Synthesis, Structure and Magnetic Property of [Ce(DMSO)$_2$(H$_2$O)Fe(CN)$_6$]

Y.M. Xie* and J.H. Wu

College of Materials Science and Engineering, Huaqiao University, Quanzhou, Fujian 362021, P.R. China

The title complex, [Ce(DMSO)$_2$(H$_2$O)Fe(CN)$_6$] (**1**), was obtained by solution reactions and structurally characterized by X-ray diffraction. The title complex is characteristic of a novel cyano-bridged two-dimensional stair-like layered structure. The magnetic property of the title complex is reported herein. The $\chi_M T$ value at 300 K is *ca*. 0.92 emu K mol^{-1}. The temperature dependence behavior of molar magnetic susceptibility of the complex clearly indicates the presence of an antiferromagnetic interaction.

INTRODUCTION

Due to the extensive applications in preparing magnetic materials, chemical sensor materials, fluorescent materials, zeolitic-type materials, and so forth, cyanide-bridged lanthanide-transition metal complexes have attracted continuous interest for about two decades [1-7]. Most of the known cyanide-bridged lanthanide-transition metal complexes contain such ligands as DMF, urea and caprolactam, while DMSO is not common. Therefore, our recent efforts in synthesizing novel cyano-bridged complexes have focused largely on the systems containing DMSO ligand. In this work, we report a new cyano-bridged bimetallic complex [Ce(DMSO)$_2$(H$_2$O)Fe(CN)$_6$] (**1**) with a novel cyano-bridged two-dimensional stair-like structure containing DMSO as ligand.

EXPERIMENTAL

Reagents and Apparatus

All reactants were of A.R. grade, obtained commercially

*Corresponding author. E-mail: xym8790@yahoo.com.cn

and used without further purification.

X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) using a ω scan technique. The CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL^{TM} Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Synthesis of [Ce(DMSO)$_2$(H$_2$O)Fe(CN)$_6$] (1)

DMSO (0.1 ml) was added to a 30 ml aqueous solution of Ce(NO)$_3$·6H$_2$O (1 mmol), then 20 ml aqueous solution of K$_3$[Fe(CN)$_6$] (2 mmol) was added. Slow evaporation of the

Table 1. Crystal Data of $[Ce(DMSO)_2(H_2O)Fe(CN)_6]$

Empirical formula	$C_{10}H_{14}CeFeN_6O_3S_2$
Formula weight	526.36
X-rays	$MoK\alpha$
Crystal system	monoclinic
Space group	$P2/n$
Unit cell dimensions	$a = 7.850(3)$ Å
	$b = 10.728(4)$ Å
	$c = 11.172(5)$ Å
	$\beta = 97.032(7)°$
Z	2
V	933.8(7) Å^3
D_x	1.872 mg m^{-3}
Absorption coefficient	3.425 mm^{-1}
Crystal size	$0.22 \times 0.14 \times 0.06$ mm
No. of reflections collected/unique	6958/2108 [$R_{(int)} = 0.0283$]
Refinement	full matrix least squares on F^2
Goodness-of-fit on F^2	1.064
Data/restraints/parameters	1974/6/115
Final R indices	$R_1 = 0.0246$, $wR_2 = 0.0654$
R indices (all data)	$R_1 = 0.0264$, $wR_2 = 0.0663$
Index ranges	$-8<=h<=10$, $-13<=k<=13$, $-14<=l<=11$
Measurement	Rigaku Mercury CCD diffractometer
Monochromator	graphite
Structure determination	Siemens SHELXTL

Table 2. Selected Bond Lengths and Bond Angles of $[Ce(DMSO)_2(H_2O)Fe(CN)_6]$

Bond Lengths (Å)		Bond Angles (°)	
Ce(1)-O(1W)	2.381(5)	C(1)-N(1)-Ce(1)	169.4(3)
Ce(1)-O(1) × 2	2.384(3)	C(2)-N(2)-Ce(1)#1	170.3(3)
Ce(1)-N(1) × 2	2.553(4)	N(1)-C(1)-Fe(1)	178.3(3)
Ce(1)-N(2)#2 × 2	2.588(3)	N(2)-C(2)-Fe(1)	177.7(3)
Fe(1)-C(1) × 2	1.933(3)	N(3)-C(3)-Fe(1)	176.9(3)
Fe(1)-C(2) × 2	1.943(3)	N(1)-Ce(1)-N(1)#1	169.22(19)
Fe(1)-C(3) × 2	1.927(3)	N(1)-Ce(1)-N(2)#2	94.36(13) × 2
N(1)-C(1)	1.135(5)	N(1)#1-Ce(1)-N(2)#2	77.21(11) × 2
N(2)-C(2)	1.147(4)	N(2)#2-Ce(1)-N(2)#3	78.67(15)
N(3)-C(3)	1.152(5)		

Symmetry codes: #1 -x+3/2, y, -z+3/2; #2 -x+1, -y+1, -z+1; #3 x+1/2, -y+1, z+1/2.

resultant mixture at room temperature gave well-shaped orange single crystals.

