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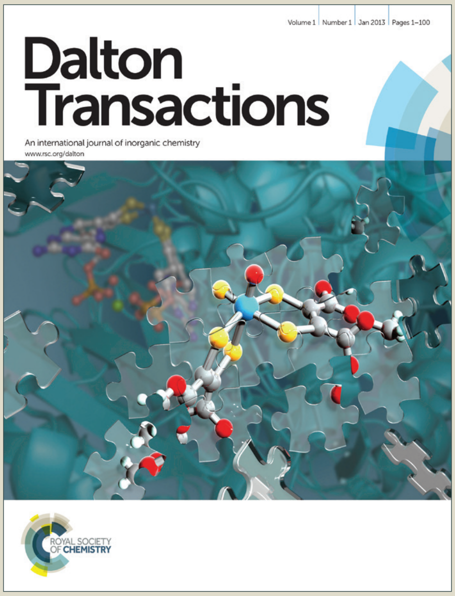

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COMMUNICATION

Magnetic analysis of a tetranuclear octahedral high-spin cobalt(II) complex based on a newly derived magnetic susceptibility equation

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Here we report a versatile magnetic susceptibility equation for tetranuclear octahedral high-spin cobalt(II) complexes and a magnetic analysis for a tetranuclear defect cubane cobalt(II) complex based on the equation. We concluded that the interaction is essentially ferromagnetic despite the decrease in the χT product on cooling from 300 K, and the decrease is due to the spin-orbit coupling.

1. Introduction

Magnetic properties of coordination compounds have been extensively studied for more than half a century. However, it is still very difficult to understand the relationship between structure and magnetic properties of some octahedral high-spin cobalt(II) complexes, because effects of the ligand field and the spin-orbit coupling work at the same time.[1] Lines[2] and Figgis[3] showed the way to analyse the magnetic properties of mononuclear octahedral high-spin cobalt(II) complexes by considering an axially distorted ligand field and spin-orbit coupling, pointing out the importance of considering the axial distortion in analysis. For the complexes containing two equivalent octahedral high-spin cobalt(II) ions, Lines developed a magnetic susceptibility equation for a pure octahedral case,[4] and Sakiyama developed susceptibility equations for distorted octahedral cases based on the ligand field theory.[5]

Various types of tetranuclear octahedral high-spin cobalt(II) complexes have been reported,[6,7] and several magnetic studies have been done. On the other hand, most of the time, it is difficult to understand the magnetic behaviour without considering the distorted ligand field. Therefore in this study we aim to develop a versatile magnetic susceptibility equation for tetranuclear octahedral high-spin cobalt(II) complexes, considering the local distorted ligand field, spin-orbit coupling, and exchange interaction. We also demonstrate theoretical χT versus T curves, and we show a result of magnetic analysis for a tetranuclear defect cubane cobalt(II) complex.

