# Mono(di)nuclear Europium(III) Complexes of Macrobi(tri)cyclic Cryptands Derived from Diazatetralactams as Luminophores in Aqueous Solution

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To increase the excellent light-emitting properties of the $Eu^{3+}$ ion, macrobicyclic and macrotricyclic ligands **7** – **10**, incorporating a 18-membered tetralactam ring (acting as a lanthanide binding site) and a sensitizer group (2,2′-bipyridine or 2,2′-bipyridine 1,1′-dioxide moiety), were synthesized. The mononuclear and dinuclear europium cryptates derived from these ligands were isolated and characterized. Their luminescent properties and those of the corresponding cryptates containing a phenanthroline group (see **11** and **12**) were examined in $H_2O$ and $D_2O$ solutions at 77 and 300 K. It results that the tetralactam moiety plays a major role in the efficient shielding of the complexed $Eu^{3+}$ ion from the water environment. The cryptands incorporating the bipyridine unit are the most promising labels according to their photophysical properties (excitation maxima, emission decay lifetime, relative luminescent yield). In contrast with literature data, introduction of *N*-oxide groups in the bipyridine chromophore weakens the luminescence properties of the cryptate.

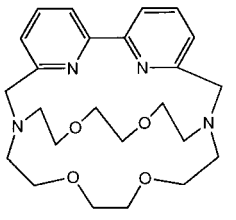
**Introduction.** – A significant part of the importance of the europium(III) ion arises from its unusual luminescent properties: large difference between the excitation and emission wavelengths (*Stokes* shift $> 200$ nm), emission spectrum in the visible range ($580\text{ nm} < \lambda_{em} < 720\text{ nm}$) characterized by narrow bands ($< 10$ nm full width at half-height), and long-lived luminescence ($\tau > 100$ μs) observed under ambient conditions [1]. This long lifetime makes such an ion particularly attractive as luminescent marker as it provides a minimization of the interference of nanosecond-lived background fluorescence and allows enhancement of the sensitivity by time-resolved detection procedures [2]. However, the absorption band of the $Eu^{3+}$ ion ($\lambda$ 393 nm) is narrow and weak ($\varepsilon < 3\ M^{-1} \cdot cm^{-1}$); consequently, direct excitation of the ion results only in low luminescence intensity. A second problem relates to the possible presence of water molecules (and $OH^-$ ions) in the first coordination sphere of the $Eu^{3+}$ ion owing to its pronounced hard *Lewis* acid character. When solvents containing OH groups are coordinated to europium ions, efficient nonradiative deactivation of the metal emissive states takes place *via* weak vibronic coupling between f electronic states of the central ion and vibrational states of high-frequency O–H oscillators [3]. The result is that luminescence of the free $Eu^{3+}$ ion is weak.

To enhance absorption, the $Eu^{3+}$ ion is usually chelated with ligands that have broad, intense absorption bands ($\varepsilon \approx 10^3 - 10^5\ M^{-1} \cdot cm^{-1}$). In these complexes, metal-centered luminescence occurs upon light absorption by allowed ligand-centered

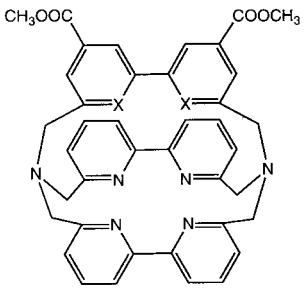
transitions, followed by ligand-to-metal intramolecular energy transfer. This overall process was recently termed the 'antenna effect' [4]. In addition, the ligands offering at least 8–9 hard donor atoms, like O- and N-atoms which are able to coordinate the lanthanide ion into the first coordination sphere, provide an efficient shielding of the ion from interactions with solvent molecules (water).

Long lifetime emitting europium(III) compounds as sensitive labels or probes have already been used in many domains of biology; either for analytical purposes or for molecular-mechanism studies. First they have been used as labels in time-resolved fluoroimmunoassays (TR-FIA) [5]. Several europium-complex-based detection systems for heterogeneous TR-FIA (*Wallac Oy* [6], *Cyberfluor* [7]) or homogeneous TR-FIA (*Cis-Bio* [8]) have been commercialized and are available for routine diagnostic use. The reported detection limit for the europium probes is $5 \cdot 10^{-14}$ M [9]. More recently, these metallo-organic labels have been applied to protein labeling, DNA sequencing and mapping, enzyme analysis, cellular applications, and receptor-ligand interactions [10]. Europium complexes have also been shown to be excellent donors in luminescence resonance-energy-transfer (LRET) experiments for homogeneous assays [8b][11].

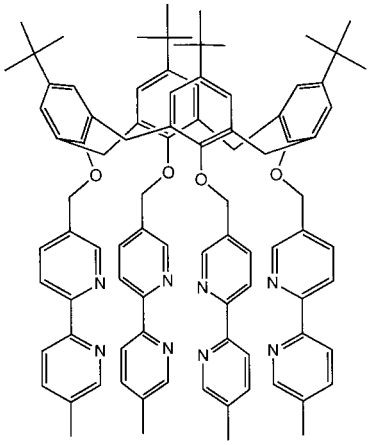
This explains the strong motivation for the synthesis of organic complexing agents for the $Eu^{3+}$ ion. The ligand must incorporate a chromophoric group characterized by suitable excitation properties and should shield the metal ion from water molecules in order to transfer energy to the bound ion with a reasonable efficiency and to lengthen the excited-state lifetime (*vide supra*). In addition, the complexes must have reasonable water solubility, be characterized by a high kinetic stability, and contain additional functional groups to allow conjugation to biomolecules. Current research has demonstrated that macrocycles (branched macrocycles and cryptands), *e.g.*, **1**–**4**, are useful as potential ligands for the encapsulation of the europium ion [12]. The number of different types of macrocyclic sensitizers is quite limited, and most have been based on the tris-bipyridine ligand first defined by *Lehn* and coworkers [13]. In these compounds, the macrocyclic platform is based essentially on oxamacrocycles ([18]-$N_2O_4$, see [14]), on azamacrocycles ([9]-$N_3$, see [15]; [12]-$N_4$, see [16]; [18]-$N_6$, see



**1**




**2** X = N
**3** X = N→O



**4**

[17]; [18]-$N_2$-(2,2′-bipyridine)$_2$, see [12b][15b][18]; [18]-$N_2$-(1,10-phenanthroline), see [19]), or on calix[4]arenes [20–22].

On the other hand, carboxamide groups are known to favour the complexation of 4f-block metal ions. They have better ligating properties for $Ln^{3+}$ ions than the ether O-atoms or diaza heterocyclic subunits such as 2,2′-bipyridine [12b] and stabilize the complexes in hydroxylic solvents. Recent reports described the crucial role played by carboxamide groups for the control of structural, electronic, and photophysical properties of europium podates [23]. Ligands with amide coordinating groups have been thus extensively used in $Ln^{III}$ complexes. Some of these include diamide chelates [24], macrocyclic dilactams [25], linear and macrocyclic polyamino ligands, or calix[4]arenes with amide pendant groups [21][26]. For example, cyclen appended with four primary amide groups afforded a nine-coordinate $Eu^{III}$ complex, and its X-ray crystal structure showed that coordination involves the carbonyl O-atoms [27]. The behaviour as luminescent probes of $Eu^{III}$ complexes derived from sensitizer cyclen or calix[4]arene containing four side-arm carboxamide coordinating atoms has also been reported [28].

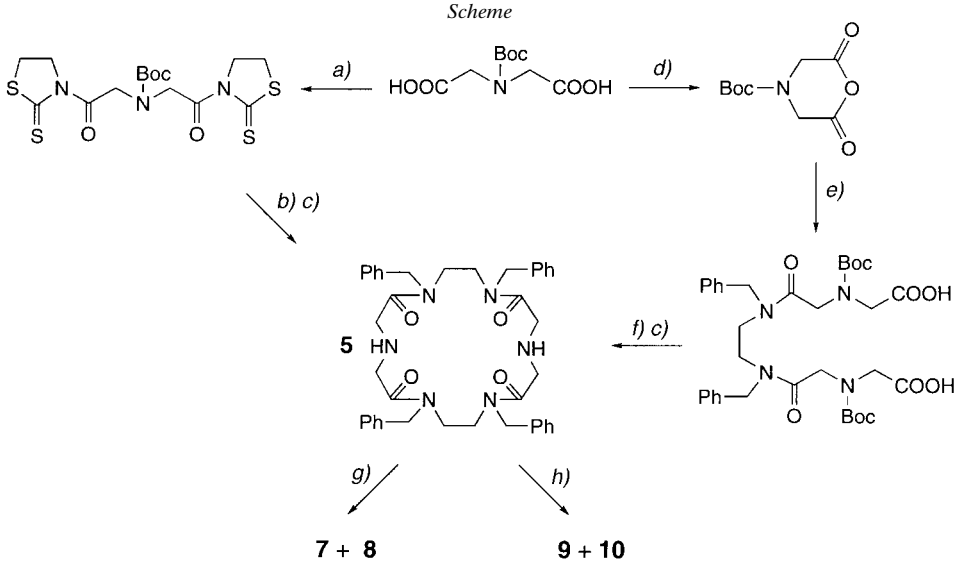
Recently, macrocyclic tetralactams have gained an important place in host-guest chemistry because of their ability to form complexes with ions and neutral molecules [29]. In particular, we have reported their complexing properties toward calcium ion [30]. Similar features between calcium and europium ions prompted us to design luminescent europium complexes with cage-type ligands containing chromophoric groups (as light collectors) and tetralactam rings (as chelate moieties). Thus, we planned the preparation of luminescent europium cryptates derived from ligands which present four functional features: *i*) an 18-membered diazatetralactam as base backbone ring which offers coordinating space for the $Eu^{3+}$ ion; *ii*) 2,2′-bipyridine (bpy) or 2,2′-bipyridine 1,1′-dioxide (bpy$O_2$) chromophoric groups which exhibit intense absorption bands in the near UV region and have their lowest excited state sufficiently high in energy to be able to transfer excitation to the luminescent $^5D_0Eu^{3+}$ level [31]; *iii*) benzyl substituents at the N-atom of the amide functions to avoid the quenching of the excited state of the europium ion by interactions with high-energy vibrations like N–H groups of amide moieties [32]; in addition, introducing bulky lipophilic groups in the ligand may provide an efficient hydrophobic environment for the enclosed metal ion; *iv*) additional functional groups (carboxylic acid ester groups) for attaching the label to macrobiomolecules.

