

Synthesis, Crystal Structure and Properties of a New One-Dimensional 3d-4f Compound

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A new heterometallic complex $K_2\{[Eu(H_2O)_4]_2[Fe^{II}(bipy)(CN)_4]\} \cdot 9H_2O \cdot CH_3OH$ [bipy=2,2'-bipyridine] was synthesized. The compound has been characterized by X-ray structure analysis, elemental analyses, IR spectrum, TGA thermogram and magnetic susceptibility. The complex consists of novel one-dimensional ladder structure. The crystal belongs to monoclinic system with a space group $P2_1/c$, $a = 1.3946(4)$ nm, $b = 2.0450(6)$ nm, $c = 2.9722(8)$ nm, $\beta = 99.025(5)^\circ$, $V = 8.372(4)$ nm³, $Z = 4$, $D_c = 1.562$ g · cm⁻³.

Keywords 3d-4f heterometallic, cyano-bridged complex, crystal structure, magnetic property

Introduction

Recently cyano bridged 3d-4f heterometallic compounds have attracted much attention because of their interesting structures and magnetic characteristics.¹ The most successful and often the sole strategy for preparing these materials consists in assembling two building blocks that are transition and lanthanide metal complexes, one with terminal ligands that are able to act as bridging ligands and the other with available co-ordination sites. The $[M(CN)_4]^{2-}$ ($M = Ni, Pd, Pt$),^{1f,2} $[M(CN)_6]^{3-}$ ($M = Cr, Fe$),³ and $[Fe(L)(CN)_4]^-$ ($L = bipy, phen$)⁴ units exhibit various geometrical structures and cyanide groups are good at bridging metals. These characteristics enable them as potential flexible building blocks to construct various architectures. Lanthanide metal cations are able to interact with cyanometallate anions giving polymeric arrays of various connectivity. So the cyano-bridged 3d-4f heterometallic complexes exhibit rich structures, such as: ion pair,² binuclear,³ trinuclear,^{1d} tetranuclear,^{1e} 1D,^{1f} 2D^{1g} and 3D^{1h} structures. Lanthanide metal cations have higher coordination numbers and reveal larger flexibility of coordination environment compared to 3d transition metals. In contrast, to the best of our knowledge, derivatives of $[Fe(bipy)(CN)_4]^{2-}$ with 4f ions have not been reported. Here we report the 1D polymer $K_2\{[Eu(H_2O)_4]_2[Fe^{II}(bipy)(CN)_4]\} \cdot 9H_2O \cdot CH_3OH$ with novel ladder structure, which is derived from the building block $[Fe(bipy)(CN)_4]^{2-}$.

Experimental

Reagents

Chemicals were purchased from commercial sources as reagents pure for analysis and used as received. $K_2[Fe(bipy)(CN)_4] \cdot 3H_2O$ was prepared as described in the literature.⁵

Physical measurements

Elemental analyses of carbon, hydrogen and nitrogen were carried out by the Elementar Carlo EL elemental analyzer. The infrared spectroscopy on KBr pellets was performed on a Nicolet 7199B spectrophotometer in the 4000—400 cm⁻¹ range. Thermogravimetric measurements were carried out with a Dupont 1090 apparatus in the temperature range 298—1073 K with a heating rate of 283 K · min⁻¹ under air atmosphere. Magnetic susceptibility data in the temperature range 5.0—300 K were collected with an applied field of 0.5T of a Quantum Design model MPMS-7 magnetometer.

X-ray crystal structure determination

Crystal data and structure refinement details for the compound are given in Table 1. Selected bond lengths and angles for the compound are listed in Table 2. Data were collected with Mo K α radiation ($\lambda = 0.071073$ nm) using an Enraf-Nonius CCD-4 diffractometer at 273 K. The sample selected for investigation has dimension of 0.25 mm × 0.20 mm × 0.20 mm. A total of 34386 reflections were measured to give 14787 independent reflections ($R_{int} = 0.0546$). The structures were solved

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with direct methods with SHELXL-97 program⁶ and refined with the full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were assigned to calculated positions. The structure was then refined on F^2 using SHELXL-97. The final R value was 0.0588 [$I > 2\sigma(I)$].

