Inorg. Chem. **2002**, *41*, 4058–4062

Inorganic Chemistry
Article

Synthesis, Structure, and Magnetic Properties of Dinuclear Cobalt(II) Complexes with a New Phenol-Based Dinucleating Ligand with Four Hydroxyethyl Chelating Arms

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Received February 5, 2002

A new end-off type acyclic ligand with four hydroxyethyl arms, 2,6-bis[bis(2-hydroxyethyl)aminomethyl]-4-methylphenol [H(bhmp)], formed dinuclear cobalt(II) complexes $[Co_2(bhmp)(OAc)_2]BPh_4$ (**1**) and $[Co_2(bhmp)(OBz)_2]BPh_4$ (**2**). The complex **1**·2.5CH$_3$CN ($C_{50}H_{62.5}BCo_2N_{4.5}O_9$) crystallizes in the monoclinic space group *C*2/*c* with dimensions $a = 25.424(5)$ Å, $b = 13.376(2)$ Å, $c = 29.913(6)$ Å, $\beta = 105.930(3)°$, and $V = 9781(3)$ Å^3 and with $Z = 8$. X-ray diffraction analysis revealed a μ-phenoxo–bis(μ-acetato)dicobalt(II) core structure containing two octahedral cobalt(II) ions. Electronic spectra were investigated for **1** and **2** in the range 400–1800 nm, and the data were typical for the octahedral high-spin cobalt(II) complexes. Magnetic susceptibility was measured for **1** and **2** over the temperature range 4.5–300 K, and the data were analyzed well using our theoretical method. The best fitting parameters were $\kappa = 0.77$, $\lambda = -116$ cm^{-1}, $\Delta = 572$ cm^{-1}, and $J = -0.44$ cm^{-1} for complex **1** and $\kappa = 0.96$, $\lambda = -93$ cm^{-1}, $\Delta = 616$ cm^{-1}, and $J = -0.33$ cm^{-1} for complex **2**.

Introduction

The magnetism of dinuclear high-spin cobalt(II) complexes is a challenging area because the orbital angular momentum causes difficulties in the magnetic analysis.[1] In general, the orbital angular momentum is partially quenched in a ligand field of a certain symmetry.[2] For instance, in a ligand field of O_h symmetry, only the orbital angular momenta of T terms (T_{1g}, T_{1u}, T_{2g}, and T_{2u}) remain as a result of the quenching. When the symmetry is decreased to D_{3h}, only E terms (E′ and E″) have orbital angular momenta. Thus, the effect of the orbital angular momentum is highly dependent on the symmetry around the metal ion. To our knowledge, the magnetism of the high-spin cobalt(II) complexes is classified into three groups: (1) an ideal octahedral or slightly distorted octahedral case, in which a ground term possesses an orbital angular momentum; (2) a tetrahedral, square-planer, trigonal-bipyramidal, or highly distorted octahedral case, in which a ground term does not have an orbital angular momentum; and (3) a highly distorted lower symmetric case, in which a ground term has an orbital angular momentum. In group 1, under an ideal O_h symmetry, the ground $^4T_{1g}$ term possesses the orbital angular momentum. Thus, to analyze the magnetic data, the effect of the orbital angular momentum should be taken into account.[1] In group 2, the ground term does not have an orbital angular momentum; thus, a spin-only treatment is valid for the complexes in this group. The effect of the higher term possessing an orbital momentum can be treated as a second-order Zeeman effect.[2] In group 3, the ground term possesses an orbital angular momentum due to the admixture with higher states.[2] At this stage, an appropriate method should be selected to consider the symmetry around the cobalt(II) ion for magnetic analysis.