In this paper, we describe the synthesis of the new macrobicyclic ligands **7** and **9** and the luminescence study, in aqueous solution, of their mononuclear $Eu^{III}$ cryptates together with the related photophysical data for the $Eu^{III}$ complex of the macrobicyclic ligand **11** containing a 1,10-phenanthroline subunit (for preliminary reports, see [33]). We also report the synthesis and photophysical properties of the binuclear $Eu^{III}$ complexes of the corresponding macrotricyclic cryptands of cylindrical type **8**, **10**, and **12**. To the best of our knowledge, this is the first report on luminescent properties of dinuclear europium(III) cryptates.

**Results and Discussion.** – *NaBr Complexes of the Macrobi- and Macrotricyclic Cryptands* **7**–**10**. The macrocyclic molecules **7**–**10** are accessible by a stepwise procedure involving the synthesis of the intermediate macrocyclic unit **5** and its

subsequent bridging (*Scheme*). The 18-membered diazatetralactam building block **5** was synthesized following two methods: a direct macrocyclization or a stepwise approach. The direct macrocyclization was performed by the reaction of the bis[thiazolidine-2-thione] derivative of [(*tert*-butoxycarbonyl)imino]bis[acetic acid] and *N*,*N*′-dibenzylethane-1,2-diamine (19% overall yield starting from iminobis[acetic acid]). The stepwise approach, described previously [34], involved a cyclization step, mediated by diphenylphosphoryl azide (DPPA) as *in situ* activating coupling agent, between an intermediate diamide diacid and *N*,*N*′-dibenzylethane-1,2-diamine (44% overall yield). In these two synthetic pathways, the macrocyclization step was realized without requiring high-dilution techniques.

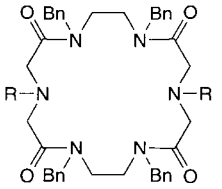
*Scheme*



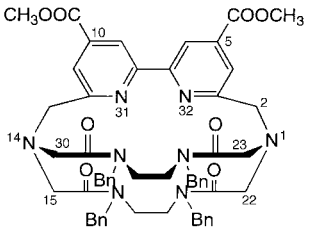

*a*) Thiazolidine-2-thione/dicyclohexylcarbodiimide (DCC)/4-(dimethylamino)pyridine(DMAP)/AcOEt. *b*) *N*,*N*′-Dibenzylethane-1,2-diamine/$CH_2Cl_2$. *c*) $CF_3COOH/CH_2Cl_2$. *d*) DCC/THF. *e*) *N*,*N*′-Dibenzylethane-1,2-diamine/THF, 50°, 24 h. *f*) *N*,*N*′-Dibenzylethane-1,2-diamine/$Et_3N$/diphenylphosphoryl azide/THF. *g*) Dimethyl 6,6′-bis(bromomethyl)-2,2′-bipyridine-4,4′-dicarboxylate/$Na_2CO_3$/MeCN, reflux, 20 h. *h*) Dimethyl 6,6′-bis(bromomethyl)-2,2′-bipyridine-4,4′-dicarboxylate 1,1′-dioxide/$Na_2CO_3$/MeCN, reflux, 20 h.

The amine groups of **5** are secondary, allowing subsequent ring closure reactions with a dihalide. Dropwise addition of dimethyl 6,6′-bis(bromomethyl)-2,2′-bipyridine-4,4′-dicarboxylate to a solution of compound **5** ($3.4 \cdot 10^{-3}$ M) in refluxing MeCN and in the presence of $Na_2CO_3$ gave, after liquid chromatography, the macrobicyclic cryptand **7** and the macrotricyclic cryptand **8**, both complexed to the $Na^+$ ion in 10 and 38% yield, respectively. Under similar reaction conditions, the sodium complex of macrobi- and macrotricyclic cryptands **9** and **10** were prepared from **5** and dimethyl 6,6′-bis(bromomethyl)-2,2′-bipyridine-4,4′-dicarboxylate 1,1′-dioxide in 7 and 21% yield, respectively.

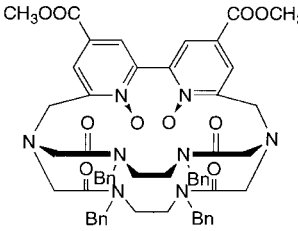
The preferential orientation of these macrocyclization reactions towards the macrotricyclic cryptand of dimeric structure has been previously noticed by us during



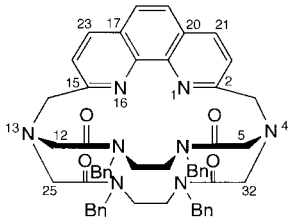
**5** R = H
**6** R = $CH_2CONMe_2$



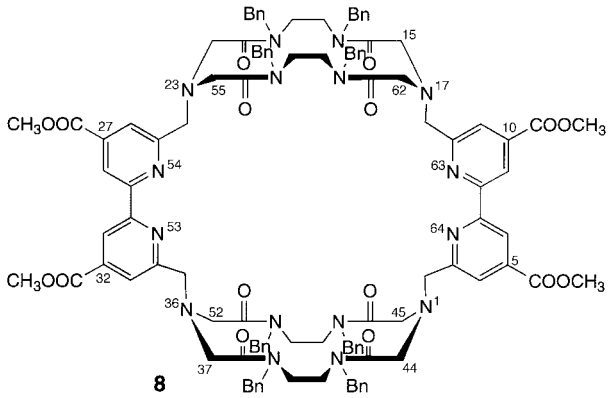
**7**



**9**



**11**



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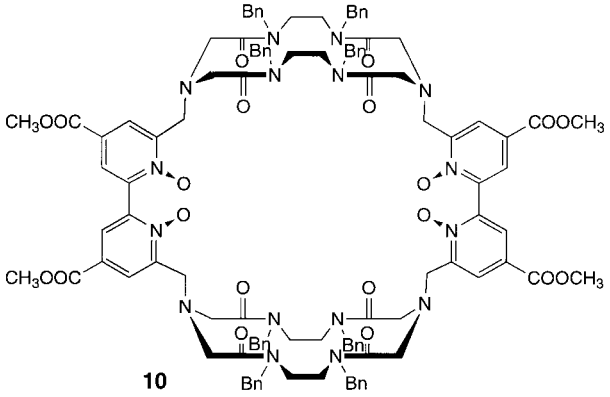
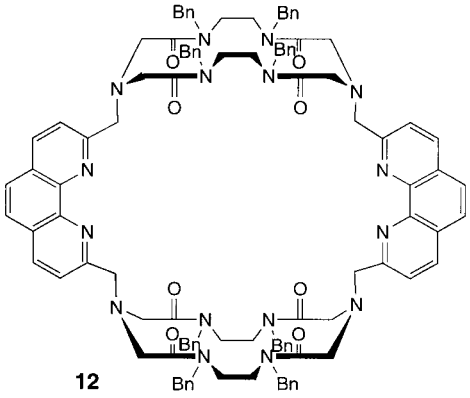


**10**



**12**

the preparation of the cryptands **11** and **12** incorporating phenanthroline units [34]. This is in marked contrast with the predominant macrobicycle formation reported by *Lehn* and coworkers [14b] [35] for analogous cryptands derived from [18]-$N_2O_4$ or [18]-$N_2$-(2,2′-bipyridine)$_2$ rings following the same procedure. For the formation of these

latter compounds, a marked sodium template effect has been found facilitating the cyclization process in favour of the monomer species. On the other hand, the selectivity of the macrocyclization reaction, based on the tetralactam ring **5**, is strongly dependent on the nature of the alkaline carbonate employed. Thus for the reaction of **5** with dimethyl 6,6′-bis(bromomethyl)-2,2′-bipyridine-4,4′-dicarboxylate in the presence of $K_2CO_3$ or $Cs_2CO_3$, polymeric forms were predominant, while the monomer *vs.* dimer selectivity, *i.e.*, **7** *vs.* **8**, was greatly improved (*ca.* 10-fold increase) when $Li_2CO_3$ was used instead of $Na_2CO_3$. It is thought that, apart from the best fit between the size of ion and the dimension of the molecular cavity, other considerations such as the highest affinity of the amide function for cations of high charge density ($Li^+ > Na^+$, $K^+$, $Cs^+$) and perhaps the base strength of the reaction medium might explain these results.

