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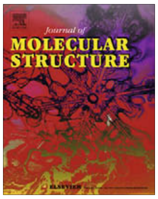

Study of structure and two-dimension correlation infrared spectroscopy on three rare-earth/3-methylbenzoic acid complexes

Lingyan Zhao [a], Yiping Chen [a,*], Hanhui Zhang [a,b], Chaoyu Li [a], Ruiqing Sun [a], Qiyu Yang [a]

[a] Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, PR China
[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

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Three rare-earth complexes with 3-methylbenzoic acid (HL) have been hydrothermally synthesized directly: $Yb(C_8H_7O_2)_3$ **1** and $Ln(C_8H_7O_2)_3{\cdot}(4,4'\text{-bipy})_{0.5}$ (Ln = Eu **2**, Gd **3**) (4,4′-bipy = 4,4′-bipyridine).The crystal structures were determined by single crystal X-ray diffraction with the following data: **1**: monoclinic, $P2_1/n$, $a = 13.574(3)$, $b = 8.0438(2)$, $c = 20.652(4)$ Å, $\beta = 96.14(3)°$; **2**: triclinic, P-1, $a = 8.1788(2)$, $b = 12.952$ (3), $c = 12.968(3)$ Å, $\alpha = 94.400(3)°$, $\beta = 92.260(4)$, $\gamma = 101.360(4)$; the complex **1** is a one-dimensional chain. However, due to the existence of the second ligand-4,4′-bipy, the complexes **2** and **3** are a two-dimensional layer, the Lanthanide contraction makes the difference of the structure between the complexes at the same time. Additionally, in order to explore the structural characteristic, the 2D-IR correlation spectroscopy containing the temperature-induced structural variations and magnetism-induced structural variations is used. Photo-luminescent properties of **1** and **2** are discussed in detail.

1. Introduction

Because of the metal-organic frameworks (MOFs) intriguing topological structure and potential application as functional materials, such as magnetism, zelite-like catalysis activity, gas storage, ion change and optical properties, etc. [1], they always attracts great attentions. Due to the diversity of the coordination modes of carboxylate groups to metal atoms, the carboxylate-containing ligands can come into being many novel structures. The rare-earth ions not only having large radii and high coordination number but also having very stronger luminescence are widely applied in constructing the supra-molecular architectures. The coordination compound of rare-earth ion and carboxylate already have been studied over the past decade, which contains benzoic acid and its derivative ligands, for example: (1) 2-nitrobenzoic acid, 3-nitrobenzoic acid and 4-nitrobenzoic acid [2]; (2) 3-methoxybenzoic acid and 2,3-dimethoxybenzoic acid [3]; (3) amino-benzoic acid [4]; (4) hydroxyl-benzoic acid [5] and other intricate compounds [6–10]. However, these compounds are merely the coordination mode of the rare-earth ions and the carboxylate group, and mainly the oxygen atom of the carboxylate group is coordinated with the rare-earth ion.

Now the key question is how to make the structure novel and innovative, which requires that the second ligand joins into the coordination compounds. The second ligand will make the structure very rich and colorful. The second ligand can change the zero-dimension into one-dimension or one-dimension chain into two-dimension layered structure by the second ligand functioning as the bridge. In addition, the important property of the rare-earth ions is lanthanide contraction, which affects the coordination-mode of the rare-earth ion. The effect of the lanthanide contraction on the structure of the rare-earth compounds has been reported [11–17] that three different structures, namely two-dimensional single layer, two-dimensional double layer and three-dimensional array are obtained by the coordination of 3,5-pyrazoldicarboxylic acid and lanthanide (Ln = La, Ce, Eu, Er and Lu). The crystal structures of these complexes indicate that their dimensional diversity is controlled by lanthanide contraction [18].

In order to further investigate the structure characteristics of the rare-earth complexes with 3-methylbenzoic acid (HL) and gain better knowledge on the different factors that may influence the structure of the rare-earth complexes, we have synthesized $Yb(C_8H_7O_2)_3$ **1** and $Ln(C_8H_7O_2)_3{\cdot}(4,4'\text{-bipy})_{0.5}$ (Ln = Eu **2**, Gd **3**) (4,4′-bipy = 4,4′-bipyridine). Due to the entry of the second ligand-4,4′-bipy in **2** and **3**, their structures are obviously different from **1**, The aim is that whether the second ligand-4,4′-bipy coordinates with the rare-earth ions, which decides the structure of the rare-earth complexes. The influence of the second ligand-4, 4′-bipy and lanthanide contraction on the structure of three rare-earth complexes have been studied. Due to **2** and **3** are iso-structural, **2** was only researched.

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[*] Corresponding author. Tel.: +86 591 22866340.
E-mail address: ypchen007@gmail.com (Y. Chen).

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Table 1
Crystal data and structure refinement for **1**, **2** and **3**.

