A Unique Two-Dimensional Terephthalate-Bridged Structure with Alternate Tetra- and Penta-Coordinate Cobalt(II) Sites. Synthesis, Crystal Structure and Magnetic Properties of [{$Co_3(tp)_2(OH)_2(phen)_2$}$_n$]

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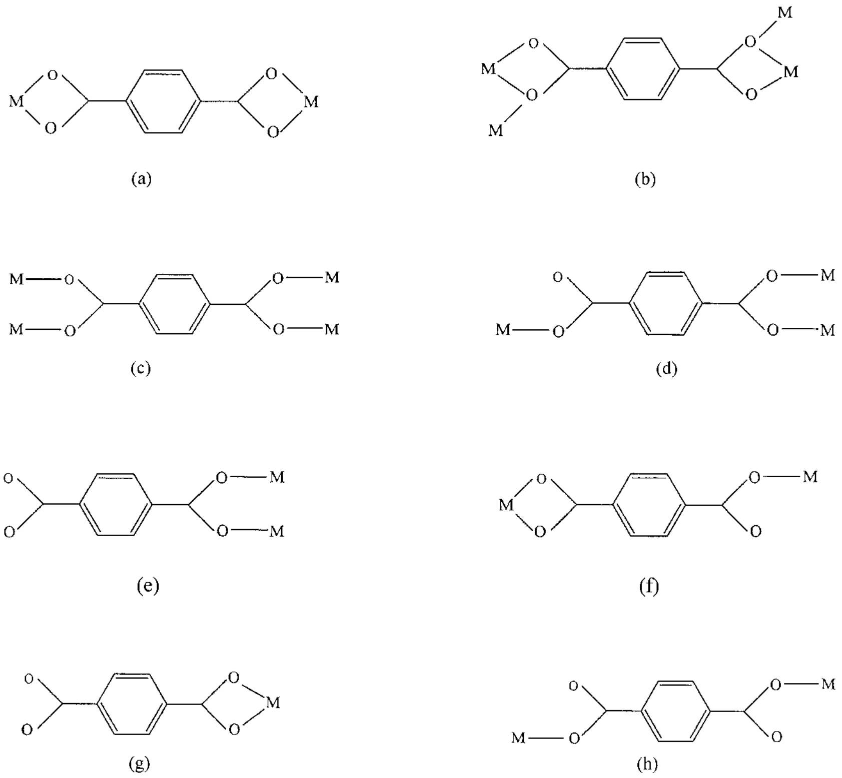
A two-dimensional (2D) cobalt coordination polymer [{$Co_3(tp)_2(OH)_2(phen)_2$}$_n$] (**1**), bridged by the terephthalate (tp) ligand, was synthesized under hydrothermal conditions, and its structure was determined by single-crystal X-ray diffraction. Complex **1** crystallized in the triclinic space group $P\bar{1}$ with $a = 8.2620(11)$ Å, $b = 10.4409(12)$ Å, $c = 11.0840(10)$ Å, $\alpha = 111.332(8)^\circ$, $\beta = 91.394(10)^\circ$, $\gamma = 91.638(10)^\circ$, $Z = 2$, $V = 889.65(18)$ Å^3. A structure refinement showed that complex **1** is the first example of a two-dimensional (2D) framework with both carboxylate bridges and μ-hydroxo bridges, in which cobalt atoms adopt square-pyramidal and square-planar geometries. Complex **1** exhibited a interesting magnetic behavior: the shape of the μ_{eff} curve indicates a ferrimagnetic-like behavior between 300–41.0 K, immediately followed by a strong decay of the magnetic moment. Moreover, complex **1** was characterized by IR spectroscopy, inductively coupled plasma (ICP), elemental and thermogravimetric (TGA) analyses.

