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研究简报

氰基桥联双核镝(Ⅲ)-铁(Ⅲ)配合物 $[DyFe(CN)_6(DMF)_4(H_2O)_3]\cdot 1.25H_2O$ 的合成与结构表征

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Synthesis and Structural Characterization of a Cyano-bridged Dinuclear Dysprosium (Ⅲ)-Iron (Ⅲ) Complex $[DyFe(CN)_6(DMF)_4(H_2O)_3]\cdot 1.25H_2O$

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A dinuclear complex $[DyFe(CN)_6(DMF)_4(H_2O)_3]\cdot 1.25H_2O$ (DMF = N, N-dimethylformamide) **1** based on the cyanide as linkage was prepared and structurally characterized by X-ray single-crystal structure analysis. The Dy (Ⅲ) ion is eight coordinations in a square-antiprism arrangement and the Fe (Ⅲ) ion is six coordinations oriented octahedrally. The neutral units $[DyFe(CN)_6(DMF)_4(H_2O)_3]$ are held together by hydrogen bonds formed by lattice water molecules, coordinated water molecules and nitrogen atoms of cyanide coming from other distinct complex units to afford a three-dimensional framework. CCDC: 192314.

Keywords: ***crystal structure*** ***cyano-bridged*** ***dinuclear Dy (Ⅲ)-Fe (Ⅲ) complex***

0 Introduction

Recently, several research groups have employed a hybrid approach, in which $[M(CN)_6]^{n-}$ building block have been combined with transition metal ions or lanthanide ions complexes in order to exploit the features of the ligands in the formation of different structures[1~8]. Cyano-bridged complexes are generally obtained by reacting hexacyanometalate with mononuclear assembler complex in which some of the coordination sites can be occupied by some assistant ligands (or terms as the third ligands). Several cyano-bridged dinuclear lanthanide (Ⅲ) hexacyanoferrates have been reported on the DMF and water molecules occupying

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some coordinating sites of lanthanide ions[9~11] among which different amounts of coordinated water molecules have been found. In order to gain more insights into the influences on the structure of aimed products from lanthanide contraction and different synthetic methods, we experiment all of lanthanide ions to react with potassium hexacyanoferrate on the existence of DMF molecules and use several synthetic strategies, however similar dinuclear products were usually obtained. Herein, we reported the synthesis and crystal structure of a new dinuclear Dy (Ⅲ) -Fe (Ⅲ) complex, $[DyFe(CN)_6(DMF)_4(H_2O)_3] \cdot 1.25H_2O$ **1**.

1 Experimental

1.1 General

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Infrared spectra were measured on Nicolet 5DX FT-IR spectrophotometer in $4cm^{-1}$ resolution in the $4000 \sim 400cm^{-1}$ region using a KBr pellet, and elemental analyses were carried out on a Perkin-Elmer 240C analyzer.

1.2 Synthesis of $[DyFe(CN)_6(DMF)_4(H_2O)_3] \cdot 1.25H_2O$ 1

The complex **1** was prepared by mixing 1: 1 molar ratio of $DyCl_3$ (0.5mmol) and $K_3[Fe(CN)_6]$ (165mg, 0.5mmol) in EtOH/H_2O/ DMF mixture solvent (5 mL) with volume ratio of 2: 2: 1. The reaction mixture was stirred for about one hour and filtered. Then the filtration was left to stand at room temperature. Orange prismatic crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent with yield of 65% (crystals). Selected IR peaks (cm^{-1}): 1653(s, C = O(MDF)), 2125(m, CN), 2943(s, OH(H_2O)). Calcd. for $DyFeC_{18}H_{36.5}N_{10}O_{8.25}$: C, 29.05; H, 4.95; N, 18.84. Found: C, 29.09; H, 5.01; N, 18.75.

1.3 Crystallography

An orange crystal of complex **1** with approximate dimension of $0.26 \times 0.24 \times 0.16mm^3$ was used for data collection on a Siemens Smart CCD diffractometer with the graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$Å) at 298 K. A total of 10188 reflections measured in the range of $1.47° < \theta < 25.03°$ by using ω scan technique at 293K, Siemens SAINT[12] software was used for data reduction. Empirical absorption corrections SADABS[13] based on measurements of equivalent reflections were used. 4382 reflections with $I > 2\sigma(I)$ out of 5382 unique reflections ($R_{int} = 0.0232$) were considered as observed. The structures were solved by the direct method using the Siemens SHELXTLTM Version 5 package of crystallographic software[14] . The difference Fourier maps based on these atomic positions yields the other 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 hydrogen atoms were added theoretically, riding on their respective parent atoms and refined with fixed thermal factors. Crystal data: monoclinic, space group $P2_1/n$, cell parameters: $a = 13.9838(4)$, $b = 8.8904(3)$, $c = 24.9425(8)$ Å, $\beta = 96.302(1)°$; $Z = 4$; $D_c = 1.602g \cdot cm^{-3}$; final $R = 0.0365$, w$R = 0.0916$.

