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Syntheses, characterization, and luminescence of two lanthanide complexes $[Ln_2(acetate)_6(H_2O)_4]\cdot 4H_2O$ (Ln=Tb(1), Sm(2))

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Abstract: Two dinuclear compounds $[Ln_2(acetate)_6(H_2O)_4]\cdot 4H_2O$ (Ln=Tb(1), Sm(2)) were obtained by the hydrothermal reaction of Ln_2O_3 with malonic acid at 150 °C. Both compounds were characterized by elemental analyses, infrared spectra, and single crystal X-ray diffraction. The results showed that complexes **1** and **2** were isomorphous and crystallize in triclinic space group $P\bar{1}$. The coordination geometry around Ln(III) ions in the complexes **1** and **2** was a distorted tricapped trigonal prism with a nine coordination. In the crystal, the molecular organization was further stabilized by well-defined weak hydrogen bonding interactions between the neutral dinuclear molecular units that led to the formation of a three-dimensional network. The fluorescence properties of the two complexes **1** and **2** in organic solvents were also studied. The results show that the ligand acetate favored energy transfer to the emitting energy level of Tb(III) in complex **1**. Some factors that influence the fluorescent intensity were also discussed in the article.

Keywords: rare earth dinuclear complexes; X-ray crystal structure; malonic acid; fluorescence; rare earths

In recent years, increasing attention has been paid to the design and synthesis of lanthanide-based carboxylate complexes due to their unusual coordination characteristics, exceptional optical and magnetic properties[1–3], and precursors for oxides[4]. Compared to transition metals, lanthanides have much higher coordination numbers and more flexible coordination geometry, which makes it difficult to control the preparation of lanthanide complexes but are helpful in the formation of unusual multidimensional architectures[5]. The reported carboxylate complexes based on lanthanides show beautiful and interesting topological structures, such as 1D chains[6], 2D grids[7], 3D porous structures, and interpenetrating networks[8]. However, for lanthanide compounds, it is well-known that they exhibit excellent photophysical properties that can contribute to f-f transitions with an extremely narrow bandwidth[9]. Therefore, studies of the new complexes of lanthanides with carboxylic acid are important both inherently and in their applications, such as catalysis, adsorption, magnetic materials, separation sensors, and luminescent sensors[10].

Extensive study on the oxalate compounds of rare earth elements has been carried out by many researchers in view of their important applications. However, not much work has been done on rare earth malonates. Malonic acid is the next higher homologue of oxalic acid, but with a fairly active methylene group between the two carboxylate groups. Although the malonate ion is a simple dicarboxylate ligand, it exhibits a rather flexible stereochemistry and variable modes of binding with metal ions in the crystalline state[11].

The authors, previously, have made a systematic study of rare earth complexes with phenoxy acetic acids at low pH values[12]. The studies showed that below pH 5.0, phenoxy acetic acids commonly yield chain-like compounds with lanthanide ions. When the pH value is increased to close to 7.0, the ligands may be partially or completely deprotonated. It is possible for the carboxylate oxygen atoms to participate in coordination simultaneously, yielding a discrete lanthanide cluster[13]. Taking into account the intriguing luminescent properties of Sm^{3+} and Tb^{3+}, and as a continuation and expansion of the related studies of phenoxy acetic acids series, malonic acid assembled with Ln_2O_3 under hydrothermal conditions was used and two dinuclear lanthanides $[Ln_2(acetate)_6(H_2O)_4]\cdot 4H_2O$ (Ln=Tb(**1**), Sm(**2**)) was obtained containing acetate resulting from partial decomposition of malonic acid. Herein, the synthesis, characterizations, and luminescent properties of $[Ln_2(acetate)_6(H_2O)_4]\cdot 4H_2O$

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(Ln=Tb(**1**), Sm(**2**)) was reported.

1 Experimental

1.1 Synthesis of the complexes

1.1.1 $[Tb_2(CH_3COO)_6(H_2O)_4]\cdot 4H_2O$ (**1**) For the synthesis of the complex 0.16 g (1.5 mmol) of $CH_2(COOH)_2$ and 4,4'-bipyridyl (0.214 g, 0.5 mmol) were mixed with ethanol (0.5 ml), and water (5 ml). To this mixed solution was added a suspension of 0.40 g (0.5 mmol) Tb_4O_7 in 2 ml of water. Then, the mixture was placed in a Teflon-lined stainless vessel (15 ml), and the vessel was sealed and heated to 150 ℃ for 96 h. After cooling to room temperature, the resulting solution was filtered off. The filtrate was left in air to evaporate the solvent and colorless crystals were obtained after 4 d. The yield was 78%. Elemental analysis calcd. for $C_{12}H_{34}O_{20}Tb_2$ (%): C 17.64, H 4.17, Tb 38.94; found: C 17.70, H 4.29, Tb 38.88. IR (KBr pellet): $\bar{\nu}$=3426.0 (br, s), 3224.0 (s), 1625.1 (vs), 1576.0 (vs), 1430.2 (m), 1379.2 (vs), 1322.4 (m), 1115.5 (m), 1030.2 (m), 947 (m), 728.3 (m), and 540.1 (m) cm^{-1}.

