

Controlled Assembly of Dinuclear Metallorings into 1D Coordination Polymer and Mixed-metal Rare Earth Complexes with Red-to-Green Luminescence Properties

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Novel rings connected by chains 1D coordination polymer of rare earth complex have been rationally synthesized by the reaction of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and L, 1,4-bis{[(2'-benzylaminoformyl)phenoxy]methyl}benzene. The functional terminal groups (*N*-benzylsalicylamide) can activate both Eu^{3+} and Tb^{3+} to give out their characteristic lights and the mixed-metal complexes of different ratio of these metals have also been prepared. According to the principle of paints, these complexes give out red-to-green luminescence under UV light, so the complexes with yellow and orange luminescence properties have been realized.

The design and synthesis of extended frameworks via metal-ligand coordination have received intense attention because of their promising applications.¹ Over the past decade, 1D and multidimensional infinite structures with specific topologies have been obtained by assembly of suitable metal ions with bridging ligands, and the principles of recognition-driven, spontaneous self-assembly have been further elucidated. In these processes, the combination of binding constraints and geometrical requirements has been considered as one of the key factors.²

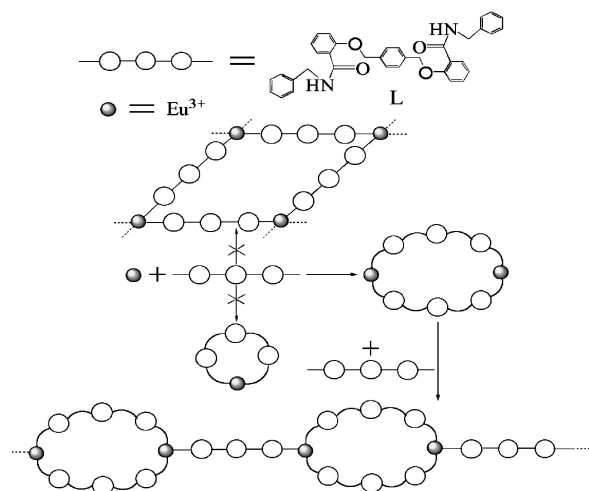
It has been demonstrated that if discrete metallosupramolecular species contain additional peripheral binding sites they can assemble into 1D polymeric structure.³ Similarly, the metallorings with two metal junctions, which contain additional binding sites, can also assemble into 1D polymer by the link of bridging ligands. It is important to understand the principles when designing and synthesizing some intricate and functional metallosupramolecular structure.

We report here a novel 1D metallosupramolecular polymer⁴ $\{[\text{Eu}(\text{NO}_3)_3]_2\text{L}_3\}_n$ generated from the reaction of $\text{Eu}(\text{NO}_3)_3$ with a new aryl amide type bifunctional bridging ligand L. The ligand L was prepared by the replacement reaction of 1,4-bis(bromomethyl)benzene and *N*-benzylsalicylamide. The complex was obtained in 63% yield by the reaction of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and L. Colorless crystals suitable for X-ray diffraction were obtained by slow evaporation of the complex solution (methanol and ethyl acetate).

The main features of the ligand can be summarized as follows: 1) The semirigid nature of the skeleton; 2) The distance of two donor atoms is about 15 Å. Therefore, the ligand cannot be bent to form a single molecular ring or spread linearly to form a lattice structure. The semirigid bis-monodentate nature of L makes it suitable for the synthesis of larger size rings; so two ligands have been slightly distorted to form a dinuclear metalloring with two suitable metal centers (Eu^{3+}).⁵ At the same time, these metal centers with high coordination number feature⁶ have additional peripheral binding sites. So these dinuclear metallorings can be linked by other bis-monodentate ligands to form a

1D coordination polymer (Scheme 1).

The complex crystallizes in triclinic, space group $P\bar{1}$. Every asymmetric unit contains two Eu^{3+} centers and three L ligands (Figure 1) with both centers lying on the joints of the 1D coordination polymer. Each metal center binds to nine oxygen donor



Scheme 1. The formation process of 1D coordination polymer.

