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New 3-D Bimetallic Magnetic Compounds, $[Ni(dipn)]_3[M(CN)_6]_2 \cdot 7H_2O$ (M^{III} = Fe, Co; dipn = *N*,*N*-di(3-aminopropyl)amine)

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New cyanide-bridged bimetallic compounds of the formula $[Ni(dipn)]_3[M(CN)_6]_2 \cdot 7H_2O$ (M^{III} = Fe (**1**), Co (**2**); dipn = N,N-di-(3-aminopropyl)amine) were prepared and their crystal structures and magnetic properties were investigated. They are isostructural. In the crystal of **1** each $[Fe(CN)_6]^{3-}$ makes bond to three $[Ni(dipn)]^{2+}$ cations to form a 2-D sheet and the 2-D sheets are connected by $[Ni(dipn)(H_2O)]^{2+}$ cations providing a 3-D network structure. **1** shows a ferromagnetic ordering in the bulk with T_C = 7.8 K.

Keywords: three-dimensional compound; bimetallic compound; ferromagnet; molecular-based magnet

INTRODUCTION

Design of magnetic compounds with multi-functional properties using paramagnetic metal complexes as constituent is a current subject of molecular magnetism. From this viewpoint, we have extensively studied cyanide-bridged bimetallic compounds consisting of $[Ni(diamine)_2]^{2+}$ and $[M(CN)_6]^{3-}$ [1]. So far the following network compounds have been structurally and magnetically studied: $PPh_4[Ni(pn)_2][M(CN)_6]$ (M^{III} = Cr, Fe, Co; pn = 1,2-propanediamine)

with a 1-D chain structure[2], $[Ni(en)_2]_3[M(CN)_6]_2$ (M^{III} = Cr, Mn, Fe, Co; en = ethylenediamine) with a 1-D ladder structure[3,4], $[Ni(N\text{-}men)_2]_3[M(CN)_6]_2$ (M^{III} = Fe, Co; N-men = N-methylethylenediamine) with a 2-D honeycomb structure[1], and $[Ni(L)_2]_2[Fe(CN)_6]X$ (L = pn, 1,1-dmen (=1,1-dimethylethylenediamine) of a 2-D structure based on Fe_4Ni_4 square unit[5].

An important knowledge drawn from the magnetic studies of these complexes is that 3-D bimetallic networks have a bright prospect for developing magnetic materials. With a hope to provide 3-D bimetallic compounds, $[Ni(dipn)]^{2+}$ (dipn = N,N-di(3-aminopropyl)-amine) was used in this work to afford $[Ni(dipn)]_3[M(CN)_6]_2{\cdot}7H_2O$ (M^{III} = Fe (**1**), Co(**2**)). Structures and magnetic properties of the complexes are reported.

EXPERIMENTAL

Preparations

$[Ni(dipn)]_3[Fe(CN)_6]_2{\cdot}7H_2O$ (1): $NiCl_2{\cdot}6H_2O$ (71 mg, 0.30 mmol) was dissolved in a DMF-water mixture (1:1 in volume, 10 cm^3). To this were successively added dipn (39 mg, 0.3 mmol) and an aqueous solution of $K_3[Fe(CN)_6]$ (66 mg, 0.2 mmol), and the resulting brown turbid mixture was allowed to stand to form dark brown crystals **1**. Thermogravimetric (TG) analyses were made for **1** to determine the number of water molecules. Elemental analyses were obtained for $[Ni(dipn)]_3[Fe(CN)_6]_2{\cdot}H_2O$ (**1'**) prepared by heating **1** at 150 °C and then allowing to stand in air. (yield; 58 %) Anal. Found: C, 35.33; H, 5.07; N, 29.40; Fe, 11.4; Ni, 17.5 %. Calcd. for $C_{33}H_{53}N_{21}OFe_2Ni_3$: C, 35.62; H, 5.28; N, 29.08; Fe, 11.0; Ni, 17.4 %.

$[Ni(dipn)]_3[Co(CN)_6]_2{\cdot}7H_2O$ (2): This was obtained as purple crystals in a way similar to that of **1** except for using $K_3[Co(CN)_6]$. (yield; 76 %) Elemental analyses were obtained for $[Ni(dipn)]_3[Co(CN)_6]_2{\cdot}H_2O$ (**2'**) prepared by similar method for **1'**. Anal. Found: C, 35.62; H, 5.17; N,

29.24; Co, 11.7; Ni, 17.5 %. Calcd. for $C_{33}H_{53}N_{21}OCo_2Ni_3$: C, 35.40; H, 5.25; N, 28.90; Co, 11.6; Ni, 17.3 %.