Much attention has been paid to inorganic-organic hybrid materials owing to their potential applications in catalysis, magnetism, separation, gas storage and molecular recognition.[1] The organic components offer great potential for chemical and structural diversity. For example, organic polycarboxylates are most widely used as bridging ligands for designing inorganic-organic hybrid materials with interesting magnetic properties. The terephthalate (tp) ligand, as a bridge among paramagnetic metal centers, has been extensively studied.[2–13] Magnetic interactions transmitted through phenyldicarboxylate bridges are usually weak,[3,4,11–13] and coupling interactions can be influenced by such factors as the separation of the metal centers[2,6,8,9,12,13] and bridging modes,[3,4,10,13] as well as the dihedral angles between the carboxylato planes and the phenyl ring.[2–6,10,11,13] The terephthalate ligand has been used in many synthetic systems, for it can form either short bridges via one carboxylato end, or long bridges via the benzene ring. Also, the coordination modes of the carboxyl groups in the terephthalate, as reported in papers, are summarized in Scheme 1.[2–22] The synthesis and structures of coordination polymers containing only of coordination mode of the terephthalate ligand have been reported more often.[2–15,17–22] Comparatively, coordination polymers based on two coordination modes of the terephthalate ligands have been reported, but obviously seldom.[16] Moreover, because reports on inorganic–organic frameworks with unsaturated metal sites are scanty in the literature,[23–26] the synthesis of this hybrid material can not only help us to understand how to design inorganic-organic frameworks with unsaturated metal sites, but also to provide frameworks with higher selectivity in catalysis. In particular, cobalt ions may be used for the preparation of multi-dimensional inorganic-organic hybrid materials with unsaturated metal sites. We are reporting on the synthesis and crystal structure of a novel two-dimensional complex containing mixed coordination metal centers and mixed coordination modes of the terephthalate ligands, namely [{$Co_3(tp)_2(OH)_2(phen)_2$}$_n$] (**1**).

Experimental

Preparation of [{$Co_3(tp)_2(OH)_2(phen)_2$}$_n$] (1). Complex **1** was synthesized by sealing up a mixture of $CoCl_2 \cdot 6H_2O$ (0.48 g, 2.0 mmol), terephthalic acid (0.50 g, 3.0 mmol), 1,10-phenanthroline (0.2 g, 1.0 mmol), KOH (0.45 g, 8.0 mmol) and H_2O (20 mL) with a mole ratio of 2:3:1:8:1111 in a 30 mL Teflon-lined autoclave, and crystallized at 160 °C for five days. The deep-red crystal was isolated by filtration and washed with distilled water (yield: 75% based on phen). Found: C, 53.19; H, 2.84; N, 6.40; Co, 19.32%. Calcd for **1**, $C_{20}H_{13}Co_{1.5}N_2O_5$: C, 53.37; H, 2.89; N, 6.23; Co, 19.64%.

Measurements. C, H and N analysis was carried out with a Perkin-Elmer 2400 elemental analyzer, and the Co of an inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV ICP spectrometer. Infrared spectra were measured on KBr disks with a Perkin-Elmer Spectrum One FT-IR spectrometer in the 4000–400 cm^{-1} regions. A thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 instrument with a heating rate of 20 °C min^{-1} in air. Magnetic measurements were obtained using an MPMS-XL magnetometer



Scheme 1. Typical coordination modes for the terephthalate ligand.

at $H = 5000$ Oe in the 4–300 K temperature range.

X-ray Crystal Structure Determination. Crystals of **1** with a size of 0.20 mm × 0.13 mm × 0.10 mm, and suitable for single-crystal X-ray diffraction, were selected. The data collections were made at room temperature on a Siemens P4 four-circle diffractometer with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) and ω–2θ scans. The structure was solved by direct methods and refined by a full-matrix least-squares approach on F^2 using the SHELXTL (Version 5.1) program.[27] All of the non-hydrogen atoms were refined anisotropically. The H atom attached to the O5 atom was located from difference Fourier maps. Hydrogen atoms attached to C atoms were placed geometrically. Crystal data and structure refinement details for **1** are given in Table 1; selected bond lengths and angles for **1** are given in Table 2.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 203050.

