Structures and Magnetic Properties of a New Cobalt(II) Linear Trimer with Phenylcinnamic Acid

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Linear trinuclear cobalt(II) complex with α-phenylcinnamic acid (phcinaH), $[Co_3(phcina)_6(quin)_2]$ (quin = quinoline) was synthesized and characterized by X-ray crystallography and magnetic susceptibility measurement. The magnetic susceptibility of the linear trimer, which has one octahedral and two trigonal-bipyramidal coordination was analyzed by modified Lines model.

There has been considerable interest in multinuclear metal complexes because of their structures and properties. Synthesis and characterization of nanometer-sized transition-metal complexes is fundamental study in the development of molecular magnets.[1,2] Extensive work on Co(II) clusters has been reported and one of the most attracting interest is magneto-structural correlations.[3–11] With the objective of theory, Co(II) cluster with a focus on dimer has been investigated, where attracting puzzle is handling large orbital contribution of octahedral Co(II) ion.[3–6] In 1971, Lines reported a statistical approximation for the analysis of the magnetic coupling for binuclear octahedral Co(II) complex.[3] On the other hand, in tetrahedral, square-planar, trigonal-bipyramidal, and distorted octahedral cases, contribution of orbital angular momentum is negligible in respect of ground state; therefore spin-only approximation is valid. Here we report on synthesis, crystal structure and magnetic behavior of a new linear cobalt(II) trimer complex, $[Co_3(phcina)_6(quin)_2]$ (**1**) (phcina = α-phenylcinnamate, quin = quinoline). The magnetic susceptibility was analyzed by modified Lines' approximation as required to apply the complex **1**, in which trimer unit there are one octahedral and two trigonal-bipyramidal Co ions.

1 was prepared as follows. $Co(NO_3)_2{\cdot}6H_2O$ (1.82 g) was added to aqueous slurry (50 mL) of NaOH (0.25 g) and α-phenylcinnamic acid (1.41 g) in a Teflon-liner autoclave and heated to 100 °C for 48 h under hydrothermal condition. 0.20 g of obtained powder and 1 mL of quinoline were added to ethanolic solution (100 mL) and heated under reflux for 1 h, then filtered and left to crystallize. The purple block crystals were obtained and washed with ethanol and dried in the air. Anal. Calcd for $Co_3C_{108}O_{12}N_2H_{78}$: C, 73.10; N, 1.52; H, 4.71; Found: C, 73.10; N, 1.58; H, 4.54%.

The X-ray structure analysis of **1** revealed the molecular structure shown in Figure 1 consisting of a centrosymmetric, and linear, array of three cobalt atoms with three bridging phenylcinnamate between adjacent pairs.[9] The outer cobalt atoms, Co(1) and Co(1′) are each coordinated to a quinoline molecule to give distorted trigonal-bipyramidal coordination. The O–Co(1)–O bond angles in the trigonal site of $\{CoO_5\}$ range from 106.1(1) to 133.8(1)° and the bond distances range from 1.968(2) to 2.052(3) Å. The bond distances in the axial site are 2.265(3) and 2.113(4) Å for Co(1)–O(2) and Co(1)–N(1), respectively. The central cobalt atom, Co(2) has regular octahedral coordination. The O–Co(2)–O bond angles in the $\{CoO_6\}$ site range from 87.5(1) to 92.5(1)° and the bond distances range from 2.042(3) to 2.090(3) Å. Co(1)–Co(2) intracluster and Co(1)–Co(1′) nearest intercluster separations are 3.57 and 7.37 Å, respectively.

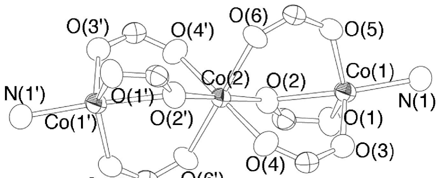

Figure 1. ORTEP representation at 50% probability level of linear trimer complex of **1**. Phenyl groups are omitted for clarity.

The magnetic properties of **1** were measured by SQUID magnetometor over the temperature range of 2–300 K.

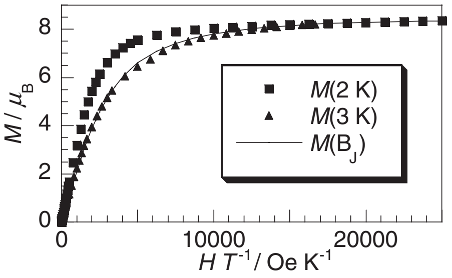

Figure 2. Field dependence of the magnetization per Co_3. The solid curve is fit by Brilloun function.

Figure 2 shows the field dependence of the magnetization per Co_3 cluster up to 50 kOe at 2 K and 3 K. The solid curve in Figure 2 is the fit of the data to the Brilloun function:

$$M(H/T) = pgS\mu_B B_J(H/T) \tag{1}$$

$$B_J(H/T) = \frac{2S+1}{2S}\frac{1}{\tanh\left[(2S+1/2S)\dfrac{gS\mu_B}{k_B}\dfrac{H}{T}\right]} - \frac{1}{2S}\frac{1}{\tanh\left[(1/2S)\dfrac{gS\mu_B}{k_B}\dfrac{H}{T}\right]}$$

