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Assembly, crystal structures and luminescent properties of the lanthanide nitrate coordination polymers with 1,5-bis{[(2'-(2-picolylaminoformyl))phenoxyl]methyl}naphthalene

Xu-Huan Yan, Chun-Li Yi, Xiao-Guang Huang, Wei-Sheng Liu, Yu Tang*, Min-Yu Tan

Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

ARTICLE INFO

Article history: Received 23 December 2010 Accepted 28 January 2011 Available online 23 February 2011

Keywords: Amide type bridging ligand Lanthanide Coordination polymers Luminescent properties

ABSTRACT

A new amide type bridging ligand, 1,5-bis{[(2'-(2-picolylaminoformyl))phenoxyl]methyl}naphthalene (L), and its complexes with lanthanide ions (Ln Sm, Eu, Gd, Tb, and Dy) have been designed and assembled. The crystal structures of {[EuL(NO₃)₃(CH₃OH)](H₂O)}_n and [TbL(NO₃)₃(CH₃OH)]_n display one-dimensional (1-D) zig-zag coordination polymeric chains. At the same time, the solid state luminescent properties of the Sm, Eu, Tb, and Dy complexes were investigated at room temperature. The complexes all exhibit characteristic luminescence emissions of the central metal ions under UV light excitation. The lowest triplet state energy level (T₁) of the ligand indicates that the triplet state energy level of the ligand matches better to the resonance level of Tb(III) ion than other lanthanide ions.

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Over the past decade, the construction of supramolecular coordination polymers has attracted great interest because of their potential applications as some functional materials [1]. Remarkably, the vast majority of the reported frameworks are based on transition metal centers. Lanthanide centers have recently attracted the attention of crystal engineers due to their various tantalizing applications such as fluoroimmuno-assays, light-emitting diodes, laser systems, and optical amplification for telecommunication and fascinating topological architectures which can be achieved by their higher coordination numbers and more flexible coordination geometry [2]. As a consequence of the parity rule (and sometimes due to the change in spin multiplicity), lanthanide ions are very poor at absorbing light directly. This problem may be overcome by using a strongly absorbing chromophore to sensitize Ln(III) emission in a process known as the "antenna effect". Considering this, we designed and synthesized a new amide type bridging ligand 1,5-bis{[(2'-(2picolylaminoformyl))phenoxyl]methyl}naphthalene (L), because: (1) the amide ligands that have high extinction coefficients in the near ultraviolet-visible range provide effective absorption of excitation energy, which promotes more effective energy transfer to the lanthanide ions; (2) the ligands possess spheroidal cavities, therefore stabilizing their complexes and shielding the encapsulated ions from interaction with the surroundings; (3) the presence of O and N atoms and aromatic rings may form hydrogen bonds and $\pi-\pi$ stacking interactions, thus to extend and stabilize the whole framework series [3]. The lanthanide (Ln Sm, Eu, Gd, Tb, and Dy) complexes with this ligand have also been synthesized. At the same time, we obtained the crystal structures of the complexes $\{[EuL(NO_3)_3(CH_3OH)](H_2O)\}_n$ and $[TbL(NO_3)_3(CH_3OH)]_n$, which demonstrate one-dimensional (1-D) zig-zag coordination polymeric chain structures. Under the excitation of UV light, Sm(III), Eu(III), Tb(III), and Dy(III) complexes all exhibit characteristic emissions of corresponding central lanthanide ions. The lowest triplet state (T₁) energy level of the ligand L matches better to the resonance level of Tb(III) than other lanthanide ions.

