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Self-Assembly of a Trinuclear Luminescent Europium Complex

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Functional molecules containing lanthanides have already found many applications in medicine and biology, especially for medical imaging purposes (MRI contrast agents)^[1] and luminescent probes.^[2] However, the development of new lanthanide complexes combining both responsive features is of importance for the enhancement of imaging and diagnostic procedures. The design of suitable receptors for lanthanides is challenging because it must take into account several antagonistic requirements. The application of Ln^{III} complexes as MRI contrast agents requires high stability and the presence of exchangeable water molecules to exhibit a good relaxivity. Efficient ligands for Gd^{III} coordination are therefore derived from macrocyclic ligands providing a high thermodynamic and kinetic stability and one or two positions for water coordination.^[1] Good luminescent properties of lanthanide complexes are achieved with organic ligands possessing suitable chromophores for efficient sensitization of the lanthanide luminescence. One of the most investigated type of ligands for Ln^{III} complexation are receptors bearing the β -diketonate structural motif, and various ligands were recently reviewed by Binnemans.^[3] Suitable diketonate complexes can be advantageously used for fluoroimmunologic assays^[4] and for responsive systems based on luminescence quenching.^[5] Diketonate-containing ligands are often combined with other ligands (bipy, terpy, phen)^[6] 1) to complete the coordination sphere and 2) to enhance luminescent properties of new materials.^[7] Pyridyl-substituted diketo-

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nates provide an additional coordination within one receptor to give rise to binuclear complexes.^[8] Analogous ligands (bis(2-pyridylcarbonyl)amine (Hbpca) and bis(2-pyrimidylcarbonyl)amine (Hbpmca)) can be obtained upon replacement of the connecting carbon with an amidic nitrogen. This structural motif was successfully used for the preparation of coordination complexes with different transition-metal ions, in which the carbonyl groups may bridge neighboring cations.^[9] The only example of lanthanide-containing compounds in which Ln^{III} is coordinated by carbonyl groups, is reported for binuclear Fe^{III}–Dy^{III} complexes.^[10]

To better satisfy a high coordination number of Ln^{III}, we have prepared a new ligand by introducing terminal carboxylic groups on the Hbpca backbone to achieve the Ln^{III} coordination in the pentacoordinate cavity (Scheme 1). The



Scheme 1. Synthesis of **L1** and **L2**. Reagents: i) SOCl₂, DMF, CH₂Cl₂/toluene; ii) NH₄Cl/SiO₂, TsCl, NEt₃.

topology of this coordination site can be compared to some pentadentate ligands, namely derivatized dicarbazone^[11] and terpyridine ligands^[12] used for fluorimetric assays.^[4] As shown previously for transition metals, the amidic carbonyl groups point to the opposite side of the cavity, which makes them available for some additional complexation. After deprotonation of the amidic and carboxylic groups, the negatively charged ligand compensates the positive charge of lanthanides, which is supposed to increase the thermody-

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namic stability of the resulting complexes. In this work, we report on the preparation, structure, and characterization of the europium complex with bis(6-carboxypyridine-2-carbonyl)amine (L2). The luminescent properties of this neutral complex are reported in view of possible applications in imaging techniques.

The L1 precursor was synthesized by adapting the conditions usually used for the synthesis of diacylamide compounds (Scheme 1, see the Supporting Information). The ¹H NMR spectrum of **L1** in CD₃CN (see Figure S1 in the Supporting Information) shows well-resolved peaks of three aromatic protons and a singlet for the terminal methyl protons, in agreement with C_2 symmetry. Attempts to transform L1 to L2 by hydrolysis of the ester group in basic media led to the hydrolysis of the amidic group. To isolate the Eu^{III} complexes with L2, the solution of L1 in DMF was treated with NaH. The DMF solution containing one equivalent of [Eu(Otf)₃] was slowly added to the resulting mixture under stirring. The hydrolysis of the terminal methyl ester groups occurs by the concerted complexation of the ester group to the Eu^{III} cation acting as a Lewis acid and the action of NaH, as was described for the alkaline hydrolysis of tertbutyl esters.^[13] Finally, diffusion of water into a filtered DMSO solution of the complex provides X-ray quality cubic crystals showing a strong red-orange photoluminescence upon the UV light irradiation.

