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Research paper

Synthesis, crystal structure and magnetic properties of a cyanide-bridged one-dimensional Fe^{III}Co^{II} metamagnet

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ABSTRACT

A new cyanide-bridged Fe^{III}Co^{II} bimetallic complex $\{[Fe(Tp)(CN)_3Co(L_{N3O2})]ClO_4 \cdot 2H_2O\}_n$ (Tp$^-$ = hydrotris (pyrazolyl)borate, L_{N3O2} = 2,13-dimethyl-6,9-dioxa-3,12,18-triaza-bicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentene) (**1**) has been synthesized based on the building blocks of $[Co^{II}(L_{N3O2})(H_2O)_2](ClO_4)_2$ and Bu$_4$N $[Fe^{III}(Tp)(CN)_3]$. X-ray single crystal diffraction analysis shows that complex **1** has a cyanide-bridged Fe(III) and Co(II) alternating one-dimensional (1D) zigzag-like structure. Magnetic investigations on complex **1** indicate the ferromagnetic coupling between Fe(III) and Co(II) through cyanide bridge. Complex **1** displays long-range antiferromagnetic ordering with T_N = 2.6 K. The typical metamagnet behaviors have been observed with the critical field of *ca.* 1.2 kOe at 2.0 K.

1. Introduction

Molecule-based magnetic materials have aroused much attention in the past several decades because of their potential applications in high-density information storage and important theoretical values such as quantum tunneling effect [1–4]. Therefore, a large number of complexes with novel topological structures have been designed and synthesized and many of them exhibit interesting magnetic properties [5–8]. During the process of preparing new magnetic complexes, the selection of magnetic spin carriers and bridging linkages and co-ordination ligands usually play very important roles.

As a famous bridging ligand, cyanide group usually displays its unique advantage for assembling bimetallic even trimetallic magnetic complexes because cyanide-bridged complexes are commonly synthesized by stepwise assembly strategy based on building blocks containing different magnetic carriers [9–20]. Although there are many combinations of different magnetic carriers for cyanide-bridged complexes, the Fe^{III}Co^{II} system has still been focused much attentions and many cyanide-bridged Fe^{III}Co^{II} complexes with interesting magnetic properties such as single-molecule magnets, single-chain magnets, spin-crossover magnets and photoswitchable magnets have been reported [21,22]. As one of the limited cyanide-containing building blocks, *fac*-tricyanide-containing building block [Fe(Tp)(CN)$_3$]$^-$ and its derivatives have played important roles in the development of cyanide-bridged complexes [22–24]. In addition, the seven-coordinated $[Co^{II}(L_{N5})(X)_2]^{2+}$ and $[Co^{II}(L_{N3O2})(X)_2]^{2+}$ units with pentadentate equatorial ligands have been explored as important magnetic blocks

because of the high-spin state and the large magnetic anisotropy of central Co(II) spin carrier [11a,13a,25]. Herein, we report a new cyanide-bridged 1D Fe^{III}Co^{II} bimetallic complex $\{[Fe(Tp)(CN)_3Co (L_{N3O2})]ClO_4 \cdot 2H_2O\}_n$ (Tp$^-$ = hydrotris(pyrazolyl)borate, L_{N3O2} = 2,13-dimethyl-6,9-dioxa-3,12,18-triaza-bicyclo[12.3.1]octadeca-1(18), 2,12,14,16-pentene) (**1**) has been synthesized, building blocks of $[Co^{II}(L_{N3O2})(H_2O)_2](ClO_4)_2$ and Bu$_4$N[Fe^{III}(Tp)(CN)$_3$] (Scheme 1). The structure of the complex has been determined by X-ray single crystal diffraction analysis and the magnetic properties of the complex have been investigated.

2. Experimental section

2.1. Materials and physical measurements

All the chemicals were obtained commercially without further purification. The $[Co^{II}(L_{N3O2})(H_2O)_2](ClO_4)_2$ precursor and the cyanide-containing building blocks Bu$_4$N[Fe^{III}(Tp)(CN)$_3$] prepared by the procedures reported previously [11a,24]. *WARNING*: Cyanides are extremely toxic and should be handled with caution.