Results and Discussion

Synthesis. The reactions of a carboxylic or dicarboxylic acid with a cobalt ion are known to result in several complexes, which depend on the concentration, the pH, the temperature and the synthetic method. The wide range of stable compounds is due to such factors as the range of the coordination modes of the carboxylate ion (monodentate, didentate of syn-syn, syn-anti, and anti-anti types, and tridentate) and the stable coordination geometries (tetrahedral, pyramidal and octahedral) of Co, as well as the presence and number of coordinated water or hydroxide molecules.[3,8,14,16] The isolation of single phases is a problem under certain conditions. Hydrothermal synthesis is becoming one of the most reliable techniques for producing single phases of high crystallinity. Complex **1** was constructed through a self-assembly process under mid-temperature hydrothermal conditions. In contrast to the synthesis of $[\{Co(tp)(phen)(H_2O)\}_n]$, which can be prepared under various conditions of the concentration and nature of reactants,[8] the preparation of $[\{Co_3(tp)_2(OH)_2(phen)_2\}_n]$ (**1**) requires strict conditions. In the preparation of **1**, the molar ratio of metal:terephthalic acid:hydroxide (2:3:8) is important; this molar ratio, which is higher than those in some of the related complexes (2:1:4 and 1:1:2),[3,16] may contribute to the formation of the tetra- and penta-coordination cobalt.

Structures. As shown in Fig. 1(a), three cobalt(II) centers, with an inversion center on Co(1), are clustered by virtue of the bis(didentate) functionalities of tp units as well as the bridging capacity of the OH groups. Co(1) has a square-planar geometry with two carboxylato-oxygen atoms from two bis(didentate) tp ligands and two oxygen atoms from two bridging OH groups. Two cross-bond angles of 180.0°, O(5)–Co(1)–O(5A) and O(1)–Co(1)–O(1A) show that the Co(1) ion is located in a square plane, and that there is no axial displacement. It is very rare that the coordination geometry around Co(II) is square-planar. Previous evidence based on magnetic measurements indicates that four-coordinated low-spin complexes of cobalt are likely to have a square-planar arrangement.[28] Also, apparently, the best evidence obtained by X-ray diffraction techniques indicates that the cobalt atom has a square-planar environment in some cobalt complexes.[29] The Co(1)–O bond lengths (Co(1)–O(5) 1.909(2) Å, Co(1)–O(1) 1.9545(19) Å) are shorter than the corresponding Co(2)–O bond lengths

Table 1. Crystal Data and Structure Refinement for [{$Co_3(tp)_2(OH)_2(phen)_2$}$_n$] (**1**)

Empirical formula	$C_{20}H_{13}Co_{1.5}N_2O_5$
Formula weight	449.72
Shape	Prism
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 8.2620(11)$ Å $\alpha = 111.332(8)°$
	$b = 10.4409(12)$ Å $\beta = 91.394(10)°$
	$c = 11.0840(10)$ Å $\gamma = 91.638(10)°$
Volume	889.65(18) $Å^3$
Z, Calculated density	2, 1.679 $g\,cm^{-3}$
Absorption coefficient	1.451 mm^{-1}
$F(000)$	455
Theta range for data collection	1.97 to 24.99°
Limiting indices	$-1 \le h \le 9$, $-11 \le k \le 11$, $-13 \le l \le 13$
Reflections collected/unique	3876/3056 [R(int) = 0.0227]
Data/restraints/parameters	3056/0/263
Goodness-of-fit on F^2	1.009
Final R indices [$I > 2\sigma(I)$]$^{a)}$	$R_1 = 0.0308$, $wR_2 = 0.0822$
R indices (all data)	$R_1 = 0.0400$, $wR_2 = 0.0845$
Largest diff. peak and hole	0.265 and −0.296 e $Å^{-3}$

a) $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (°) for [{$Co_3(tp)_2(OH)_2(phen)_2$}$_n$] (**1**)