Table 1 Crystallographic data for $K_2[\{Eu(H_2O)_4\}_2\{Fe^{II}(bipy)(CN)_4\}_4] \cdot 9H_2O \cdot CH_3OH$

Empirical formula	$C_{57}H_{70}Eu_2Fe_4K_2N_{24}O_{18}$
Formula weight	1984.84
Crystal system	Monoclinic
Space group	$P2(1)/c$
	$a = 1.3946(4)$ nm
Unit cell dimension	$b = 2.0450(6)$ nm, $\beta = 99.025(5)^\circ$
	$c = 2.9722(8)$ nm
Volume, Z	$8.372(4)$ nm ³ , 4
$F(000)$	3904
Density	1.562 g \cdot cm ⁻³
Absorption coefficient	2.322 mm ⁻¹
Crystal size	0.25 mm \times 0.20 mm \times 0.20 mm
θ Range	$1.21^\circ - 25.03^\circ$
	$-16 \leq h \leq 14$,
Limiting indices	$-24 \leq k \leq 23$
	$-16 \leq l \leq 35$
T	$273(2)$ K
Reflections collected/unique	34386/14787 ($R_{int} = 0.0546$)
Data/restraints/parameters	14787/1/990
Goodness of fit indicator	1.004
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0588$, $wR_2 = 0.1495$
Largest diff. peak and hole	2097, 1111 e \cdot nm ⁻³

Synthesis of the compound

$K_2[Fe(bipy)(CN)_4] \cdot 3H_2O$ (0.2 mmol) was dissolved in methanol (25 mL), followed by the addition of a methanolic solution of $Eu(NO_3)_3 \cdot 6H_2O$ (0.1 mmol, 5 mL) with stirring. The red precipitate formed immediately was filtered off and washed thoroughly with acetonitrile. The remaining solid was dissolved in warm water. After a few days, red single crystal was obtained. The yield is about 27%. IR (KBr) ν : 2059, 2094 cm⁻¹. Anal. calcd for $C_{57}H_{70}Fe_4K_2N_{24}O_{18}Eu_2$: C 34.49, H 3.55, N 16.9; found C 34.70, H 3.82, N 17.02.

Results and discussion

IR spectra

The bimetallic assembly of the compound shows two sharp ν_{CN} bands at ca. 2059 and ca. 2094 cm⁻¹, indicating the existence of two types of cyanide groups in the crystal lattice. The lower frequency band corresponds to that of $K_2[Fe(bipy)(CN)_4] \cdot 3H_2O$ and can be ascribed to

a non-bridging cyanide group. The higher frequency band is attributed to the bridging cyanide group.⁷

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for $K_2[\{Eu(H_2O)_4\}_2\{Fe^{II}(bipy)(CN)_4\}_4] \cdot 9H_2O \cdot CH_3OH$.