In the magnetic analysis of homo dinuclear high-spin cobalt(II) complexes, the classification above is also valuable. It is not difficult to understand the magnetism of the dinuclear complexes containing two cobalt(II) ions classified into group

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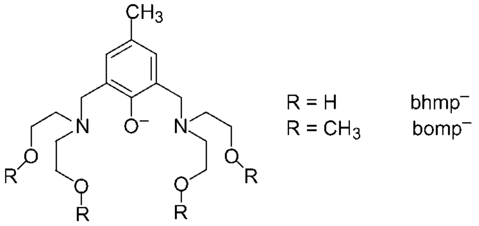
10.1021/ic0255297 CCC: $22.00

Chart 1. Chemical Structures of bhmp− (R = H) and bomp− (R = CH_3)



2 because the spin-only treatment is possible. However, it is much more difficult to elucidate the magnetism of the dinuclear complexes containing two cobalt(II) ions classified into group 1 because of the T ground term with an orbital angular momentum, and there have been only a few successful examples.[3−6] In 1971, Lines reported a theory for the analysis of the magnetic coupling between two high-spin cobalt(II) ions of pure O_h symmetry using a temperature-dependent Hamiltonian.[3] This remarkable theory enabled the analysis of the magnetic data of some dinuclear cobalt(II) complexes,[5] but it was limited to only highly symmetrical cases. This limitation sometimes causes problems in the magnetic analysis since the symmetry around the real cobalt(II) ions is at best axial.[1] Taking the anisotropy into account, Drillon and co-workers made a successful low-temperature study.[4] In a whole-temperature-range magnetic analysis for the dinuclear complexes classified into group 1, Lines's theory[3] had been the only efficient way until we developed a new approximation method.[6] In order to introduce a distortion around the cobalt(II) ions, we adopted the axial splitting parameter Δ, which was used by Lines[7] and Figgis[8] for mononuclear complexes to avoid over-parametrization. In our approximation method, the magnetic coupling between the two cobalt(II) ions is assumed to be effective only between the lowest energy levels of each cobalt(II) ion among the six energy levels generated from the $^4T_{1g}$ ground term by spin−orbit coupling. This approximation method gives a good result because the energy gap between the lowest and the second-lowest energy levels (∼300 cm^{-1}) is, in general, much larger than the magnetic coupling J ($|J| < 5$ cm^{-1}). It should be emphasized that the result obtained by our method is identical to that obtained by Lines's theory when the splitting parameter Δ is zero.

In this study, a new acyclic end-off type dinucleating ligand, 2,6-bis[bis(2-hydroxyethyl)aminomethyl]-4-methylphenol [H(bhmp)], was synthesized (Chart 1), and, with the intention of revealing the relationship between the structure and magnetism of dinuclear cobalt(II) complexes, new dinuclear cobalt(II) complexes $[Co_2(bhmp)(OAc)_2]BPh_4$ (**1**) and $[Co_2(bhmp)(OBz)_2]BPh_4$ (**2**) were synthesized.

Experimental Section

Measurements. Elemental analyses (C, H, and N) were obtained at the Elemental Analysis Service Centre of Kyushu University. IR spectra were recorded on a Hitachi 270-50 spectrometer. ^1H and ^{13}C NMR spectra (400 MHz) were measured on a JEOL JNM-α400 spectrometer in $CDCl_3$ using $SiMe_4$ as the internal standard. Electronic spectra were measured in *N*,*N*-dimethylformamide (DMF) on Jasco V-560 (400−900 nm) and Hitachi 330 (900−1800 nm). Molar conductances were measured in DMF on a DKK AOL-10 conductivity meter at room temperature. The temperature dependence of the magnetic susceptibilities was measured with a Quantum Design MPMS-5S SQUID susceptometer operating at a magnetic field of 0.5 T between 4.5 and 300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constant.[1] The effective magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.828(\chi_A T)^{1/2}$, where χ_A is the atomic magnetic susceptibility. All the magnetic calculations were made using the MagSaki[9] magnetic software program of our laboratory.