Co(1)–O(5)	1.909(2)
Co(1)–O(1)	1.9545(19)
Co(2)–O(5)	1.932(2)
Co(2)–O(3)	1.950(2)
Co(2)–N(1)	2.026(2)
Co(2)–N(2)	2.030(3)
Co(2)–O(2)	2.283(2)
O(5)#1–Co(1)–O(5)	180.000(1)
O(5)#1–Co(1)–O(1)	88.76(9)
O(5)–Co(1)–O(1)	91.24(9)
O(5)–Co(2)–O(2)	93.09(9)
O(3)–Co(2)–O(2)	101.85(9)
N(1)–Co(2)–O(2)	88.98(9)
N(2)–Co(2)–O(2)	89.05(9)
Co(1)–O(5)–Co(2)	113.11(12)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+2$, $-z+1$.

(Co(2)–O(5) 1.932(2) Å, Co(2)–O(2) 2.283(2) Å). The geometry around the Co(2) ion is square-based pyramidal with one carboxylato-oxygen atom from the bis(didentate) tp ligand and with two nitrogen atoms from phen, one oxygen atom from the bridging OH group, and one carboxylato-oxygen atom from the bis(monodentate) tp ligand. The deviation of the metal atom from the mean plane, O(5)O(3)N(1)N(2), is 0.1229 Å. However, the Co(2)–O(4)[2.887 Å] distance shows some weak interaction between the cobalt and uncoordinated oxygen of the bis(monodentate) tp ligand, which may be viewed as being a semi-chelating coordination mode.[30] Thus, the environment of the Co(2) in **1** can also be described as a distorted octahedron: the two phen nitrogens [N(1) and N(2)] and two oxygen atoms [O(5) and O(3)] comprise an equatorial plane, while the axial positions are filled by the other two carboxylato-oxygens [O(2) and O(4)]; the axial Co–O distances [2.283(2) Å and 2.887(2) Å] are extremely elongated compared with the equatorial Co–O distances [1.932(2) Å and 1.950(2) Å]. In the fundamental building block of **1**, the bent Co(1)–OH–Co(2) unit is not quite symmetrical: one Co–$O_{hydroxo}$ distance is longer than the other. The Co(1)···Co(2) separation is 3.21 Å and the Co–(OH)–Co angle is 113.11(12)°. The dihedral angle between phen and the bis(didentate) tp lignad is 43.4°; the dihedral angle between phen and the bis(monodentate) tp lignad is 117.9°; the dihedral angle between the bis(monodentate) and bis(didentate) tp units is 114.7°. The trinuclear $Co_3(tp)_2(OH)_2(phen)_2$ species with two six-membered rings may be considered to be a basic subunit for the structure. Such subunits are polymerized through the bis(monodentate) and bis(didentate) tp units, i.e. every two Co_3 subunits are linked together, sharing their bis(monodentate) tp bridges, to form a zig-zag chain (Fig. 1(b)). The phen rings in adjacent subunits are parallel. The adjacent zig-zag chains are further inter-connected by the bis(didentate) tp bridges to form a two-dimensional layer containing a regular rhombus (Fig. 1(c)). The parallel phen rings are located on both sides of the layer.

Co(II) atoms usually exhibit an octahedral geometry in their coordination polymers.[14,31] Cobalt atoms with alternative octahedral and tetrahedral geometries or alternative octahedral and square-pyramidal geometries are found in one-dimensional (1D),[32] two-dimensional (2D)[33] and three-dimensional (3D) structures,[24,34] as reported in some papers. However, to our knowledge, complex **1** is the first example of a two-dimensional framework with both carboxylate bridges and μ-hydroxo bridges, in which cobalt atoms adopt square-pyramidal and square-planar geometries. The tetra- and penta-coordination of Co in **1** is attributed to, at least in part, the μ-OH bridges, which are stronger donors than the carboxylate oxygen atoms, thus decreasing the coordination number.

