



Isomorphous and isostructural lanthanide coordination polymers based on 2-(4-chlorobenzoyl)benzoic acid: Synthesis, structure, characterization, and luminescent properties



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ABSTRACT

Self-assembly of a flexible ligand Hcbba (2-(4-chlorobenzoyl)benzoic acid) and lanthanide salts yield a series of three-dimensional (3D) coordination polymers under hydrothermal conditions, namely, $[\text{Ln}(\text{cbba})_3\text{H}_2\text{O}]_\infty$ (Ln = La(**I**), Pr(**II**), and Nd(**III**)). Their structures were determined by single-crystal X-ray diffraction analyses and characterized by elemental analyses and infrared spectroscopy, which verified that they are isomorphous and isostructural. Findings indicate that the subunit of cavate cages ($\text{Ln}_2\text{O}_2(\text{OCO})_2$) are observed in **I–III**, which are connected into a one-dimensional (1D) chain through cbba[−] anions in $\mu_2\text{-}\eta^1\text{:}\eta^1$ fashion and further assembled into 3D architecture via C–H $\cdots\pi$ and C–H $\cdots\text{Cl}$ interactions between the neighboring parallel 1D chains. **I–III** feature that the double-stranded helix entangled by one left- and one right-handed helical chain coaxially along *c* axis in each 1D infinite chain. Luminescent properties reveal that **II** and **III** may be potential ion-selective luminescent probes for Hg^{2+} and Ag^+ , respectively.

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1. Introduction

Lanthanide-organic frameworks (LnOFs) have evoked great interest not only the combination of organic and inorganic fragments that can generate a large amount of novel topological structures but also allow that rational design strategies for constructing porous materials with high surface areas, predictable structures, tunable pore sizes and may find potentially industrial applications in gas storage and separation, adsorption catalysis, ion exchange, guest exchange, molecular magnetism, molecular recognition, nonlinear optics and luminescent, etc [1–9]. Additionally, lanthanide ions own larger radius and higher affinity for hard donor centers and ligands with oxygen or hybrid oxygen–nitrogen atoms, which are in favor of the construction of coordination polymers [10–15]. What's more, lanthanide ions with special luminescent resulting from 4f electrons, which illustrated the coordination polymers are intriguing and remarkably suitable for the development of optical devices as well as probes for chemical species [16–20]. Specifically, the conformational freedom nature of the flexible linker Hcbba exhibits several interesting characteristics which may provide

more possibility for the construction of novel structures and microporous MOFs: (a) carboxyl and carbonyl may potentially provide various coordination modes and favor the construction of multi-dimensional MOFs. (b) halogen (Cl) atoms may function as electron donor to form hydrogen bonds. (c) specific spatial structure of two benzenes benefit the construction of C–H $\cdots\pi$ and $\pi\cdots\pi$ interactions.

Up to now, only several transition metal coordination polymers based on 2-(4-chlorobenzoyl)benzoic acid has been reported. Following our ongoing efforts towards the synthesis and isolation of lanthanide-containing coordination polymers [21–24]. In this work, we describe the synthesis, structures, and luminescent properties of three 3D coordination polymers obtained from the self-assembly of flexible bridging ligands 2-(4-chlorobenzoyl)benzoic acid and Ln(III) ions, which are formulated as $[\text{La}(\text{cbba})_3\text{H}_2\text{O}]$, $[\text{Pr}(\text{cbba})_3\text{H}_2\text{O}]_\infty$, and $[\text{Nd}(\text{cbba})_3\text{H}_2\text{O}]_\infty$.

2. Experimental section

2.1. Materials and physical measurements

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 240 CHN Elemental Analyzer. IR

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spectra in the range of 400–4000 cm^{-1} were recorded with an AVATAR 360 FT-IR spectrometer (KBr pellets were used). The crystal structure was determined with a Bruker Smart CCD X-ray single-crystal diffractometer. TG analysis was conducted with a Perkin–Elmer TGA7 instrument in flowing N_2 at a heating rate of $10^\circ\text{C min}^{-1}$. Excitation and emission spectra were obtained with an F-7000 FL spectrofluorometer at room temperature.

