

A series of 3D lanthanide complexes based on H bond and halogen-halogen interactions: Synthesis, structure, spectroscopic and thermal properties

WU Junchen (吴俊辰)^{1,2}, LI Hua (李华)³, REN Ning (任宁)^{4*}, ZHANG Jianjun (张建军)^{1,2*}, WANG Shuping (王淑萍)²

(1. Testing and Analysis Center, Hebei Normal University, Shijiazhuang 050024, China; 2. College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, China; 3. Shijiazhuang College, Shijiazhuang 050035, China; 4. College of Chemical Engineering and Material, Handan University, Handan 056005, China)

Received 31 March 2016; revised 31 May 2016

Abstract: Four lanthanide coordination complexes, namely, $[\text{Ln}(2,3\text{-DCIBA})_3(5,5'\text{-dmebipy})(\text{H}_2\text{O})_2]$ ($\text{Ln}=\text{Sm}(1), \text{Eu}(2), \text{Dy}(3), \text{Ho}(4)$); 2,3-DCIBA=2,3-dichlorobenzoate; 5,5'-dmebipy=5,5'-dimethylbipyridine) were synthesized and characterized by elemental analysis, infrared spectroscopy and single crystal X-ray diffraction. Findings indicated that complex 3 was a dinuclear molecule, and the center Dy^{3+} was eight-coordinated. Each dinuclear units could be connected by H bond and halogen-halogen interactions. Luminescent property of complex 2 suggested the typical intense emissions of Eu^{3+} ions. Thermal analysis showed that the complexes decomposed in three steps: the coordination water was lost firstly then the neutral ligand 5,5'-dmebipy was lost and lastly the 2,3-DCIBA ligand was lost.

Keywords: lanthanide complexes; crystal structure; supramolecular; H bond; halogen-halogen interactions; luminescent property; TG/DSC; rare earths

Lanthanide organic coordination complexes have provoked great interest for their fascinating architectures^[1–5] and potential applications^[6–11] as functional materials. Many lanthanide organic coordination complexes have been synthesized^[12–14]. Particularly, the intriguing luminescent properties resulting from 4f electrons illustrate that the lanthanide complexes are remarkably candidates for the development of optical devices^[15–17]. However, low absorptivity and emission intensity were caused by the selection rules^[18]. The problem can be solved by the coordination of organic ligand that transfers energy to the lanthanide ions^[19,20].

From this point of view, our team often choose halogenated aromatic carboxylic acids as the first ligand for the following reasons: (1) delocalized π -electron system can sensitize the lanthanide ions; (2) the oxygen atoms from carboxylic groups of the ligand have high affinity for the Ln^{3+} ions^[21]; (3) there may be weak halogen-halogen interactions between adjacent ligand by which the supramolecule can be constructed. Carter et al. and Kastan et al. synthesized a series of novel lanthanide complexes with p-chlorobenzoic acid in recent years^[22,23]. Metal-organic frameworks have been beneath the attention of many researchers^[24,25], the design and synthesis of the supramolecule are very important.

Therefore, following our ongoing efforts towards lanthanide complexes^[26–28], in this work, four complexes

were synthesized with 2,3-DCIBA being as the first ligand, 5,5'-dmebipy being as the coligand. The thermal decomposition mechanisms of the complexes were studied using TG/DSC technology. The luminescent property of complex 2 was also discussed.

1 Experimental

1.1 Materials and physical techniques

All reagents and solvents employed were commercially available and used without further purification. Analyses for C, H and N were carried out on a Vario-ELIII elemental analyzer. IR spectra were measured on a BRUKER TENSOR27 spectrometer in the range of 4000–400 cm^{-1} with KBr medium pellets. Powder X-ray diffraction identification was carried out for the crystalline analyses by a Bruker D8 Advance X-ray diffractometer in a scanning range of 5° – 60° (2θ) with Cu $K\alpha$ radiation ($\lambda=0.15418$ nm). The thermogravimetry (TG), differential thermogravimetric (DTG), differential scanning calorimetric (DSC) analyses of the title complexes were conducted by a TG/DSC system, which was a Netzsch STA 449 F3 instrument under the simulated atmosphere (the gas flow of the nitrogen is 30 mL/min and the oxygen is 15 mL/min). Fluorescence spectra were measured on an F-4600 Hitachi spectrophotometer in the solid state at room temperature.

Foundation item: Project supported by the National Natural Science Foundation of China (21073053, 21473049) and the Natural Science Foundation of Hebei Province, China (B2016205207)

* **Corresponding authors:** ZHANG Jianjun, REN Ning (E-mail: jjzhang6@126.com, ningren9@163.com; Tel.: +86-311-80786457)

DOI: 10.1016/S1002-0721(16)60138-2

1.2 Preparation of [Ln(2,3-DCIBA)₃(5,5'-dmebipy)(H₂O)]₂(Ln=Sm(1),Eu(2),Dy(3),Ho(4))

The ligand of 2,3-dichlorobenzoic acid (2,3-DCIHBA) (6 mmol) and 5,5'-dmebipy (2 mmol) were dissolved in 95% ethanol solution together. The pH of the mixture solution was adjusted to 6–7 by adding 1 mol/L NaOH solution. Then the ligand solution was added to the LnCl₃·6H₂O aqueous solution dropwise and the mixture was stirred for 6 h at room temperature. Then it was deposited for 12 h. The resulting precipitate was filtered off, washed with 95% ethanol and dried. The mother liquors were placed for about two weeks to get crystals which were suitable for X-ray diffraction analysis. Elemental analyses: Calc(%) for **1**: C 42.95, H 2.294, N 3.036, Sm 16.30. Found(%): C 42.52, H 2.581, N 2.945, Sm 16.53. Calc(%) for **2**: C 42.88, H 2.290, N 3.031, Eu 16.44. Found(%): C 42.95, H 2.528, N 2.992, Eu 16.46. Calc(%) for **3**: C 42.56, H 2.273, N 3.008, Dy 17.38. Found(%): C 42.65, H 2.618, N 2.794, Dy 17.50. Calc(%) for **4**: C 42.29, H 2.258, N 2.989, Ho 17.60. Found(%): C 42.11, H 2.459, N 2.898, Ho 17.43.

