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# Magnetic behavior of dinuclear cobalt(II) complexes assumed to be caused by a paramagnetic impurity can be explained by tilts of local distortion axes

Katsuya Tone [a], Hiroshi Sakiyama [a,*], Masahiro Mikuriya [b], Mikio Yamasaki [c], Yuzo Nishida [a]

[a] *Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, 1-4-12 Kojirakawa, Yamagata 990-8560, Japan*
[b] *School of Science and Technology, Kwansei Gakuin University, Gakuen 2-1, Sanda 669-1337, Japan*
[c] *X-ray Research Laboratory, Rigaku Corporation, Matsubara 3-9-12, Akishima, Tokyo 196-8666, Japan*

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**Abstract**

A pair of dinucleating ligands *sym*-hmp$^-$ [*sym*-hmp$^-$: 2,6-bis[(2-hydroxyethyl)methylaminomethyl]-4-methylphenolate] incorporated two cobalt(II) ions to form a dinuclear cobalt(II) complex $[Co_2(sym\text{-hmp})_2](BPh_4)_2$ (**1**). Magnetic susceptibility indicated the antiferromagnetic exchange interaction; however, the susceptibility increased again below 20 K. Usually, such an increase is assumed to be caused by a paramagnetic impurity. However, the tilts of local distortion axes around cobalt(II) ions were found to cause the increase despite the antiferromagnetic interaction.


*Keywords:* Dinuclear cobalt(II) complex; Dinucleating ligand; Crystal structure; Magnetic studies

The magnetic behavior of octahedral high-spin cobalt(II) complexes is difficult to explain due to the orbital angular momentum [1]. In the magnetic behavior of dinuclear octahedral high-spin cobalt(II) complexes, the local spin–orbit coupling in a mononuclear unit is the dominant factor and is strongly affected by local distortion [2,3] around each cobalt(II) ion. The second dominant effect is the exchange interaction between the cobalt(II) ions, which is considered to be an interaction between the effective (1/2) spins [1,2] generated by the spin–orbit coupling. At this stage, two factors complicate the problem; one is the large anisotropy of the effective (1/2) spins, and the other is the orientation of the local distortion axes. Here, we report on the relationship between the crystal structure of a dinuclear cobalt(II) complex and its characteristic magnetic behavior for the purpose of solving the problem.

A pair of dinucleating ligands *sym*-hmp$^-$ [*sym*-hmp$^-$: 2,6-bis[(2-hydroxyethyl)methylaminomethyl]-4-methylphenolate] [4] incorporated two cobalt(II) ions to form a dinuclear cobalt(II) complex $[Co_2(sym\text{-hmp})_2](BPh_4)_2$ (**1**), which crystallized in the form **1** · 4.5DMF · 0.5(2-PrOH) (**1′**) [5]. A single-crystal X-ray analysis [6] revealed that the two cobalt(II) ions were bridged by two phenolate oxygen atoms of the ligands and the coordination geometries of both cobalt(II) ions were distorted octahedral (Fig. 1). The symmetry of the dinuclear core was approximated $C_2$, and the coordination geometries were twisted along the Co···Co axis.

For magnetic measurements, high-quality single crystals were powdered and used. When decreasing the temperature, the magnetic susceptibility ($\chi_A$) deviated from the Curie law (Fig. 2) because of the antiferromagnetic exchange interaction; however, the susceptibility increased again below 20 K. Usually, such an increase within a low-temperature range despite the antiferromagnetic interaction is assumed to be caused by a paramagnetic impurity

* Corresponding author. Tel.: +81 23 628 4601; fax: +81 23 628 4591.
*E-mail address:* saki@sci.kj.yamagata-u.ac.jp (H. Sakiyama).

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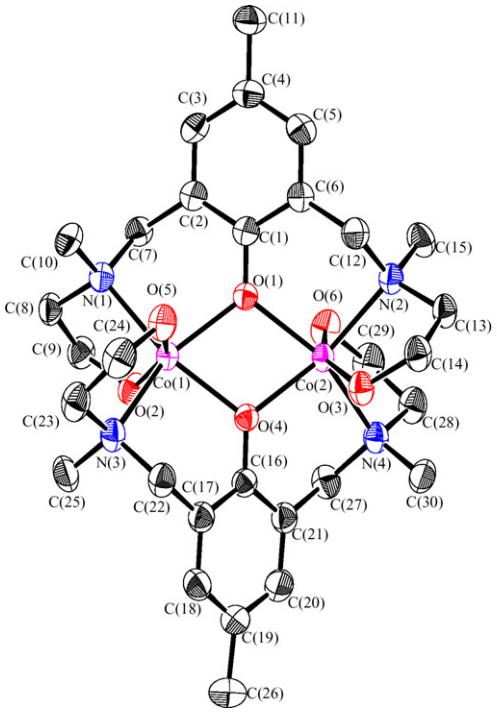


