported so far.

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