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Syntheses, structures, molecular and cationic recognitions and catalytic properties of two lanthanide coordination polymers based on a flexible tricarboxylate

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ABSTRACT

Two lanthanide coordination polymers, namely, $\{[La(TTTA)(H_2O)_2]\cdot 2H_2O\}_n$ (La-TTTA) and $[Nd(TTTA)(H_2O)_2]\cdot 2H_2O\}_n$ (Nd-TTTA) have been hydrothermally synthesized through the reaction of lanthanide ions (La^{3+} and Nd^{3+}) with the flexible tripodal ligand 2,2′,2″-[1,3,5-triazine-2,4,6-triyltris(thio)]tris-acetic acid (H_3TTTA). La-TTTA and Nd-TTTA are isostructural and both show three dimensional structures. La-TTTA and Nd-TTTA show good recognition of amine molecules via quenching the luminescent intensities in amines emulsions. They can also recognize Fe^{3+}, Cu^{2+}, Mg^{2+}, Cr^{3+} and Co^{2+} ions with the quenching the peak around 361 nm when the compounds immersed in ionic solutions. The two compounds act as efficient Lewis acid catalysts for the cyanosilylation of benzaldehyde and derivatives in high yields shortly due to the strong Lewis acidity and the possible open sites of the lanthanide ions.

1. Introduction

Studies on the synthesis and design of coordination polymers (CPs) have been extensively developed in recent years, owing to their dynamic structures and promising applications in gas storage and separation, luminescence, catalysis, magnetism, and drug delivery [1]. The design of organic linkers and the coordination tendencies of metal ions besides crystallization conditions have led to a large number of open framework structures quite often endowed with novel topological structures as well as unique functionalities [2]. Especially, exploring highly symmetrical multi-topic ligands and suitable metal salts to construct supramolecular architectures is of higher interest [3]. Flexible ligands, which have been less studied than the rigid ligands, can adopt additional different conformations according to the geometric requirements of different metal ions and may afford unpredictable and interesting supramolecular networks [4]. The self-assembly between metal ions and flexible ligands is also proven to be a most effective synthetic design to achieve chiral, helical frameworks and high-nuclear complexes [5], single-helices [6] with potential applications in selective catalysis, separation and so on [7]. Indeed, the structural frameworks are frequently influenced by external factors, such as solvent systems, pH values, temperature, geometric requirements of metal atoms, metal–ligand ratio, structure of connecting ligands, and nature of counter anions [8]. Moreover, self-assembly of inorganic and organic luminescent moieties into porous coordination polymers can used as luminescent materials for chemical sensing, light-emitting and environmental monitoring [9].

Recently, we have focused on the flexible tripodal ligand 2,2′,2″-[1,3,5-triazine-2,4,6-triyltris(thio)]tris-acetic acid (H_3TTTA) which can be constructed with different metal ions to novel complexes with abundant topologies and interesting applications. Due to its flexibility, the three arms could show significant deviation from the central triazine ring. Besides, the different degrees of protonation will cause numbers of coordination sites which will achieve affluent, unpredictable topologies and interesting properties. Though some complexes based on H_3TTTA with fluorescence and magnetic properties were reported previously [10], the applications on cyanosilylation reaction have never been explored yet. As we know, cyanosilylation reaction is widely used to test the Lewis acid catalysis of complexes. Moreover, The Lewis acid used for the addition of trimethylsilyl cyanide (TMSCN) in aldehydes and ketones primarily includes compounds based on lanthanides metal compounds [11]. Therefore, lanthanide coordination polymers exhibit great potential as Lewis acids in heterogeneous catalysis.

In present work, we have produced two lanthanide coordination polymers assembled with H_3TTTA. We report their syntheses, crystal structures, molecular and cationic recognitions

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and catalytic properties. To date, research on the properties of complexes with H_3TTTA and the similar ligands are mainly focused on the luminescence and magnetism and so on. There are few reports about molecular and cationic recognition as well as catalytic properties of these compounds.

2. Experimental

2.1. Materials and physical methods

The ligand was prepared according to the previous procedure [12]. All other reagents were commercially available and used as purchased. The elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 400–4000 cm^{-1} on a Nicolet spectrometer. Thermal analyses were performed on integrated thermal STA 449C analyzers from room temperature to 800 °C with a heating rate of 10 °C/min under flowing nitrogen. The fluorescence spectra of compounds in different solvents and solutions were performed on a QuantaMaster TM 40 & Time-Master spectrophotometer. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D/max2500VB3+/PC diffractometer equipped with Cu-*Kα* radiation ($\lambda = 1.5406$ Å).

2.2. Synthesis of La-TTTA

A mixture containing H_3TTTA (0.035 g, 0.1 mmol) and $La(NO_3)_3 \cdot 6H_2O$ (0.086 g, 0.2 mmol) in 3 mL water was sealed in a Teflon-lined autoclave and heated to 80 °C under autogenous pressure for two days and then allowed to cool to room temperature. After filtration, the white block crystals were washed with water and dried in air. Anal. Calcd for $C_{18}H_{20}La_2N_6O_{20}S_6$ (*Mr*: 1110.58): C, 19.47; H, 1.82; N, 7.57%. Found: C, 19.08; H, 1.89; N, 7.51%. IR (cm^{-1}): 3426(m), 1582(s), 1479(s), 1419(s), 1385(s), 1269 (w), 1226(m), 848(w).

