Encapsulation of Lanthanide Ions in Calixarene Receptors. A strongly Luminescent Terbium(3+) Complex

Nanda Sabbatini,*[a] Massimo Guardigli,[a] Andrea Mecati,[a] Vincenzo Balzani,[a] Rocco Ungaro,*[b] Eleonora Ghidini,[b] Alessandro Casnati,[b] and Andrea Pochini[b]

[a] *Dipartimento di Chimica 'G. Ciamician,' Università di Bologna, Via Selmi 2, 40126 Bologna, Italy*
[b] *Istituto di Chimica Organica dell'Università, Viale delle Scienze, 43100 Parma, Italy*

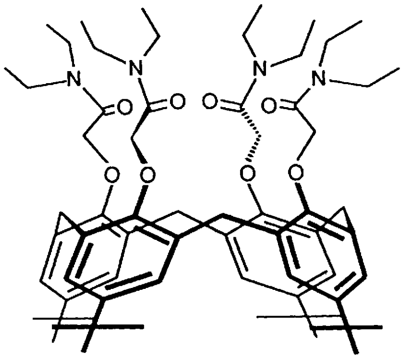
Complexes in which the Eu^{3+}, Tb^{3+}, and Gd^{3+} ions are encapsulated in the *p*-t-butylcalix[4]arene-tetra-acetamide ligand, (**1**) have been synthesized and their photophysical properties investigated; the Tb^{3+} complex exhibits a high luminescence quantum yield (0.2) and a long luminescence lifetime (1.5 ms) upon ligand excitation in aqueous solution.

Preorganization is an important factor in determining the complexation ability of multidentate cation ligands[1] or other molecular receptors.[2] Recently, calixarenes have gained an important place in host–guest chemistry because of their ability to form complexes with ions and neutral molecules.[3,4] In particular, functionalization of the lower rim (phenolic OH groups) of calix[4]arenes with suitable binding groups has produced a series of new, powerful, and selective cation receptors and carriers.[4]

Some of us have recently reported on the synthesis of a *p*-t-butylcalix[4]arene-tetra-acetamide (**1**) and its complexation properties towards alkali metal cations.[5] This ligand exists in a fixed 'cone' conformation in both the free and complexed states and the *X*-ray crystal structure of its KSCN complex shows that the cation is encapsulated in a polar environment of eight oxygen atoms (four ester and four amide) which form an antiprism.[5]

Encapsulation of Eu^{3+} and Tb^{3+} ions in suitable ligands is known to yield highly luminescent species which can be used as probes for a variety of applications.[6] We have synthesized the complexes of (**1**) with the Eu^{3+}, Tb^{3+}, and Gd^{3+} ions and we have found that the Tb^{3+} complex exhibits excellent luminescence properties.[7] The luminescence of the $[\mathrm{Eu} \subset (\mathbf{1})]^{3+}$ complex has also been studied in the solid state.[8]

The complexes were synthesized following the method used for the prepararation of the (2.2.1) and (2.2.2) cryptates.[9] $EuCl_3{\cdot}6H_2O$, $TbCl_3{\cdot}6H_2O$, or $GdCl_3{\cdot}6H_2O$ (Ventron, 99.9%) were dissolved in dried acetonitrile and trimethyl orthoformate was added as a drying agent. After refluxing for 1 h a slight excess of the ligand dissolved in a small amount of acetonitrile was added. The solution was refluxed again for 3 h and filtered quickly. The 1:1 complexes were isolated by precipitation with diethyl ether. Satisfactory elemental analyses were obtained in all cases. The $[\mathrm{Eu} \subset (\mathbf{1})]Cl_3$ complex was also identified by FAB MS [*m/z* 1359, $(M\mathrm{H})^+$].



(**1**)

The Eu^{3+}, Tb^{3+}, and Gd^{3+} complexes show solubility characteristics quite different from those of the free ligand and the analogous complex with the K^+ ion. The free ligand and the K^+ complex are more soluble in apolar solvents, *e.g.* $CHCl_3$, whereas the Eu^{3+}, Tb^{3+}, and Gd^{3+} complexes dissolve only in polar solvents like water and alcohols.

Figure 1 presents the absorption spectrum of the free ligand and the excitation spectrum of the $[\mathrm{Tb} \subset (\mathbf{1})]^{3+}$ complex in methanol. The two bands at ~270 and ~280 nm correspond to transitions in the aromatic groups of the ligand. The excitation spectrum of the $[\mathrm{Eu} \subset (\mathbf{1})]^{3+}$ complex is similar to that of the Tb^{3+} complex, but much weaker. The analogy between the absorption spectrum of the free ligand and the excitation spectra of the Eu^{3+} and Tb^{3+} complexes shows that energy transfer from the ligand to the encapsulated metal ion takes place.