Synthesis of Na(bhmp). To an aqueous solution (40 mL) containing *p*-cresol (5.41 g, 50.0 mmol), NaOH (2.00 g, 50.0 mmol), and bis(2-hydroxyethyl)amine (10.55 g, 100 mmol) were added paraformaldehyde (3.00 g, 100 mmol) and ethanol (20 mL), and the resulting solution was refluxed for 4 h. On cooling to 0 °C Na(bhmp) was obtained as a white powder. Yield: 7.60 g (42%). Selected IR data (ν/cm^{-1}) using KBr disks: 3500−3200, 2980, 1658, 1608, 1444, 1366, 1300, 1146, 1052, 866 and 764. ^1H NMR ($CDCl_3$: δ, ppm): 2.22 (*s*, 3H, CH_3), 2.69 (*t*, 8H, NCH_2R), 3.67 (*t*, 8H, OCH_2), 3.73 (*s*, 4H, $ArCH_2N$), 6.79 (*s*, 2H, ArH). ^{13}C NMR ($CDCl_3$; δ, ppm): 20.40 (CH_3), 55.63 (NCH_2R), 57.12 ($ArCH_2N$), 59.25 (OCH_2), 123.48 (ArH), 128.04 ($ArCH_3$), 130.13 (Ar), 153.71 (ArO).

$[Co_2(bhmp)(OAc)_2]BPh_4$ (1). To a methanolic solution (15 mL) of Na(bhmp) (0.19 g, 0.52 mmol) was added cobalt(II) acetate tetrahydrate (0.25 g, 1.00 mmol), and the resulting solution was refluxed for 1 h to give a deep violet solution. The addition of sodium tetraphenylborate (0.17 g, 0.50 mmol) resulted the precipitation of pink microcrystals. Yield: 0.32 g (67%). Anal. Found: C, 60.16; H, 6.27; N, 3.36; Co, 13.5. Calcd for $C_{45}H_{55}BCo_2N_2O_9$: C, 60.28; H, 6.18; N, 3.12; Co, 13.15. Selected IR data (ν/cm^{-1}) using KBr disks: 3600−3300, 3100, 2988, 1588, 1472, 1422, 1340, 1258, 1016, 866, 730, 702, 606. Molar conductance [Λ/S cm^2 mol^{-1}]: 37.

$[Co_2(bhmp)(OBz)_2]BPh_4$ (2). This was prepared as pink microcrystals by a method similar to that of **1** using cobalt(II) benzoate instead of cobalt(II) acetate tetrahydrate. Yield: 0.60 g (58%). Anal. Found: C, 64.44; H, 5.82; N, 2.77; Co, 11.8. Calcd for $C_{55}H_{59}BCo_2N_2O_9$: C, 64.72; H, 5.83; N, 2.74; Co, 11.63. Selected IR data (ν/cm^{-1}) using KBr disks: 3600−3300, 2988, 1600, 1562, 1474, 1390, 1258, 1046, 1128, 868, 704, 604. Molar conductance [Λ/S cm^2 mol^{-1}]: 40.

Single-Crystal X-ray Analysis of Complex $1\cdot2.5CH_3CN$. Experimental data were summarized in Table 1. All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation. The data were collected to a maximum 2θ value of 55.0°. Of the 45995 reflections, 11123 were unique ($R_{\text{int}} = 0.044$). A symmetry-related absorption correction using the program REQAB[10] was applied which resulted

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Table 1. Crystallographic Data for **1**·2.5CH$_3$CN

empirical formula	$C_{50}H_{62.50}BCo_2N_{4.50}O_9$
a/Å	25.424(5)
b/Å	13.376(2)
c/Å	29.913(6)
β/deg	105.930(3)
V/Å^3	9781(3)
Z	8
fw	999.24
space group	$C2/c$ (No. 15)
T/°C	-160 ± 1
λ/Å	0.71070
D_{calcd}/g cm^{-3}	1.357
μ(Mo Kα)/cm^{-1}	7.38
$R(F_o^2)^a$	0.052
$R_w(F_o^2)^b$	0.081

^{a} $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$. ^{b} $R_w = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

in transmission factors ranging from 0.77 to 0.89. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[11] and expanded using Fourier techniques.[12] Most of the non-hydrogen atoms were refined anisotropically, while the disordered atoms were refined isotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 11123 observed reflections. All calculations were performed using the teXsan[13] crystallographic software package of Molecular Structure Corporation.

