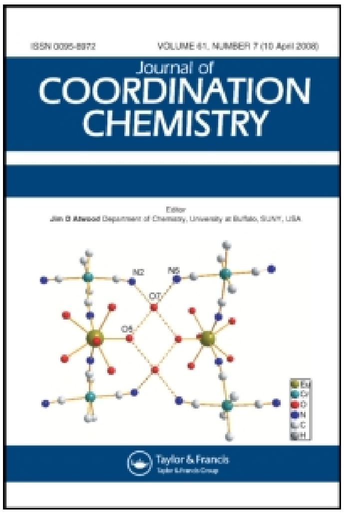

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Synthesis, Crystal structures and Magnetic properties of two new Hetero-bimetallic assemblies

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SYNTHESIS, CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF TWO NEW HETERO-BIMETALLIC ASSEMBLIES

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Two new cyanide-bridged 3d–4f hetero-dinuclear complexes, namely $Ln(DMF)_4(H_2O)_3(\mu\text{-CN})Co(CN)_5 \cdot H_2O$ (Ln = Nd (**1**) and Gd (**2**), DMF = *N*,*N*-dimethylformamide), were synthesized by the facile reaction of $LnCl_3 \cdot 6H_2O$ and $K_3Co(CN)_6$. Characterization includes microanalysis, IR spectrometric identifications, X-ray crystallographic analysis and magnetic properties. Both **1** and **2** crystallize in the centrosymmetric monoclinic space group $P2_1/n$ (No. 14) with $Z = 4$. The lanthanide(III) ions are eight-coordinate in a square-antiprism arrangement, while cobalt(III) ions are six-coordinate in an octahedral environment in each complex. A cyanide bridge links an Ln(III) ion to a Co(III) ion. Molecules in the crystal cell of each compound are held together by van der Waals forces and a network of hydrogen bonding. Magnetic analysis shows that antiferromagnetic interactions are observed below 7 K for both **1** and **2**, which are attributed to intermolecular interactions between the Ln(III) ions in the network through hydrogen bonds. This series of compounds may be of importance in photo-induced magnetism because of the cyanide bridge between 3d and 4f metals.

Keywords: Synthesis; Crystal structure; Magnetic properties; Cyanide bridge; Hexacyanide; Ln–Co complex

INTRODUCTION

Prandtl and Mohr first reported the synthesis of $LnFe(CN)_6 \cdot nH_2O$ in the late 1930s [1]. In the early 1970s, Milligan and co-workers determined the crystal structure of $LnFe(CN)_6 \cdot 5H_2O$ using single-crystal X-ray diffraction techniques [2]. In the last decade, extensive research dealing with the synthesis and structures of complexes with polycyanometalates and lanthanide metal ions has been carried out, driven by interest in molecular magnetism [3]. Important structural information was summarized in a brief review [4]. Several representative compounds with different dimensionality have been reported: three-dimensional hexacyanometalates(III) $LnFe(CN)_6 \cdot nH_2O$ (Ln = La–Nd, $n = 5$; Ln = Sm–Nd, $n = 4$) and $LnCr(CN)_6 \cdot 5H_2O$ (Ln = La–Lu) [5];

