Seven-Coordinate Luminophores: Brilliant Luminescence of Lanthanide Complexes with $C_{3v}$ Geometrical Structures


Abstract: Enhanced Luminescence properties of mononuclear lanthanide complexes with asymmetric seven-coordination structure are reported for the first time. The lanthanide complexes are composed of a lanthanide ion (EuIII or TbIII), three tetramethyl heptanediocinatot and one triphenyl phosphate oxide. The coordination geometries of the lanthanide complexes are evaluated using single crystal X-ray analyses and shape-measurement calculations. The complexes are categorized to be seven-coordinate mononuclear octahedral structure (point group: $C_{3v}$). The seven-coordinate lanthanide complexes show high intrinsic emission quantum yields, extra-large radiative rate constants and unexpected small non-radiative rate constants. The brilliant luminescence properties are elucidated in terms of the asymmetric coordination geometry and small vibrational quanta related to the thermal relaxation.

Introduction

Luminescent metal complexes have attracted considerable attention in the fields of inorganic chemistry, photophysics and materials science for photofunctional molecules for applications such as photocatalysts, display materials and a bio-imaging.[1-3] A typical luminescent metal complex is composed of one metal ion and characteristic organic ligands in a three-dimensional structure. The three-dimensional geometries of coordination structures dominate their photochemical and photophysical properties. The coordination numbers of the metal complex are generally known to be even numbers (two, four and six for coordination geometries of the lanthanide complexes are evaluated in terms of the asymmetric coordination geometry and small vibrational quanta related to the thermal relaxation.

The brilliant luminescence properties are elucidated in terms of the asymmetric coordination geometry and small vibrational quanta related to the thermal relaxation.

![Figure 1. Ideal coordination geometrical structures of a) eight-coordinate square anti-prism, b) eight-coordinate trigonal dodecahedron, c) nine-coordinate mononuclear square anti-prism, d) seven-coordinate mononuclear dodecahedron and e) seven-coordinate mononuclear trigonal prism. Chemical structures of f) Ln(tmmh)(tppo) with seven-coordination structure and g) Ln(hfa)(tppo) with eight-coordinate structure.](image-url)

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Supporting information for this article is given via a link at the end of the document.
In this study, we have attempted to synthesize mononuclear luminescent lanthanide complexes (Eu\(^{3+}\) and Tb\(^{3+}\) complexes) with characteristic seven-coordination structures. Three bidentate \(\beta\)-diketonato ligands with large steric hindrance, tetramethylheptanedionato (thm; six-coordination) and monodentate triphenyl phosphine oxide (tppo; one-coordination) were introduced to construct the seven-coordination structure shown in Figure 1f. The geometrical structures of the prepared lanthanide complexes were characterized using single-crystal X-ray analyses and shape-measurement calculations. Based on the structural analyses, the formation of an ideal seven-coordination structure was successfully categorized as the \(C_{eqv}\) group. The emission properties were evaluated using the intrinsic emission quantum yields, emission lifetimes, \(k_r\) and \(k_{nr}\) (non-radiative rate constant). The seven-coordination lanthanide complexes exhibited an extra large \(k_{nr}\), although fBu groups in the thm ligand promote non-radiative transitions via the vibrational frequency of C-H bonds.\(^{[26]}\) The small \(k_{nr}\) was explained using the spectral overlap between 4f-4f transitions of lanthanide ions and the harmonic overtones of the vibration frequencies of the organic ligands. This study provides significant results that are directly related to molecular science, photophysical chemistry and photonic device applications.

