General Paper

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, λ , the orbital reduction factor, κ , and the axial splitting parameter, Δ .

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-9GIN 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 χ_A and μ_{eff} values for five types of trinuclear cobalt(II) structures, including triangle-shape and linear-shape structures, and displays the theoretical curves of χ_A versus T and μ_{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 , ν , Δ , and κ , are used in mode 1, and parameter θ 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,

Figure1. Equilateral-triangle-shaped(a), isosceles-triangle-shaped (b), and line-shaped (c) trinuclear cobalt(II) structures.

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
ν	–	Distortion parameter defined as $\Delta/(\kappa\lambda)$
Δ	cm^{-1}	Axial splitting parameter
θ	K	Weiss constant
κ	–	Orbital reduction factor
λ	cm^{-1}	Spin-orbit coupling parameter
μ_{eff}	μ_{B}	Effective magnetic moment
χ_{A}	$\text{cm}^3 \text{mol}^{-1}$	Atomic magnetic susceptibility
χ_{M}	$\text{cm}^3 \text{mol}^{-1}$	Molar magnetic susceptibility

J, J', ν, Δ , and κ , are used in mode 2, and parameter θ is optional. Mode 3 is for isosceles-triangle-shaped tricobalt complexes (**Figure 1b**), including two types of cobalt(II) ions ($\text{Co}_{\text{A}1} = \text{Co}_{\text{A}2} \neq \text{Co}_{\text{B}}$). Eight parameters, $J, J', \nu_{\text{A}}, \nu_{\text{B}}, \Delta_{\text{A}}, \Delta_{\text{B}}, \kappa_{\text{A}}$, and κ_{B} , are used in mode 3, and parameter θ is optional. Mode 4 is for line-shaped tricobalt complexes (**Figure 1c**), including three equivalent cobalt(II) ions ($\text{Co}_{\text{A}1} = \text{Co}_{\text{A}2} = \text{Co}_{\text{B}}$). Four parameters, J, ν, Δ , and κ , are used in mode 4, and parameter θ is optional. Mode 5 is for line-shaped tricobalt complexes (**Figure 1c**), including two types of cobalt(II)

Table 2. Calculation modes

Mode	Shape	Cobalt(II) ions	Interaction (s)
1	Equilateral triangle	$\text{Co}_{\text{A}1} = \text{Co}_{\text{A}2} = \text{Co}_{\text{A}3}$	J
2	Isosceles triangle	$\text{Co}_{\text{A}1} = \text{Co}_{\text{A}2} = \text{Co}_{\text{B}}$	$J \neq J'$
3	Isosceles triangle	$\text{Co}_{\text{A}1} = \text{Co}_{\text{A}2} \neq \text{Co}_{\text{B}}$	$J \neq J'$
4	Linear	$\text{Co}_{\text{A}1} = \text{Co}_{\text{A}2} = \text{Co}_{\text{B}}$	J
5	Linear	$\text{Co}_{\text{A}1} = \text{Co}_{\text{A}2} \neq \text{Co}_{\text{B}}$	J

ions ($\text{Co}_{\text{A}1} = \text{Co}_{\text{A}2} \neq \text{Co}_{\text{B}}$). Seven parameters, $J, \nu_{\text{A}}, \nu_{\text{B}}, \Delta_{\text{A}}, \Delta_{\text{B}}, \kappa_{\text{A}}$, and κ_{B} , are used in mode 5, and parameter θ is optional (**Table 2**).

6 MAGNETIC SUSCEPTIBILITY EQUATIONS

Magnetic susceptibility equations are shown below.