Eu(1)—N(4)	0.2436(8)	Eu(1)—O(3)	0.2448(8)
Eu(1)—N(11)	0.2452(10)	Eu(1)—N(13)	0.2463(8)
Eu(1)—O(1)	0.2469(7)	Eu(1)—N(3)	0.2473(9)
Eu(1)—O(4)	0.2484(7)	Eu(1)—O(2)	0.2503(8)
Fe(1)—C(3)	0.1860(10)	Fe(1)—C(2)	0.1949(12)
Fe(1)—C(1)	0.1929(11)	Fe(1)—N(16)	0.1995(8)
N(4)-Eu(1)-O(3)	143.0(3)	N(4)-Eu(1)-N(11)	87.7(3)
O(3)-Eu(1)-N(13)	73.5(3)	N(4)-Eu(1)-N(13)	143.2(3)
N(4)-Eu(1)-O(1)	74.0(3)	N(11)-Eu(1)-N(13)	103.2(3)
N(11)-Eu(1)-O(1)	77.1(3)	O(3)-Eu(1)-O(1)	70.6(3)
N(4)-Eu(1)-N(3)	99.2(3)	N(13)-Eu(1)-O(1)	142.6(3)
N(11)-Eu(1)-N(3)	145.1(3)	O(3)-Eu(1)-N(3)	80.0(3)
O(1)-Eu(1)-N(3)	72.2(3)	N(13)-Eu(1)-N(3)	91.7(3)
O(3)-Eu(1)-O(4)	138.1(3)	N(4)-Eu(1)-O(4)	73.7(3)
N(13)-Eu(1)-O(4)	76.4(3)	N(11)-Eu(1)-O(4)	141.5(3)
N(3)-Eu(1)-O(4)	72.4(3)	O(1)-Eu(1)-O(4)	126.6(3)
O(3)-Eu(1)-O(2)	124.7(3)	N(4)-Eu(1)-O(2)	77.2(3)
N(3)-Eu(1)-O(2)	143.2(3)	N(11)-Eu(1)-O(2)	71.7(3)
C(3)-Fe(1)-C(55)	87.7(4)	O(1)-Eu(1)-O(2)	137.9(3)
C(55)-Fe(1)-C(1)	89.8(4)	O(4)-Eu(1)-O(2)	71.4(3)
C(55)-Fe(1)-C(2)	91.0(5)	C(3)-Fe(1)-C(1)	90.6(4)
C(3)-Fe(1)-N(15)	176.3(4)	C(3)-Fe(1)-C(2)	85.2(4)
C(1)-Fe(1)-N(16)	89.1(4)	C(2)-Fe(1)-N(15)	92.1(4)
N(15)-Fe(1)-N(16)	80.5(3)	C(2)-Fe(1)-N(16)	90.5(4)

TGA Thermogravimetric analysis

The thermogravimetric curve of the complex presents three steps: the first step shows a continuous mass loss from room temperature up to about 123 $^\circ$ C; a plateau is observed between 123 and 312 $^\circ$ C. The total mass loss up to the midpoint between 123 and 312 $^\circ$ C corresponds to the mass of all water molecules. A successive mass loss was observed upon further heating, suggesting decomposition of the sample.

Description of the crystal structure

The structure of the cation of the complex is shown in Figure 1. The structure of the compound reveals that it is a tetranuclear macrocycle. The square cores of the compound composed of the alternately cyanide bridged Fe(II) and Eu(III) ions. Each Fe(II) ion is coordinated by two nitrogen atoms of bipy and four carbon atoms of cyanide, taking a distorted octahedral geometry. Each Eu(III) ion is eight coordinated by four oxygen atoms from four water molecules [the mean length of Eu—O

is 0.2448(8)—0.2503(8) nm] and four nitrogen atoms from four bridging CN groups [the mean length of Eu—N is 0.2436(8)—0.2473(9) nm], taking a dodecahedral geometry. The structure of the compound consists of $[\{\text{Eu}(\text{H}_2\text{O})_4\}_2\{\text{Fe}^{\text{II}}(\text{bipy})(\text{CN})_4\}_4]^{2-}$ anions (Figure 1), disordered potassium cations and crystal water molecules. In the chain structure two CN^- groups of each $[\text{Fe}(\text{bipy})(\text{CN})_4]^{2-}$ unit bridge two europium atoms with an $\text{Fe}^{\text{II}}\cdots\text{Eu}^{\text{III}}$ distance of 0.53248 nm, similar to those observed in $[\text{Fe}_2(\text{CN})_4(\text{phen})_4\text{Yb}_2\text{Cl}_6(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}_2] \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$.⁸ Within each asymmetric unit, the $[\text{Fe}(\text{bipy})(\text{CN})_4]^{2-}$ unit acts as a dimonodentate ligand towards $\text{Eu}(\text{H}_2\text{O})_4^{3+}$ units through two of its four cyanide groups on *cis* positions, generating a ladder structure (Figure 2).

