



Luminescent europium(III) complexes of tripodal heptadentate N₇ ligands containing three imidazole groups

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ABSTRACT

Luminescent Eu^{III} complexes with tripodal heptadentate N₇ ligands containing three imidazole groups, [Eu^{III}(H₃L^{2-H})(ac)](ClO₄)₂·H₂O (**1**), [Eu^{III}(H₃L^{2-Me})(ac)](ClO₄)₂·2EtOH (**2**), and [Eu^{III}(H₃L^{4-Me})(ac)](ClO₄)₂·H₂O (**3**), were synthesized and characterized, where H₃L^{2-H}, H₃L^{2-Me}, and H₃L^{4-Me} are the tripodal ligands derived from the 1:3 condensation of tris(2-aminoethyl)amine and either 4-formylimidazole, 2-methyl-4-formylimidazole, and 4-methyl-5-formylimidazole, respectively, and ac denotes an acetate ion. Single-crystal X-ray analyses revealed that each Eu^{III} ion is coordinated by a tripodal heptadentate N₇ ligand and two oxygen atoms of the acetate ion as a bidentate ligand. The complexes displayed sharp emission bands based on the f–f transitions by excitation at 261 nm in acetonitrile. The emission intensities increased in the order **1** < **2** < **3** in acetonitrile, while the emission spectra were quenched in aqueous solution due to the partial dissociation of the acetate ion and tripodal ligand.

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1. Introduction

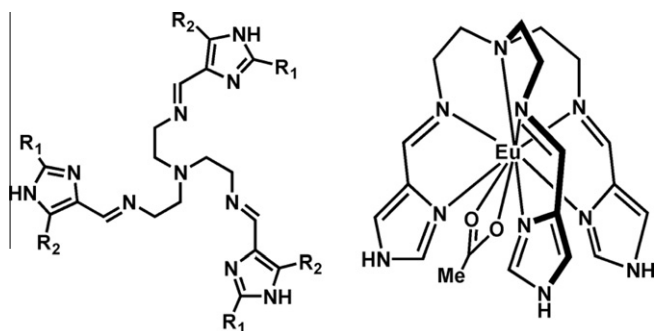
Luminescent lanthanide complexes have attracted considerable attention due to their potential uses as fluorescent sensors and luminescent probes [1–7]. Lanthanide complexes have specific luminescence properties such as large Stokes shifts, sharp emission profiles and long luminescence lifetimes that conventional organic dyes do not have. The lanthanide complexes applicable for an analytical probe must fulfill the following requirements: (i) presence of a suitable absorbing group for strong luminescence with a large luminescence quantum yield and a molar extinction coefficient, in addition to a long luminescence lifetime; (ii) high thermodynamic and kinetic inertness and (iii) solubility in an aqueous buffer [8]. To achieve these properties, it is desired to design a suitable ligand that can completely encapsulate the lanthanide ion. Recently, many luminescent lanthanide complexes with encapsulating ligands have been synthesized [9]. Among them, the tripodal macrocyclic ligands derived from tris(2-aminoethyl)amine and 2,3-dihydroxyterephthalic acid have been demonstrated to provide hosts for the lanthanide ions, three arms of a suitably designed tripodal ligand that can encapsulate the central ions, and the lanthanide complexes are highly luminescent [10]. These results

demonstrate the effectiveness of the tripodal ligand for strong luminescence properties even in solution.

Matsumoto et al. have studied the metal complexes of polydentate ligands involving imidazole groups [11]. We [12–21] and Brewer et al. [22–26] have studied the transition metal complexes of pendant-armed tripodal ligands containing three imidazole groups (see the structure in Scheme 1), where the ligand encapsulates the transition metal ion such as Cu, Co and Fe ions, and the resulting complexes are moderately soluble in water due to the imidazole groups. Since the tripodal heptadentate ligand can encapsulate one lanthanide ion leading to a highly thermodynamically stable lanthanide complex and the resulting lanthanide complexes may be moderately soluble in a polar solvent due to the imidazole groups, it is anticipated that the lanthanide complex can be a good candidate for a stable luminescent complex both in the solid state and solution state. In this study, in order to investigate the structures and luminescent properties of the lanthanide complexes of the tripodal ligands (see the structures in Scheme 1), three Eu^{III} complexes with the formulas of [Eu^{III}(H₃L^{2-H})(ac)](ClO₄)₂·H₂O (**1**), [Eu^{III}(H₃L^{2-Me})(ac)](ClO₄)₂·2EtOH (**2**), and [Eu^{III}(H₃L^{4-Me})(ac)](ClO₄)₂·H₂O (**3**) were synthesized, where H₃L^{2-H} denotes tris{[2-((4-formylimidazole)methylidene)amino]ethyl}amine, H₃L^{2-Me} denotes tris{[2-((2-methyl-4-formylimidazole)methylidene)amino]ethyl}amine, H₃L^{4-Me} denotes tris{[2-((4-methyl-5-formylimidazole)methylidene)amino]ethyl}amine, and ac denotes acetate. We report here the syntheses, crystal structures

