

Unprecedented ferromagnetic interaction in an erbium(III)–copper(II) coordination polymer

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Abstract

Two 3D Ln(III)–Cu(II) coordination polymers $[\text{Er}_2\text{Cu}_3(\text{pydc})_6(\text{H}_2\text{O})_6]_n$ (**1**) and $[\text{Tb}_2\text{Cu}_3(\text{pydc})_6(\text{H}_2\text{O})_6]_n$ (**2**) were hydrothermally prepared from pyridine-2,4-dicarboxylic acid (H_2pydc) and characterized by single-crystal X-ray diffraction analysis. The magnetic studies show that an unexpected ferromagnetic interaction between metal centers exists in **1** while **2** behaves as an antiferromagnet. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

The 3d–4f heterometallic coordination polymers have been intensively investigated because of their interesting magnetic and luminescent properties [1–4]. Among these 3d–4f complexes, particular attention has been paid to gadolinium(III)/copper(II) couples which display magnetic properties amenable to a rather simple analysis based on a spin-only Hamiltonian because the $^8\text{S}_{7/2}$ single-ion ground state of gadolinium(III) has no first-order orbital momentum to complicate the magnetic analysis. Ferromagnetic interaction has been observed in a number of gadolinium(III)–copper(II) complexes [5–7]. However, little attention has been paid to the fact that almost all the erbium(III)–copper(II) complexes reported by now are antiferromagnets [8–11]. To the best of our knowledge, only one erbium(III)–copper(II) compound reported recently by Navarro et al. is ferromagnet [12]. It should be mentioned that the number of erbium(III)–copper(II) compounds for which structural and magnetic data are

available is restricted and that the factors governing the nature and magnitude have not been clarified. Here, we report two Ln(III)–Cu(II) coordination polymers formulated as $[\text{Er}_2\text{Cu}_3(\text{pydc})_6(\text{H}_2\text{O})_6]_n$ (**1**) and $[\text{Tb}_2\text{Cu}_3(\text{pydc})_6(\text{H}_2\text{O})_6]_n$ (**2**), compound **1** displays an unprecedented ferromagnetic behavior while **2** behaves as an antiferromagnet.

2. Experimental

2.1. General

All chemicals are analytical grade and were used without further purification. The hydrothermal reaction was performed in a 23 mL Teflon-lined stainless steel autoclave under autogenous pressure. Infrared spectra were recorded on a Magna 750 FR-IR spectrometer using KBr pellets. C, H and N microanalyses were measured with an elemental Vairo EL III analyzer. Thermal analyses were performed using a thermal analyst 2100TA Instrument and a SDT 2960 Simultaneous TGA-DTA Instrument. The polycrystalline magnetic susceptibility data were collected on a Quantum Design PPMS model 6000 magnetometer in the temperature range from 2 to 300 K.

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2.2. Synthesis of the complexes

Both **1** and **2** were prepared by the same method, as follows: a mixture of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1 mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.029 g, 0.15 mmol), H_2pydc (0.048 g, 0.3 mmol) in H_2O (5 mL) was sealed in a 23 mL Teflon-lined bomb at 160 °C for 6 days, then slowly cooled to room temperature by 5 °C/h. Blue prismatic crystals were recovered by filtration, washed by distilled water, and air-dried (Yield: 83%, and 87%, based on $\text{Ln}(\text{NO}_3)_3$ for **1** and **2**, respectively). The positions of the diffraction peaks of the experimental and simulated XRD patterns correspond well, thus indicating phase purity of the as-synthesized samples (Figure S1). Elemental analysis and IR data for compounds **1** and **2** are listed in Table 4.

2.3. X-ray crystallography

Data collections were performed at 293(2) K on a Mercury CCD diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and all calculations were performed using the SHELXL package [13]. The structure were refined by full matrix least squares with anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms belonging to the water molecules were found in the electron density map and refined isotropically, the other H atoms were generated geometrically and

treated as riding. The crystallographic data are summarized in Table 1 and selected bond lengths and bond angles of **1** and **2** are listed in Tables 2 and 3.

3. Results and discussion

3.1. Crystal structures and magnetic properties

X-ray diffraction analyses reveal that **1** and **2** are isostructural with our previous report of $[\text{Sm}_2\text{Cu}_3(\text{pydc})_6(\text{H}_2\text{O})_6]_{\text{ln}}$ [14]. Both of them contain 2D carboxyl-bridged layers which are further pillared together through pydc ligands to generate the final 3D structures (Fig. 1). The asymmetric unit of **1** contains one eight-coordinated Er^{III} ion and one and a half five-connected Cu^{II} ions. In the 2D carboxyl-bridged layer, each Er^{III} ion connects to