2.2. Synthesis of the coordination polymers I–III

[La(cbba)₃H₂O]_∞ (I) was synthesized from the reaction mixture of 2-(4-Chlorobenzoyl)benzoic acid and lanthanum chloride at a molar ratio of 1:1 (0.1 mmol:0.1 mmol) in 10 mL distilled water. The resultant mixture was homogenized by stirring for 30 min at ambient temperature and then transferred into 20 mL Teflon-lined stainless steel autoclave under autogenous pressure at 160°C for 3 days and then cooled to room temperature at a rate of 5°C/h . After filtration, the product was washed with distilled water and then dried to afford colorless block-shaped crystals suitable for X-ray diffraction analysis. Elemental analysis calculated (mass fraction, the same hereafter, %) for $\text{C}_{42}\text{H}_{26}\text{O}_{10}\text{Cl}_3\text{La}$ (935.91): C, 53.64; H, 2.73. Found: C, 53.90; H, 2.80. IR data (KBr pellet, cm^{-1}): 3590(w), 3460(br), 3061(w), 2355(w), 1665(s), 1615(s), 1587(s), 1565(s), 1537(m), 1484(m), 1444(m), 1401(s), 1289(w), 1254(w), 1149(w), 1093(s), 1015(m), 933(s), 887(w), 843(m), 770(w), 748(s), 715(w), 691(w), 677(w), 653(w), 591(w), 561(w), 532(w), 481(w), 426(w).

[Pr(cbba)₃H₂O]_∞ (II) was synthesized by identical experimental procedures to that of I except that lanthanum chloride was replaced by praseodymium nitrate. After filtration, the product was washed with distilled water and then dried and primrose transparent crystals suitable for X-ray diffraction analysis were finally isolated. Elemental analysis calculated (%) for $\text{C}_{42}\text{H}_{26}\text{O}_{10}\text{Cl}_3\text{Pr}$ (937.91): C, 53.99; H, 2.50. Found: C, 53.78; H, 2.79. IR data (KBr pellet, cm^{-1}): 3433(br), 2926(w), 2367(w), 2346(w), 1664(m), 1614(s), 1586(s), 1560(w), 1483(w), 1444(w), 1401(s), 1289(w), 1251(w), 1092(w), 1014(w), 964(w), 933(m), 887(w), 842(w), 772(w), 748(m), 716(w), 677(w), 652(w), 531(w), 483(w), 421(w).

[Nd(cbba)₃H₂O]_∞ (III) was synthesized by identical experimental procedures to that of I except that lanthanum chloride was replaced by neodymium nitrate. After filtration, the product was washed with distilled water and then dried and purplish transparent crystals suitable for X-ray diffraction analysis were finally isolated. Elemental analysis calculated (%) for $\text{C}_{42}\text{H}_{26}\text{O}_{10}\text{Cl}_3\text{Nd}$ (941.25): C, 53.88; H, 2.61. Found: C, 53.59; H, 2.78. IR data (KBr pellet, cm^{-1}): 3429(br), 2927(w), 2377(w), 2345(w), 1661(m), 1617(s), 1587(s), 1560(w), 1484(w), 1443(w), 1401(s), 1276(w), 1151(w), 1091(w), 1014(w), 965(w), 933(m), 844(w), 772(w), 749(m), 716(w), 677(w), 652(w), 531(w), 439(w), 420(w).

2.3. Crystallographic data collection and refinement

Single-crystal diffraction data I–III were collected. Suitable single crystals of the coordination polymers on a Bruker Smart CCD X-ray single-crystal diffractometer with graphitic monochromated $\text{MoK}\alpha$ -radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K. All independent reflections were collected in a range of $1.50\text{--}25.00^\circ$ for I, 1.49 to 25.00° for II, and 2.15 to 25.00° for III (determined in the subsequent refinement). Multi-scan empirical absorption corrections were applied to the data using the SADABS. The crystal structure was solved by direct methods and Fourier synthesis. Positional and thermal parameters were refined by the full-matrix least-squares method on F^2 using the SHELXTL software package. The final least-square cycle of refinement gave, $R_1 = 0.0399$, $wR_2 = 0.0803$ for I, $R_1 = 0.0636$, $wR_2 = 0.0870$ for II, $R_1 = 0.0273$, and $wR_2 = 0.0600$ for III. The weighting scheme, $w = 1/[\sigma^2(F_0^2) + (0.0316P)^2 + 0.17.99P]$

for I, $w = 1/[\sigma^2(F_0^2) + (0.0459P)^2 + 6048P]$ for II, and $w = 1/[\sigma^2(F_0^2) + (0.0278P)^2 + 2.62P]$ for III, Where $P = (F_0^2 + 2F_c^2)/3$. A summary of the key crystallographic information is given in Table 1. Selected bond lengths, bond angles and the parameters of hydrogen bonds for the coordination polymers I–III are listed in Table 2 and Table 3, respectively. Table 4.

