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<tr>
<td>Citation</td>
<td>European journal of inorganic chemistry, 28: 4769-4774</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2015-10</td>
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<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/62879">http://hdl.handle.net/2115/62879</a></td>
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<td>Rights</td>
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Seven-Coordinated Luminophores: Brilliant Luminescence of Lanthanide Complexes with $C_{3v}$ Geometrical Structures

Kei Yanagisawa, Takayuki Nakanishi, Yuichi Kitagawa, Tomohiro Seki, Tomoko Akama, Masato Kobayashi, Tetsuya Taketsugu, Hajime Ito, Koji Fushimi, Yasuchika Hasegawa

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 (Eu$^{3+}$ or Tb$^{3+}$), three tetramethyl heptanedionato 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: $C_{6v}$). 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. 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, eight and ten for lanthanide complexes). Metal complexes with odd coordination numbers, in particular seven-coordination structures, have rarely been reported. Ahmed and Iftikhar predicted that asymmetric seven-coordination structures would promote the enlargement of $k_r$ and $\Phi_f$. Eliseeva and co-workers have also reported the dinuclear lanthanide complexes with six oxygen atoms and one nitrogen atom. While seven-coordination may influence the orbit splitting of metals, multinuclear complexes have a difficulty for analyzing the physicochemical property in detail. Zuo and co-workers studied on seven-coordinate lanthanide porphyrinate and phthalocyaninate complexes with tripodal phosphate oxide ligand for single-molecule magnet. The seven-coordination would be due to the steric hindrance of macrocyclic molecules. Based on such background, an investigation of a simple mononuclear lanthanide complex surrounded by seven oxygen atoms is expected lead to further understanding and development of coordination chemistry and photophysical science.

Lanthanide complexes with characteristic narrow emission bands and long emission lifetimes based on the 4f-4f transitions have been regarded as attractive luminescent materials for applications such as lasers, electroluminescence devices and bio-probes. Various types of luminescent lanthanide complexes have been reported to date. Lanthanide complexes with asymmetric coordination structures exhibit high emission quantum yields ($\Phi_f$) and large radiative rate constants ($k_r$). Lanthanide complexes generally provide eight-coordinate square anti-prism structures that are categorized as $D_{4h}$ in point group theory (8-SAP, Figure 1a). Recently, Hasegawa and co-workers have synthesized more asymmetric lanthanide complexes with eight-coordinate trigonal dodecahedron (8-TDH: $D_{3d}$, Figure 1b) and nine-coordinate mononuclear square anti-prism (9-SAP: $C_{3v}$, Figure 1c) structures. $k_r$ for the lanthanide complexes with 8-TDH and 9-SAP structures are larger than those of typical 8-SAP structures, based on the Laporte rule related to the transition probability. The ideal asymmetric lanthanide complex with a seven-coordination structure would construct a unique mononuclear octahedron (7-MCO: $C_{3v}$, Figure 1d) or mononuclear trigonal prism (7-MCTP: $C_{3v}$, Figure 1e), which would promote the enlargement of $k_r$ and $\Phi_f$.

![Image](image_url)

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 octahedron and e) seven-coordinate mononuclear trigonal prism. Chemical structures of f) Ln(tmh)$_3$(tppo) with seven-coordination structure and g) Ln(hfa)$_3$(tppo)$_2$ with eight-coordinate structure.
In this study, we have attempted to synthesize mononuclear luminescent lanthanide complexes (EuIII and TbIII complexes) with characteristic seven-coordination structures. Three bidentate β-diketonato ligands with large steric hindrance, tetramethylheptanedionato (tmh; 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 C3v group. The emission properties were evaluated using the intrinsic emission quantum yields, emission lifetimes, k and kkr (non-radiative rate constant). The seven-coordinate lanthanide complexes exhibited an extra large kkr and an unexpectedly small knr, although fBu groups in the tmh ligand promote non-radiative transitions via the vibrational frequency of C-H bonds. The small knr 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, photophysics, and photonic device applications.

Results and Discussion

The seven-coordination lanthanide complexes were synthesized by the reaction of precursor Ln(tmh)3(MeOH)2 with tppo in methanol under reflux (Supporting information). Single crystals of the Ln(tmh)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(tmh)3(tppo) and Tb(tmh)3(tppo) showed seven-coordinate structures, which were comprised of three tmh and one tppo ligands (Figure 2). The bond length between Eu and O atoms for Eu(tmh)3(tppo) (average length in EuO = 2.338 Å) was shorter than that for previous reported Eu(hfa)3(tppo)2 (average length in EuO = 2.415 Å, hfa: hexafluoroacetylacetonato, Figure 1g). We consider that Eu(tmh)3(tppo) shows a tighter packing structure. In contrast, the carbonyl bond for Eu(tmh)3(tppo) (average length in C=O = 1.27 Å) was longer than that for Eu(hfa)3(tppo)2 (average length in C=O = 1.25 Å). The longer C=O bond in tmh might be caused by electron-donation effect on fBu group.

