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Photoluminescent Dinuclear Lanthanide Complexes with Tris(2-pyridyl)carbinol Acting as a New Tetradentate Bridging Ligand

Masayuki Watanabe,*[†,‡] Takuya Nankawa,[‡] Teppei Yamada,[‡] Takaumi Kimura,[†] Kosuke Namiki,[‡] Masaki Murata,[‡] Hiroshi Nishihara,*[‡] and Shoichi Tachimori[†]

Department of Materials Science, Japan Atomic Energy Research Institute,
Tokai-mura Ibaraki, 319-1195, Japan, and Department of Chemistry, School of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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A tripodal ligand, tris(2-pyridyl)carbinol, affords a novel tetradentate coordination mode in homodinuclear lanthanide complexes, which exhibit remarkably short distances between metal ions. The strong luminescences of Eu(III) and Tb(III) complexes with the ligand demonstrate that the ligand has a suitable excited state for energy transfer from the ligand to the Eu(III) and Tb(III) centers, respectively.

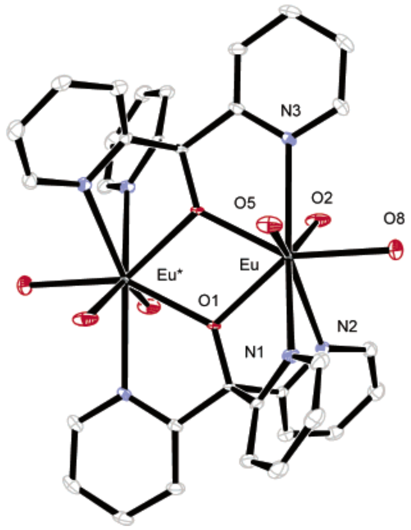

Figure 1. ORTEP drawing of complex **2**. The ellipsoids of thermal vibration represent a 50% probability. H atoms and triflates have been omitted except for coordinating oxygen. Selected bond distances (Å) and angles (°): Eu−N1 2.619(2), Eu−N2 2.548(2), Eu−N3 2.552(2), Eu−O1 2.292(1), Eu−O2(H_2O) 2.413(2), Eu−O5(triflate) 2.383(2), Eu−O8(triflate) 2.380(2), O1−Eu−N1 64.85(5), O1−Eu−N2 64.86(5), N1−Eu−N2 68.40(6).

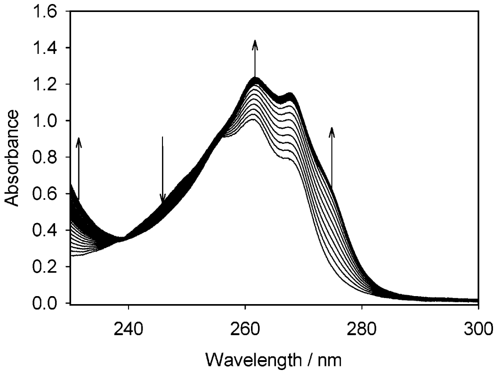

Figure 2. Spectrophotometric titration of **1** with $Eu(NO_3)_3$ in acetonitrile. Arrows indicate spectral changes observed on the titration. Concentration of **1** is 1.0×10^{-4} M and of $Eu(NO_3)_3$ is 3.0×10^{-3} M.

The rational design and synthesis of ligands capable of forming stable and strongly luminescent lanthanide complexes have attracted a great deal of attention due to their potential application as luminescent probes.[1] To achieve strong luminescence, concurrent control of solvation and hydration around the lanthanide ion, and its high coordination number, should be incorporated into the ligand design. To this end, one promising strategy is encapsulating the lanthanide ion with the ligand, which has a large absorption cross section with suitable excitation energy that can be transferred to a metal excitation state.[2] Consequently, a pyridyl group, due to its large absorption cross section and modular synthesis, is reasonable for use in designing strongly luminescent lanthanide complexes. The stability of the lanthanide complex with nitrogen donor ligands against moisture, however, is generally not significant.[3,4] Due to the oxophilicity of a lanthanide ion (hard acid−hard base interaction), an oxygen donor ligand appears attractive for strong complexation of lanthanide ions. Further, when the oxygen donor consists of

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* To whom correspondence should be addressed. E-mail: mw@popsvr.tokai.jaeri.go.jp (M.W.); nisihara@chem.s.u-tokyo.ac.jp (H.N.). Fax: +81-29-282-6723 (M.W.); +81-3-5481-8063 (H.N.).