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two-dimensional hexacyanometalates(III) $Ln(bipm)(H_2O)_4Fe(CN)_6 \cdot 3H_2O$ (Ln = La, Nd) and $Sm(DMF)_m(H_2O)_nFe(CN)_6 \cdot H_2O$ ($m = 4$, $n = 2$; $m = 2$, $n = 3$) [6]; one-dimensional hexacyanometalates(III) $[Sm(DMA)_2(H_2O)_4Fe(CN)_6 \cdot 5H_2O]_n$ [7], $\{Yb_2(DMF)_{10}[M(CN)_4]_3\}_n$ (M = Ni, Pt) and $[Eu(DMF)_4M(CN)_4]_n$ (M = Ni, Pt) [8], *cis*-$[Gd(DMF)_4(H_2O)_2Cr(CN)_6]_n \cdot nH_2O$, and *trans*-$[Gd(bpy)(H_2O)_4Cr(CN)_6]_n \cdot 4nH_2O \cdot 1.5n$bpy [9]. Discrete 3d–4f molecular compounds have also been reported as follows: trinuclear complexes $\{[Gd(DMA)_3(H_2O)_4]_2[Fe(CN)_6]\}[Fe(CN)_6] \cdot 3H_2O$ [10] and $\{[Nd(bipy)_2(H_2O)_4]_2Fe(CN)_6\} \cdot [Fe(CN)_6] \cdot 8H_2O$ [11]; dinuclear complexes $Ln(DMF)_4(H_2O)_3Fe(CN)_6 \cdot H_2O$ (Ln = La, Ce, Pr, Tm, Er, Yb, Lu) [12], $Sm(DMF)_4(H_2O)_4Fe(CN)_6 \cdot H_2O$ [13] and $Ln(DMF)_4(H_2O)_3Co(CN)_6 \cdot H_2O$ (Ln = Ce, Sm, Yb, Lu) [14]. Following these studies of complexes with 3d–4f ions, we are interested in the molecular magnetism and photo-induced molecular magnetism [15] of this series of complexes. This article describes the synthesis, characterization and magnetic properties of two new cyano-bridged 3d–4f hetero-dinuclear complexes $Ln(DMF)_4(H_2O)_3$-(μ-CN)$Co(CN)_5 \cdot H_2O$ [Ln = Nd (**1**) and Gd (**2**)].

EXPERIMENTAL

General Procedures

All chemicals and solvents were used as purchased without further purification.

Synthesis of $Ln(DMF)_4(H_2O)_3(\mu\text{-}CN)Co(CN)_5 \cdot H_2O$ (Ln = Nd (1) *and Gd* (2)*, DMF = N,N-dimethylformamide)*

The procedures for synthesizing **1** and **2** were identical. $LnCl_3 \cdot 6H_2O$ (1.0 mmol) was dissolved in DMF (10 cm^3). An equimolar quantity of $K_3Co(CN)_6$ (0.332 g, 1.0 mmol) was dissolved in deionized water (10 cm^3). The solution of $LnCl_3 \cdot 6H_2O$ in DMF was allowed to layer onto the potassium hexacyanocobaltate solution in a 30-cm^3 test tube for a few days. Crystals of **1** and **2** were obtained after filtration of the reactants. Some single crystals were suitable for X-ray crystallographic analysis.

$Nd(DMF)_4(H_2O)_3(\mu\text{-}CN)Co(CN)_5 \cdot H_2O$ (1) Pale purple crystals. Yield 90%. Anal. Calcd. for $C_{18}H_{36}CoN_{10}NdO_8$(%): C, 29.87; H, 5.01; N, 19.93. Found: C, 30.19; H, 4.90; N, 19.65. IR (cm^{-1}, KBr): 3388 (ν-OH, hydrogen bonding), 2945 (ν-CH_3, C–H stretches), 2163, 2151, and 2134 (ν-C$\equiv$N), 1642 (δ-HOH), 1442 (δ_{as}-CH_3), 1383 (δ_s-CH_3, C–H stretches), 1249 (aldehydic C–H bend), 1060 (C–N stretches), 425 (ν-Fe–C).

$Gd(DMF)_4(H_2O)_3(\mu\text{-}CN)Co(CN)_5 \cdot H_2O$ (2) Colorless crystals. Yield 88%. Anal. Calcd. for $C_{18}H_{36}CoGdN_{10}O_8$(%): C, 29.35; H, 4.93; N, 19.01. Found: C, 29.23; H, 4.83; N, 19.23. IR (cm^{-1}, KBr): 3356 (ν-OH, hydrogen bonding), 2947 (ν-CH_3, C–H stretches), 2166, 2152, and 2135 (ν-C$\equiv$N), 1642 (δ-HOH), 1438 (δ_{as}-CH_3), 1382 (δ_s-CH_3, C–H stretches), 1249 (aldehydic C–H bend), 1059 (C–N stretches), 418 (ν-Fe–C).

