A Novel One-Dimensional Chain Cyano-Bridged Complex $[Sm(DMF)_4(H_2O)_2Mn(CN)_6{\cdot}H_2O]_n$: Long-Range Magnetic Ordering, T_c = 18 K and Coercive Force H_c = 600 Oe

Bing Yan, Zhida Chen,* Shixi Wang,† and Song Gao
State Key Laboratory of Rare Earth Material Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China
†*Department of Chemistry, Jining Teachers College, Jining 272125, P. R. China*

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A novel cyano-bridged heteronuclear complex $[Sm(DMF)_4(H_2O)_2Mn(CN)_6{\cdot}H_2O]_n$ has been synthesized based on the reaction of $K_3Mn(CN)_6$, $Sm(NO_3)_3{\cdot}6H_2O$ and *N*,*N*-dimethylformamide (DMF). The crystal structure shows that title complex is a one-dimensional chain complex with two *cis*-CN bridging ligands between Sm atom and Mn atom. The measurement of magnetic property evidences an antiferromagnetic interaction between Sm and Mn atom. It is very interesting that title complex exhibits unusual magnetic properties, such as long-range magnetic ordering, critical temperature T_c = 18 K and stronger coercive force H_c = 600 Oe.

Recently a considerable effort has been devoted to the research of cyano-bridged lanthanide-transition metal complexes, which can show abundant structures and magnetochemistry.[1–15] In this paper, we employed *N*,*N*-dimethylformamide (DMF) as a hybrid ligand to synthesize the cyano-bridged chain complex $[Sm(DMF)_4(H_2O)_2Mn(CN)_6{\cdot}H_2O]_n$, which displays a remarkable variety of magnetic behavior and a rich structural chemistry.

An ORTEP drawing of this complex molecule with the atom numbering scheme is given in Figure 1.[16] The Sm atom is eight coordinated consisting of six oxygen atoms from four DMF molecules and two H_2O molecules as well as two nitrogen atoms from the two *cis*-bridging CN ligands. The bond distances of Sm–N are 2.527(6) Å (Sm–N(1)) and 2.532(5) Å (Sm–N(5)), respectively. The bond distances between Sm and the O atoms from H_2O molecules range from 2.394(4) to 2.456(5) Å; and range 2.363(4) to 2.402(5) Å between Sm and the O atoms from DMF molecules. The bond angle consisting of the bridging CN and Sm (C(1)–N(1)–Sm and C(5)–N(5)–Sm) are 159.5(5)°, 161.9(5)° respectively. The bond angle of N(1)–Sm–N(5) is 76.10(5)°. The geometry of the $Mn(CN)_6^{3-}$ ion is approximately octahedron with the coordination of six CN ligands. The bond lengths of Mn–C range from 1.978(7) to 2.001(6) Å, and the bond distances of the two *cis*-bridging CN, Mn1–C1 and Mn1–C5 are 1.993(6) Å and 2.001(6) Å, respectively. The two cyano-bridged coordination in the complex leads to the distortion of the bond angle C1–Mn1–C5 (94.8(2)°). The bond angle of Mn–C–N ranges from 173.0(6)° to 178.7(6)°. The C–N bond distances range from 1.141(9) to 1.162(9) Å.

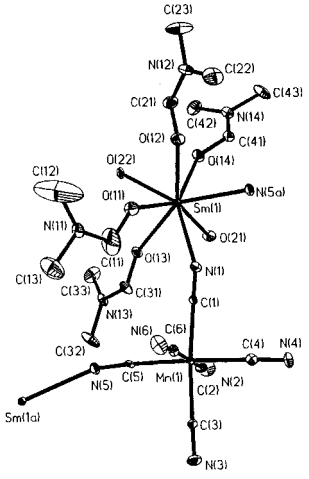

Figure 1. Crystal structure of $Sm(DMF)_4(H_2O)_2Mn(CN)_6{\cdot}H_2O$.

There exist two types of hydrogen bond in the unit cell. One is the intrachain hydrogen bond between the coordinated water molecule in one complex unit and the CN of another complex unit. Another is the interchain hydrogen bond which is involved in the one uncoordinated water molecule in the space among the unit cells of the complex. The O atom of the uncoordinated water molecule forms the hydrogen bond with the H atom of the coordinated water molecule while the H atom of the crystallized water molecule forms the other hydrogen bond with the terminal group CN, which can be regarded as a intermolecular hydrogen bond tetrahedron. It is interesting to note that because there exist C(1)–Mn–C(5) of 94.8(2)° and N(1)–Sm–N(5) of 76.10(5)° in the two *cis*-bridging CN, the one-dimensional chain structure between Sm and Mn, –Mn–C(1)N(1)–Sm–N(5)C(5)–Mn–C(1)N(1)–Sm–, seems as if to be the β-folding chain of protein molecule.

The viable temperature susceptibility (1.5 ~ 300 K) was measured by a MagLab-2000 magnetometer under the applied magnetic field of 10000 Oe. The χ_m^{-1} versus T is nearly a straight line above 25 K, which it obeys the Curie–Weiss law. The Curie and Weiss constants, C and θ, are 2.09 cm^3 K mol^{-1} and –20.22 K, respectively, based on the equation $\chi_m = C/(T-\theta)$. The negative Weiss constant indicates an overall intramolecular antiferromagnetic interaction between the adjacent Sm^{III} (S = 5/2) and Mn^{III} (S = 1) ions through the cyano bridge at higher temperature range, which is due to the strong L S coupling of Sm(III). We further measured magnetic susceptibility for the crystal sample of SmMn in the lower range of temperature (4 ~ 56 K) under the applied magnetic field of 500 Oe (Figure 2), which shows that there exists weak ferrimagnetic behavior between 4 K and 25 K. The $\chi_m T$ value is 1.35 cm^3 K mol^{-1} at 55.2 K and decreases slowly with decreasing temperature, down to a minimum value of 0.98 cm^3 K mol^{-1} at 25 K. Upon cooling, the $\chi_m T$ value increases sharply up to a maximum value of 6.86 cm^3 K mol^{-1} at 12 K and then decreases quickly below this temperature. The weak ferrimagnetic behavior for the one-dimensional structural complex suggests the onset of three-dimensional magnetic ordering.

