Synthesis and Luminescence Properties of New Dinuclear Complexes of Lanthanide(III) Ions

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Dedicated to the memory of Professor Marian Elbanowski

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As a result of coordination of the ligand **L**, containing two tridentate binding units, to samarium(III), europium(III), terbium(III), and dysprosium(III) ions, new dinuclear architectures containing two ions with coordination number 9 were formed. The structures of the complexes have been assigned on the basis of their solution spectroscopic and microanalytical data, and confirmed by X-ray crystallography in the case of the europium(III) complex **2**. The structural analysis of the dinuclear complex **2** showed the presence of two europium centers [Eu(1) and Eu(2)] and four ligands **L**. Each europium ion is coordinated by 9 donor atoms with typical Eu–N and Eu–O distances.

Introduction

The coordination chemistry of lanthanides has become increasingly significant in the last few years due to the wide variety of potential applications of their complexes in many important areas of inorganic chemistry,[1] biology,[2] and medicine.[2c,3] The complexes of lanthanides also play a role as accelerators of hydrolytic cleavage of RNA model compounds,[4] and their applications as MRI contrast agents are very popular, especially complexes of Gd^{III}.[5] Lanthanide complexes are well known to undergo luminescence in the visible and near-IR wavelength regions,[1a,6] and have found widespread applications as fluorescence bio-markers.[2c,7] The design and synthesis of dinuclear complexes of lanthanides constitute a special area of study in bioinorganic chemistry, in particular because of their uses as spectroscopic probes for active sites in metalloproteins.[8]

During the course of our studies on the self-assembly and properties of supramolecular grid-type metal complexes, ligand **L** was shown to successfully form tetranuclear [2 × 2]G architectures upon correct stoichiometric combination with a range of first row transition metal ions.[9] In the resultant grid complexes, the metal ions are octahedrally coordinated by two N,N,O ligand donor sets. Grid complexes of this type may be expected to exhibit interesting photophysics and redox chemistry.

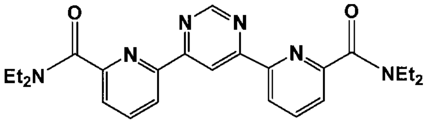

Figure 1. Structure of ligand **L**

In view of the fact that lanthanide ions prefer to be coordinated by relatively hard oxygen donor ligands, it was anticipated that ligand **L** would be able to form stable coordination architectures upon appropriate stoichiometric combination with specific lanthanide salts. However, ligand **L** possesses an insufficient number of donor sites to satisfy the coordination requirement of lanthanide(III) ions. The reaction between **L** and lanthanide ions may, therefore, be expected to result in a variety of possible outcomes depending on factors such as the M:L ratio, solvent, counterions etc.

In this report we describe our initial investigations into the lanthanide coordination chemistry of **L**, and demonstrate that this ligand is able to form structurally novel multinuclear lanthanide complexes of 2:4 M:**L** stoichiometry with Sm^{3+}(**1**), Eu^{3+}(**2**), Tb^{3+}(**3**), and Dy^{3+}(**4**).

The lanthanide complexes with **L** were characterized on the basis of ESI-MS, microanalysis and, in the case of the Eu^{3+} complex **2**, X-ray crystallography. Of particular significance is the fact, that the complexes are luminescent upon irradiation with UV light. A detailed investigation

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into the luminescence properties of the lanthanide complexes was therefore also undertaken in order to obtain the photophysical properties characteristic of the $[M_2L_4]^{6+}$ {M = lanthanide(III)} system.

Results and Discussion

Initial investigations into the lanthanide complexation by **L** focussed upon the reaction between 1:1 stoichiometric combinations of M^{III}/**L** [M^{III} = Sm^{III} (**1a**), Eu^{III} (**2a**), Tb^{III} (**3a**), and Dy^{III} (**4a**)] in the hope of obtaining $[M_4L_4]^{12+}$ grid-type products. Evidence for the existence of $[M_4L_4]^{12+}$ species for the lanthanide ion systems, which may be of a grid-type structure, was obtained using ESI-MS. The ESI-MS data indicate, that many kinds of multinuclear structures co-exist in solution, which may be formulated as grids or helicates. Since we could not obtain crystals suitable for X-ray analysis, thereby confirming the structural identities of the components in the mixture, we decided to change the molar ratio of M^{III}/**L** to 2:3, and we obtained, unexpectedly, new dinuclear complexes of Sm^{III} (**1**), Eu^{III} (**2**), Tb^{III} (**3**), and Dy^{III} (**4**). The dinuclear nature of these species was confirmed by the X-ray crystal structure of the Eu^{III} complex **2**.

