



Synthesis, structure and luminescence properties of lanthanide complex with a new tetrapodal ligand featuring salicylamide arms

Xue-Qin Song^{a,b}, Xiao-Guang Wen^b, Wei-Sheng Liu^{a,*}, Da-Qi Wang^c

^a College of Chemistry and Chemical Engineering and State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

^b School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

^c Department of Chemistry, Liaocheng University, Liaocheng 252000, China

ARTICLE INFO

Article history:

Received 29 March 2009

Received in revised form

1 July 2009

Accepted 12 July 2009

Available online 31 August 2009

Keywords:

Lanthanide coordination polymer

Salicylamide

Crystal structure

Hydrogen-bond

Luminescence properties

ABSTRACT

A new tetrapodal ligand 1,1,1-tetrakis[[(2'-(2-furfurylaminoformyl))phenoxy]methyl]methane (L) has been prepared and their coordination chemistry with Ln^{III} ions has been investigated. The structure of $\{[Ln_4L_3(NO_3)_{12}] \cdot H_2O\}_\infty$ ($Ln = Nd, Eu$) shows the binodal 4,3-connected three-dimensional interpenetration coordination polymers with topology of a $(8^6)_3(8^3)_4$ notation. $[DyL(NO_3)_3(H_2O)_2] \cdot 0.5CH_3OH$ and $[ErL(NO_3)_3(H_2O)(CH_3OH)] \cdot CH_3COCH_3$ is a 1:1 mononuclear complex with interesting supramolecular features. The structure of $[NdL(H_2O)_6] \cdot 3ClO_4 \cdot 3H_2O$ is a 2:1 mononuclear complex which further self-assembled through hydrogen bond to form a three-dimensional supramolecular structures. The result presented here indicates that both subtle variation of the terminal group and counter anions can be applied in the modulation of the overall molecular structures of lanthanide complex of salicylamide derivatives due to the structure specialties of this type of ligand. The luminescence properties of the Eu^{III} complex are also studied in detail.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

The design and construction of polymeric metal-organic hybrid complexes are of considerable interest in recent years, due to their appealing structural topologies and potential application in catalysis, adsorption/separation, host-guest chemistry, and the promising photo-, electro-, and magnetofunctional materials [1–3]. Metal-organic frameworks containing lanthanide ions as connectors is particularly attractive because of the magnetic and electronic properties of $4f$ ions, which should result in the application of lanthanide polymers in sensors, lighting devices, and optical storage [4]. Lanthanide ions, with their high coordination flexibility and their lack of preferential geometries, are good candidates to provide unique opportunities for the discovery of unusual network topologies [5–7], thus leading us to this interesting and challenging field. So far, much work is focused on using multicarboxylate ligands to prepare lanthanide-containing MOFs [8,9]. By contrast, based on a query to the Cambridge Structural Database (CSD), we find that the synthesis of multi-dimensional lanthanide-containing MOFs by using amide ligands is less developed [10].

Owing to the structural features of salicylamide derivatives which afforded diverse types of lanthanide supramolecular complexes upon variation of the backbone and terminal groups,

some lanthanide complexes with intriguing structure as well as interesting luminescence properties have been reported [11]. In order to further understand the influence on the structure as well as the regularity of luminescence properties of their complexes, it is necessary to extend such a studying area for improving desirable properties. At the same time, we have tried to merge the role of anions in this self-assembly. As a part of our systematic investigation of self-assembly based on salicylamide ligands, we report herein the synthesis of a new tetrapodal ligand featuring salicylamide arms, namely, 1,1,1-tetrakis[[(2'-(2-furfurylaminoformyl))phenoxy]methyl]methane (L) and describe the synthesis and crystal structure of the resulting complexes. Two three-dimensional polymeric coordination complexes, namely, $[Nd_4L_3(NO_3)_{12} \cdot 6H_2O]_\infty$, $\{[Eu_4L_3(NO_3)_{12}] \cdot 6H_2O\}_\infty$, three mononuclear complex with interesting supramolecular properties, namely, $\{[DyL(NO_3)_3(H_2O)_2] \cdot 0.5CH_3OH\}$, $\{[ErL(NO_3)_3(H_2O)(CH_3OH)] \cdot CH_3COCH_3\}$ and $\{[NdL_2(H_2O)_6] \cdot 3ClO_4 \cdot 3H_2O\}$, were structurally characterized by single-crystal X-ray diffraction together with the luminescence properties of the Eu^{III} complex.