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

$$\chi_{\text{M}} = \frac{\chi_z + 2\chi_x}{3}$$

$$\chi_{z(x)} = N \frac{F_{1,z(x)}}{F_2}$$

$$F_{1,z(x)} = \sum_{n=\pm 1} \left[\frac{E_{z(x),n}^{(1)2}}{k(T-\theta)} \left\{ \frac{2}{8} \text{Exp} \left(\frac{-E_n^{(0)} - \frac{25}{9}A}{kT} \right) + \frac{2}{8} \text{Exp} \left(\frac{-E_n^{(0)} - \frac{25}{9}B}{kT} \right) + \frac{20}{8} \text{Exp} \left(\frac{-E_n^{(0)} - \frac{25}{9}C}{kT} \right) \right\} - 6E_{z(x),n}^{(2)} \text{Exp} \left(\frac{-E_n^{(0)}}{kT} \right) \right] + 3 \sum_{n \neq \pm 1} \left[\left\{ \frac{E_{z(x),n}^{(1)2}}{k(T-\theta)} - 2E_{z(x),n}^{(2)} \right\} \text{Exp} \left(\frac{-E_n^{(0)}}{kT} \right) \right]$$

$$(n = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6)$$

$$F_2 = \sum_{n=\pm 1} \left[\frac{2}{8} \text{Exp} \left(\frac{-E_n^{(0)} - \frac{25}{9}A}{kT} \right) + \frac{2}{8} \text{Exp} \left(\frac{-E_n^{(0)} - \frac{25}{9}B}{kT} \right) + \frac{4}{8} \text{Exp} \left(\frac{-E_n^{(0)} - \frac{25}{9}C}{kT} \right) \right] + \sum_{n \neq \pm 1} \left[\text{Exp} \left(\frac{-E_n^{(0)}}{kT} \right) \right]$$

$$(n = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6)$$

$$(A, B, C) = (3J/4, 3J/4, -3J/4) \quad (\text{mode 1})$$

$$(A, B, C) = (J - J'/4, 3J'/4, -J/2 - J'/4) \quad (\text{mode 2})$$

$$(A, B, C) = (J, 0, -J/2) \quad (\text{mode 4})$$

[Magnetic susceptibility equation for modes 3 and 5]

$$\chi_{\text{M}} = \frac{\chi_z + 2\chi_x}{3}$$

$$\chi_{z(x)} = N \frac{2 F_{A,1,z(x)}}{F_{A,2}} + N \frac{F_{B,1,z(x)}}{F_{B,2}}$$

$$F_{A,1,z(x)} = \sum_{n=\pm 1} \left[\frac{2 K^2}{24 k T} \left\{ \text{Exp} \left(\frac{-\frac{25}{9} A}{k T} \right) \right\} + \frac{2 L^2}{24 k (T - \theta)} \left\{ \text{Exp} \left(\frac{-\frac{25}{9} B}{k T} \right) \right\} + \frac{20 M^2}{24 k (T - \theta)} \left\{ \text{Exp} \left(\frac{-\frac{25}{9} C}{k T} \right) \right\} - 2 E_{A,z(x),n}^{(2)} \right] \\ + \sum_{n \neq \pm 1} \left[\left\{ \frac{E_{A,z(x),n}^{(1)2}}{k (T - \theta)} - 2 E_{A,z(x),n}^{(2)} \right\} \text{Exp} \left(\frac{-(E_{A,n}^{(0)} - E_{A,0}^{(0)})}{k T} \right) \right]$$

$$(n = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6)$$

$$F_{A,2} = \sum_{n=\pm 1} \left[\frac{2}{8} \text{Exp} \left(\frac{-(E_{A,n}^{(0)} - E_{A,0}^{(0)}) - \frac{25}{9} A}{k T} \right) + \frac{2}{8} \text{Exp} \left(\frac{-(E_{A,n}^{(0)} - E_{A,0}^{(0)}) - \frac{25}{9} B}{k T} \right) + \frac{4}{8} \text{Exp} \left(\frac{-(E_{A,n}^{(0)} - E_{A,0}^{(0)}) - \frac{25}{9} C}{k T} \right) \right] \\ + \sum_{n \neq \pm 1} \left[\text{Exp} \left(\frac{-(E_{A,n}^{(0)} - E_{A,0}^{(0)})}{k T} \right) \right]$$

