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Synthesis of Eu(III) and Tb(III) Complexes with Two New Aryl Amide Type Tetrapodal Ligands and Their Luminescence Properties

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Lanthanide complexes have been attracted much attention for their important applications [1]. In particular, Eu(III) and Tb(III) are characterized by long-lived (ms timescale) and strong luminescent electronically excited states, which makes them important in analytical chemistry [2]. Among these, the complexes of Eu(III) and Tb(III) with alkyl amide have been widely investigated, but their luminescence was very weak. The energy transfer from ligand to central metal (antenna effect) should be the main reason for this. Aryl amide ligand is anticipated to have stronger antenna effect to Eu(III) and Tb(III), and few complexes of this kind have been reported [3]. So we used N-benzylsalicylamide and two different rigid central skeletons to synthesis two new aryl amide type tetrapodal ligands L_I (1,1,1,1-tetrakis-{[(2-benzylaminoformyl)phenoxyl]methyl}methane) and L_{II} (1,2,4,5-tetrakis-{[(2-benzylaminoformyl)phenoxyl]methyl}benzene). Their complexes of $Eu(NO_3)_3$ and $Tb(NO_3)_3$ were also synthesized and characterized. The results suggested that these complexes of two ligands had different metal-to-ligand stoichiometry in spite of identical conductivity. Furthermore, their luminescence properties were also studied. The results indicated that the tetrapodal ligand with alkyl being used as the central skeleton has a stronger antenna effect to Eu(III) and Tb(III) than that with phenol.

The two ligands could be easily prepared from the replacement reaction of 1,1,1,1-tetrakis-(*p*-tosyloxymethyl)-methane [4] and 1,2,4,5-tetrakis-(bromomethyl) benzene [5] with N-benzylsalicylamide [6]. The synthetic routes are shown in Figure 1. Their complexes were synthesized with corresponding ligands and lanthanide nitrate salts in chloroform and ethyl acetate.

Analytical data of the complexes are listed in Table 1. The elemental analytical data and the content of metal confirm 3:2 (complexes of L_I) and 1:1 (complexes of L_{II})

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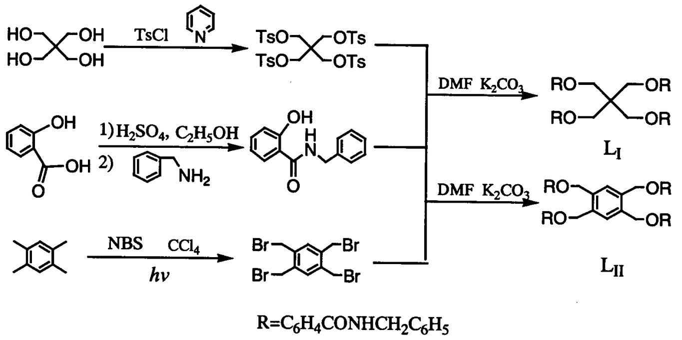

Figure 1. Preparation of ligands L_I and L_{II}.

metal-to-ligand stoichiometry respectively. The difference in stoichiometry is a surprising result. Considering the structure of two ligands, it can be explained as follows: (1) The branches of two ligands have half-rigid nature, which makes them as bridging ligands to form complicated coordination polymer instead of encapsulating structure [3]. (2) The different rigid central skeleton leads to great differences in coordination structure of their complexes, and this also may be the key factor that make these complexes different in coordination stoichiometry. The study on confirmed structure is in process.

Free ligands L_I and L_{II} both exhibit two absorption bands at about 1649 cm^{-1} (C=O) and 1105 cm^{-1} (Ar–O–). The complexes also exhibit these two bands, but the low energy band (1105 cm^{-1}) almost remain unchanged and the high energy band (1649 cm^{-1}) red shifts to about 1607 cm^{-1} ($\Delta\nu = 42$ cm^{-1}), indicating that only the oxygen atom of C=O takes part in coordination to the metal ions. For the four complexes, there are new absorption bands at about 1628 cm^{-1} (complexes of L_I) or 1645 cm^{-1} (complexes of L_{II}), which were occurred from the C=O of coordinated $CH_3COOC_2H_5$. Additionally, bands at 1384 cm^{-1} in the spectra of complexes indicate that free nitrate groups (D_{3h}) exist. Two intense absorptions associated with the asymmetric stretching appear in the ranges 1290–1306 (ν_4) and 1482–1489 (ν_1) cm^{-1}, clearly indicating that the NO_3^- groups (C_{2v}) are coordinated [7]. The separation of the two bands is about 180 cm^{-1} in the complexes, which indicates that the NO_3^- groups are bidentate ligands [8].