2. Results and discussion

The ground term of free high-spin cobalt(II) ion is ^4F. In the weak field of O symmetry, the ^4F term splits into $^4T_1$, $^4T_2$, and $^4A_2$ terms from the lower energy, and the ground $^4T_1$ term has the first-order orbital angular momentum. Considering the axial distortion and spin-orbit coupling, the ground $^4T_1$ term splits into six Kramers doublets, which should be considered in analysing the temperature-dependence of magnetic susceptibility. This splitting is considered to be a zero-field splitting (ZFS), but is different from the normal ZFS of a term without first-order orbital angular momentum. The Hamiltonian can be written as $\mathbf{H} = \mathit{\Delta}(\mathbf{L}_z^2 - 2/3) - (3/2)\kappa\lambda\mathbf{L}\cdot\mathbf{S} + \beta[-(3/2)\kappa\mathbf{L}_u + g_e\,\mathbf{S}_u]\cdot H_u$ $(u = x, y, z)$, where $\mathit{\Delta}$ is the axial splitting parameter, κ is the orbital reduction factor including the admixing, and λ is the spin-orbit coupling parameter.[1] Using the Hamiltonian, Zeemann energies [$E_n^{(0)}$ (n = ±1, ±2, ±3, ±4, ±5, ±6)] and first- and second-order Zeeman coefficients [$E_{u,n}^{(1)}$ and $E_{u,n}^{(2)}$ ($u = z, x$; n = ±1, ±2, ±3, ±4, ±5, ±6)] are obtained as the functions of the parameters $\mathit{\Delta}$, κ, and λ.[5,8] Although the order of the six Kramers doublets varies with the functions of the three parameters, the lowest Kramers doublet is always the same term of effective 1/2 spin.[2] When considering the exchange interaction between octahedral high-spin cobalt(II) ions, the $|J|$ value is generally much smaller than the energy separation between the lowest and the second-lowest Kramers doublets (~100-200 cm^{-1}). Therefore, considering the interaction only between the lowest Kramers doublets of cobalt(II) ions is a good approximation.[5] Thus, in the case of tetranuclear octahedral high-spin cobalt(II) complexes, exchange interaction can be treated in the same way as tetranuclear copper(II) complexes.

Hatfield and coworkers developed a magnetic susceptibility equation for tetranuclear copper(II) complexes based on a Hamiltonian as follows: $\mathbf{H} = -J\mathbf{S}_{A1}\cdot\mathbf{S}_{A2} - J'(\mathbf{S}_{A1}\cdot\mathbf{S}_{B1} + \mathbf{S}_{A2}\cdot\mathbf{S}_{B2}) - J''(\mathbf{S}_{A1}\cdot\mathbf{S}_{B2} + \mathbf{S}_{A2}\cdot\mathbf{S}_{B1}) - J'''\mathbf{S}_{B1}\cdot\mathbf{S}_{B2}$.[9] In the same way we can develop a magnetic susceptibility equation for tetranuclear octahedral high-spin cobalt(II) complexes, considering the six Kramers doublets generated from the ground $^4T_1$ term. Assuming the isotropic interaction, the magnetic susceptibility equation is written as follows:

$$\chi_{\mathrm{M}} = \frac{4\,(\chi_z + 2\,\chi_x\,)}{3}$$

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

$$F_{1,z(x)} = \sum_{n=\pm 1} \left[\frac{{E^{(1)}_{z(x),n}}^{2}}{k\,(T-\theta)} \left\{ \frac{10}{16}\mathrm{Exp}\left(\frac{-E^{(0)}_{n} - \frac{25}{9}A}{k\,T}\right) + \frac{2}{16}\mathrm{Exp}\left(\frac{-E^{(0)}_{n} - \frac{25}{9}B}{k\,T}\right) + \frac{2}{16}\mathrm{Exp}\left(\frac{-E^{(0)}_{n} - \frac{25}{9}C}{k\,T}\right) + \frac{2}{16}\mathrm{Exp}\left(\frac{-E^{(0)}_{n} - \frac{25}{9}D}{k\,T}\right) \right\} - 2\,E^{(2)}_{z(x),n}\,\mathrm{Exp}\left(\frac{-E^{(0)}_{n}}{k\,T}\right) \right] + \sum_{n\neq\pm 1} \left[\left\{ \frac{{E^{(1)}_{z(x),n}}^{2}}{k\,(T-\theta)} - 2\,E^{(2)}_{z(x),n} \right\} \mathrm{Exp}\left(\frac{-E^{(0)}_{n}}{k\,T}\right) \right]$$

