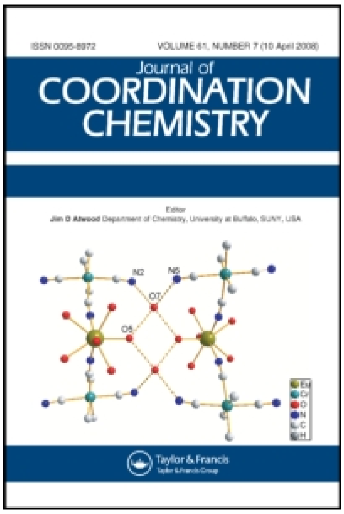

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A cyano-bridged hetero-tetranuclear [Sm_2(o-phen)$_2$(DMF)$_6$(H_2O)$_2$(μ-CN)$_4$$Fe_2(CN)_8$] · 5$H_2O$ · CH_3OH: synthesis, structure, Mössbauer spectrum, and magnetism

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A cyano-bridged hetero-tetranuclear $[Sm_2(o\text{-}phen)_2(DMF)_6(H_2O)_2(\mu\text{-}CN)_4Fe_2(CN)_8]\cdot5H_2O\cdot CH_3OH$: synthesis, structure, Mössbauer spectrum, and magnetism

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Two new hetero-tetranuclear complexes, $[Sm_2(o\text{-}phen)_2(DMF)_6(H_2O)_2(\mu\text{-}CN)_4Fe_2(CN)_8]\cdot5H_2O\cdot CH_3OH$ (**1**) and $[Sm_2(o\text{-}phen)_2(DMF)_6(H_2O)_2(\mu\text{-}CN)_4Co_2(CN)_8]\cdot5H_2O$ (**2**), have been prepared from reaction of $SmCl_3\cdot6H_2O$, $K_3[Fe(CN)_6]\cdot3H_2O$ or $K_3[Co(CN)_6]$, and o-phen in methanol/DMF, and characterized. The structure of **1** consists of a cyano-bridged discrete cyclic tetranuclear complex in which the Sm(III) and Fe(III) centers are linked by four CN groups. Mössbauer spectrum of ^{57}Fe indicates that both Fe(III) atoms in **1** have the same low-spin ($S=1/2$) electronic ground state. From comparison of the magnetic data of **1** and **2**, at low temperature for **1** indicates weak ferromagnetic coupling between Sm(III) and Fe(III).

Keywords: Samarium; Ferricyanide; Cyanide-bridged lanthanide complexes; Crystal structure; Mössbauer effect; Magnetic properties

1. Introduction

Cyanide-bridged 3d–4f complexes may open new perspectives as optical and magnetic molecular media of rare earth elements [1–4]. A series of cyano-bridged 3d–4f heterobimetallic complexes based on $[M(III)(CN)_6]^{3-}$ (M = Fe, Co, Cr) have been synthesized to clarify the intermetallic magnetic interactions and to develop new molecule-based magnets [5–12]. Among Sm(III)–$Fe(CN)_6^{3-}$ complexes with cyano-bridges, different molecular structures have been found: dinuclear $[Sm(DMF)_4(H_2O)_4Fe(CN)_6]\cdot H_2O$ [8] and $[Sm(DMF)_4(H_2O)_3Fe(CN)_6]\cdot H_2O$ [9], 2-D $[Sm(DMSO)_2Fe(CN)_6\cdot H_2O]_n$ [10] and 1-D $[Sm(DMF)_2(H_2O)_4Fe(CN)_6\cdot5H_2O]_n$ [11], $[Sm(DMF)_4(H_2O)_2Fe(CN)_6\cdot H_2O]_n$ [12] and $[Sm(bpy)(H_2O)_4Fe(CN)_6]_n\cdot5nH_2O\cdot$ 1.5nbpy [6c] (bpy = 2,2-bipyridine, DMF = *N*,*N*-dimethylformamide; DMSO = dimethyl sulfoxide, DMA = *N*,*N*′dimethylacetamide; bpy = 2,2-bipyridine). In contrast, discrete tetranuclear Sm(III)–$Fe(CN)_6^{3-}$ complexes have not been reported. This work reports the preparation, characterization including X-ray single crystal structural analysis, ^{57}Fe-Mössbauer spectrum, and magnetic properties of the

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first discrete $[Sm_2(o\text{-}phen)_2(DMF)_6(H_2O)_2(\mu\text{-}CN)_4Fe_2(CN)_8]5H_2O \cdot CH_3OH$ (**1**). In addition, preparation and magnetic data of $[Sm_2(o\text{-}phen)_2(DMF)_6(H_2O)_2(\mu\text{-}CN)_4Co_2(CN)_8] \cdot 5H_2O$ (**2**) are also reported. The cobalt(III) center in **2** is diamagnetic and used to analyze the magnetic interactions in **1** with the empirical approach.

