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Magnetic analyses of isosceles tricobalt(II) complexes containing two types of octahedral high-spin cobalt(II) ions

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ABSTRACT

The observed magnetic data for two isosceles tricobalt(II) complexes have been successfully analyzed, considering the axial distortion around each cobalt(II) ion, the local spin-orbit coupling, the anisotropic exchange interactions, and the intermolecular exchange interactions. The complexes each contains two types of octahedral high-spin cobalt(II) ions (Co_A and Co_B) in the shape of an isosceles triangle (Co_{A1}-Co_B-Co_{A2}), and the contribution of the orbital angular momentum is significant. The exchange interaction between the Co_A and Co_B ions is practically negligible ($J = \sim 0$), whereas the interaction between the Co_{A1} and Co_{A2} ions is ferromagnetic ($J' > 0$) for both complexes.

Keywords: Tricobalt(II) Complex; Magnetic Properties; Spin-Orbit Coupling; Exchange Interaction

1. INTRODUCTION

Magnetic analysis of multinuclear octahedral high-spin cobalt(II) complexes is a challenging subject because the orbital angular momentum makes the theoretical treatment difficult [1]. One of the most difficult points is that the local spin-orbit coupling is much larger than the exchange interactions [2]. Another difficult point is that the effect of local distortion is generally too large to be ignored, and that the anisotropic treatment is necessary [2,3].

For mononuclear octahedral high-spin cobalt(II) complexes, Lines [2] and Figgis [3] solved the problem, considering the axial distortion and spin-orbit coupling. For dinuclear complexes containing two equivalent octahedral high-spin cobalt(II) ions, Lines [4] developed a magnetic susceptibility equation for pure octahedral coordination geometries, and Sakiyama [5-10] developed susceptibility equations for distorted octahedral geometries considering the local axial distortion, local spin-orbit

coupling, and isotropic/anisotropic exchange interaction. Palii *et al*. [11-13] derived analytical expressions for the components of the exchange parameter, the g-tensor, and the temperature independent paramagnetism (TIP), based on the application of irreducible tensor operator technique. Recently, Lloret *et al*. [14] proposed an empirical expression.

In spite of progress in the theoretical treatment of dinuclear high-spin cobalt(II) complexes, magnetic analysis of the trinuclear octahedral high-spin cobalt(II) complexes had not been successfully performed. In this study, a magnetic susceptibility equation was obtained for tricobalt(II) complexes in the shape of an isosceles triangle (Co_{A2}-Co_B-Co_{A2}), considering local distortions, local spin-orbit couplings, exchange interactions, and the intermolecular exchange interactions. Magnetic analyses were successfully performed for two trinuclear high-spin cobalt(II) complexes $[Co_3(L1)_2(OCOMe)_2(NCS)_2]$ (1) and $[Co_3(L2)_2(OCOMe)_2(NCS)_2]$ (2) (see **Figure 1**), whose crystal structures and magnetic data were previously reported [15].

2. EXPERIMENT

Magnetic Analysis

The entire calculation was performed on a Power Macintosh 7300/180 computer using the MagSaki(T) program
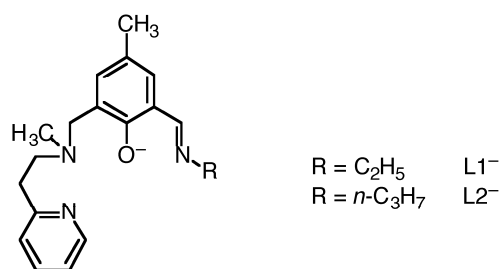
Figure 1. Chemical structures of L1$^-$ (R = C_2H_5) and L2$^-$ (R = n-C_3H_7).