The ESI-MS investigations of all complexes were performed on acetonitrile solutions at concentrations of approximately 10^{-4} mol·L^{-1}. For example, the ESI mass spectrum of **1** showed peaks corresponding to multiply charged species containing the $[Sm_2L_4]^{6+}$ unit. These data confirmed the presence of dinuclear complex **1** in solution.

Photophysical Properties

The luminescence lifetimes of Eu^{III} excited states were measured with the use of a detection system consisting of a nitrogen laser-pumped dye laser. Excitation spectra assigned to the $^7F_0-^5D_0$ transition of the Eu^{III} ion were obtained with the same pulsed dye laser. The laser was continuously scanned from 578 to 581.5 nm while monitoring the $^5D_0-^7F_2$ emission at 618 nm. Details of the instrumentation, and procedures used for determining emission lifetimes of europium complexes have been described elsewhere.[10] The electronic absorption spectra for a 10^{-5} mol·L^{-1} acetonitrile solution of complex **2** and **L** are shown in Figure 2.

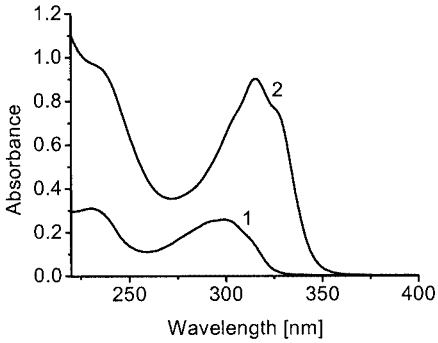

Figure 2. Electronic absorption spectra for acetonitrile solutions of ligand **L** (1.2 × 10^{-5} mol·L^{-1}), and of the Eu^{III} complex **2** (1.07 × 10^{-5} mol·L^{-1})

Two absorption maxima are present, which correspond to π-π* transition bands of the ligand. The absorption maxima, molar extinction coefficients (ε) for the free ligand, and its complexes with lanthanide(III) ions in acetonitrile are listed in Table 1. All the studied complexes show bathochromic shifts of the absorption maxima (ca. 18 nm) indicating ligand-lanthanide interaction. Similar bathochromic shifts have been reported for lanthanide complexes with other azaaryl ligands.[1a,11]

The luminescence properties of Sm^{III}, Eu^{III}, Tb^{III}, and Dy^{III} complexes have been studied in acetonitrile solution at room temperature. The emission spectra of the lanthanide(III) complexes, excited into the lowest energy LC absorption band, showed the well-known structured luminescence of the lanthanide ions.

The excitation spectrum for complex **2** consists of a broad curve with a maximum at ca. 330 nm, assigned to the π-π* transition of the ligand. For a given ligand, the Ln^{III} complexes displayed similar excitation spectra with identical excitation maxima. The emission from the lowest luminescent level to the ground state manifold, i.e. $^4G_{5/2}-^6H_{7/2}$ (598 nm) for Sm^{III}, $^5D_0-^7F_2$ (618 nm) for Eu^{III}, $^5D_4-^7F_5$ (547 nm) for Tb^{III}, and $^4F_{9/2}-^6H_{15/2}$ (576 nm) for Dy^{III} was measured. Strong red (Figure 3) and strong green emissions were observed for the Eu^{III} and Tb^{III} complexes, whereas the emissions of the Sm^{III} and Dy^{III} complexes were weak (Table 1).

The close agreement between the absorption and excitation spectra (see Figures 2 and 3) shows, that the excitation of Ln^{III} ions is caused by an indirect process, i.e. a ligand-to-metal energy transfer, the ligand units acting as an antenna.[1a]

The Eu^{III} ion is unique in that both the ground state $^7F_0$, and excited emissive state $^5D_0$ are non-degenerate. Since the $^7F_0-^5D_0$ transition occurs between non-degenerate energy levels, neither of which can be split by a ligand field, a single environment gives rise to only a single transition. If more than one Eu^{III} environment is present, each will have its own characteristic transition energy. The lifetime of the $^5D_0$ level of Eu^{III} is also a sensitive probe of local structure, particularly in the case of Eu^{III} ions in the presence of OH-oscillators.[12]

The excitation spectrum of complex **2** in the solid state showed two compounds with the $^7F_0-^5D_0$ transition (Figure 4).