3. Results and discussion

3.1. The IR spectra of the coordination polymers

Coordination polymers I–III are insoluble in common solvents such as CH_3COCH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OH , and $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, but they are slight soluble in DMSO and DMF. The structures of the coordination polymers are identified by satisfactory elemental analysis as well as FT-IR and X-ray analyses. The FT-IR spectra of the six as-synthesized coordination polymers are similar. The strong and broad absorption bands in the ranges of $3460\text{--}3329 \text{ cm}^{-1}$ in I–III are assigned to the stretching vibrations of $\nu(\text{O–H})$ in water molecules in coordination [25–27]. The sharp peaks of $\delta_{\text{O–C–O}}$ vibration in plane emerge in the range of $748\text{--}653 \text{ cm}^{-1}$. The features present in the range of 591 cm^{-1} can be ascribed to the bend vibrations of $\nu(\text{Ar–CO–Ar})$ in cbba^- ligands. Another features in the region of $1665\text{--}1536 \text{ cm}^{-1}$ and $1484\text{--}1401 \text{ cm}^{-1}$ may be ascribed to the asymmetric (COO^-) and symmetric (COO^-) stretching of carboxyl groups of cbba^- ligands in I–III. The values of $\Delta[\nu_{\text{as}} - \nu_{\text{s}}]$ are about $264\text{--}260 \text{ cm}^{-1}$, which indicate that the carboxyl groups are coordinated with the metal ions via both bidentate-chelating

Table 1
Summary of crystallographic data for coordination polymers I–III.

Data	I	II	III
Empirical formula	$\text{C}_{42}\text{H}_{26}\text{Cl}_3\text{O}_{10}\text{La}$	$\text{C}_{42}\text{H}_{26}\text{Cl}_3\text{O}_{10}\text{Pr}$	$\text{C}_{42}\text{H}_{26}\text{Cl}_3\text{O}_{10}\text{Nd}$
Formula weight	935.89	937.89	941.22
Temperature/K	296(2)	296(2)	296(2)
Wavelength/ \AA	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$C2/c$	$C2/c$	$C2/c$
$a/\text{\AA}$	28.5420(16)	28.561(2)	28.5550(19)
$b/\text{\AA}$	10.1480(6)	10.1580(8)	10.0900(7)
$c/\text{\AA}$	28.2810(17)	28.301(2)	28.2580(19)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	106.2490(11)	106.2330(14)	106.4270(12)
$\gamma/^\circ$	90	90	90
Z	8	8	8
Density (calculated)	1.581 Mg/m^3	1.580 Mg/m^3	1.601 Mg/m^3
$F(000)$	3728	3744	3752
Crystal size/ mm^3	$0.23 \times 0.20 \times 0.18$	$0.20 \times 0.19 \times 0.17$	$0.21 \times 0.20 \times 0.17$
θ for data collection/ $^\circ$	1.500 to 24.999	1.485 to 25.000	2.151 to 24.999
Limiting indices	$-29 \leq h \leq 33$ $-12 \leq k \leq 11$ $-33 \leq l \leq 33$	$-32 \leq h \leq 33$ $-12 \leq k \leq 11$ $-31 \leq l \leq 33$	$-31 \leq h \leq 33$ $-11 \leq k \leq 11$ $-31 \leq l \leq 33$
Reflns collected/unique	19,612/6902 $[R_{\text{int}}] = 0.0552]$	19,666/6925 $[R_{\text{int}}] = 0.0413]$	19,490/6860 $[R_{\text{int}}] = 0.0332]$
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	6902/0/505	6925/0/505	6860/0/505
Goodness-of-fit on F^2	1.041	1.028	1.034
Volume/ \AA^3	7864.2(8)	7883.4(11)	7809.4(9)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0399$, $wR_2 = 0.0803$	$R_1 = 0.0636$, $wR_2 = 0.0870$	$R_1 = 0.0273$, $wR_2 = 0.0600$
R indices (all data)	$R_1 = 0.0656$, $wR_2 = 0.0979$	$R_1 = 0.0525$, $wR_2 = 0.0934$	$R_1 = 0.0369$, $wR_2 = 0.0634$
ρ_{min} and ρ_{max} ($\text{e} \cdot \text{\AA}^{-3}$)	0.553 and -0.585	0.629 and -0.431	0.515 and -0.419

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