 $[Eu_3(L2)_3(H_2O)_6]$ crystallizes in the cubic system (space group $Pa\bar{3}$) and contains eight trimeric complexes in the unit cell.^[14] The X-ray crystal structure of $[Eu_3(L2)_3(H_2O)_6]$ shows that this complex is formed by three molecules of L2 interconnected with three europium cations around a crystallographic threefold axis (Figure 1 and S2 in the Supporting Information). Each europium cation in the crystal structure is nine-coordinated by five donor atoms of one ligand (pentacoordinated cavity), two oxygen atoms of the amidic carbonyl groups of the neighboring ligand, and the two remaining positions are occupied by water molecules (Figure 2). The coordination sphere of Eu^{III} can be described as a distorted mono-capped square antiprismatic site, in which one water molecule caps the rectangular face formed by two carbonyl and two carboxylate oxygens. The final edifice is electroneutral due to the full compensation of the europium positive charge by the two carboxylates and the deprotonated amide nitrogen. A view of the crystal packing is given in Figures S3 and S4 in the Supporting Information. The Eu–O and Eu–N bond lengths in [Eu₃(L2)₃- $(H_2O)_6$] are with the expected range (see Table S1 in the Supporting Information). The bond lengths in the CO-N-CO group are symmetrical with the C-O bonds shorter than in lanthanide complexes with real β-diketonate ligands. These data suggest the presence of the diketo form of the N-deprotonated L2 with a lower π -electron delocalization.

The triangular arrangement of europium cations can be compared with the arrangement in trinuclear sandwich complexes obtained from Ln^{III} and *cis*-inositol,^[15] in which lanthanides form similar two-dimensional arrays. In the complex with Eu^{III}, the cations are only eight-coordinated: six



Figure 1. Crystal structure of $[Eu_3(L2)_3(H_2O)_6]$. View of the trinuclear complex a) along and b) perpendicular to the threefold axis.



Figure 2. View of the coordination environment around Eu^{III} cations in $[Eu_3(L2)_3(H_2O)_6]$ with the atomic numbering scheme.

coordination bonds are provided by two ligands and the two remaining positions are occupied by water molecules. However, the intermetallic distance of 3.745 Å is much shorter than in $[Eu_3(L2)_3(H_2O)_6]$, in which the distance between Eu cations is 6.4969(4) Å.

The ¹H NMR spectrum of the complex $[Eu_3(L2)_3(H_2O)_6]$ in DMSO (Figure 3) shows three different aromatic signals, which are shifted upfield and broadened due to the paramagnetic contribution of Eu^{III} cations. The ES-MS spectrum of the DMSO/CH₃CN solution (7×10^{-5} M) clearly confirms the presence of the trinuclear edifice in solution with peaks at *m*/*z* 1393.9 ([Eu₃(L2)₃+H⁺]⁺) and *m*/*z* 697.8 ([Eu₃(L2)₃ +2H⁺]²⁺).

The trinuclear complex was investigated by using Eu^{III} as a structural probe to correlate the coordination environment in the solid state and in solution. The high-resolution excitation and emission spectra of isolated $[Eu_3(L2)_3(H_2O)_6]$ crys-



Figure 3. ¹H NMR spectrum of $[Eu_3(L2)_3(H_2O)_6]$.

tals were recorded at temperatures from 10 to 300 K. The emission spectrum (Figure 4a) obtained upon irradiation through the ligand-centered excited states (λ_{exc} =280 nm) is dominated by the intense hypersensitive Eu(${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) tran-



Figure 4. The emission spectra of $[Eu_3(\textbf{L2})_3(H_2O)_6]$ in the solid state at a) 10 K ($\lambda_{ex}{=}280$ nm), b) 295 K ($\lambda_{ex}{=}280$ nm), and c) in DMSO ($\lambda_{ex}{=}279$ nm, 295 K).

sition at 616 nm and does not significantly change with temperature (Figure 4a,b). The excitation profiles upon monitoring different Eu(${}^{5}D_{0}$) transitions can be superimposed and show a broad band with the maximum at 284 nm with a significant tail up to 400 nm (see Figure S5 in the Supporting Information), which allows efficient ligand $(\pi\pi)^{*} \rightarrow Eu^{III}$ energy transfers. The very weak $Eu({}^{5}D_{0}\leftarrow^{7}F_{0})$ transition is unique and indicates a single type of environment around the Eu^{III} cations related by a crystallographic threefold axis. The considerable splitting of the ${}^{7}F_{1}$ (3 transitions), ${}^{7}F_{2}$ (5 transitions), and ${}^{7}F_{4}$ (9 transitions) states is compatible with the low local C_{s} -symmetry of the Eu^{III} site found in the crystal structure of $[Eu_{3}(L2)_{3}(H_{2}O)_{6}]$ (see Table S2 in the Supporting Information).