2. Experimental

2.1. *Materials*

$SmCl_3 \cdot 6H_2O$, $K_3[Fe(CN)_6] \cdot 3H_2O$ or $K_3[Co(CN)_6]$, 1,10-phenanthroline (o-phen), and other materials of analytical grade (Aldrich Co.) were used as supplied.

2.2. *Preparation of $[Sm_2(o\text{-}phen)_2(DMF)_6(H_2O)_2(\mu\text{-}CN)_4Fe_2(CN)_8] \cdot 5H_2O \cdot CH_3OH$ (1) and $[Sm_2(o\text{-}phen)_2(DMF)_3(H_2O)_2Co_2(CN)_8] \cdot 4H_2O$ (2)*

A mixed solution of $SmCl_3 \cdot 6H_2O$ (365 mg, 1 mmol) in 10 mL H_2O and 1,10-phenanthroline (180 mg, 1 mmol) in 10 mL CH_3OH was stirred for 1 h then $K_3Fe(CN)_6 \cdot 3H_2O$ (0.422 mg, 1 mmol) in 10 mol H_2O was added. To the resulting solution, 10 mL dmf was added, and the mixture was further stirred for 30 min, and allowed to stand for crystallization. After three weeks orange-red crystals of **1** suitable for X-ray diffraction analysis separated. The procedure of preparation for **2** is similar to that of **1** except $K_3Fe(CN)_6 \cdot 3H_2O$ was replaced by $K_3Co(CN)_6$. After three weeks light crystals separated. Anal. Calcd (%) for $C_{55}H_{76}Sm_2Fe_2N_{22}O_{13}$ (**1**): C, 38.28; H, 4.55; N, 18.32. Found: C, 38.32; H, 4.72; N, 18.36. Selected IR ν_{CN} (KBr cm^{-1}) 2086, 2132 (terminal), and 2140 (bridged). Anal. Calcd (%) for $C_{54}H_{72}Sm_2Co_2N_{22}O_{12}$ (**2**): C, 39.54; H, 4.40; N, 18.80. Found: C, 39.48; H, 4.32; N, 19.02. Selected IR ν_{CN} (KBr cm^{-1}) 2079, 2135 (terminal), and 2159 (bridged).

2.3. *Physical measurements*

IR spectra were recorded on a Bio-Rad FTS40FTIR spectrophotometer using KBr pellets in the 400–4000 cm^{-1} region. The ^{57}Fe Mössbauer spectrum was measured by ^{57}Co(Rh) source on a WissEl Mössbauer measuring system. Both source and sample were kept at 77 K in a cryostat equipped with a closed-cycle refrigerator. The isomer shift is relative to α-iron at 295 K. Variable-temperature (2–300 K) magnetic susceptibility measurements for **1** and **2** were carried out with a Quantum Design MPMS SQUID magnetometer under fixed field strength of 1 T.

2.4. *X-ray crystal structure analysis*

Crystallographic data were collected at 200 K on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct and Fourier methods and refined by full-matrix least-squares methods based on F^2 using the program NRCVAX package. All non-hydrogen atoms were readily located and refined using anisotropic thermal parameters. Crystallographic

Table 1. Crystal data and structure refinement for $[Sm_2(\text{o-phen})_2(DMF)_4(H_2O)_2Fe_2(\mu\text{-}CN)_4(CN)_8]_2 \cdot 5H_2O \cdot CH_3OH$ (**1**).

Formula	$C_{55}H_{76}Sm_2Fe_2N_{22}O_{13}$
Formula weight	1681.78
Space group	Monoclinic $C2/c$
a (Å)	33.3865
b (Å)	12.6608
c (Å)	17.3195
β (°)	99.1350
V (Å^3)	7228.10
Z	4
D_{Calc} (Mg m^{-3})	1.545
λ (Mo-Kα) (Å)	0.71073
T (K)	200(2)
Collected reflections	29691
Independent reflections	6614 [$R(\text{int}) = 0.0446$]
Goodness-of-fit on F^2	1.004
R_1[a]	0.0323
wR_2[b]	0.0967

$^{a}R_1 = \Sigma|F_o - F_c|/\Sigma|F_o|$, $^{b}wR_2 = (\Sigma_w |F_o - F_c|^2/\Sigma |Fo|^2)^{1/2}$.

details for the structure of **1** are summarized in table 1. CCDC reference number: 616748.