Measurements

Elemental analyses were performed on an Elemetar Vario EL at the Central Facilities for Science and Technology Research, Keio University. Infrared spectra (IR) were recorded from KBr disks on a BIO-RAD FTS-165 FT-IR spectrophotometer at 25°C over the range 400–4000 cm^{-1}. Magnetic properties were investigated with a

TABLE I Summary of crystal data for **1** and **2**

	1	*2*
Formula	$C_{18}H_{36}CoN_{10}NdO_8$	$C_{18}H_{36}CoGdN_{10}O_8$
Formula weight	723.72	736.73
Crystal size (mm)	0.50 × 0.30 × 0.30	0.40 × 0.30 × 0.30
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a (Å)	19.879(6)	19.812(4)
b (Å)	8.885(2)	8.863(1)
c (Å)	17.524(4)	17.524(2)
β (°)	95.93(2)	96.07(1)
U (Å)^3	3078(1)	3059.8(8)
Z	4	4
D_c (Mg m^{-3})	1.561	1.559
F(000)	1460	1476
$2\theta_{max}$ (°)	55.0	55.0
μ(Mo Kα) (mm^{-1})	2.260	2.751
No. of reflections observed ($I > 2\sigma(I)$)	8471	8292
No. of reflections unique (R_{int})	7074 (0.047)	7755 (0.148)
No. of reflections used	5926	5649
No. of parameters	344	344
$R1$	0.042	0.086
wR	0.168	0.290
Goodness-of-fit	1.06	1.13

$R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$; $w = [\sigma^2(F_o) + (0.1287P)^2 + 1.8376P]^{-1}$ for **1**, $w = [\sigma^2(F_o) + (0.1859P)^2 + 24.9683P]^{-1}$ for **2**, where $P = (F_o^2 + 2F_c^2)/3$.

superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S).

X-ray Crystallography

Single crystals of **1** and **2** were coated and glued on the top of a glass fiber with epoxy resin. The intensity data were collected on a Rigaku AFC-7R four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 24°C. There was no significant decay of the crystals during data collection. The intensities were corrected for Lorentz polarization and absorption effects by applying ψ scans, transmission factors for **1** and **2**, were 0.8775–0.9995 and 0.8400–0.9994, respectively. The structures were solved by direct methods using the SIR92 program [16] and refined on F^2 by the full-matrix least-squares method with the SHELXL-97 program [17] using anisotropic thermal parameters for all nonhydrogen atoms. The hydrogen atoms connected to carbon atoms were located at the calculated positions and refined isotropically. However, the hydrogen atoms of the water molecules were not included in the models, because these hydrogen atoms could not be found even in the difference Fourier maps. All calculations were carried out on an SGI O2 workstation with a teXsan software package [18]. The crystal data for **1** and **2** are summarized in Table I.

RESULTS AND DISCUSSION

Synthesis

All compounds were obtained by the facile reaction of $LnCl_3 \cdot 6H_2O$ and equimolar $K_3Co(CN)_6$ in DMF and aqueous solutions, respectively. The slow diffusion of

$LnCl_3 \cdot 6H_2O$ into $K_3Co(CN)_6$ leads to the growth of crystals suitable for X-ray crystallographic analysis. This is the general method of obtaining cyanide-bridged bimetallic assemblies, described in several preceding papers [14,19].