Based on the crystal data, the coordination geometry was calculated using the shape factor S, to estimate the degree of distortion of the coordination structure in the first coordination sphere. The S value is given by

\[
S = \min \left[ \frac{1}{m} \sum_{i=1}^{m} (\delta_i - \theta_i)^2 \right],
\]

where m, \( \delta_i \) and \( \theta_i \) are the number of possible edges (m = 15 in this study[28]), the observed dihedral angle between planes along the \( i \)th edge and the dihedral angle for the ideal structure, respectively. The estimated S values of lanthanide complexes were summarized in Tables S2 and S3. For Eu(tmh)3(tppo), the S value calculated for a seven-coordinate monocapped octahedral structure (7-MCO, point group: C3v, S = 7.6) was smaller than that for the seven-coordinate monocapped trigonal prismatic structure (7-MCTP, point group: D3h, S = 13.8), which suggests that the coordination structure is closer to 7-MCO rather than 7-MCTP. As a result, the coordination geometry of Eu(tmh)3(tppo) was determined to be distorted 7-MCO. Tb(tmh)3(tppo) was also estimated as 7-MCO using a similar calculation (S = 8.8, S = 14.1). The characteristic structures of the lanthanide complexes are expected to provide larger kkr and higher \( \Phi_{ef} \).

Figure 3a shows the emission spectra of Eu(tmh)3(tppo) and Eu(hfa)3(tppo) in the solid state. The spectra were normalized with respect to the magnetic dipole transition intensities at around 590 nm (1D2-7F1, which are insensitive to the surrounding environment of the lanthanide ions[29]). The emission bands at around 615 nm were due to the hypersensitive transitions, which are strongly dependent on the surrounding environment of the lanthanide ions. The emission bands at around 615 nm were due to the hypersensitive transitions, which are strongly dependent on the surrounding environment of the lanthanide ions. The Stark splitting structure of the electric dipole transition bands for Eu(tmh)3(tppo) was critically investigated.

<table>
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<tr>
<th>complex</th>
<th>( r_{\text{rad}} )</th>
<th>( k_{\text{nr}} )</th>
<th>( k_{\text{kr}} )</th>
<th>( \Phi_{\text{eff}} )</th>
<th>point group</th>
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<td>Eu(tmh)3(tppo)</td>
<td>0.76</td>
<td>1.05×102</td>
<td>2.61×102</td>
<td>80</td>
<td>C3v</td>
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<tr>
<td>Eu(hfa)3(tppo)</td>
<td>0.67</td>
<td>8.63×102</td>
<td>2.86×102</td>
<td>75</td>
<td>D4h</td>
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<tr>
<td>Tb(tmh)3(tppo)</td>
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<td>1.04×103</td>
<td>1.49×102</td>
<td>88</td>
<td>C3v</td>
</tr>
<tr>
<td>Tb(hfa)3(tppo)</td>
<td>0.12</td>
<td>1.02×102</td>
<td>7.31×103</td>
<td>12</td>
<td>D4h</td>
</tr>
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[a] Emission lifetimes \( r_{\text{rad}} \) measured by excitation at 355 nm (Nd: YAG, third harmonics), [b] radiative rate constants \( k_{\text{r}} \) for EuIII complexes estimated from \( \Phi_{\text{eff}} = \frac{4}{3} \times \frac{\lambda}{10^3} \times \tau_{\text{rad}} \), [c] non-radiative rate constants \( k_{\text{nr}} = \frac{1}{r_{\text{rad}}} - \frac{1}{r_{\text{rad}}} \) and [d] intrinsic emission yield \( \Phi_0 = \frac{k_{\text{r}}}{k_{\text{r}} + k_{\text{nr}}} \). The \( k_{\text{r}} \) of TbIII complexes were calculated under the assumption that the emission lifetimes at 77 K were the radiative emission lifetime \( r_{\text{rad}} \).
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) was based on the asymmetric coordination structure in solid state. The observation of intense Eu(5D0-7F2) transition 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 C3v 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 radiative rate constant of Eu(tmh)3(tppo) (kr = 0.7×10^3 s^-1) is slightly larger than that of Eu(hfa)3(tppo)2 (kr = 0.5×10^3 s^-1) in solution.

The emission lifetime decay profiles of the EuIII complexes are shown in Figure 3b. The emission lifetime (τobs) for Eu(tmh)3(tppo) is slightly shorter than that for Eu(hfa)3(tppo)2. Their τobs, kr, knr, Φff and the point groups were summarized in Table 1. Eu(tmh)3(tppo) exhibited a high Φff of 80% due to the extra-large kr (1.05×10^3 s^-1) and relatively small knr (2.61×10^2 s^-1). The Φff is as high as previous reported poly-enolates with EuIII systems.

