Different Crystal Structures of Novel Cyano-Bridged Complexes: One-Dimensional Chain of $[Sm(DMA)_2(H_2O)_4Fe(CN)_6 \cdot 5H_2O]_n$ and Trinuclear $\{[Gd(DMA)_3(H_2O)_4]_2Fe(CN)_6\}Fe(CN)_6 \cdot 3H_2O$

Bing Yan and Zhida Chen*
State Key Laboratory of Rare Earth Material Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, P. R. China

(Received August 1, 2000; CL-000736)

Two novel cyano-bridged rare earth–iron complexes have been synthesized based on the reaction of $K_3Fe(CN)_6$, $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Sm, Gd) and *N,N*-dimethylacetamide (DMA). It is interesting that the two complexes exhibit the different coordination form and crystal structure, in which $[Sm(DMA)_2(H_2O)_4Fe(CN)_6 \cdot 5H_2O]_n$ ($[SmFe]_n$), shows one-dimensional chain structure with approximately parallel two CN bridging ligands between Sm atom and Fe atom, while $\{[Gd(DMA)_3(H_2O)_4]_2Fe(CN)_6\}Fe(CN)_6 \cdot 3H_2O$ ($[Gd_2Fe]$) is an isolated trinuclear Gd(1)–Fe–Gd(2) complex with two approximately perpendicular CN bridging ligands between the two Gd atoms and Fe atom. Among $[SmFe]_n$ complex exhibits critical temperature T_c = 3.5 K.

Recently there has been great interest in the research field of cyano-bridged lanthanide–transition metal complexes, which can show abundant structures and magnetochemistry.[1–12] In this paper, we employed *N,N*-dimethylacetamide (DMA) as a hybrid ligand to synthesize two novel cyano-bridged complexes: one-dimensional $[Sm(DMA)_2(H_2O)_4Fe(CN)_6 \cdot 5H_2O]_n$ ($[SmFe]_n$) and trinuclear $\{[Gd(DMA)_3(H_2O)_4]_2Fe(CN)_6\}Fe(CN)_6 \cdot 3H_2O$ (Gd_2Fe).

$K_3[Fe(CN)_6]$ (0.330 g, 1.0 mmol) in a minimum amount of water was slowly added to a DMA (2.0 mL) solution of $Ln(NO_3)_3 \cdot 6H_2O$ (0.444 g for Sm and 0.453 g for Gd, 1.0 mmol). The clear mixed solution was then filtered and then kept standstill. After about two weeks, well-shaped yellow single crystals were obtained. Yield/% (Fe) for $[SmFe]_n$: 20; for Gd_2Fe: 31. IR, UV and elemental analysis data for the two complexes (SmFe and Gd_2Fe) are available upon request from the authors.

Figure 1 shows the crystal structure of $[SmFe]_n$. The Sm atom is eight coordination consisting of six oxygen atoms from two DMA molecules and four water molecules as well as two nitrogen atoms from the two bridging CN. The bond distances of Sm–N are 2.528(5) Å (Sm–N1) and 2.549(5) Å (Sm–N6), respectively. The bond distances between Sm and the O atoms from H_2O molecules range from 2.404(5)–2.550(5) Å; and range from 2.321(4) to 2.329(4) Å between Sm and the O atoms from DMA molecules. The bond angles consisting of the bridging CN and Sm ((C(1)–N(1)–Sm and C(2)–N(6)–Sm)), are 175.8(5)°, 177.8(5)° respectively. The bond angle of N(1)–Sm–N(6) is 142.26(19)°. The geometry of the $Fe(CN)_6^{3-}$ group is an approximate octahedron with the coordination of six CN ligands. The bonds distances of Fe–C range from 1.933(7) to 1.953(7) Å, and the bond distances of the two bridging Fe–C(1) and Fe–C(6) are 1.947(6) Å and 1.939(6) Å, respectively. The two cyano-bridged coordination in the SmFe complex leads to a little distortion of the bond angle C(1)–Fe(1)–C (6) (179.3(2)°). The Fe–C–N bond angles range from 176.9(6)° to 178.7(6)°. With two bridging CN groups (N(1)–Sm–N(6), 142.26(19)°), one-dimensional –Fe–C(1)N(1)–Sm–N(6)C(6)–Fe–C(1)N(1)–Sm– chain is formed and seems as if the β-folding chain of protein molecule. This form is different from those of the isolated dinuclear cyano-bridged Ln–Fe complexes.[2,4,5]

