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A 3-D Gd(III)–Cu(I) coordination polymer based on nicotinate and oxalate ligands: synthesis, crystal structure, and magnetic properties

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A new 3d–4f coordination polymer, [GdCu(nic)₂(ox)_{0.5}Br(H₂O)₂] (**1**) [nic = nicotinate, ox = oxalate], was synthesized and characterized by elemental analysis, infrared (IR) spectroscopy, thermal analysis and single crystal X-ray diffraction. Compound **1** exhibits a 3-D network constructed from Gd-carboxylate chain, Cu(nic)₂ subunits and ox ligands. Furthermore, the magnetism is studied in this article.

Keywords: Hydrothermal synthesis; 3d–4f System; Crystal structure; Magnetic behavior

1. Introduction

The design and synthesis of lanthanide-transition metal complexes (LTMCs) are of interest with intriguing structural motifs and may provide a new strategy for achieving solid functional materials with applications in gas storage, luminescent materials, etc. [1–3]. A variety of heterometallic coordination polymers have been obtained from spontaneous assembly of metal ions and ligands containing mixed-donors such as pyridinecarboxylate, carbonyls, cyanides, amino acids, etc. [4–7]. The construction of open heterometallic coordination frameworks, however, is still a formidable task because of the variable coordination numbers of lanthanides, their low stereochemical preference and the competitive reactions between lanthanide and transition metals coordinated by ligands. Fortunately, the different Lewis acidities of lanthanide and transition metal ions provide the impetus to construct multi-dimensional heterometallic coordination frameworks with useful physical–chemical properties and intriguing structural topologies [8]. When using bifunctional ligands with both a carboxylate and an N-donor (e.g. pyridine carboxylic acid, pyrazine carboxylic acid, etc.), the lanthanides have a strong preference for O-donors forming lanthanide carboxylate subunits, while transition metal ions such as Ag(I) or Cu(I)/Cu(II) ions bind more easily

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to N-donors to link the lanthanide carboxylate subunits. Based on these, many high-dimensional heterometallic coordination frameworks have been constructed [9].

We chose nicotinic acid (nic) as a potential linker between lanthanide and transition metal ions, and oxalate as an additional bridging ligand. One 3d–4f coordination polymer, $[\text{GdCu}(\text{nic})_2(\text{ox})_{0.5}\text{Br}(\text{H}_2\text{O})_2]$ (**1**), was obtained under hydrothermal conditions and characterized by elemental analysis, infrared (IR) spectroscopy, thermogravimetric analysis (TGA) and single crystal X-ray diffraction. Compound **1** exhibits a 3-D network constructed from a Gd-carboxylate chain, $\text{Cu}(\text{nic})_2$ subunits and ox ligands. For compound **1**, the Cu(II) ions were reduced to copper(I) in the hydrothermal reaction, as previously reported with nicotinic acid [10].

2. Experimental

2.1. Materials and instruments

All chemicals were commercially available and used as received without purification. Elemental analyses for C, H, and N were carried out using a Vario EL III Elemental Analyzer. IR spectra were recorded ($4000\text{--}400\text{ cm}^{-1}$) as KBr disks on a Bruker 1600 Fourier transform infrared (FTIR) spectrometer. TGA were performed on a simultaneous SDT thermal analyzer (STA449C, Netzsch) under a flow of N_2 at a heating rate of $10^\circ\text{C min}^{-1}$ between ambient temperature and 800°C . Magnetic properties were studied with a Quantum Design superconducting quantum interference device (SQUID) magnetometer on the MPMS-7 system.

2.2. Synthesis of compound 1

A mixture of CuBr_2 (0.112 g, 0.5 mmol), Gd_2O_3 (0.087 g, 0.25 mmol), Hnic (0.0615 g, 0.5 mmol), sodium oxalate (0.067 g, 0.5 mmol), HClO_4 (1 mL) and H_2O (10 mL) was stirred for 30 min in air and then sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 120°C for 72 h. The mixture was cooled to room temperature at a rate of 5°C h^{-1} , and yellow block crystals were obtained in a yield of 42% based on Gd. Calcd for $\text{C}_{13}\text{H}_{12}\text{CuGdN}_2\text{O}_8$ (**1**): C, 24.96; H, 1.92; N, 4.48. Found: C, 24.93; H, 1.90; N, 4.52. IR bands (KBr pellets, cm^{-1}): $\nu = 3381(\text{s}), 2917(\text{vs}), 2852(\text{vs}), 1608(\text{s}), 1554(\text{s}), 1461(\text{s}), 1377(\text{m}), 1192(\text{w}), 1049(\text{w}), 756(\text{w}), 724(\text{w}), 698(\text{w}), 554(\text{w})$.

