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Photoluminescence via Two Different Excited States in a Mononuclear Europium(III) Complex with Tetradentate Schiff Base Ligands

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A europium(III) complex with tetradentate Schiff base ligands $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$ was prepared, and its structure was determined by X-ray crystal structure analysis. The complex has an eight-coordinate mononuclear structure with two Schiff base ligands in a *meridional* form. The complex displays emission bands resulting from f–f transitions by excitation at 357 or 234 nm in acetonitrile.

The tetradentate Schiff base salen ligand (H_2salen: *N*,*N*′-bissalicylidene-1,2-ethanediamine) is a versatile ligand, and many transition-metal complexes with salen and its related ligands have been reported. Lanthanide(III) complexes with salen-type ligands form various structures. For example, mononuclear,[1–4] dinuclear,[5–7] tetranuclear,[8] pentanuclear,[9] and polynuclear[10–12] lanthanide(III) complexes have been prepared by different synthetic methods, under various conditions. Photoluminescence is one of the distinctive properties of lanthanide(III) complexes. Many different photoluminescent europium(III) complexes have been reported.[13] As for europium(III) complexes with the salen ligand, photoluminescence properties of mononuclear pipH[Eu(salen)$_2$] and dinuclear [Eu$_2$(salen)$_3$]•0.3DMSO have been reported.[3,5] However, the structures of these complexes have not been determined by X-ray crystal structure analysis. When discussing the photoluminescence of Schiff base lanthanide(III) complexes, the crystal structure should be taken into account. In this study, we report on the preparation, crystal structure, and photoluminescence properties of the newly prepared mononuclear europium(III) complex with tetradentate Schiff base ligands, $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$ ($H_2$3,5Clsalen: *N*,*N*′-bis-3,5-dichlorosalicylidene-1,2-ethanediamine). The Schiff base ligands used in this study are well known and prepared easily. However, the europium(III) complexes show new notable photoluminescence properties. To the best of our knowledge, this is the first study of photoluminescence via two excitation states in a Schiff base–europium(III) complex. The Schiff base–europium(III) complexes can be developed systematically as new luminescence materials.

A yellow-white europium(III) complex, $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$, was prepared by the reaction of europium(III) acetate with the Schiff base ligand in methanol. The Schiff base ligand (0.203 g, 0.50 mmol) and $Eu(CH_3COO)_3 \cdot 4H_2O$ (0.100 g, 0.25 mmol) were added to a methanol solution (30 cm^3) containing triethylamine (4 mmol). The reaction mixture was stirred at 60 °C for 1 h. The resulting yellow-white precipitate was collected by filtration and washed with methanol.[14] The reaction of H_2salen with $Eu(CH_3COO)_3 \cdot 4H_2O$ yielded a yellow precipitate in a similar manner. However, the molecular structure of the compound could not be assigned by elemental analysis.[15]

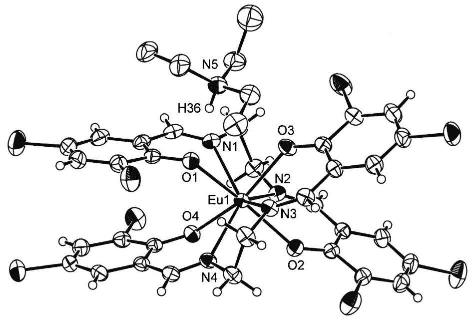

Figure 1. An ORTEP drawing of $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$ with 30% probability ellipsoids. Hydrogen atoms attached to the carbon atoms of the triethlylammonium cation are omitted for simplicity. Selected bond lengths (Å): Eu1–O1 2.377(2); Eu1–O2 2.285(2); Eu1–O3 2.285(2); Eu1–O4 2.322(2); Eu1–N1 2.583(3); Eu1–N2 2.579(3); Eu1–N3 2.588(2); Eu1–N4 2.558(3).