[†] Japan Atomic Energy Research Institute.

[‡] The University of Tokyo.

(1) Bünzli, J.-C. G. *Lanthanide Probes in Life, Chemical and Earth Sciences*; Bünzli, J.-C. G., Choppin, G. R., Eds; Elsevier: Amsterdam, 1989, pp 219−293.

(2) Sabatini, N.; Guardigli, M.; Manet, I. *Handbook on the Physics and Chemistry of Rare Earths*; Elsevier: Amsterdam, 1996; Vol. 23, pp 69−119. Beeby, A.; Bushby, L. M.; Maffeo D.; Williams, J. A. G. *J. Chem. Soc., Dalton Trans.* **2002**, 48−54.

(3) Forsberg, J. H. *Coord. Chem. Rev.* **1973**, *10*, 195−226.

(4) Yashiro, M.; Ishikubo, A.; Takarada, T.; Komiyama, M. *Chem. Lett.* **1995**, *24*, 665−666. Ionova, G.; Rabbe, C.; Guillaumont, R.; Ionov, S.; Madic, C.; Krupa, J.-C.; Guillaneux, D. *New J. Chem.* **2002**, *26*, 234−242.

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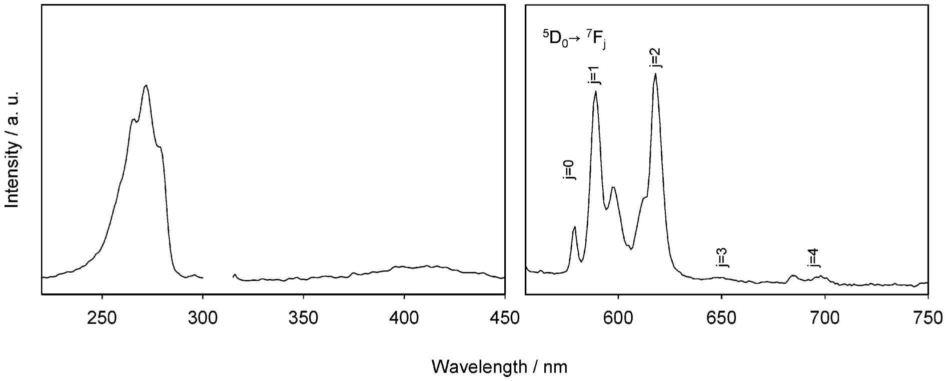
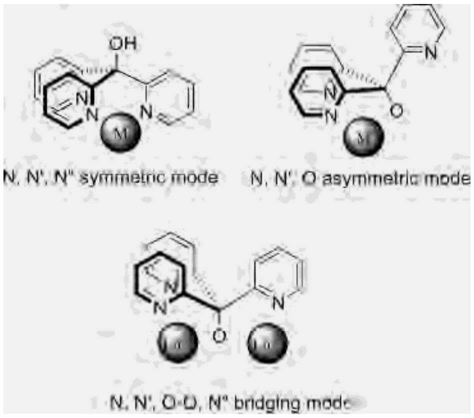


Figure 3. Excitation (left) and luminescence (right) spectra of aqueous **2** at 298 K. The emission and excitation wavelengths for the spectra are 619.0 and 263.0 nm, respectively. The concentration of **2** is 3.3 × 10^{-5} M.

