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Lanthanide coordination polymers constructed by a new semirigid bridging salicylamide ligand: Synthesis, supramolecular structure and luminescence properties

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ABSTRACT

A new semirigid *exo*-bidentate ligand was designed, synthesized, and used as building blocks for constructing lanthanide polymers both with interesting supramolecular structures and luminescent properties. Among a series of lanthanide nitrate complexes which have been characterized by elemental analysis, X-ray powder diffraction, IR spectroscopy and molar conductance analysis, five new coordination polymers have been determined using X-ray diffraction analysis. All the coordination polymers exhibit the same metal-to-ligand molar ratio of 1:1 and the semirigid *exo*-bidentate ligand as a bridging ligand, reacts with lanthanide nitrates forming a zigzag chain which further interconnected to three dimensional supramolecular structure in aid of cooperative C–H···O hydrogen bond and π–π stacking interactions. The europium and terbium containing compounds exhibit luminescence of the referring trivalent lanthanide ions, giving a red luminescence for EuIII and a green luminescence for TbIII triggered by an efficient antenna effect of the picolylsalicylamide group.

1. Introduction

The emergence of hybrid materials constructed of metal nodes and organic bridging ligands, coordination polymers, has significantly enriched the domain of porous materials [1]. Many factors have been found to influence the network and the topology of coordination polymers, such as the coordination geometry of the metal ions, solvents systems, counter anions, and metal-to-ligand ratios. In principle, selection and synthesis of the organic bridging ligands represents a key step in the design of the architectures of the coordination polymers with specific functionalities. By carefully modifying the size and flexibility of the ligand, numerous 1D, 2D, and 3D architectures have been constructed [2]. Europium and terbium-based complexes are of special interest for optical excitation and emission studies because they exhibit high luminescent quantum efficiencies, and the details of their excitation and emission spectra are particularly sensitive to structural details of the coordination environment [3]. In recent years, various organic ligands used for constructing lanthanide coordination polymers have been synthesized [4–6]. Among these numerous ligands, the salicylamide derivatives provide a fascinating prospect in preparing lanthanide coordination polymers possessing strong luminescence properties [7] which prompts us to synthesize and investigate analogs of the extensive series of these ligands.

In a recent paper [7b], we described the crystal structure and luminescent properties of lanthanide complex with a ligand which incorporated 2,3-dimethoxy-naphthalene as a backbone and picolylsalicylamide as pendant arms. The results indicated that the bidentate naphthalene-bridged space ligand is a useful building block in the construction of polymeric and discrete lanthanide complexes with interesting supramolecular properties. Furthermore, The introduction of the methoxyl substituents on the naphthalene backbone lowers the triplet energy leading to a better match with the acceptor $^5D_0$ state of the europium ion than the $^5D_4$ state of terbium.

In this study, we designed and synthesized the new semirigid *exo*-bidentate ligands 1,4-bis{[(2′-picolylaminoformyl)phenoxyl]methyl}-2,5-bismethoxybenzene (L), As a result, six novel lanthanide coordination polymers were obtained and characterized by elemental analysis, X-ray powder diffraction, IR spectroscopy and molar conductance analysis, five of them, namely, $\{[Nd(L)(NO_3)_3{\cdot}CH_3OH{\cdot}H_2O]{\cdot}2CH_3OH\}_\infty$ (**1**), $\{[Sm(L)(NO_3)_3{\cdot}CH_3OH{\cdot}H_2O]{\cdot}2CH_3OH\}_\infty$ (**2**), $\{[Eu(L)(NO_3)_3{\cdot}H_2O]{\cdot}C_4H_8O_2\}_\infty$ (**3**),$\{[Gd(L)(NO_3)_3{\cdot}H_2O]{\cdot}C_4H_8O_2\}_\infty$ (**4**), $\{[Er(L)(NO_3)_3{\cdot}H_2O]{\cdot}C_4H_8O_2\}_\infty$ (**6**) were characterized *via* single-crystal X-ray diffraction analysis. The contraction of the radius of lanthanide ions imposes evident influences upon the coordination geometry. Indeed, the title

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compounds can be grouped into two types: the large Nd and Sm lanthanides form type I; the small ones, Eu, Gd, and Er, form type II. The results presented herein indicated that the new semirigid bridging ligand exhibited a good antennae effect with respect to the TbIII ion due to efficient ligand to metal energy transfer.

2. Experimental

2.1. Materials and instrumentation

Picolylamine was obtained from Alfa Aesar Co. Other commercially available chemicals were of analytical grade and were used without further purification. The lanthanide nitrates [8] were prepared according to the literature method.

The metal ions were determined by EDTA titration using xylenol orange as indicator. Carbon, nitrogen and hydrogen analyses were performed using an EL elemental analyzer. Melting points were determined on a Kofler apparatus. Powder X-ray diffraction patterns (PXRD) were determined with Rigaku-D/Max-II X-ray diffractometer with graphite-monochromatized Cu Kα radiation. Infrared spectra (4000–400 cm^{-1}) were obtained with KBr discs on a Therrno Mattson FTIR spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ solution at room temperature on a Bruker 400 instrument operating at a frequency of 400 MHz and referenced to tetramethylsilane (0.00 ppm) as an internal standard. Chemical shift multiplicities are reported as s = singlet, d = doublet, t = triplet and m = multiplet. Fluorescence measurements of the well grinded thick solid samples were made on FLS920 of Edinburgh Instrument equipped with a xenon lamp as the excitation source (front-face mode). Samples were placed between two quartz cover slips and the excitation and emission slit of 0.2 nm were used. The 77 K solution-state phosphorescence spectra of the GdIII complex was recorded with solution samples (a 1:1 ethyl acetate–MeOH (v/v) mixture) loaded in a quartz tube inside a quartz-walled optical Dewar flask filled with liquid nitrogen in the phosphorescence mode on a Hitachi F-4500 spectrophotometer [9]. Quantum yields were determined by an absolute method [10] 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 line width of the dye-laser output were 10 ns and 0.18 cm^{-1}, respectively. The emission spectra of the sample were collected by two lenses in a monochromator (WDG30), detected by a photomultiplier and processed by a Boxcar Average (EGG model 162) in line with a microcomputer. Reported quantum yields and luminescence lifetimes are averages of at least three independent determinations. The estimated errors for quantum yields and luminescence lifetimes are 10%.