Characterization. The IR spectrum shows that two of the characteristic bands of the dicarboxylate unit are at 1573(vs)

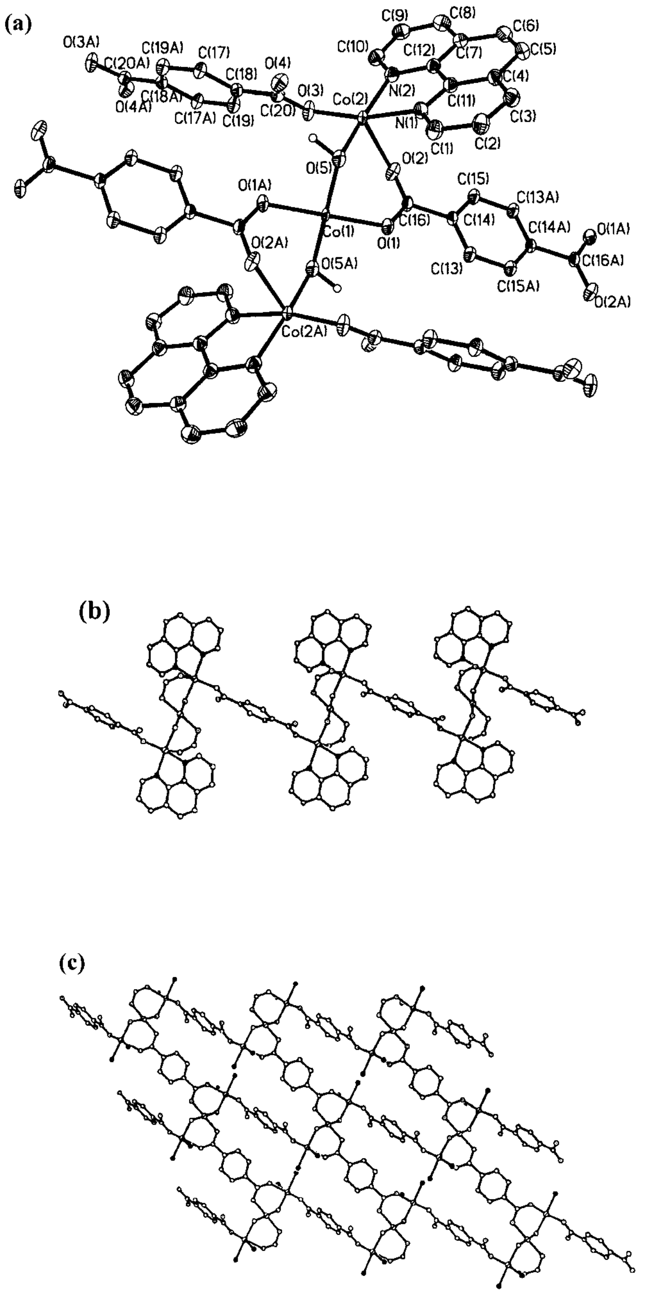


Fig. 1. (a) Coordination environment of cobalt ions in **1**. (b) The one-dimensional zig-zag chain structure in **1**. (c) A view of two-dimensional structure of **1**. Hydrogen atoms and carbon atoms of phen are omitted for clarity.

cm^{-1} and 1514(sh) cm^{-1} for the antisymmetric stretching, and the other is at 1369 cm^{-1} for symmetric stretching. The separations between $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ and $\nu_{\mathrm{sym}}(\mathrm{CO_2})$ are, respectively, at 204 cm^{-1} and 145 cm^{-1}. The splitting of $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ indicates that the tp carboxylate groups function in two different coordination modes,[35] which are in agreement with the crystal structures of **1**. The absorption band at 1424 cm^{-1} can be assigned to the skeletal bending vibration of the phen ligand. A broad band of medium-intensity at 3422 cm^{-1} is assigned to δ(OH).[36]