Infrared Spectra

The IR spectra for **1** and **2** were similar, displaying the following notable identification peaks: very broad peaks around 3380 cm^{-1} with the characteristics of ν-*OH* (hydrogen bonding) and ν-*NH*; sharp peaks around 2950 cm^{-1}, assigned to ν-*CH* stretches of CH_3; three very strong and sharp peaks at 2162, 2150 and 2135 cm^{-1}, assigned to bridging and terminal ν-*CN* modes; a strong and sharp peak at 1650 cm^{-1}, characteristic of ν-*HOH* and ν-*CO* of DMF. The peaks at 1438 and 1382 cm^{-1} arise from aldehydic C–H bends and the peak at 1059 cm^{-1} is from ν-*CN* stretches.

Crystal Structures

Taking into account the presence of four *N*,*N*-dimethylformamide ligands, three water molecules, a discrete hexacyanocobaltate(III) moiety and one additional crystalline water molecule, the molecular formulas of **1** and **2** have the stoichiometry $Ln(DMF)_4(H_2O)_3Co(CN)_6 \cdot H_2O$ [Ln = Nd (**1**) and Gd (**2**)]. Obviously, **1** and **2** are isomorphous. A representative molecular structure of **1** is shown in Fig. 1. Selected geometric parameters for **1** and **2** are presented in Table II.

The molecular units within the crystal lattice are separated by normal van der Waals contact distances. The Ln(III) ion is in a slightly distorted square antiprism (D_{4d}) geometry, eight-coordinated by four DMF ligands, three water molecules and a discrete

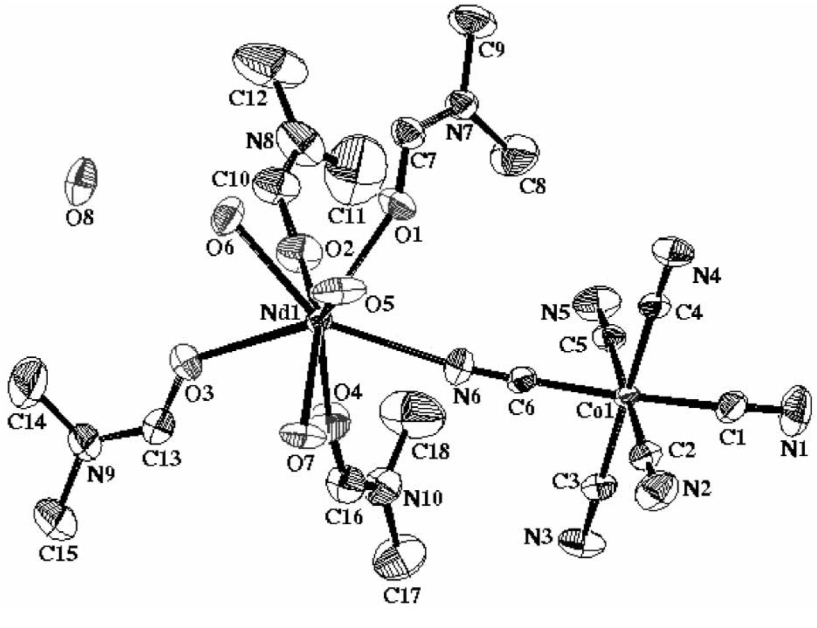

FIGURE 1 A perspective view of molecular structure of **1**. Hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at 50% probability level.