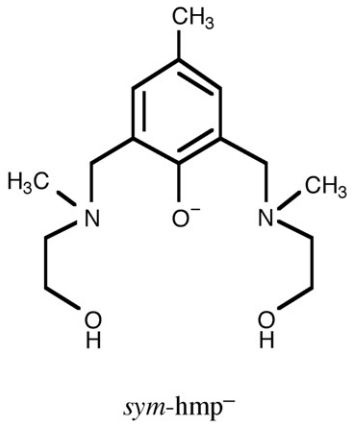


*sym*-hmp$^-$

Fig. 1. X-ray structure of $[Co_2(sym\text{-hmp})_2]^{2+}$. Selected distances (Å): Co(1)–O(1) 2.031(1), Co(1)–O(2) 2.088(2), Co(1)–O(4) 2.066(1), Co(1)–O(5) 2.182(2), Co(1)–N(1) 2.195(1), Co(1)–N(3) 2.228(2), Co(2)–O(1) 2.052(1), Co(2)–O(3) 2.176(1), Co(2)–O(4) 2.032(1), Co(2)–O(6) 2.136(1), Co(2)–N(2) 2.206(2), Co(2)–N(4) 2.193(2), Co(1)···Co(2) 3.2370(4).

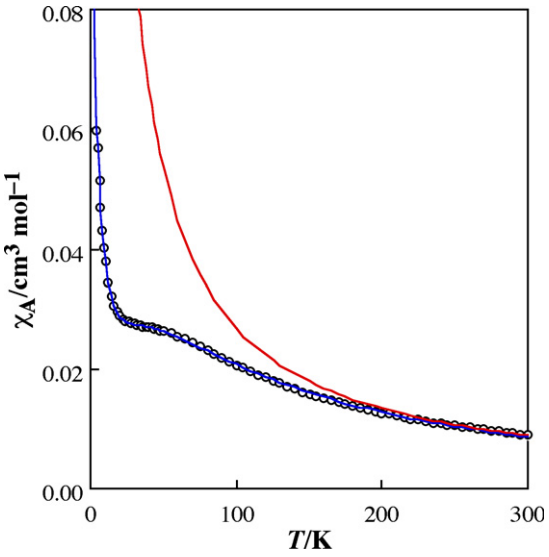


Fig. 2. Temperature dependencies of $\chi_A$ (O) of complex **1**′. A fitted curve is drawn with the parameters $\kappa = 0.77$, $\lambda = -173\ cm^{-1}$, $\Delta = -706\ cm^{-1}$, $\phi = 32.3°$, $\psi = 83.6°$, and $J = -27.3\ cm^{-1}$ using an equation [8] in this study. The other curve is based on the Curie law.

[1]. However, we concluded that this was not the case for the two following reasons. (1) The increase in susceptibility was well reproduced using different samples prepared separately. (2) In order to analyze the observed data assuming the paramagnetic impurity, about 6% of the impurity was necessary. It is improbable that the different single-crystal samples would always include 6% of the impurity because these samples are analytically pure within 0.5%.

Previously, one of the authors theoretically predicted [7] that despite the antiferromagnetic interaction, the magnetic susceptibility would increase within a low-temperature range due to the anisotropy of the exchange interaction. In the prediction, axial distortion around each cobalt(II) ion was considered and the local distortion axes were assumed to be parallel to the molecular principal axis. When the local distortion is so-called "negative" ($\Delta = \sim -800\ cm^{-1}$), the $z$ component of the magnetic susceptibility is higher than the others ($\chi_z > \chi_x = \chi_y$) within a higher-temperature range (Fig. 3a). Moreover, when the exchange interaction is antiferromagnetic, the $z$ component of the exchange integral is the largest ($|J_z| > |J_x| = |J_y|$). In other words, the higher $\chi_z$ curve drops significantly within a low-temperature range, whereas, the lower $\chi_x$ and $\chi_y$ curves do not drop within a low-temperature range. Therefore, superimposing the susceptibilities in all directions results in the increase in the magnetic susceptibility within a low-temperature range. However, in the case of complex **1**′, the increase below 20 K was higher than we expected and could be simulated when the two local distortion axes were assumed to tilt toward the $y$ direction, as described below.

In order to describe the orientation of the local distortion axis, the tilt angle $\phi$ and tilt direction angle $\psi$ were introduced (Fig. 4a). The local symmetry was assumed to be axial; however, the molecular symmetry became rhombic due to the tilts of the local distortion axes. When