**Results and Discussion**

The seven-coordination lanthanide complexes were synthesized by the reaction of precursor Ln(thm)\(_3\)((MeOH)\(_2\)) with tppo in methanol under reflux (Supporting information). Single crystals of the Ln(thm)\(_3\)(tppo) were prepared by recrystallization from methanol solutions at room temperature. The crystal data obtained from single-crystal X-ray analyses is summarized in Table S1. The ORTEP views of Eu(thm)\(_3\)(tppo) and Tb(thm)\(_3\)(tppo) showed seven-coordinate structures, which were comprised of three thm and one tppo ligands (Figure 2). The bond length between Eu and O atoms for Eu(thm)\(_3\)(tppo) (average length \(\text{Eu-O} = 2.338\ \text{Å}\)) was shorter than that for previous reported Eu(hfa)\(_3\)(tppo)\(_2\) (average length \(\text{Eu-O} = 2.415\ \text{Å}\), hfa: hexafluoroacetylacetone, Figure 1g). We consider that Eu(thm)\(_3\)(tppo) shows a tighter packing structure. In contrast, the carbonyl bond for Eu(thm)\(_3\)(tppo) (average length \(\text{C-O} = 1.27\ \text{Å}\)) was longer than that for Eu(hfa)\(_3\)(tppo)\(_2\) (average length \(\text{C-O} = 1.25\ \text{Å}\)). The longer C=O bond in thm might be caused by electron-donation effect on fBu group.

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<th>Table 1. Photophysical properties and point groups of the lanthanide complexes</th>
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<td>complex</td>
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<td>Eu(thm)(_3)(tppo)</td>
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[a] Emission lifetimes \(\tau_{rad,exp}\) measured by excitation at 355 nm (Nd: YAG, third harmonics), [b] radiative rate constants \(k_r\) for Eu\(^{3+}\) complexes estimated from \(k_r = \tau_{rad,exp}^{-1}\), [c] non-radiative rate constants \(k_{nr} = \frac{1}{\tau_{obs}} - \frac{1}{\tau_{rad,exp}}\) and [d] the intrinsic emission yield \(\Phi_{ff} = \frac{\tau_{rad}}{\tau_{rad,exp}} = 0.54\). The \(k_r\) of Tb\(^{3+}\) complexes were calculated under the assumption that the emission lifetimes at 77 K were the radiative emission lifetime \(\tau_{rad,exp}^{0}\).
different from that for Eu(hfa)₃(tppo)₂. The relative spectral integration for Eu(tmh)₃(tppo) was 1.7 times larger than that for the corresponding Eu(hfa)₃(tppo)₂. The large spectral integration for Eu(tmh)₃(tppo) is based on the asymmetric coordination structure in solid state. The observation of intense Eu(5D₀→7F₂) transition (with respect to Eu(5D₀→7F₁)) is the signature of the lack of center of inversion. Both 7-MCO and 8-SAP structures have no inversion center.

We also measured the emission spectrum of Eu(tmh)₃(tppo) in methanol. The spectral shape is different from that in the solid state. The coordination structure of Eu(tmh)₃(tppo) in methanol might be not the same as seven-coordinate Cᵥ structure. The emission spectrum and the emission lifetime decay are shown in Figure S1 and S2, respectively. The luminescence properties of Eu(tmh)₃(tppo) in methanol are summarized in Table S5.

The emission lifetime decay profiles of the Eu III complexes are shown in Figure 3b. The emission lifetime (τₒᵤᵤ) for Eu(tmh)₃(tppo) is slightly shorter than that for Eu(hfa)₃(tppo)₂. Their τₒᵤᵤ, κᵣ, κᵦᵦ, Ψff and the point groups were summarized in Table 1. Eu(tmh)₃(tppo) exhibited a high Ψff of 80% due to the extra-large κᵣ (1.05×10³ s⁻¹) and relatively small κᵦᵦ (2.61×10² s⁻¹). The Ψff is as high as previous reported poly-enolates with EuIII systems[34-36].

Figure 3. a) Emission spectra of i) Eu(tmh)₃(tppo) and ii) Eu(hfa)₃(tppo)₂ in the solid state at room temperature excited at 350 nm. The spectra were normalized with respect to the magnetic dipole transition (5D₀→7F₁). b) Emission lifetime decays of i) Eu(tmh)₃(tppo) and ii) Eu(hfa)₃(tppo)₂ in the solid state at room temperature exited at 355 nm (third harmonics of a Q-switched Nd-YAG laser: fwhm = 5 ns, λ = 1064 nm).