Results and Discussion

Crystal Structure of Complex 1·2.5CH$_3$CN. The crystal structure consists of [Co$_2$(bhmp)(OAc)$_2$]$^+$ complex cations, tetraphenylborate anions, and acetonitrile molecules in a 1:1:2.5 molar ratio. The structure of the complex cation is depicted in Figure 1. Selected distances and angles with their estimated standard deviations are listed in Table 2. The complex cation consists of one dinucleating ligand bhmp$^-$, two cobalt(II) ions, and two acetate ions. The two cobalt(II) ions are bridged by one phenolic oxygen of bhmp$^-$ and two acetate ions, forming a μ-phenoxo−bis(μ-acetato)dicobalt(II) core structure. The Co(1)···Co(2) separation is 3.3563(5) Å. A similar separation [3.3360(3) Å] was found in the related dinuclear cobalt(II) complex [Co$_2$(bomp)(OAc)$_2$]BPh$_4$ (**3**) [H(bomp) = 2,6-bis[bis(2-methoxyethyl)-aminomethyl]-4-methylphenol].[6] The bridging angle Co(1)−O(1)−Co(2) is 112.21(6)°, and a similar bridging angle [113.03(6)°] was found in complex **3**.[6]

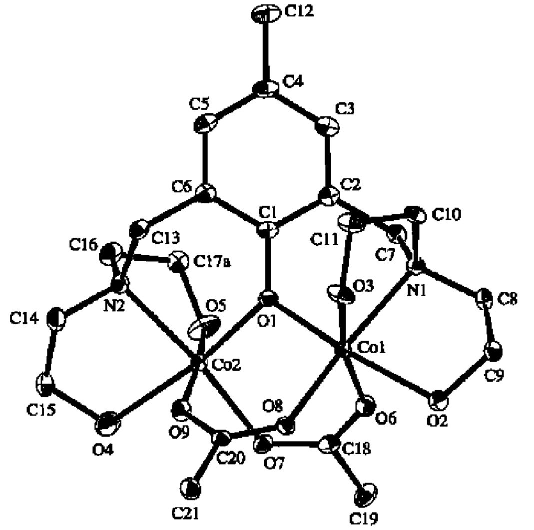

Figure 1. ORTEP[14] view of the complex cation [Co$_2$(bhmp)(OAc)$_2$]$^+$ in **1** with the atom-numbering scheme.

Table 2. Selected Distances (Å) and Angles (deg) for **1**·2.5CH$_3$CN

Distances (Å)			
Co(1)−O(1)	2.027(1)	Co(2)−O(1)	2.016(1)
Co(1)−O(2)	2.178(1)	Co(2)−O(4)	2.158(2)
Co(1)−O(3)	2.070(1)	Co(2)−O(5)	2.073(1)
Co(1)−O(6)	2.090(1)	Co(2)−O(7)	2.093(1)
Co(1)−O(8)	2.070(1)	Co(2)−O(9)	2.113(1)
Co(1)−N(1)	2.178(2)	Co(2)−N(2)	2.163(2)
Co(1)···Co(2)	3.3563(5)		

Angles (deg)			
O(1)−Co(1)−O(2)	164.62(5)	O(1)−Co(2)−O(4)	162.39(6)
O(1)−Co(1)−O(3)	99.16(5)	O(1)−Co(2)−O(5)	99.70(6)
O(1)−Co(1)−O(6)	89.93(5)	O(1)−Co(2)−O(7)	101.57(5)
O(1)−Co(1)−O(8)	101.11(5)	O(1)−Co(2)−O(9)	90.19(5)
O(1)−Co(1)−N(1)	90.42(5)	O(1)−Co(2)−N(2)	91.21(5)
O(2)−Co(1)−O(3)	91.54(5)	O(4)−Co(2)−O(5)	93.28(6)
O(2)−Co(1)−O(6)	78.36(5)	O(4)−Co(2)−O(7)	90.73(5)
O(2)−Co(1)−O(8)	90.06(5)	O(4)−Co(2)−O(9)	77.05(6)
O(2)−Co(1)−N(1)	81.17(5)	O(4)−Co(2)−N(2)	79.62(6)
O(3)−Co(1)−O(6)	168.93(6)	O(5)−Co(2)−O(7)	87.69(5)
O(3)−Co(1)−O(8)	88.77(5)	O(5)−Co(2)−O(9)	170.11(6)
O(3)−Co(1)−N(1)	77.18(5)	O(5)−Co(2)−N(2)	78.87(6)
O(6)−Co(1)−O(8)	95.70(5)	O(7)−Co(2)−O(9)	90.31(5)
O(6)−Co(1)−N(1)	96.58(5)	O(7)−Co(2)−N(2)	162.88(5)
O(8)−Co(1)−N(1)	163.14(5)	O(9)−Co(2)−N(2)	101.10(5)
Co(1)−O(1)−Co(2)	112.21(6)		