TABLE II Selected bond distances (Å) bond angles (°) for **1** and **2**

	Nd (*1*)	*Gd* (**2**)
Ln(1)–O(1)	2.410(4)	2.396(9)
Ln(1)–O(2)	2.437(5)	2.420(10)
Ln(1)–O(3)	2.438(4)	2.406(8)
Ln(1)–O(4)	2.408(5)	2.384(10)
Ln(1)–O(5)	2.475(4)	2.431(9)
Ln(1)–O(6)	2.481(4)	2.447(8)
Ln(1)–O(7)	2.465(4)	2.433(8)
Ln(1)–N(6)	2.543(5)	2.516(10)
Co(1)–C(1)	1.891(5)	1.90(1)
Co(1)–C(2)	1.900(5)	1.897(10)
Co(1)–C(3)	1.889(5)	1.90(1)
Co(1)–C(4)	1.882(5)	1.89(1)
Co(1)–C(5)	1.902(4)	1.90(1)
Co(1)–C(6)	1.899(4)	1.894(9)
C≡N (mean)	1.149	1.138
C(6)≡N(6)	1.135(7)	1.13(1)
Co(1)–C(1)–N(1)	177.8(5)	178(1)
Co(1)—C(2)–N(2)	178.9(5)	178(1)
Co(1)–C(3)–N(3)	178.3(5)	178(1)
Co(1)–C(4)–N(4)	178.4(4)	178.7(9)
Co(1)–C(5)–N(5)	178.1(5)	178(1)
Co(1)–C(6)–N(6)	176.7(4)	175.2(9)
Co–C≡N (mean)	178.0	177.7
Ln(1)–N(6)–C(6)	165.1(4)	167.5(9)

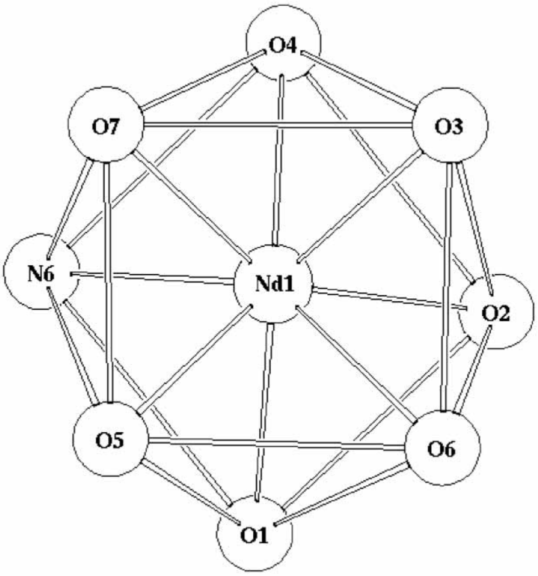

FIGURE 2 The coordination geometry of the Ln(III) ions consists of a slightly distorted square antiprism.

hexacyanocobaltate(III) moiety, all bonded to the central Ln metal (Fig. 2). The top face of the prism, composed of the atoms of O(3), O(5), O(6) and O(7), is essentially planar with a mean deviation of 0.0015 and 0.0119 Å, while the bottom face, defined by O(1), O(2), O(4) and N(6), is slightly distorted from planarity by a mean deviation of 0.2044 and 0.1986 Å for **1** and **2**, respectively. The dihedral angles between the two mean planes are 3.69 and 3.20° for **1** and **2**, respectively.