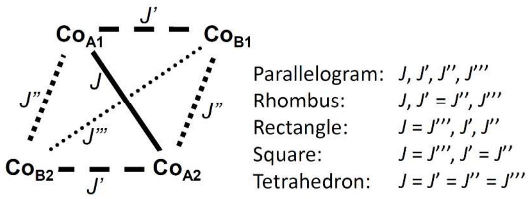
$$(n = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6)$$

$$F_{2} = \sum_{n=\pm 1} \left[\frac{5}{16}\mathrm{Exp}\left(\frac{-E^{(0)}_{n} - \frac{25}{9}A}{k\,T}\right) + \frac{3}{16}\mathrm{Exp}\left(\frac{-E^{(0)}_{n} - \frac{25}{9}B}{k\,T}\right) + \frac{3}{16}\mathrm{Exp}\left(\frac{-E^{(0)}_{n} - \frac{25}{9}C}{k\,T}\right) + \frac{3}{16}\mathrm{Exp}\left(\frac{-E^{(0)}_{n} - \frac{25}{9}D}{k\,T}\right) + \frac{1}{16}\mathrm{Exp}\left(\frac{-E^{(0)}_{n} - \frac{25}{9}E}{k\,T}\right) + \frac{1}{16}\mathrm{Exp}\left(\frac{-E^{(0)}_{n} - \frac{25}{9}G}{k\,T}\right) \right] + \sum_{n\neq\pm 1} \left[\mathrm{Exp}\left(\frac{-E^{(0)}_{n}}{k\,T}\right) \right]$$

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

$A = (-K/2) - P$
$B = (-K/2) + P$
$C = K/2 - \sqrt{L^2 + M^2}$
$D = K/2 + \sqrt{L^2 + M^2}$
$E = K/2 + P - \sqrt{K^2 + 3\,L^2 - 2\,K\,P + P^2}$
$G = K/2 + P + \sqrt{K^2 + 3\,L^2 - 2\,K\,P + P^2}$
$K = (J + J''') / 2$
$L = (J' - J'') / 2$
$M = (J - J''') / 2$
$P = (J' + J'') / 2$

This equation contains nine parameters λ, κ, v, J, J', J'', J''', θ, and TIP, where v is defined as $v = \Delta / (\kappa\,\lambda)$. The parameters θ (K) and TIP are options to consider the intermolecular interaction and the temperature-independent paramagnetism, respectively. The factor 25/9 in the equation originates from the relationship between the true 3/2 spin and the effective 1/2 spin.[2] The orientation of each cobalt(II) ion is important; however, the effect of orientation would give no effect on the result as far as we consider isotropic interactions. Therefore, the equation is versatile for various shaped tetranuclear octahedral high-spin cobalt(II) complexes, including parallelogram-shaped, rhombus-shaped, rectangle-shaped, square-shaped, and tetrahedron-shaped complexes (Scheme 1). For example, in tetranuclear cubane cobalt(II) complexes (Fig. 1a), four cobalt(II) ions are located at the vertices of the tetrahedron, so the tetrahedron-shaped model can be used. In the same way, for defect cubane complexes (Fig. 1b), rhombus-shaped or parallelogram-shaped model can be used.



Scheme 1 Exchange coupling model for tetranuclear cobalt(II) complexes.

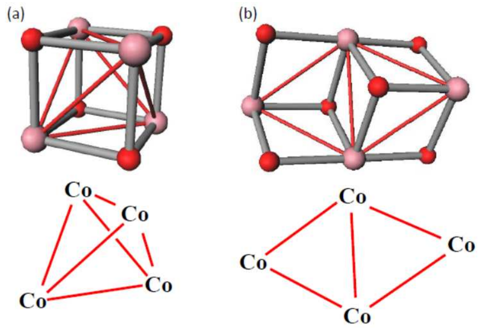


Fig. 1 Structures of tetranuclear cobalt(II) complexes; cubane structure (a) and defect cubane structure (b).