2.2. Synthesis of the ligand

The synthetic route for the ligand (L) is shown in Scheme 1. Picolylsalicylamide was synthesized according to the literature procedure [11] and puried by chromatography on silica, gradient elution from petroleum to 1:4 petroleum–ethyl acetate. 1,4-bis(bromomethyl)-2,5-dimethoxy-benzene was prepared by the literature procedure [12] except that 1,4-dimethyl benzene was replaced by 1,4-dimethoxy benzene.

To a solution of picolylsalicylamide (2.39 g, 10.5 mmol) in dry acetone was added 1.52 g (11 mmol) dried K_2CO_3, and the mixture was stirred for 30 min at room temperature, 1.61 g (5 mmol) 1,4-bis(bromomethyl)-2,5-dimethoxybenzene in 20 ml of dry acetone was added dropwise in 30 min and the resulting solution stirred and heated to reflux for 10 h. After cooling down, inorganic salts were separated by filtration and the solvent removed from the filtrate under reduced pressure. The crude product was recrystallized with ethyl acetate to give a white solid. 2.85 g, Yield 92%. m. p. 134–135 °C. *Anal.* Calc. for $C_{36}H_{34}N_4O_6$: C, 69.89; H, 5.54; N, 9.06. Found: C, 70.07, H, 5.52, N, 9.03%. IR (KBr, ν, cm^{-1}): 3325(s), 2940(m), 2830(w), 1639 (s, C=O), 1599(m), 1525(s), 1485 (m), 1211(m), 1240(s), 1209(s), 752(s). ^1H NMR ($CDCl_3$, 400 MHz): δ: 3.60(s, 6H, OCH_3), 4.75(d, 4H, $NHCH_2$, J = 5.2 Hz), 5.26 (s, 4H, OCH_2), 6.94 (s, 2H, Ar), 7.09 (m, 6H), 7.25 (t, 2H), 7.43 (m, 2H), 7.55 (m, 2H), 8.24 (m, 2H), 8.35 (d, 2H, J = 4.4 Hz), 8.90 (t, 2H, NH).

2.3. Synthesis of the complexes

0.1 mmol (0.062 g) of ligand and 1 equiv of the lanthanide nitrates were dissolved in a hot methanol + ethyl acetate (v/v = 1:10) solution to make a concentrated solution. Then the flask was cooled, and the mixture was filtered into a sealed 10–20 mL glass vial for crystallization at room temperature. After about two weeks single crystals of **1**, **2**, **3**, **4**, **6** suitable for crystal analysis and micro crystals of 5 were obtained. Elemental analysis, molar conductance and IR data for all complexes are summarized in Tables 1 and 2, respectively.

2.4. X-ray single-crystal diffraction analysis

Crystals of complexes **1**, **2**, **3**, **4**, **6** with approximate dimensions of 0.29 × 0.21 × 0.18 mm^3, 0.25 × 0.21 × 0.17 mm^3, 0.21 × 0.18 × 0.15 mm^3, 0.28 × 0.21 × 0.18 mm^3, 0.23 × 0.18 × 0.15 mm^3, suitable for X-ray diffraction, were obtained in good yield by slow evaporation of the mixed solvent (ethyl acetate/methanol = 10:1, v/v) in air over two weeks. The crystals belonged to the triclinic space group $P\bar{1}$ (number 2). The data were collected at 296 K using a Bruker Smart APEX II CCD diffractometer equipped with graphite-monochromatized Mo Cu Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix leastsquares methods on F^2 data using the software package SHELXS-97 [13]. Hydrogen atoms were placed at calculated positions and refined isotropically. Crystallographic data as well as details of data collection and refinement for these complexes are summarized in Table 3, and important bond lengths are listed in Table 4.

3. Results and discussion

3.1. Physical measurements

A ethyl acetate solution of one equivalent of lanthanide(III) nitrate salt was added to a ethyl acetate solution of one equivalent of L. After stirring the reaction solution for 3–4 h, methanol was added to give a clear solution which volatilized to obtain the desired complexes as analytically pure solids. The analytical data for the newly synthesized complexes, listed in Table 1, conforms to a 1:1 metal-to-L stoichiometry. All complexes are soluble in DMF, DMSO, ethanol, methanol, and slightly soluble in ethyl acetate. The molar conductance of the complexes in methanol (see Table 1) indicates that all complexes act as non-electrolytes.

As shown in Table 2, the characteristic band of carbonyl group of free ligand L is shown at 1639 cm^{-1}. The IR spectra of all six complexes are very similar. Consistent with the successful formation of the desired complexes, IR spectroscopy of the six complexes revealed a new band at ca. 1617 cm^{-1}, corresponding to the carbonyl group. Weak absorptions observed in the range of 2900–2950 cm^{-1} can be attributed to the $< xml_del > \upsilon < /xml_del > \nu_{CH_2}$ of the ligand. The ν_3 of the free nitrate group disappears in the spectra of the complexes which is in agreement with the results