Table 1. Analytical data for the complexes.

Complexes	Content of metal found % (calc.)	IR (cm^{-1})		λ ($Scm^2\ mol^{-1}$) (CH_3OH, 25°C)
		C=O	Ar–O	
$[Eu(NO_3)_3]_3(L_I)_2 \cdot CH_3COOC_2H_5$	14.5 (14.9)	1606	1110	175.6
$[Tb(NO_3)_3]_3(L_I)_2 \cdot CH_3COOC_2H_5$	15.9 (15.5)	1608	1110	179.3
$[Eu(NO_3)_3](L_{II}) \cdot 2H_2O \cdot CH_3COOC_2H_5$	10.5 (10.3)	1606	1108	195.3
$[Tb(NO_3)_3](L_{II}) \cdot 2H_2O \cdot CH_3COOC_2H_5$	10.4 (10.7)	1609	1108	198.2

The molar conductivity of the complexes is 170–200 $Scm^2\ mol^{-1}$, indicating that two free nitrate groups existed in each molar complex and these complexes are all 2:1 (160–220) type of electrolytes [9], which is consistent with the result of IR spectra.

As we know, the better the triplet-state level of the ligand matches with the lowest excited state level of metal center, the more effective energy transfer will occur, thus, the luminescence emission will be more completely quenched. So the antenna effect ability of the ligand can be found from the ligand luminescence emission in the complex luminescence spectra. This ability is only determined by the nature of ligand. So the change in structure of ligand will influence the antenna effect ability of ligand. In this paper, although there are differences in coordination number and environment of the metal ion, they should not be the obstacles to our qualitative investigation in the antenna effect of the two ligands.

The complexes of L_I and L_{II} all have strong luminescence properties. In order to compare the influence of different skeleton on antenna effect, the luminescence spectra of the ligands and their Eu(III) and Tb(III) complexes in solid state were recorded at room temperature. The emission spectra of the complexes are shown in Figure 2.

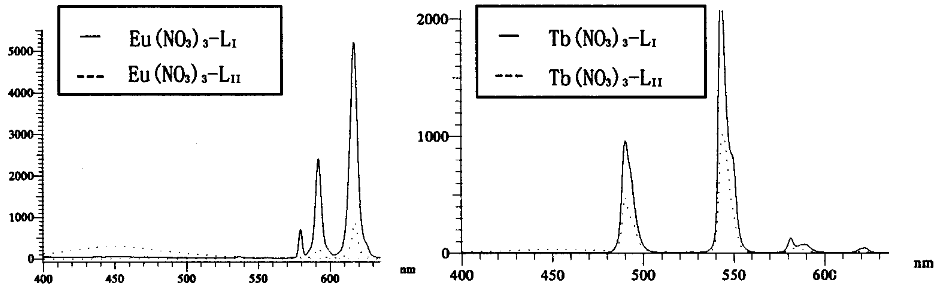

Figure 2. Emission spectra of complexes in solid state (excited at 325 nm).

Excited by the absorption band at 325 nm, the free ligands exhibit broad emission bands ($\lambda_{max} = 450$ nm), which is due to the π-π^* transition of the ligand. All the complexes show the characteristic emissions of Eu(III) and Tb(III) respectively, indicating that both ligands are good chelates to transfer energy to metal ions. In the two spectra of Eu(III) complexes, the relative intensity of $^5D_0 \to {}^7F_2$ is more intense than that of $^5D_0 \to {}^7F_1$, showing that the Eu(III) ion does not lie in a centro-symmetric coordination site [10]. The spectra of Tb(III) complexes showed the expected sequence of $^5D_4 \to {}^7F_J$ transitions (J = 6, 5, 4, 3). In addition, the complexes of L_I showed no emission bands at 450 nm, but the emission bands in the complexes of L_{II} are still visible, suggesting that the energy transfer (antenna effect) in the complexes of L_I is more effective [11]. This result is consistent with that of our recent reports [12]. So we can conclude that the antenna effect of alkyl, being used as the central skeleton, is stronger than that of phenyl and the main reason should be the rigidity of the skeleton.

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