Elemental analyses (C, H and N) were carried out on an Elementary Vario El instrument. The infrared spectra of solid samples on KBr pellets were recorded on a Nicolet 7199B FT/IR spectrophotometer in the region of 4000–1000 cm^{-1}. Magnetic properties measurements on crystal samples were carried out on a Quantum Design MPMS SQUID magnetometer. The powder XRD data were measured on a Bruker D8 Advance X-ray diffractometer equipped with Cu-Kα radiation
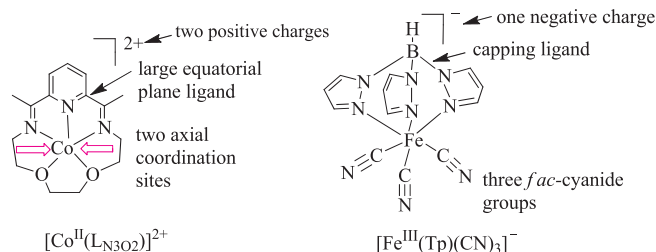
Scheme 1. The structures of building blocks $[Co^{III}(L_{N3O2})]^{2+}$ and *fac*-$[Fe^{III}(Tp)(CN)_3]^-$.

(λ = 0.15418 nm, cathode voltage 40 kV and cathode current 30 mA). Magnetic measurements on crystal samples were carried out on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for diamagnetism estimated based on Pascal's tables.

2.2. Synthesis of complex {[Fe(Tp)(CN)₃Co(L_{N3O2})]ClO₄·2H₂O}ₙ (1)

Complex **1** was prepared as following procedures: $Bu_4N[Fe^{III}(Tp)(CN)_3]$ (0.1 mmol) dissolved in 15 mL water/methanol (v/v = 1/5) was added to the CH_3OH/CH_3CN (v/v = 2/1) solution (15 mL) containing $[Co^{II}(L_{N3O2})(H_2O)_2](ClO_4)_2$ (0.1 mmol). The mixture was filtered and the filtrate was allowed to evaporate at the room temperature without disturbing. Block brown crystals suitable for X-ray diffraction analysis can be obtained after about two days with high yield of 82.4%. Anal. Calcd. for $CoFeBC_{27}H_{33}N_{12}O_7Cl$ (**1**): C, 40.60; H, 4.16; N, 21.05. Found: C, 40.35; H, 4.30; N, 20.79. Main IR bands (cm^{-1}): 2142 (m, $\nu C\equiv N$), 2130 (w, $\nu C\equiv N$),1086 (vs νClO_4).

2.3. X-ray data collection and structure refinement of complex 1

The structures were obtained by the direct methods and refined by full-matrix least-squares methods (SHELXL-97) on F^2. Structural measurements were performed on a Bruker APEX II CCD using graphite-monochromatized Mo-$K\alpha$ radiation (λ = 0.71073 Å) and the ω-scan techniques at room temperature. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Images were created by using DIAMOND program. The crystal data of **1** was shown in Table 1.

Table 1
Crystal data and structure-refinement parameters for **1**.

Empirical formula	$CoFeBC_{27}H_{33}N_{12}O_7Cl$
Formula weight	798.69
Temperature (K)	123(2)
Crystal system	Monoclinic
space group	$P2_1/c$
a (Å)	13.139(3)
b (Å)	17.163(3)
c (Å)	15.576(3)
B (°)	105.09(3)
Volume (Å^3)	3391.2(12)
Z	4
$\rho_{Calcd.}$ (g cm^{-3})	1.564
μ(Mo-$K\alpha$) (mm^{-1})	1.059
$F(0\,0\,0)$	1640
θ (°)	3.01–25.00
Measured reflections	22,661
Unique reflections [R_{int}]	5952 [0.0988]
Reflections (I > 2σ (I))	4091
GOF on F^2	1.015
R_1 [I > 2sigma(I)]	0.0772
wR_2 (all data)	0.2329