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$\text{H}_3\text{L}^{2\text{-H}}$: $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{H}$

$\text{H}_3\text{L}^{2\text{-Me}}$: $\text{R}_1 = \text{Me}$, $\text{R}_2 = \text{H}$

$\text{H}_3\text{L}^{4\text{-Me}}$: $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{Me}$

Scheme 1. Structures of tripodal ligands ($\text{H}_3\text{L}^{2\text{-H}}$, $\text{H}_3\text{L}^{2\text{-Me}}$, $\text{H}_3\text{L}^{4\text{-Me}}$) and $[\text{Eu}^{\text{III}}(\text{H}_3\text{L}^{2\text{-H}})(\text{ac})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**).

and luminescent properties of these compounds. Part of our result was reported in 2007 [27].

2. Experimental

2.1. Caution

Perchlorate salts of metal complexes are potentially explosive. Only small quantities of material should be prepared and the samples should be handled with care.

2.2. Materials

All reagents and solvents used in this study are commercially available from Tokyo Kasei Co., Ltd. and Wako Pure Chemical Industries, Ltd. and were used without further purification.

2.3. Preparations

2.3.1. $[\text{Eu}^{\text{III}}(\text{H}_3\text{L}^{2\text{-H}})(\text{ac})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**)

A solution of tris(2-aminoethyl)amine (0.073 g, 0.5 mmol) in 10 mL of methanol and a solution of 4-formylimidazole (0.144 g, 1.5 mmol) in 10 mL of methanol were mixed, and the mixture was stirred at 50 °C for 1 h and then cooled to room temperature. To the resultant ligand solution ($\text{H}_3\text{L}^{2\text{-H}}$) was added a solution of $\text{Eu}^{\text{III}}(\text{ac})_3 \cdot 4\text{H}_2\text{O}$ (0.200 g, 0.5 mmol) in 10 mL of methanol and the mixture was stirred for 30 min at room temperature. A solution of NaClO_4 (0.122 g, 1 mmol) in 10 mL of methanol was added and

Table 2

Relevant coordination bond distances and hydrogen bond distances (Å) for $[\text{Eu}(\text{H}_3\text{L}^{2\text{-H}})(\text{ac})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**), $[\text{Eu}(\text{H}_3\text{L}^{2\text{-Me}})(\text{ac})](\text{ClO}_4)_2 \cdot 2\text{EtOH}$ (**2**), and $[\text{Eu}(\text{H}_3\text{L}^{4\text{-Me}})(\text{ac})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**3**) at 296 K.

| Complex | (1) | (2) | (3) |
|------------------------------------|-----------|-----------|-----------|
| <i>Coordination bond distances</i> | | | |
| Eu–N(1) | 2.672(9) | 2.728(9) | 2.713(12) |
| Eu–N(2) | 2.545(8) | 2.510(9) | 2.548(16) |
| Eu–N(3) | 2.526(8) | 2.558(7) | 2.579(13) |
| Eu–N(5) | 2.526(8) | 2.538(10) | 2.525(12) |
| Eu–N(6) | 2.552(8) | 2.681(7) | 2.528(12) |
| Eu–N(8) | 2.494(9) | 2.484(7) | 2.509(12) |
| Eu–N(9) | 2.548(8) | 2.551(10) | 2.608(12) |
| Eu–O(1) | 2.468(6) | 2.509(6) | 2.412(12) |
| Eu–O(2) | 2.463(7) | 2.462(6) | 2.453(9) |
| N(2)–Eu(1)–N(5) | 76.6(3) | 74.9(3) | 82.2(5) |
| N(2)–Eu(1)–N(8) | 129.2(3) | 128.3(3) | 128.8(5) |
| N(5)–Eu(1)–N(8) | 86.5(3) | 86.5(3) | 83.1(5) |
| N(3)–Eu(1)–N(6) | 73.6(3) | 77.5(3) | 72.0(4) |
| N(3)–Eu(1)–N(9) | 108.1(3) | 108.8(3) | 116.2(4) |
| N(6)–Eu(1)–N(9) | 70.9(3) | 76.7(3) | 73.8(4) |
| <i>Hydrogen bond distances</i> | | | |
| N(4)–O(1) ^a | 2.910(12) | | |
| N(7)–O(3) | 3.028(15) | | |
| N(10)–O(11) | 2.775(13) | | |
| O(2)–O(11) ^b | 2.699(11) | | |
| O(7)–O(11) | 2.944(16) | | |
| N(4)–O(1) ^c | | 2.767(9) | |
| N(7)–O(12) | | 2.818(14) | |
| N(10)–O(11) | | 2.845 | |
| O(3)–O(11) | | 2.867 | |
| O(7)–O(12) | | 2.79(3) | |
| N(4)–O(2) ^d | | | 2.866(17) |
| N(7)–O(3) ^e | | | 2.938(19) |
| N(10)–O(3) | | | 2.94(2) |
| N(10)–O(7) | | | 2.99(3) |