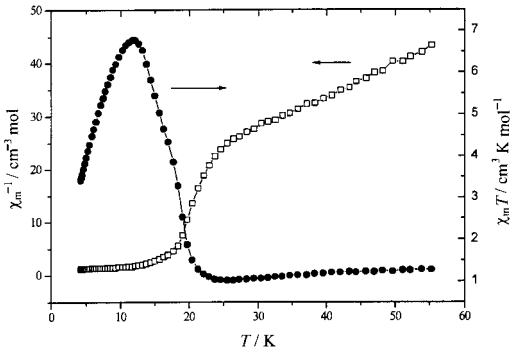

Figure 2. Viable-temperature magnetic susceptibility of $[Sm(DMF)_4(H_2O)_2Mn(CN)_6{\cdot}H_2O]_n$ (4 ~ 56 K).

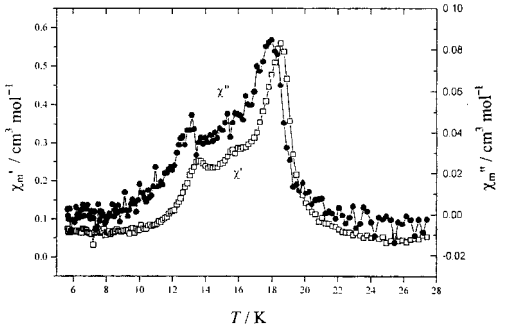

Figure 3. Plot of the in-phase (○) and out-of-phase (●) ac magnetic susceptibility for SmMn complex under 111Hz.

In Figure 3, the temperature dependence of the alternating current magnetic susceptibility shows that both in-phase, χ', and out-of-phase, χ'', components of the ac magnetic susceptibility exist for SmMn in the range of temperature 5 ~ 28 K. The measurements were made by cooling the compound in a close zero field and then measuring at driving frequency of 111 Hz with zero-applied dc field. The observance of χ'' is due to long-range magnetic ordering in certain extent, and consequently a strong coercive behavior is expected. When the external magnet field is reversed with a certain frequency in the ac susceptibility experiment, the magnetization of the sample must respond to this oscillating external magnetic field. In the case of a simple paramagnet the magnetization of the sample can relax very rapidly (nanoseconds), and can follow the oscillating external field. Thus no out-of-phase component (imaginary part) of the ac susceptibility is expected for the simple paramagnet. If the magnetization of the sample relaxes slowly, then there must be a nonzero imaginary component. Such is the case for the crystals sample of SmMn. The SmMn complex exhibits three temperature dependent χ'' peaks, respectively in the regions 16 ~ 19.5 K, 15 ~ 17 K and 12 ~ 14 K. The dominant peak is within 16 ~ 19.5 K. This is consistent with the χ' versus temperature plots, where there are also three peaks in the ranges 12 ~ 14.5 K, 14.5 ~ 16.5 K and 16 ~ 20 K,, respectively (Figure 3). The physical meaning of these three peaks may be due to the three magnetic phase transfer, which belongs to the three-dimensional magnetic ordering behavior. The fact that the one-dimensional structural complex of SmMn exhibits three-dimensional magnetic ordering behavior verifies that the interchain hydrogen bond interaction play an important role in the magnetic interaction for SmMn complex. Now we have not the sufficient reason to interpret the strange and interesting magnetic behavior. The T_c is best determined to be 18 K by the first $\chi'(T)$ peak maximum, which is higher than the critical temperature (T_c = 11.7 K) of the three-dimensional Ln–Cr(CN)$_6$ reported in reference 1. The origin of the magnetic ordering and relatively strong H_c in one-dimensional network should be ascribed to the strong magnetic anisotropy of Sm(III).

Figure 4 shows field-dependent magnetization (M–H) hysteresis data for the SmMn complex under the applied magnetic field from –1000 to +1000 Oe at 5.7 K. It is interesting to note that this hysteresis loop reveals a stronger coercive field H_c of 600 Oe and a remnant magnetization M_R of 0.69 Nβmol^{-1}. This interesting magnetic behavior is ascribed to the stronger interaction between different chain of the complex. The excellent magnetic property of $[SmMn]_n$ complex is found only in quite a few cyano-bridged rare earth-transition metal complexes.[1,11,12] The magnetization curve at the range of 0–5 T indicated that the SmMn complex has not attained saturation magnetization at 5 T.

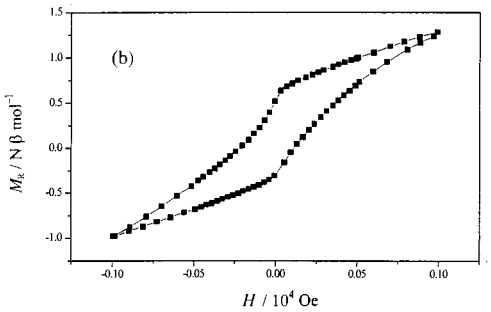

Figure 4. Hysteresis loop of SmMn complex at 5.7 K.

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16 Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144100. Copies of the data can be obtained free of charge on applications to the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code (+44) (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk). Crystal system monoclinic, space group $P2_1/n$, a = 12.990(3), b = 12.787(3), c = 19.131(4) Å, β = 109.29(3)°, Z = 4, R = 0.0502.