Scheme 1. Coordination Mode for Tris(2-pyridyl)carbinol (**1**)



alkoxide or carboxylic acid, the ligand would form multinuclear complexes with a variety of geometries due to the hardness,[5] the oxophilicity, and the high coordination number of the lanthanide ion. In this study, we investigated the complexation of a ligand involving pyridyl groups and an oxygen donor with lanthanide ions. Tris(2-pyridyl)carbinol (**1**), which has three pyridine moieties with a hydroxyl group in the apical position, aligns with our interest because of its variety of coordination modes. Note that the previously known coordination modes of **1** are two tridentate modes: the N,N′,N″ symmetric coordination mode for Hg(II)[6] and Co(III)[7] complexes, and the N,N′,O asymmetric coordination mode for Co(III)[8] and Ru(II)[9] complexes, as shown in Scheme 1.

We herein report the first examples of lanthanide complexes of **1**, which involve another novel coordination mode, the tetradentate N,N′,O−O,N″ bridging mode, as shown in Scheme 1. This unique coordination mode forms homodinuclear complexes of Eu(III) and Tb(III) with remarkably short metal-to-metal distances. In addition, we found that **1** reaches a suitable excitation state to transfer its absorbed energy to Eu(III) and Tb(III) metal centers.

Ligand **1** was prepared in 40% yields using the published method.[10] 2-Lithio-pyridine, prepared from 2-bromopyridine and *n*-butyllithium in −80 °C, was reacted with di(2-pyridyl)-ketone, quenched with a small amount of MeOH, and recrystallized with acetone.[11]

Mixing an acetonitrile solution of **1** with 1 equiv of Ln(OTf)$_3$·3H$_2$O (Ln = Eu, Tb) afforded [Ln$_2$**1**$_2$(OTf)$_4$(H$_2$O)$_2$] (Eu, **2**; Tb, **3**).[11] Suitable crystals of **2** for X-ray crystallography were obtained by recrystallization from acetonitrile and ether.[12] The X-ray crystal structure of a neutral complex, **2**, is shown in Figure 1. The structure of **3** is as isomorphous as that of **2** (Figure S1 of Supporting Information). These two complexes have a homodinuclear and an eight-coordination structure in common with **1**, which coordinates in a tetradentate manner, and the alkoxo-oxygen contributes as a bridging donor. The structure has a center of symmetry in the middle of two metal centers. Two triflates and one water molecule coordinate to each lanthanide ion. Compound **1** could well shield the water molecule from coordinating, due to the fact that it encapsulates two metal ions in two ligands. The bond lengths of **3** are shorter by ca. 0.02 Å than those of **2** due to lanthanide contraction, which corresponds to the

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(5) Abraham, U.; Dell'Amico, D. B.; Calderazzo, F.; Porta, C. D.; Englert, U.; Marchetti, F.; Merigo, A. *Chem. Commun.* **1999**, 2053−2054. Bryzyska, W.; Rzaczynska, Z.; Swita, E.; Mrozek, R.; Glowiak, T. *J. Coord. Chem.* **1997**, *41*, 1.

(6) Canty, A. J.; Chaichit, N.; Gatehouse, B. M.; George, E. E. *Inorg. Chem.* **1981**, *20*, 4293−4300.

(7) Szalda, D. J.; Keene, F. R. *Inorg. Chem.* **1986**, *25*, 2795−2799.

(8) White, D. L.; Faller, J. W. *Inorg. Chem.* **1982**, *21*, 3119−3122.

(9) Keene, F. R.; Szalda, D. J.; Wilson, T. A. *Inorg. Chem.* **1987**, *26*, 2211−2216.

(10) Wibaut, J. P.; De Jonge, A. P.; Van der Voort, H. G. P.; Otto, P. H. L. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 1054−1066.