	1	**2**	**3**
Formula	$C_{24}H_{21}O_6Yb$	$C_{29}H_{21}EuNO_6$	$C_{29}H_{25}GdNO_6$
Formula mass	578.45	631.43	640.75
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	*P*-1	*P*-1
a (Å)	13.574(3)	8.1788(17)	8.1704(16)
b (Å)	8.0438(16)	12.952(3)	12.919(3)
c (Å)	20.652(4)	12.968(3)	12.957(3)
α (°)	90	94.400(3)	94.33(3)
β (°)	96.14(3)	92.260(4)	92.60(3)
γ (°)	90	101.360(4)	100.98(3)
V (Å^3)	2242.0(8)	1340.7(5)	1336.3(5)
Z	4	2	2
F (000)	1132	626	636
Crystal size (mm)	0.25 × 0.12 × 0.07	0.23 × 0.14 × 0.06	0.33 × 0.18 × 0.16
θ range (°)	3.02–27.47	3.07–27.51	3.08–27.51
GooF	1.007	1.000	1.099
Observed reflections ($I > 2\sigma(I)$)	4148	5619	5730
Final *R* factors ($I > 2\sigma(I)$)	$R_1 = 0.0370$	$R_1 = 0.0481$	$R_1 = 0.0294$
	$wR_2 = 0.1040$	$wR_2 = 0.0665$	$wR_2 = 0.0856$
Final *R* factors (all data)	$R_1 = 0.0519$	$R_1 = 0.0508$	$R_1 = 0.0306$
	$wR_2 = 0.0931$	$wR_2 = 0.1056$	$wR_2 = 0.0673$
Independent reflections (R_{int})	5131(0.0601)	5886 (0.0285)	5875 (0.0253)
Largest diff. map peak and hole e Å^{-3}	0.914 and −0.894	1.286 and −0.815	1.009 and −0.973

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

2. Experimental

2.1. General procedures

All chemicals purchased were of reagent grade or better and were used without further purification. The IR spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR Fourier transform spectrometer with pressed KBr pellets in the range 400–4000 cm^{-1}. The temperature variation was controlled by a Portable programmable temperature controller (Model 50–886, Love Control Corporation) during the process of increasing temperature from 323 to 393 K at intervals of 10 K. The magnetism variation was made by ourselves and its rang is 0–50 mT. 2D-IR correlation spectra were obtained by treatment of the series of dynamic spectra with 2D-COS IR correlation analysis software provided by Tsinghua University. The luminescence spectra were reported on an Edinburgh-Instrument spectra-Fluorimeter (solid).

2.2. Synthesis of [Yb ($C_8H_7O_2$)$_3$] **1**

Compound **1** was prepared by hydrothermal reaction. A mixture of $(CH_3COO)_3Yb \cdot 4H_2O$ (0.25 mmol, 0.076 g), 3-methylbenzoic acid (0.25 mmol, 0.045 g), 4,4′-bipy (0.05 g), absolute ethanol (1 mL), H_2O (4 mL) and pH 4 were sealed into a bomb equipped with a teflon liner, heated at 150 °C for 2d and then cooled to room temperature at 24 h. Very longer colorless needle crystals for 1 were obtained. IR data (KBr pellet, υ [cm^{-1}]): 3449, 2922, 1732, 1636, 1595, 1527, 1487, 1408, 1287, 1226, 1165, 1084, 807, 785, 756, 669, 578, 517, 490, 438.

2.3. Synthesis of [Eu ($C_8H_7O_2$)$_3$·(4,4′-bipy)$_{0.5}$] **2** and [Gd ($C_8H_7O_2$)$_3$·(4,4′-bipy)$_{0.5}$] **3**

Compound **2** was prepared by hydrothermal reaction. A mixture of $Eu(NO_3)_3 \cdot 5H_2O$ (0.25 mmol, 0.107 g), 3-methylbenzoic acid (0.25 mmol, 0.045 g), 4,4′-bipyridine (0.05 g), absolute ethanol (1 mL), H_2O (4 mL) and pH 4 was sealed into a bomb equipped with a teflon liner, heated at 150 °C for 2d, and then cooled to room temperature at 24 h. The synthesis of **3** is similar to **2**, only the $Eu(NO_3)_3 \cdot 5H_2O$ was replaced by the $Gd(NO_3)_3 \cdot 5H_2O$. Light yellow needle crystals for **2** were obtained IR data (KBr pellet, υ [cm^{-1}]): 3059, 2920, 1596, 1530, 1487, 1408, 1286, 1226, 1086, 1068, 1042, 999, 911, 804, 758, 685, 676, 616, 570, 516, 489, 421.

2.4. X-ray crystallography

Suitable single crystals of **1** were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker Rigaku R-AXIS RAPID diffractometer with graphite mono-chromatized MoKα radiation (λ = 0.71073 Å). Suitable single crystals of **2** and **3** were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite mono-chromatized MoKα radiation (λ = 0.7107 Å). Crystal structures were solved by the direct method and refined by full-matrix least-squares techniques against F^2 using the SHELXS-97 [19a] crystallographic software package. All non-hydrogen atoms were refined anis-tropically. Hydrogen atoms were fixed at calculated positions and refined by using a riding mode. All calculations were performed using the SHELXL-97 [19b] program. The Crystal data **1, 2** and **3** were given in Table 1. Selected bond lengths and bond angles of **1** and **2** were listed in Table 2. Selected bond lengths and bond angles of **3** was listed in Table 3.

3. Results and discussion

3.1. Structural descriptions of [Yb ($C_8H_7O_2$)$_3$] **1** and [Eu ($C_8H_7O_2$)$_3$ · (4,4′-bipy)$_{0.5}$] **2**

The X-ray crystal structure analysis reveals that the structure of **1** is a one-dimensional chain framework, crystallizing in monoclinic space group $p2_1/n$. The asymmetric unit of **1** contains three HLs. The Yb ion is coordinated with seven oxygen atoms from one chelating bidentate carboxyl group (O5 and O6) and five dimonodentate carboxyl groups(O1, O2A, O3, O4 and O7A), as shown in Fig. 1. The average distance of Yb–O is 2.2922(8) Å.

The X-ray crystal structure analysis reveals that the structure of **2** is a two-dimensional layer framework, crystallizing in