

Crystal structures and fluorescence properties of lanthanide complexes prepared with 2,2'-biphenyldicarboxylic acid and 2,2':6',2''-terpyridine

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Received 4 March 2013; revised 7 April 2013

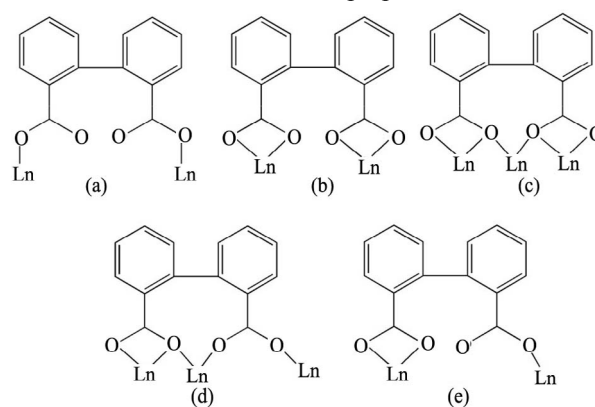
Abstract: Five lanthanide complexes of $\text{Ln}_2(\text{dpdc})_2(\text{tpy})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ [$\text{Ln}=\text{La}$ (1), Ce (2), Pr (3), Sm (4), Gd (5), $\text{H}_2\text{dpdc}=\text{2,2'}$ -biphenyldicarboxylic acid and $\text{tpy}=\text{2,2':6',2''}$ -terpyridine)] were prepared at room temperature and characterized by X-ray diffraction, FT-IR and thermo-gravimetric analysis. The results showed that complexes 1–5 were isostructural and consisted of dinuclear units [$\text{Ln}_2(\text{dpdc})_2(\text{tpy})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$] bridged by two dpdc^{2-} ligands. The dinuclear units with strong intramolecular hydrogen bonds were assembled into 2D supramolecular layers by the weak $\pi \cdots \pi$ stacking interactions between pyridine rings of tpy. The TG analysis showed that the complexes 1–5 behaved higher thermal stability with no mass loss at < 320 °C. The lanthanide contraction effect and the solid state luminescence properties of complexes 1–5 were also investigated. The luminescence emission spectra of complexes 1–5 exhibited ligands emission bands and complex 3 and 4 had no typical emission in the visible region.

Keywords: lanthanide complexes; crystal structure; luminescence property; preparation; rare earths

Recently, lanthanide complexes have attracted attention because of their superior functional properties and potential applications in catalysis, magnetism, optoelectronic devices, medicine, separation, ions recognition, etc.^[1–6]. Especially, lanthanide elements have a special configuration 4f electrons and variable coordination environments, so that the lanthanide complexes have applications in optical field^[7–9]. Based on the sharp f-f transitions and high quantum yields, it is often thought that lanthanide compounds are the most important components in pursuit of new luminescence materials^[10–12]. However, it is still a great challenge to synthesize expected lanthanide complexes because of a lot of changing factors. Among these factors, the selection of suitable ligands is very important. It is well known, lanthanide ions have high affinity with hard bases such as oxygen or nitrogen atoms, so aromatic multicarboxylic acid such as benzene-1,3,5-tricarboxylic acid^[13], benzene-1,2,4,5-tetracarboxylic acid^[14], mellitic acid^[15], etc., and nitrogen containing heterocyclic ligands such as 1,10-phenanthroline^[16], 2,4,6-tris-2-pyridyl-1,3,5-triazine^[17], etc., are often chosen to construct lanthanide complexes. In these ligands, 2,2'-biphenyldicarboxylic acid as an aromatic dicarboxylic acid, its deprotonated anions dpdc^{2-} can offer flexible, multidentate coordination sites, and therefore may potentially provide various coordination modes (Scheme 1) to form various lanthanide complexes under

appropriate synthesis conditions^[18,19]. The nitrogen containing heterocyclic ligand of 2,2':6',2''-terpyridine (tpy) has been studied on their potential use as extractants of lanthanide elements in the reprocessing of nuclear waste^[20], and as “antenna” ligand to harvest the absorption of photon energy and to enhance the efficiency of emission^[21].

In this work, we focused on the synthesis of five lanthanide complexes with dpdc^{2-} and tpy ligands, that is $\text{Ln}_2(\text{dpdc})_2(\text{tpy})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ [$\text{Ln}=\text{La}$ (1), Ce (2), Pr (3), Sm (4), Gd (5), $\text{H}_2\text{dpdc}=\text{2,2'}$ -biphenyldicarboxylic acid and $\text{tpy}=\text{2,2':6',2''}$ -terpyridine], and an investigation of their structures and fluorescence properties.



Scheme 1 Coordination modes of dpdc^{2-} in lanthanide complexes

Foundation item: Project supported by National Basic Research Program of China (2010CB732300) and Foundation of Zhejiang Province Education Commission of China (Y201224213)

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DOI: 10.1016/S1002-0721(12)60334-2

1 Experimental

1.1 Synthesis of lanthanide complexes

All chemicals of reagent grade were commercially available (Aladdin) and used without further purification. The lanthanide complexes of $\text{Ln}_2(\text{dpdc})_2(\text{tpy})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ [$\text{Ln}=\text{La}$ (**1**), Ce (**2**), Pr (**3**), Sm (**4**), Gd (**5**)] were prepared similarly by using different $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ raw materials. The synthesis of complex **1** is described as follows. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.0433 g, 0.100 mmol) in ethanol (2 mL) and 2,2'-biphenyldicarboxylic acid (0.0448 g, 0.1 mmol) in ethanol (3 mL) were mixed and heated to 60 °C under stirring. Then the hot solution (60 °C) of 2,2':6',2''-terpyridine (0.0236 g, 0.1 mmol) in 15 mL ethanol was added into the above synthesis solution. After heating and stirring, a clear solution was obtained and cooled naturally to room temperature. After being stood about 15 d, the crystals of the complex **1** were formed.