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developed by Sakiyama. Nine independent parameters $\kappa_A, \lambda_A, \Delta_A, \kappa_B, \lambda_B, \Delta_B, J, J'$, and θ were determined as described below. First, the susceptibility data above 50 K (or 100 K) were fitted using six local parameters $\kappa_A, \lambda_A, \Delta_A, \kappa_B, \lambda_B$, and Δ_B, excluding the effect of exchange interactions between cobalt(II) ions. Secondly, fixing the six local parameters, the susceptibility data in the entire temperature range (2 - 300 K) were fitted to determine the remaining parameters J, J', and θ, and finally all the parameters were optimized.
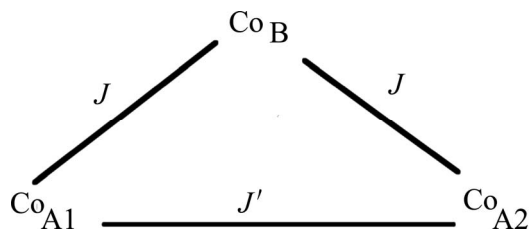
3. RESULTS AND DISCUSSION

3.1. Magnetic Susceptibility Equation for Isosceles Tricobalt(II) Complexes

In a trinuclear octahedral high-spin cobalt(II) complex, each cobalt(II) ion (O symmetry) has a local $^4T_1(^4F)$ ground term, which is split into six Kramers doublets due to a spin-orbit coupling. When the cobalt(II) ion is axially distorted, the order of the six Kramers doublets changes; however, the second-lowest doublet is always more than 100 cm^{-1} higher than the lowest doublet [2]. Since the local spin-orbit coupling is much larger than the exchange interactions, the exchange interaction is effective only between the lowest doublets of cobalt(II) ions. Therefore, it is appropriate to assume that the exchange interaction causes no effect to the higher doublets [2,5].

Here we want to obtain a magnetic susceptibility equation for an isosceles tricobalt(II) core, as shown in **Figure 2**. Full Hamiltonian is written as $\mathbf{H} = \mathbf{H}_{LF} + \mathbf{H}_{LS} + \mathbf{H}_{ZE} + \mathbf{H}_{ex}$, where $\mathbf{H}_{LF}$, $\mathbf{H}_{LS}$, $\mathbf{H}_{ZE}$, and $\mathbf{H}_{ex}$ are the ligand field term, LS coupling term, Zeeman term, and the exchange term of the Hamiltonian, respectively. The Hamiltonians $\mathbf{H}_{LF}$, $\mathbf{H}_{LS}$, and $\mathbf{H}_{ZE}$ are as follows: (see Equations (1)-(3))

$$\mathbf{H}_{LF} = \Delta_{A1}\left(\mathbf{L}^2_{z,A1} - \frac{2}{3}\right) + \Delta_{A2}\left(\mathbf{L}^2_{z,A2} - \frac{2}{3}\right) + \Delta_B\left(\mathbf{L}^2_{z,B} - \frac{2}{3}\right), \quad (1)$$

Figure 2. Isosceles tricobalt(II) core.

$$\mathbf{H}_{LS} = -\frac{3}{2}\kappa_{A1}\lambda_{A1}\mathbf{L}_{A1}\cdot\mathbf{S}_{A1} - \frac{3}{2}\kappa_{A2}\lambda_{A2}\mathbf{L}_{A2}\cdot\mathbf{S}_{A2} - \frac{3}{2}\kappa_B\lambda_B\mathbf{L}_B\cdot\mathbf{S}_B, \quad (2)$$

If we assume isotropic exchange interactions between local true spins ($S_{A1} = S_{A2} = S_B = 3/2$), the exchange part of the Hamiltonian can be written as

$$\mathbf{H}_{ex} = -J\left(\mathbf{S}_{A1}\cdot\mathbf{S}_B + \mathbf{S}_{A2}\cdot\mathbf{S}_B\right) - J'\mathbf{S}_{A1}\cdot\mathbf{S}_{A2}. \quad (4)$$

Since the local $^4T_1$ ground term is split by spin-orbit coupling larger than the exchange interactions, the local effective spins ($s_{A1} = s_{A2} = s_B = 1/2$) for the local lowest Kramers doublets are introduced [2,8].