*Europium(III) Complexes.* The $Eu^{III}$ complexes were prepared by refluxing a solution of macrobicyclic (**7**, **9**, and **11**) or macrotricyclic (**8**, **10**, and **12**) cryptands, all complexed to the $Na^+$ ion, in MeOH in the presence of $EuCl_3 \cdot 6H_2O$ (1.05 or 2.1 equiv., resp.). They were isolated by precipitation with $Et_2O$ (40–80% yield). These $Eu^{III}$ complexes were soluble in MeOH and $H_2O$.

The electrospray ionisation (ESI) mass-spectrometric data and elemental analyses of the $Eu^{III}$ complexes establish complexation of one and two $Eu^{3+}$ ions per molecule of macrobicyclic and macrotricyclic cryptand, respectively. In the ESI-MS (positive mode), no $[Eu(L)]^{3+}$ and $[2Eu(L)]^{6+}$ (L = ligand) ions are detected, but intense peaks attributable to the expected species in association with one or several counterions are observed. The isotope pattern expected in the presence of both Cl- and Eu-atoms (the europium ion has two major isotopes, $^{151}Eu$ and $^{153}Eu$) was used for the characterization of the observed ions. It is noteworthy that the ESI-MS of the dinuclear complexes display only peaks corresponding to species containing two $Eu^{3+}$ ions without complications resulting from monodemetalation. In addition, no peak ascribed to the free ligands **7**–**12** is observed in the ESI-MS obtained in MeOH and from rather low concentrations ($10^{-6}$–$10^{-7}$ M), indicating a high affinity of these ligands for the $Eu^{3+}$ ion.

The IR data provide support for O-atom coordination and are a diagnostic feature for amide O-atom and heterocyclic *N*-oxide group environments [26a][36]. The spectra of mono- and dinuclear complexes show similar patterns in the 1620–1600 $cm^{-1}$ region and indicate that the amide-carbonyl groups are binding cooperatively (single amide-carbonyl band, coordination red shift of 20–40 $cm^{-1}$). For $bpyO_2$-based cryptates, a marked decrease in the N–O stretching band vibration wavenumber from the $Na^+$ to the $Eu^{3+}$ cryptates ($\Delta\tilde{\nu} = 25\ cm^{-1}$) is observed, reflecting the tight binding of the $Eu^{3+}$ ion to the bipyridine 1,1′-dioxide moiety of the ligands.

The absorption spectra of the complexes are characterized by absorption bands in the UV region due to $\pi$-$\pi^*$ transitions. The $\pi$-$\pi^*$ transitions of the phenyl rings ($\varepsilon =$ 1000 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ for **6**) are masked by the more intense $\pi$-$\pi^*$ transitions of the bipyridine unit (*e.g.*, $\varepsilon = 7100\ dm^3 \cdot mol^{-1} \cdot cm^{-1}$ for **7**). In aqueous solutions, red shifts of the $\pi$-$\pi^*$ transition for the bipyridine moiety of **7** and **8** ($\Delta\lambda = 6$–$16$ nm) and for the phenanthroline moiety of **11** and **12** ($\Delta\lambda = 5$–$10$ nm) are observed upon binding the $Eu^{3+}$ ion. These shifts of the absorption to lower energy from the free ligands to their $Eu^{III}$ complexes are indicative of a perturbation produced by the coordinated metal ion and are similar to those previously reported for other complexes of $Eu^{3+}$ ion with

ligands derived from phenanthroline or 2,2′-bipyridine [17][18b]. On the other hand, complexation leads to a shift of the $\pi$-$\pi$* transition of the bipy$O_2$ moiety towards higher energies. This hypsochromic shift could arise from non-coplanarity of the two O-atoms of the bipy$O_2$ unit owing to the distorted conformation that this moiety is constrained to assume on chelate formation. A similar effect (blue shift of 19 nm) is observed upon complexation of the $Eu^{3+}$ ion with 2,2′-bipyridine 1,1′-dioxide in methanolic solution.

The luminescence study of the complexes (*vide infra*) also supports the participation of the N- or O-atoms of the heterocyclic unit(s). Moreover, the luminescence lifetimes of the complexes in aqueous solution ($\tau$ 0.4 – 0.85 ms) are significantly larger than the lifetime of $EuCl_3$ in the same solvent ($\tau$ 0.11 ms [37]); this indicates the substitution of water molecules around the metal ion by coordinating atoms of the ligand, related to a close distance of the ligand and the metal ion.

The features observed by IR, UV, and fluorescence techniques can be explained by the chelation of the $Eu^{3+}$ cation at the same time by all the carbonyl groups and the N- or O-atoms of the heteroarene moieties, and confirm the cryptate structure of the $Eu^{3+}$ complexes with ligands **7** – **12**, *i.e.*, the cation-inclusion nature of the complexes. In a structural study of $Ca^{2+}$ complexes derived from 18-membered dioxatetralactam or bibranched diazatetralactam [30b,e], we have shown that the metal ion cannot be lodged in the cavity of the tetralactam ring as the amide functions are unable to converge towards the centre of the cavity; these amide groups point towards the cation outside the mean-plane of the tetralactam macrocycle. The same structural behaviour is proposed for the $Eu^{3+}$ complexes of ligands **7** – **12**, the macrobi- or macrotricyclization creating the ion encapsulation.

*Luminescence Properties.* Excitation of the aqueous solutions of the $Eu^{3+}$ complexes of **7** – **12** into the lowest-energy ligand-centred absorption band give rise to the well-known structured emission of the $Eu^{3+}$ ion. This suggests that energy transfer takes place from the excited ligand to the emitting metal ion. Comparison of the absorption and luminescence excitation spectra shows that the emitting state is clearly populated through absorption by the heterocyclic unit(s). Representative excitation spectra are shown in *Fig. 1* for the complexes derived from ligands **7**, **8**, and **10**. A through-space intramolecular energy transfer may also occur *via* excitation of the $\pi$-$\pi$* state of the side-chain aromatic rings, as reported for lanthanide complexes containing phosphinic or phosphonic groups incorporating benzyl or phenyl units [38]. In the cryptands **7** – **12**, the involvement of these phenyl groups cannot be unequivocally assessed because their absorption bands are overlapped by the heterocycle absorption. On the other hand, the $Eu^{3+}$ complex of the ligand **6** bearing two carboxamide side-arms is luminescent in MeOH, and the comparison of its absorption and excitation spectra shows that the energy transfer involves the phenyl groups (insert in *Fig. 1*). However, the luminescence intensity of $[Eu \subset \mathbf{6}]^{3+}$ is weak compared to those observed for the $Eu^{3+}$ complexes of **7** – **12**, in agreement with a lowest absorption efficiency and a highest distance from the bound ion of the phenyl groups with respect to the coordinating heterocyclic units.

The europium emission spectra are essentially identical for all cryptands **7** – **12**, although the total intensity and the excited-state lifetime is cryptand-dependent. As expected, all emissions arise from the $^5D_0$ state, and the most intense bands corresponding to the $^5D_0 \rightarrow {}^7F_j$ ($\Delta J = 0, 1, 2, 3, 4$) transitions are observed (*Fig. 2*). The

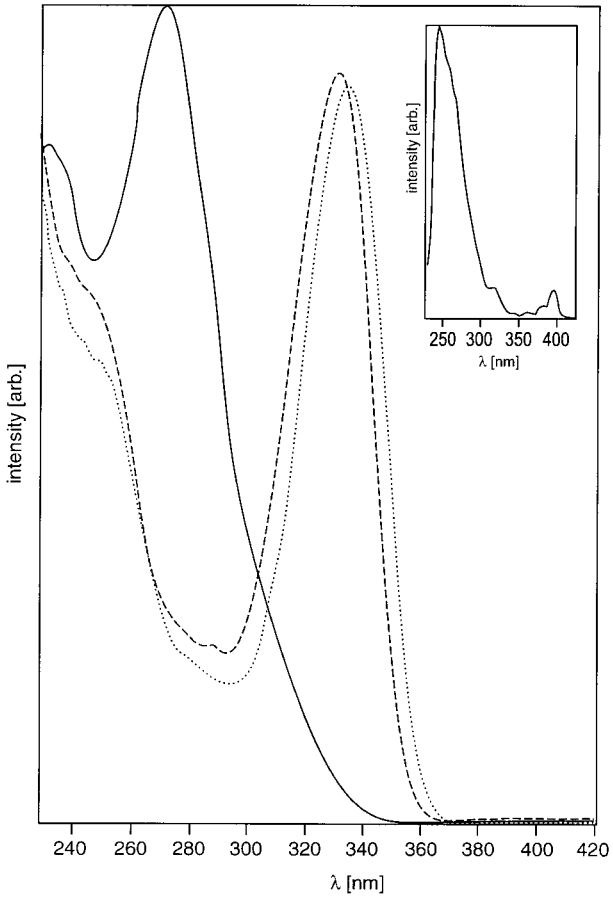



Fig. 1. *Corrected excitation spectra of [Eu⊂**7**]*$^{3+}$ (– – –), *[2Eu⊂**8**]*$^{6+}$ (····), *and [2Eu⊂**10**]*$^{6+}$ (—) *complexes in water* ($\lambda_{em}$ 616 nm; $c = 1.0 \cdot 10^{-6}$ M). Insert: corrected excitation spectrum of [Eu⊂**6**]$^{3+}$ in MeOH ($\lambda_{em}$ 616 nm; $c = 2.0 \cdot 10^{-3}$ M).

spectra are dominated by the $^5D_0 \rightarrow {}^7F_2$ transition; 55–65% of the total emission is centered on the 616 nm peak. Unlike the $^5D_0 \rightarrow {}^7F_1$ transition which is magnetic-dipole allowed and is little affected by changes in the coordination environment, the $^5D_0 \rightarrow {}^7F_2$ is electric-dipole allowed and is hypersensitive, so that the emission intensity is a sensitive function of $Eu^{3+}$ ion environment [1]. The ratio between the intensities of the $^5D_0 \rightarrow {}^7F_1$ and the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transitions is equal for the complexes of ligands **7** and **8**, implying a similar symmetry around the $Eu^{3+}$ ion induced by the mononuclear or dinuclear ligand and the solvent. A comparable trend is observed for the complexes of **11** and **12**. This intensity ratio is lower for [Eu⊂**9**]$^{3+}$ than for [2Eu⊂**10**]$^{6+}$, suggesting a slightly different europium surrounding in the dinuclear complex with respect to the mononuclear complex in this latter series.