2. Experimental

2.1. Materials

The commercially available chemicals were used without further purification. All of the solvents used were of analytical reagent grade.

* Corresponding author. Fax: +86 931 8912582.

E-mail address: liuws@lzu.edu.cn (W.-S. Liu).

2.2. Methods

The metal ions were determined by EDTA titration using xylenol orange as indicator. C, N and H were determined using an Elementar Vario EL. Melting points were determined on a Kofler apparatus. IR spectra were recorded on Nicolet FT-170SX instrument with pressed KBr pellets in the 400–4000 cm^{-1} region. ^1H NMR spectra were measured on a Bruker DRX 300 spectrometer in CDCl_3 solution with TMS as internal standard. Fluorescence measurements were made on FLS920 of Edinburgh Instrument equipped with quartz cuvettes of 1 cm path length with a xenon lamp as the excitation source. An excitation and emission slit of 2.5 nm were used for the measurements of luminescence in solid state. The 77 K solution-state phosphorescence spectra were recorded with solution samples loaded in a quartz tube inside a quartz-walled optical Dewar flask filled with liquid nitrogen in the phosphorescence mode. Quantum yields were determined by an absolute method using an integrating sphere on FLS920 of Edinburgh Instrument. The luminescence decays were recorded using a pumped dye laser (Lambda Physics model FL2002) as the excitation source. The nominal pulse width and the linewidth of the dye laser output were 10 ns and 0.18 cm^{-1} , respectively. The emission of a sample was collected by two lenses into a monochromator (WDG30), detected by a photomultiplier and processed by a Boxcar Average (EGG model 162) in line with a microcomputer. Reported luminescence lifetimes are averages of at least three independent determinations.

2.3. Crystal structure determination

X-ray single-crystal diffraction of all complexes was performed on CCD area diffractometer with $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) at 298 K. In each case, semiempirical absorption correction was applied (SADABS) and the program SAINT was used for integration of the diffraction profiles [12]. The structures were solved by direct methods using SHELXS of the SHELXL package and refined with SHELXL [13]. The non-H atoms were modeled with anisotropic displacement parameters and refined by full-matrix least-squares methods on F^2 . Generally, C-bound hydrogen atoms were placed geometrically and refined as riding. Isotropic

displacement parameters of hydrogen were derived from their parent atoms. The hydrogen atoms of the water molecules were located by a difference Fourier map and refined with distance restraints for O–H and H...H (0.90 and 1.50 \AA , respectively), and one variable isotropic U for Nd^{III} perchlorate complex. In the structure of Nd^{III} complex, the terminal furfurylamine group exhibits disorder over two positions and the occupancy ratios were found to 0.529/0.471. In all cases of refinements, structural restraints were applied for solvent molecules, benzene or furan rings of the ligand, the full details of which are given in the ESI CIF files. Details of crystallographic parameters, data collection and refinements are listed in Table 2. Representative bond distances and angles for Nd^{III} , Eu^{III} , Dy^{III} , Er^{III} nitrate and Nd^{III} perchlorate complexes are listed in Table S1, S2 and S3, respectively. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC 705664–705668.