The synthetic route for the ligand L is shown in Scheme 1. A mixture of picolylsalicylamide [4] (5 mmol, 1.142 g) and potassium carbonate (5 mmol, 0.690 g) in 50 cm^3 acetone were refluxed for 30 min, then 1,5-bis(bromomethyl)naphthalene (2.2 mmol, 0.691 g) was added to the solution. The reaction mixture was stirred and refluxed for 12 h and the hot solution was filtered off. The collected organic phase was concentrated in vacuum. Then the resulted solid was recrystallized with acetone to get the ligand L. Yield: 60%. m.p.: 113–116 °C. ¹H NMR (CDCl₃, 200 MHz): 4.52–4.54 (d, 4 H, —CH₂—N), 5.64 (s, 4 H, --CH₂---O), 6.97--8.29(m, 22 H, Ar---H), 8.66 (s, 2 H, N—H). IR (KBr) v: 3372(m), 1651(s, CO), 1596(m), 1542(s), 1446 (m), 1450(s), 1300(s), 1229(s, Ar-O-C), 1163(w), 1104(w), 984 (m), 759(s), 637(s). The lanthanide complexes were prepared by the reaction of Ln(NO₃)₃·6H₂O (Ln Sm, Eu, Gd, Tb, and Dy) and L in 1:1 molar ratio in ethyl acetate and chloroform as white powder. The data of the elemental analysis indicate that the complexes conform to a 1:1 metal-to-ligand stoichiometry [5]. The complexes have the similar IR spectra, of which the characteristic bands have similar shifts, suggesting that they have a similar coordination structure [5]. The molar conductances of the complexes in methanol indicate that all

^{*} Corresponding author. Fax: +86 9318912582. *E-mail address:* tangyu@lzu.edu.cn (Y. Tang).

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Scheme 1. The synthetic route for the ligand L.

complexes act as non-electrolytes [6], implying that all nitrate groups are in coordination sphere.

After several weeks of slow evaporation of the ethyl acetatemethanol solution, the colorless crystals suitable for X-ray analysis of the complexes $\{[EuL(NO_3)_3(CH_3OH)](H_2O)\}_n$ and $[TbL(NO_3)_3(CH_3OH)](H_2O)\}_n$ (CH₃OH)]_n were obtained [7]. The single-crystal X-ray analysis reveals that they possess the same topological structures despite the fact that one crystal water molecule occurs in $\{[EuL(NO_3)_3(CH_3OH)](H_2O)\}_n$. Therefore, only $[TbL(NO_3)_3(CH_3OH)]_n$ is selected for investigation here in detail as a representative example. The crystal analysis unambiguously reveals that the [TbL(NO₃)₃(CH₃OH)]_n crystallizes in the triclinic space group P-1. As shown in Fig. 1a, each Tb(III) ion is coordinated with nine oxygen donor atoms, six of which belong to three bidentate nitrate groups, two belong to carbonyl groups from two bridging ligands and the remaining one to coordinated methanol molecule. The Tb(III) center lies in a distorted tricapped trigonal prism coordination environment. The Tb—O distances are between 2.276(2) and 2.515(2) Å, which are comparable to the corresponding Tb–O bond lengths found in related complexes [8]. At the same time, each ligand binds to two Tb(III) ions using its two oxygen atoms of the amide groups. So the whole structure consists of an infinite array of Tb (III) ions bridged by bidentate ligands and a one-dimensional (1-D) zig-zag coordination polymeric chain is formed. Different from previous reports [3d, 9], an asymmetric unit of compound [TbL (NO₃)₃(CH₃OH)]_n contains two crystallographically independent

ligands and the Tb–Tb separations linked by the bridging ligand are *ca*. 15.78 and 17.46 Å. Through careful study, we found that the major reason is the strong intermolecular hydrogen bonds between the oxygen atoms (O14) of the coordinated methanol molecules and the nitrogen atoms (N1) of terminal pyridyl groups. The schematic view of this 1-D zig-zag chain is shown in Fig. 1b. A deeper view of the compound $[TbL(NO_3)_3(CH_3OH)]_n$ indicates that there are strong intramolecular hydrogen bonds between the amide nitrogen atoms (N2 and N3) and the ether oxygen atoms (O2 and O3).

There were also intermolecular hydrogen bonds between the coordinated ligands and nitrate groups which play an important role in the crystal packing of the complex. In the complex, the coordination chains are linked by intermolecular hydrogen bonds C(6)—H(6B)··O(12) [H(6B)··O(12), 2.50 Å and C(6)—H(6B)··O(12), 128°] to form a two-dimensional (2-D) layer supramolecular structure, as shown in Fig. 2a. In addition, the layers are linked by intermolecular hydrogen bonds C(25)—H(25A)··O(6) [H(25A)··O(6), 2.59 Å and C(25)—H(25A)··O(6), 138°] to form an infinite three-dimensional (3-D) supramolecular framework (Fig. 2b). It is no doubt to note that the robust hydrogen bonds may have a template effect and participate in the stabilization of the complex architectures and may enhance the luminescent properties.