The values of the luminescence lifetimes determined in $10^{-6}$ M aqueous solutions and under various experimental conditions, the decay-rate constants, and the number

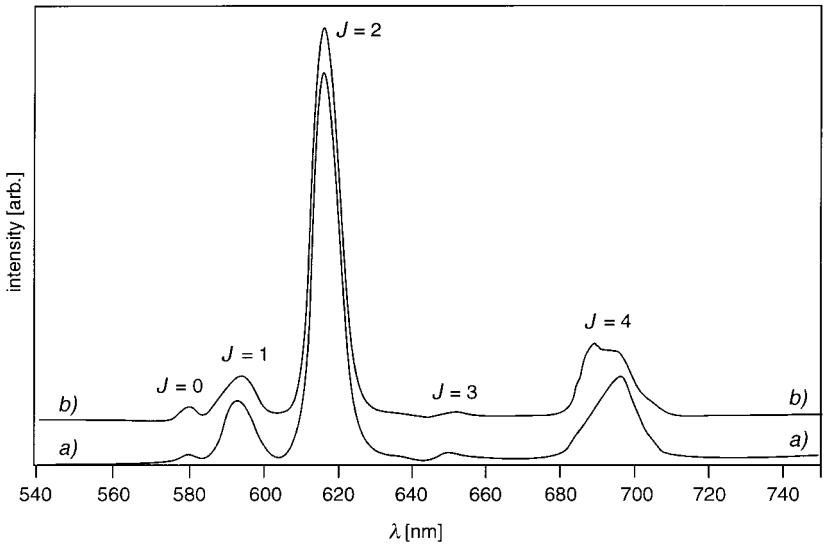



Fig. 2. *Corrected emission spectra of* a) *[Eu* ⊂ **9***]*$^{3+}$ *and* b) *[2Eu* ⊂ **10***]*$^{6+}$ *in water* ($1.0 \cdot 10^{-6}$ M, 300 K). The bands arise from $^5D_0 \rightarrow {}^7F_j$ transitions; the *J* values are shown on the spectra.

of coordinated water molecules are given in *Table 1*, together with analogous data from the literature for $[Eu \subset \mathbf{1}]^{3+}$ [14a], $[Eu \subset \mathbf{2}]^{3+}$ [14a], and $[Eu \subset \mathbf{3}]^{3+}$ [12a]. The experimental luminescent lifetime of $[Eu \subset \mathbf{7}]^{3+}$ in $H_2O$ solution at 300 K ($\tau$ 0.74 ms) is higher than those of analogous europium complexes derived from macrobicyclic bipyridine ligands where the macrocyclic backbone is based on [18]-$N_2O_4$ ($\tau$ 0.28 ms for $[Eu \subset \mathbf{1}]^{3+}$) or [18]-$N_2$-(2,2′-bipyridine)$_2$ ($\tau$ 0.34 ms for $[Eu \subset \mathbf{2}]^{3+}$). A similar trend is observed for the europium cryptates of macrobicyclic phenanthroline ligands: the luminescence lifetime is lowered by a factor of 2.5 by substituting the tetralactam ring of **11** by the [18]-$N_2O_4$ ring ($\tau$ 0.27 ms [13]) in the corresponding europium complexes. With regard to analogous europium complexes based on calix[4]arene ligands carrying two or four 2,2′-bipyridine subunits [20a] (*e.g.*, **4**), a direct comparison of the photophysical data is rather difficult since all the reported measurements were carried out in MeCN solutions. Their luminescence efficiency in water could be expected to be substantially lower. However, the lifetime of 1.63 ms observed in MeCN for $[Eu \subset \mathbf{7}]^{3+}$ compares favourably with those reported for the calix[4]arene complexes ($\tau$ 0.6 – 1.6 ms [20a]). On the other hand, upon solvent deuteration, the lifetimes of $[Eu \subset \mathbf{7}]^{3+}$ and $[Eu \subset \mathbf{11}]^{3+}$ are increased by a factor of 2.1 and 2.3, respectively, indicative of some coupling between the metal ion and O–H oscillators which favour radiationless deactivation of the excited state [3].

The number of water molecules ($n_{H_2O}$) bound to the inner coordination sphere of the europium ion may be quantified by the use of the well-known empirical relation proposed by *Horrocks* and *Sudnick* [39] where $n = 1.05\ (1/\tau_{H_2O} - 1/\tau_{D_2O})$ and in which $\tau$ is the lifetime (in ms) of the complex in $H_2O$ and $D_2O$. The formula is reported to be accurate up to 0.5 water molecules. This provides an opportunity to investigate the degree to which the present tetralactam moiety is capable to shield the ion from the

Table 1. *Luminescence Lifetimes*[a]), *Rate Constants, and Average Number of Coordinated Water Molecules* ($n_{H_2O}$)

| | Lifetime[b]) [ms] | | | | Rate constants [$s^{-1}$] | | | $n_{H_2O}$[f]) |
|---|---|---|---|---|---|---|---|---|
| | $\tau_H^{300K}$ | $\tau_D^{300K}$ | $\tau_H^{77K}$ | $\tau_D^{77K}$ | $k_r$[c]) | $k_{nr}(OH)$[d]) | $k_{nr}(T)$[e]) | |
| [Eu⊂**7**]$^{3+}$ | 0.74 | 1.55 | 1.03 | 1.88 | 530 | 700 | 100 | 0.7 |
| [2Eu⊂**8**]$^{6+}$ | 0.69 | 1.82 | 0.82 | 1.83 | 550 | 900 | < 50 | 0.9 |
| [Eu⊂**9**]$^{3+}$ | 0.41 | 1.28 | 0.46 | 1.82 | 550 | 1650 | 250 | 1.7 |
| [2Eu⊂**10**]$^{6+}$ | 0.52 | 0.99 | 0.63 | 1.58 | 630 | 900 | 400 | 0.9 |
| [Eu⊂**11**]$^{3+}$ | 0.67 | 1.56 | 1.26 | 1.87 | 540 | 850 | 100 | 0.9 |
| [2Eu⊂**12**]$^{6+}$ | 0.85 | 1.59 | 1.13 | 1.85 | 540 | 550 | 100 | 0.6 |
| [Eu⊂**1**]$^{3+}$[g]) | 0.28 | 1.20 | – | 1.60 | 630 | 2750 | 200 | 2.7 |
| [Eu⊂**2**]$^{3+}$[g]) | 0.34 | 1.50 | – | 1.50 | 670 | 2250 | < 50 | 2.4 |
| [Eu⊂**3**]$^{3+}$[h]) | 0.40 | 0.70 | 0.80 | 1.10 | 900 | 1100 | 500 | 1.1 |

[a]) In aerated $1.0 \cdot 10^{-6}$M aqueous solution. [b]) The lifetimes of the $Eu^{3+}$ complexes of **7**–**12** were determined by excitation into the lowest-energy ligand-centered absorption band and recording the intensity of the emitted light of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition (616 nm); experimental error $\leq 10\%$. [c]) From the lifetimes in $D_2O$ solution at 77 K, assumed to be purely radiative; $k_r = 1/\tau_D^{77K}$. [d]) From the lifetimes in $H_2O$ and $D_2O$ solutions at 300 K; $k_{nr}(OH) = 1/\tau_H^{300K} - 1/\tau_D^{300K}$. [e]) From the lifetimes in $D_2O$ solution at 300 and 77 K; $k_{nr}(T) = 1/\tau_D^{300K} - 1/\tau_D^{77K}$, in the hypothesis of the absence of equilibria between the emitting state and other excited states. [f]) Calculated at 300 K *via* $n = 1.05\ (1/\tau_{H_2O} - 1/\tau_{D_2O})$; uncertainty $\pm 0.5$ [39]. [g]) Data from [14a]. [h]) Data from [12a].

environment. Thus, only 0.7–0.9 $H_2O$ molecules surround the metal ion at 300 K in [Eu⊂**7**]$^{3+}$ and [Eu⊂**11**]$^{3+}$, whereas *ca.* 2.5 water molecules are present in the case of the complexes reported in the literature. These features demonstrate that the europium ion is much better protected by the macrobicycles **7** and **11** from the undesired interaction with water molecules and, thus, that an effective solvent shielding of the ion has been achieved by the tetralactam moiety. The presence of only one coordinated water molecule in these complexes is in agreement with the expected eight-coordinating nature of the tetralactam cryptands since the $Eu^{3+}$ ion prefers a coordinating number of 8–9 [1].