3. Results and discussion

3.1. *Synthesis*

Complex **1** was synthesized by the reaction of $SmCl_3 \cdot 6H_2O$ in water with o-phen (1,10-phenanthroline) in CH_3OH and $K_3[Fe(CN)_6] \cdot 3H_2O$ in water, the resulting yellow precipitates were dissolved in a small amount of DMF. In this method, the o-phen is a blocking ligand which plays a role in building the tetranuclear Sm_2–Fe_2 structure.

3.2. *Structure of 1*

The crystal structure of **1** with ORTEP drawing is shown in figure 1, and selected bond distances and angles relevant to the metal coordination sphere are listed in table 2. Crystallographic analysis of **1** revealed that its crystal is a discrete hetero-tetranuclear, $[Sm_2(\text{o-phen})_2(DMF)_4(H_2O)_2Fe_2(\mu\text{-}CN)_4(CN)_8]_2 \cdot 5H_2O \cdot CH_3OH$. The structural framework is similar to the corresponding tetranuclear complex of $[Gd_2(\text{urea})_8(H_2O)_4Cr_2(\mu\text{-}CN)_4(CN)_8]$ [5g], in which the complex is a neutral molecular square with two eight-coordinate Gd(III) ions linked by two $Cr(CN)_6$ moieties, each $Cr(CN)_6$ bridged two Gd(III) ions using two *cis* cyano ligands and each Gd(III) ion in turn links two $Cr(CN)_6$ units *cis* fashion. The structure of **1** shows (figure 1) alternation of Sm(III) and Fe(III) units linked by two cyanide bridges in *cis* geometry with respect to Fe(III). The coordination sphere around each Sm(III) comprises three oxygen atoms (O(1), O(2), and O(3)) of dmf, one oxygen atom (O(4)) of water, two nitrogen atoms (N(1), N(2)) of the cyanide bridges, and two nitrogen atoms (N(7) and (N(8)) of o-phen.

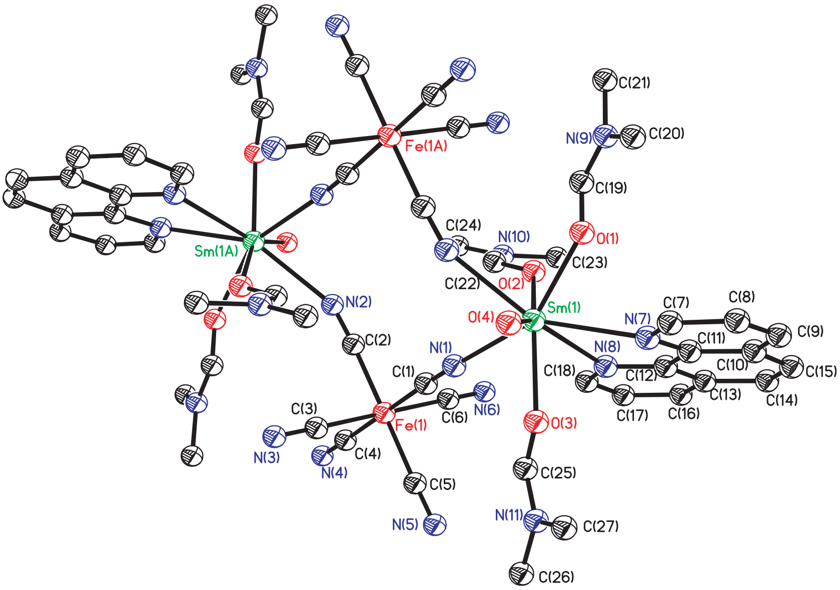

Figure 1. Perspective drawing of **1** with atom numbering scheme. Thermal ellipsoids are drawn at 30% probability level. The solvent molecules were omitted for clarity.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Sm–O(1)	2.352(3)	Sm–O(2)	2.412(3)
Sm–O(3)	2.413(3)	Sm–O(4)	2.373(2)
Sm–N(1)	2.485(3)	Sm–N(2a)	2.518(3)
Sm–N(7)	2.608(3)	Sm–N(8)	2.605(4)
Fe–C(1)	1.931(4)	Fe–C(2)	1.932(4)
Fe–C(3)	1.956(4)	Fe–C(4)	1.930(4)
Fe–C(5)	1.943(4)	Fe–C(6)	1.957(4)
O(1)–Sm(1)–O(3)	138.13(10)	O(1)–Sm(1)–N(1)	147.31(10)
O(4)–Sm(1)–O(2)	149.48(9)	O(3)–Sm(1)–O(2)	134.81(10)
N(8)–Sm(1)–N(7)	62.99(12)	C(1)–Fe(1)–C(4)	179.49(17)
C(1)–N(1)–Sm(1)	167.3(3)	C(7)–N(7)–Sm(1)	121.7(3)
C(11)–N(7)–Sm(1)	119.4(3)	C(18)–N(8)–C(12)	118.1(4)
C(18)–N(8)–Sm(1)	121.9(3)	C(12)–N(8)–Sm(1)	119.3(3)
N(1)–C(1)–Fe(1)	177.5(4)	N(2)–C(2)–Fe(1)	175.6(3)
N(3)–C(3)–Fe(1)	178.0(3)	N(4)–C(4)–Fe(1)	178.1(4)
N(5)–C(5)–Fe(1)	178.3(4)	N(6)–C(6)–Fe(1)	178.6(4)

