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A novel 2D oxalate- and dissymmetrical oxamidato-bridged heterometallic CuII–GdIII complex: Synthesis, crystal structure and magnetic properties

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ABSTRACT

A novel 2D framework, $\{[Cu_2(aeoe)_2Gd_2(C_2O_4)(H_2O)_6]\cdot 7H_2O\}_n$ (1) $(H_4aeoe = N'-(2-aminoterephthalic acid)-N''-(ethylenediamine) oxamidato), has been synthesized and characterized by elemental analysis, IR spectrum, thermogravimetric analysis (TGA), single-crystal X-ray diffraction and magnetic properties. Single-crystal structural analysis shows that complex 1 displays a novel 2D layered structure. The asymmetry unit of complex 1 contains a heterotetranuclear <math>Cu^{II}_2Gd^{III}_2$ building block. The Cu(II) ions are in a distorted square pyramidal CuN3O2 surrounding. The Gd(III) ions are eight-coordinated and surrounded by two oxygen atoms from oxamide group, one oxygen atom from carboxylate, two oxygen atoms from oxalate and three oxygen atoms from coordination water molecules. The framework formed using dissymmetrical oxamide and oxalate anions as mixed ligands is the first examples of 3d–4f complexes involving dissymmetrical oxamide. Its magnetic properties have also been investigated, and show weak ferromagnetic coupling between the Cu(II)-Gd(III) ions.

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1. Introduction

The design and construction of 3d–4f heterometallic coordination polymers have attracted special attention, not only for their diversified and tunable frameworks or electronic structures [1– 3], but also for their potential applications as multifunctional materials [4–9]. Among all the heteronuclear systems, the majority are associated with Cu–Ln complexes, which contain 1-D chains [10–12], 2-D grids [13–16] and 3-D networks [17–19].

To obtain the heterometallic complexes, a successful strategies is the "complex as ligand" approach, i.e., utilizing a metal complex as a ligand to coordinate an appropriate additional metal ion [20– 22]. Along this line, the heterospin systems of macrocyclic oxamides have been extensively investigated [23–25]. However, only a few kinds of coordination polymers based on macrocyclic oxamidate compound [Cu(L)] and Ln³⁺ have been reported [26–29]. So it is significant to elucidate the magnetic coupling between 3d and 4f metal ions via oxamidate bridges. With this in mind, we used dissymmetrical oxamide and oxalate anions as mixed ligands to assemble 3d–4f coordination polymers. Herein, we report the hydrothermal synthesis, crystal structure, and magnetic properties of a novel 2D 3d–4f coordination polymer {[Cu₂(aeoe)₂Gd₂(C₂O₄) (H₂O)₆]·7H₂O}_n (1). To our knowledge, it is the first reported heterometallic 3d–4f compound containing dissymmetrical oxamide.

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2. Experimental

2.1. Materials and methods

All chemicals and solvents were in analytical grade and used as commercially available. Elemental analyses for C, H and N were carried out on a Perkin-Elmer 2400II analyzer. The infrared spectra were recorded on an Avater-360 spectrometer using KBr pellets in a range of 400–4000 cm⁻¹. Thermogravimetric analysis was carried out on an TGA/SDTA851^e analyzer in a nitrogen atmosphere, and the complexes were heated to 1000 °C at a heating rate of $10 \,^{\circ}$ C min⁻¹. Magnetic measurement was carried out on polycrystalline samples with a MPMS-7SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all atoms.

2.2. Synthesis of { $[Cu_2(aeoe)_2Gd_2(C_2O_4)(H_2O)_6] \cdot 7H_2O$ }_n (1)

A mixture of Na₂[Cu(aeoe)]·3H₂O [30] (0.2 mmol, 0.096 g), Gd(NO₃)₃·6H₂O (0.2 mmol, 0.093 g) and Na₂C₂O₄ (0.05 mmol, 0.007 g) in 10 ml of H₂O was stirred for 1 h at room temperature, and then the reaction mixture was sealed in a Teflon-lined reactor and kept at 100 °C for 100 h under autogenous pressure. After being slowly cooled to the room temperature, red crystals of **(1)** were obtained Yield: 0.87 g (65%). *Anal.* Calc. for C₂₆H₄₄Cu₂Gd₂₋N₆O₂₉: C, 23.20; H, 3.29; N, 6.24. Found: C, 23.03; H, 3.11; N, 6.19%. IR (KBr, cm⁻¹): $v_{c=0}$ 1651 cm⁻¹, $v_{as(COO⁻)}$ 1557 cm⁻¹, $v_{s(COO⁻)}$ 1432 cm⁻¹ and 1407 cm⁻¹.

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2.3. X-ray crystallography

The single crystal used for data collection was selected and mounted on a Bruker Smart APEX diffractometer with a CCD detecusing graphite monochromated ΜοΚα radiation tor (λ = 0.071073 nm). Lorentz and polarization factors were made for the intensity data and absorption corrections were performed using SADABS. The crystal structures were solved using SHELXTL and refined using full matrix least-squares. The hydrogen atom positions were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbon atoms. Crystal data collection and refinement parameters are given in Table 1. The selected bond lengths and angles are given in Table 2.