The presence of directly coordinated water molecules to $Eu^{3+}$ was also evidenced by the increase in the luminescence lifetimes of [Eu⊂**7**]$^{3+}$ and [Eu⊂**11**]$^{3+}$ upon the addition of $F^-$ anion. It has been established that some anions ($F^-$, phosphate) replace water in the coordination sphere of the europium ion, thus limiting the radiationless decay of the excited state through the O–H vibrations [40]. This is clearly shown in the case of [Eu⊂**7**]$^{3+}$ where the lifetime, in the presence of $4 \cdot 10^{-1}$M $F^-$, increases in $H_2O$ ($\tau$ 1.14 ms) but not in $D_2O$ ($\tau$ 1.60 ms). Unlike in the case of [Eu⊂**2**]$^{3+}$ [40b], no increase of the lifetimes is noticed for the complexes of **7** and **11** in the presence of the largest phosphate anions, indicating the absence of interactions between $Eu^{3+}$ and phosphate anions. This suggests again that these cryptands derived from macrocyclic tetralactams wrap about the metal ion uniformly.

In comparison with [Eu⊂**7**]$^{3+}$, [Eu⊂**9**]$^{3+}$ containing a bipyridine 1,1′-dioxide moiety presents markedly less favourable luminescence properties (see *Table 1*). Its lifetime in $H_2O$ at 300 K is lowered by a factor of *ca.* 2, and the hydration state of its excited state is 1.7. The higher deactivation by water molecules exhibited by [Eu⊂**9**]$^{3+}$ compared to [Eu⊂**7**]$^{3+}$ was not expected from the results reported in the literature concerning bipyridine and bipyridine *N,N′*-oxide cryptates [12]. In fact, a significant

gain in light-conversion efficiency was observed for $[Eu \subset \mathbf{3}]^{3+}$ in comparison with the europium cryptate of the parent ligand **2**, and this was ascribed, at least in part, to the better shielding of the bound cation by the two O-atoms of the *N*-oxide coordination sites of the ligand **3**. In the tetralactam-based cryptand series, a smaller cavity inside the cryptand **9** leading to a molecular distortion and a localization of the $Eu^{3+}$ ion more exposed to solvent water molecules could explain these results.

For the europium homodinuclear complexes, all the measured luminescence decays are monoexponential, suggesting the presence of two metal sites with very similar environments. On the other hand, it is interesting to note that the luminescence lifetimes for the macrotricyclic complexes with respect to the macrobicyclic ones are in fact similar within the experimental error of *ca.* 10%. However, upon solvent deuteration, the lifetime at 300 K of $[2Eu \subset \mathbf{10}]^{6+}$ is increased by a factor of 1.9 compared to a factor of 3.1 for $[Eu \subset \mathbf{9}]^{3+}$, indicative of a smaller number of coordinating solvent molecules in the former complex. A same trend is observed at 77 K. The experimentally determined number of coordinating water molecules is $0.9 \pm 0.5$ for $[2Eu \subset \mathbf{10}]^{6+}$ *vs.* $1.7 \pm 0.5$ for $[Eu \subset \mathbf{9}]^{3+}$. This indicates that the shielding of the $Eu^{3+}$ ion is increased in the macrotricyclic complex relative to the macrobicyclic complex, presumably because **10** is more flexible than **9**, and the $bpyO_2$ units can approach the metal ion more closely in the case of this macrotricyclic ligand. For the complexes derived from ligands **7** *vs.* **8** or **11** *vs.* **12**, the average number of coordinated $H_2O$ molecules is similar (*Table 1*).

To discuss the metal luminescence, the radiative and nonradiative decay rate constant of the $^5D_0$ $Eu^{3+}$ emitting states were estimated by measuring the luminescence lifetimes under various experimental conditions. The values were obtained according to the approach described by *Sabbatini* and coworkers [12] and to *Eqn. 1* where $k_{obs}$ is the observed rate constant, $k_r$ the natural rate constant for the emission of photons, $k_{nr}(T)$ the nonradiative temperature-dependent decay-rate constant, and $k_{nr}(OH)$ the rate constant for the nonradiative energy transfer to the OH vibrational manifold of OH oscillators in the first coordination sphere.

$$k_{obs} = 1/\tau_{obs} = k_r + k_{nr}(T) + k_{nr}(OH) \quad (1)$$

The estimated $k_r$ values are around $550\ s^{-1}$ and are larger than those found for the free $Eu^{3+}_{aq}$ ion ($300\ s^{-1}$). Thus, it seems that the quenching of the excited state of the $Eu^{3+}$ ion by the C–H high-vibrational modes of the ligands **7**–**12** can play a role in the nonradiative process. However, these $k_r$ values compare well with those reported for other complexes. Beside those shown in *Table 1* (with exception of $[Eu \subset \mathbf{3}]^{3+}$), we may consider the following $k_r$ values: $[Eu \subset (2.2.1)]^{3+} \cdot 2F^-$, $560\ s^{-1}$; $[Eu \subset (bpy.bpy.bpy)]^{3+}$, $590\ s^{-1}$; $[Eu \subset (macrobpy)(bpy)_2]^{3+}$, $530\ s^{-1}$; $[Eu \subset (calix[4]arenetetraacetamide)]^{3+}$, $500\ s^{-1}$ [12a]. Consequently, the $CH_2$ groups of the tetralactam ring in these complexes do not induce a characteristic quenching of the $Eu^{3+}$ excited state by C–H vibrational modes.

As one can see from *Table 1*, the temperature-independent term receives the most important contribution from the decay through coupling with O–H vibrations. In aqueous solution, the term $k_{nr}(OH)$ plays an important role in the radiation process for the complexes derived from ligands **7**–**11**, particularly for **9**, whereas it is small in the case of $[2Eu \subset \mathbf{12}]^{6+}$.

As far as $k_{nr}(T)$ is concerned, this is negligible or of minor importance for the complexes derived from tetralactam cryptands incorporating bipyridine or phenanthroline chromophores, showing that no upper-lying excited state of other configurations is thermally accessible from the $^5D_0$ $Eu^{3+}$ luminescent state. This term becomes larger in the analogous complexes containing *N*-oxide groups ($[Eu \subset \mathbf{9}]^{3+}$ and $[2Eu \subset \mathbf{10}]^{6+}$). Although the value of the zero-zero energy for the $^3\pi\pi^*$ ligand level is not available for these two latter europium complexes, the value estimated for the complex $[Eu \subset (bpy.bpy.bpyO_2)]^{3+}$ ($^3E_{oo} = 20500\ cm^{-1}$ [31b]) suggests that in $[Eu \subset \mathbf{9}]^{3+}$ and $[2Eu \subset \mathbf{10}]^{6+}$, the energy gap between the ligand excited triplet states and the metal emitting state is sufficiently high, thereby preventing radiationless decay *via* a back transfer of energy. Most likely, for these two complexes, the temperature-dependent decay may take place, at least in part, *via* charge-transfer states involving the *N*-oxide groups, as reported for the $[Eu \subset \mathbf{3}]^{3+}$ cryptate.

To evaluate these new europium complexes for practical luminescent molecular devices, it is necessary to take into account their absorption efficiency and luminescence quantum yield. *Table 2* lists these data as well as the energy-transfer efficiency ($\eta_{en.tr.}$) and the efficiency of incident-light-emitted-light conversion (overall efficiency) for the $Eu^{3+}$ cryptates derived from ligands **7**–**10** and from reference ligands **2** and **3**. The $[2Eu \subset \mathbf{8}]^{6+}$ cryptate is the most convenient label choice with respect to UV absorption properties ($\lambda, \varepsilon$). It can be excited at a wavelength of *ca.* 330 nm, which is a more convenient excitation wavelength for instrumental reasons related to the UV transmision of lenses, filters, cuvettes, and glass slides and for minimizing endogenous fluorescence due to biological chromophores. Moreover, its molecular extinction coefficient is increased by a factor of 1.6 with respect to $[Eu \subset \mathbf{7}]^{3+}$, owing to the presence of two chromophoric units in the ligand. The replacement of the bpy unit by the $bpyO_2$ unit gives rise to higher absorptivity, but the cryptates $[Eu \subset \mathbf{9}]^{3+}$ and $[2Eu \subset \mathbf{10}]^{6+}$ were mainly excited at shorter wavelengths ($\lambda_{exc}$ 275–285 nm).

Table 2. *Absorption Emission Data*[a]) *and Efficiency of the Incident-Light-Emitted-Light Conversion*[b])

| | Absorption | | | Emission | | | Overall efficiency |
|---|---|---|---|---|---|---|---|
| | $\lambda_{max}$ | $\varepsilon_{max}$ | Absorption efficiency[c]) | Luminescence quantum yield[d]) | | Energy transfer efficiency[e]) | |
| | [nm] | [M · cm$^{-1}$] | (· $10^2$) | $H_2O$ (· $10^2$) | $D_2O$(· $10^2$) | $\eta_{en.tr}$(· $10^2$) | $\eta_{overall}$(· $10^2$) |
| $[Eu \subset \mathbf{7}]^{3+}$ | 323 | 9100 | 2.1 | 4 | 8 | 10 | 0.08 |
| $[2Eu \subset \mathbf{8}]^{6+}$ | 328 | 15000 | 3.4 | 5 | 18 | 13 | 0.17 |
| $[Eu \subset \mathbf{9}]^{3+}$ | 285 | 21000 | 4.7 | 1.5 | 3 | 7[f]) | 0.07 |
| $[2Eu \subset \mathbf{10}]^{3+}$ | 273 | 39300 | 8.7 | 4 | 6 | 12[f]) | 0.35 |
| $[Eu \subset \mathbf{2}]^{3+}$[g]) | 306 | 29000 | 6.5 | 2 | – | 9 | 0.13 |
| $[Eu \subset \mathbf{3}]^{3+}$[h]) | 306 | 17000 | 3.8 | 9 | 17 | 25 | 0.35 |

[a]) In water solution at 300 K. [b]) Evaluated for $1.0 \cdot 10^{-6}$ M solutions and 1-cm optical length. [c]) Evaluation in correspondence with the $\lambda_{max}$ values. [d]) Excitation in ligand-centered bands; experimental errors ±30%. [e]) Evaluated using $\eta_{en.tr} = \Phi \cdot \tau_D^{77K}/\tau_H^{300K}$. [f]) Evaluated on the assumption that the thermally activated decay process does not involve any equilibrium between the metal emitting state and other excited states [12a]. [g]) Data from [14a]. [h]) Data from [12a].