where p is the effective molar fraction. The best fit of M(H/T) at 3 K with $S = 9/2$, $p = 0.89$ and $g = 2.1$ indicates **1** has ferromagnetic interaction between the nearest Co(II)^{HS} ions, Co(1)–Co(2) and Co(1′)–Co(2). The magnetization curve at 2 K has larger curvature than that of Brillouin function with $S = 9/2$, indicating that the ground state at 2 K is bigger than $S = 9/2$ and the interaction between adjacent trimers may be ferromagnetic. The temperature dependence of the susceptibility at 50 kOe per Co_3 cluster is shown in Figure 3. The effective magnetic moment of **1** at 300 K is 4.43 μ_B per Co ion, which is larger than the spin-only value 3.87 μ_B of Co(II)^{HS} and this difference comes from spin-orbit coupling. In order to approximate statistically the magnetic susceptibilities of octahedral Co(II) ions, which have large orbital contribution due to ground $^4T_1$ term, Lines introduced the fictitious spin $5/3\mathbf{s}$ ($s = 1/2$).[3] Here the linear trimer, which has one octahedral and two trigonal-bipyramidal Co ions, requires to apply modified Lines' approximation. For linear trimer, Hamiltonian is

$$H = -\frac{5}{3}J(\mathbf{s_1 s_2} + \mathbf{s_{1'} s_2}) - 2J'\mathbf{s}^{\mathrm{cl}}\mathbf{s}^{\mathrm{cl}} - g_0\mu_B H_0 \sum_i s_i^z \qquad (2)$$

where J is the exchange integral between adjacent Co atoms (1, 2 and 1′, 2) in the trimer, and J' is the nearest-neighbor cluster exchange integral. Here the plus sign and the minus sign of J and J' refer to ferromagnetic and antiferromagnetic interaction, respectively. For nearest neighbor clusters, the coordination number of 2 is assumed, and $\mathbf{s}^{\mathrm{cl}}$ is the total spin of a cluster. In Eq 2 the fictitious spin $5/3\mathbf{s}$ ($s = 1/2$) and $s = 1/2$ spins are considered for octahedral Co(2) and trigonal-bipyramidal Co(1) and Co(1′) ions, respectively. The magnetic susceptibility per trimer is as follows:

$$\chi_{trimer} = \frac{Ng_0^2\mu_B^2}{k_BT}F_{3'}(T) \qquad (3)$$

$$F_{3'}(T) = \frac{10 + \exp\left[\left(-\frac{5J}{2} - 6J'\right)\frac{1}{k_BT}\right] + \exp\left[\left(\frac{5}{6}J - 6J'\right)\frac{1}{k_BT}\right]}{8 + 4\exp\left[\left(-\frac{5J}{2} - 6J'\right)\frac{1}{k_BT}\right] + 4\exp\left[\left(\frac{5}{6}J - 6J'\right)\frac{1}{k_BT}\right]} \qquad (4)$$

The solid curve in Figure 3 is the fit of the data to the Eq 3 with $J/k_B = 17$ K, $2J'/k_B = 4$ K and $g_0 = 4.6$. The dashed lines are fit with $g_0 = 10/3 + k$; $k = 0.75$ (spin-orbit reduction factor for octahedral Co(II)^{HS} ion) using Lines' approximation and $g_0 = 4.8$ using $s = 1/2$ Heisenberg Hamiltonian. This simple approach is consistent with experimental magnetic susceptibility. The fitting with large g_0 value of **1** indicates large orbital contribution. For many clusters such as Co multinuclear complexes, simple approach may be valid as a primary approximation. Strict approximation of orbital contribution for **1** is now in progress.

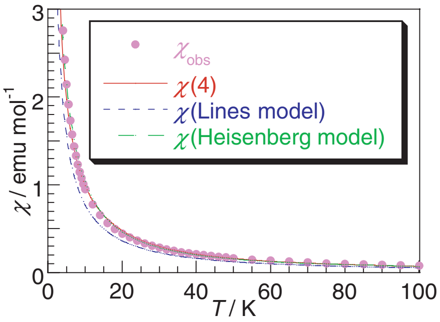

Figure 3. Temperature dependence of the magnetic susceptibility per Co_3. The solid curves are mentioned in text.

In conclusion, we synthesized and characterized a new cobalt trimer complex, $[Co_3(phcina)_6(quin)_2]$ with α-phenylcinnamate. This complex has $S = 9/2$ state. The magnetic susceptibility of linear trimer, which has one octahedral and two trigonal-bipyramidal coordination was analyzed by modified Lines model and fitted with $J = 12\,\mathrm{cm}^{-1}$ (ferromagnetic interaction between adjacent Co atoms), $J' = 1.4\,\mathrm{cm}^{-1}$ (ferromagnetic interaction between nearest-neighbor trimers) and $g_0 = 4.6$.

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12 Crystallographic data for $[Co_3(phcina)_6(quin)_2]$; $Co_3O_{12}N_2C_{108}H_{78}$, $M_r = 1772.61$, triclinic, space group $P1$, $a = 13.427(2)$, $b = 13.825(2)$, $c = 14.213(2)$ Å, $\alpha = 107.643(3)$, $\beta = 113.653(3)$, $\gamma = 98.355(3)°$, $V = 2192.7(6)$ Å^3, $Z = 1$, $D_{\mathrm{calcd}} = 1.342\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\ K}\alpha) = 8.30\,\mathrm{cm}^{-1}$, $R_1(I > 4\sigma) = 0.0629$, $R_w(\mathrm{all\ data}) = 0.1575$. Diffraction data were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo Kα radiation. The structure was solved by direct methods and refined by SHELXL. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-219936.

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