Here we demonstrate χT versus T curves using the equation (Fig. 2). First, when decreasing the temperature from 300 K, χT product is not constant even in the cases with no interaction (J = 0 cm^{-1}); this is due to the thermal population onto the six Kramers doublets generated by the spin-orbit coupling. The χT product decreases when $|\lambda|$ and κ are close to their upper limits (Fig. 2a), but the χT product increases when $|\lambda|$ and κ are much smaller than the upper limits (Fig. 2b). In addition, the shape of the curve varies with the function of the local distortion,[3] although it is not shown here. These are all due to the spin-orbit coupling. Next, if we focus on the low temperature range, the χT product decreases when the interaction is antiferromagnetic, while the χT product increases when the interaction is ferromagnetic. This is quite normal; however, it is only in the low temperature range. In the higher temperature range, sometimes the χT product decreases in spite of the ferromagnetic interaction, and sometimes the χT product increases despite the antiferromagnetic interaction. Therefore, the magnetic behaviour in the higher temperature range is unrelated to the exchange interaction.

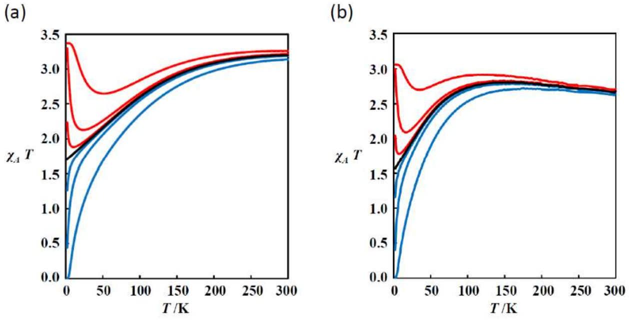


Fig. 2 Theoretical χT versus T curves for tetranuclear cobalt(II) complexes with the variation of J [The curves represent from the bottom J = J' = J'' = J''' = –5, –1, –0.2, 0, +0.2, +1, and +5 cm^{-1}, respectively.] when λ = –170 cm^{-1}, κ = 0.9, and Δ = 0 cm^{-1} (a) and when λ = –100 cm^{-1}, κ = 0.7, and Δ = 0 cm^{-1} (b), where θ and TIP are not used.

Now we analyse the magnetic data observed for a defect cubane complex $[Co_4(\mu_3\text{-}OH)_2(H_2O)_6(ntp)_2]\cdot 2H_2O$, where $H_3(ntp)$ = $N(CH_2CH_2COOH)_3$.[7] For this purpose, we developed a computer software MagSaki(tetra), which included optimization programs. First, assuming all the interactions are equal (J = J' =

$J'' = J'''$), we decided to determine six parameters λ, κ, ν, J, θ, and TIP. Generally it is too difficult to determine six parameters based on a simple curve; however, it is possible to determine all the parameters in this case, reducing the six-parameter problem to a three-parameter problem plus three one-parameter problems; this is because the individual parameters have a different effect on the χT versus T curve, and the effective temperature ranges of the problems are different from each other. The observed χT versus T data above 100 K is strongly dependent on only three parameters λ, κ, and ν, and there are at most three local minima [usually at $\nu < 0$, $\nu = \sim 0$, and $\nu > 0$] for the objective function, which should be minimized. For the compound we found only one local minimum at (λ, κ, ν) = (~ -110 cm^{-1}, ~ 0.93, ~ -3.0). Analysing the data in the whole temperature range, we found only one parameter set (J, λ, κ, ν, θ, TIP) = (+2.54 cm^{-1}, −105 cm^{-1}, 0.93, −3.5, −1.67 K, 0.000433 cm^3 mol^{-1}) after optimization. Further analysis was also possible assuming the rhombus-shaped model, using the brute force method, finding all the local minima. In the case assuming $J = J' = J''$ and $J''' = 0$ cm^{-1}, the obtained parameters were $J = J' = J'' = +3.37$ cm^{-1}, $J''' = 0$ cm^{-1} (fixed), $\lambda = -108$ cm^{-1}, $\kappa = 0.93$, $\nu = -3.5$, $\theta = -1.65$ K, and TIP = 0.000422 cm^3 mol^{-1}. Furthermore, in the case assuming $J \neq J' = J''$ and $J''' = 0$ cm^{-1}, the obtained parameters were $J = +0.76$ cm^{-1}, $J' = J'' = +4.22$ cm^{-1}, $J''' = 0$ cm^{-1} (fixed), $\lambda = -108$ cm^{-1}, $\kappa = 0.93$, $\nu = -3.5$, $\theta = -1.66$ K, and TIP = 0.000414 cm^3 mol^{-1}. This is the most appropriate one, judging from the crystal structure. The obtained theoretical χT *versus* T curve is shown in Fig. 3. This result indicates three things: (1) the decrease in χT from 300 K to 50K is due to the thermal population on the Kramers doublets caused by the spin-orbit coupling, (2) a small increase below 20 K to ~10 K is due to the ferromagnetic interaction within a tetranuclear unit, and (3) a sudden decrease below 10 K is due to the intermolecular antiferromagnetic interaction. The theoretical no-interaction curve is also shown in Fig. 3, assuming $J = J' = J'' = J''' = 0.00$ cm^{-1}, $\lambda = -108$ cm^{-1}, $\kappa = 0.93$, $\nu = -3.5$, $\theta = -1.66$ K, TIP = 0.000414 cm^3 mol^{-1}. The observed data is gradually deviating upwards from the theoretical no-interaction curve on cooling. Therefore the interaction is apparently ferromagnetic despite the decrease in χT.