An X-ray crystal structure analysis of $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$ was carried out.[16] An ORTEP drawing of the complex is shown in Figure 1. The two tetradentate Schiff base ligands display *meridional* coordination,[17] and the complex has a mononuclear structure. The geometry around the europium(III) ion can be described as an eight-coordinate square antiprism. The five-membered N–N chelate rings assume a *gauche* form. The H36 atom of the triethylammonium cation is strongly hydrogen-bonded to the O1 atom of the complex anion {N5…O1: 2.816(4) Å}. The dihedral angles between the adjacent two phenyl rings are 8.9(2)° for the two salicylaldehyde moieties containing O1 and O4 atoms and 42.1(1)° for the two salicylaldehyde moieties containing O2 and O3 atoms. Similar crystal structures of mononuclear lanthanide(III) complexes, pipH[Er(salen)$_2$] (pip: piperidine) and [Eu(Hsalen)(salen)], have been reported.[1,2] The amine proton of the pipH cation is also hydrogen-bonded to the phenolate oxygen atoms of the complex anion in pipH[Er(salen)$_2$] (N…O: 2.746 and 2.832 Å). On the other hand, no counter cation is present in [Eu(Hsalen)(salen)].

Emission and excitation spectra of $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$ in acetonitrile are shown in Figure 2. By excitation with 357 or 234 nm light, the complex displays a sharp strong emission band at 613 nm ($^5D_0 \rightarrow {}^7F_2$) with weak emission bands at 580 nm ($^5D_0 \rightarrow {}^7F_0$), 589, 595 nm ($^5D_0 \rightarrow {}^7F_1$), 654, 658 nm ($^5D_0 \rightarrow {}^7F_3$), and 697, 706 nm ($^5D_0 \rightarrow {}^7F_4$). The $^5D_0 \rightarrow {}^7F_2$ transition is predominantly electric-dipolar in character, and the emission intensity of the transition is sensitive to the coordination environment around the europium(III) ion.[18] Two separate excitation peaks are observed at 357 and 234 nm.

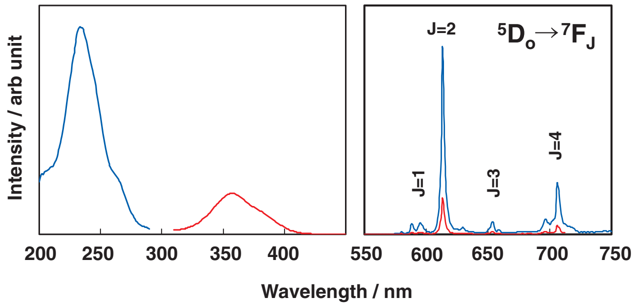

Figure 2. Emission and excitation spectra of $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$ in acetonitrile at 298 K. The emission spectra were measured by excitation at 357 nm (—) or 234 nm (—). The excitation spectra were measured with emission wavelength at 613 nm. The concentration is 2.00×10^{-6} M. Measurements were carried out in the same conditions.

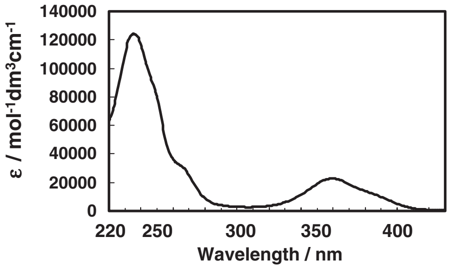

Figure 3. Electronic spectrum of $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$ in acetonitrile.