1 and **2** are also similar to those isomorphous complexes $Ln(DMF)_4(H_2O)_3Co(CN)_6 \cdot H_2O$ (Ln = Ce, Sm, Yb, Lu) and $Ln(DMF)_4(H_2O)_3Fe(CN)_6 \cdot H_2O$ (Ln = La, Ce, Pr, Tm, Yb, Er, Yb, Lu) [12,14]. However, the Sm(III) ion in $Sm(DMF)_4(H_2O)_4Fe(CN)_6 \cdot H_2O$ was nine coordinate [13]. In fact, one of the Sm–O bond distances in $Sm(DMF)_4(H_2O)_4Fe(CN)_6 \cdot H_2O$ is 2.885(5) Å, which is too long to be considered as a bonding interaction. The mean Nd–O and Gd–O bond distances of 2.445 (2.408–2.543) and 2.416 (2.384–2.516) Å for **1** and **2**, respectively, which are consistent with the sum of the radii of neodymium/gadolinium and oxygen [20], are close to the reported Nd–O bond distances in $Nd(bipm)(H_2O)_4Fe(CN)_6 \cdot 3H_2O$ (2.424–2.533 Å) [6b], $NdCo(CN)_6 \cdot 5H_2O$ (2.53–2.56 Å) [19], $Co_2Nd(O_2CCMe_3)_6(C_9H_7N)_2(NO_3)$ (2.358–2.565 Å) [21] and the reported Gd–O bond distances in $\{[Gd(DMA)_3(H_2O)_4]_2[Fe(CN)_6]\}[Fe(CN)_6] \cdot 3H_2O$ (2.472–2.547 Å) [7], $[CoGd(piv)_5(C_9H_7N)(H_2O)] \cdot 0.5C_9H_7N$ (2.295–2.475 Å) and $[Co_2Gd(piv)_6(C_9H_7N)_2(NO_3)]$ (2.299–2.463 Å) [22]. The Nd–N and Gd–N bond distances for **1** and **2** are 2.543(5) and 2.516(10) Å, respectively, which are similar to Nd–N bond distances in $Nd(bipm)(H_2O)_4Fe(CN)_6 \cdot 3H_2O$ (2.511–2.729 Å) [6b], $NdCo(CN)_6 \cdot 5H_2O$ (2.54–2.58 Å) [19], and for Gd–N bond distances in $\{[Gd(DMA)_3(H_2O)_4]_2[Fe(CN)_6]\}[Fe(CN)_6] \cdot 3H_2O$ (2.543 and 2.559 Å) [7].

The cobalt ion is in approximately octahedral (O_h) geometry, six-coordinated by six CN groups. The mean C≡N bond distances of 1.149 (1.135–1.159) and 1.138 Å (1.13–1.15) Å for **1** and **2**, respectively, are consistent with the summation of the triple bond radii of C and N atoms (0.603 and 0.55 Å) [23], and also similar to those in $Ln(DMF)_4(H_2O)_3Fe(CN)_6 \cdot H_2O$ (Ln = La, Ce, Pr, Tm, Er, Yb, Lu) (1.144–1.150 Å) [12] and $Ln(DMF)_4(H_2O)_3Co(CN)_6 \cdot H_2O$ (Ln = Ce, Sm, Yb, Lu) (1.141–1.152 Å) [14]. The mean Co–C bond distances of 1.892 (1.882–1.902) and 1.897 (1.89–1.90) Å in **1** and **2**, which are in accord with the sum of the radii of cobalt and carbon atoms [23], are similar to the reported Co–C bond distances in $Ln(DMF)_4(H_2O)_3Co(CN)_6 \cdot H_2O$ (Ln = Ce, Sm, Yb, Lu) (1.886–1.911 Å) [14]. The rest of the bond distances for **1** and **2** are consistent with reported values [12,14]. The interaction of 3d orbitals for the Co(III) ions and the CN^- orbitals leads to strong directional bonding. The mean Co–C≡N angles are approximately 178.0 (176.7–178.9) and 177.7 (175.2–178.7)° for **1** and **2**, respectively, similar to those in $LnCo(CN)_6 \cdot 5H_2O$ (Ln = Pr, Nd) (177–179.4°) [21] and $Ln(DMF)_4(H_2O)_3Co(CN)_6 \cdot H_2O$ (Ln = Ce, Sm, Yb, Lu) (176.1–177.9°) [14]. However, little directional influence is observed for the electrostatic bonding of the Ln(III) ions to the CN^- groups. The bond angles of the Ln–N≡C are 165.1(4) and 167.5(9)° for **1** and **2**, respectively, close to those in $Ln(DMF)_4(H_2O)_3Co(CN)_6 \cdot H_2O$(Ln = Ce, Sm, Yb, Lu) (163.0–164.2°) [14].

Hydrogen bonding and van der Waals cohesive forces are important in the intermolecular network of the crystal lattices of these compounds. The molecular units in the crystal cells of each compound are separated by normal van der Waals contact distances. According to the data of Hamilton and Ibers [24], hydrogen bonding of the O–H···N and O–H···O types may be present when O···N and O···O contact distances are within 3.2 Å. Such distances (see Table III) occurred in the crystal lattices of **1** and **2** where the crystalline water molecules are involved in the network of hydrogen bonding (Fig. 3).

