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Cation-Controlled Self-Assembly of a Hexameric Europium Wheel

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The assembly of sophisticated high-nuclearity coordination complexes with relatively simple ligands allows the combination of their nanoscopic size with the magnetic or optical properties of the metals which should lead to interesting new materials. The number of fascinating metal-based supramolecular architectures such as metallacoronates, circular helicates, and wheels is rapidly increasing.[1] The incorporation of lanthanides(III) in such highly organized polymetallic complexes is of great interest in supramolecular chemistry in view of their interesting magnetic and luminescent properties.[2] Indeed, the creation of polymetallic architectures is crucial for the design of lanthanide-based devices such as light converters[3] or MRI contrast agents.[4] Despite this, the assembly of lanthanide-based supramolecular architectures has lagged behind that of other systems due to the difficulty in controlling the coordination environment of these ions which display high and variable coordination numbers with little stereochemical preferences.[5] The first example of self-assembly of dinuclear helical species containing lanthanide ions was reported in 1992.[6] The groups of Piguet and Bünzli have subsequently prepared a large number of N-donor podating ligands to explore intramolecular Ln−Ln energy transfer.[2c] We have recently described the self-assembly of homotrinuclear lanthanide complexes M_3L_2 directed by a potentially dodecadentate flexible tripodal ligand containing three tetradentated carboxyterpyridine arms.[7]

Here we report how the simple asymmetric tetradentate ligand 2,2′:6′,2″-terpyridine-6-carboxylic acid (HL) lead to the self-assembly of a large rare earth ring[8] and to the first one containing the Eu^{III} ion which, due to its peculiar spectroscopic properties, is one of the lanthanides (together with Tb^{III}) best suitable for the design of luminescent probes and sensors.[5] We also describe how the formation of the polymetallic ring can be controlled by the ligand/cation ratio.

The reaction of $\mathrm{Eu(Otf)_3}$ with 2 equiv of HL in the presence of triethylamine in methanol leads to the formation of the mononuclear eight-coordinate complex $[\mathrm{Eu(L)_2}](\mathrm{Otf})$, **1** (Figure 1). The molecular structure of **1** was confirmed by X-ray crystallographic analysis on a single crystal.[9] A previous X-ray crystallographic analysis on single crystals of poorer quality revealed a neutral nine-coordinate Eu(III) complex with the triflate counterions occupying the ninth coordination position.[10] This indicates that the eight-coordinate $[\mathrm{EuL_2}]^+$ species can easily accommodate an additional ligand leading to a nine-coordinate structure. The ^{1}H NMR spectrum of deuterated methanol solutions of **1** shows only 10 narrow signals for the two terpyridinecarboxylate ligands, indicating an overall two-fold symmetry for the solution species. The ^{1}H NMR spectrum of deuterated acetonitrile solutions of **1** shows very broad signals which could be explained by the presence in solution of several species exchanging on the NMR time scale.

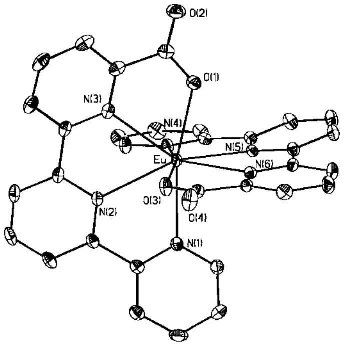

Figure 1. Crystal structure of the cation $[\mathrm{EuL_2}]^+$, **1**, with thermal ellipsoids at 30% probability.