As shown by *Sabbatini et al.* [12], the efficiency of energy conversion from the excited state of the ligand to the emitting state of the metal ($\eta_{en.tr}$) can be estimated from the ratio between the experimental quantum yield ($\Phi$) and the quantum yield upon metal excitation (in our case obtained from the experimental lifetimes). With the assumption that the decay process at 77 K in deuterated water is purely radiative, $\eta_{en.tr}$ can be defined by *Eqn. 2*.

$$\eta_{en.tr} = \Phi \cdot \tau_D^{77K}/\tau_H^{300K} \quad (2)$$

For the dinuclear complexes, $\eta_{en.tr}$ is higher than for the mononuclear complexes (see *Table 2*). This enhancement of the efficiency of the ligand-to-metal energy transfer may be related to a closer vicinity of the chromophore and the metal ion in the macrotricyclic cryptands. This stronger ligand-metal interaction is also indicated by the UV spectral data: the red shift of the bpy absorption (for free dimethyl 6,6′-dimethyl-2,2′-bipyridine-4,4′-dicarboxylate, $\lambda$ 308 nm) is more pronounced for $[2Eu \subset \mathbf{8}]^{6+}$ than for $[Eu \subset \mathbf{7}]^{3+}$. The same tendency can be seen between the $Eu^{3+}$ cryptates of $bpyO_2$ ligands **9** and **10** where a blue shift is observed upon complexation (for free dimethyl 6,6′-dimethyl-2,2′-bipyridine-4,4′-dicarboxylate 1,1′-dioxide, $\lambda$ 290 nm). This efficiency is markedly lowered, by a factor of 2–3 in these latter $bpyO_2$-based cryptates, as compared to $[Eu \subset \mathbf{3}]^{3+}$. It seems that the weaker interaction between the $bpyO_2$ group in the cryptands **9** and **10** and the metal ion overcomes the favourable effect of the inclusion of a $bpyO_2$ unit in a ligand, which was ascribed to an efficient population of the lowest triplet level of the ligand due to $bpyO_2$-localized levels [12a][41]. In contrast, the efficiency of the ligand-to-metal energy transfer is slightly higher in bpy-based cryptates with respect to the $[Eu \subset \mathbf{2}]^{3+}$ reference complex.

Finally, the absorption and luminescent features of the studied $Eu^{3+}$ cryptates can be determined by the evaluation of the efficiency of incident-light-emitted-light conversion which is defined as the product of the absorption efficiency and the luminescence quantum yield [12]. In water solutions, the $[2Eu \subset \mathbf{10}]^{6+}$ cryptate shows the highest overall efficiency (0.35%), owing to the higher absorption efficiency. It is worthwhile noting that this value is similar to that of the reference complex $[Eu \subset \mathbf{3}]^{3+}$. On the other hand, the luminescence intensity for the bpy-based cryptates, with $\lambda_{exc}$ 300 nm, are rather high. As a matter of fact, the overall efficiency for $[Eu \subset \mathbf{7}]^{3+}$ is 0.08% in spite of the relatively low molar extinction coefficient resulting from the presence in the ligand of only one chromophore. The $[2Eu \subset \mathbf{8}]^{6+}$ cryptate displays an overall efficiency (0.17%) higher than that reported for $[Eu \subset \mathbf{2}]^{3+}$ (0.13%), which is considered interesting for a luminescent label [12].

**Conclusion.** – The results described here provide a facile route to a novel class of cryptand molecules containing 18-membered tetralactam and heterocyclic moieties. These macrobicyclic and macrotricyclic cryptands form mononuclear or dinuclear europium cryptates, respectively. The coordination of the metal ion is chiefly achieved by the amide carbonyl groups and the heteroatoms of the chromophoric units. These $Eu^{3+}$ cryptates show the typical $Eu^{3+}$ luminescence and have relatively long luminescence decays at room temperature in aqueous solution. These long luminescence lifetimes may be related to the very efficient encapsulation of the complexed $Eu^{3+}$ ion by the tetralactam moiety, the degree of shielding depending on the nature of

the heterocyclic unit and the bi- or tricyclic structure of the ligand. The bpy-based cryptates show interesting luminescence properties (decay times, quantum yields, excitation wavelengths). Introduction of the *N*-oxide groups in the bpy chromophore impairs the luminescent properties of the corresponding cryptates, where thermally activated decay processes are more important.

Functionalization of the bpy unit by carboxylic acid ester groups should allow the attachment of these cryptates to biomolecules, thus enabling them to be used in biological assays. It will be necessary, at that time, to take into account the possible effects that the coupling of the label to the biological substrates and the biological medium may have on the luminescence properties of these complexes. Preliminary experiments carried out with $[Eu \subset \mathbf{7}]^{3+}$ indicate that no effect on the chemical stability and no luminescence quenching occurs in human serum medium for this complex. On the contrary, we observe an increase of the luminescence lifetime in that medium ($\tau$ 1.10 ms).

Our synthetic approach allowing a substantial variation of the heterocyclic moiety of the macrocycle, we are currently investigating the introduction of more-absorbing chromophoric units in this series of cryptands with the aim to gain a more intense luminescence.

## Experimental Part

*General*. Commercially available chemicals were used without further purification. M.p.: uncorrected. Absorption spectra ($\lambda$ in nm, $\varepsilon$ in $M^{-1} \cdot cm^{-1}$); *Lambda-17-Perkin-Elmer* spectrophotometer; in $H_2O$ or MeOH; molar extinction coefficients determined from absorbance measurements with at least two different concentrations of compounds. IR Spectra ($\tilde{\nu}$ in $cm^{-1}$): *Perkin-Elmer-883* spectrometer; KBr pellets. $^1$H-NMR Spectra: *Bruker-AC-200* spectrometer; chemical shift $\delta$ in ppm rel. to $SiMe_4$ (= 0 ppm). Fast-atom-bombardment (FAB) MS: *Nermag-R10-10C* mass spectrometer (pos. mode); glycerol-thioglycerol (gly-thiogly) or 3-nitrobenzyl alcohol (NBA) matrix. Electrospray-ionization (ESI) MS: *Autospec-OATOF* (high resolution) and *Finnigan-TSQ-700* spectrometers (pos. mode). Elemental analyses were carried out by the 'Service Commun de Microanalyse élémentaire UPS-INP' in Toulouse.

The following compounds were prepared as described in the literature: **6**, **11**, and **12** [34]; *dimethyl 6,6′-bis(bromomethyl)-2,2′-bipyridine-4,4′-dicarboxylate* [42]; *dimethyl 6,6′-bis(bromomethyl)-2,2′-bipyridine-4,4′-dicarboxylate 1,1′-dioxide* [43].

*1,7,10,16-Tetrakis(phenylmethyl)-1,4,7,10,13,16-hexaazacyclooctadecane-2,6,11,15-tetrone* (**5**). A soln. of *N*,*N*′-dibenzylethane-1,2-diamine (600 mg, 2.5 mmol) in $CH_2Cl_2$ (40 ml) was added at r.t. to a stirred soln. of 3,3′-{[(*tert*-butoxycarbonyl)imino]bis(1-oxoethane-2,1-diyl)}bis[thiazolidine-2-thione] [29] (830 mg, 2.5 mmol) in $CH_2Cl_2$ (300 ml). Then the mixture was stirred for an additional 48 h and evaporated. The org. soln. was washed with 1N NaOH, sat. aq. NaCl soln., dried ($Na_2SO_4$), and evaporated, and the solid residue chromatographed (silica gel, $CH_2Cl_2$/acetone 98 : 2 → 95 : 5): 4,13-bis[(*tert*-butoxy)carbonyl]-protected **5** (310 mg, 28%).

Removal of the Boc protecting group by $CF_3COOH/CH_2Cl_2$ treatment according to the procedure previously described [34] afforded **5** (quant.). Physical and anal. properties: identical with those described [34].