2.3. X-ray crystallography

Single crystal X-ray diffraction data collection for compound **1** was performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Data collection and reduction were performed using SMART and SAINT software [11]. A multi-scan absorption correction was applied using SADABS [11]. The two structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package [11]. Water hydrogens were tentatively located in difference Fourier maps and were refined with distance restraints of $\text{O-H} = 0.82$ and $\text{H}\cdots\text{H} = 1.35 \text{ \AA}$, each within a standard

deviation of 0.01 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Crystal parameters and details of the data collection and refinement are given in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. Crystal structures

[GdCu(nic)₂(ox)_{0.5}Br(H₂O)₂] (**1**) is a 3-D heterometallic coordination polymer constructed from Gd-carboxylate chain, Cu(nic)₂ subunits and ox. A thermal ellipsoid

Table 1. Crystallographic data and structure refinement summary for compound **1**.

Empirical formula	C ₁₃ H ₁₂ BrCuGdN ₂ O ₈
Formula weight	624.95
Crystal system	Monoclinic
Size (mm)	0.30 × 0.27 × 0.21
Space group	<i>P</i> 2(1)/ <i>c</i>
Unit cell dimensions (Å, °)	
<i>a</i>	14.1373(2)
<i>b</i>	12.3960(2)
<i>c</i>	9.8979(10)
β	93.448(10)
Volume (Å ³), <i>Z</i>	1731.43(4), 4
Calculated density (mg cm ⁻³)	2.397
Absorption coefficient (mm ⁻¹)	7.378
<i>F</i> (000)	1184
Parameters	235
Goodness-of-fit on <i>F</i> ²	1.063
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0374
<i>wR</i> ₂ (all data) ^b	0.1083

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

$$^b wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum(F_o^2)^2\}^{1/2}.$$

Table 2. Selected bond distances (Å) and angles (°).

Gd(1)–O(3) ^{#1}	2.306(6)	N(1)–Cu(1)–Br(1)	105.6(2)
Gd(1)–O(1)	2.319(6)	N(2)–Cu(1)–Br(1)	101.9(3)
Gd(1)–O(2) ^{#2}	2.324(6)	O(2) ^{#2} –Gd(1)–O(4) ^{#3}	104.1(2)
Gd(1)–O(4) ^{#3}	2.379(5)	O(3) ^{#1} –Gd(1)–O(1W)	142.6(2)
Gd(1)–O(1W)	2.420(6)	O(2) ^{#2} –Gd(1)–O(1W)	72.9(2)
Gd(1)–O(5)	2.443(5)	O(1)–Gd(1)–O(5)	138.0(2)
Gd(1)–O(6) ^{#4}	2.460(5)	O(1W)–Gd(1)–O(5)	128.85(2)
Gd(1)–O(2W)	2.528(6)	O(2) ^{#2} –Gd(1)–O(6) ^{#4}	77.2(2)
Cu(1)–N(1)	1.952(7)	O(4) ^{#3} –Gd(1)–O(2W)	74.6(2)
Cu(1)–N(2)	1.955(7)	O(1W)–Gd(1)–O(2W)	71.6(2)
Cu(1)–Br(1)	2.5136(2)	O(3) ^{#1} –Gd(1)–O(1)	102.4(2)
N(1)–Cu(1)–N2	150.9(3)	O(1) ^{#2} –Gd(1)–O(2)	86.9(2)

Symmetry codes: ^{#1}1 + *x*, 1/2 – *y*, 1/2 + *z*; ^{#2}*x*, 1/2 – *y*, –1/2 + *z*; ^{#3}1 + *x*, *y*, *z*; and ^{#4}2 – *x*, 1 – *y*, 2 – *z*.

