



Research paper

Two unique hydroxyl bridged lanthanide polymers incorporating mixed carboxylate ligands: Syntheses, structures, luminescence and magnetic property



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ABSTRACT

Two lanthanide–organic coordination polymers incorporating both substituted imidazole dicarboxylate and benzene monocarboxylate auxiliary ligand, namely, $\{[\text{Gd}_2(\mu_3\text{-OH})(\text{pimda})(\text{imba})(\text{H}_2\text{pimda})(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}]_n\}$ (**1**) and $\{[\text{Tb}_2(\mu_3\text{-OH})(\text{pimda})(\text{imba})(\text{H}_2\text{pimda})(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}]_n\}$ (**2**) ($\text{H}_2\text{pimda} = 2\text{-propyl-1H-imidazole-4,5-dicarboxylic acid}$ and $\text{H}_2\text{imba} = 4\text{-(1H-imidazole-1-yl) benzoic acid}$) have been obtained under the hydrothermal conditions, and have been structurally characterized by elemental analysis, IR spectrum and single X-ray diffraction. The polymers are isostructural, both crystallizing in the triclinic system, with space group of $P\bar{1}$. They display one dimensional (1-D) double-stranded ribbon chains based on hydroxyl-bridged $[\text{Ln}_4\text{pimda}_2]$ tetranuclear unit as second building block, which are interlinked forming 2-D corrugated layer. The extensive hydrogen bondings further extend these 2-D lamellar networks into 3-D supramolecular architecture. The emission spectrum of polymer **1** exhibits ligand-to-ligand charge-transfer (LLCT) transition luminescence; polymer **2** shows characteristic $f\text{-}f$ transition luminescence, which can be considered as a fluorescent molecular sensor for zinc(II) ions in environment. Variable-temperature magnetic susceptibility measurement reveals that multi-bridging fashion of carboxylic group in **1** results in depopulation of the stark levels for a single Gd(III) ion and/or possible antiferromagnetic interactions between adjacent Gd(III) cations within the carboxylate bridged binuclear unit.

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1. Introduction

In recent years, construction of coordination polymers (CPs) with new network is of interest for the development of new functional materials and in fundamental studies of crystal engineering and supramolecular chemistry. The rare-earth metal CPs bridged by carboxylic groups have attracted great deal of interest in chemistry and materials science fields owing to their extraordinary molecular architectures and fascinating chemical/physical properties [1,2]. A number of luminescent Ln-CPs can act as sensor through specific host-guest interactions and tune the luminescent properties by taking advantage of lanthanide optical properties, including long luminescence lifetime, high color purity, large Stokes shift, as well as the wide emission range, which originated

from $f\text{-}f$ transitions via an “antenna effect”. These optical properties of microporous Ln-MOFs make them especially attractive for potential applications in fluorescence probes and luminescence bioassays [3,4]. However, the luminescence intensity of lanthanide(III) is often quenched by the non-radiative exchange of electronic energy of lanthanide(III) due to the high vibration modes from O–H, C–H bondings [5]. Given the very low molar absorption coefficients for direct excitation of the trivalent metal ions, sensitized luminescence using a light-harvesting “antenna” chromophore is often exploited in order to avoid deactivation processes. The role of the aromatic carboxylic ligand, especially for aromatic amines, aromatic carboxylic acids, and β -diketones provide efficient energy transfer to lanthanide(III) ions [6,7]. A variety of multi-carboxylate triazine/imidazoline/pyridine-based ligands has been employed for constructing coordination polymers, which exhibits various coordination fashions with gas adsorptions, magnetic and luminescent properties, and so on [8–10]. The conjugational aromatic carboxylic acid ligands can

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form asymmetry complexes with lanthanide ions and absorb light then transfer energy efficiently to lanthanide(III) ions, as a result of sensitizing luminescence by overcoming the problem of the Laporte forbidden $f-f$ transitions [11]. However, systematic study based on the combination of two conjugational aromatic carboxylic acid ligands in order to shield lanthanide center against the solvent with facile energy transition has been seldom documented [12]. Meanwhile, the compatible gadolinium chelates incorporating mixed carboxylates were developed as a magnetic resonance imaging contrast agent due to the Gd(III) cation having an $^8S_{7/2}$ ground state without first-order orbital momentum. The compounds are most appropriate to get further insights in the studying on magnetic properties of lanthanide polynuclear systems, while the situation with the magnetic coupling between lanthanide ions is much less advanced [13]. As a continuation of our previous investigation [14] and for better understanding the influence exerted by the auxiliary aromatic carboxylic ligand on structures and properties of Gd(III) and Tb(III) compounds, we wish to describe here the syntheses, structures of two lanthanide coordination polymers based on the 2-propyl-1H-imidazole-dicarboxylate and 4-(1H-imidazole-1-yl) benzoic acid ligands. The powder X-ray diffraction (PXRD) patterns, photo-luminescence, thermal decomposition and magnetic properties are also investigated.