$$s_{U,x} = \frac{S_{U,x}}{\alpha_U}, \ s_{U,y} = \frac{S_{U,y}}{\beta_U}, \ s_{U,z} = \frac{S_{U,z}}{\gamma_U}$$
$$(U = A1, A2, \text{ and } B) \quad (5)$$

Assuming axial symmetry for local effective spins ($\beta_U = \alpha_U$ and $s_{U,y} = s_{U,x}$), the exchange Hamiltonian can be rewritten as

$$\mathbf{H}_{ex} = -J_{eff}\left(\mathbf{s}_{A1}\cdot\mathbf{s}_B + \mathbf{s}_{A2}\cdot\mathbf{s}_B\right) - J'_{eff}\mathbf{s}_{A1}\cdot\mathbf{s}_{A2} + D_{eff}\left(s_{A1,z}s_{B,z} + s_{A2,z}s_{B,z}\right) + D'_{eff}s_{A1,z}s_{A2,z} \quad , (6)$$

where $J_{eff} = J\alpha_{A1}\alpha_B = J\alpha_{A2}\alpha_B$, $J'_{eff} = J'\alpha_{A1}\alpha_{A2}$,
$$D_{eff} = J\left(\alpha_{A1}\alpha_B - \gamma_{A1}\gamma_B\right) = J\left(\alpha_{A2}\alpha_B - \gamma_{A2}\gamma_B\right),$$

and $D'_{eff} = J'\left(\alpha_{A1}\alpha_{A2} - \gamma_{A1}\gamma_{A2}\right)$.

The coefficients α_U and γ_U (U = A1, A2, and B) can be expressed by the local parameters κ_U, λ_U, and Δ_U [2,8], where κ_U is the orbital reduction factor, λ_U is the spin-orbit coupling parameter, and Δ_U is the axial splitting parameter. The zero-field splitting parameter (D_{quin}) within an effective quintet state, generated from the three local effective spins (1/2), can be expressed as $D_{quin} = D_{eff}/3 + D'_{eff}/6$ [16].

At this stage, the susceptibility equation can be expressed as follows:

$$\chi_M = \frac{2N}{3}\left(\frac{F_{1,A} + 2F_{3,A}}{F_{2,A}} + \frac{F_{1,B} + 2F_{3,B}}{2F_{2,B}}\right), \quad (7)$$

where θ is the Weiss constant to describe the intermolecular exchange interactions. This interaction is actually temperature-dependent, but it is approximated as a constant in this study. The zero-field energies and first- and second-order Zeeman coefficients for each cobalt(II) ion $E_{A,n}^{(0)}$, $E_{B,n}^{(0)}$, $E_{A,z(x)n}^{(1)}$, $E_{B,z(x)n}^{(1)}$, $E_{A,z(x)n}^{(2)}$, and $E_{B,z(x)n}^{(2)}$ ($n = \pm1$ - ±6) can be expressed using equations reported previously [5,6].

$$\mathbf{H}_{ZE} = \beta\left[-\frac{3}{2}\kappa_{A1}\mathbf{L}_{A1} + g_e\mathbf{S}_{A1} - \frac{3}{2}\kappa_{A2}\mathbf{L}_{A2} + g_e\mathbf{S}_{A2} - \frac{3}{2}\kappa_B\mathbf{L}_B + g_e\mathbf{S}_B\right]H. \quad (3)$$

$$F_{1,A(B)} = \frac{1}{4}\sum_{n=\pm 1}\left(\frac{\left(4E_{A,z,n}^{(1)}-E_{B,z,n}^{(1)}\right)^2}{27k(T-\theta)}-2E_{A(B),z,n}^{(2)}\right)\exp\left[\frac{-E_{A(B),n}^{(0)}-J_{eff}+J'_{eff}/4}{kT}\right]$$