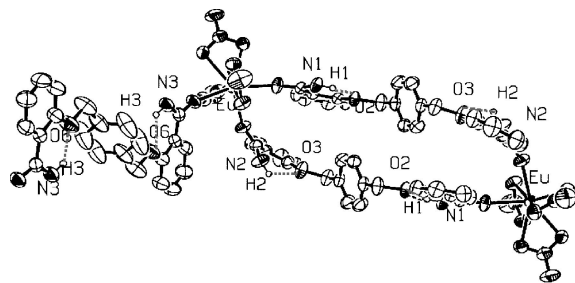


Figure 1. ORTEP drawing of the molecular structure of $[\text{Eu}(\text{NO}_3)_3]_2\text{L}_3$ (intramolecular hydrogen bonds indicated by dashes). Benzyl groups and H atoms (except those involved in hydrogen bond) are omitted for clarity.

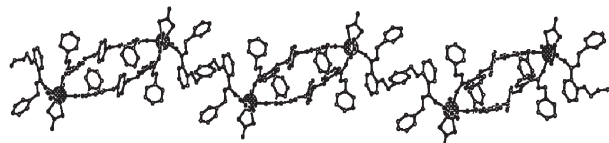


Figure 2. The 1D rings connected by chains coordination polymer of $\{[\text{Eu}(\text{NO}_3)_3]_2\text{L}_3\}_n$, (black ball represents Eu^{3+}).

atoms, three of which belong to carbonyl groups from three different ligands, six to three bidentate nitrate groups. These nitrate groups occupy the binding sites in the vertical plane of the chains, preventing further aggregation,⁷ and two bis-monodentate ligands bind to two metal centers to form 34-membered rings. The other bis-monodentate ligands link the neighboring rings (Figure 2) to form a novel 1D coordination polymer. The assembly consists of two independent, enantiomeric metal centers bridged by two ligands, and is comprised of rings connected by chains. As determined by single-crystal X-ray analysis, the cross-ring Eu–Eu separation is about 16.65 Å and the separation of two metal centers between neighboring rings is about 17.97 Å, which is slightly longer than that of intrarings. Furthermore, the skeletons of two ligands are near to each other and the vertical separation of their least-square planes is 4.064 Å. This gives an optimal charge separation, which presumably has a beneficial influence on the formation of the metalloring entities.⁸

Like most of the coordination polymers, hydrogen bonds are involved in this complex, but all of them are belonged to intramolecular hydrogen bonds (Figure 1, linked by dashes). The corresponding benzyl groups of two ligands in these rings have no overlap section in the vertical orientation in spite of their parallelism. So the common intermolecular interactions (π – π stacking and hydrogen bond) in coordination polymers do not exist in the structure we reported here, and an independent 1D coordination polymer comprised of rings connected by chains of rare earth complex is firstly obtained.

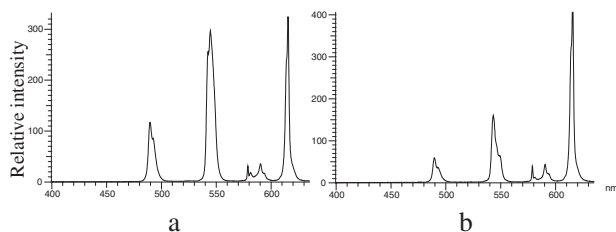


Figure 3. Fluorescence spectrum (excitation at 325 nm) of complexes with yellow and orange luminescence properties (the main emission bands at 498 and 545 nm are ascribed to Tb^{3+} and that at 616 nm to Eu^{3+}).

The complexes of this ligand with $\text{Eu}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$ have been synthesized and characterized. The analytic data show that they have the same composition and coordination circumstances. At the same time, the Eu^{3+} and Tb^{3+} ions have the same valence and similar radius. On the basis of these results, it is easy to infer that they have the same 1D coordination polymer structure.

As expected, the functional terminal groups, *N*-benzylsalicylamide, have maintained the conjugate chromogen of salicylic acid to activate both Eu^{3+} and Tb^{3+} ions to give out their characteristic lights. According to the principle of paints, a series of mixed-metal coordination polymers of Eu^{3+} and Tb^{3+} in ionic

level have been synthesized by adjusting the proportions of $\text{Eu}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$ when preparing complexes. Although the accurate contents of two ions in these complexes cannot be known, their luminescence properties changed from red to green little by little, indicating both ions existed in the polymers. So the lanthanide complexes with luminescence properties from red to green have been realized. For example, the complex of mixed-salt ($\text{Eu}(\text{NO}_3)_3\text{:Tb}(\text{NO}_3)_3 = 10\text{:}1$) shows yellow luminescence (Figure 3a) and another one ($\text{Eu}(\text{NO}_3)_3\text{:Tb}(\text{NO}_3)_3 = 20\text{:}1$) shows orange (Figure 3b) luminescence under UV light.

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