CCDC: 192314.

2 Results and Discussion

In order to illustrate that if using different anion lanthanide salt as original material such as nitrate, chloride and perchlorate, and varying the composition of the solvent mixture of water and ethanol and DMF may obtain products with distinct structure, however, similar dinuclear complexes were usually obtained on the crystalline cell determination. This observation imply that the structure model of the present compound is preferred in the preparation of cyano-bridged dinuclear lanthanide (Ⅲ) hexacyanoferrates.

2.1 Crystal Structure

The molecular structure of **1** is shown in Fig. 1 and the selected bond lengths and bond angles are listed in Table 1. The structure unit consists of neutral group $[DyFe(CN)_6(DMF)_4(H_2O)_3]$ and one a quarter of uncoordinated lattice water molecules. In $[DyFe(CN)_6(DMF)_4(H_2O)_3]$, Fe (Ⅲ) and Dy (Ⅲ) ions are bridged together by cyanide ligand to form a dimetallic moiety with the Dy···Fe separation of 5.445(3)Å. The Dy (Ⅲ)

Table 1　Selected Bond Lengths(Å) and Bond Angles(°)

Dy(1)-O(41)	2.336(3)	Dy(1)-O(11)	2.349(4)	Dy(1)-O(31)	2.354(4)
Dy(1)-O(21)	2.363(4)	Dy(1)-O(2w)	2.381(4)	Dy(1)-O(3w)	2.387(3)
Dy(1)-O(1w)	2.406(3)	Dy(1)-N(3)	2.429(5)	Fe(1)-C(2)	1.933(6)
Fe(1)-C(1)	1.941(6)	Fe(1)-C(6)	1.938(5)	Fe(1)-C(5)	1.941(5)
Fe(1)-C(3)	1.942(5)	Fe(1)-C(4)	1.958(6)	N(3)-C(3)	1.146(6)
N(6)-C(6)	1.153(6)	N(5)-C(5)	1.130(6)	N(2)-C(2)	1.148(7)
N(1)-C(1)	1.151(7)	N(4)-C(4)	1.149(7)	O(11)-C(13)	1.222(7)
O(41)-Dy(1)-O(11)	140.7(1)	O(41)-Dy(1)-O(31)	125.0(1)	O(11)-Dy(1)-O(31)	74.8(1)
O(41)-Dy(1)-O(21)	73.8(1)	O(11)-Dy(1)-O(21)	81.8(2)	O(31)-Dy(1)-O(21)	74.0(1)
O(41)-Dy(1)-O(2w)	74.7(1)	O(11)-Dy(1)-O(2w)	71.1(1)	O(31)-Dy(1)-O(2w)	139.7(1)
O(21)-Dy(1)-O(2w)	80.5(1)	O(41)-Dy(1)-O(3w)	136.6(1)	O(11)-Dy(1)-O(3w)	76.9(1)
O(31)-Dy(1)-O(3w)	76.8(1)	O(21)-Dy(1)-O(3w)	147.4(1)	O(2w)-Dy(1)-O(3w)	114.6(1)
O(41)-Dy(1)-O(1w)	75.0(1)	O(11)-Dy(1)-O(1w)	111.9(1)	O(31)-Dy(1)-O(1w)	141.5(1)
O(21)-Dy(1)-O(1w)	143.3(1)	O(2w)-Dy(1)-O(1w)	73.0(1)	O(3w)-Dy(1)-O(1w)	68.7(1)
O(41)-Dy(1)-N(3)	73.8(1)	O(11)-Dy(1)-N(3)	143.5(1)	O(31)-Dy(1)-N(3)	72.7(1)
O(21)-Dy(1)-N(3)	104.4(2)	O(2w)-Dy(1)-N(3)	145.1(1)	O(3w)-Dy(1)-N(3)	80.0(1)
O(1w)-Dy(1)-N(3)	84.8(1)	C(2)-Fe(1)-C(1)	89.8(2)	C(2)-Fe(1)-C(6)	88.1(2)
C(1)-Fe(1)-C(6)	89.9(2)	C(2)-Fe(1)-C(5)	88.7(2)	C(1)-Fe(1)-C(5)	92.1(2)
C(6)-Fe(1)-C(5)	176.3(2)	C(2)-Fe(1)-C(3)	92.1(2)	C(1)-Fe(1)-C(3)	177.6(2)
C(6)-Fe(1)-C(3)	88.7(2)	C(5)-Fe(1)-C(3)	89.4(2)	C(2)-Fe(1)-C(4)	177.9(2)
C(1)-Fe(1)-C(4)	90.0(2)	C(6)-Fe(1)-C(4)	93.9(2)	C(5)-Fe(1)-C(4)	89.2(2)
C(3)-Fe(1)-C(4)	88.2(2)	C(3)-N(3)-Dy(1)	163.0(4)	N(1)-C(1)-Fe(1)	176.8(5)
N(2)-C(2)-Fe(1)	179.4(5)	N(3)-C(3)-Fe(1)	177.2(5)	N(4)-C(4)-Fe(1)	178.5(5)
N(5)-C(5)-Fe(1)	178.4(5)	N(6)-C(6)-Fe(1)	178.7(5)		