$$+\frac{1}{4}\sum_{n=\pm 1}\left(\frac{\left(2E_{A,z,n}^{(1)}+E_{B,z,n}^{(1)}\right)^2}{3k(T-\theta)}-2E_{A(B),z,n}^{(2)}\right)\exp\left[\frac{-E_{A(B),n}^{(0)}-D_{quin}+J'_{eff}/4}{kT}\right]$$

$$+\frac{1}{4}\sum_{n=\pm 1}\left(\frac{\left(2E_{A,z,n}^{(1)}+E_{B,z,n}^{(1)}\right)^2}{27k(T-\theta)}-2E_{A(B),z,n}^{(2)}\right)\exp\left[\frac{-E_{A(B),n}^{(0)}+D_{quin}+J_{eff}/2+J'_{eff}/4}{kT}\right]$$

$$+\frac{1}{4}\sum_{n=\pm 1}\left(\frac{{E_{B,z,n}^{(1)}}^2}{3k(T-\theta)}-2E_{A(B),z,n}^{(2)}\right)\exp\left[\frac{-E_{A(B),n}^{(0)}-3J'_{eff}/4}{kT}\right]+\sum_{n\neq\pm 1}\left(\frac{{E_{A(B),z,n}^{(1)}}^2}{kT}-2E_{A(B),z,n}^{(2)}\right)\exp\left[\frac{-E_{A(B),n}^{(0)}}{kT}\right]\quad(n=\pm 1\sim\pm 6),$$

(8)

$$F_{2,A(B)} = \frac{1}{4}\sum_{n=\pm 1}\exp\left[\frac{-E_{A(B),n}^{(0)}-J_{eff}+J'_{eff}/4}{kT}\right]+\frac{1}{4}\sum_{n=\pm 1}\exp\left[\frac{-E_{A(B),n}^{(0)}-D_{quin}+J_{eff}/2+J'_{eff}/4}{kT}\right]$$

$$+\frac{1}{4}\sum_{n=\pm 1}\exp\left[\frac{-E_{A(B),n}^{(0)}+D_{quin}+J_{eff}/2+J'_{eff}/4}{kT}\right]+\frac{1}{4}\sum_{n=\pm 1}\exp\left[\frac{-E_{A(B),n}^{(0)}-3J'_{eff}/4}{kT}\right]+\sum_{n\neq\pm 1}\exp\left[\frac{-E_{A(B),n}^{(0)}}{kT}\right]\quad(n=\pm 1\sim\pm 6),$$

(9)

$$F_{3,A(B)} = \frac{1}{4}\sum_{n=\pm 1}\left(\frac{\left(4E_{A,x,n}^{(1)}-E_{B,x,n}^{(1)}\right)^2}{27k(T-\theta)}-2E_{A(B),x,n}^{(2)}\right)\exp\left[\frac{-E_{A(B),n}^{(0)}-J_{eff}+J'_{eff}/4}{kT}\right]$$

$$-\frac{1}{4}\sum_{n=\pm 1}\left(\frac{\left(2E_{A,x,n}^{(1)}+E_{B,x,n}^{(1)}\right)^2 T}{9D_{quin}(T-\theta)}-2E_{A(B),x,n}^{(2)}\right)\exp\left[\frac{-E_{A(B),n}^{(0)}-D_{quin}+J_{eff}/2+J'_{eff}/4}{kT}\right]$$

(10)

$$+\frac{1}{4}\sum_{n=\pm 1}\left(\frac{\left(2E_{A,x,n}^{(1)}+E_{B,x,n}^{(1)}\right)^2 T}{9D_{quin}(T-\theta)}+\frac{4\left(2E_{A,x,n}^{(1)}+E_{B,x,n}^{(1)}\right)^2}{27k(T-\theta)}-2E_{A(B),x,n}^{(2)}\right)\exp\left[\frac{-E_{A(B),n}^{(0)}+D_{quin}+J_{eff}/2+J'_{eff}/4}{kT}\right]$$

$$+\frac{1}{4}\sum_{n=\pm 1}\left(\frac{{E_{B,x,n}^{(1)}}^2}{4k(T-\theta)}-2E_{A(B),x,n}^{(2)}\right)\exp\left[\frac{-E_{A(B),n}^{(0)}-3J'_{eff}/4}{kT}\right]+\sum_{n\neq\pm 1}\left(\frac{{E_{A(B),x,n}^{(1)}}^2}{kT}-2E_{A(B),x,n}^{(2)}\right)\exp\left[\frac{-E_{A(B),n}^{(0)}}{kT}\right]\quad(n=\pm 1\sim\pm 6).$$