The Ln(tmh)₃(tppo) exhibited small κᵦᵦ values, although the tBu groups in the complexes are composed of high-vibrational frequency C-H bonds (2950 cm⁻¹).[25] High-vibrational C-H bonds generally promote effective thermal relaxation from the excited state of lanthanide complexes.[39] We have suggested that introducing low-vibrational frequency group such as C-F (1200 cm⁻¹) instead of C-H was available for suppression of the thermal quenching like Eu(hfa)₃(tppo). In order to analyze the effect of the vibrational frequency of the ligands, the spectral

have reported that the energy gaps between the emitting level of the terbium ion and the exited triplet state of the hfa ligand in Tb(hfa)₃(tppo)₂ were 1700 cm⁻¹. The back energy transfer from lanthanide ion to the ligands is enhanced when the energy gap is less than 1850 cm⁻¹. Therefore, the combination of TbIII with hfa ligand is expected to enhance back energy transfer, resulting in low intrinsic emission quantum yield at room temperature.

In order to determine the energy of the triplet state of tmh ligand, the emission spectrum of the Gd(tmh)₃(tppo) was measured. Figure 5 presented broad peak with maxima at around 410 nm (24390 cm⁻¹), which would be the phosphorescence of tmh ligand. Since the energy gap of TbIII and the triplet state energy of the ligand is about 3500 cm⁻¹, the back energy transfer would be suppressed substantially, resulting in the small κᵦᵦ of Tb(tmh)₃(tppo).

Figure 5. Emission spectrum of Gd(tmh)₃(tppo) in the solid state at 77 K, which presents the phosphorescence of organic ligands.

The Ln(tmh)₃(tppo) exhibited small κᵦᵦ values, although the tBu groups in the complexes are composed of high-vibrational frequency C-H bonds (2950 cm⁻¹). High-vibrational C-H bonds generally promote effective thermal relaxation from the excited state of lanthanide complexes. We have suggested that introducing low-vibrational frequency group such as C-F (1200 cm⁻¹) instead of C-H was available for suppression of the thermal quenching like Eu(hfa)₃(tppo). In order to analyze the effect of the vibrational frequency of the ligands, the spectral

Figure 4. a) Emission spectra of i) Tb(tmh)₃(tppo) and ii) Tb(hfa)₃(tppo)₂ in the solid state at room temperature excited at 350 nm. The spectra were normalized with respect to the spectral integration area at T₀→F₁ transitions. b) Emission lifetime decays of b) Tb(tmh)₃(tppo) and c) Tb(hfa)₃(tppo)₂ in the solid state at 77 K and 298 K exited at 355 nm.

The Ln(tmh)₃(tppo) exhibited small κᵦᵦ values, although the tBu groups in the complexes are composed of high-vibrational frequency C-H bonds (2950 cm⁻¹). High-vibrational C-H bonds generally promote effective thermal relaxation from the excited state of lanthanide complexes. We have suggested that introducing low-vibrational frequency group such as C-F (1200 cm⁻¹) instead of C-H was available for suppression of the thermal quenching like Eu(hfa)₃(tppo). In order to analyze the effect of the vibrational frequency of the ligands, the spectral
overlap between the energy gap of 4f-4f transitions and the vibrational harmonics was estimated from IR measurements and calculations. Pecoraro et al. reported that one of the important parameters to suppress vibrational relaxation was the distance between the lanthanide ion and the highly oscillated functional groups. We have focused on the carbonyl group, which is the closest group to the lanthanide ion. The IR spectra of carbonyl groups for Eu(tmh)₃(tppo) and Eu(hfa)₃(tppo)₂ are shown in Figure 6a. The vibrational frequency of carbonyl groups for Eu(tmh)₃(tppo) (ν_C=O = 1573 cm⁻¹) was smaller than that for Eu(hfa)₃(tppo)₂ (ν_C=O = 1654 cm⁻¹).