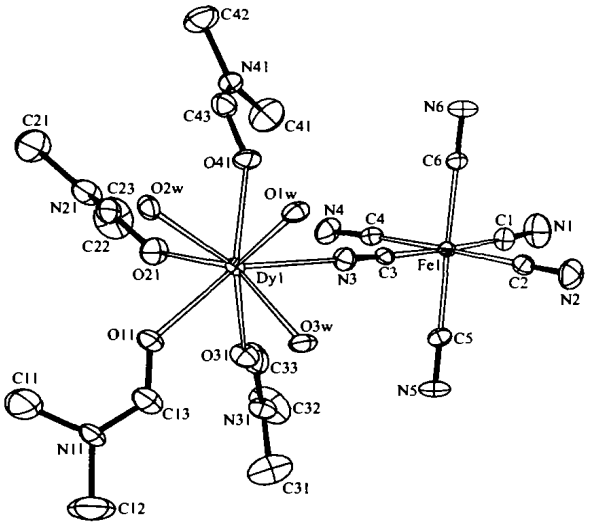

Fig. 1　ORTEP view of **1** with packing water molecules omitted

ion is eight-coordinated by one nitrogen atom from bridging cyanide group and seven oxygen atoms among which four from four DMF molecules and the other three from three coordinated water molecules. Like other analogous complexes of the series[10, 11], the coordination geometry of Dy (Ⅲ) ion is a square antiprism. The Fe (Ⅲ) ion coordinated by six cyanide groups can be described as an octahedral coordination arrangement with normal coordination geometry. The average bond distance of Dy-O(DMF) is 2.351(2) Å, of which the shortest Dy-O(41) bond length is 2.336(3) Å, this may be due to the steric hindrance of block DMF molecules. And the average bond length Dy-O(H_2O) is 2.391(2) Å. The distances of the six Fe-C bonds with cyanide groups and the six C-N bonds of cyanide are nearly equivalent which are in the narrow ranges of 1.933(6) ~ 1.958(6) and 1.130(6) ~ 1.153(6) Å, respectively. It should be noted that one of two uncoordinated water molecules, O5w (0.25 site occupancy), has a shorter distance of 2.937(1) Å with the Dy atoms, this can be considered as weak contact. The bridging Dy(1) -N(3) -C(3) bond angle deviates from linearity by 17.0o as the case found in the analogous complexes[9, 10]. Three-dimissional framework has been formed through the O – H···O and O-H···N hydrogen bonds as shown in Fig. 2 with the O···O separation of 2.635(3)Å and the average O···N separation of 2.858 (2)Å.

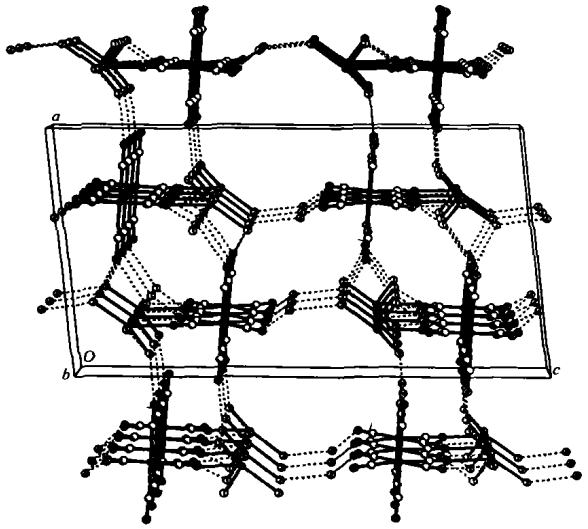

Fig. 2 View of the 3-D framework of **1** assembled through the hydrogen bonds with DMF omitted for clarity

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