Addition of small amounts of $\mathrm{Eu(Otf)_3}$ leads to the self-assembly of the polynuclear complex $[\mathrm{Eu}\subset(\mathrm{EuL_2})_6](\mathrm{Otf})_9$, **2**, as indicated by the large changes in the ^{1}H NMR spectrum. In addition to the broad signals, 20 narrow peaks appear at $0.16 < [\mathrm{Eu(L)_2}](\mathrm{Otf}){:}\mathrm{Eu(Otf)_3} < 0.5$ ratios, indicating the presence of a rigid solution species presenting two terpyridinecarboxylate ligands in distinct environnements. At a $[\mathrm{Eu(L)_2}](\mathrm{Otf}){:}\mathrm{Eu(Otf)_3}$ ratio of 0.16 the ^{1}H NMR spectrum shows only the presence of the rigid solution species presenting 20 narrow peaks for the terpyridinecarboxylate ligands. An X-ray crystallographic analysis[11] revealed this species to have a unique cyclic structure $[\mathrm{Eu}\subset(\mathrm{EuL_2})_6]^{9+}$ in which six $\mathrm{EuL_2}$ (Eu(1)) components are connected by six bridging carboxylates to yield a ring encapsulating an octahedral Eu(III) cation (Eu(2)) (Figure 2). In the complex $[\mathrm{Eu}\subset(\mathrm{EuL_2})_6](\mathrm{Otf})_9$, **2**, each Eu(1) is nine-coordinated by six nitrogens and two oxygens from the two terpyridinecarboxylate ligands and one oxygen from a bridging terpyridinecarboxylate ligand of the adjacent $\mathrm{EuL_2}$ unit. The polyhedron of the Eu(1) coordination sphere is best described as a distorted monocapped square antiprism. The angle between the mean planes of the two terpyridines is smaller (76.7°) than in the monomeric complex **1** (94.5°), and the two terpyridines are more distorted from planarity. The mean Eu(1)−O distance (2.407(12) Å) is significantly longer than the mean Eu−O distance found in complex **1**(2.31(1) Å). A seventh europium ion, Eu(2), is encapsulated in the ring center and has a regular octahedral coordination sphere composed of six symmetry-related carboxylate oxygens from the coordinated terpyridine carboxylate ligands not involved in the ring formation (Figure 3). Only a few examples of lanthanide complexes with octahedral geometry of the donor atoms have been described.[12] The Eu(2)−O distance (2.272(6) Å) is similar to the mean Eu−O distance found in complex **1**(2.31(1) Å). The six crystallographically equivalent europium ions of the centrosym-

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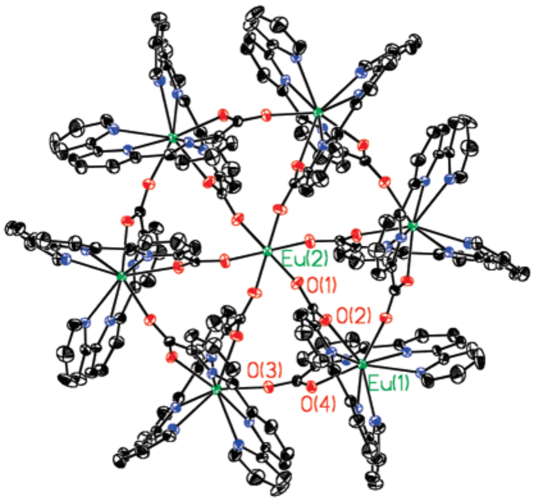

Figure 2. Crystal structure of the cation $[Eu\subset(EuL_2)_6]^{9+}$, **2**, with thermal ellipsoids at 30% probability.

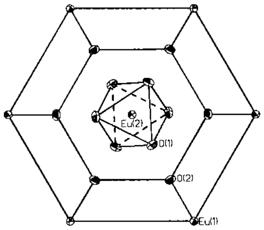

Figure 3. Top view of the coordination polyhedron of Eu(2) and of the hexagon formed by the carboxylate oxygens and by the six Eu(1) ions.

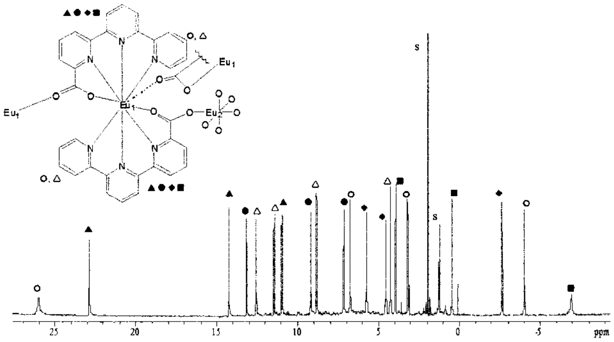

Figure 4. ^1H NMR spectrum of $[Eu\subset(EuL_2)_6]$ $(Otf)_9$ in CD_3CN. The same shaped dots indicate peaks attributed to protons belonging to the same pyridine. Open circles indicate peaks attributed to the protons of the two undifferenciated terminal pyridines. Filled circles indicate the peaks of the four disubstituted undifferenciated pyridines.

metric cation $[Eu\subset(EuL_2)_6]^{9+}$, which are related by a S_6 axis, are located in the corners of a pseudohexagon. The diameter of the pseudohexagon, defined as the distance of two opposite europium ions, is 12.5 Å. Preliminary results indicate that the same ring architecture can be obtained for Gd^{III}.

