Cyano-bridged One-dimensional Sm^{III}–Fe^{III} Molecule-based Magnet with an Ordering Temperature of 3.4 K

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A new cynao-bridged Sm^{III}–Fe^{III} bimetallic coordination polymer has been prepared by the reaction of $(n\text{-}Bu_4N)_3Fe(CN)_6$ and $Sm(NO_3)_3\cdot 6H_2O$ in a DMF–H_2O media. The complex consists of alternate $Sm(DMF)_4(H_2O)_2$ and $Fe(CN)_6$ units bridged by two *cis*-cyano ligands to form a zigzag chain. It behaves as a molecule-based magnet with $T_c = 3.4$ K. At 2 K, hysteresis was observed with a coercive field of 200 Oe.

In the past decades, considerable attention has been paid to coordination compounds built from hexacyanometalate units. Recently, a series of cyano-bridged 3d–4f dinuclear, trinuclear, tetranuclear, or polymeric assemblies based on $[M(CN)_6]^{3-}$ have been synthesized in order to learn the nature of the intermetallic magnetic exchange interactions and to search new molecule-based magnets.[1] As far as Sm^{3+}–$Fe(CN)_6{}^{3-}$ complexes are concerned, different molecular structures have been found, dinuclear $[Sm(DMF)_4(H_2O)_4Fe(CN)_6]\cdot H_2O$[2] and $[Sm(DMF)_4(H_2O)_3Fe(CN)_6]\cdot H_2O$,[3] two-dimensional $[Sm(DMSO)_2Fe(CN)_6\cdot H_2O]_n$,[4] and one-dimensional polymer $[Sm(DMA)_2(H_2O)_4Fe(CN)_6\cdot 5H_2O]_n$ (DMF = *N*,*N*-dimethylformamide; DMSO = dimethyl sulfoxide, DMA = *N*,*N*-dimethylacetamide).[5] Nevertheless, it is interesting to note that there is only one example that has a 1D structure.

Herein, we report a new cyano-bridged one-dimensional Sm–Fe complex $[Sm(DMF)_4(H_2O)_2Fe(CN)_6\cdot H_2O]_n$ (**1**).[6] **1** was synthesized by the reaction of $(n\text{-}Bu_4N)_3Fe(CN)_6$ in DMF solution with equimolor $Sm(NO_3)_3\cdot 6H_2O$ in water, and yellow single crystals were grown by evaporation. It is worth mentioning that dimeric $Sm(DMF)_4(H_2O)_4Fe(CN)_6$ or $Sm(DMF)_4(H_2O)_3Fe(CN)_6$ was obtained when $K_3Fe(CN)_6$ was empolyed.[2,3]

$$K_3Fe(CN)_6 + Sm^{3+} \xrightarrow[\text{DMF}]{H_2O} Sm(DMF)_4(H_2O)_3Fe(CN)_6 \text{ (dimer)}$$

$$(n\text{-}Bu_4N)_3Fe(CN)_6 + Sm^{3+} \xrightarrow[\text{DMF}]{H_2O} [Sm(DMF)_4(H_2O)_2Fe(CN)_6\cdot H_2O]_n. \ (\mathbf{1})$$

X-ray diffraction structural characterization shows that the complex is isostructural with $Sm(DMF)_4(H_2O)_2Cr(CN)_6\cdot H_2O$,[1h] and consists of a neutral chain with alternate Sm^{3+} and $[Fe(CN)_6]^{3-}$ ions (Figure 1). $[Fe(CN)_6]^{3-}$ anions in a cis fashion link Sm(III) atoms, and in turn Sm^{3+} ions are coordinated by two *cis*-cyano nitrogen atoms forming a zigzag chain (Figure 2, top). The Fe center in **1** is in slightly distorted octahedral geometry, viz., C(1)–Fe(1)–C(2) and C(1)–Fe(1)–C(5) angles are 85.06° and 92.39°, respectively. The values of the Fe–C bonds are in the range 1.934–1.950 Å. The Fe–C–N angles of the iron and cyanides are almost linear (173.68–178.38°). Each Sm^{3+} ion is eight-coordinated by two N atoms (N(2A) and N(5)) from different $[Fe(CN)_6]^{3-}$ units (the length of Sm–N = 2.543–2.545 Å), four O atoms from four DMF molecules and two O atoms from two water molecules (the length of Sm–O = 2.367–2.433 Å). The angle of N(5)–Sm(1)–N(2A) is 75.66°. The bond angles of Sm(1)–N(5)–C(5) and Sm(1)–N(2A)–C(2A) (A denotes symmetry code: $-x + 3/2$, $y - 1/2$, $-z + 1/2$) are 161.63 and 157.96°, respectively. Adjacent Sm···Fe separation is 5.539 Å.