3.2. Structural Features of 1 and 2

The crystal structures of 1 and 2 have been reported previously [15]; thus, only the structural features are briefly mentioned here. Both 1 and 2 have tricobalt(II) structures as shown in **Figure 3**, and the structures are very similar. Both ligands L1⁻ and L2⁻ have an N₂O coordination site and an NO site (see **Figure 1**). The N₂O site of a ligand incorporates a cobalt(II) ion (Co$_A$), and another cobalt(II) ion (Co$_B$) is incorporated by two NO sites of the two ligands, forming a trinuclear structure in the shape of an isosceles triangle. Co$_A$ and Co$_B$ are bridged by a phenolic oxygen atom of the ligand and an oxygen atom from an external acetate ion. Two Co$_A$ ions (Co$_{A1}$ and Co$_{A2}$) are bridged by two pairs of *syn-anti* bidentate oxygen atoms of two acetate ions. The coordination geometry for each cobalt(II) ion is distorted octahedral.
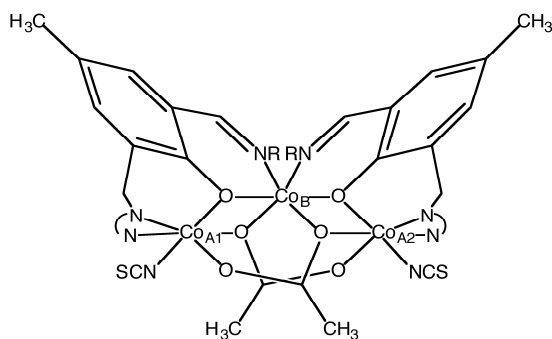
3.3. Magnetic Data Analysis

Magnetic data for complexes 1 and 2, as well as the preparations and crystal structures, were reported earlier [15], but no theoretical analysis of the data was made. The temperature dependencies of χ_M and μ_{eff} for the Co₃ unit for 1 and 2 are shown in **Figures 4** and **5**, respectively. The μ_{eff} values for the Co₃ unit for 1 and 2 at room temperature are 8.36 and 8.45 μ_B, respectively. These values
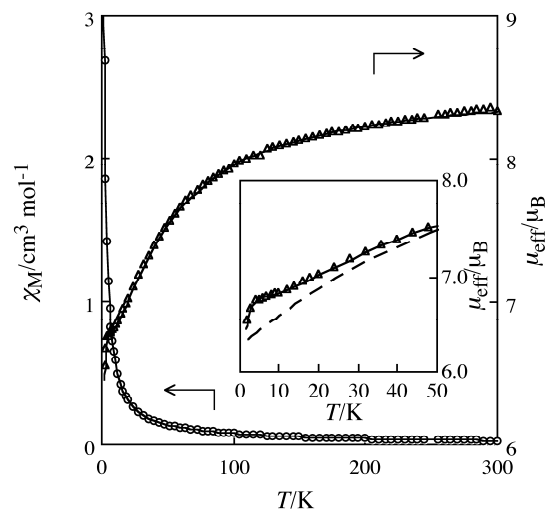
are larger than the spin-only value of the high-spin cobalt(II) ion (6.71 μ_B; $\mu_{SO} = [3\{4S(S+1)\}]^{1/2}$; $S = 3/2$) but close to the value expected when the spin momentum and orbital momentum exist independently [9.00 μ_B; $\mu_{LS} = [3\{L(L+1)+ 4S(S+1)\}]^{1/2}$; $L = 3$, $S = 3/2$]. This indicates a contribution of the orbital angular momentum typical of the local $^4T_1$ ground term. Moreover, the characteristic slopes of μ_{eff} curves are typical for the result of spin-orbit coupling. Therefore, the data were analyzed using the equation in Section 3.1, considering the local axial distortions, the local spin-orbit couplings, the anisotropic exchange in- teractions, and the intermolecular exchange interactions. The obtained parameters are summarized in **Table 1**.