Symmetry operations:

- ^a $x, -y + 1/2, z + 1/2$.
^b $-x + 2, -y + 1, -z + 1$.
^c $x, y + 1, z$.
^d $-x + 2, -y + 2, -z + 1$.
^e $x, -y + 5/2, z + 1/2$.

the resultant mixture was stirred for 30 min and then filtered. The filtrate was left to stand for several days to give colorless crystals, 49% yield. *Anal.* Calc. for $[\text{Eu}^{\text{III}}(\text{H}_3\text{L}^{2\text{-H}})(\text{ac})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} = \text{C}_{20}\text{H}_{29}\text{N}_{10}\text{O}_{11}\text{Cl}_2\text{Eu}$: C, 29.72; H, 3.62; N, 17.33. Found: C, 30.02; H, 3.56; N, 17.69%.

2.3.2. $[\text{Eu}^{\text{III}}(\text{H}_3\text{L}^{2\text{-Me}})(\text{ac})](\text{ClO}_4)_2 \cdot 2\text{EtOH}$ (**2**)

The complex (**2**) was prepared in a similar way to **1**, using 2-methyl-4-formylimidazole, instead of 4-formylimidazole. Since good quality crystals were not obtained in methanol, the reaction was performed in ethanol, 34% yield. *Anal.* Calc. for

Table 1

X-ray crystallographic data for $[\text{Eu}^{\text{III}}(\text{H}_3\text{L}^{2\text{-H}})(\text{ac})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**), $[\text{Eu}^{\text{III}}(\text{H}_3\text{L}^{2\text{-Me}})(\text{ac})](\text{ClO}_4)_2 \cdot 2\text{EtOH}$ (**2**), and $[\text{Eu}^{\text{III}}(\text{H}_3\text{L}^{4\text{-Me}})(\text{ac})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**3**) at 296 K.

| Complex | $[\text{Eu}(\text{H}_3\text{L}^{2\text{-H}})(\text{ac})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (1) | $[\text{Eu}(\text{H}_3\text{L}^{2\text{-Me}})(\text{ac})](\text{ClO}_4)_2 \cdot 2\text{EtOH}$ (2) | $[\text{Eu}(\text{H}_3\text{L}^{4\text{-Me}})(\text{ac})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (3) |
|---|---|--|--|
| Formula | $\text{C}_{20}\text{H}_{29}\text{O}_{11}\text{N}_{10}\text{Cl}_2\text{Eu}$ | $\text{C}_{27}\text{H}_{45}\text{O}_{12}\text{N}_{10}\text{Cl}_2\text{Eu}$ | $\text{C}_{23}\text{H}_{35}\text{O}_{11}\text{N}_{10}\text{Cl}_2\text{Eu}$ |
| Formula weight | 808.38 | 924.58 | 850.46 |
| Space group | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) |
| a (Å) | 17.286(7) | 19.282(5) | 16.543(8) |
| b (Å) | 10.879(4) | 9.1247(17) | 12.600(5) |
| c (Å) | 17.424(7) | 23.359(7) | 16.565(8) |
| β (°) | 92.843(1) | 109.428(12) | 103.656(17) |
| V (Å ³) | 3272(2) | 3875.9(17) | 3355(3) |
| Z | 4 | 4 | 4 |
| D_{calc} (g cm ⁻³) | 1.641 | 1.584 | 1.683 |
| μ (cm ⁻¹) | 21.41 | 18.21 | 20.93 |
| R^a, R_w^b | 0.0585, 0.1588 | 0.0616, 0.1657 | 0.0877, 0.2386 |

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$.

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