X-ray Crystallographic Studies

Each single crystal of $[Ni(dipn)]_3[Fe(CN)_6]_2 \cdot 7H_2O$ (**1**) and $[Ni(dipn)]_3[Co(CN)_6]_2 \cdot 7H_2O$ (**2**) was sealed in a glass tube and used for crystallographic studies. Pertinent crystallographic parameters are summarized below. Full crystallographic data for **1** and **2** have been deposited at the CCDC (deposition numbers: 173496 – 173498).

Crystal data for 1: Formula = $C_{30}H_{65}N_{21}Fe_2Ni_3O_7$, F. W. = 1119.77, crystal system = monoclinic, space group = *C*2/c (#15), T = 23 °C, a = 24.097(4), b = 14.344(3), c = 16.681(2) Å, β = 100.57(1)°, V = 5667(1) Å^3, Z = 4, D_c = 1.312 g cm^{-3}, No. of reflections ($I > 3.00\sigma(I)$) = 4480, R = 0.059, Rw = 0.097.

Crystal data for 2: Formula = $C_{30}H_{65}N_{21}Co_2Ni_3O_7$, F. W. = 1125.95, crystal system = monoclinic, space group = *C*2/c (#15), T = 23 °C, a = 24.466(4), b = 14.534(3), c = 16.475(3) Å, β = 100.04(1)°, V = 5768(1) Å^3, Z = 4, D_c = 1.296 g cm^{-3}, No. of reflections ($I > 3.00\sigma(I)$) = 2875, R = 0.057, Rw = 0.081, T = -30 °C, a = 23.980(9), b = 14.197(6), c = 16.599(3) Å, β = 100.703(2)°, V = 5552(3) Å^3, Z = 4, D_c = 1.347 g cm^{-3}, No. of reflections ($I > 3.00\sigma(I)$) = 3050, R = 0.068, Rw = 0.113.

RESULTS AND DISCUSSION

Crystal and Network Structures

Compounds **1** and **2** are isostructural. An ORTEP view of **1** is shown in Figure 1 together with the atom numbering scheme.

The asymmetric unit of **1** consists of one $[Fe(CN)_6]^{3-}$ anion, one $[Ni(1)(dipn)]^{2+}$ and one half of $[Ni(2)(dipn)(H_2O)]^{2+}$ cations and three water molecules (Figure 1). Each $[Fe(CN)_6]^{3-}$ makes bond to three $[Ni(1)(dipn)]^{2+}$ cations and one $[Ni(2)(dipn)(H_2O)]^{2+}$ cation, with the two non-bridging cyanide groups in *cis* positions. The Ni(1) has a pseudo octahedral $\{NiN_6\}$ chromophore and the Ni(2) has a $\{NiN_5O\}$

chromophore; the dipn ligand assumes *mer* coordination mode in both chromophores. The nearest Fe···Ni(1), Fe···Ni(2) and Ni(1)···Ni(2) interatomic separations are 5.012(1), 5.043(1) and 8.428(1) Å, respectively. The Fe-CN-Ni(1) linkages extend on the *bc* plane to form a 2-D sheet structure consisting of cyclic Fe_4Ni_4 and Fe_2Ni_2 units, and the 2-D sheets are connected by the Fe-CN-Ni(2) linkage providing a 3-D network structure (Figure 2). The six water molecules are captured in the crystal lattice.

The structure of **2** at 23 ºC is similar to that of **1**. No marked change was recognized in the structure of **2** between 23 ºC and –30 ºC.

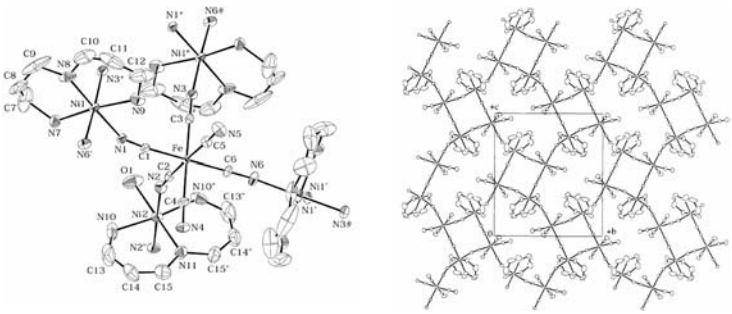

FIGURE 1 Left: An ORTEP view of the unit of **1** (lattice water are omitted). Right: A projection of polymeric structure of **1** onto *ab* plane.