Atom Co(1) has a six-coordinate distorted octahedral geometry with O(1), O(2), O(3), and N(1) of bhmp$^-$ and O(6) and O(8) of the two acetate groups. The coordination geometry around Co(2) is also distorted octahedral with O(1), O(4), O(5), and N(2) of bhmp$^-$ and O(7) and O(9) of the acetate groups. The geometries around Co(1) and Co(2) are very similar to each other, and the complex cation has a pseudo-C_2 axis along C(12), C(4), C(1), and O(1). The least-squares plane of the aromatic ring of bhmp$^-$ and the plane defined by Co(1), Co(2), and O(1) are twisted with a dihedral angle of 45°. This dihedral angle is similar to that of the related cobalt(II) complex **3** (46°).

A characteristic feature in the structure of complex **1** is the distortion around the cobalt atoms. The bond distances between cobalt atoms and equatorial alcoholic oxygens [2.178(1)−2.158(2) Å] are longer than those between cobalt and axial alcoholic oxygens [2.070(1)−2.073(1) Å], whereas, in the case of complex **3**, the bond distances between cobalt atoms and axial ether oxygens [2.200(1)−2.229(1) Å] are longer than the equatorial ones [2.156(1)−2.160(1) Å]. Thus, the distortion pattern around cobalts in complex **1** is different from that in complex **3**, presumably because of the less-hindered hydroxy groups of bhmp$^-$.

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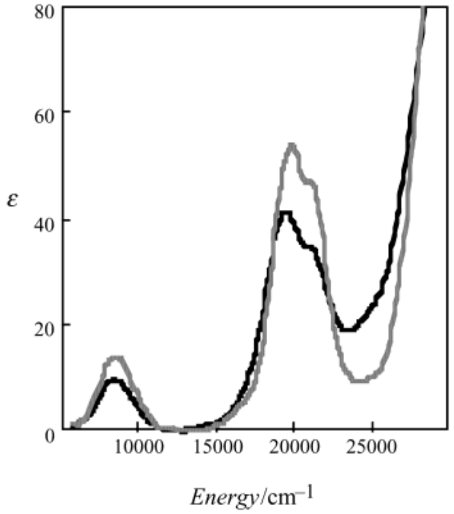

Figure 2. Electronic spectra for the complexes **1** (solid line) and **2** (shaded line) in DMF.

Table 3. Electronic Spectral Components for **1** and **2** (cm^{-1})

	complex **1**		complex **2**	
transition	obsd[a]	calcd	obsd[a]	calcd
$^4T_1 \rightarrow {}^2T_2(^2G), {}^2T_1(^2G)$	21500(32)	20700, 22300	21200(46)	20400, 22000
$^4T_1 \rightarrow {}^4T_1(^4P)$	19300(42)	19300	19300(52)	19300
$^4T_1 \rightarrow {}^4T_2(^4F)$	8300(10)	8300	8400(14)	8400

[a] The ε values are in parentheses.