3. Results and discussion

3.1. Crystal structure of complex 1

Single-crystal X-ray diffraction analysis reveals that complex **1** is a 2D framework formed by heterotetranuclear $Cu^{II}_{2}Gd^{III}_{2}$ building blocks. As shown in Fig. 1, the Cu(II) ions are in a distorted square pyramidal. The square-plane environment of Cu(II) formed by one oxygen atom and three nitrogen atoms from oxamidate bridges. And the apical position being occupied by another carboxylate oxygen atom with the bond length 2.548(5) Å. The Cu–N distances are distributed in the range 1.906(5)–2.032(5) Å, and the Cu–O distance is 1.912(4) Å, which are similar to the values reported in the literature [62]. The Gd(III) ions are eight-coordinated and surrounded by two oxygen atoms from oxamide group, one oxygen atom from carboxylate, two oxygen atoms from oxalate and three oxygen atoms from 2.325(4) to 2.514(4) Å. The Cu–Gd distance through the oxamido bridge is 5.734(1) Å.

The oxalate acts as bridge to link the adjacent $Cu^{II}_{2}Gd^{III}_{2}$ building blocks to create an infinite 1D chain with a Gd–Gd separation of 6.246(9) Å. These 1D chains are linked by coordinative bonds between carboxylic oxygen atoms and Cu ions to form a novel 2D coordination polymer, as illustrated in Fig. 2.

Table	1
	_

Crystal data and structure refinement for complexes 1.

1	
Empirical formula	$C_{26}H_{44}Cu_2Gd_2N_6O_{29}$
Formula weight	1346.25
T (K)	298(2)
Wavelength/nm	0.071073
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.165(1)
b (Å)	10.181(1)
<i>c</i> (Å)	14.731(2)
α (°)	109.260(2)
β(°)	97.079(2)
γ (°)	99.826(2)
$V(Å^3)$	1118.4(3)
Ζ	1
D_{Calc} (g cm ⁻³)	1.999
μ (mm ⁻¹)	3.965
F(000)	660
Crystal size/mm ³	$0.26 \times 0.19 \times 0.16$
θ range (deg)	2015-25.00
Independent reflns	$3889(R_{int} = 0.0210)$
Goodness-of-fit (GOF) on F^2	1.031
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0375, wR2 = 0.0948$
R indices (all data)	$R_1 = 0.0488, wR2 = 0.0994$

 $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|, \ wR_2 = \left[\sum w(|F_0|^2 - |F_c|^2)^2 / \sum w(F_0^2)^2 \right]^{1/2}.$

Table 2

Selected bond lengths (Å) and angles (deg) for complex 1.

Cu(1)-N(2)	1.906(5)	Cu(1)-N(1)	1.971(5)
Cu(1)-O(6)	1.912(4)	Cu(1)-N(3)	2.032(5)
Gd(1)-O(5)	2.325(4)	Gd(1)-O(2W)	2.347(5)
Gd(1)-O(1)#1	2.379(4)	Gd(1)-O(3W)	2.380(4)
Gd(1)-O(7)	2.391(4)	Gd(1)-O(2)#1	2.413(4)
Gd(1)-O(8)#2	2.421(4)	Gd(1)-O(1W)	2.514(4)
Gd(1)#1-O(1)	2.379(4)	Gd(1)#1-O(2)	2.413(4)
Gd(1)#2-O(8)	2.421(4)		
N(2)-Cu(1)-O(6)	166.2(2)	N(2)-Cu(1) -N(1)	84.6(2)
O(6)-Cu(1)-N(1)	95.26(19)	N(2)-Cu(1)-N(3)	83.1(2)
O(6)-Cu(1)-N(3)	96.4(2)	N(1)-Cu(1)-N(3)	167.6(2)
O(5)-Gd(1) - O(2W)	147.71(17)	O(5)-Gd(1)-O(1)#1	87.56(17)
O(2W)-Gd(1)-O(1)#1	108.2(2)	O(5)-Gd(1)-O(3W)	88.19(17)
O(2W)-Gd(1)-O(3W)	90.85(19)	O(1)#1-Gd(1)-O(3W)	149.88(16)
O(5)-Gd(1)-O(7)	142.28(15)	O(2W)-Gd(1)-O(7)	69.58(17)
O(1)#1-Gd(1)-O(7)	80.34(17)	O(3W)-Gd(1)-O(7)	85.00(18)
O(5)-Gd(1)-O(2)#1	79.34(16)	O(2W)-Gd(1)-O(2)#1	81.17(17)
O(1)#1-Gd(1)-O(2)#1	67.21(14)	O(3W)-Gd(1)-O(2)#1	140.72(16)
O(7)-Gd(1)-O(2)#1	126.38(17)	O(5)-Gd(1)-O(8)#2	75.65(15)
O(2W)-Gd(1)-O(8)#2	134.49(16)	O(1)#1-Gd(1)-O(8)#2	77.07(16)
O(3W)-Gd(1)-O(8)#2	72.99(16)	O(7)-Gd(1)-O(8)#2	66.88(15)
O(2)#1-Gd(1)-O(8)#2	136.85(15)	O(5)-Gd(1)-O(1W)	73.18(15)
O(2W)-Gd(1)-O(1W)	75.83(18)	O(1)#1-Gd(1)-O(1W)	134.28(14)
O(3W)-Gd(1)-O(1W)	72.10(15)	O(7)-Gd(1)-O(1W)	137.93(16)
O(2)#1-Gd(1)-O(1W)	68.65(15)	O(8)#2-Gd(1)-O(1W)	133.28(16)