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The energy of the Eu(${}^{5}D_{0} \leftarrow {}^{7}F_{0}$) transitions is modified by the composition of the europium coordination sphere (the nephelauxetic effect) and can be calculated according to Frey and Horock's equation [Eq. (1)], in which $\tilde{\nu}_{0}$ = 17374.0 cm⁻¹ is the energy of the Eu(${}^{5}D_{0} \leftarrow {}^{7}F_{0}$) transition in the free metal ion, C_{CN} is equal to 1.0 for the nine-coordinate Eu^{III} cation, n_{i} is the number of atoms of type i, and δ_{i} is the capacity of the atom i to accept the electronic density of the metal ion.^[16] The coordination sphere of each europium cation is considered as that of the crystal structure: two heterocyclic nitrogens, two oxygen atoms of carboxylic groups, two water molecules, two carbonyl oxygens, and one negatively charged nitrogen of the amide group.

$$\tilde{\nu} = \tilde{\nu}_0 + C_{CN} \sum n_i \delta_i \tag{1}$$

If we consider $\delta_i = -15.3$ for the deprotonated nitrogen, the application of Equation (1) gives the value 17241.5 cm⁻¹ (580 nm). The position of the Eu(${}^{5}D_{0} \rightarrow {}^{7}F_{0}$) transition was found to be 17227 cm⁻¹ at 10 K, which corresponds to 17239 cm⁻¹ at 295 K by taking into account the temperature correction 1 cm⁻¹ per 24 K.^[17] The resulting difference of 2.5 cm⁻¹ suggests that the negatively charged nitrogen has a stronger nephelauxetic effect than expected above. The straightforward calculation gives $\delta_i = -17.8$ cm⁻¹, which is in line with a general effect of anionic ligands. The alternative consideration of β -diketonate oxygens instead of carbonyl ones for the prediction of $\tilde{\nu}$ gives the value 17245.1 cm⁻¹, which differs from that of the experiment by 6.1 cm⁻¹. This comparison is consistent with the diketo configuration of L2 discussed above.

The Eu(⁵D₀) lifetimes in the solid state were obtained upon irradiation through ligand-centered excited states (28169 cm⁻¹) at temperatures between 10 and 300 K. Monoexponential luminescent decays support the presence of only one type of the Eu^{III} site. The average lifetime for different transitions (see Table S3 and Figure S5 in the Supporting Information) at 10 K is 0.47(4) ms and slightly decreases with temperature to 0.41(2) ms at 300 K. Such a lifetime is comparable to the one of other Eu^{III} complexes containing two water molecules in the first coordination sphere.^[18]

The excitation spectrum of $[Eu_3(L2)_3]$ in DMSO (see Figure S7 in the Supporting Information) coincides with the absorption spectrum with the maximum absorbance at 284–286 nm as found in the solid state. Except for some broadening, the europium-centered emission spectra in DMSO, D₂O, and H₂O show the same pattern as in the solid state, which confirms the presence of the same trinuclear structure in solution (Figure 4c and Figure S8 in the Supporting Information). Compared to the results in the solid state, $[Eu_3(L2)_3]$ in DMSO shows a considerable lengthening of the luminescent lifetime (τ =1.57 ms). This can be explained by the replacement of water molecules containing O–H oscillators with DMSO in the first coordination sphere of Eu^{III}. The absolute quantum yield, Φ_{abs} , of the $[Eu_3(L2)_3]$ lu-

minescence in DMSO at 295 K was estimated to be about 37%. The solution structure of $[Eu_3(L2)_3]$, especially the number of water molecules in the first coordination sphere, was evaluated by using Horrocks and Sudnick's equation^[18] [Eq. (2)] corrected for closely diffusing oscillators.^[19]

$$q = 1.1(k_{H_2O} - k_{D_2O} - 0.31) \tag{2}$$

The lifetimes measured for $[Eu_3(L2)_3]$ in water (0.42 ms) and deuterated water (2.41 ms) (see Table S3 in the Supporting Information) give q = 1.8(1), which confirms that 1) two water molecules are present in the first coordination sphere and 2) the trinuclear complex is maintained in solution. Although the quantum yield in water falls to about 13%, this value is still compatible with potential applications in sensing devices. The decrease of Φ_{abs} by about 70% compared to value in the DMSO solution is accompanied by the decrease of the luminescent lifetime ($\tau_{H_2O}/\tau_{DMSO}=0.3$, Table S3).

In summary, the self-assembly of the new receptor L2 with Eu^{III} results in the formation of the trinuclear discrete complex. Its crystal structure reveals the two-dimensional arrangement of europium cations with an unusual topology, in which each Eu^{III} is nine-coordinated by two neighboring ligands and two water molecules. Despite the coordination of water molecules to the Eu^{III} cations in $[Eu_3(L2)_3(H_2O)_6]$, the trinuclear complex exhibits remarkable luminescent properties and the presence of three metal ions in proximity may constitute a significant advantage for designing homoand heterometallic sensing systems. Current investigations are focused on the analogous trinuclear complexes with paramagnetic lanthanides, which are of a special interest as potential MRI contrast agents.

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