The peak maxima of the $^7F_0-^5D_0$ excitation spectrum were found at 579.77 and 580.33 nm. The two compounds indicated by the analysis of the excitation spectrum of complex **2** suggest, that the Eu^{III} ions interact with two different types of binding sites, each with a different number of residual Eu hydration.

The lifetimes of the $^5D_0$ excited state for solid complex **2** were obtained by measuring the luminescence decays at wavelengths of 579.77 and 580.33 nm. The lifetime values were calculated using the mono-exponential decay method.

Table 1. Absorption and luminescence data of the ligand **L** and complexes **1**−**4** in acetonitrile solution

Compound	Absorption		Fluorescence			Lum. quant.yield
	$\lambda_{max.}$ [nm]	$\varepsilon \times 10^4$ [L·mol^{-1}·cm^{-1}]	λ_{ex} [nm]	λ_{em} [nm]	I_{lum} [a.u.]	Φ[a]
L	299.4	2.15	–	–	–	–
1	317.0	8.56	328	598	448	0.0016
2	316.5	8.79	328	618	36800	0.059
3	316.0	9.35	328	547	32100	0.049
4	317.0	9.63	328	576	1880	0.0033

[a] Excitation at 328 nm; $Ru(bpy)_3^{2+}$ (Φ = 0.028 in water) was used as a standard for all Ln^{III} complexes; experimental error ca. 30%.

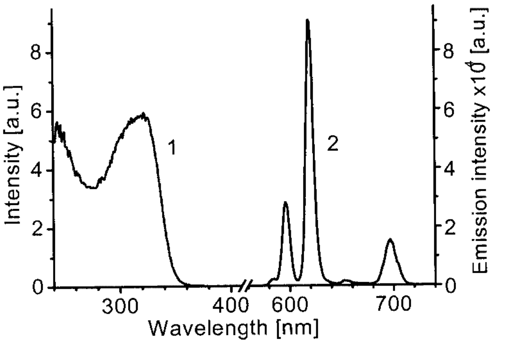

Figure 3. Excitation (1) and emission (2) spectra of complex **2** in acetonitrile solution, [Eu^{III}] = 1.07 × 10^{-5} mol·L^{-1}

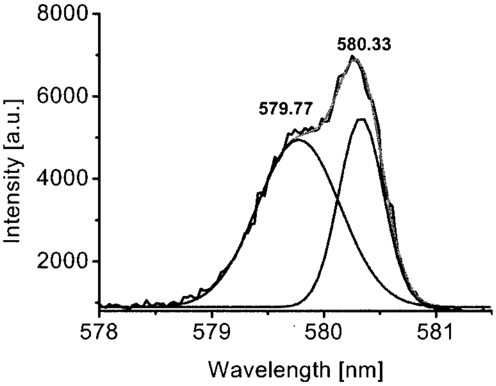

Figure 4. The $^7F_0$−$^5D_0$ selective excitation spectra of complex **2** in the solid state, obtained by analyzing at 618 nm ($^5D_0$−$^7F_2$ transition), and its deconvolution using a Gaussian-type function. Experimental data (dark line), calculated data (light line)

Two separate lifetime values of 280 and 511 μs were obtained, respectively. The hydration numbers of the Eu^{III} ions in complex **2** were found directly from the lifetime measurements using the equation: $n_{H2O} = 1.05k_{obsd.}$ (ms^{-1}) −0.7, where $k_{obsd.}$ is the reciprocal of the excited state lifetime.[13]

The numbers of water molecules bound in the inner coordination sphere of the Eu^{III} ions were determined as 3 and 1. The presence of the two species was found on the excitation spectrum of complex **2** (Figure 4). The peak at the shorter excitation wavelength (579.77 nm) can be assigned to the Eu complex with three molecules of H_2O in the inner coordination sphere, and the peak at the longer wavelength (580.33 nm) to the Eu complex with one molecule of H_2O. The presence of one and three-coordinated H_2O molecules in complex **2** is in agreement with crystallographic data.

Crystallographic Characterization of Complex 2

Single crystals of complex **2** were obtained by slow diffusion of *tert*-butyl methyl ether into a solution of the complex in acetonitrile, and its structure was determined by X-ray crystallography. The structure of the Eu^{III} complex is shown in Figure 5.