Intra- and interchain hydrogen bonds have been found between the water molecules and the nitrogen atoms of CN groups [O(2W)···N(4) (symmetry code: $-x + 1/2$, $y - 1/2$, $-z + 1/2$) 2.778 Å, O(2W)–H(2B)···N(4) 175.85°; O(2W)···N(6) (symmetry code: x, $y - 1$, z) 2.757 Å, O(2W)–H(2A)···N(6) 169.12°], and these hydrogen bonds link the one-dimensional chains into

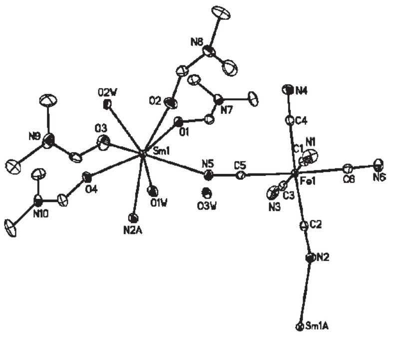

Figure 1. Perspective drawing of the unit.

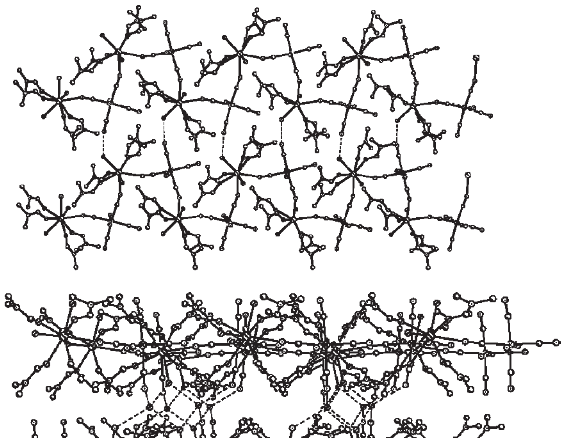

Figure 2. Two-dimensional layer (top) and three-dimensional network (bottom) formed by hydrogen bonds of **1**.

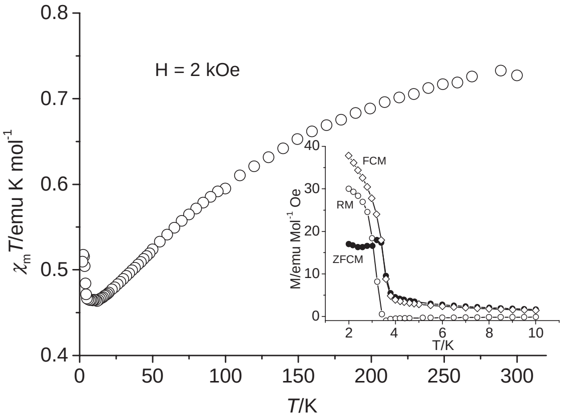

Figure 3. The $\chi_m T$ vs T plot for **1**. Inset: FCM, ZFCM, and RM plots for **1**.

the two-dimensional layer structure. The layers are further extended into a three-dimensional supramolecular network by hydrogen bonds involving the uncoordinated water molecules (Figure 2).

The strong bands of IR spectra at 2148 and 2123 cm^{-1} can be attributed to the stretching of CN group.