The Ln(tmh)3(tppo) exhibited small knr values, although the C8Bu 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) are shown in Figure 6a. The vibrational frequency of carbonyl groups for Eu(tmh)₃(tppo) (\(\nu_{c=o} = 1573 \text{ cm}^{-1}\)) was smaller than that for Eu(hfa)₃(tppo) (\(\nu_{c=o} = 1654 \text{ cm}^{-1}\)).

![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) 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 supporting information. The Franck-Condon integrals between the energy gap of 4f transitions and the vibrational harmonics of organic ligands. The Franck-Condon factor decreases with an increase in vibrational quanta, which is the harmonic number matched with the energy gap of the lanthanide ion. The energy gaps of Eu³⁺ (5D₀-7F₂) and Tb³⁺ (5D₀-7F₂) have been reported to be 12297 and 14800 cm⁻¹, respectively. The \(\nu\) was estimated by the following equation including anharmonic constant (\(\kappa_x = 6.5 \times 10^4\) cm⁻¹ MeV⁻¹).

\[
\Delta \nu \nu_{\nu + 1} = 9 - 2(\nu + 1) \kappa_x + \ldots
\]

where \(G\), \(\nu\) are vibrational energy and vibrational frequency, respectively. \(\nu\) for Eu(tmh)₃(tppo) and Eu(hfa)₃(tppo) were calculated to be 9 and 8, respectively (Figure 4b). The Franck-Condon factor estimated for Eu(hfa)₃(tppo) (8-SAP: \(D_4\)) is nine times larger than that for Eu(tmh)₃(tppo) (7-MCO: \(C_5\)). The Franck-Condon factor for Tb(tmh)₃(tppo) (\(\nu = 11\)) was also estimated to be eleven times larger than that for Tb(tmh)₃(tppo) (\(\nu = 10\)). 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 \(k_r\) 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 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 \(k_r\) and small \(\kappa_x\) 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)methanone) without single-crystal X-ray analysis. In contrast, We insisted on the importance of direct seven-coordinate crystal structure and their photophysical property analysis based on the X-ray analysis of Ln(tmh)₃(tppo). Various type of lanthanide complexes with photosensitized ligand have been reported. Tb(tmh)₃(tppo) exhibited excitation peak in UV region (Figure S3). Luminescent seven-coordinate Eu⁶⁺ 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 \(k_r\). 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.

**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: tmh (1.46 g, 8.1 mmol for Eu³⁺ complex or 1.32 g, 7.2 mmol for Tb³⁺ complex) was added to the solution with ethanol (20 mL). The solution was added dropwise to the solution until pH 7. Approximately, after stirring for 3 h at room temperature, the reaction mixture was reprecipitated by cold water. The produced precipitation was filtered, and resulting powder was recrystallized from methanol to afford colorless rod-shaped 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)₃ (1.0 g, 1.4 mmol) were dissolved in methanol (50 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): v₁ = 1573 (at, C=O), 1138 cm⁻¹ (at, P=O); ESI-MS: m/z: calc for C₅₁H₇₂EuO₇P [M+H⁺]: 981.42; found: 981.41, calc for C₆₅H₇₄O₇Pb [M+H⁺]: 987.42; found: 987.43, elemental analysis calc (%) for C₅₁H₇₂EuO₇P: C 62.50, H 7.34; found: C 62.56, H 7.32; calc (%) for C₆₅H₇₄O₇Pb: C 62.06, 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 paraffin oil. All measurements were made using a Rigaku RAXIS RAPID imaging plate area detector with graphite – monochromated MoKα radiation. Non-hydrogen atoms were refined anisotropically. All calculations were 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.

**Emission measurements:**

Emission and excitation spectra of the lanthanide complexes were measured with a HORIBA Fluorolog-3 spectrophotometer and corrected for the response of the detector system. The emission quantum yields were obtained using JASCO F-6300-H spectrometer attached with JASCO ILF-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 (τₑ) were measured using the third harmonics (355 nm) of a Q-switched Nd: YAG laser (Spectra physics, INDI-50, fwhm = 5 ns, λ = 1064 nm) and a photomultiplier (Hamamatsu Photonics, R5108, response time ≤ 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 Eu³⁺ complexes, Eu(tmh)₃(tppo) and Eu(tfa)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.

**Acknowledgements**

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Area of “New Polymeric Materials Based on Element-Blocks” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (Japan; grant number 2401). One of the authors, K. Yanagisawa was supported by The Ministry of Education, Culture, Sports and Technology through Program for Leading Graduate Schools (Hokkaido University "Ambitious Leader’s Program").

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

References:


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.