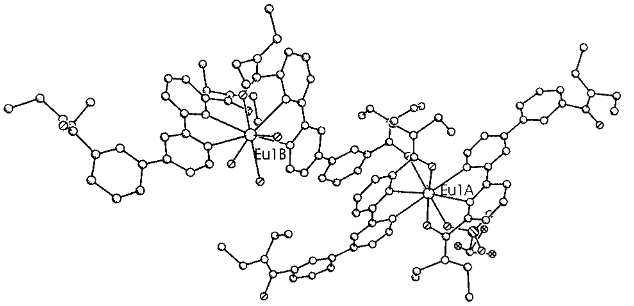

Figure 5. Molecular structure of complex **2** in the crystal. $Eu_2(C_{24}H_{28}N_6O_2)_4(CF_3SO_3)_6\cdot 6H_2O$

In the crystal structure the complex exists as a binuclear compound. The europium(III) ions are nine-coordinate, and the geometry around the central ions can be described as distorted, tri-capped trigonal prismatic. Both ions are coordinated (almost symmetrically) by two ligands, that utilize three centers each: two aromatic ring nitrogen atoms, and one carbonyl oxygen atom, all from the same half of the molecule. Only one out of four ligands (D) joins two europium ions, and effectively acts as a tetradentate ligand. The coordination of Eu1A is completed by one of the triflate counterions and one water molecule, while Eu1B has three water molecules at the coordination sites.

One Eu^{III} ion is coordinated by six donor atoms from two molecules of the ligand **L** [each ligand comprises bis(tridentate) N,N,O (carbonyl) donor sets], and three remaining positions are occupied by oxygen atoms of water molecules. The second Eu^{III} ion is also nine-coordinate, but its coordination environment is filled by six donor atoms from two molecules of the ligand **L**. The seventh position is occupied by the oxygen atom of a triflate ion, the eighth site contains the oxygen atom of a water molecule, and in the ninth site there is an oxygen carbonyl atom of ligand **L** (D), which is coordinated to the first Eu^{III} ion, and plays a role as bridge between two metal ions. To the best of our knowledge, only six complexes with Eu^{III}-triflate bonds are known.[4e,14]

Two binuclear complexes **2**, related by a center of symmetry at (1/2, 1/2, 1/2), form a dimer connected via two water molecules, and two triflate molecules by means of hydrogen bonds (Figure 6).

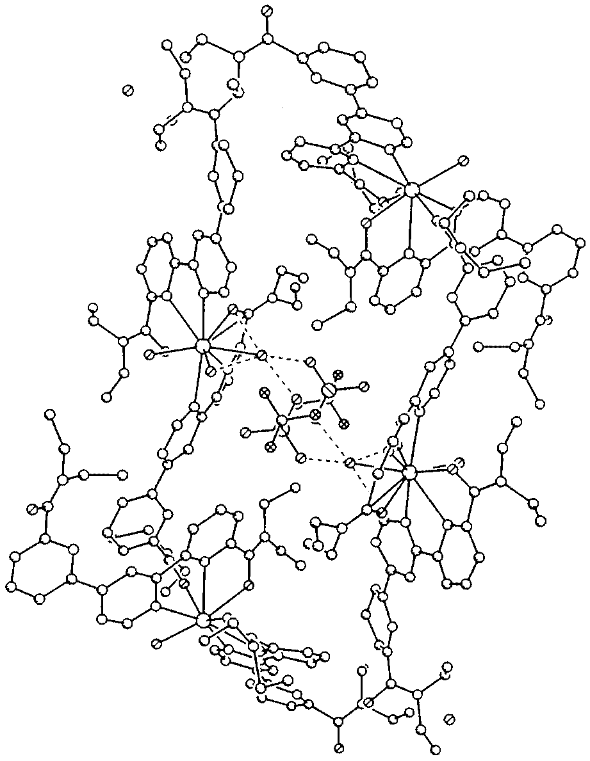

Figure 6. Hydrogen-bonded centrosymmetric dimer (see text)

These dimers, in turn, are connected by O(water)···O(carbonyl) hydrogen bonds, and make infinite chains along the *y* direction. In the crystal structure, the water molecules, which can both donate and accept hydrogen bonds act as a kind of "glue", which connects the molecules in the crystal structure. This structure is additionally strengthened by a number of weak C−H···O hydrogen bonds.