2.3. Synthesis of Nd-TTTA

Nd-TTTA was obtained in a similar manner to La-TTTA using $Nd(NO_3)_3 \cdot 6H_2O$ (0.086 g, 0.2 mmol). After filtration, the crystals were washed with water and dried in air. Anal. Calcd for $C_9H_{10}NdN_3O_{10}S_3$ (*Mr*: 560.62): C, 19.28; H, 1.80; N, 7.50%. Found: C, 19.13; H, 1.92; N, 7.43%. IR (cm^{-1}): 3424(m), 1580(s), 1474(s), 1418(s), 1384(s), 1270(w), 1224(m), 848(w).

2.4. Crystal structure determination and refinement

The X-ray intensity data for the two compounds were collected on a Rigaku Saturn 724+CCD diffractometer with graphite monochromatized Mo *Kα* radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by direct methods using difference Fourier synthesis with SHELXTS [13], and refined by full-matrix least-squares method using the SHELXL-97 program [14]. The non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms except for those of guest molecules were added according to theoretical models. Crystal data and details of the structure determination for La-TTTA and Nd-TTTA are listed in Table 1. Selected bond lengths and angles for La-TTTA and Nd-TTTA are listed in Table S1.

2.5. Catalytic test for cyanosylation reaction

Aldehyde (1.0 mmol) in trimethylsilyl cyanide (TMSCN, 2 mmol) was successively placed into a 10 mL screw-cap vial and compound (2.5 mol%) was then added to initiate the reaction with ultrasound for 2 h in the sealed vial. After the reaction completed, the catalyst was removed by centrifugation and then filtered with ethyl acetate quickly. The conversion of aldehydes was determined by gas chromatography (GC, Agilent 7890 A) analysis and GC–MS (HP 6890) spectra with those of authentic samples.

Table 1
Crystal data and structure refinements for La-TTTA and Nd-TTTA.

Compound	**La-TTTA**	**Nd-TTTA**
Empirical formula	$C_{18}H_{20}La_2N_6O_{20}S_6$	$C_9H_{10}N_3NdO_{10}S_3$
Formula weight	1110.58	560.62
Temperature (K)	193	193
Crystal system	Triclinic	Monoclinic
Space group	$P\overline{1}$	$P21/c$
a (Å)	8.9930(18)	8.7281(17)
b (Å)	13.214(3)	14.495(3)
c (Å)	14.518(3)	15.445(5)
α (°)	86.89(3)	90.00
β (°)	87.01(3)	121.07(2)
γ (°)	86.08(3)	90.00
D_c (g/cm^3)	2.149	2.225
Z	2	4
F (0 0 0)	1,080	1,092
Reflections collected	14,845	6,903
Unique reflections	4560	2578
μ (mm^{-1})	2.910	3.535
Goodness-of-fit on F^2	0.931	1.086
R_1 [$I > 2\sigma(I)$]	0.0714	0.1414
wR_2 [$I > 2\sigma(I)$]	0.1890	0.3259
R_1 (all data)	0.0887	0.1459
wR_2 (all data)	0.2057	0.3278

3. Results and discussion

3.1. Synthetic and spectral aspects

The two compounds were characterized by powder XRD, TG analysis, and FT-IR spectroscopy. The experimental powder XRD patterns were measured at room temperature as shown in Fig. S1. The peak positions of the simulated and experimental PXRD patterns are in agreement with each other, suggesting the good phase purity of the two compounds. TG analysis revealed that all these materials have good thermal stabilities, since they start to decompose beyond 300 °C (Figs. S2 and S3).

The characteristic absorption peaks of the main functional groups in FT-IR spectra for all the compounds are shown in Fig. S4. The asymmetric stretching vibrations $\upsilon_{as}(COO^-)$ of the two compounds were observed in about 1582, 1580, 1597 cm^{-1} and symmetric stretching vibrations $\upsilon_s(COO^-)$ in 1385, 1384, 1403 cm^{-1}. The difference $\Delta(\upsilon_{as}(COO^-) - \upsilon_s(COO^-))$ was about 200 cm^{-1}, characteristic for coordinated carboxylate groups [15].

3.2. Crystal structural description of La-TTTA and Nd-TTTA

Single-crystal X-ray analyses indicate that the only small difference between La-TTTA and Nd-TTTA is the coordination mode of La1 metal center. The bond length of La1–O3 is 2.896 (7) Å, which is a little longer than the common La–O bond lengths. However, regarding La1–O3 as a weak coordination bond, La-TTTA and Nd-TTTA are isostructural. Herein, the structures and properties of La-TTTA are described in detail as a representative example. La-TTTA crystallizes in the triclinic space group $P\overline{1}$. The ORTEP view of La-TTTA is shown in Fig. 1. La ion is ten-coordinated by five $TTTA^{3-}$ ligands and two water molecules to finish distorted monocapped square anti-prism coordination geometry. The La–O (carboxylate) bond distances vary from 2.473(7) to 2.896(7) Å, and the average La–O (water) bond distance is 2.566(7) Å. The O–La–O