TABLE III Possible hydrogen bond distances (Å) for **1** and **2**

D···*A*	*Nd* (*1*)	*Gd* (**2**)
O(8)···N(1)	2.815(6)[a]	2.82(1)[e]
O(8)···N(2)	2.888(6)[b]	2.91(2)[f]
O(8)···O(6)	2.670(5)	2.67(1)
N(4)···O(5)	2.820(6)[c]	2.84(1)[g]
N(4)···O(6)	2.851(6)[d]	2.86(1)[g]

Symmetry transformation: [a] $x+1/2$, $-y+3/2$, $z+1/2$; [b] $x+1/2$, $-y+1/2$, $z+1/2$, [c] $-x+1/2$, $y-1/2$, $-z+1/2$; [d] $-x+1/2$, $y+1/2$, $-z+1/2$, [e] $x-1/2$, $-y-1/2$, $z+1/2$; [f] $x-1/2$, $-y+1/2$, $z-1/2$; [g] $-x+3/2$, $y+1/2$, $-z+1/2$.

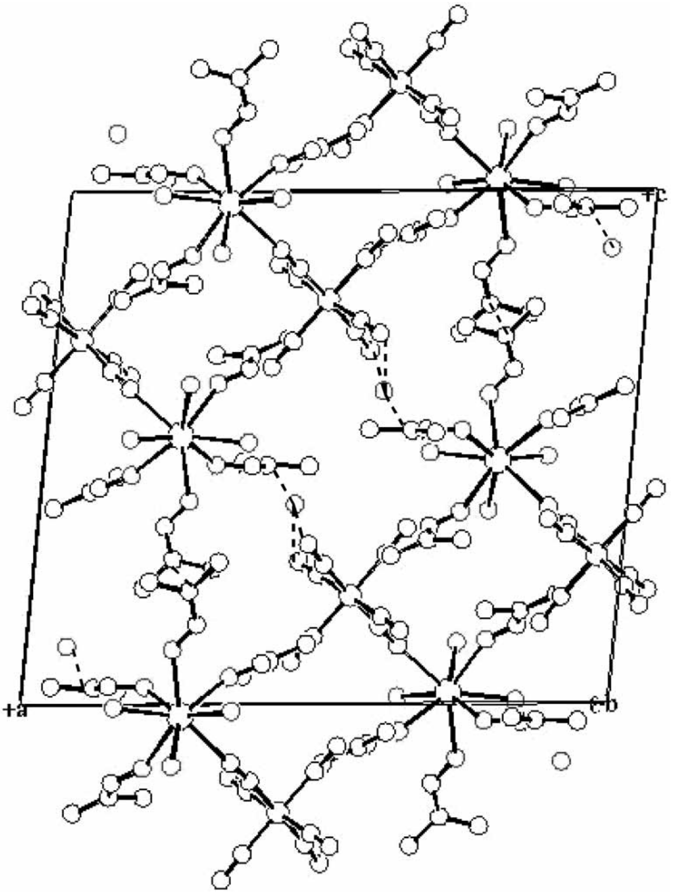

FIGURE 3 The crystal structure of **1** viewed down the crystallographic *b* axis showing hydrogen bonds as dashed lines.