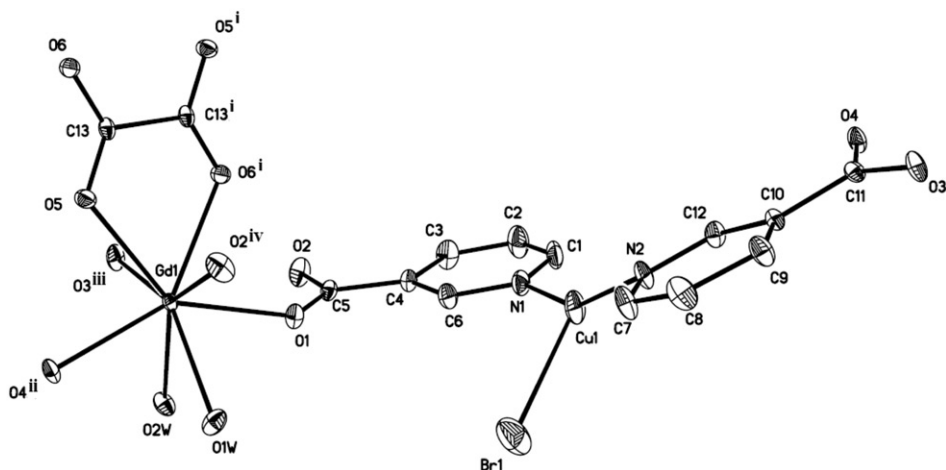


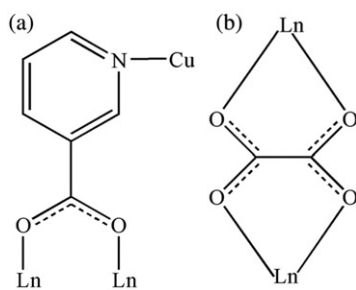
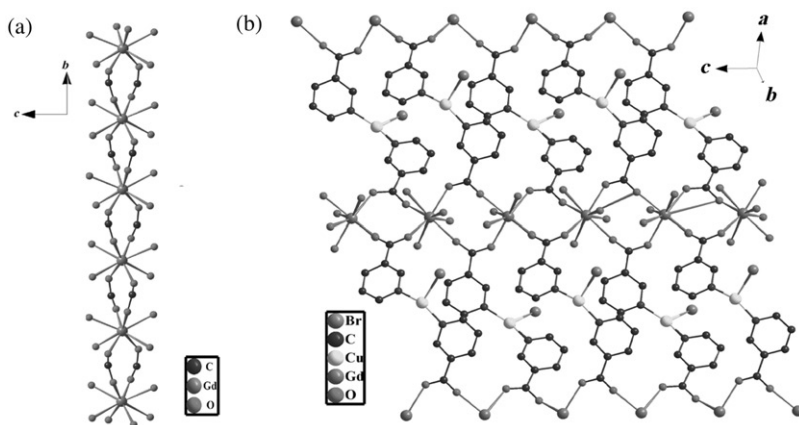
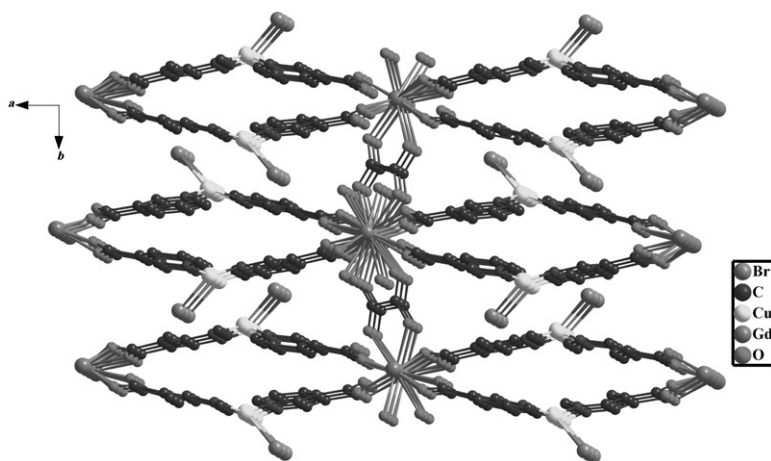
Figure 1. Thermal ellipsoid plot of the asymmetric unit of compound **1** (30% probability ellipsoids). All hydrogens were omitted for clarity. Symmetry code: (i) $2 - x, 1 - y, 2 - z$; (ii) $1 + x, y, z$; (iii) $1 + x, 1/2 - y, 1/2 + z$; (iv) $x, 1/2 - y, -1/2 + z$.

plot of compound **1** is shown in figure 1. In the asymmetric unit of compound **1**, there is one Gd(III), one Cu(I), two nic ligands, half an oxalate, one bromide, and two coordinated waters. The nic ligands in compound **1** exhibit a coordination mode with the carboxylate bidentate linking two Gd(III) ions and the nitrogen linking one Cu(I) (scheme 1a); oxalates are μ_4 bridging and chelating linking two Gd(III) ions (scheme 1b).