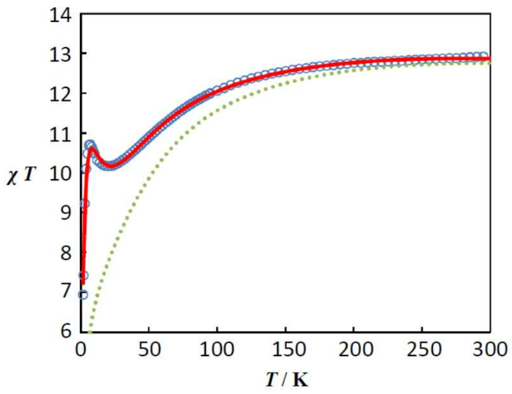


Fig. 3 Temperature dependencies of the χT products: the observed data (circles), an optimized theoretical curve with the parameters $J = +0.76$ cm^{-1}, $J' = J'' = +4.22$ cm^{-1}, $J''' = 0$ cm^{-1} (fixed), $\lambda = -108$ cm^{-1}, $\kappa = 0.93$, $\nu = -3.5$, $\theta = -1.66$ K, TIP = 0.000414 cm^3 mol^{-1} (solid curve), and a theoretical no-interaction curve with the parameters $J = J' = J'' = J''' = 0.00$ cm^{-1}, $\lambda = -108$ cm^{-1}, $\kappa = 0.93$, $\nu = -3.5$, $\theta = -1.66$ K, TIP = 0.000414 cm^3 mol^{-1} (dotted curve).

3. Conclusions

A versatile magnetic susceptibility equation was obtained for tetranuclear octahedral high-spin cobalt(II) complexes, considering the local distorted ligand field, spin-orbit coupling, and exchange interaction. This equation can be used for various shaped tetranuclear cobalt(II) complexes, including parallelogram-shaped, rhombus-shaped, rectangle-shaped, square-shaped, and tetrahedron-shaped complexes. The χT versus T data were analysed for a defect cubane complex $[Co_4(\mu_3\text{-}OH)_2(H_2O)_6(ntp)_2]\cdot 2H_2O$, and the result indicated that (1) the decrease in χT from 300 K to 50K is due to the spin-orbit coupling, (2) an increase below 20 K to ~10 K is due to the ferromagnetic interaction within a tetranuclear unit, and (3) a sudden decrease below 10 K is due to the intermolecular antiferromagnetic interaction. Importantly, the interaction is essentially ferromagnetic despite the decrease in χT from 300 K to 50K.

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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