Colorless crystals for **1**, yield: 28% based on $\text{La}(\text{III})$. IR (KBr pellet, cm^{-1}): 3440s, 1598s, 1446s, 1446m, 1386s, 1290m, 1010w, 771s, 651w.

Colorless crystals for **2**, yield: 30% based on $\text{Ce}(\text{III})$. IR (KBr pellet, cm^{-1}): 3413m, 1614s, 1533s, 1482w, 1448s, 1412s, 1367s, 1158w, 1017m, 861m, 764s, 718m, 688w.

Pale green crystals for **3**, yield: 45% based on $\text{Pr}(\text{III})$. IR (KBr pellet, cm^{-1}): 3444m, 1679s, 1596s, 1450w, 1396s, 1355w, 1297m, 1135w, 925w, 757s, 701w.

Pale yellow crystals for **4**, yield: 23% based on $\text{Sm}(\text{III})$. IR (KBr pellet, cm^{-1}): 3448m, 1685s, 1579m, 1446m, 1413s, 1294s, 1133w, 921m, 755s, 701m, 665w.

Pale yellow crystals for **5**, yield: 14% based on $\text{Gd}(\text{III})$.

IR (KBr pellet, cm^{-1}): 3405w, 1600s, 1579s, 1448m, 1384s, 1299m, 1164m, 1010w, 865w, 773s, 651w.

1.2 Structure characterization of complexes

The single crystal X-ray diffraction analyses for the crystals of complexes **1–5** were performed at 298(2) K on a RIGAKU RAXIS-RAPID diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071073$ nm). All calculations were carried out with SHELXTL-97 programs^[22,23]. The structure parameters were refined by full matrix least-square method with anisotropic displacement atomic parameters for non-hydrogen atoms. All the other H atoms were generated geometrically and treated as riding. The crystal data, collection and refinement of complexes **1–5** are summarized in Table 1.

The FT-IR spectra of samples were recorded on a Shimadzu FTIR-8900 spectrometer, and the sample to be measured was ground with KBr and pressed into thin wafer. Thermo-gravimetric analysis (TG) of sample was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer under nitrogen at a heating rate of 10 °C/min from room temperature to 800 °C. Solid-state power luminescence spectra of samples were recorded on an F-4600 Hitachi fluorescence spectrofluorimeter.

2 Results and discussion

As is well-known, the single crystals of coordination polymers $[\text{Ln}_2(\text{dpdc})_3(\text{tpy})_2 \cdot \text{H}_2\text{O}]_n$ ($\text{Ln}=\text{Nd}$ and Yb) and the coordination complexes $[\text{Er}_2(\text{dpdc})_2(\text{Hdpdc})(\text{tpy})_2]$ can be prepared in de-ionized water (pH=8), at 170 °C for 3 d with the cooling of 10 °C/h^[24]. Herein, we focused on the preparation of lanthanide complexes of

Table 1 Crystal data and structure refinements for complexes **1–5**^a

Compounds	1	2	3	4	5
Formula	$\text{C}_{29}\text{H}_{21}\text{LaN}_4\text{O}_8$	$\text{C}_{29}\text{H}_{21}\text{CeN}_4\text{O}_8$	$\text{C}_{29}\text{H}_{21}\text{PrN}_4\text{O}_8$	$\text{C}_{29}\text{H}_{21}\text{SmN}_4\text{O}_8$	$\text{C}_{29}\text{H}_{21}\text{GdN}_4\text{O}_8$
Formula mass	692.41	693.62	694.41	703.85	710.75
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$
a/nm	2.4888(5)	2.4933(5)	2.5024(5)	2.4996(5)	2.5048(5)
b/nm	1.9870(4)	1.9760(4)	1.9736(4)	1.9710(4)	1.9643(4)
c/nm	1.1723(2)	1.1662(2)	1.1675(2)	1.1650(2)	1.1642(2)
$\alpha/^\circ$	90	90	90	90	90
$\beta/^\circ$	111.65(3)	111.79(3)	111.95(3)	111.86(3)	112.04(3)
$\gamma/^\circ$	90	90	90	90	90
Volume/ nm^3	5.389(2)	5.335(2)	5.348(2)	5.327(2)	5.310(2)
Z	8	8	8	8	8
$D_{\text{calcd}}/(\text{g}/\text{cm}^3)$	1.707	1.727	1.725	1.755	1.778
μ/mm^{-1}	1.646	1.767	1.883	2.266	2.559
$F(000)$	2752	2760	2768	2792	2808
$\theta/^\circ$	3.01–27.45	3.22–27.43	2.03–27.56	1.76–27.46	2.05–27.52
$R_1, wR_2 [I > 2\sigma(I)]$	0.0407, 0.0895	0.0365, 0.0813	0.0455, 0.1292	0.0511, 0.1284	0.0492, 0.1326
R_1, wR_2 (all data)	0.0676, 0.1227	0.0471, 0.0848	0.0520, 0.1369	0.0823, 0.1726	0.0640, 0.1598
GOF	1.064	1.076	1.058	1.139	1.100

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

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