Excited by the absorption band at 327 nm, the free ligand exhibits a broad emission band (λ_{max} = 447 nm). And the solid state luminescent properties of the Sm(III), Eu(III), Tb(III), and Dy(III) complexes were investigated at room temperature (the excitation and emission slit widths were 2.5 and 1.0 nm except for Sm(III) complex with the excitation and emission slit widths being 2.5 and 2.5 nm). The solid state excitation and emission spectra of the complexes at room temperature are shown in Fig. 3. The excitation spectrum of {[EuL (NO₃)₃(CH₃OH)](H₂O)}_n has negligible contribution from the ligand and exhibits a series of sharp lines characteristic of the Eu(III) energy-level structure and can be assigned to transitions between the ⁷F_{0,1} and ⁵L₆, ⁵D_{2,1} levels [10]. The intensity of the ⁵D₀ \rightarrow ⁷F₁ transition (magnetic dipole), which indicates that the coordination environment of the Eu (III) ion is asymmetric [11], which is confirmed by crystallographic



Fig. 1. (a) The local coordination environment of Tb(III) in compound $[TbL(NO_3)_3(CH_3OH)]_n$. (b) 1-D coordination polymer chain of Tb(III) complex (hydrogen atoms are omitted for clarity). The key bond distances and angles (Å and °): Tb(1)–O(4) 2.2759(18), Tb(1)–O(1) 2.2880(18), Tb(1)–O(14) 2.427(2), Tb(1)–O(13) 2.434(2), Tb(1)–O(5) 2.448(2), Tb(1)–O(11) 2.482(2), Tb(1)–O(7) 2.484(2), Tb(1)–O(8) 2.487(2), Tb(1)–O(10) 2.515(2) and O(4)–Tb(1)–O(1) 149.29(8), O(5)–Tb(1)–O(7) 51.41(7), O(13)–Tb(1)–O(11) 51.63(7), O(8)–Tb(1)–O(10) 51.03(6).



Fig. 2. (a) 2-D supramolecular layer structure generated by intermolecular hydrogen bonds. (b) 3-D supramolecular structure of [TbL(NO₃)₃(CH₃OH)]_n generated by intermolecular hydrogen bonds. (The hydrogen atoms without formed hydrogen bonds and the benzyl groups of the ligands are omitted for clarity).

analysis. For the complex [TbL(NO₃)₃(CH₃OH)]_n, the excitation spectrum exhibits a broad excitation band (BEB) between 250 and 500 nm. indicating that energy can transfer efficiently from the ligand to the Tb (III) center. There are four characteristic peaks shown in Fig. 3b, which are assigned to the ${}^{5}D_{4} \rightarrow {}^{7}F_{I}$ (I = 6, 5, 4, 3) transitions. The solid state luminescence lifetime values of the Eu(III) and Tb(III) complexes were determined to be 0.687 ± 0.001 ms and 0.805 ± 0.001 ms from the luminescence decay profile at room temperature by fitting with a monoexponential curve. For the Sm(III) and Dy(III) complexes, the characteristic emission bands can also be observed in the emission spectra, which are attributed to ${}^{4}G_{5/2} \rightarrow {}^{6}H_{I}$ (I = 5/2, 7/2) and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{I}$ (J = 15/2, 13/2) transitions respectively. The fluorescence quantum yield, Φ , of the Sm(III), Eu(III), Tb(III), and Dy(III) complexes in the solid state were found to be 0.39%, 3.12%, 7.97%, and 0.82% using an integrating sphere, respectively. The emission intensity and fluorescence quantum yield of the Tb(III) complex are the strongest among these four complexes under the same conditions.