(11) The elemental analysis of compounds follows. Anal. Calcd (%) for **1** as $C_{16}H_{13}N_3O$: C, 72.98; H, 4.98; N, 15.96. Found (%): C, 72.72; H, 5.04; N, 15.87. Anal. Calcd (%) for **2** as $C_{36}H_{28}Eu_2F_{12}N_6O_{16}S_4$: C, 29.60; H, 1.93; N, 5.75. Found (%): C, 30.00; H, 1.78; N, 5.65. Anal. Calcd (%) for **3** as $C_{36}H_{28}Tb_2F_{12}N_6O_{16}S_4$: C, 29.32; H, 1.91; N, 5.70. Found (%): C, 29.45; H, 1.80; N, 5.55. Anal. Calcd (%) for **4**·4H$_2$O as $C_{32}H_{32}Eu_2N_{10}O_{18}$: C, 33.46; H, 2.81; N, 12.20. Found (%): C, 33.19; H, 2.76; N, 11.90. Anal. Calcd (%) for **5**·2H$_2$O as $C_{32}H_{28}Tb_2N_{10}O_{16}$: C, 34.12; H, 2.50; N, 12.43. Found (%): C, 33.83; H, 2.35; N, 12.63.

(12) Crystal data for **2**·2MeCN follow. $C_{40}H_{34}Eu_2F_{12}N_8O_{16}S_4$, $M = 1542.89$, triclinic, space group $P1$, $a = 10.917(3)$ Å, $b = 11.418(2)$ Å, $c = 13.152(3)$ Å, $\alpha = 65.272(11)°$, $\beta = 63.269(10)°$, $\gamma = 71.971(13)°$, $V = 1314.9(6)$ Å^3, $F(000) = 898$, 10322 reflections collected, 5853 unique ($R_{int} = 0.016$). The final R1 and wR2 are 0.018, 0.023 (all data), respectively. CCDC 210852. For **3**·2MeCN: $C_{40}H_{34}Tb_2F_{12}N_8O_{16}S_4$, $M = 1556.82$, triclinic, space group $P1$, $a = 10.891(3)$ Å, $b = 11.400(3)$ Å, $c = 13.089(3)$ Å, $\alpha = 65.41(2)°$, $\beta = 63.28(3)°$, $\gamma = 72.29(3)°$, $V = 1306.1(6)$ Å^3, $F(000) = 1520$, 14890 reflections collected, 7202 unique ($R_{int} = 0.031$). The final R1 and wR2 are 0.028, 0.035 (all data), respectively. CCDC 210853. Reflection data were collected at 93 ± 1 K (Rigaku Mercury diffractometer coupled with CCD area detector) with graphite monochromated Mo Kα radiation (0.7107 Å).

Table 1. Luminescence Lifetimes and Derived Hydration States of **2**−**5**

complex	τH_2O/ms	τD_2O/ms	qH_2O^a
$[Eu_2\mathbf{1}_2(OTf)_4(H_2O)_2]$ (**2**)	0.37	3.1	2.3
$[Tb_2\mathbf{1}_2(OTf)_4(H_2O)_2]$ (**3**)	1.1	3.0	2.6
$[Eu_2\mathbf{1}_2(NO_3)_4(H_2O)_2]$ (**4**)	0.38	3.1	2.2
$[Tb_2\mathbf{1}_2(NO_3)_4(H_2O)_2]$ (**5**)	1.1	2.7	2.4

[a] The number of water molecules which coordinate to lanthanide ion and derived using $q = 1.11(1/\tau H_2O - 1/\tau D_2O - 0.31)$ for Eu complexes and $q = 5.0(1/\tau H_2O - 1/\tau D_2O - 0.06)$ for Tb complexes at 298 K.

difference in ionic radii for eight-coordination between Eu(III), 1.07 Å and Tb(III), 1.04 Å.[13] The metal-to-metal distances are remarkably short for dinuclear lanthanide complexes: 3.785(2) Å for **2** and 3.743(2) Å for **3**.[14]

