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Luminescent hybrid lanthanide sulfates and lanthanide sulfonate-carboxylates with 1,10-phenanthroline involving *in-situ* oxidation of 2-mercaptobenzoic acid

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ABSTRACT

A series of lanthanide sulfates and lanthanide sulfonate-carboxylates, $[Ln_2(phen)_2(SO_4)_3(H_2O)_2]_n$ (**I**; $Ln = Nd$ (**1a**), Sm (**1b**), Eu (**1c**), $phen = 1,10$ -phenanthroline) and $[Ln(phen)(2-SBA)(BZA)]_n$ (**II**; $Ln = Sm$ (**2a**), Eu (**2b**), Dy (**2c**), $2-SBA = 2$ -sulfobenzoate, $BZA = benzoate$) have been hydrothermally synthesized from lanthanide oxide, 2-mercaptobenzoic acid with $phen$ as auxiliary ligand and characterized by single-crystal X-ray diffraction, elemental analyses, IR spectra, TG analyses and luminescence spectroscopy. Interestingly, SO_4^{2-} anions in **I** came from the *in situ* deep oxidation of thiol groups of 2-mercaptobenzoic acid while 2-sulfobenzoate and benzoate ligands in **II** from the middle oxidation and desulfuration reactions of 2-mercaptobenzoic acid. Compounds **I** are organic-inorganic hybrid lanthanide sulfates, which have rare one-dimensional column-like structures. Complexes **II** are binuclear lanthanide sulfonate-carboxylates with 2-sulfobenzoate and benzoate as bridges and 1,10-phenanthroline as terminal. Photoluminescence studies reveal that complexes **I** and **II** exhibit strong lanthanide characteristic emission bands in the solid state at room temperature.

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1. Introduction

In recent years, some *in situ* ligands or metal reactions, including hydroxylation of aromatic rings [1], alkylation [2], acylation [3], substitution [4], cycloaddition [5], decarboxylation [6], carbon-carbon bond formation [7], transformation of inorganic and organic sulfur [2,8], have attracted increasing interest for sake of obtaining the new chemistry reactions, as well as generation of novel coordination polymers [9]. As we know, *in situ* ligand may contain three benefits: Firstly, *in situ* ligand synthesis produces the possibility of novel ligand and simultaneous metal coordination. Secondly, in some cases, *in situ* ligand synthesis can be used as a simple and friendly synthesis route. Thirdly, *in situ* ligand synthesis has been used to gain ligands that are hard to obtain through assembly synthetic routes [10]. It is hard to access the ligands *in situ* reaction by conventional methods. Solvothermal (containing hydrothermal) method can be a good choice, up to now, solvothermal-microwave as well as ultrasound method have been observed *in situ* reactions [11].

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In situ ligand formation has largely been a serendipitous process. It depends on the condition of chemistry reaction, such as pH, catalysts, time and temperature. Disulfide bond formation has been usually observed in thioate systems under hydrothermal or solvothermal conditions [12,13], such as 2-mercaptobenzoic acid or others. It well known that the oxidation by oxygen catalyzed by metal ions of thiols produces several compounds including sulfenates, sulfinates and sulfonates in basic solutions [14,15]. However, *in situ* oxidation and desulfuration reactions of 2-mercaptobenzoic acid to produce sulfonate-metal complexes or metal sulfate are scarcely found under hydrothermal or solvothermal conditions.

The synthesis and characterization of novel hybrid organic-inorganic materials have been attracted great of current interest owing to their fascinating structural diversity and potential applications in many fields such as catalysis, material science, optoelectronic- and magnetic-chemistry [16]. The organic-inorganic hybrids by incorporating $phen$ ligand in the structure of lanthanide sulfates [17] or sulfobenzoates [18] are rare. Sulfobenzoate is a good ligand for the preparation of metal-organic complexes owing to its rigidity and more donor O atoms. Some transition metal complexes with 2-sulfobenzoate (2-SBA), 3-sulfobenzoate (3-SBA) and 4-sulfobenzoate (4-SBA) have been investigated [19], and lanthanide complexes with sulfobenzoate were relatively less reported. Herein, we report two series of organic-inorganic lanthanide complexes with $phen$ as

auxiliary ligand: $[Ln_2(phen)_2(SO_4)_3(H_2O)_2]_n$ (**I**: $Ln=Nd$ (**1a**), Sm (**1b**), Eu (**1c**)) and $[Ln(phen)(2-SBA)(BZA)]_n$ (**II**: $Ln=Sm$ (**2a**), Eu (**2b**), Dy (**2c**)), involving *in situ* oxidation and desulfuration reactions of 2-mercaptobenzoic acid. Complexes **I** and **II** both contain 2D supermolecular structure by the π - π stacking interactions between the aromatic rings. In **I**, the SO_4^{2-} anions came from the deep oxidation of 2-mercaptobenzoic acid under the hydrothermal conditions, which is first reported. Interestingly, in **II**, the middle oxidation and desulfuration reactions of 2-mercaptobenzoic acid simultaneously occurred, resulting in the formation of 2-sulfobenzoate and benzoate ligands. The thermal stability and application properties as the potential fluorescent material of two lanthanide organic-inorganic materials have also been studied by the thermogravimetric analysis (TGA) and fluorescent properties.