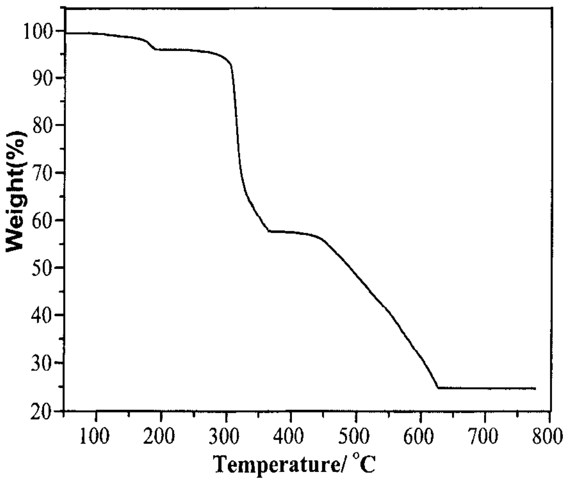


Fig. 2. Thermogravimetric analysis for **1**.

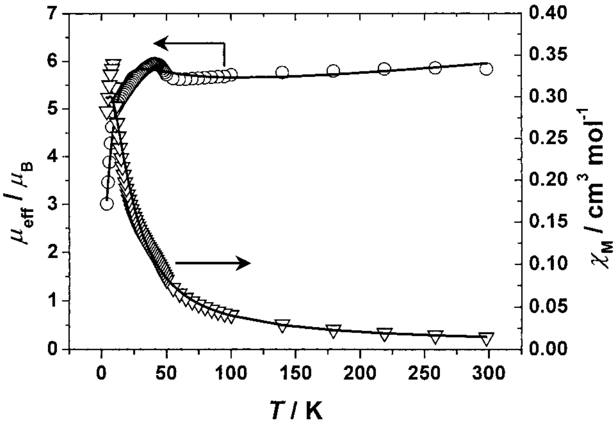


Fig. 3. Plots of μ_{eff} and χ_{M} versus temperature for **1**.

A TGA analysis of **1** is shown in Fig. 2. A first loss of 3.98% related to the interstitial water was observed between 110 and 190 °C. Upon further heating, the residue began to decompose at around 270 °C, followed by a quick exothermic weight loss (38.02%) due to burning of the phen ligands (calcd 39.14%). The loss of the tp ligand occurred upon heating until 420 °C, due to the strong bonds with metal ions. Heating to 620 °C gave a black solid, which could be cobalt oxide, based on the IR spectrum.

Magnetic Properties. The dependence of the magnetic susceptibility of **1** on the temperature in the range of 4–300 K under an applied field of 5000 Oe was studied. As illustrated in Fig. 3, the μ_{eff} value per $\mathrm{Co_3}$ unit at 298 K is ca. 5.83 μ_{B}, slightly higher than the spin-only value (5.74 μ_{B}) of three Co atoms, two of which adopt a square-based pyramidal geometry with $S = 3/2$ in the terminal position; the central cobalt(II) ion has a square-planar geometry with $S = 1/2$. Upon cooling down, the μ_{eff} slowly decreases from 5.83 μ_{B} at room temperature to 5.62 μ_{B} at 60.0 K. Below this minimum, μ_{eff} increases to a maximum of 5.95 μ_{B} at 41.0 K, and then decreases to 3.01 μ_{B} at 4.0 K. The shape of the μ_{eff} curve indicates a ferrimagnetic-like behavior in the range of 300–41.0 K, immediately followed by a strong decay of the magnetic moment.