Dissolution of the crystals of **2** in methanol leads to disruption of the cyclic structure as indicated by the ^1H NMR spectrum presenting only 10 peaks, probably due to displacement of bridging carboxylates by methanol molecules. Conversely the ^1H NMR spectrum of the crystals of complex **2** (which presents a M:L ratio = 1:1.7) in deuterated acetonitrile (Figure 4) shows the presence of 20 narrow signals in agreement with the retention in acetonitrile solution of its solid-state structure. Since only complex **2** is present in solution at the stoechiometric ratio Eu:L = 1:1.7, it seems likely that in the absence of the excess of cation several different oligomeric species are present in solution and that the presence of an additional cation favors the self-assembly of bis(terpyridinecarboxylate) europium species to form an hexameric wheel capable of strongly binding the Eu^{III} cation.

Furthermore, preliminary ^1H NMR studies indicate that the presence of additional lanthanide cations of different sizes also yields a controlled self-assembly. While the addition of 0.16 equiv of Ln^{III} ions larger than Eu(III) to an acetonitrile solution of complex **1** results in a complicated mixture of species, the addition of smaller Ln^{III} ions such as Ho, Tm, Yb, or Lu leads to only one other self-assembled species in addition to complex **2**. This new species shows the same solution symmetry as **2**. The presence of two different lanthanides in an organized molecular edifice is of particular interest since it can result in new intramolecular directional energy transfers leading to light-converting devices.

Complex **2** is to our knowledge the first example of cation-assisted self-assembly of a lanthanide nanowheel leading to a system containing europium ions in two different coordination environments. Moreover, **2** is a very rare example of a large polynuclear lanthanide complex with a very symmetric ring structure.

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Supporting Information Available: Details of the synthesis and characterization of the ligand and of complexes **1** and **2**, ^1H NMR spectra of **1** in the presence of 0.16 equiv of La, Lu (S1), Yb (S2), Ho (S3), Tm (S4), description of the crystal structure of **1**, crystal data, refinement details, positional parameters, bond distances and angles, and thermal parameters for structures of **1** and **2** (PDF). An X-ray cyrstallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) *Crystal data*: (**1**) $[Eu(L)_2](Otf)\cdot 0.5H_2O$, C33 H21 Eu F3 N6 O7.50 S, $M = 862.58$, monoclinic, space group $C2/c$, $a = 31.537(3)$ Å, $b = 8.8546(8)$ Å, $c = 23.933(2)$ Å, $\beta = 110.637(2)°$, $V = 6254.5(10)$ Å^3, $Z = 8$, $\rho_c = 1.832$ g cm^{-3}, $\mu = 2.154$ mm^{-1}, $T = 193(2)$ K. Of the 15032 reflections collected, 7265 were unique ($R_{int} = 0.0408$). Refinement on all data converged at R1 = 0.0385, wR2 = 0.0873.
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(11) *Crystal data*: (**2**) $[Eu\subset(EuL_2)_6](Otf)_9\cdot 10CH_3CN$, C221 H150 Eu7 F27 N46 O51 S9, $M = 6131.13$, hexagonal, space group $P6(3)/m$, $a = 22.9958(7)$ Å, $b = 22.9958(7)$ Å, $c = 31.3192(17)$ Å, $V = 14342.9(10)$ Å^3, $Z = 2$, $\rho_c = 1.420$ g cm^{-3}, $\mu = 1.662$ mm^{-1}, $T = 223$ K. Of the 51321 reflections collected, 11116 were unique ($R_{int} = 0.090$). Refinement on all data converged at R1 = 0.0607, wR2 = 0.1934.
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