2. Experimental

2.1. Materials and physical measurements

All reagents used in the syntheses were of analytical grade and used as received. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Vario EL III elemental analyzer. The infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded by using KBr pellet on an Avatar TM 360 E. S. P. IR spectrometer. Thermogravimetric analysis (TGA) was performed under atmosphere with a heating rate of $10\text{ }^\circ\text{C}/\text{min}^{-1}$ using TGA/SDTA851e. The PXRD patterns were measured using a Bruker D8 Advance powder diffractometer at 40 kV, 40 mA for Cu $K\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$), with a scan speed of 0.2 s/step and a step size of 0.02 (2θ). UV–visible spectra were recorded at $25\text{ }^\circ\text{C}$ by a Shimadzu Model 1601 spectrophotometer, in quartz cells of 1 cm, using DMF as a solvent. Variable-temperature magnetic susceptibilities were measured using a MPMS-7 SQUID magnetometer under a 0.2 T applied magnetic field and over the range of 2–300 K. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.2. Syntheses of title complexes

2.2.1. $\{[\text{Gd}_2(\text{OH})(\text{pimda})(\text{imba})(\text{H}_2\text{pimda})\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}\}_n$ (**1**)

H_3pimda acid (0.0419 g, 0.2 mmol) and H_2imba (0.021 g, 0.2 mmol) in a solution of water/alcohol ($v/v = 1.2$, 10 mL) were mixed with an aqueous solution (10 mL) of 0.2 mmol $\text{Gd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, 0.089 g. After stirring for 20 min in air, the pH value was adjusted to 4.5 with nitric acid, and the mixture was placed into 25 mL Teflon-lined autoclave under autogenous pressure being heated at $155\text{ }^\circ\text{C}$ for 72 h, then the autoclave was cooled over a period of 24 h at a rate $5\text{ }^\circ\text{C}/\text{h}$. After filtration, the product was washed with distilled water and then dried, light yellow crystals of **1** suitable for X-ray diffraction analysis were obtained. For **1**, yield: 0.0354 g (36%) based on gadolinium element. Elemental analysis (%): calcd for $\text{C}_{26}\text{H}_{31}\text{N}_6\text{O}_{14}\text{Gd}_2$: C 32.32, H 3.23, N 8.69, found: C 32.27, H 3.26, N 8.58. IR (KBr pellet, cm^{-1}): 3423s, 3236br, 1590s, 1529s, 1462s, 1460m, 1338s, 1212s, 867m, 810vs, 793s, 667s, 565m. Procedure of preparation of **2** is reported in the Supporting Information.

2.3. Crystallographic data collection and refinement

Single-crystal diffraction data of complexes **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at room temperature. The structures were solved using direct methods and successive Fourier difference synthesis (SHELXS-97) [15], and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all nonhydrogen atoms (SHELXL-97) [16]. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The summary crystallographic data and selected bond lengths and angles for complexes are listed in Tables 1 and 2, respectively.

3. Results and discussion

3.1. IR spectrum and structural description for title complexes

In the IR spectra of both complexes, the weaker absorption peaks in the frequency region of $3100\text{--}3500\text{ cm}^{-1}$ are attributed to O–H bonding stretching vibration of water molecules. The sharp bands in the ranges of $1600\text{--}1500$ and $1462\text{--}1375\text{ cm}^{-1}$ are attributed to asymmetric and symmetric stretching vibrations of carboxylic groups, respectively. While, the obvious absorption peak maximum at about 1700 cm^{-1} indicates stretching vibrations for the deprotonation of carboxylic groups of dicarboxylic ligand [17].

Single-crystal X-ray diffraction study reveals that complexes **1** and **2** are isostructural, and they both crystallize in triclinic system with space group of P_{-1} . Therefore, only the structure of **1** is described as a representative. The asymmetry unit contains two independent Gd(III) ions bridged by hydroxyl oxygen, one H_2pimda ligand, one Himba ligand, one coordinated water molecules and

Table 1
Crystal data and structure refinement details for polymers **1** and **2**.

Parameter	Polymer 1	Polymer 2
Crystal shape/color	Block/colorless	Block/light yellow
Empirical Formula	$\text{C}_{26}\text{H}_{31}\text{Gd}_2\text{N}_6\text{O}_{14}$	$\text{C}_{26}\text{H}_{31}\text{N}_6\text{O}_{14}\text{Tb}_2$
Formula weight	966.07	968.40
Temperature	293(2) K	293(2) K
Crystal system	Triclinic	Triclinic
Space group	P_{-1}	P_{-1}
Unit cell dimensions (\AA , deg.)	a = 9.0233(4) b = 9.3386(4) c = 18.6728(9) $\alpha = 102.5968(6)$ $\beta = 96.1711(7)$ deg. $\gamma = 91.4604(8)$ deg.	a = 9.1542(15) b = 9.5057(17) c = 19.073(3) $\alpha = 102.866(4)$ deg. $\beta = 96.485(3)$ deg. $\gamma = 91.427(4)$ deg.
$V(\text{\AA}^3)$	1524.75(12)	1605.5(5)
Z	2	2
ρ (g cm^{-3})	2.104	2.003
$F(000)$	938	940
Absorption coefficient (mm^{-1})	4.393	4.446
θ Range for data collection ($^\circ$)	2.24 to 27.92 deg.	2.20 to 27.50 deg.
Limiting indices ranges	$-11 \leq h \leq 11$ $-12 \leq k \leq 11$ $0 \leq l \leq 24$	$-11 \leq h \leq 11$ $-10 \leq k \leq 12$ $-22 \leq l \leq 24$
Max. and min. transmissions	0.4344 and 0.3098	0.6405 and 0.5016
Data/restraints/parameters	6846/76/425	6972/79/451
GOF	1.079	1.045
R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0562$ $wR_2 = 0.1796$	$R_1 = 0.0395$ $wR_2 = 0.1048$
R_1, wR_2 (all data)	$R_1 = 0.0645$ $wR_2 = 0.2038$	$R_1 = 0.0472$ $wR_2 = 0.1121$
Largest diff. peak and hole ($e/\text{\AA}^3$)	2.696 and -4.010	2.217 and -1.721

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \frac{\sum_w [F_o^2 - F_c^2]^2 / \sum_w (|F_w|^2)^2}{\sum_w (|F_w|^2)^2}$$

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