![Figure 6](image)

The vibrational frequencies of coordinated carbonyl groups in the Eu³⁺ complexes were also estimated from density functional theory (DFT) calculations at the B3LYP-D3 level with the Stuttgart RECP basis set for Eu and cc-pVDZ for the other atoms. The results indicated that the vibrational frequency of the carbonyl stretching for Eu(tmh)₃(tppo) and Eu(hfa)₃(tppo)₂ were 1548-1554 and 1633 cm⁻¹, respectively (see Table S4, supporting information). The vibrational frequencies of the coordination sites were supported by DFT calculations with the lanthanide ions. The vibrational transition probability is proportional to the Franck-Condon factor, i.e., the overlap integrals between the energy gap of 4f-4f transitions and the vibrational harmonics of organic ligands. The Franck-Condon factor for Tb(tmh)₃(tppo) (ν = 11) was also estimated to be eleven times larger than that for Tb(tmh)₃(tppo)₂ (ν = 10). From these calculations, it was concluded that the vibrational relaxation in Ln(tmh)₃(tppo) would be effectively suppressed because of the small vibrational quanta of the carbonyl groups, which would result in a small k_v constant.

Conclusions

In summary, we have successfully synthesized novel lanthanide complexes with characteristic seven-coordinate geometrical structures. This is the first reported mononuclear luminescent complex surrounded by seven oxygen atoms. The ideal seven-coordinate structure is useful for comparison with the previous eight-coordinate structure as a strong luminescent material. The lanthanide complexes exhibited extra large radiative rate constants due to their asymmetric coordination geometries. It was experimentally revealed that the asymmetric seven-coordinate geometry enhances the luminescence properties by the large k_v and small k_r constants. We have also proposed that the vibrational frequency of carbonyl groups is effective for thermal relaxation, and IR spectra calculations of the carbonyl groups for Eu³⁺ complexes supported the experimental results. The photophysical results reported here should contribute to the design of lanthanide complexes with remarkable luminescence properties.

Werts and co-workers have shown the chemical structure of seven-coordinate Mₖ-EuFOD complex (FOD: 1,1,1,2,2-pentafluoro-6,6-dimethylheptane-3,5-dione, Mₖ: Michler’s ketone, bis(4-(dimethylamino)phenyl)methane) without single-crystal X-ray analysis. In contrast, We insisted on the importance of direct seven-coordinate crystal structure and their photophysical property based on the X-ray analysis of Ln(tmh)₃(tppo). Various type of lanthanide complexes with photosensitized ligand have been reported. Various Tb(tmh)₃(tppo) exhibited excitation peak in UV region (Figure S3). Luminescent seven-coordinate Eu³⁺ complex excited at around 450 nm (visible region) may be ideal phosphor for applications such as LEDs, biomarkers, and chemical sensing devices. Recently, Marta and co-workers reported similar system of lanthanide complex. We hope all seven-coordinate complexes would give large k_v. In the future, other seven-coordinate complexes could be synthesized and the photophysical properties will be revealed. Seven-coordinate lanthanide complexes have the potential to break
new ground in the fields of photophysical, coordination and materials chemistry.

**Experimental Section**

**Materials:**

Europium chloride hexahydrate (99.9%), terbium chloride pentahydrate (99.9%) were purchased from Kanto Chemical Co., Inc. 2,2,6,6-tetramethylheptane-3,5-dion and triphenyl phosphine oxide were obtained from Tokyo Kasei Organic Chemicals. Europium acetate monohydrate (99.9%), terbium acetate tetrahydrate (99.9%) and ammonia solution (28%) were purchased from Wako Pure Chemical Industries Ltd. All other chemicals and solvents were reagent grade and were used without further purification.

**Apparatus:**

Infrared spectra were recorded with a JASCO FTIR-420 spectrometer. Mass spectra were measured using Thermo Scientific Exactive. Elemental analyses were performed with an Exeter Analytical CE440.