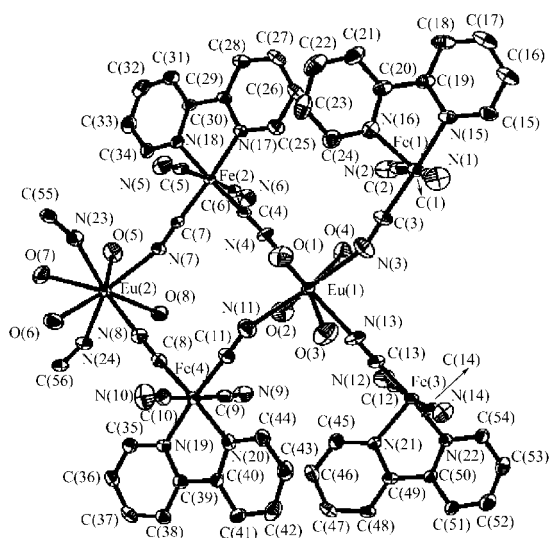


Figure 1 ORTEP drawing of the anion $[\{\text{Eu}(\text{H}_2\text{O})_4\}_2\{\text{Fe}^{\text{II}}(\text{bipy})(\text{CN})_4\}_4]^{2-}$ with the atom numbering scheme for the unique atoms, showing the 30% probability thermal motion ellipsoid.

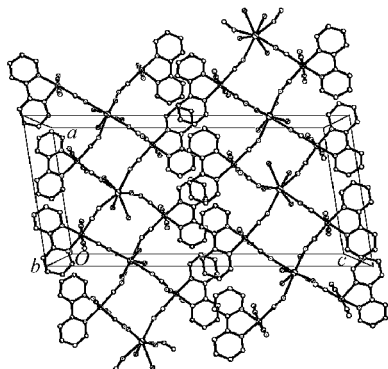


Figure 2 Stacking of the adjacent one-dimensional ladder chains running along the *b*-axis.

Magnetic properties

The $\chi_M T$ and χ_M vs. *T* plot for $\text{K}_2[\{\text{Eu}(\text{H}_2\text{O})_4\}_2\{\text{Fe}^{\text{II}}(\text{bipy})(\text{CN})_4\}_4] \cdot 9\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ obtained under a 0.5*T* field is shown in Figure 3, χ_M being the molar

magnetic susceptibility. At room temperature, the $\chi_M T$ value is $2.76 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$. As the temperature is lowered, the $\chi_M T$ value shows a gradual decrease, reaching the minimal value ($0.51 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$) at 16 K. With a further decrease of the temperature, $\chi_M T$ increases reaching a maximum value of $0.67 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 5.0 K.

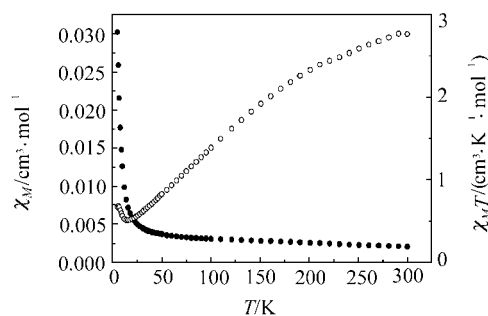


Figure 3 Plots of the temperature dependence of $\chi_M T$ and χ_M for the complex **1**. The (•) represents the χ_M value; the (○) represents the $\chi_M T$ value.

Concluding remarks

The synthesis, magnetic susceptibility and crystal structure of a novel 1D heterometallic chain, where a cyano-bridged Eu(III) dimer is linked by four tetra-cyano-mono-(2,2'-bipyridine)-ferrate(II) anion are described. We are now studying the structure of other similar extended systems based on $[\text{Fe}(\text{bipy})(\text{CN})_4]^{2-}$ and hope to report in the near future some interesting results.

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