*Dimethyl 6,6′-{[2,6,11,15-Tetraoxo-1,7,10,16-tetrakis(phenylmethyl)-1,4,7,10,13,16-hexaazacyclooctadecane-4,13-diyl]bis(methylene)}-2,2′-bipyridine-4,4′-dicarboxylate}sodium(1+) Bromide (={Dimethyl 16,21,24,29-Tetraoxo-17,20,25,28-tetrakis(phenylmethyl)-1,14,17,20,25,28,31,32-octaazatetracyclo[12.8.8.1$^{3,7}$.1$^{8,12}$]dotriaconta-3,5,7(32),8,10,12(31)-hexaene-5,10-dicarboxylate}sodium(1+) Bromide*; $[Na \subset \mathbf{7}]Br$) *and {Dimethyl 6,6′-{[4,4′-Bis(methoxycarbonyl)-2,2′-bipyridine-6,6′-diyl]bis(methylene)bis[2,6,11,15-tetraoxo-1,7,10,16-tetrakis(phenylmethyl)-1,4,7,10,13,16-hexaazacyclooctadecane-13,4-diyl]bis(methylene)}-2,2′-bipyridine-4,4′-dicarboxylate}disodium(2+) Dibromide* (={*Tetramethyl 16,21,28,43,46,51,56,61-Octaoxo-17,20,39,42,47,50,57,60-octakis(phenylmethyl)-1,14,17,20,23,36,39,42,47,50,53,54,57,60,63,64-hexadecaazaheptacyclo[34.8.8.8$^{14,23}$.1$^{3,7}$.1$^{8,12}$.1$^{25,29}$.1$^{30,34}$]tetrahexaconta-3,5,7(64),8,10,12(63),25,27,29(54),30,32,34(53)-dodecaene-5,10,27,32-tetracarboxylate}disodium(2+) Dibromide;* $[2Na \subset \mathbf{8}]Br_2$). A mixture of **5** (500 mg, 0.74 mmol) and $Na_2CO_3$ (797 mg, 7.5 mmol) in anh. MeCN (220 ml) under Ar was heated to reflux for 30 min. Then, dimethyl 6,6′-bis(bromomethyl)-2,2′-

bipyridine-4,4′-dicarboxylate (339 mg, 0.74 mmol) was added in one portion (not soluble in MeCN). The resulting suspension was refluxed under efficient magnetic stirring for further 20 h. After cooling to r.t., the insoluble solid was filtered off and the filtrate evaporated. The solid residue was chromatographed (silica gel, $CH_2Cl_2$/MeOH 95 : 5 → 80 : 2, then $CH_2Cl_2$/MeOH/30% aq. $NH_4OH$ soln. 80 : 20 : 0.5): [Na ⊂ **7**]Br (86 mg, 10%) and [2Na ⊂ **8**]$Br_2$ (330 mg, 38%).

[Na ⊂ **7**]Br: White powder. M.p. >230°. UV/VIS ($H_2O$: 317 (7100). IR (KBr): 1729 (COOMe); 1646 (C=O, amide); 1566, 983, 771, 738 (py). $^1$H-NMR ($CDCl_3$): 2.0–5.0 (*m*, 34 H, Me, $CH_2$); 6.8–7.5 (*m*, 20 arom. H); 7.6–8.6 (*m*, 4 H, bpy). FAB-MS (gly-thiogly): 1009.5 ($[M+K]^+$). Anal. calc. for $C_{56}H_{58}N_8O_8 \cdot NaBr \cdot CH_2Cl_2$ (1159): C 59.07, H 5.22, N 9.67; found: C 59.44, H 5.27, N 9.47.

[2Na ⊂ **8**]$Br_2$; White powder. M.p. >230°. UV/VIS ($H_2O$): 312 (19600). IR (KBr): 1731 (COOMe); 1635 (C=O, amide); 1569, 989, 962, 766, 741 (py). $^1$H-NMR ($CDCl_3$): 2.0–5.0 (*m*, 68 H, Me, $CH_2$); 6.6–7.9 (*m*, 44 arom. H bpy); 8.6 (*m*, 4 H, bpy). FAB-MS (gly-thiogly): 2061.5 ($[M+H+NaBr+H_2O]^+$), 1981.7 ($[M+Na+H_2O]^+$). Anal. calc. for $C_{112}H_{116}N_{16}O_{16} \cdot 3NaBr \cdot 7H_2O$ (2377): C 56.59, H 5.51, N 9.43; found: C 56.52, H 5.51, N 9.80.

*{Dimethyl 1,1′-Dioxido-6,6′-{[2,6,11,15-tetraoxo-1,7,10,16-tetrakis(phenylmethyl)-1,4,7,10,13,16-hexaazacyclooctadecane-4,13-diyl]bis(methylene)}-2,2′-bipyridine-4,4′-dicarboxylate}sodium(1+) Bromide* (= *{Dimethyl 31,32-Dioxido-16,21,24,29-tetraoxo-17,20,25,28-tetrakis(phenylmethyl)-1,14,17,20,25,28,31,32-octaazatetracyclo-[12.8.8.1$^{3,7}$.1$^{8,12}$]dotriaconta-3,5,7(32)8,10,12(31)-hexaene-5,10-dicarboxylate}sodium(1+) Bromide;* [Na ⊂ **9**]Br) *and {Dimethyl 1,1′-Dioxido-6,6′-{[4,4′-bis(methoxycarbonyl)-2,2′-bipyridine-6,6′-diyl]bis(methylene)bis[2,6,11,15-tetraoxo-1,7,10,16-tetrakis(phenylmethyl)-1,4,7,10,13,16-hexaazacyclooctadecane-13,4-diyl]bis(methylene)}-2,2′-bipyridine-4,4′-dicarboxylate}disodium(2+) Dibromide* (= *{Tetramethyl 53,54,63,64-Tetraoxido-16,21,28,43,46,51,56,61-octaoxo-17,20,39,42,47,50,57,60-octakis(phenylmethyl)-1,14,17,20,23,36,39,42,47,50,53,54,57,60,63,64-hexadecaazaheptacyclo[34.8.8.8$^{14,23}$.1$^{3,7}$.1$^{8,12}$.1$^{25,29}$.1$^{30,34}$]tetrahexaconta-3,5,7(64),8,10,12(63),25,27,29(54),30,32,34(53)-dodecaene-5,10,27,32-tetracarboxylate}disodium(2+) Dibromide;* [2Na ⊂ **10**]$Br_2$). As described for **7** and **8**, using dimethyl 6,6′-bis(bromomethyl)-2,2′-bipyridine-4,4′-dicarboxylate 1,1′-dioxide (138 mg, 0.28 mmol) and **5** (191 mg, 0.28 mmol). Chromatography (silica gel, $CH_2Cl_2$/MeOH 97 : 3 → 90 : 10) gave [Na ⊂ **9**]Br (28 mg, 7%) and [2Na ⊂ **10**]$Br_2$ (73 mg, 21%).

[Na ⊂ **9**]Br: White powder. M.p. >230°. UV/VIS ($H_2O$): 290. $^1$H-NMR ($CD_3CN$): 2.8–5.4 (*m*, 34 H, Me, $CH_2$); 6.9–7.9 (*m*, 20 arom. H); 7.6–8.2 (*m*, 4 H, $bpyO_2$). FAB-MS (NBA/DMSO): 1025 ($[M+Na]^+$), 1003 ($[M+H]^+$). Anal. calc. for $C_{56}H_{58}N_8O_{10} \cdot NaBr \cdot 4CH_2Cl_2$ (1446): C 49.85, H 4.60, N 7.75; found: C 51.12, H 4.68, N 7.66.

[Na ⊂ **10**]$Br_2$: White powder. M.p. >230°. UV/VIS ($H_2O$): 290. IR (KBr): 1728 (COOMe); 1634 (C=O, amide); 1278, 1247, 821 (N–O). $^1$H-NMR ($CD_3CN$): 2.5–5.5 (*m*, 68 H, Me, $CH_2$); 6.6–7.8 (*m*, 40 arom. H); 7.9–8.6 (*m*, 8 H, $bpyO_2$). FAB-MS (gly/DMSO): 2006.7 ($[M+H]^+$); 1990.7 ($[(M-O)+H]^+$), 1973.7 ($[(M-2O)+H]^+$), 1003.4 ($[M+2H]^{2+}$), 995.3 ($[M-2O)+2H]^{2+}$). Anal. calc. for $C_{112}H_{116}N_{16}O_{20} \cdot 4NaBr \cdot 4H_2O$ (2490): C 54.03, H 5.02, N 9.00; found: C 53.96, H 5.00, N 9.35.

*{Dimethyl 16,21,24,29-Tetraoxo-17,20,25,28-tetrakis(phenylmethyl)-1,14,17,20,25,28,31,32-octaazatetracyclo-[12.8.8.1$^{3,7}$.1$^{8,12}$]dotriaconta-3,5,7(32),8,10,12(31)-hexaene-5,10-dicarboxylate}europium(3+) Tris(trifluoroacetate)* ([Eu ⊂ **7**]$(CF_3COO)_3$). Under Ar, $EuCl_3 \cdot 6H_2O$ (17.3 mg, $4.7 \cdot 10^{-5}$ mol) was added to a stirred soln. of [Na ⊂ **7**]Br (50 mg, $4.4 \cdot 10^{-5}$ mol) in $CH_2Cl_2$/MeOH 1 : 2 (15 ml). After 30 h of reflux, the soln. was evaporated. Chromatography (gel-permeation column *Sephadex LH20*, MeOH/$CF_3COOH$ pH 4) yielded pure [Eu ⊂ **7**]$(CF_3COO)_3$ (60 mg, 84%). Yellow powder. UV/VIS ($H_2O$): 337 (6740), 323 (9120). IR (KBr): 1736 (COOMe), 1708, 1686 ($COO^-$), 1605 (C=O, amide), 988, 966 (py), 769, 741 (py). ESI-MS (MeOH): 412.4 ($[M+Eu+CF_3COO+H]^{3+}$). Anal. calc. for $C_{56}H_{58}EuN_8O_8(CF_3COO)_3 \cdot 9H_2O$ (1624): C 45.85, H 4.72, N 6.90; found: C 45.85, H 5.05, N 6.49.