The orbital reduction factor κ corresponds to the delocalization of unpaired electrons from metal ions to ligand, but it also contains the admixture of the upper $^4T_1(^4P)$ state into the $^4T_1(^4F)$ ground state. The κ value is known to be ~0.93 for the free cobalt(II) ion [4,17], and the obtained κ_A and κ_B values for both complexes are close to the free ion value. Comparing the axial splitting parameters Δ_A and Δ_B, Δ_B is larger than Δ_A for both complexes. All the Δ values for both complexes are normal for octahedral high-spin cobalt(II) complexes (~ 200 - ~ 800 cm^{-1}) [3]. The spin-orbit coupling parameter λ for the free cobalt(II) ion is theoretically expected to be ~ −172 cm^{-1} [18], but is generally smaller in the complexes. For complex 1, the λ_A value is normal (~70% of the free ion value), whereas the λ_B value is slightly smaller than the normal value. This occurs presumably because the assumed symmetry is less suitable for Co$_B$. That is, the local distortion axes are assumed to be parallel in this study, and this assumption may not be adequate. A similar tendency is also seen for complex 2.

The magnetic susceptibility below 50 K cannot be fitted without consideration of the exchange interactions. If we assume that there is no exchange interaction ($J = 0.00$ cm^{-1}, $J' = 0.00$ cm^{-1}, and $\theta = 0.00$ K), the calculated susceptibility curves are lower than the observed susceptibility below ~50K for both complexes as shown in

Figure 4. Temperature dependencies of χ_M (O) and μ_{eff} (Δ) of complex **1**. Solid curves are drawn with the parameters $\kappa_A = 0.93$, $\lambda_A = −151$ cm^{-1}, $\Delta_A = 604$ cm^{-1}, $\kappa_B = 0.93$, $\lambda_B = −101$ cm^{-1}, $\Delta_B = 714$ cm^{-1}, $J = +0.01$ cm^{-1}, $J' = +1.51$ cm^{-1}, and $\theta = −0.61$ K. The dashed curve in the insert is drawn with the parameters $\kappa_A = 0.93$, $\lambda_A = −151$ cm^{-1}, $\Delta_A = 604$ cm^{-1}, $\kappa_B = 0.93$, $\lambda_B = −101$ cm^{-1}, $\Delta_B = 714$ cm^{-1}, $J = 0.00$ cm^{-1}, $J' = 0.00$ cm^{-1}, and $\theta = 0.00$ K.
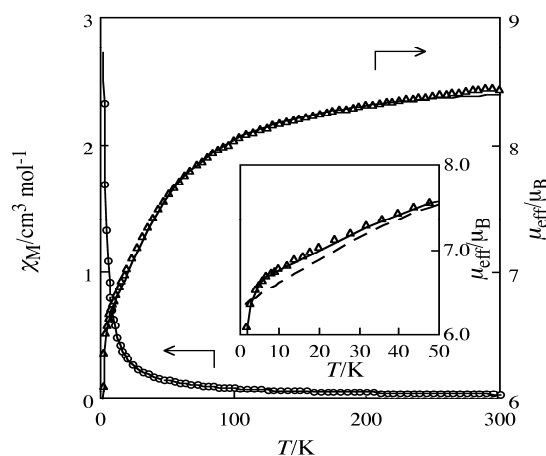
Figure 5. Temperature dependencies of χ_M (O) and μ_{eff} (Δ) of complex **2**. Solid curves are drawn with the parameters $\kappa_A = 0.93$, $\lambda_A = −136$ cm^{-1}, $\Delta_A = 531$ cm^{-1}, $\kappa_B = 0.93$, $\lambda_B = −115$ cm^{-1}, $\Delta_B = 674$ cm^{-1}, $J = +0.01$ cm^{-1}, $J' = +1.76$ cm^{-1}, and $\theta = −1.08$ K. The dashed curve in the insert is drawn with the parameters $\kappa_A = 0.93$, $\lambda_A = −136$ cm^{-1}, $\Delta_A = 531$ cm^{-1}, $\kappa_B = 0.93$, $\lambda_B = −115$ cm^{-1}, $\Delta_B = 674$ cm^{-1}, $J = 0.00$ cm^{-1}, $J' = 0.00$ cm^{-1}, and $\theta = 0.00$ K.