Electronic Spectra of Complexes 1 and 2. Electronic spectra for **1** and **2** are shown in Figure 2. The spectral features of the complexes are very similar to each other, and they are typical for the octahedral high-spin cobalt(II) complexes,[2] as shown by the X-ray analysis for complex **1**. However, the spectrum for **2** is slightly higher in intensity than that for **1**. This may indicate that the coordination geometry around cobalt(II) ions in complex **2** is more distorted than that in **1** and the Laporte forbidden rule is thus much more relaxed. The peak positions of the spectral components obtained by the Gaussian curve analysis are summarized with their molar absorption coefficients in Table 3. The strongest absorption band around 19300 cm^{-1} was assigned to $^4T_1 \rightarrow {}^4T_1(^4P)$, the weak shoulder around 21500 cm^{-1} was assigned to $^4T_1 \rightarrow {}^2T_2(^2G)$, $^2T_1(^2G)$, and the broad band around 8300 cm^{-1} was assigned to $^4T_1 \rightarrow {}^4T_2(^4F)$ for complex **1**. For complex **2**, the spectral components were assigned in the same way.

A spectral simulation was also made using calculations from the angular overlap model (AOM). In this study, the average value was used for e_σ, and the π orbital contribution was neglected. Optimization of the AOM parameter e_σ and Racha parameters B and C was performed using the AOMX[2] program developed by Adamsky. The observed data were well simulated by the calculation from the AOM with the parameters $e_\sigma = 3140$ cm^{-1}, $B = 810$ cm^{-1}, and $C = 2570$ cm^{-1} for complex **1** and $e_\sigma = 3170$ cm^{-1}, $B = 800$ cm^{-1}, and $C = 2460$ cm^{-1} for complex **2**. The obtained parameters are normal for octahedral high-spin cobalt(II) complexes with the N and O donor atoms ($e_\sigma = \sim 4000$ cm^{-1} for N and ~ 3000 cm^{-1} for O).[15]

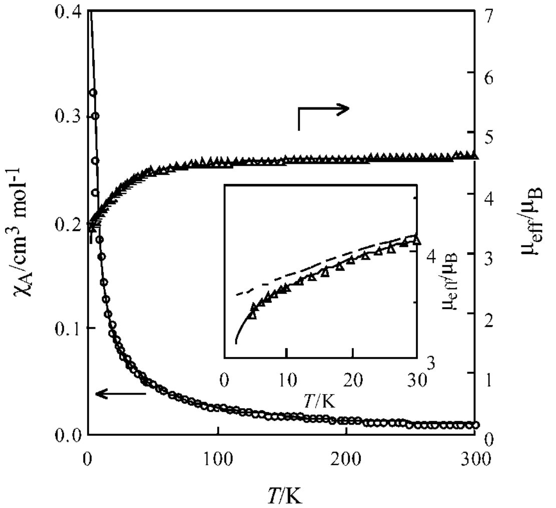

Figure 3. Temperature dependencies of χ_A (○) and μ_{eff} (△) of the complex **1**. Solid curves are drawn with the parameters $\kappa = 0.77$, $\lambda = -116$ cm^{-1}, $\Delta = 572$ cm^{-1}, and $J = -0.44$ cm^{-1}. Dashed curves are drawn with the parameters $\kappa = 0.77$, $\lambda = -116$ cm^{-1}, $\Delta = 572$ cm^{-1}, and $J = 0$ cm^{-1}.

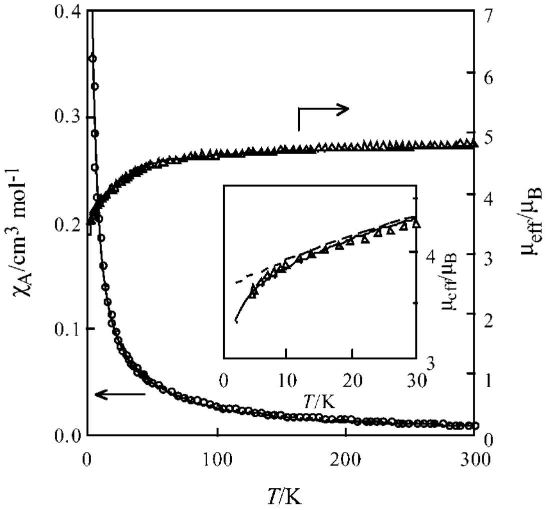

Figure 4. Temperature dependencies of χ_A (○) and μ_{eff} (△) of the complex **2**. Solid curves are drawn with the parameters $\kappa = 0.96$, $\lambda = -93$ cm^{-1}, $\Delta = 616$ cm^{-1}, and $J = -0.33$ cm^{-1}. Dashed curves are drawn with the parameters $\kappa = 0.96$, $\lambda = -93$ cm^{-1}, $\Delta = 616$ cm^{-1}, and $J = 0$ cm^{-1}.