The eight-coordinate Sm lies in a distorted dodecahedral environment. The bond angles (°) of C(3)–Fe(1)–C(6) = 178.97(15), C(2)–Fe(1)–C(5) = 179.08(17), C(2)–Fe(1)–C(3) = 88.00(16), and C(1)–Fe(1)–C(3) = 92.45(15) around the Fe(III) atom reveal distorted octahedral geometry of $Fe(CN)_6$. The Sm-Fe intermolecular distance is 5.528 Å and the Sm–Fe–Sm angle is 93.60°, indicating cyclic *cis* geometry. The shortest intermolecular contact is through weak hydrogen bonding (2.774 Å) with Fe–CN(4) $\cdots$ H–O(4)′ between the nitrogen of terminal NC ligand and water hydrogen (H–O(4)) of an adjacent molecule (figure 2).

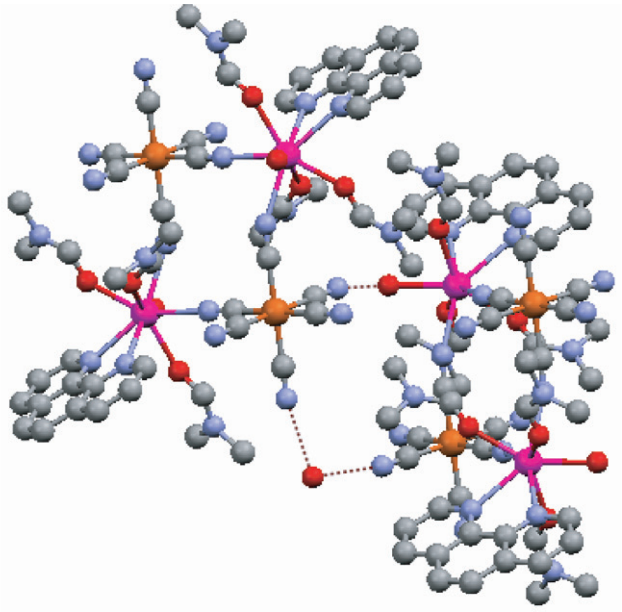

Figure 2. Perspective view of the shortest intermolecular contact through the weak hydrogen bonding as shown by dotted lines.

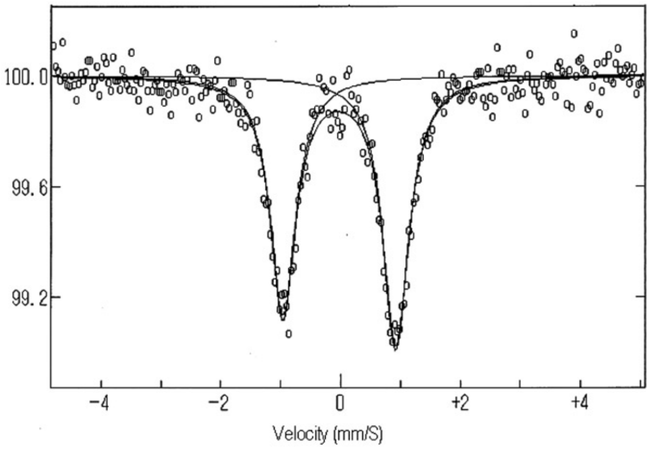

Figure 3. Mössbauer spectra at 78 K for **1**.