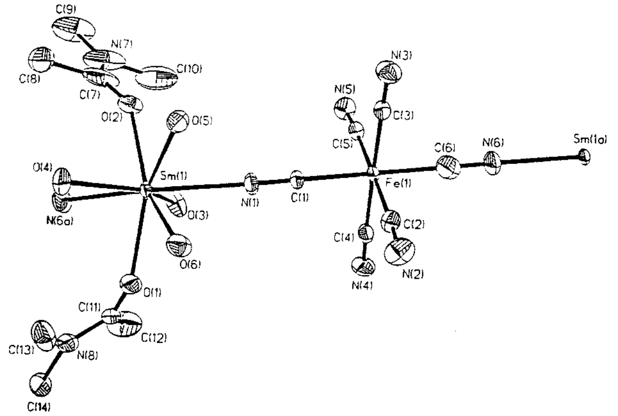

Figure 1. Crystal structure of $[SmFe]_n$ complex.

Figure 2 shows the crystal structure of Gd_2Fe complex. The two Gd atoms belong to eight-coordination, in which seven coordinated oxygen atoms come from the three DMA molecules and the four water molecules and each has one coordinated nitrogen atom from the bridging cyanide ligands. While

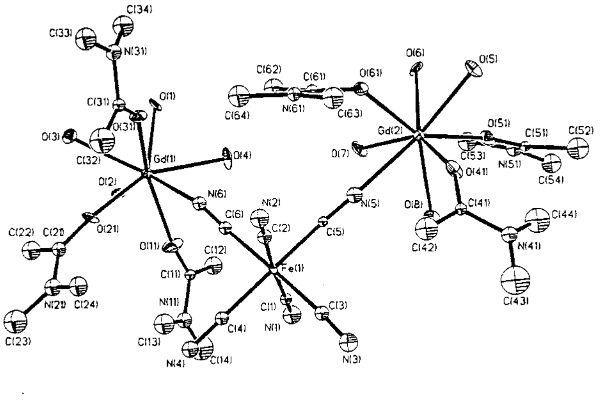

Figure 2. Crystal structure of Gd_2Fe complex.

each Fe atom is bridged with two Gd atoms through two cyano group (C(5)N(5) and C(6)N(6)). It is interesting that the DMA molecules coordinated to Gd atom have two kinds of conformations, in which the only difference is that, besides the coordinated oxygen atoms of acetamide group of DMA, the other atoms rotate by 180° around the O–Gd axis. The distances of Gd–N are 2.559(14) Å (Gd(1)–N(6)) and 2.543(15) Å (Gd(2)–N(5)), respectively. The distances between Gd1, Gd2 and the O atoms of the coordinated H_2O molecules are in the range of 2.472(11)–2.547(12) Å, 2.453(12)–2.492(12) Å, respectively. The distances between Gd1, Gd2 and the O atoms of coordinated DMA are within 2.303(11)–2.341(11), 2.316(11)–2.349(11) Å, respectively. The bond angles between the bridging CN and Gd1, Gd2 (C–N–Gd) are 163.1(13)°, 176.8(13)°, respectively. Fe atom in Gd_2Fe has six coordinated cyano groups, and forms distorted octahedral conformation. The crystal structure for Gd_2Fe complex indicates that there is a central cyano-bridged framework. The bond length of Fe–C is ranged in 1.892(14)–1.947(15) Å, in which the bond lengths of Fe(1)–C(5) and Fe(1)–C(6) involved in the bridging CN are 1.892(14) Å and 1.921(16) Å, respectively. The bond angle of C–Fe–C is led to the distortion due to the two CN coordinated and the bond angle of C(5)–Fe(1)–C(6) is 89.1 (6)°. The bond angle of Fe–C–N is ranged in 174.0(14)° and 170.0(15)°. The examples of this trinuclear structure is very few in Ln–Fe cyano-bridged complexes.

In spite of the same reaction condition and similar reactant, $[SmFe]_n$ and Gd_2Fe show the quite different crystal structures. $[SmFe]_n$ complex has one-dimensional chain structure with *trans*-CN-bridge between Fe atom and Sm atom, while Gd_2Fe forms an isolated trinuclear structure due to the two *cis*-CN bridge between on Fe atom and two Gd atoms. This is corresponded to the rare earth element structural chemicstry.