**Preparation of Ln(tmh)$_3$(MeOH):**

Europium chloride hexahydrate (1.0 g, 2.7 mmol) or Terbium chloride pentahydrate (1.0 g, 2.4 mmol) was dissolved in distilled water (5 mL) in a 100 mL flask. A solution of 2,2,6,6-tetramethylheptane-3,5-dion and triphenyl phosphine oxide (1.46 g, 8.1 mmol for EuIII complex or 1.32 g, 7.2 mmol for TbIII complex) was added to the solution with ethanol (20 mL). Ammonia solution was added dropwise to the solution until pH 7, approximately. After stirring for 3 h at room temperature, the reaction mixture was recrystallized by cold water. The precipitated precipitation was filtered, and resulting powder was recrystallized from methanol to afford colorless block crystals of the titled compound. Yield: 2.07 g (99%).

**Preparation of Ln(tmh)$_3$(tppo):**

Triphenyl phosphine oxide (0.4 g, 1.4 mmol) and Ln(tmh)$_3$(MeOH)$_2$ (1.0 g, 1.4 mmol) were dissolved in methanol (30 mL). The solution was heated at reflux while stirring for 12 h. The reaction mixture was recrystallized in methanol. Recrystallization gave colorless rod-shaped crystals of the lanthanide complexes. Yield: 1.1 g (84%); IR (KBr): ν = 1573 (at, C=O), 1138 cm$^{-1}$ (at, P=O); ESI-MS: [M+H]$^+$: 981.42; found: 981.41, calcd for C$_{51}$H$_{72}$O$_7$P$^+$ [M+H]$^+$: 987.42; found: 987.43; elemental analysis calcd (%) for C$_{51}$H$_{72}$EuO$_7$P: C 62.50, H 7.35; found: C 62.11, H 7.31.

**Crystallography:**

Colorless single crystals of the lanthanide complexes were mounted on a MiTeGen micromesh using parafin oil. All measurements were made using a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo K$_{α}$ radiation. Non-hydrogen atoms were refined anisotropically. All calculation was performed using the crystal-structure crystallographic software package. CIF data was confirmed by using the checkCIF/PLATON service. CCDC-1400251 for Eu(tmh)$_3$(tppo) and CCDC-1400286 for Tb(tmh)$_3$(tppo) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Optical measurements:**

Emission and excitation spectra of the lanthanide complexes were measured with a HORIBA Fluorolog-3 spectrophurometer and corrected for the response of the detector system. The emission quantum yields were obtained using JASCO F-6300-H spectrometer attached with JASCO ILS-53 integrating sphere unit. The wavelength dependence of the detector response and the beam intensity of the Xe light source for each spectrum were calibrated using a standard light source. Emission lifetimes ($\tau$) were measured using the third harmonics (355 nm) of a Q-switched Nd: YAG laser (Spectra physics, INDI-50, fwhm = 5 ns, $\lambda$ = 1064 nm) and a photomultiplier (Hamamatsu Photonics, R5108, response time $\leq$ 1.1 ns). The Nd: YAG laser response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles.

**Computational details:**

All calculations were performed with the GAUSSIAN 09 program. The structure of the seven- and eight-coordinate Eu$^{3+}$ complexes, Eu(tmh)$_3$(tppo) and Eu(hfa)$_3$(tppo)$_2$, were optimized in the gas phase at the B3LYP-D3 level with the Stuttgart RECP and cc-pVDZ basis sets for Eu and the other atoms, respectively. Then, the normal mode analysis of each molecule at the optimized structure was executed at the same level to obtain vibrational frequencies and IR intensities. The vibrational frequencies were corrected with the scaling factor of 0.9614, which was reported as the optimal value for the B3LYP functional.

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**Keywords:** lanthanides • luminescence • O ligands • structural analysis • DFT calculation


This work reported that lanthanide complexes with seven-coordination showed brilliant luminescence properties due to the asymmetric geometrical structure. The complexes exhibited extra-large radiative rate constants and unexpected small non-radiative rate constants.

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