Development of MagSaki(Tri) Software for the Magnetic Analysis of Trinuclear High-spin Cobalt(II) Complexes

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MagSaki(Tri) software was developed for the purpose of analyzing the magnetic data of trinuclear octahedral high-spin cobalt(II) complexes. The software enables analyses for five types of trinuclear cobalt(II) structures, including equilateral triangle shapes, isosceles triangle shapes, and linear shapes, to obtain magnetic parameters: the interaction parameters, $J$ and $J'$, the spin-orbit coupling parameter, $\lambda$, the orbital reduction factor, $\kappa$, and the axial splitting parameter, $\Delta$.

Keywords: Magnetic analysis, Octahedral high-spin cobalt(II) complex, Spin-orbit coupling, Ligand field, Trinuclear cobalt(II) complex

1 INTRODUCTION

The magnetic properties of coordination compounds have been extensively studied for more than half a century; however, it is still difficult to simulate magnetic data for some high-spin cobalt(II) complexes, because effects of the ligand field and the spin-orbit coupling work at the same time [1]. In the early studies by Lines [2] and Figgis [3], considering the axial ligand field turned out to be important. Then, Sakiyama developed magnetic susceptibility equations for dinuclear octahedral high-spin cobalt(II) complexes considering the axial ligand field [4–7], and software was also developed [8,9]. Regarding trinuclear octahedral high-spin cobalt(II) complexes, such software has not been reported, although the magnetic analysis was successfully done [10].

Therefore, in this paper, a MagSaki(Tri) software is reported for the purpose of analyzing the magnetic data of trinuclear cobalt(II) complexes, including triangle-shaped and linear structures (Figure 1).

2 MAGNETIC PARAMETERS

The main symbols for the magnetic parameters are summarized in Table 1.

3 METHOD

The software was developed using REALbasic software [11] on a SONY PCG-9G1N computer (OS: Windows XP Home edition). Magnetic susceptibility equations were obtained in the same way as described in reference [12].

4 FUNCTION OF MAGSAKI(TRI) SOFTWARE

The software calculates theoretical $\chi_A$ and $\mu_{\text{eff}}$ values for five types of trinuclear cobalt(II) structures, including triangle-shape and linear-shape structures, and displays the theoretical curves of $\chi_A$ versus $T$ and $\mu_{\text{eff}}$ versus $T$. The software optimizes magnetic parameters to fit the theoretical curves to the observed data.

5 CALCULATION MODES

The software has five calculation modes for trinuclear high-spin cobalt(II) complexes. Mode 1 is for equilateral-triangle-shaped tricobalt complexes (Figure 1a), including three equivalent cobalt(II) ions ($\text{Co}_{A1} = \text{Co}_{A2} = \text{Co}_{A3}$). Here, equivalent cobalt(II) ions have equal parameter values. Four parameters, $J$, $\nu$, $A$, and $\kappa$, are used in mode 1, and parameter $\theta$ is optional. Mode 2 is for isosceles-triangle-shaped tricobalt complexes (Figure 1b), including three equivalent cobalt(II) ions ($\text{Co}_{A1} = \text{Co}_{A2} = \text{Co}_{B}$). Five parameters,

Figure 1. Equilateral-triangle-shaped (a), isosceles-triangle-shaped (b), and line-shaped (c) trinuclear cobalt(II) structures.
$J, J', v, A, \Delta$, and $\kappa$, are used in mode 2, and parameter $\theta$ is optional.

Mode 3 is for isosceles-triangle-shaped tricobalt complexes (Figure 1b), including two types of cobalt(II) ions ($CoA_1 = CoA_2 \neq CoB$). Eight parameters, $J, J', v_A, v_B, \Delta_A, \Delta_B, \kappa_A$, and $\kappa_B$, are used in mode 3, and parameter $\theta$ is optional. Mode 4 is for line-shaped tricobalt complexes (Figure 1c), including three equivalent cobalt(II) ions ($CoA_1 = CoA_2 = CoB$). Four parameters, $J, v, \Delta, \kappa$, are used in mode 4, and parameter $\theta$ is optional. Mode 5 is for line-shaped tricobalt complexes (Figure 1c), including two types of cobalt(II) ions ($CoA_1 = CoA_2 \neq CoB$). Seven parameters, $J, v_A, v_B, \Delta_A, \Delta_B, \kappa_A$, and $\kappa_B$, are used in mode 5, and parameter $\theta$ is optional (Table 2).