The Eu−O and Eu−N distances are well within typical ranges. The mean values are as follows (in parentheses are the mean values from the December 2002 version of the Cambridge Structural Database[15]): Eu(1A)−O(water): 2.45(2) [2.45(6)], Eu−O(carbonyl): 2.43(2) [2.40(6)], and Eu−N(aromatic): 2.60(2) [2.62(8)]. The conformation of the ligand molecules can be described by the values of the dihedral angles between the least-squares planes of the pyridine rings. Three ligands, which are bound to a single Eu ion, have quite similar values for these twist angles (15°−23°), while the ligand D, which binds two Eu ions, is significantly more twisted, the dihedral angle being 46(1)°.

Conclusion

We have described four new photoactive lanthanide complexes. Ligand **L**, containing two N,N,O tridentate binding sites for complexation, is a good Eu^{III} and Tb^{III} sensitizer. The europium complex **2** shows excellent luminescence properties with a high quantum yield, and effective intramolecular energy transfer from the ligand to the Eu^{III} ions. These factors, along with the stability of this complex in solution, make these compounds good candidates as luminescence and laser materials. ES-MSI and luminescence indicate, that the structure found in the crystal is essentially maintained in solution.

In conclusion, the investigated complexes may be of use in several fields of lanthanide coordination chemistry or as luminescent supramolecular nano-devices.

Experimental Section

General Remarks: CH_3CN was freshly distilled under argon from CaH_2. Ligand **L** was prepared according to the literature.[9] The lanthanide triflates were used without further purification from Aldrich. ESI-mass spectra were determined in acetonitrile using a Waters Micromass ZQ apparatus. Microanalyses were obtained using an Elementor Vario El III microanalyzer.

All absorption spectra, in acetonitrile or aqueous solution, were recorded with a Shimadzu UVPC 2001 spectrophotometer, between 200 and 400 nm, in 10 × 10 mm quartz cells. The concentration of Ln^{III} ions was $1-2 \times 10^{-5}$ mol·L^{-1} in all experiments. Excitation and emission spectra were measured at room temperature on a Perkin−Elmer MPF3 spectrofluorimeter with excitation and emission slits at 5 nm.

The quantum yields of the metal-centered luminescence were determined using published procedures, with $Ru(bpy)_3{}^{2+}$ as a standard,[16] in CH_3CN at room temperature. The refractive indexes were 1.346 for solutions in CH_3CN, and 1.333 for solutions in water. The excitation wavelength was 326 or 328 nm for all lanthanide ions.

Sm^{III} Complex 1: A mixture of $Sm(CF_3SO_3)_3$ (9.1 mg, 15 µmol) and ligand **L** (9.9 mg, 23 µmol) in CH_3CN (5 mL) was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure to yield a white powder in quantitative yield. ESI-MS: *m*/*z* (%) = 1314 (8) $\{[Sm_2(\mathbf{L})_4](CF_3SO_3)_4\}^{2+}$, 827 (3) $\{[Sm_2(\mathbf{L})_4](CF_3SO_3)_3\}^{3+}$, 583 (100) $\{[Sm_2(\mathbf{L})_4](CF_3SO_3)_2\}^{4+}$, 437 (20) $\{[Sm_2(\mathbf{L})_4](CF_3SO_3)\}^{5+}$, 339 (5) $\{[Sm_2(\mathbf{L})_4]\}^{6+}$. $Sm_2\mathbf{L}_4(CF_3SO_3)_6\cdot 6H_2O$ (3033.31): calcd. C 40.39, H 4.12, N 11.08, S 6.34; found C 40.45, H 3.92, N 10.35, S 6.80.

Sm^{III} Complex 1a: A solution of ligand **L** (10.4 mg, 24 µmol) and $Sm(CF_3SO_3)_3$ (14.5 mg, 24 µmol) in CH_3CN (5 mL) was stirred at room temperature for 19 h. The white complex was isolated in quantitative yield by evaporation of the solvent. ESI-MS: *m*/*z* (%) = 1910.2 (3) $\{[Sm_4(\mathbf{L})_4](CF_3SO_3)_{10}\}^{+2}$, 1316.4 (7) $\{[Sm(\mathbf{L})_2](CF_3SO_3)_2\}^{+}$, 1180.1 (7) $\{[Sm_3(\mathbf{L})_2](CF_3SO_3)_7\}^{2+}$, 1096.9 (10) $\{[Sm_2(\mathbf{L})_3](CF_3SO_3)_4\}^{2+}$, 881.9 (100) $\{[Sm_4(\mathbf{L})_4](CF_3SO_3)_8\}^{4+}$, 736.3 (18) $\{[Sm_3(\mathbf{L})_2](CF_3SO_3)_6\}^{3+}$, 681.9 (2) $\{[Sm_2(\mathbf{L})_3]$-