$$(n = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6)$$

$$F_{B,1,z(x)} = \sum_{n=\pm 1} \left[\frac{2 K^2}{24 k T} \left\{ \text{Exp} \left(\frac{-\frac{25}{9} A}{k T} \right) \right\} + \frac{2 L^2}{24 k (T - \theta)} \left\{ \text{Exp} \left(\frac{-\frac{25}{9} B}{k T} \right) \right\} + \frac{20 M^2}{24 k (T - \theta)} \left\{ \text{Exp} \left(\frac{-\frac{25}{9} C}{k T} \right) \right\} - 2 E_{B,z(x),n}^{(2)} \right] \\ + \sum_{n \neq \pm 1} \left[\left\{ \frac{E_{B,z(x),n}^{(1)2}}{k (T - \theta)} - 2 E_{B,z(x),n}^{(2)} \right\} \text{Exp} \left(\frac{-(E_{B,n}^{(0)} - E_{B,0}^{(0)})}{k T} \right) \right]$$

$$(n = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6)$$

$$F_{B,2} = \sum_{n=\pm 1} \left[\frac{2}{8} \text{Exp} \left(\frac{-(E_{B,n}^{(0)} - E_{B,0}^{(0)}) - \frac{25}{9} A}{k T} \right) + \frac{2}{8} \text{Exp} \left(\frac{-(E_{B,n}^{(0)} - E_{B,0}^{(0)}) - \frac{25}{9} B}{k T} \right) + \frac{4}{8} \text{Exp} \left(\frac{-(E_{B,n}^{(0)} - E_{B,0}^{(0)}) - \frac{25}{9} C}{k T} \right) \right] \\ + \sum_{n \neq \pm 1} \left[\text{Exp} \left(\frac{-(E_{B,n}^{(0)} - E_{B,0}^{(0)})}{k T} \right) \right]$$

$$(n = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6)$$

$$K = \left(4 \left| E_{A,z(x),n}^{(1)} \right| - \left| E_{B,z(x),n}^{(1)} \right| \right) / 3$$

Figure 2. Theoretical χT versus T curves for trinuclear cobalt(II) complexes of equilateral triangle shape with the variation of J [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 θ and TIP are not used.

$$L = E_{B, z(x), n}^{(1)}$$

$$M = \left(2 \left| E_{A, z(x), n}^{(1)} \right| + \left| E_{B, z(x), n}^{(1)} \right| \right) / 3$$

$$(A, B, C) = (J - J' / 4, 3 J' / 4, -J / 2 - J' / 4) \quad (\text{mode } 3)$$

$$(A, B, C) = (J, 0, -J / 2) \quad (\text{mode } 5)$$

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 $\sim 100 \text{ K}$, 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 is positive, the low-temperature data are affected by J' (**Figure 4a**), but when J is negative, the curves are not affected so much by J' (**Figure 4b**). The theoretical curves are more affected by J than J' .

Figure 3. Theoretical χT versus T curves for trinuclear cobalt(II) complexes of equally-spaced linear shape with the variation of J [The curves represent from the bottom $J = -10, -5, -1, -0.2, 0, +0.2, +1, +5$, and $+10 \text{ cm}^{-1}$, respectively.] when $J' = 0 \text{ cm}^{-1}$, $\lambda = -170 \text{ cm}^{-1}$, $\kappa = 0.9$, and $\Delta = 0 \text{ cm}^{-1}$ (a) and when $J' = 0 \text{ cm}^{-1}$, $\lambda = -100 \text{ cm}^{-1}$, $\kappa = 0.7$, and $\Delta = 0 \text{ cm}^{-1}$ (b), where θ and TIP are not used.

Figure 4. Theoretical χT versus T curves for trinuclear cobalt(II) complexes of isosceles triangle shape with the variation of J' when $J > 0$ (a) and when $J < 0$ (b). [The curves represent from the bottom ($J / \text{cm}^{-1}, J' / \text{cm}^{-1}$) = (0,0), (+10, -10), (+10, -5), (+10, 0), (+10, +5), and (+10, +10), respectively for (a) and ($J / \text{cm}^{-1}, J' / \text{cm}^{-1}$) = (-10, -10), (-10, -5), (-10, 0), (-10, +5), (-10, +10), and (0,0), respectively for (b), when $\lambda = -170 \text{ cm}^{-1}$, $\kappa = 0.9$, and $\Delta = 0 \text{ cm}^{-1}$.]

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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