### 6 MAGNETIC SUSCEPTIBILITY EQUATIONS

Magnetic susceptibility equations are shown below.

**[Magnetic susceptibility equation for modes 1, 2, and 4]**

$$X_M = \frac{X_z + 2 X_x}{3}$$

**[Magnetic susceptibility equation for modes 3 and 5]**

$$X_M = \frac{X_z + 2 X_x}{3}$$

### Table 1. List of the main symbols [1,4–10]

| Symbol | Unit   | Meaning         |
|--------|--------|-----------------|
| $J, J', J'', J'''$ | cm$^{-1}$ | Interaction parameters |
| $T$ | K | Absolute temperature |
| $v$ | – | Distortion parameter defined as $\Delta/(\kappa \lambda)$ |
| $A$ | cm$^{-1}$ | Axial splitting parameter |
| $\theta$ | K | Weiss constant |
| $\kappa$ | – | Orbital reduction factor |
| $\lambda$ | cm$^{-1}$ | Spin-orbit coupling parameter |
| $\mu_{\text{eff}}$ | | Effective magnetic moment |
| $\chi_A$ | cm$^3$ mol$^{-1}$ | Atomic magnetic susceptibility |
| $\chi_M$ | cm$^3$ mol$^{-1}$ | Molar magnetic susceptibility |

### Table 2. Calculation modes

| Mode | Shape | Cobalt(II) ions | Interaction (s) |
|------|-------|-----------------|-----------------|
| 1    | Equilateral triangle | $CoA_1 = CoA_2 = CoA_3$ | $J$ |
| 2    | Isosceles triangle | $CoA_1 = CoA_2 = CoB$ | $J \neq J'$ |
| 3    | Isosceles triangle | $CoA_1 = CoA_2 \neq CoB$ | $J \neq J'$ |
| 4    | Linear | $CoA_1 = CoA_2 = CoB$ | $J$ |
| 5    | Linear | $CoA_1 = CoA_2 \neq CoB$ | $J$ |

$J, J', v, A, \Delta$, and $\kappa_B$ are used in mode 5, and parameter $\theta$ is optional (Table 2).

F_{ij} = \sum_{n=1}^{2} \left[ \frac{E_n^{(i)} \lambda_n}{k(T-\theta)} \right] + 3 \sum_{n=1}^{2} \left[ \frac{E_n^{(i)} \lambda_n}{k(T-\theta)} - 2 E_n^{(i)} \right] \left[ \frac{E_n^{(i)}}{kT} \right]

F_z = \sum_{n=1}^{2} \left[ \frac{E_n^{(i)}}{kT} \right]

$\chi_M = \chi_z + \frac{2 \chi_x}{3}$

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(A, B, C) = (3 $J$/4, 3 $J$/4, 3 $J$/4) (mode 1)

(A, B, C) = (J $-J'/4$, 3 $J'/4$, 3 $J'/4$) (mode 2)

(A, B, C) = (J, 0, $-J'/2$) (mode 4)
\[ \chi_{(t)} = N \frac{2 F_{A,1,1(t)}}{F_{A,2}} + N \frac{F_{B,1,1(t)}}{F_{B,2}} \]

\[ F_{A,1,1}(x) = \sum_{n=\pm 1} 2 K^2 \left( \frac{25}{9} A \right) \left( \frac{25}{9} A \right) + 2 L^2 \left( \frac{25}{9} B \right) \left( \frac{25}{9} B \right) + 20 M^2 \left( \frac{25}{9} C \right) \left( \frac{25}{9} C \right) \]