$(CF_3SO_3)_3\}^{3+}$, 515.9 (2) $\{[Sm_3(\mathbf{L})_2](CF_3SO_3)_5\}^{4+}$, 365.5 $\{[Sm_4(\mathbf{L})_4](CF_3SO_3)_4\}^{8+}$. $Sm_4\mathbf{L}_4(CF_3SO_3)_{12}$ (4120.3): calcd. C 31.48, H 2.74, N 8.16, S 9.34; found C 30.06, H 2.56, N 9.01, S 7.85. Excitation, λ = 326 nm. Luminescence spectrum (MeCN, 2×10^{-5} M, at 20 °C): λ_{em} = 566 nm ($^4G_{5/2}\rightarrow{}^6H_{5/2}$), 597 nm ($^4G_{5/2}\rightarrow{}^6H_{7/2}$), 647 nm ($^4G_{5/2}\rightarrow{}^6H_{9/2}$).

Eu^{III} Complex 2: A solution of ligand **L** (11.9 mg, 28 µmol) and $Eu(CF_3SO_3)_3$ (11.0 mg, 18 µmol) in CH_3CN (5 mL) was stirred at room temperature for 24 h. The white complex was isolated in quantitative yield by evaporation of the solvent. ESI-MS: *m*/*z* (%) = 1316 (30) $\{[Eu_2(\mathbf{L})_4](CF_3SO_3)_4\}^{2+}$, 827 (7) $\{[Eu_2(\mathbf{L})_4](CF_3SO_3)_3\}^{3+}$, 583 (100) $\{[Eu_2(\mathbf{L})_4](CF_3SO_3)_2\}^{4+}$, 436 (100) $\{[Eu_2(\mathbf{L})_4](CF_3SO_3)\}^{5+}$, 340 (10) $\{[Eu_2(\mathbf{L})_4]\}^{6+}$. $Eu_2\mathbf{L}_4(CF_3SO_3)_6{\cdot}6H_2O$ (3036.59): calcd. C 40.35, H 4.12, N 11.07, S 6.34; found C 39.23, H 4.03, N 10.67, S 6.02.

Eu^{III} Complex 2a: An equimolar mixture of $Eu(CF_3SO_3)_3$ (7.5 mg, 17 µmol) and ligand **L** (10.4 mg, 17 µmol) in CH_3CN (5 mL) was stirred at room temp. for 16 h. The solvent was evaporated under reduced pressure to yield a yellowish powder. ESI-MS: *m*/*z* (%) = 1914.5 (3) $\{[Eu_4(\mathbf{L})_4](CF_3SO_3)_{10}\}^{2+}$, 1314.9 (10) $\{[Eu_2(\mathbf{L})_4](CF_3SO_3)_4\}^{2+}$, 1226.0 (10) $\{[Eu_4(\mathbf{L})_4](CF_3SO_3)_9\}^{3+}$, 1181.5 (3) $\{[Eu_3(\mathbf{L})_2](CF_3SO_3)_7\}^{2+}$, 1097.9 (23) $\{[Eu_2(\mathbf{L})_3](CF_3SO_3)_4\}^{2+}$, 881.9 (100) $\{[Eu_4(\mathbf{L})_4](CF_3SO_3)_8\}^{4+}$, 827.4 (5) $\{[Eu_2(\mathbf{L})_4](CF_3SO_3)_3\}^{3+}$, 738.1 (14) $\{[Eu_3(\mathbf{L})_2](CF_3SO_3)_6\}^{3+}$, 682.5 (20) $\{[Eu_2(\mathbf{L})_3](CF_3SO_3)_3\}^{3+}$, 673.8 (10) $\{[Eu_4(\mathbf{L})_4](CF_3SO_3)_7\}^{5+}$, 582.8 (15) $\{[Eu_2(\mathbf{L})_4](CF_3SO_3)_2\}^{4+}$, 538.3 (25) $\{[Eu_4(\mathbf{L})_4](CF_3SO_3)_6\}^{6+}$, 435.2 (10) $\{[Eu_2(\mathbf{L})_4](CF_3SO_3)\}^{5+}$, 366.9 (10) $\{[Eu_4(\mathbf{L})_4](CF_3SO_3)_4\}^{8+}$, 350.0 (3) $\{[Eu_2(\mathbf{L})_3](CF_3SO_3)\}^{5+}$. $Eu_4\mathbf{L}_4(CF_3SO_3)_{12}$ (4126.77): calcd. C 31.43, H 2.75, N 8.15, S 9.32; found C 30.16, H 2.55, N 7.97, S 8.53. UV/Vis ($c = 1.8 \times 10^{-5}$ M): λ = 303 nm, 314 nm, 326 nm. Excitation λ = 326 nm. Luminescence spectrum (MeCN, at 20 °C): λ_{em} = 590 nm ($^5D_0\rightarrow{}^7F_1$), 615 nm ($^5D_0\rightarrow{}^7F_2$), 648 nm ($^5D_0\rightarrow{}^7F_3$), 691 nm ($^5D_0\rightarrow{}^7F_4$).