The Gd1(III) is eight-coordinate with four oxygens of four different nic ligands, two oxygens of one chelating oxalate and two waters. The Gd1 can be described as having a bicapped trigonal prismatic geometry with Gd \cdots O bond distances and O \cdots Gd \cdots O bond angles ranging from 2.306(6) to 2.528(6) Å and 66.52(2) $^\circ$ to 144.5(2) $^\circ$, respectively, all of which are within the range of those observed for eight-coordinate Gd(III) complexes with oxygen donors [12]. The Cu(I) ion is a T-shaped configuration, defined by two nitrogens from two nic ligands and bromide. The Cu \cdots N bond distances are 1.952(7) and 1.955(7) Å, Cu \cdots Br bond distance of 2.5136(2) Å, and the N \cdots Cu \cdots N angle of 150.9(3) $^\circ$, similar to other Cu(I) structures with T-shaped configuration [13]. In the polymeric structure of compound **1**, the carboxylate groups of the nic ligands connected adjacent Gd(III) ions to form a Gd-carboxylate infinite chain running along the bc-plane of the unit cell (figure 2a). The distance between adjacent Gd(III) ions is 4.949(3) Å. The Cu(nic) $_2$ subunits connect the chains to form a layer (figure 2b). The oxalates exhibit μ_4 bridging and chelating to link two Gd(III) ions from neighboring layers resulting in a 3-D network (figure 3). O–H \cdots O and O–H \cdots Br hydrogen bonds involving the carboxyl oxygens of the nic ligands, coordinated water and bromide further enhance the stability of the 3-D structure.

3.2. IR analysis

The broad band at 2850–3381 cm^{-1} may be assigned to $\nu(\text{O–H})$ of water. The features at 1608, 1554 and 1461, 1377 cm^{-1} are associated with the asymmetric (COO) and symmetric (COO) stretching vibrations [14].

Scheme 1. Coordination modes of nicotinic acid (IN) and oxalate ligands in **1**.Figure 2. (a) View of a Gd-carboxylate infinite chain and (b) one layer of compound **1** (all hydrogens omitted for clarity).Figure 3. The 3-D network of compound **1** running along the ab plane of the unit cell (all hydrogens omitted for clarity).

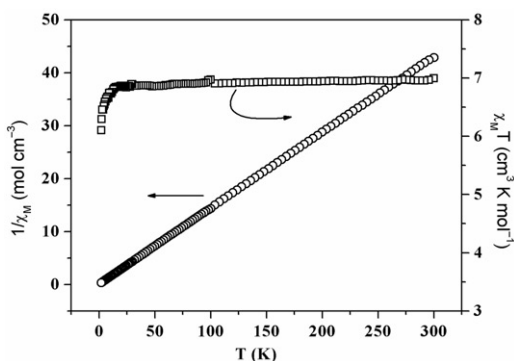


Figure 4. Plots of $\chi_M T$ and $1/\chi_M$ vs. T for compound **1**.

3.3. Thermogravimetric analysis

TGA of compound **1** was performed in a N_2 atmosphere to $800^\circ C$ at a constant rate of $10^\circ C \text{ min}^{-1}$. For compound **1**, the TGA trace (Supplementary material) showed a gradual weight-loss step of 5.9% ($90\text{--}170^\circ C$), corresponding to gradual loss of coordinated water ($2H_2O$, Calcd 5.1%), followed by a plateau ($170\text{--}320^\circ C$). The weight-loss step above $320^\circ C$ corresponds to decomposition of the framework structure.

3.4. Magnetic properties

Magnetic susceptibility measurements were performed from 2 to 300 K with an applied field of 1000 Oe. Experimental susceptibilities were corrected for diamagnetism of the constituent atoms. Plots of $\chi_m T$ and $1/\chi_m$ versus T are presented in figure 4. The experimental value at room temperature ($6.99 \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$) is slightly lower than the calculated value for one Gd(III) ($S=7/2$) with noninteracting ions ($7.88 \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$). With decrease of temperature, the $\chi_m T$ decreases gradually to $6.87 \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ at 20 K and then abruptly decreases to $6.1 \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ at 2 K, which indicates antiferromagnetic coupling between Gd(III) ions. The plot of $1/\chi_m$ versus T follows the Curie–Weiss law with Weiss constant $\theta = -0.54 \text{ K}$. The observed behavior indicates weak antiferromagnetic interactions between adjacent paramagnetic gadolinium centers. The magnetic behavior is similar to that of discrete gadolinium–copper complexes [9d–9g], with weak antiferromagnetic or ferromagnetic interactions from adjacent paramagnetic gadolinium and copper centers.

4. Conclusion

We have synthesized a new 3d–4f heterometallic coordination polymer $[GdCu(\text{nic})_2(\text{ox})_{0.5}\text{Br}(\text{H}_2\text{O})_2]$ (**1**) under hydrothermal conditions. Compound **1** is a 3-D heterometallic coordination framework constructed from Gd-carboxylate chains, $\text{Cu}(\text{nic})_2$ subunits and ox ligands, unusual in the reference [9a]. Magnetic studies

indicate that interactions between Gd(III) ions is antiferromagnetic. This synthetic approach can be used to prepare other lanthanide–transition metal heterometallic coordination polymers with particular functions.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC 743732. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>); also available from the author on request.

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