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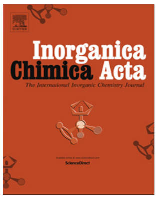

A cyanide-bridged one-dimensional $Cr^{III}Co^{II}$ metamagnet based on the *trans*-dicyanidechromate(III) building block

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ABSTRACT

A cyanide-bridged $Cr^{III}Co^{II}$ bimetallic complex $[Cr(bpb)(CN)_2Co(L_{N5})\cdot 2H_2O\cdot ClO_4]_n$ (bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate, L_{N5} = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene) (**1**) has been synthesized by the reaction of $[Co^{II}(L_{N5})(H_2O)_2](ClO_4)_2$ with the *trans*-dicyanidechromate(III) building block $K[Cr^{III}(bpb)(CN)_2]$. X-ray single crystal diffraction analysis shows that complex **1** exhibits a cyanide-bridged Cr(III) and Co(II) alternating one-dimensional (1D) wave-like structure. Magnetic investigations show that complex **1** displays over all ferromagnetic coupling between Cr(III) and Co(II) through cyanide bridge with long-range antiferromagnetic ordering of T_N = 9.4 K. The typical metamagnet behaviors were observed with the critical field of *ca.* 2.6 kOe at 2.0 K.

1. Introduction

The study on the design, synthesis and magnetic property of molecular coordination complexes has aroused continuously much attention in the fields of chemistry, physics and material science [1–4]. Up to date, a large number of complexes with novel topological structures have been prepared and many of them exhibit interesting magnetic properties and bifunctional even multifunctional properties [5–8]. Although there are many uncertainties for the final structure and property during the process of assembling new complexes, some important agreements and rules have been achieved. Generally, the suitable design and selection of magnetic spin carrier, bridging linkage and coordination ligand play very important roles for the resulting complexes.

As one famous bridging ligand, cyanide group usually displays some unique advantages such as the controllability and predictability for the structures and magnetic coupling nature of the final complexes [9–12]. In addition, cyanide-bridged complexes are generally synthesized by stepwise assembly strategy, which provides favorable prerequisite for heterospin complexes [13–18]. The combination of different magnetic spin carriers usually offers more chance and possibility than the only spin center for interestingly magnetic property [19–21]. The seven-coordinate $[Co^{II}(L_{N5})(X)_2]^{2+}$ and $[Co^{II}(L_{N3O2})(X)_2]^{2+}$ units with pentadentate equatorial ligands and labile axial ones (L_{N5} = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene, L_{N3O2} = 2,13-dimethyl-6,9-dioxa-3,12,18-triaza-bicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentene) exhibit their excellent features for interesting magnetic properties because of the high-spin state and the large magnetic anisotropy of central Co(II) spin carrier [11b,13a,22]. As our continuous work, we have focused on the design and development of $[Fe(bpb)(CN)_2]^-$ and $[Cr(bpb)(CN)_2]^-$ building blocks (bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate) with equatorial ligands and two axial cyanide groups, which are very suitable for low-dimensional cyanide-bridged complexes [11c,17b]. Recently, we synthesized a cyanide-bridged 1D $Cr^{III}Co^{II}$ complex $[Cr(bpb)(CN)_2Co(L_{N5})\cdot 2H_2O\cdot ClO_4]_n$ (**1**) based on the reaction of $[Co^{II}(L_{N5})(H_2O)_2](ClO_4)_2$ with the *trans*-dicyanidechromate(III) building block $K[Cr^{III}(bpb)(CN)_2]$ (Scheme 1). To the best our knowledge, there is still no report on the cyanide-bridged 1D $Cr^{III}Co^{II}$ complex. 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. The $[Co^{II}(L_{N5})(H_2O)_2](ClO_4)_2$ precursor and the cyanide-containing building blocks $K[Cr^{III}(bpb)(CN)_2]$ prepared by the procedures reported previously [11b,c]. *WARNING*: Cyanides are extremely toxic and should be handled with caution.

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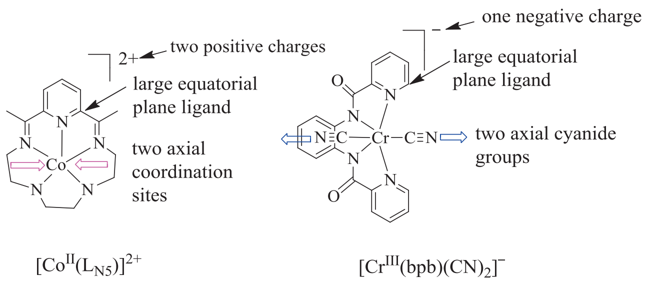

Scheme 1. The structures of building blocks $[Co^{III}(L_{N5})]^+$ and $[Cr^{III}(bpb)(CN)_2]^-$.

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 4000–400 cm^{-1}. Magnetic properties measurements on crystal samples were carried out on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism estimated based on Pascal's tables.

2.2. Synthesis of complex $[Cr(bpb)(CN)_2Co(L_{N5})\cdot 2H_2O\cdot ClO_4]_n$ (**1**)

Complex **1** were prepared by the commonly slow evaporation as following: $K[Cr^{III}(bpb)(CN)_2]$ (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 $[Co^{II}(L_{N5})(H_2O)_2](ClO_4)_2$ (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 $CoCrC_{35}H_{39}ClN_{11}O_8$ (**1**): C, 47.33; H, 4.43; N, 17.35. Found: C, 47.15; H, 4.50; N, 17.22. Main IR bands (cm^{-1}): 2144 (m, $\nu C{\equiv}N$), 1089(vs νClO_4).