3. Results and discussions

3.1. Synthesis and general characterization

As shown in Scheme 1, the central Co(II) ion of building block $[Co^{III}(L_{N3O2})]^{2+}$ is relatively strongly coordinated by a pentadentate macrocyclic ligand L_{N3O2} at its equatorial plane, however, there are two weakly bonded and replaceable ligands at its two *trans* positions. On the other hand, the central Fe(III) ion in *fac*-$[Fe^{III}(Tp)(CN)_3]^-$ is strongly coordinated by one capping tridentate ligand Tp and three *fac* cyanide groups. The building blocks of $[Co^{III}(L_{N3O2})]^{2+}$ and *fac*-$[Fe^{III}(Tp)(CN)_3]^-$ are all excellent precursors for the design and synthesis of low-dimensional cyanide-bridged complexes. As a consequence, the reaction of *fac*-$[Fe^{III}(Tp)(CN)_3]^-$ and $[Co^{II}(L_{N3O2})]^{2+}$ with 1:1 M ratio led to one-dimensional cyanide-bridged single cationic chain structure with free ClO_4^- groups as counterpart anion.

The PXRD diagram (Fig. S1) of complex **1** is in good agreement with the calculated pattern, indicating the phase purity of the solid. The title complex has also been characterized by IR spectra (Fig. S2). In the IR spectra of complex **1**, the peak of 2130 cm^{-1} is assigned to the free unbridged cyanide group and the peak of 2142 cm^{-1} can be assigned to the bridging cyanide groups. Observation of a strong broad peak centered at ca. 1086 cm^{-1} suggests the presence of ClO_4^- anions.

3.2. Crystal structure of complex 1

Single crystal X-ray diffraction analysis shows that complex **1** has a cyanide-bridged 1D zigzag-like structure, in which each [Fe(Tp)(CN)₃]$^-$ unit links two $[Co^{II}(L_{N3O2})]^+$ segments through its two of its three *fac*-cyanide groups. The molecular structures of the complexes are showed in Fig. 1 and the selected bond distances and angles are listed in Table 2.

The Fe(III) ion in complex **1** is coordinated by three nitrogen atoms from the capping Tp$^-$ ligand at one side and three *fac*-cyanide carbon atoms at the other side, forming slightly distorted FeN₃C₃ coordination environment. The Fe–C bond lengths are similar within a narrow range of 1.925(6)–1.936(6) Å. The Fe–N bond distances range from 1.972(5) to 1.988(5) Å. The bond distances around Fe(III) clearly indicate that the central Fe(III) ion is low-spin state. The bridging Fe–C≡N linkages are 171.8(5)° for Fe1–C1–N1, 174.2(5)° for Fe1–C2–N2B, which is slightly smaller than that of non-bridging Fe–C≡N angle with 175.9(6)° for Fe1–C3–N3.

The cobalt(II) ion in complex **1** is seven-coordinated by five nitrogen atoms and two oxygen atoms in which the five equatorial positions are occupied by the N₃O₂ atom set from the macrocyclic L_{N3O2} plane ligand and two axial sites are coordinated by two cyanide nitrogen atoms, forming a slightly distorted pentagonal-bipyrimidal coordination geometry. The Co–N_cyanide bond distances are 2.118(5) Å for Co1–N1 and 2.114(5) Å for Co1–N2A. The Co–N_equatorial bond lengths locate with the range of 2.105(5)–2.227(7) Å. The Co–O bond distances are 2.241(6) Å for Co1–O1 and 2.233(6) Å for Co1–O2, respectively. The bond angles of Co–N≡C are fashionable bent with 156.4(5)° for Co1–N1–C1 and 156.4(5)° for Co1–N2A–C2A, respectively. The nearest adjacent Fe···Co distance through cyanide bridge in the same chain is 5.040(7) Å for Fe1···Co1. The shortest distance for metal···metal between chains is 7.685(7) Å for Fe1···Fe1 in complex **1**.

There exist obviously π–π interchain interactions between the pyrazole rings from two neighboring 1D chains of complex **1**, which link the 1D chains of complex **1** into two-dimensional (2D) bilayer-like supramolecular structures (Fig. 2). In addition, there are hydrogen bonds between free water molecules and cyanide nitrogen atoms and oxygen atoms from ClO_4^- anions in these 2D supramolecular structures.

3.3. Magnetic properties of complex 1

The magnetic susceptibilities of complex **1** have been measured in