The magnetic susceptibilities of **1** were measured using a SQUID magnetometer between 2 and 300 K in a field of 2 kOe. The $\chi_m T$ versus T plot is shown in Figure 3. As the temperature is lowered, the $\chi_m T$ value decreases steadily reaching a minimum at 9 K. With a further decrease in temperature, $\chi_m T$ increases rapidly. The magnetic susceptibility above 70 K obeys the Curie–Weiss law with the Weiss constants of $\theta = -40.8$ K and $C = 0.83$ emu mol^{-1} K based on the equation $\chi_m = C/(T - \theta)$. However, the nature of the magnetic coupling between the adjacent Sm(III) and Fe(III) ions can not be simply determined from the decrease of $\chi_m T$ because of the superposition of the thermal depopulation of the low-lying excited states of Sm(III), orbital contribution of low-spin Fe(III), and the Sm(III)–Fe(III) magnetic interaction.[1h]

The increase in $\chi_m T$ at low temperatures signifies the existence of 3D magnetic ordering. Indeed, as shown in inset of Figure 3, FCM and ZFCM measurements[7] show that two curves diverge at 3.4 K. Moreover, remnant magnetization (RM) curve reveals that the magnetization vanishes at 3.4 K, indicating that **1** exhibits a magnetic phase transition at 3.4 K.

The magnetization curve at 2 K shows regular increase with the increase of magnetic field, as shown in Figure 4. The value at 50,000 Oe is only 0.64 $N\beta$. Such a small value might signify the presence of antiferromagnetic Sm(III)–Fe(III) interaction in complex **1**. However, it should be pointed out that the nature of Sm(III)–Fe(III) interaction is better determined by the comparison of $\chi_m T$ curves of isostructural SmFe and SmCo species.[8] Unfortunately, we cannot synthesize the isomorphous Co(III) compound, and such a comparison could not be done. The hysteresis loop at 2 K (Inset of Figure 4) is observed with a coercive field of 200 Oe, further confirming that **1** is a molecule-based magnet.

In summary, the new cyano-bridged one-dimensional Fe(III)–Sm(III) complex synthesized by using $(n\text{-Bu}_4\text{N})_3\text{Fe(CN)}_6$ exhibits three-dimensional magnetic ordering below 3.4 K. This method might be used for the synthesis of new 1D Fe(III)–Ln(III) complexes that may exhibit interesting magnetic properties.

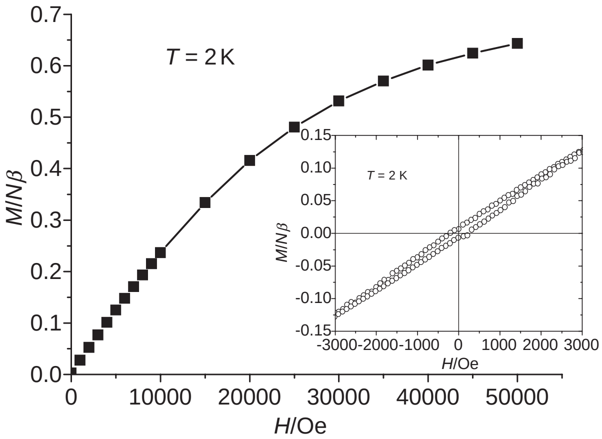

Figure 4. The field dependence of magnetization at 2.0 K for **1**. Inset: Hysteresis loop at 2.0 K.

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References and Notes

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6 Crystal data for **1**: $C_{18}H_{34}FeN_{10}O_7Sm$, fw 708.74, monoclinic, $a = 12.961(3)$ Å, $b = 12.683(3)$ Å, $c = 18.898(4)$ Å, $\beta = 109.89(3)^\circ$, space group $P2_1/n$, $V = 2921.3(10)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.612$ g/cm^3, of the 5726 reflections collected, 5065 were unique, GOF = 1.007, $R1 = 0.0234$, $R_w = 0.0618$ for all data. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-271970. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

7 The magnetization was measured while cooling the sample under 50 Oe to give the FCM curve. ZFCM was obtained by cooling the sample to 2 K under zero magnetic field, and then measuring the magnetization under 50 Oe.

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