2.4. Synthesis of the ligand

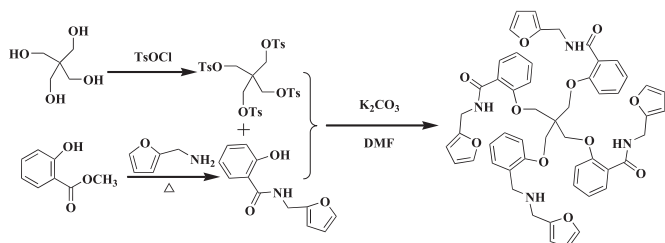
The ligand 1,1,1-tetrakis[[(2'-(2-furfurylaminoformyl))phenoxy]methyl]methane (L) (Scheme 1) was prepared similar to the literature procedure [11f]. Yield 76%. m.p.: 161.7 $^{\circ}\text{C}$. Analytical data, Calc. for $\text{C}_{53}\text{H}_{48}\text{N}_4\text{O}_{12}$: C, 68.23; H, 5.19; N, 6.01; Found: C, 68.52, H, 5.21, N, 6.04; IR (KBr, ν , cm^{-1}): 3417, 3314 (m, NH), 1648 (s, C=O), 1601 (m), 1537 (m), 1299 (m), 1224 (m), 750 (m). ^1H NMR (CDCl_3 , 300 MHz): δ : 4.16 (s, 8H, OCH_2), 4.48 (d, $J=5.4$, 8H, NHCH_2), 6.11 (m, 8H, Ar), 6.82 (d, $J=8.1$, 4H, Ar), 6.98 (s, 4H, Ar), 7.13 (t, 4H, Ar), 7.20 (t, 4H, NH), 7.44 (m, 4H), 8.0 (dd, 4H, Ar).

2.5. Syntheses of the complexes

One millimole of ligand and 1 equiv (1 mmol) of the lanthanide nitrates or perchlorates were dissolved in a minimum methanol+acetone+ethyl acetate ($v:v=1:1:8$) solution under reflux. Then the flask was cooled, and the mixture was filtered into a sealed 25–40 ml glass vial for crystallization at room temperature. After about three weeks crystals suitable for analysis were obtained. Elemental analysis data and IR spectra data characteristic of the complexes are listed in Table 1.

3. Results and discussion

The tetrapodal ligand was prepared by the ether base coupling of pentaerythritol benzenesulfonate and the furfurylsalicylamide in a 1:4 ratio in dry DMF in the presence of an excess of anhydrate K_2CO_3 (Scheme 1). Purification of L was accomplished by column chromatography over silica, eluting with petroleum ether/ethyl acetate ($v:v=2:1$) to give a pale white solid with the yield of 76%.



Scheme 1. The synthetic route of the ligand.

Table 1
Elemental analytical and IR spectral data for the complexes.

Compound	Elemental analyses ^a				IR ($\lambda_{\text{max}}/\text{cm}^{-1}$) ν (C=O)
	C	H	N	Ln	
$\text{Nd}_4\text{L}_3(\text{NO}_3)_{12}(\text{H}_2\text{O})_6$	45.38 (45.17)	3.70 (3.72)	7.93 (7.95)	13.59 (13.65)	1607
$\text{Eu}_4\text{L}_3(\text{NO}_3)_{12}(\text{H}_2\text{O})_6$	44.69 (44.84)	3.68 (3.69)	7.90 (7.89)	14.34 (14.27)	1606
$\text{DyL}(\text{NO}_3)_3(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})_{0.5}$	48.38 (48.19)	4.10 (4.08)	7.37 (7.35)	12.12 (12.19)	1607 1644
$\text{ErL}(\text{NO}_3)_3(\text{CH}_3\text{OH})(\text{H}_2\text{O})(\text{C}_3\text{H}_6\text{O})$	49.29 (49.10)	4.37 (4.34)	7.05 (7.03)	11.96 (12.00)	1604 1632
$\text{NdL}_2(\text{H}_2\text{O})_9(\text{ClO}_4)_3$	51.41 (51.53)	4.67 (4.65)	4.52 (4.54)	5.81 (5.84)	1605 1638

^a Data in parentheses are calculated values.

Download English Version:

<https://daneshyari.com/en/article/1331312>

Download Persian Version:

<https://daneshyari.com/article/1331312>

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