Magnetic Properties

The temperature dependence of the magnetic susceptibilities for compounds **1** and **2** was examined in the temperature range 5–300 K. The plots of $\chi_M T$ *versus* T are presented in Fig. 4. Obviously, the profiles of the plots for **1** and **2** are similar, indicating similar

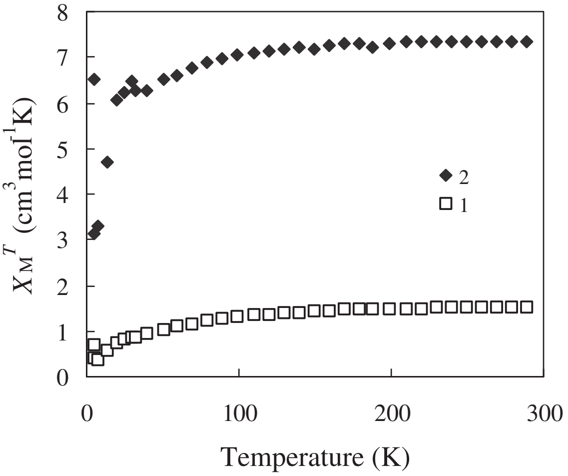

FIGURE 4 $\chi_M T$ *vs.* temperature (K) plot at $H = 5$ kG for **1** and **2**.

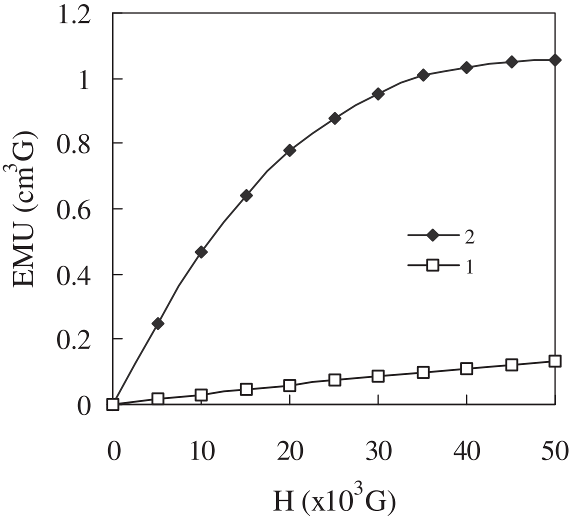

FIGURE 5 Magnetization *vs.* H at 5 K for **1** and **2**.

magnetic behavior. The experimental $\chi_M T$ values at 300 K are 1.52 and 7.33 for **1** and **2**, respectively, which are close to the calculated $\chi_M T$ values for noninteracting metal ions of 1.64 and 7.88. The $\chi_M T$ values should decrease with decreasing temperature; however, clear rebounds are observed when the temperature is lowered to 7 K for both **1** and **2**, indicative of an antiferromagnetic interaction. Since there is no intramolecular interaction between the paramagnetic Ln(III) ions and the diamagnetic Co(III)$_{LS}$ ions, it is proposed that the intermolecular interactions take place in the three-dimensional network through hydrogen bonds below 7 K [14a]. The cooperativity arising from the network enhances the weak interaction between the Ln(III) ions, enabling it to be observed at very low temperature.

The field dependences of the magnetization for compounds **1** and **2** were examined in the range 0–50 kG at 5 K. The plots of *EMU versus H* are shown in Fig. 5. As a result, the different magnetic phenomena for **1** and **2** are revealed, i.e., the magnetization is increased and saturated rapidly for **1** by increasing the applied field but only slowly for **2**. This is ascribed to the nature of the thermal population of Ln(III) Stark components [14a].

In summary, two new hetero-dinuclear lanthanide cyanide-bridged hexacyanocobaltate complexes have been synthesized and characterized by X-ray crystallographic analysis. These complexes are among a few rare earth and cobalt hetero-bimetallic assemblies. Interestingly, the weak antiferromagnetic interactions, resulting from intermolecular interactions between the Ln(III) ions in the network, were observed for both **1** and **2** below 7 K. It proposed that the cooperativity arising from the network structure through hydrogen bonds plays an important role in molecular magnetization for this series of compounds. In addition, these compounds are of importance in photo-induced magnetism because of the cyanide bridge between 3d and 4f metals. Some photo-induced magnetic properties have been observed for certain compounds in research currently ongoing in our group.

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Supplementary Data

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 203315 for **1** and CCDC No. 203316 for **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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