The free ligand shows a phosphorescence band with maximum at 420 nm (τ 1.8 s) in dichloromethane–methanol (1:1, v/v) at 77 K. Such a band is also observable for the Gd^{3+} complex ($\lambda_{max.}$ 410 nm; τ 69 ms), but not for the Eu^{3+} and Tb^{3+} complexes because of the ligand-to-metal energy transfer.

Table 1 presents the luminescence lifetimes and quantum yields of the Eu^{3+} and Tb^{3+} calixarene complexes upon ligand excitation. Figure 2 shows schematically the energy level diagram and the absorption and decay processes for the Tb^{3+}

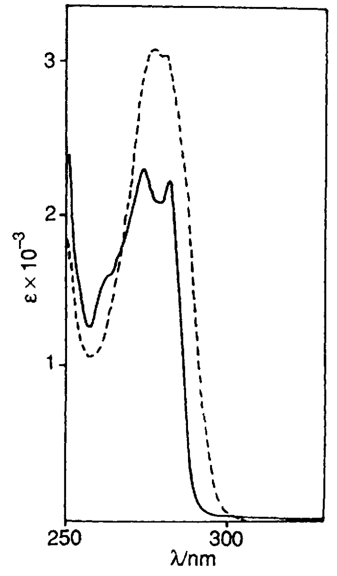


Figure 1. Absorption spectrum of (**1**) (- - -) and excitation spectrum of $[\mathrm{Tb} \subset (\mathbf{1})]^{3+}$ (——) in methanol.

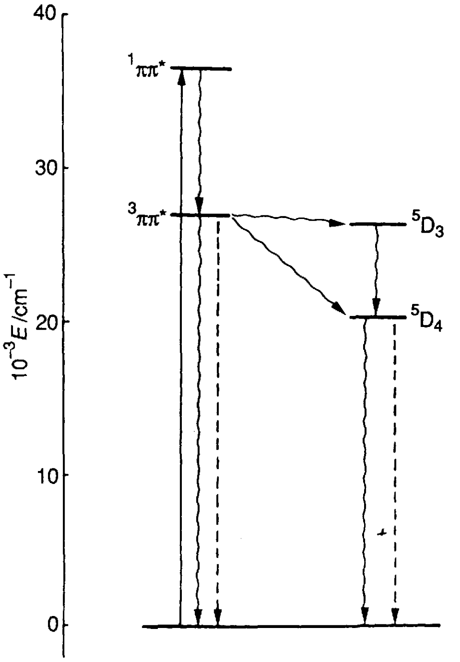


Figure 2. Schematic energy level diagram for the $[\mathrm{Tb}\subset(\mathbf{1})]^{3+}$ complex (the energy of the triplet state of the ligand corresponds to the highest energy feature of the phosphorescence spectrum).

Table 1. Luminescence properties.[a]

	Lifetime/ms[b]				Quantum yield[c]
Compound	300 K $\tau(H_2O)$	300 K $\tau(D_2O)$	77 K $\tau(H_2O)$	77 K $\tau(D_2O)$	300 K $\phi(H_2O)$
$[\mathrm{Eu}\subset(\mathbf{1})]^{3+}$	0.65	1.9	1.8	2.0	2.0×10^{-4}
$[\mathrm{Tb}\subset(\mathbf{1})]^{3+}$	1.5	2.6	1.6	2.8	2.0×10^{-1}

[a] Water solution, excitation in the ligand (λ 273 nm). [b] Measured in correspondence with the most intense emission band ($^5D_0 \rightarrow {}^7F_2$, λ 614 nm for Eu^{3+} and $^5D_4 \rightarrow {}^7F_5$, λ 542 nm for Tb^{3+}). Experimental error $\leqslant 10\%$. No oxygen effect. [c] Experimental error $\leqslant 30\%$.

complex.† The Tb^{3+} complex shows a high luminescence quantum yield and a long luminescence lifetime in water at room temperature. These properties, taken together with the high molar absorptivity of the ligand (Figure 1) and the high solubility of the complex in water, make the Tb^{3+} calixarene complex an interesting label for time-resolved fluoroimmunoassay.[10]

The high luminescence quantum yield upon ligand excitation is most likely due to both efficient ligand-to-metal energy transfer and excellent shielding of the encapsulated metal ion from interaction with water molecules. By using the Horrocks and Sudnick equation[11] it is possible to deduce that only one water molecule is co-ordinated to the central metal ion in the calixarene complex.

For the Eu^{3+} complex, the relatively short lifetime and the very low luminescence quantum yield are ascribed to the presence of a ligand-to-metal charge-transfer state (observed as a shoulder around 300 nm in the absorption spectrum) which may efficiently deactivate the singlet excited state of the ligand and the $^5D_0$ emitting state of the metal ion to the ground state.[12]

A full discussion of the photophysical properties of the complexes of lanthanide ions with the *p*-t-butylcalix[4]arene tetra-acetamide ligand will be reported elsewhere.

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† The energy of the triplet state of the ligand has been deduced from the highest energy feature observed in the phosphorescence spectrum of the Gd^{3+} complex.