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

The structures were obtained by the direct methods (SHELXS-97) 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 123 K. 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. Crystallographic data for the structures have been deposited at the Cambridge Crystallographic Data Center (CCDC 1524046 for **1**), which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, United Kingdom; Fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

3. Results and discussion

X-ray single crystal diffraction analysis shows that complex **1** has a cyanide-bridged 1D wave-like structure [23], in which each $[Cr(bpb)(CN)_2]^-$ unit links two $[Co^{II}(L_{N5})]^+$ segments through its two *trans* cyanide groups. The molecular structure of the complex is showed in Fig. 1 and the relatively detailed bond parameters are listed in Table 1.

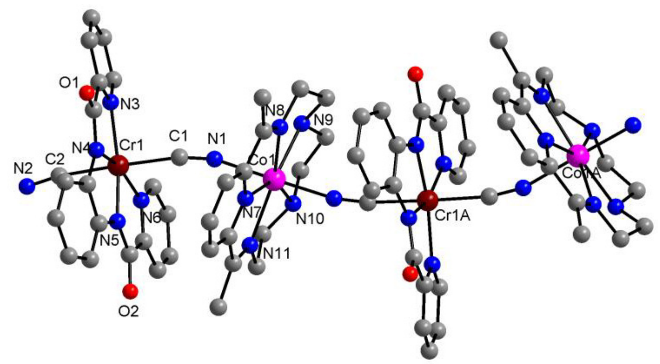

Fig. 1. The 1D chain-like structure of complex **1** (H atoms, free water molecules and counterions are omitted for clarity).

The Cr(III) ion in complex **1** is coordinated by four nitrogen atoms from the bpb^{2-} ligand at the equatorial plane and two cyanide carbon atoms at the *trans* axial sites, forming slightly distorted CrN_4C_2 coordination geometry. The Cr–C bond length is 2.055(5) Å for Cr1–C1 and 2.065(5) Å for Cr1–C2, respectively. The $Cr–N_{pyridine}$ bond distances (2.081(5) and 2.082(4) Å) are significantly larger than those of $Cr–N_{amide}$ bond distances (1.970(5) and 1.970(5) Å), indicating that the amide nitrogen atoms from starting ligand H_2bpb coordinate to Cr(III) ion as the negative ion after deprotonation. The $Cr–C{\equiv}N$ linkages slightly deviate from strictly line with 168.8(5)° for Cr1–C1–N1 and 171.2(4)° for Cr1–C2–N2, respectively. The C1–Cr1–C2 bond angle is 173.7(2)°. All the bond parameters around Cr(III) ion can be comparable to those of other cyanide-bridged heterometallic complexes based on $K[Cr^{III}(bpb)(CN)_2]$ build block and its derivatives [11c,17b].

The cobalt(II) ions in complex **1** are seven-coordinated by seven nitrogen atoms in which the five equatorial positions are occupied by the N_5 atom set from the macrocyclic planar ligand L_{N5} and two axial sites are coordinated by two cyanide nitrogen atoms, forming a significantly distorted pentagonal-bipyramidal coordination geometry. The $Co–N_{cyanide}$ bond distances are 2.110(5) Å for Co1–N1 and 2.108(5) Å Co1–N2, respectively, which are slightly smaller than those of $Co–N_{equatorial}$ bond lengths (2.204(5)–2.291(5) Å). The $Co–N{\equiv}C$ bond angles are fashionable bent (164.1(4)° for Co1–N1–C1 and 169.3(4)° for Co1–N2–C2). The N1–Co1–N2 bond angle is 178.60(19)°. The nearest adjacent Cr···Co distance through cyanide bridge in the same chain is 5.201(5) Å for Cr1···Co1. The shortest distance for metal···metal between chains is 8.484(5) Å in complex **1**.

There are affluent hydrogen bonds involving free water molecules, oxygen atoms from bpb^{2-} ligand and free ClO_4^- anions, and nitrogen atoms of ligand L_{N5} in the packing diagrams of the title complex (see Table 2), which link the 1D chains of complex **1** into three-dimensional (3D) supramolecular structures (Fig. 2, Supplementary information). In addition, it is noteworthy there is cyclic water cluster formed by four waters between the chains of complex **1**.

The magnetic susceptibilities of complex **1** have been measured in the temperature range of 2–300 K under an applied of 1000 Oe. A plot of $\chi_m T$ versus T is presented in Fig. 3, where χ_m represents the molar magnetic susceptibility per $Cr^{III}Co^{II}$ unit. The $\chi_m T$ value is 4.42 emu K mol^{-1} at room temperature, which is significantly higher than the expected value of 3.75 emu K mol^{-1} for two uncoupled spin carriers (S = 3/2) based on g = 2.0, indicating a relevant contribution of spin-orbital coupling of Co(II) ions. Upon lowering of temperature, the $\chi_m T$ value slowly increases until around 50 K, and then it increases sharply to a maximum value of 34.65 emu K mol^{-1} at about 9.4 K, after that it decreases abruptly to reach a minimal value of 0.81 emu K mol^{-1} at 2.0 K. The variation tendency of the $\chi_m T$ curve indicates the existence of obvious intrachain ferromagnetic coupling and interchain antiferromag-