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



Fig. 1. Perspective view of the $Cu^{II}_2Gd^{III}_2$ building unit (Symmetry transformations used to generate equivalent atoms: #1–x, 1–y, 1–z; #2–x, 1–y, 2–z; #3 1–x, 1–y, 1–z).

3.2. Thermogravimetric analysis

The thermal property of **1** (Fig. 3) has been measured in the N₂ flowing atmosphere with the heating rate of 10 °C·min⁻¹ from 25 to 1000 °C. The TGA curve of **1** can be divided into there steps of weight loss. The weight loss of 9.34% during the first step from 25 to 70 °C corresponds to the release of seven water molecules (calc. 9.36%). The following weight loss of 14.96% occurs from 70 to 340 °C which is attributed to the loss of six coordination water molecules and the oxalate ligand (calcd. 14.56%). Finally, the decomposition of complex **1** began at 440 °C.

3.3. Magnetic properties of complex 1

The magnetic susceptibility of the complex has been measured in the range of 2–300 K. The curves of χ_M and $\chi_M T$ versus T are shown in Fig. 4. At room temperature, the experimental $\chi_M T$ value is 8.14 cm³ mol⁻¹ K. This is close to the expected value for uncoupled CullGdIII (8.13 cm³ mol⁻¹ K). The $\chi_M T$ value first slightly increased, from 8.14 cm³ mol⁻¹ K at 300 K to 8.17 cm³ mol⁻¹ K at 55 K, but then rose sharply to 8.35 cm³ mol⁻¹ K at 6 K. This is clearly indicative of ferromagnetic behavior. The slight decrease in $\chi_M T$ at very low temperatures (6–1.8 K) may indicate the presence of an intermolecular antiferromagnetic component or B.-L. Liu et al. / Inorganica Chimica Acta 392 (2012) 1-4



Fig. 2. Perspective view of the 2D coordination polymer 1 (left). Space-filling representation of the 2D coordination polymer (right). Hydrogen atoms and water molecule are omitted for clarity.



Fig. 3. Thermogravimetric analyses (TGA) curves for complex 1.



Fig. 4. χ_{M} (\bigcirc) versus *T* and $\chi_{M}T$ (\Box) versus *T* plots for the complex **1**.

zero-field splitting. To our knowledge, no formula in literatures is available to reproduce the magnetic susceptibility of such a complex system. Therefore, its magnetic properties was preliminarily investigated. On the basis of the crystal structure, the magnetic interactions of Gd...Gd through the oxalate bridge are supposed to be much weaker than that of $Cu \cdots Gd$ through the oxamido bridge. So the magnetic analysis was carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian $\hat{H} = -2J\hat{S}_{Cu}\hat{S}_{Gd}$. The expression of the magnetic susceptibility for a Cu(II)-Gd(III) binuclear unit is

$$\chi_{M} = \frac{4Ng^{2}\beta^{2}}{KT} \left[\frac{7\exp(-8J/KT) + 15}{7\exp(-8J/KT) + 9} \right]$$

and further using molecular field approximation (zj') to deal with magnetic exchange interactions between binuclear units

$$\chi'_M = \frac{\chi_M}{1 - (2zJ'/Ng^2\beta^2)\chi_M}$$

The least-squares fit to the experimental data was found with $J = 0.79 \text{ cm}^{-1}$, $z_{j'} = -0.027 \text{ cm}^{-1}$, g = 2.01, and the agreement factor defined as $R = \Sigma (\chi_{obsd} - \chi_{calcd})^2 / \Sigma \chi_{obsd}^2$ is 8.62×10^{-6} . The J value suggests a pronounced weak intramolecular ferromagnetic interaction between the copper(II) and gadolinium(III) ions through the oxamido bridges.

4. Conclusion

In conclusion, we succeeded in the synthesis of a novel dissymmetrical oxamido-bridged complex with oxalate co-ligands under hydrothermal reaction conditions. Replacement of the oxalate coligand by potentially bridging ligands (N₃⁻, SCN⁻, Fe(CN)₆³⁻, $Cr(CN)_6^{3-}$) should be an alternative approach in this direction. Such studies are currently underway in our laboratory.

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Appendix A. Supplementary material

CCDC 855555 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.ica.2012.06.043.

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