2. Experimental

2.1. Reagents and general techniques

All chemicals were of AR grade commercially available and used without further purification. The elemental analyses for C, H, N and O were performed with an Elementar Vario EL III elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR Fourier transform spectrometer with pressed KBr pellets in the

range of 400–4000 cm^{-1} . Powder X-ray diffraction (PXRD) patterns were acquired on D/MXA-2500 diffractometer measurements using Mo-K α radiation in the ambient environment. Thermo-gravimetric analyses were recorded in Perkin-Elmer TGA 7 thermal analyzer at a heating rate of 10 $^\circ C/min$. The steady fluorescence spectra with solid sample of complexes series **I** and **II** were obtained on Edinburgh-Instrument spectra-Fluorimeter.

2.2. Synthesis of $[Ln_2(phen)_2(SO_4)_3(H_2O)_2]_n$ (**I**, $Ln=Nd$ (**1a**), Sm (**1b**) and Eu (**1c**))

A mixture of 2-mercaptobenzoic acid (0.1233 g, 0.8 mmol), 1,10-phenanthroline (0.1585 g, 0.8 mmol), $Bi(NO_3)_3 \cdot 5H_2O$ (0.0970 g, 0.2 mmol), 0.2 mmol of Ln_2O_3 (0.0672 g Nd_2O_3 (**1a**), 0.0697 g Sm_2O_3 (**1b**) and 0.0703 g Eu_2O_3 (**1c**)) and 10 ml H_2O was stirred for 30 min and the pH was adjusted to 3.3 with HNO_3 , then sealed in a 23 ml Teflon-lined autoclave. The mixture was heated to 160 $^\circ C$ for 3 days. Accordingly columnar crystals were isolated by filtering, washed with distilled water and dried in air. Yield: 40% (**1a**), 35% (**1b**) and 36% (**1c**) (based on Ln_2O_3). Calc for $C_{24}H_{20}N_4O_{14}S_3Nd_2$ (**1a**): C, 29.62; H, 2.03; N, 5.67; O, 23.08 wt%; Found: C, 29.59; H, 2.05; N, 5.75; O, 23.02 wt%. Anal. Calc for $C_{24}H_{20}N_4O_{14}S_3Sm_2$ (**1b**): C, 29.25; H, 2.04; N, 5.65; O, 22.78 wt%; Found: C, 29.23; H, 2.03; N, 5.68; O, 22.74 wt%. Anal. Calc for $C_{24}H_{20}N_4O_{14}S_3Eu_2$ (**1c**): C, 29.16; H, 2.03; N, 5.69; O, 22.71 wt%;

Table 1

Crystal data and structure refinement for **1** and **2**.

Compound	1a	1b	
Empirical formula	$C_{24}H_{20}N_4O_{14}S_3Nd_2$	$C_{24}H_{20}N_4O_{14}S_3Sm_2$	
Formula weight	973.10	985.32	
Crystal system	Triclinic	Triclinic	
Space group	<i>P</i> -1	<i>P</i> -1	
<i>a</i> (Å)	10.228(6)	10.195(9)	
<i>b</i> (Å)	12.302(5)	12.316(11)	
<i>c</i> (Å)	12.516(6)	12.552(10)	
α (deg)	72.360(17)	71.920(3)	
β (deg)	75.740(14)	75.750(4)	
γ (deg)	83.322(17)	83.600(5)	
<i>V</i> (Å ³)	1453.1(12)	1451(2)	
<i>D_c</i> (g/cm ³)	2.224	2.255	
<i>Z</i>	2	2	
<i>F</i> (000)	944	952	
μ (mm ⁻¹)	3.892	4.303	
Reflns collected/unique	14,160/6466	12,101/6326	
<i>R</i> _{int}	0.0225	0.0513	
GOOF on <i>F</i> ²	1.029	1.067	
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0238, 0.0781	0.0476, 0.1313	
Compound	2a	2b	2c
Empirical formula	$C_{26}H_{17}N_2O_7SSm$	$C_{26}H_{17}N_2O_7SEu$	$C_{26}H_{17}N_2O_7SDy$
Formula weight	651.85	653.45	663.99
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	10.511(6)	10.506(5)	10.472(5)
<i>b</i> (Å)	10.774(6)	10.763(7)	10.737(7)
<i>c</i> (Å)	11.548(8)	11.545(6)	11.509(4)
α (deg)	82.098(2)	82.032(2)	82.26(2)
β (deg)	78.140(2)	78.125(2)	78.11(2)
γ (deg)	70.975(2)	71.00(2)	70.85(2)
<i>V</i> (Å ³)	1206.4(13)	1204.4(12)	1193.1(10)
<i>D_c</i> (g/cm ³)	1.794	1.802	1.848
<i>Z</i>	2	2	2
<i>F</i> (000)	642	644	650
μ (mm ⁻¹)	2.571	2.741	3.270
Reflns collected/unique	11,854/5449	11,882/5448	11,698/5390
<i>R</i> _{int}	0.0260	0.0205	0.0198
GOOF on <i>F</i> ²	1.008	0.996	1.003
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0257, 0.0650	0.0208, 0.0607	0.0221, 0.0765

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

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

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