RESULTS AND DISCUSSION

Figure 1 is a perspective view of the [Ce(DMSO)$_2$(H$_2$O)Fe(CN)$_6$] molecule with atomic labeling scheme. The structure of complex consists of neutral stair-like layers. The Ce^{3+} ion is seven coordinate being bound by two O atoms from two DMSO molecules (the average Ce-O$_{DMSO}$ = 2.384(3) Å), one O atom from a water molecule (Ce-O$_{H2O}$ = 2.381(5) Å) and four N atoms from four bridging CN$^-$ groups (the average Ce-N = 2.570(4) Å), yielding a distorted pentagonal bi-pyramid with a pentagon defined by O1, N2(1/2+x, 1-y, 1/2 +z), N2(1-x, 1-y, 1-z), O1(3/2-x, y, 3/2-z) and O1W atoms, and two apical atoms N1 and N1(3/2-x, y, 3/2-z), respectively. The bridging cyanide ligands coordinating to the Ce^{3+} ions are in a nearly linear arrangement, [C(1)-N(1)-Ce(1) = 169.4(3) and C(2)-N(2)-Ce(1)(-x+3/2, y, -z+3/2) = 170.3(3)°], and every two bridging cyanide ligands surrounding to one Ce^{3+} center form the angles from 77.21(11), 78.67(15), 94.36(13) to 169.22(19)°, respectively.

Meanwhile, the Fe^{3+} ion is coordinated by six cyanide groups to form an approximately regular octahedron with the Fe-C and C-N bond distances in the normal ranges of 1.927(3)-1.943(3) and 1.135(5)-1.152(5) Å, respectively. The cyano-bridged Ce…Fe distances are in the range of *ca.* 5.593-5.662 Å, comparable with that found in the reference [8]. The [Fe(CN)$_6$]$^{3-}$ unit connects to three [Ce(DMSO)$_2$(H$_2$O)]$^{3+}$ units through three equatorial CN$^-$ groups, and vice versa, forming an approximately rectangular "grid" of Ce$_2$Fe$_2$, which inter-links along the c direction to form a "step". The "steps" connect to each other through the axial CN$^-$ groups of [Fe(CN)$_6$]$^{3-}$ units to form a "stair" running along the a direction (Fig. 2). The shortest inter-layer Ce…Fe distance is *ca.* 7.720 Å, obviously longer than that of intra-layer. Meanwhile, there is no hydrogen bonding among the layers and, therefore, the van de Waals' force should be the only contribution to the stability of the crystal packing (Fig. 3).

The susceptibility measurement for complex **1** is shown in Fig. 4 as $\chi_M T$ *vs.* *T*, where χ_M is the molar magnetic susceptibility per Ce(III)Fe(III) unit. The $\chi_M T$ value at 300 K is *ca.* 0.92 emu K mol^{-1}, slightly smaller than the 1.08 emu K
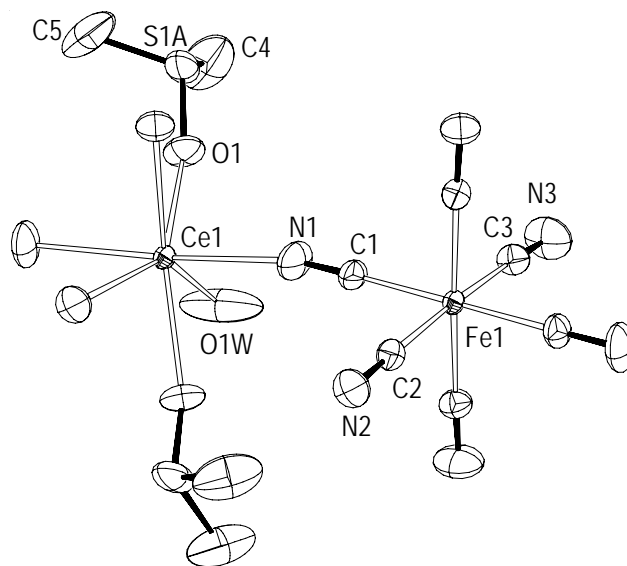