Figures 4 and **5**. This indicates the existence of ferromagnetic interaction in both complexes. Considering both the intramolecular and intermolecular interactions, the data were successfully analyzed. The result indicated that the exchange interaction between Co$_A$ (Co$_{A1}$ and Co$_{A2}$) and Co$_B$ is practically negligible ($J = ~ 0$), but the interaction between Co$_{A1}$ and Co$_{A2}$ is ferromagnetic ($J' > 0$). As mentioned above, Co$_A$ and Co$_B$ are bridged by a phenolic oxygen atom and an oxygen atom of an acetate

Figure 3. Schematic drawing of the tricobalt(II) structure for 1 (R = C$_2$H$_5$) and 2 (R = n-C$_3$H$_7$).

Table 1. Magnetic parameters and discrepancy factors for complexes 1 and 2.

Complex	κ_A	λ_A/cm^{-1}	Δ_A/cm^{-1}	κ_B	λ_B/cm^{-1}	Δ_B/cm^{-1}	J/cm^{-1}	J'/cm^{-1}	θ/K	$R(\chi_A)$*	$R(\mu_{eff})$*
1	0.93	−151	604	0.93	−101	714	+0.01	+1.51	−0.61	9.0×10^{-6}	1.3×10^{-6}
2	0.93	−136	531	0.93	−115	674	+0.01	+1.76	−1.08	9.2×10^{-6}	5.9×10^{-6}

*The discrepancy factors are defined as $R(\chi_A) = \Sigma[(\chi_{A,calc} - \chi_{A,obs})^2]/(\chi_{A,obs})^2$ and $R(\mu_{eff}) = \Sigma[(\mu_{eff,calc} - \mu_{eff,obs})^2]/(\mu_{eff,obs})^2$.

ion, whereas Co$_{A1}$ and Co$_{A2}$ are bridged by two pairs of *syn-anti* bidentate oxygen atoms of two acetate ions. Since an exchange interaction parameter is described as the sum of the ferromagnetic and antiferromagnetoic components and a phenolate bridge generally contributes to an antiferromagnetic interaction, the result ($J' > J$) is consistent with this idea.

Judging from the obtained parameters, we can explain the temperature dependencies as follows. The magnetic moments decrease with decreasing the temperature, and the decrease above 50 K is mainly due to the thermal population on the Kramers doublets generated from the local $^4T_1$ ground term by the spin-orbit coupling. Below 50 K, the ferromagnetic interaction between Co$_{A1}$ and Co$_{A2}$ appears, and the drop below 10 K is due to the intermolecular antiferromagnetic interaction.

4. CONCLUSIONS

In this study, a new magnetic susceptibility equation was developed for trinuclear octahedral high-spin cobalt(II) complexes in the shape of an isosceles triangle considering the local axial distortion, the spin-orbit coupling, the exchange interactions, and the intermolecular exchange interactions. Using the equation, the magnetic data for two tricobalt(II) complexes 1 and 2 were successfully analyzed. For both complexes, ferromagnetic interaction between Co$_{A1}$ and Co$_{A2}$ ions and practically negligible interaction between Co$_A$ and Co$_B$ ions were observed.

5. ACKNOWLEDGMENTS

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