The magnetic analysis of a polynuclear system containing the Co(II) ion is far from being trivial because of the large number of adjustable parameters. However, many Co(II) complexes exhibit magnetism of $S = 3/2$ at 77 K and above.[37,38] To analyze the magnetic data of **1**, an approximate approach of a three spin system (3/2–1/2–3/2) was used at the first step for magnetic data above 60.0 K. If the interaction between the terminal cobalt(II) ions is neglected, the isotropic spin Hamiltonian expression,

$$\boldsymbol{H} = -J(S_{\mathrm{Co1}}S_{\mathrm{Co2}} + S_{\mathrm{Co2A}}S_{\mathrm{Co1}}), \tag{1}$$

can be used to evaluate the magnitude of the magnetic interaction, where $S_{\mathrm{Co2}} = S_{\mathrm{Co2A}} = 3/2$ and $S_{\mathrm{Co1}} = 1/2$. Then, the expression of the magnetic susceptibility is deduced as

$$\chi_{\mathrm{T}} = \left[\frac{Ng^2\beta^2}{4kT} \times \frac{A}{B}\right], \tag{2}$$

where

$$A = 10 + \exp\left(-\frac{5J}{2kT}\right) + 10\exp\left(-\frac{J}{kT}\right) + 35\exp\left(\frac{3J}{2kT}\right),$$

and

$$B = 2 + \exp\left(-\frac{5J}{2kT}\right) + 2\exp\left(-\frac{J}{kT}\right) + 3\exp\left(\frac{3J}{2kT}\right).$$

The simulation results gave a large g value, which departed far from the present status. Therefore, a very small amount of paramagnetic impurity (ρ) was assumed to modify Eq 2.

$$\chi_{\mathrm{d}} = \left[\frac{Ng^2\beta^2}{4kT} \times \frac{A}{B}\right](1-\rho) + \left[\frac{Ng^2\beta^2}{kT} \times S_{\mathrm{Co}}(S_{\mathrm{Co}}+1)\right]\rho \tag{3}$$

A good fit was obtained when the ρ was assumed to be 0.06%. Based on these results, we tried to further use an approximate approach similar to that previously used for 2D and quasi-2D complexes.[39–41] Based on the crystal data, the complex was considered to be approximately a uniform chain formed by the Co2–Co1–Co2A linkages. Therefore, the 1D chain can be treated as uniform Co($S = 3/2$)–Co($S = 1/2$)–Co($S = 3/2$) trimers with different intratrimeric and intrachain exchange constants, J and J_{c}. The molecular field term (zJ') was taken into account for the interchain exchange interaction in the 2D system:

$$\chi_{\mathrm{d}} = \frac{Ng^2\beta^2}{3KT}S_{\mathrm{d}}(S_{\mathrm{d}}+1), \tag{4}$$

$$\chi_{\mathrm{chain}} = \frac{Ng^2\beta^2}{3KT}S_{\mathrm{d}}(S_{\mathrm{d}}+1)\left(\frac{1+u}{1-u}\right), \tag{5}$$

where $u = \coth[J_{\mathrm{c}}S_{\mathrm{d}}(S_{\mathrm{d}}+1)/kT] - kT/[J_{\mathrm{c}}S_{\mathrm{d}}(S_{\mathrm{d}}+1)]$, and

$$\chi_{\mathrm{M}} = \frac{\chi_{\mathrm{chain}}}{1 - \chi_{\mathrm{chain}}(2ZJ'/Ng^2\beta^2)}. \tag{6}$$

Using this rough model, the susceptibility was simulated, giving the best fit with parameters $J = -5.4$ cm^{-1}, $J' = 6.0$ cm^{-1}, $zJ' = -1.0$ cm^{-1}, $g = 2.10$ and $\rho = 0.0006$. The agreement factor (R), defined as $\Sigma[(\chi_{\mathrm{M}}{}^{\mathrm{obs}} - \chi_{\mathrm{M}}{}^{\mathrm{calc}})^2/(\chi_{\mathrm{M}}{}^{\mathrm{obs}})^2]$, was 5.4×10^{-3}. These results indicated that the antiferromagnetic and ferromagnetic interactions occurred between cobalt(II) ions within the trimeric unit and between the trimeric units along the chain, respectively. One of the reasons for the decrease of μ_{eff} at very low temperature was probably due to the interchain interaction.

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