Table 2
Selected bond lengths [\AA] and angles [$^\circ$] for **1**

Bond			
Er1–O3 ⁱ	2.267 (3)	Cu1–O1 ^{iv}	1.966 (3)
Er1–O11	2.324 (3)	Cu1–O1	1.966 (3)
Er1–O4 ⁱⁱ	2.324 (3)	Cu1–O5 ^{iv}	2.404 (3)
Er1–O2	2.346 (3)	Cu1–O5	2.404 (3)
Er1–O13	2.381 (3)	Cu2–O6	1.936 (3)
Er1–O15	2.385 (3)	Cu2–O10 ^v	1.941 (3)
Er1–O9 ⁱⁱⁱ	2.437 (3)	Cu2–N2	1.974 (3)
Er1–O14	2.448 (3)	Cu2–N3 ^v	1.975 (3)
Cu1–N1 ^{iv}	1.964 (3)	Cu2–O12	2.334 (3)
Cu1–N1	1.964 (3)		
Angle			
O3 ⁱ –Er1–O11	87.96 (10)	O9 ⁱⁱⁱ –Er1–O14	132.76 (9)
O3 ⁱ –Er1–O4 ⁱⁱ	102.36 (10)	N1 ^{iv} –Cu1–N1	180.000 (1)
O11–Er1–O4 ⁱⁱ	144.92 (10)	N1 ^{iv} –Cu1–O1 ^{iv}	83.02 (12)
O3 ⁱ –Er1–O2	143.43 (10)	N1–Cu1–O1 ^{iv}	96.98 (12)
O11–Er1–O2	108.22 (11)	N1 ^{iv} –Cu1–O1	96.98 (12)
O4 ⁱⁱ –Er1–O2	83.24 (10)	N1–Cu1–O1	83.02 (12)
O3 ⁱ –Er1–O13	145.22 (10)	O1 ^{iv} –Cu1–O1	180.0
O11–Er1–O13	77.55 (10)	N1 ^{iv} –Cu1–O5 ^{iv}	91.41 (12)
O4 ⁱⁱ –Er1–O13	75.09 (10)	N1–Cu1–O5 ^{iv}	88.59 (12)
O2–Er1–O13	71.31 (10)	O1 ^{iv} –Cu1–O5 ^{iv}	91.46 (11)
O3 ⁱ –Er1–O15	74.71 (10)	O1–Cu1–O5 ^{iv}	88.54 (11)
O11–Er1–O15	142.45 (10)	N1 ^{iv} –Cu1–O5	88.59 (12)
O4 ⁱⁱ –Er1–O15	72.32 (10)	N1–Cu1–O5	91.41 (12)
O2–Er1–O15	72.76 (10)	O1 ^{iv} –Cu1–O5	88.54 (11)
O13–Er1–O15	133.54 (10)	O1–Cu1–O5	91.46 (11)
O3 ⁱ –Er1–O9 ⁱⁱⁱ	77.30 (10)	O5 ^{iv} –Cu1–O5	180.0
O11–Er1–O9 ⁱⁱⁱ	68.25 (10)	O6–Cu2–O10 ^v	172.22 (13)
O4 ⁱⁱ –Er1–O9 ⁱⁱⁱ	146.53 (10)	O6–Cu2–N2	84.57 (13)
O2–Er1–O9 ⁱⁱⁱ	78.79 (10)	O10 ^v –Cu2–N2	96.28 (13)
O13–Er1–O9 ⁱⁱⁱ	123.92 (10)	O6–Cu2–N3 ^v	94.83 (13)
O15–Er1–O9 ⁱⁱⁱ	75.46 (10)	O10 ^v –Cu2–N3 ^v	83.26 (12)
O3 ⁱ –Er1–O14	71.50 (10)	N2–Cu2–N3 ^v	172.06 (15)
O11–Er1–O14	75.96 (10)	O6–Cu2–O12	96.66 (13)
O4 ⁱⁱ –Er1–O14	75.84 (10)	O10 ^v –Cu2–O12	91.03 (12)
O2–Er1–O14	143.33 (10)	N2–Cu2–O12	92.98 (13)
O13–Er1–O14	74.35 (10)	N3 ^v –Cu2–O12	94.95 (12)
O15–Er1–O14	126.45 (10)	O9 ⁱⁱⁱ –Er1–O14	132.76 (9)
O3 ⁱ –Er1–O11	87.96 (10)	N1 ^{iv} –Cu1–N1	180.000 (1)
O3 ⁱ –Er1–O4 ⁱⁱ	102.36 (10)		

Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 - x, -y, -z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $1 - x, -y, 1 - z$; (v) $2 - x, 1 - y, 1 - z$.

Table 1
Crystallographic data for compounds **1** and **2**

Compound	1	2
Formula	$\text{C}_{42}\text{H}_{30}\text{Cu}_3\text{Er}_2\text{N}_6\text{O}_{30}$	$\text{C}_{42}\text{H}_{30}\text{Cu}_3\text{Tb}_2\text{N}_6\text{O}_{30}$
F_w	1623.86	1607.18
Crystal size (mm)	$0.30 \times 0.15 \times 0.05$	$0.18 \times 0.12 \times 0.02$
Space group	$P-1$	$P-1$
a (\AA)	9.4098 (5)	9.4316 (5)
b (\AA)	10.6220 (7)	10.6777 (8)
c (\AA)	12.2324 (7)	12.2767 (6)
α ($^\circ$)	86.095 (9)	86.101 (9)
β ($^\circ$)	81.384 (7)	81.449 (6)
γ ($^\circ$)	86.665 (7)	86.608 (8)
V (\AA^3)	1204.61 (12)	1218.28 (13)
Z	1	1
λ (Mo $K\alpha$) (\AA)	0.71073	0.71073
D_c (g/cm^3)	2.238	2.191
μ (mm^{-1})	4.86	4.263
T (K)	293(2)	293(2)
Reflections collected	7685	9601
Unique reflections	4220	5507
R_{int}	0.021	0.0336
Parameters	376	376
R_1, wR ($I > 2\sigma(I)$) ^a	0.0259, 0.0632	0.0416, 0.0870
R_1, wR (all data) ^b	0.0290, 0.0654	0.0517, 0.0948
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	$a = 0.0372,$ $b = 0.7273$	$a = 0.0391,$ $b = 3.5840$
Goodness-of-fit-on F^2	1.058	1.026
$\Delta\rho_{\text{min}}$ and $\Delta\rho_{\text{max}}$ (e \AA^{-3})	–1.584, 1.451	–1.235, 1.446

^a $R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|$.

^b $wR = \sqrt{\sum w(F_o - F_c)^2 / \sum w(F_o)^2}^{1/2}$.

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