There exists weak antiferromagnetic interaction between rare earth and Fe ions in most Ln–Fe cyano-bridged complexes.[2,4,5,12] Rare earth ions influence on the magnetic properties of Ln–Fe complexes due to the different crystal structure and spin state of Ln. $[SmFe]_n$ exhibits good magnetic property while Gd_2Fe does not. In Figure 3 the temperature dependence of the alternating current magnetic susceptibility shows that both in-phase, χ'(a), and out-of-phase, χ''(b), components of the ac magnetic susceptibility exist for $[SmFe]_n$ in the range of temperature 2.2–5.5 K. The measurements were made by cooling the compound in a close zero field and then measuring at driving frequency of 355 Hz. The observance of χ'' is due to long-range magnetic ordering in certain extent. 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. The $[SmFe]_n$ complex exhibits one temperature dependent χ'' peak in the region 2.4–4.0 K. This is consistent with the χ' versus temperature plots, where there is also a peak in the range 2.4–4.0 K. The T_c is best determined to be 3.5 K by the first $\chi'(T)$ peak maximum. The excellent magnetic property of $[SmFe]_n$ complex is only in quite a few cyano-bridged rare earth–transition metal complexes.[1, 11]

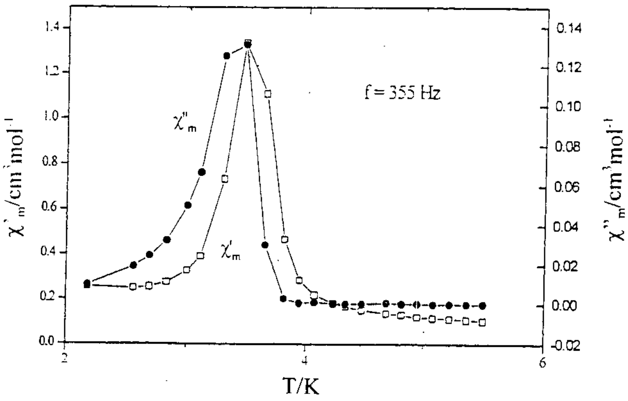

Figure 3. Plot of the in-phase and out-of-phase ac magnetic susceptibility for the $[SmFe]_n$ complex at driving frequency of 355 Hz.

This work was supported by the National Natural Science Foundation of China (29831010, 20023005), the State Key Project of Fundamental Research of China (G1998061306) and the China Postdoctoral Science Foundation (25).

References and Notes

1 F. Hulliger, M. Landolt, and H. Vetsch, *J. Solid State Chem.*, **18**, 283 (1976).
2 H. Z. Kou, G. M. Yang, D. Z. Liao, P. Cheng, Z. H. Jiang, S. P. Yan, X. Y. Huang, and G. L. Wang, *J. Chem. Crystallogr.*, **28**, 1503 (1998).
3 S. G. Granda, A. D. Morales, E. R. Buiz, and J. F. Bertran, *Acta Crystallogr., Sect. C*, **52**, 1679 (1996).
4 S. Gao, B. Q. Ma, Z. M. Wang, T. Yi, C. H. Yan, and G. X. Xu, *Mol. Cryst. Liq. Cryst.*, **335**, 221 (1999).
5 X. R. Sun, Z. D. Chen and C. M. Che, unpublished result.
6 D. W. Knoeppel, J. P. Liu, E. A. Meyers, and S. G. Shore, *Inorg. Chem.*, **37**, 4828 (1998).
7 D. W. Knoeppel and S. G. Shroe, *Inorg. Chem.*, **35**, 5328 (1996).
8 D. W. Knoeppel and S. G. Shroe, *Inorg. Chem.*, **35**, 1747 (1996).
9 J. P. Liu, E. A. Meyers, and S. G. Shore, *Inorg. Chem.*, **37**, 5410 (1998).
10 B. Yan, S. X. Wang, and Z. D. Chen, *Chem. J. Chin. Univ.*, in press.
11 B. Yan, Z. D. Chen, and S. X. Wang, *Transition. Met. Chem. (N. Y.)*, in press.
12 B. Yan, H. D. Wang, and Z. D. Chen, *Inorg. Chem. Commu*, in press.
13 Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144102 and 144103. 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). For $[SmFe]_n$: crystal system monoclinic, space group $P2_1/n$, a = 10.2744(14), b = 16.732(2), c = 17.323(2) Å, β = 97.385(3)°, Z = 4, R = 0.0412. For Gd_2Fe: crystal system orthorhombic, space group $P2_12_12$, a = 18.949(4), b = 33.293(7), c = 9.556(2) Å, β = 90°, Z = 4, R = 0.0562.