1.1.2 $[Sm_2(CH_3COO)_6(H_2O)_4]\cdot 4H_2O$ (2) A similar procedure was followed to prepare **2** except that Tb_4O_7 was replaced with Sm_2O_3. The yield was 69%. Elemental analysis calcd. for $C_{12}H_{34}O_{20}Sm_2$ (%): C 18.02, H 4.25, Sm 37.63; found: C 17.91, H 4.29, Sm 37.57. IR (KBr pellet): $\bar{n}$=3417 (br, vs), 3094 (s), 1621 (vs), 1585 (vs), 1434 (s), 1385 (vs), 1280 (s), 1185 (m), 1084 (m), 771 (m), 732 (m), 689 (s), 593 (m) 443 (m) cm^{-1}.

1.2 Instrument

All materials were of reagent grade obtained from commercial sources and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. The metal analysis was performed on an ICP AES Liberty Series II Varian apparatus. IR spectra in the 4000–400 cm^{-1} range were measured on a Thermo Nicolet 320 FT-IR spectrometer with KBr discs. The luminescent spectra for the N, N'-dimethylformamide (DMF) solution were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5.0 nm. Thermogravimetric analyses (TGA) were done at the Testing Center Laboratory of South China Normal University. TGA experiments were carried out on a Shimadzu TGA 150 instrument at a heating rate of 15 °C/min.

1.3 Crystallography

The structures of two dinuclear complexes $[Ln_2(acetic)_6(H_2O)_4]\cdot 4H_2O$ (Ln=Tb(**1**), Sm(**2**)) were determined by single crystal X-ray diffraction. Suitable single crystals were mounted on a glass fiber and the intensity data were collected on a Bruker SMART APEX II CCD diffractometer at 298 K using graphite monochromated Mo Ka radiation (λ=0.071073 nm). Absorption corrections were performed using the SADABS program[14]. The structures were determined by direct methods and refined by full-matrix least-squares against F^2 of data using SHELXTL software[15]. Anisotropic displacement parameters were assigned to all of the nonhydrogen atoms, the water H atoms were located in a different Fourier map, and the other hydrogen atoms were included in the calculations isotropically, but not refined. A summary of parameters for the data collection and refinements are given in Table 1.

CCDC reference numbers for **1** and **2** are CCDC 658052 and 658053, respectively.

2 Results and discussion

2.1 Synthesis and spectroscopic characterization of complexes 1 and 2

In the process of the assembly of the complexes **1** and **2**, partial decarboxylation of malonic acid takes place in aqueous solution. The reaction between lanthanide oxide and

Table 1 Crystallographic data for complexes 1-2

Complex	**1**	**2**
Empirical formula	$C_{12}H_{34}O_{20}Tb_2$	$C_{12}H_{34}O_{20}Sm_2$
Formula weight	816.23	799.09
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/nm	0.89374(4)	0.89662(4)
b/nm	0.93241(4)	0.93396(4)
c/nm	1.05281(4)	1.05269(5)
a /(°)	91.707(2)	91.666(2)
b /(°)	114.001(2)	113.969(2)
g /(°)	118.115(2)	118.338(2)
V/nm^3	0.67968(5)	0.68146(5)
Z	1	1
T/K	298	298
m /(mm^{-1})	5.239	4.345
D_{calcd}/(g/cm^3)	1.994	1.947
l/nm	0.071073	0.071073
R_{int}	0.0231	0.0475
Goodness-of-fit	1.088	1.063
R^a/wR^b	0.0191/0.0497	0.0363/0.0957

$^aR=\Sigma||F_o|-|F_c||/S|F_o|$; $^bwR=[\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

$w=1/[s^2(F_o^2)+(0.0661P)^2+0.3525P]$ for **1**. $w=1/[s^2(F_o^2)+(0.0293P)^2+0.2750P]$ **2**. $P=(F_o^2+2F_c^2)/3$