We have investigated the energy transfer processes in order to elucidate the phenomenon. The triplet excited energy-level T₁ datum of the ligand L is 22, 727 cm⁻¹ (440 nm), which was calculated by the low-temperature (77 K) phosphorescence spectrum of the complex [GdL(NO₃)₃]_n·3H₂O in a 1:1 methanol–ethanol mixture [12]. The triplet energy level of the ligand L is higher than the lowest excited resonance levels ${}^{4}G_{5/2}$ of Sm(III) (17,900 cm⁻¹), ${}^{5}D_{0}$ of Eu(III) (17,300 cm⁻¹), ${}^{5}D_{4}$ of Tb(III) (20,500 cm⁻¹), and ${}^{4}F_{9/2}$ of Dy(III) (21,000 cm⁻¹). This therefore supports the observation of the characteristic emissions of central Sm(III), Eu(III), Tb(III) or Dy(III) ions in the emission spectra of the complexes. And we may deduce that the triplet state energy level T₁ of this ligand L matches better to the lowest resonance level of Tb(III) ($\Delta\nu = 2227$ cm⁻¹) than that of

Sm(III) $(\Delta \nu = 4827 \text{ cm}^{-1})$, Eu(III) $(\Delta \nu = 5427 \text{ cm}^{-1})$, and Dy(III) $(\Delta \nu = 1727 \text{ cm}^{-1})$ ions, because such larger or smaller overlap between the ligands and lanthanide ions excited states result in the non-radiative deactivation of the lanthanide emitting state and quench the luminescence of the complexes [13].

In summary, we have designed and synthesized a new amide type ligand 1,5-bis{[(2'-(2-picolylaminoformyl))phenoxyl]methyl}naphthalene (L). Furthermore, the one-dimensional (1-D) lanthanide zigzag coordination polymers { $[EuL(NO_3)_3(CH_3OH)](H_2O)\}_n$ and [TbL $(NO_3)_3(CH_3OH)]_n$ were assembled using this ligand. In addition, the three-dimensional supramolecular structures were formed by the hydrogen bonds between the chains. And the robust hydrogen bonds may have a template effect and participate in the stabilization of the architectures and enhance the luminescent properties of the complexes. The Sm(III), Eu(III), Tb(III), and Dy(III) complexes all exhibit characteristic emissions of the central metal ions under the UV excitation. This indicates that the ligand L can absorb and transfer energy to lanthanide ions. From a more general perspective, these new complexes may have applications in luminescence materials. On the other hand, a series of new ligands could be designed and synthesized to optimize the luminescent properties of the lanthanide ions based on these results.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Project 20931003, 21071068), the Natural Science Foundation of Gansu Province (Project 1010RJZA121), and the program for New Century Excellent Talents in University (NCET-06-0902).



Fig. 3. Excitation and emission spectra of the samples of Eu(III) complex (a), Tb(III) complex (b), Sm(III) complex (c), and Dy(III) complex (d) in the solid state at room temperature.

Appendix A. Supplementary material

Crystallographic data for the structures reported in this paper have deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 802510 and 802511. Copies of the data can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB2 1EW, UK (email: deposit@ccdc.cam.ac. uk). Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.01.043.

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radiation ($\lambda = 0.71073$ Å). Semiempirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Analytical expressions of neutral atom scattering factors were eamployed, and anomalous dispersion corrections were incorporated. Crystal data: {[EuL(NO₃)₃(CH₃OH)] (H₂O)]₈: crystal dimensions: 0.21 × 0.20 × 0.18 mm³, $F_w = 1977.45$, Triclinic, space group P-1, a = 10.4447(8) Å, b = 10.9008(7) Å, c = 19.0476(15) Å, $\alpha = 94.550(3)^\circ$, $\beta = 90.182(3)^\circ$, $\gamma = 111.027(2)$, V = 2016.7(3) Å³, Z = 1, Dc = 1.628 mg/m³, $F_w = 0.9557$; [TbL(NO₃)₃(CH₃OH)]₈: crystal dimensions: 0.37 × 0.33 × 0.32 mm³, $F_w = 985.67$, Triclinic, space group P-1, a = 10.4462(10) Å, b = 10.8948(10) Å, c = 19.0659(18) Å, $\alpha = 94.608(4)^\circ$, $\beta = 90.209(4)^\circ$, $\gamma = 111.056(4)$, V = 2015.8(3) Å³, Z = 2, Dc = 1.624 mg/m³, F (000) = 992, GOF = 1.009, final *R* indices [I > 20(I)]: $R_1 = 0.0225$, w $R_2 = 0.0557$ [TbL(NO₃)₃(CH₃OH)], COD = 0.0606. [8] (a) X.Q. Song, W. Dou, W.S. Liu, J.N. Yao, Y.L. Guo, X.L. Tang, Design, synthesis,

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