\[ + \sum_{n=\neq \pm 1} \left[ \frac{E_{A,1,1}(x)}{k(T - \theta)} - 2 E_{A,2}(x) \right] \exp \left( \frac{-E_{A,1,1}(x)}{k(T - \theta)} \right) \]

\[ F_{A,2} = \sum_{n=\pm 1} \frac{2}{8} \exp \left( \frac{-E_{A,2}(x)}{kT} \right) + \frac{2}{8} \exp \left( \frac{-E_{A,2}(x)}{kT} \right) + \frac{4}{8} \exp \left( \frac{-E_{A,2}(x)}{kT} \right) \]

\[ F_{B,1,1}(x) = \sum_{n=\pm 1} 2 K^2 \left( \frac{25}{9} A \right) \left( \frac{25}{9} A \right) + 2 L^2 \left( \frac{25}{9} B \right) \left( \frac{25}{9} B \right) + 20 M^2 \left( \frac{25}{9} C \right) \left( \frac{25}{9} C \right) \]

\[ + \sum_{n=\neq \pm 1} \left[ \frac{E_{B,1,1}(x)}{k(T - \theta)} - 2 E_{B,2}(x) \right] \exp \left( \frac{-E_{B,1,1}(x)}{k(T - \theta)} \right) \]

\[ F_{B,2} = \sum_{n=\pm 1} \frac{2}{8} \exp \left( \frac{-E_{B,2}(x)}{kT} \right) + \frac{2}{8} \exp \left( \frac{-E_{B,2}(x)}{kT} \right) + \frac{4}{8} \exp \left( \frac{-E_{B,2}(x)}{kT} \right) \]

\[ K = \left( 4 \left| E_{A,1,1}(x) \right| - 2 E_{B,2}(x) \right) / 3 \]

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7 MAGNETIC SIMULATIONS

Here the temperature dependences of the \( \chi_A T \) product are demonstrated for three cases, an equilateral-triangle-shaped case, a line-shaped case, and an isosceles-triangle-shaped case.

Theoretical \( \chi_A T \) versus \( T \) curves for the equilateral-triangle-shaped trinuclear cobalt(II) complexes were calculated using mode 1, and the results are shown in Figure 2. When decreasing the temperature from 300 K to 100 K, the \( \chi_A T \) product is not constant even in the cases with no interaction \( (J = 0 \text{ cm}^{-1}) \) due to the single-ion spin-orbit coupling [12]. In the lower temperature range, below \( \approx 100 \text{ K} \), the \( \chi_A T \) product increases when the cobalt(II) ions are ferromagnetically coupled, but decreases when the interaction is antiferromagnetic.

Theoretical \( \chi_A T \) versus \( T \) curves for the line-shaped trinuclear cobalt(II) complexes were calculated using mode 4, and the results are shown in Figure 3. The tendency is similar to those for the above equilateral-triangle case, and the characteristic temperature dependence above 100 K is due to single-ion spin-orbit coupling.

Theoretical \( \chi_A T \) versus \( T \) curves for the isosceles-triangle-shaped trinuclear cobalt(II) complexes were calculated using mode 2, and the results are shown in Figure 4. When \( J > 0 \) (a) and when \( J < 0 \) (b), [The curves represent from the bottom \( J = -10, -5, -1, -0.2, 0, +0.2, +1, +5, \) and \( +10 \text{ cm}^{-1} \), respectively.] when \( \lambda = -170 \text{ cm}^{-1}, \kappa = 0.9, \) and \( \Delta = 0 \text{ cm}^{-1} \) (a) and when \( \lambda = -100 \text{ cm}^{-1}, \kappa = 0.7, \) and \( \Delta = 0 \text{ cm}^{-1} \) (b), where \( \theta \) and TIP are not used.

The magnetic analysis for trinuclear cobalt(II) complexes of isosceles triangle shape were performed previously [10].

8 REQUIREMENTS

The software (MagSaki(Tri) 003W) will run on Windows computers. The Macintosh version (MagSakiTri7) will run on Macintosh computers.

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