1.3 Crystal structure determination

The data of single crystal X-ray diffraction for **3** were collected on a Smart-1000 diffractometer with graphite-monochromatic Mo K α ($\lambda=0.071073$ nm) at 298(2) K. The structures were solved by SHELXS-97 program (direct methods) and refined by Full-matrix least-squares on F^2 using SHELXL-97 program. The crystallographic and refinement parameters of **3** are shown in Table 1. The selected bond lengths of **3** are listed in Table 2. Selected hydrogen bond lengths (nm) of the complex **3** are listed in Table 3.

2 Results and discussion

2.1 Infrared spectra

The characteristic infrared absorption bands of complexes **1–4** and two ligands are shown in Table 4. The characteristic peaks for carboxylate group of 2,3-DCIHBA ($\nu_{C=O}$) at 1694 cm⁻¹ disappeared in the complexes. Meanwhile there are two new characteristic bands around 1570 cm⁻¹ ($\nu_{as(COO^-)}$) and 1400 cm⁻¹ ($\nu_{s(COO^-)}$) respectively, which indicate that oxygen atoms of the carboxylate groups are coordinated to the Ln³⁺ ions. The occurrence of peaks for $\nu_{(Ln-O)}$ at 422–419 cm⁻¹ also suggests the coordination of oxygen atoms to Ln³⁺ ions. The bands $\nu_{C=N}$ and δ_{C-H} shift to higher wavenumbers in complexes compared to the free ligand 5,5'-dmebipy. It was proved that the nitrogen atoms of the 5,5'-dmebipy were also coordinated to Ln³⁺ ions.

2.2 XRD

Powder XRD spectra of complexes **1–4** were measured

Table 1 Crystal data and structure refinement of the complex **3**

Complex	3
Empirical formula	C ₆₆ H ₄₆ C ₁₁₂ N ₄ O ₁₄ Dy ₂
Formula weight	1869.47
<i>T</i> /K	298(2)
Wavelength/nm	0.071073
Crystal system	Triclinic
space group	<i>P</i> $\bar{1}$
<i>a</i> /nm	1.12960(9)
<i>b</i> /nm	1.13429(11)
<i>c</i> /nm	1.52631(13)
α (°)	94.1500(10)
β (°)	98.9410(10)
γ (°)	111.090(2)
Volume/nm ³	1.7849(3)
Z, calculated density (mg/m ³)	1, 1.739
Absorption coefficient/mm ⁻¹	2.592
<i>F</i> (000)	918
Crystal size/mm	0.13×0.10×0.05
θ range for data collection(°)	2.17 to 25.02
Limiting indices	-12≤ <i>h</i> ≤13, -13≤ <i>k</i> ≤12, -18≤ <i>l</i> ≤16
Reflections collected /unique	9174/6185 [<i>R</i> _{int}]=0.0757]
Completeness to $\theta=25.02^\circ$	98.0%
Max. and min. transmission	0.8813 and 0.7293
Data/restraints/parameters	6185/0/444
Goodness-of-fit on F^2	1.054
Final <i>R</i> indices [<i>I</i> >2 σ (<i>I</i>)]	<i>R</i> ₁ =0.0703, <i>wR</i> ₂ =0.1737
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0979, <i>wR</i> ₂ =0.1902
Largest diff. peak and hole/(10 ³ e/nm ⁻³)	2.688 and -1.550

Table 2 Selected bond lengths (nm) of the complex **3**

Bond	Bond length
Dy(1)–O(4)#1	0.2297(9)
Dy(1)–O(1)	0.2324(7)
Dy(1)–O(2)#1	0.2331(7)
Dy(1)–O(5)	0.2366(7)
Dy(1)–O(3)	0.2399(8)
Dy(1)–O(7)	0.2403(7)
Dy(1)–N(2)	0.2553(9)
Dy(1)–N(1)	0.2624(9)

#1 -x+1, -y+1, -z+1

Table 3 Selected hydrogen bond lengths (nm) of the complex **3**

D–H...A	d(D–H)/nm	d(H...A)/nm	d(D...A)/nm	<DHA/(°)
O7–H7B...O6	0.0850	0.1846	0.2661	159.98
O7–H7C...O6	0.0850	0.2274	0.2810	121.18

Table 4 IR absorption bands for the ligands and complexes (cm⁻¹)

Ligands/complexes	$\nu_{C=N}$	δ_{C-H}	$\nu_{C=O}$	$\nu_{as(COO^-)}$	$\nu_{s(COO^-)}$	$\nu_{(Ln-O)}$
2,3-DCIHBA			1694			
5,5'-dmebipy	1598	828	737			
1	1633	881	773	1573	1401	417
2	1626	885	767	1579	1402	421
3	1619	883	771	1583	1410	421
4	1659	885	771	1573	1410	419

Download English Version:

<https://daneshyari.com/en/article/7698134>

Download Persian Version:

<https://daneshyari.com/article/7698134>

[Daneshyari.com](https://daneshyari.com)