Tb^{III} Complex 3: A mixture of $Tb(CF_3SO_3)_3$ (6.7 mg, 11 µmol) and ligand **L** (7.2 mg, 17 µmol) in CH_3CN (5 mL) was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure to yield a white product in quantitative yield. ESI-MS: *m*/*z* (%) = 1322 (15) $\{[Tb_2(\mathbf{L})_4](CF_3SO_3)_4\}^{2+}$, 586 (100) $\{[Tb_2(\mathbf{L})_4](CF_3SO_3)_2\}^{4+}$, 341 (8) $\{[Tb_2(\mathbf{L})_4]\}^{6+}$. $Tb_2\mathbf{L}_4(CF_3SO_3)_6{\cdot}8H_2O$ (3074.37): calcd. C 39.85, H 4.16, N 10.93, S 6.26; found C 37.14, H 4.11, N 10.20, S 6.42.

Tb^{III} Complex 3a: A solution of ligand **L** (7.0 mg, 16 µmol) and $Tb(CF_3SO_3)_3$ (9.8 mg, 16 µmol) in CH_3CN (5 mL) was stirred at room temperature for 21 h. The white complex was isolated in quantitative yield by evaporation of the solvent. ESI-MS: *m*/*z* (%) = 2360.4 (1) $\{[Tb_2(\mathbf{L})_3](CF_3SO_3)_5\}^{+}$, 1927.2 (2) $\{[Tb_4(\mathbf{L})_4](CF_3SO_3)_{10}\}^{2+}$, 1236.4 (2) $\{[Tb_4(\mathbf{L})_4](CF_3SO_3)_9\}^{3+}$, 1192.1 (1) $\{[Tb_3(\mathbf{L})_2](CF_3SO_3)_7\}^{2+}$, 1105.4 (80) $\{[Tb_2(\mathbf{L})_3](CF_3SO_3)_4\}^{2+}$, 889.2 (37) $\{[Tb_4(\mathbf{L})_4](CF_3SO_3)_8\}^{4+}$, 687.4 (92) $\{[Tb_2(\mathbf{L})_3](CF_3SO_3)_3\}^{3+}$, 543.2 (15) $\{[Tb_4(\mathbf{L})_4](CF_3SO_3)_6\}^{6+}$, 370.1 (12) $\{[Tb_4(\mathbf{L})_4](CF_3SO_3)_4\}^{8+}$. $Tb_4\mathbf{L}_4(CF_3SO_3)_{12}$ (4154.6): calcd. C 31.22, H 2.72, N 8.09, S 9.26; found C 30.98, H 2.82, N 8.23, S 8.22. Excitation λ = 326 nm. Luminescence spectrum (MeCN, 2×10^{-5} M at 20 °C): λ_{em} = 494 nm ($^5D_4\rightarrow{}^7F_6$), 549 nm ($^5D_4\rightarrow{}^7F_5$), 588 nm ($^5D_4\rightarrow{}^7F_4$), 621 nm ($^5D_4\rightarrow{}^7F_3$).