The excitation spectrum of the complex is very similar to the electronic spectrum in acetonitrile (Figure 3). The electronic spectrum of $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$ shows absorption peaks at 360 and 236 nm ($\varepsilon = 2.28 \times 10^4\,M^{-1}\,cm^{-1}$ at 360 nm, and $1.24 \times 10^5\,M^{-1}\,cm^{-1}$ at 236 nm). The former could be assigned to π–π^* transition of the –C=N– chromophore, and the latter could be assigned to π–π^* transition of the phenolate moieties.[19,20] These results indicate that the europium(III) complex displays f–f emission bands by energy transfer from the different excited states. The photoluminescence via two different excited states has not been reported in $pipH[Eu(salen)_2]$ and $[Eu_2(salen)_3]\cdot0.3DMSO$.[3,5] The photoluminescence quantum yields in acetonitrile obtained by a comparative method are 0.277 ($\lambda_{ex} = 357$ nm) and 0.0482 ($\lambda_{ex} = 234$ nm), respectively.[21–23] The luminescence lifetimes are 0.50 ms ($\lambda_{ex} = 357$ nm) and 0.51 ms ($\lambda_{ex} = 234$ nm), respectively. It is notable that the quantum yield measured with 357 nm excitation is larger than that measured with 234 nm excitation, whereas the lifetimes are almost the same. The considerably different quantum yields by excitation at 357 or 234 nm may be originated from different energy-transfer paths from the ligand to europium(III) ion.

The europium(III) complex, $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$ is also photoluminescent in the solid state. The emission spectrum in the solid state is similar to that measured in acetonitrile.[24,25] Since the shapes of emission spectra are similar in the solid state and in acetonitrile, it is supposed that the complex keeps a mononuclear structure in acetonitrile as well as in the solid state. The quantum yield in the solid state obtained by an absolute method at room temperature is 0.31 ($\lambda_{ex} = 360$ nm).

In this study, a new mononuclear europium(III) complex with Schiff base ligands was prepared, and its photoluminescence properties were studied. Further investigations are necessary to elucidate the energy transfer from the two different excited states. The influence of different diamine moieties and counter cations for the photoluminescence properties of Schiff base–europium(III) complexes is now under investigation.

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14 Yield: $(C_2H_5)_3NH[Eu(3,5Clsalen)_2]$: 0.247 g (93%). Anal. Found: C, 42.83; H, 3.21; N, 6.43%. Calcd for $C_{38}H_{36}N_5O_4Cl_8Eu$: C, 42.96; H, 3.42; N, 6.59%.
15 Yield: 0.174 g. Anal. Found: C, 47.91; H, 4.14; N, 6.87%. The elemental analytical data does not coincident with the calculated analytical data of $(C_2H_5)_3NH[Eu(salen)_2]$ or $[Eu_2(salen)_3]$. This complex does not show photoluminescence in the solid state.
16 Single crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from acetonitrile. Crystal data: $C_{38}H_{36}N_5O_4Cl_8Eu$, $M_r = 1062.32$, monoclinic, $P2_1/n$, $a = 14.5497(3)$, $b = 19.3579(4)$, $c = 15.5456(4)$ Å, $V = 4326.8(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.631\,g\,cm^{-3}$, $\mu(Mo\,K\alpha) = 1.985\,mm^{-1}$, 11410 reflections measured, 11090 unique reflections. There was a disorder on the C34 atom of the triethylammonium ion. The R value was 0.043 for the 10455 reflections with $I > 2\sigma(I)$. The R_w value was 0.100 for all the reflections. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-775863.
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20 Electronic spectrum of $[VO(3,5Clsalen)]$ in acetonitrile shows absorption peaks at 375 nm ($\varepsilon = 7.16 \times 10^3\,M^{-1}\,cm^{-1}$) and 251 nm ($\varepsilon = 4.44 \times 10^4\,M^{-1}\,cm^{-1}$).
21 The quantum yields and lifetimes at room temperature were recorded with a Hitachi F-7000 fluorescence spectrophotometer. The luminescence quantum yield with 357 nm excitation was measured utilizing quinine sulfate as a standard ($\phi = 0.546$ in 0.500 M aqueous H_2SO_4 solution, ref 22), and that with 234 nm excitation was measured utilizing anthracene as a standard ($\phi = 0.27$ in ethanol solution, ref 23). The lifetimes were obtained by using the attachment program of time-domain phosphorescence lifetime measurement with optical chopping of excitation light.
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24 The emission and excitation spectra in the solid state are deposited (Figure S1).
25 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.