Magnetic Properties of Complexes 1 and 2. Magnetic susceptibility measurements for complexes **1** and **2** were made on polycrystalline samples in the temperature range 4.5−300 K. The temperature dependencies of χ_A and μ_{eff} per Co for **1** and **2** are shown in Figures 3 and 4. The μ_{eff} values per Co of the complexes at room temperature are 4.58 and 4.83 μ_B, respectively. These values are larger than the spin-only value of high-spin cobalt(II) (3.87 μ_B; $\mu_{so} = [4S(S+1)]^{1/2}$; $S = {}^3/_2$) but close to the value expected when the spin momentum and orbital momentum exist independently [5.20 μ_B; $\mu_{ls} = [L(L+1) + 4S(S+1)]^{1/2}$; $L = 3$, $S = {}^3/_2$]. This indicates a contribution of the orbital angular momentum typical for the $^4T_{1g}$ ground term. The magnetic moments decrease with decreasing temperature, and this can be elucidated considering three factors: the contribution of the

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Table 4. Magnetic Data for Complexes **1**−**4**

complex	κ	λ/cm^{-1}	Δ/cm^{-1}	J/cm^{-1}	g_z	g_x	D/cm^{-1}	$R(\chi_A)$	$R(\mu_{eff})$	ref
1	0.77	−116	572	−0.44	2.11	4.73	74	3.6×10^{-5}	3.6×10^{-6}	this work
2	0.96	−93	616	−0.33	2.09	4.91	69	1.6×10^{-4}	5.9×10^{-5}	this work
3	0.98	−134	749	−0.55	2.18	4.99	120	1.2×10^{-4}	8.9×10^{-5}	6
4	0.84	−138	440	−0.70	2.45	4.84	144	1.7×10^{-3}	1.6×10^{-4}	6

orbital angular momentum, an intramolecular magnetic coupling between two Co(II) ions, and an intermolecular antiferromagnetic coupling. In order to evaluate them, the experimental data were analyzed as described below.

First, the spin-only equation for the $^3/_2$ spin system based on the Heisenberg model ($H = -J\mathbf{S}_1 \cdot \mathbf{S}_2$) was used for the analysis, but the data could not be explained. Next, Lines's theory[3] was used, considering spin−orbit coupling, but the cryomagnetic data could not be fitted well. Thus, our approximation method[6] was used to consider the distortion around the cobalt(II) ions, and the data could be well analyzed. The magnetic susceptibility χ_A was calculated with the following equations:

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

$$\chi_{z(x)} = N \times \frac{\sum_{n=\pm 1}\left(\frac{{E_{z(x),n}^{(1)}}^{2}}{kT} - 2E_{z(x),n}^{(2)}\right)\exp\left[\frac{-E_n^{(0)} + \frac{25J}{36}}{kT}\right] + \sum_{n\neq\pm 1}\left(\frac{{E_{z(x),n}^{(1)}}^{2}}{kT} - 2E_{z(x),n}^{(2)}\right)\exp\left[\frac{-E_n^{(0)}}{kT}\right]}{\frac{1}{4}\sum_{n=\pm 1}\exp\left[\frac{-E_n^{(0)} - \frac{75J}{36}}{kT}\right] + \frac{3}{4}\sum_{n=\pm 1}\exp\left[\frac{-E_n^{(0)} + \frac{25J}{36}}{kT}\right] + \sum_{n\neq\pm 1}\exp\left[\frac{-E_n^{(0)}}{kT}\right]}$$