Fig. 1. ORTEP drawing of **1** with 50% thermal ellipsoids. Hydrogen atoms and disorderd S1B atom are omitted for clarity.
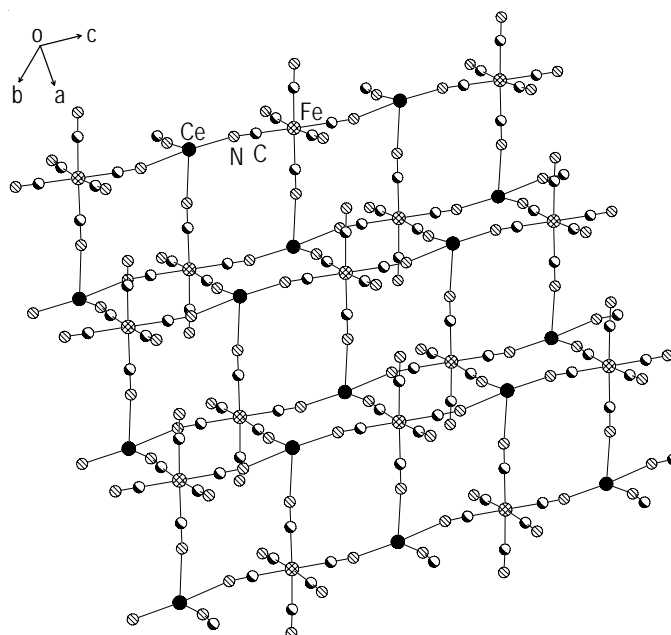

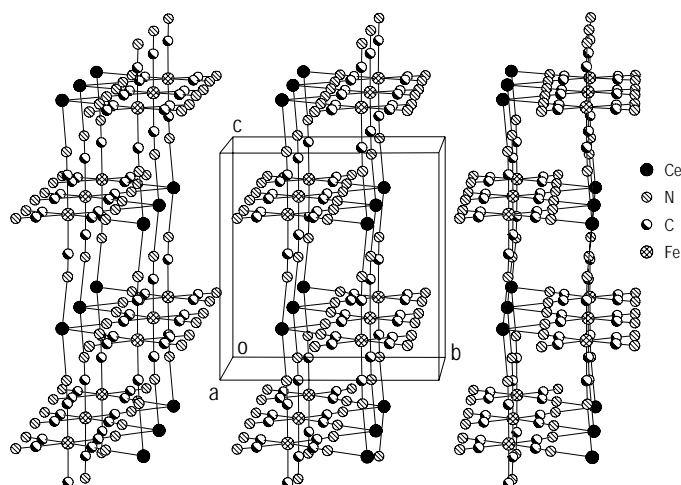**Fig. 2.** Stair-like 2-D layer of **1** with DMSO and water molecules being omitted for clarity.
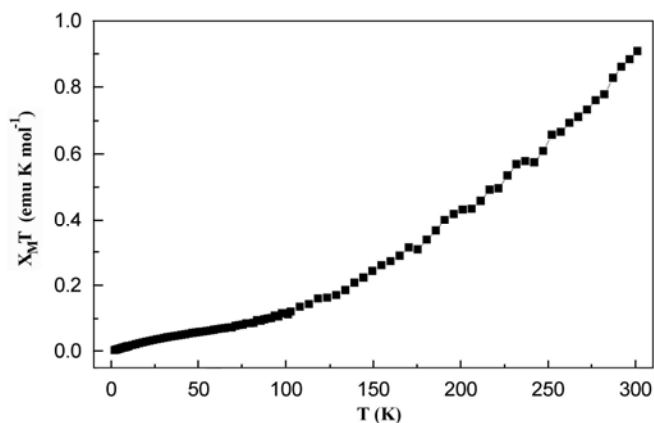
Fig. 3. Crystal packing of complex.

Fig. 4. Plot of X_MT product *vs*. *T*.

mol^{-1} that would be expected for isolated magnetic centers of Ce^{3+} and Fe^{3+} in the present structure. With the decrease of the temperature, χ_MT decreases sharply down to 0.11 emu K mol^{-1} at 100 K, then smoothly down to 0.004 emu K mol^{-1} at 2 K, which indicates the presence of an antiferromagnetic interaction.

In summary, using DMSO as ligand, one cyanide-bridged bimetallic compound was synthesized with two-dimensional stair-like structure. The title complex was structurally characterized by X-ray diffraction and its magnetic property was reported. DMSO is a very suitable electron transfer ligand so that its incorporation into the system can make the structures of 3d-4f compounds more diverse, which provide latent possibility for the application in the material.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 649424. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

ACKNOWLEDGMENTS

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