3.3. ^{57}*Fe Mössbauer spectra*

The measured ^{57}Fe Mössbauer spectra for **1** at 78 K is shown in figure 3. The isomer shift (I.S.) = −0.17 mm s^{-1} (300 K), −0.02 mm s^{-1} (78 K), and quadrupole splitting (Q.S.) = 1.82 mm s^{-1} (300 K), and 1.89 mm s^{-1} (78 K) are in the range of powder samples of 1D Ln–phen–Fe(CN)$_6$ systems [13] and indicate that both Fe(III) atoms in **1** have low-spin (S = 1/2) electronic ground state. The larger Q.S. value of Fe(III) in **1** gives large electric-field-gradient (EFG) at Fe(III) associated with the typical pattern of

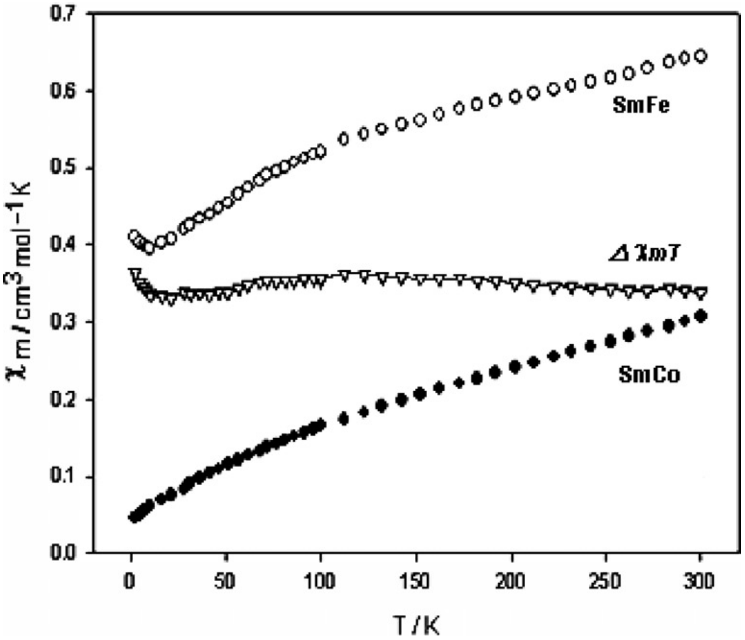

Figure 4. Temperature dependence of χ_mT for **1** (per SmFe unit) (-○-) and **2** (-●-) and $\Delta\chi_mT$ (-Δ-) between the susceptibilities of **1** and **2**.

CN-bridged $Fe(CN)_6$ in the Ln–NC–Fe–CN–Ln framework [13], also suggesting that the octahedral $Fe(CN)_6$ may distort [14].

3.4. *Magnetic susceptibility studies*

Magnetic susceptibility measurements for **1** and **2** are shown in figure 4 as χ_mT (per Sm–Fe unit) *versus* T. As the temperature is lowered, the χ_mT value per Sm–Fe unit of **1** decreases steadily reaching a minimum at 8 K, then increases with further lowering of temperature. This magnetic behavior is similar to those of dinuclear $[Sm(DMF)_4(H_2O)_3Fe(CN)_6]\cdot H_2O$, 1-D polymers of $[Sm(DMF)_4(H_2O)_2Fe(CN)_6\cdot H_2O]_n$ [12] and $[Sm(bpy)(H_2O)_4Fe(CN)_6]_n\cdot 5nH_2O\cdot 1.5nbpy$ [6c]. The temperature dependence of χ_mT for **2** [SmCo] is shown in figure 4. At 300 K the χ_mT value is approximately 0.31 cm^3 mol^{-1} K, inconsistent with the theoretical value of zero cm^3 mol^{-1} K expected for independent Sm(III) (^7F_o). This disagreement is ascribed to the presence of thermally populated electronic excited states. On lowering the temperature, the χ_mT value decreases monotonically to 0.05 cm^3 mol^{-1} K.

To obtain insights into the nature of the $[SmFe]_2$ magnetic coupling in **1**, we used an empirical approach method. Assuming intermolecular magnetic exchange interaction path-way through the Sm–NC–Fe in **1** and Sm–NC–Co in **2**. The Co(III) ion in **2** is diamagnetic and the difference in χ_mT between **1** and **2** ($\Delta\chi_mT$) and its variation with temperature can arise only from magnetic exchange interactions between Fe(III) and Sm(III). As shown in figure 4, $\Delta\chi_mT$ remains independent of T throughout the high temperature range (300–30 K) and slightly increasing with lowering of the temperature (from 10 K to 2 K), indicative of magnetic noninteraction at high temperature for the two Sm(III)–Fe(III) and a weak ferromagnetic interaction at very low temperature. The weak ferromagnetic exchange interactions of **1** below 10 K may arise from intramolecular cyanide bridging of Sm–NC–Fe or intermolecular hydrogen bonding as shown in figure 3.

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