Dy^{III} Complex 4: A mixture of $Dy(CF_3SO_3)_3$ (8.3 mg, 14 µmol) and ligand **L** (8.8 mg, 20 µmol) in CH_3CN (4 mL) was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure to yield a white powder in quantitative yield. ESI-MS: *m*/*z* (%) = 1326 (10) $\{[Dy_2(\mathbf{L})_4](CF_3SO_3)_4\}^{2+}$, 589 (100) $\{[Dy_2(\mathbf{L})_4](CF_3SO_3)_2\}^{4+}$, 441 (20) $\{[Dy_2(\mathbf{L})_4](CF_3SO_3)\}^{5+}$, 342 (10) $\{[Dy_2(\mathbf{L})_4]\}^{6+}$. $Dy_2\mathbf{L}_4(CF_3SO_3)_6{\cdot}8H_2O$ (3093.62): calcd. C 39.57, H 4.14, N 10.87, S 6.21; found C 36.53, H 4.07, N 10.09, S 6.25.

Dy^{III} Complex 4a: A solution of ligand **L** (8.2 mg, 19 µmol) and $Dy(CF_3SO_3)_3$ (11.5 mg, 19 µmol) in CH_3CN (5 mL) was stirred at room temperature for 21 h. The white complex was isolated in quantitative yield by evaporation of the solvent. ESI-MS: *m*/*z* (%) = 1325 (10) $\{[Dy_2(\mathbf{L})_4](CF_3SO_3)_4\}^{+2}$, 1108 (2) $\{[Dy_2(\mathbf{L})_3](CF_3SO_3)_4\}^{2+}$, 893 (10) $\{[Dy_4(\mathbf{L})_4](CF_3SO_3)_8\}^{4+}$, 546 (3) $\{[Dy_4(\mathbf{L})_4](CF_3SO_3)_6\}^{6+}$, 481 (5) $\{[Dy_2(\mathbf{L})_3](CF_3SO_3)_2\}^{4+}$, 447 (5) $\{[Dy_4(\mathbf{L})_4](CF_3SO_3)_5\}^{7+}$, 433 (100) [**L** + H]), 393 (5) $\{[Dy_3(\mathbf{L})_2](CF_3SO_3)_4\}^{5+}$, 150 (5) $[Dy_3(\mathbf{L})_2]^{9+}$. $Dy_4\mathbf{L}_4(CF_3SO_3)_{12}$ (4168.9): calcd. C 31.12, H 2.71, N 8.06, S9.23; found C 30.22, H 2.89, N 8.23, S 9.50. Excitation, λ = 326 nm. Luminescence spectrum (MeCN, $c = 2 \times 10^{-5}$ M, at 20 °C): λ_{em} = 483 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$), 577 nm ($^4F_{9/2}\rightarrow{}^6H_{15/2}$).

X-ray Crystallographic Study: Data were collected using the ω-scan technique in the θ range 2−25° with a KUMA KM4CCD[17] four-circle diffractometer with a CCD detector, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Accurate cell parameters were determined by a least-squares fit of the 5250 reflections of highest intensity, chosen from the whole experiment. Data were corrected for Lorentz-polarization[18] and absorption effects.[19] Due to the long *b* parameter of the unit cell, the potential overlapping of reflections was also taken into account. The structure was solved by direct methods with SHELXS-97,[20] and refined with SHELXL-97.[21] Non-hydrogen atoms were refined anisotropically, hydrogen atoms were located in calculated positions, and refined using the "riding model" with their isotropic thermal parameters set at 1.2 times the U_{eq} value of the appropriate carrier atom. The final model involves some disorder in the crystal structure (N−Et$_2$ groups and two triflates). Weak constraints to the thermal parameters of chosen atoms were applied. Crystallographic data for complex **2** are listed in Table 2.

Table 2. Crystallographic data for the structural analyses of the complex **2**

Empirical formula	$Eu_2(C_{24}H_{28}N_6O_2)_4(CF_3SO_3)_6{\cdot}6H_2O$
Molecular mass	3036.59
a (Å)	12.254(2)
b (Å)	41.250(4)
c (Å)	25.654(2)
α (°)	90
β (°)	94.03(1)
γ (°)	90
V (Å^3)	12936(2)
Z	4
Space group	$P2_1/n$
$D_{calcd.}$ (g·cm^{-3})	1.56
μ(Mo-K_α) (mm^{-1})	1.17
$R(F)$ [$F^2 > 2\sigma(F^2)$][a]	0.084
$R_w(F^2)$ [all data][b]	0.180

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [b] $Rw(F2) = (\Sigma[w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2])^{1/2}$.

CCDC-210662 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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