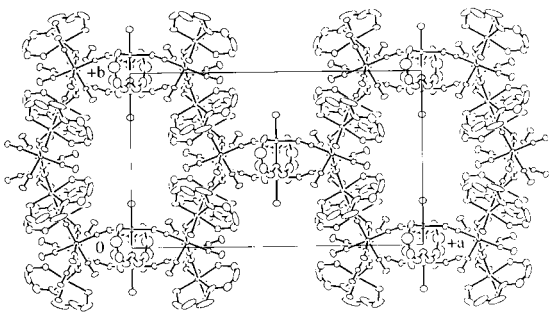

FIGURE 2 Projection of 3-D structure of **1** onto *ab* plane.

Magnetic Property of 1

Cryomagnetic property of **1** is shown in Figure 3. The $\chi_M T$ value (per Fe_2Ni_3) at room temperature is 4.30 cm^3 K mol^{-1} (5.86 μ_B) that is slightly larger than the value expected for isolated two Fe^{III} (S = 1/2) and three Ni^{II} (S = 1) ions (3.87 cm^3 K mol^{-1} and 5.56 μ_B with g = 2.03). The $\chi_M T$ value increased with decreasing temperature to a maximum value of 90.72 cm^3 K mol^{-1} (26.9 μ_B) at 6 K and then decreased below this temperature. The decrease in $\chi_M T$ below 6 K is due the saturation in χ_M. The sharp increase of $\chi_M T$ at low temperature suggests an onset of a 3-D ferromagnetic ordering in the bulk. Compound **2** simply shows paramagnetic nature due to Ni^{II}.

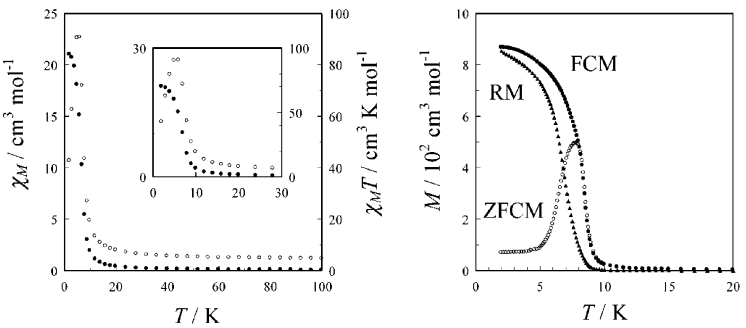

FIGURE 3 Left: $\chi_M T$ (●)*vs.* T and χ_M (○) *vs.* T curves for **1**. Right: Temperature-dependence of magnetization of **1**.

The field-cooled magnetization (FCM) under a weak applied field (5 G) shows a sharp increase around 10 K and a tendency of saturation below 2 K (Figure 4). When the applied field was switched off at 2 K, a remnant magnetization (RM) was observed which decreased upon warming and disappeared near 8 K. The zero-field cooled magnetization (ZFCM) curve showed a maximum magnetization of 495 cm^3 G mol^{-1} at 7.8 K (= T_C). Saturation magnetization and magnetic hysteresis studies have confirmed a ferromagnetic ordering in **1** (Figure. 4). The magnetization sharply increased with applied field to approach 8 $N\beta$ (S_T = 4) arising from ferromagnetic coupling of three

Ni^{II} and two Fe^{III} ions. The hysteresis curve is typical of soft magnets with a RM of 12880 cm^3 G mol^{-1} and a small coercive field of 56 G. The relatively low T_C of **1** may relate to a low-dimensional magnetic network based on the C_{2v} symmetric $[Fe(CN)_6]^{3-}$ unit.

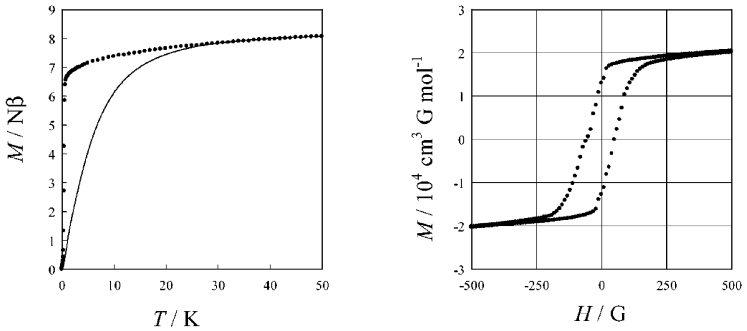

FIGURE 4 Left: *M vs. T* curve of **1** (under 5 G). The solid line is the Brillouin function for Ni_3Fe_2 with g = 2.03. Right: Magnetic hysteresis loop of **1** (measured at 2 K).

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