where $E_n^{(0)}$ is the energy of level n in the zero field ($n = \pm 1$ to ± 6), $E_n^{(1)}$ and $E_n^{(2)}$ were first- and second-order Zeeman coefficients, respectively, and other symbols have their usual meanings. The Zeeman coefficients $E_n^{(0)}$, $E_n^{(1)}$, and $E_n^{(2)}$ were calculated by equations reported previously.[6] The best-fitting parameters were $\kappa = 0.77$, $\lambda = -116$ cm^{-1}, $\Delta = 572$ cm^{-1}, and $J = -0.44$ cm^{-1} for complex **1** and $\kappa = 0.96$, $\lambda = -93$ cm^{-1}, $\Delta = 616$ cm^{-1}, and $J = -0.33$ cm^{-1} for complex **2**, where κ was the orbital reduction factor and λ was a spin-only coupling constant. The axial splitting parameter Δ is defined as the splitting of the orbital degeneracy of the $^4T_{1g}$ term by the asymmetric ligand component, in the absence of any spin−orbit coupling, and is taken to be positive when the orbital singlet is lowest. The $R(\chi_A)$ values, defined as $R(\chi_A) = \sum[(\chi_{A,calc} - \chi_{A,obs})^2]/(\chi_{A,obs})^2$, were 3.6×10^{-5} and 1.66×10^{-4}. The axial zero-field splitting parameter D is defined as the energy gap between the two Kramers doublets splitting of the lowest orbital singlet from the $^4T_{1g}$ term, and is taken to be positive when the doublet referring to $M_S = \pm^1/_2$ is lowest. The D, g_z, and g_x values can be calculated by our method and are summarized with the best-fitting parameters in Table 4.

The obtained axial splitting parameter Δ for **2** is larger than that for **1**, and this is consistent with the fact that the distortion around the cobalt(II) ion for **2** is larger than that for **1**, as discussed in the above section. The Δ values are normal for high-spin cobalt(II) complexes (∼200 to ∼800 cm^{-1}).[16] The orbital reduction factor κ corresponds to the delocalization of unpaired electrons from metal ions to ligand, but it also contains the admixture of the upper $^4T_{1g}$(^{4}P) state into the $^4T_{1g}$(^{4}F) ground state. The κ value is known to be ∼0.93 for free cobalt(II) ion[3,17] but is generally lower than this when in the complexes.[3] The κ value for complex **1** is quite normal for this kind of complex, but the value for **2** is slightly deviated from the normal value. This may be due to the fact that the grade of the approximation decreases when Δ becomes larger. Thus, the quality of the magnetic analysis for **2** was slightly worse than that for **1** because of the larger distortion for **2**. The same discussion can be made for the obtained spin−orbit coupling constant λ. Theoretically, the expected λ value is -172 cm^{-1} for the free cobalt(II) ion, and the deviation from this value increases with increasing Δ.

In the best-fitting parameters, the J values were used since the theoretically obtained cryomagnetic μ_{eff} curves assuming $J = 0$ were apparently different from the obtained data in the low-temperature region, as shown in the insertions of Figures 3 and 4. However, the obtained J values are small, and the magnetic behavior can also be attributed to the intermolecular interaction. Thus, it is impossible to separate the intramolecular interactions from the intermolecular interactions in the present cases, and we will conclude that the intramolecular magnetic interactions between the two cobalt(II) ions in complex cations are negligible for the both complexes.

Conclusion

In this study, two dinuclear cobalt(II) complexes (**1** and **2**) were made using the dinucleating ligand, bhmp$^-$, and the crystal structure of complex **1** was determined. For the purpose of analyzing the cryomagnetic data, our approximation method was used, and the experimental data were successfully analyzed. This shows that the method we developed is also suitable for the present complexes, which have a different distortion pattern from previous complexes.

Acknowledgment. We thank Dr. Thomas Schönherr and Dr. Heribert Adamsky in Heinrich-Heine-Universität Düsseldorf for providing a copy of the AOMX program.

Supporting Information Available: An X-ray crystallographic file in CIF format, results of AOM calculations, cryomagnetic data, and a set of magnetic equations. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0255297

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