*{Tetramethyl 16,21,28,43,46,51,56,61-Octaoxo-17,20,39,42,47,50,57,60-octakis(phenylmethyl)-1,14,17,20,23,36,39,42,47,50,53,54,57,60,63,64-hexadecaazaheptacyclo[34.8.8.8$^{14,23}$.1$^{3,7}$.1$^{8,12}$.1$^{25,29}$.1$^{30,34}$]tetrahexaconta-3,5,7(64),8,10,12(63),25,27,29(54),30,32,34(53)-dodecaene-5,10,27,32-tetracarboxylate}dieuropium(6+) Hexachloride* ([2Eu ⊂ **8**]-$Cl_6$). Under Ar, $EuCl_3 \cdot 6H_2O$ (47 mg, $13 \cdot 10^{-5}$ mol) was added to a stirred soln. of [2Na ⊂ **8**]$Br_2$ (150 mg, $6.3 \cdot 10^{-5}$ mol) in MeOH (20 ml). After 18 h of reflux, the soln. was concentrated. $Et_2O$ was added, resulting in the formation of a precipitate which was isolated after centrifugation: [$2Eu^{3+}$ ⊂ **8**]$Cl_6$ (128 mg, 75%). White powder. UV/VIS ($H_2O$): 338 (14000), 328 (15000). IR (KBr): 1731 (COOMe), 1612 (C=O, amide), 990, 968, 767, 742 (py). ESI-MS (MeOH): 759.8 ($[(M-2H)+2Eu+Cl]^{3+}$). Anal. calc. for $C_{112}H_{116}Cl_6Eu_2N_{16}O_{16} \cdot NaBr \cdot 8H_2O$ (2706): C 49.71, H 4.92, N 8.28; found: C 49.64, H 4.75, N 8.25.

*{Dimethyl 31,32-Dioxido-16,21,24,29-tetraoxo-17,20,25,28-tetrakis(phenylmethyl)-1,14,17,20,25,28,31,32-octaazatetracyclo[12.8.8.1$^{3,7}$.1$^{8,12}$]dotriaconta-3,5,7(32),8,10,12(31)-hexaene-5,10-dicarboxylate}europium(3+) Tri-*

*chloride* ([Eu⊂**9**]$Cl_3$). Under Ar, $EuCl_3 \cdot 6\,H_2O$ (3 mg, $8 \cdot 10^{-6}$ mol) was added to a stirred soln. of [Na⊂**9**]Br (10 mg, $7 \cdot 10^{-6}$ mol) in MeOH (5 ml). After 24 h of reflux, the soln. was concentrated. $Et_2O$ was added, resulting in the formation of a precipitate which was isolated after centrifugation: [Eu⊂**9**]$Cl_3$ (7¼mg, 74%). Yellow powder. UV ($H_2O$): 285. (21000). ESI-MS (MeOH): 1189.6 ([(*M* − H) + Eu + Cl]$^+$), 577.5 ([(*M* − H) + Eu]$^{2+}$). Anal. calc. for $C_{56}H_{58}Cl_3EuN_8O_{10} \cdot 5\,H_2O$ (1351.5): C 49.77, H 5.07, N 8.29; found: C 49.52, H 4.90, N 8.15.

*{Tetramethyl 53,54,63,64-Tetraoxido-16,21,28,43,46,51,56,61-octaoxo-17,20,39,42,47,50,57,60-octakis(phenylmethyl)-1,14,17,20,23,36,39,42,47,50,53,54,57,60,63,64-hexadecaazaheptacyclo[34.8.8.8$^{14,23}$.1$^{3,7}$.1$^{8,12}$.1$^{25,29}$.1$^{30,34}$]tetrahexaconta-3,5,7(64),8,10,12(63),25,27,29(54),30,32,34(53)-dodecaene-5,10,27,32-tetracarboxylate}dieuropium(6+) Hexachloride* ([2Eu⊂**10**]$Cl_6$). Under Ar, $EuCl_3 \cdot 6\,H_2O$ (37 mg, $10^{-4}$ mol) was added to a stirred soln. of [2Na⊂**10**]$Br_2$ (109 mg, $4.4 \cdot 10^{-5}$ mol) in MeOH (30 ml). After 48 h of reflux, the soln. was concentrated. $Et_2O$ (25 ml) was added, resulting in the formation of a precipitate which was isolated after centrifugation (132 mg). Chromatography (gel-permeation column *Sephadex LH20*, MeOH) yielded pure [2Eu⊂**10**]$Cl_6$ (66 mg, 53%). Yellow powder. UV ($H_2O$): 273 (39340). IR (KBr): 1728 (COOMe), 1604 (C=O, amide), 1244, 1229, 823 (N−O). ESI-MS (MeOH): 1189.7 ([(*M* − 2 H) + 2 Eu + 2 Cl]$^{2+}$), 793.4 ([(*M* − H) + 2 Eu + 2 Cl]$^{3+}$). Anal. calc. for $C_{112}H_{116}N_{16}O_{20}Eu_2Cl_6 \cdot NaBr \cdot 13\,H_2O$ (2860): C 47.04, H 5.00, N 7.84, O 18.46; found: C 47.06, H 5.08, N 7.74, O 18.55.

*[3,7,8,9,10,14-Hexahydro-7,10,27,30-tetrakis(phenylmethyl)-2,20:15,17-dietheno-4,13-(ethaniminoethaniminoethano)-1,4,7,10,13,16-benzohexaazacyclooctadecine-6,11,26,31(3*H*,12*H*)-tetrone]europium(3+) Trichloride* ([Eu⊂**11**]$Cl_3$). As described for [2Eu⊂**10**]$Cl_6$, using $EuCl_3 \cdot 6\,H_2O$ (8 mg, $2.1 \cdot 10^{-5}$ mol), [Na⊂**11**]Br (20 mg, $1.9 \cdot 10^{-5}$ mol), and MeOH (10 ml): white powder (9 mg, 40%). UV/VIS (MeOH): 279. IR (KBr): 1608 (COOMe). FAB-MS (gly-thiogly/$CCl_3COOH$): 1030.3 ([(*M* − H) + Eu]$^+$). Anal. calc. for $C_{54}H_{54}Cl_3EuN_8O_4 \cdot 4H_2O$ (1209.5): C 53.63, H 5.17, N 9.26; found: C 53.52, H 5.02, N 8.95.

*[7,11,12,13,14,18,27,31,32,33,34,38-Dodecahydro-11,14,31,34,45,48,57,60-octakis(phenylmethyl)-8,17:28,37-bis(ethaniminoethaniminoethano)-1,39:4,6:19,21:24,26-tetraethenodibenzo[*b,t*][1,4,7,10,13,16,19,22,25,28,31,34]dodecaazacyclohexatriacontine-10,15,30,35,44,49,56,61,(9*H*,16*H*,29*H*,36*H*)-octone]dieuropium(6+) Hexachloride* ([2Eu⊂**12**]$Cl_6$). As described for [2Eu⊂**10**]$Cl_6$, with $EuCl_3 \cdot 6\,H_2O$ (40 mg, $1.1 \cdot 10^{-4}$ mol), [2Na⊂**12**]$Br_2$ (100 mg, $4.7 \cdot 10^{-5}$ mol), and MeOH (20 ml): white powder (46 mg, 41%). UV/VIS (MeOH): 280 (26000). IR (KBr): 1608 (C=O, amide). FAB-MS (gly-thiogly/$CCl_3COOH$): 2167.4 ([*M* + 2 Eu + 3 Cl]$^+$). Anal. calc. for $C_{108}H_{108}Cl_6Eu_2N_{16}O_8 \cdot 7\,H_2O$ (2401): C 54.03, H 5.12, N 9.33; found: C 54.29, H 5.44, N 8.55.

*Luminescence Measurements.* Fluorescence spectra were obtained with a *LS5-*, *LS50-*, or *LS-50B-Perkin-Elmer* spectrofluorimeter equipped with a *Hamamatsu-R928* photomultiplier tube and with the low-temperature accessory No. *L2250136*. Metal luminescence emission and excitation spectra were recorded using the same instrument operating in time-resolved mode, with a delay time of 0.1 ms and a gate time of 0.4 ms. Excitation and emission monochromator band passes of 5 nm were used, and the emission spectra were corrected for the wavelength dependence of the photomultiplier tube. The metal luminescence excitation was acquired by monitoring the emission at 616 nm for $Eu^{III}$. Quoted lifetimes ($\tau$) are the average values of at least three independent measurements, each of which being obtained by monitoring the emission intensity at 615–620 nm after 6–10 different delay times with a gate time of 0.4 ms. The phosphorescence-decay curves were fitted to an equation of the form $I(t) = I(0)\exp(-t/\tau)$ using a curve-fitting. High correlation coefficients were observed in each case (typically 0.999 or higher). Luminescence quantum yields were obtained by the method described by *Haas* and *Stein* [44] using as standards $[Ru(bipy)_3]^{2+}$ ($\Phi_{exp} = 0.028$ in water [45]) and [Eu⊂bpy.bpy.bpy.$NH_2$]$^{3+}$ ($\Phi_{exp} = 0.02$ in water [8b]).

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