Furthermore, a 1 h reaction of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Eu, Tb) with **1** in acetonitrile forms a precipitate which was recrystallized with MeOH and H_2O and determined as $[Ln_2\mathbf{1}_2(NO_3)_4(H_2O)_2]$ (Eu, **4**; Tb, **5**) by elemental analysis[11] and spectrophotometric titration of **1** by lanthanide nitrate. The titration analysis indicates that dinuclear complexes, **4**, **5**, were formed in acetonitrile. The data were fitted by a least-squares procedure to the following equilibrium, which was supported by factor analysis indicating three species, in which solvation and anion coordination have been omitted as shown in Figure 2.[15] The calculated logarithmic formation constants, log β_{22}, are 10.849 ± 0.019 for **4** and 10.974 ± 0.016 for **5**.

$$2\mathrm{Ln}^{3+} + 2\mathbf{1} \rightleftharpoons [\mathrm{Ln}_2\mathbf{1}_2]^{4+} + 2\mathrm{H}^+ \quad \beta_{22}$$

Ligand-assisted photoluminescence properties of the lanthanide complexes of **1** were examined. The excitation and fluorescence spectra of **2** are depicted in Figure 3. The excitation spectra, which are similar to the electronic spectra of **1**, show a significant enhancement of luminescence intensity when excitation is carried out in the UV region ($\pi-\pi^*$ band of **1**, electronic spectra appear as the end point of titration in Figure 3), and no intense peaks are seen at the excitation state of the metal center, $^5L_6$, at 394 nm. This indicates that energy transfer from the ligand to metal center, sensitized emission, is clearly observed. The fluorescence spectra show that a forbidden transition, $^5D_0 \rightarrow {}^7F_0$, and a hypersensitive transition, $^5D_0 \rightarrow {}^7F_2$, are expected for the noncentrosymmetric coordination environment.[3,16]

The results of luminescence lifetime study by time-resolved laser-induced fluorescence spectroscopy are summarized in Table 1.[17] The number of coordinating water molecules, qH_2O, is calculated by Horrocks' equation for Eu complexes[18] and by Parker's equation for Tb complexes.[19] Irrespective of anions, two or three water molecules coordinate to each complex in aqueous solution. This, however, indicates that when coordinating anions are exchanged for water molecules, the ligand remains shielded from the water molecule under the moist condition.

In conclusion, homodinuclear lanthanide−carbinol complexes have been synthesized in the structurally novel tetradentate coordination mode, which is characterized by remarkably short distances between metal ions. This coordination mode provides a new possibility for designing unique complexes by synthesis of a heterodinuclear complex that involves metal−metal interactions such as multistep energy transfer or magnetic interaction. Further experiments to determine the magnetic properties of gadolinium complex with **1** are in progress.

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Supporting Information Available: Crystallographic data for the structures in CIF format. Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.

(14) Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Motevalli, M.; Wu, R. *Polyhedron* **1994**, *13*, 1−6. Yang, L.-W.; Liu, S.; Wong, E.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1995**, *34*, 2164−2178.

(15) Data analysis of spectrophotometric titration: Data analysis and the determination of formation constants with respect to the formation of lanthanide complexes were carried out by the program SPECFIT/32; this procedure is based on factor analysis and a least-squares method.

(16) Blasse, G. *Inorg. Chim. Acta* **1988**, *142*, 153−154. Thompson L. C.; Kuo, S. C. *Inorg. Chim. Acta* **1988**, *149*, 305−306.

(17) Experiment and data analysis of lifetime study: The excitation of Eu(III) and Tb(III), which was 10^{-4} mol dm^{-3}aqueous solution, was made by $^5L_6$, 394 nm, and $^5D_2$, 355 nm, respectively, with pulsed laser beam. The obtained decay curves were calculated by a single-exponential function and fitted by a least-squares method. The resulting decay rate constant k is converted to lifetime τ.

(18) Supkowski, R. M.; Horrocks, W. D. *Inorg. Chim. Acta* **2002**, *340*, 44−48.

(19) Beeby A.; Clarkson, I. M.; Dickins, R. S.; Faulkner, S.; Parker, D.; Royle, L.; Sousa, A. S.; Williams, J. A. G.; Woods, M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 493−503.