# 56. Synthesis and Properties of Sodium and Europium(III) Cryptates Incorporating the 2,2′-Bipyridine 1,1′-Dioxide and 3,3′-Biisoquinoline 2,2′-Dioxide Units

by **Jean-Marie Lehn*** and **Christine O. Roth**

Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, F–67000 Strasbourg[1])

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The sodium and europium cryptates of the new macrobicyclic ligands **2** and **3** incorporating the 2,2′-bipyridine 1,1′-dioxide and 3,3′-biisoquinoline 2,2′-dioxide units, respectively, have been prepared. The $Eu^{III}$ complexes present characteristic $^1H$-NMR spectra, showing large shifts, and are strongly luminescent in aqueous solution. These markedly improved luminescent properties, compared to the europium cryptate of the parent macrobicyclic ligand **1**, may be ascribed at least in part to a better shielding of the bound cation by the *N*-oxide sites.

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Over the past few years, there has been increasing interest in the fluorescence and photophysical properties of lanthanide cryptates as well as in their potential applications, especially for the labeling of biological materials. Thus, the $Eu^{III}$ complex of the macrobicyclic tris(bipyridine) ligand [bpy · bpy · bpy] **1** [1–6] acts as an efficient molecular device for the conversion of UV light absorbed by the ligand into visible red luminescence of the lanthanide ion [2–6]. It shows strong emission, even in dilute aqueous solution (*ca.* $10^{-5}$M); however, in heavy water, the fluorescence intensity is increased by a factor of about five [3] [6]. This was attributed to the fact that a few (*ca.* 2.5 [3]) luminescence-deactivating water molecules were still able to coordinate to the encaged $Eu^{III}$ ion, despite its marked shielding by the cryptand. Indeed, the crystal structures of the $La^{3+}$, $Eu^{3+}$, and $Tb^{3+}$ cryptates of ligand **1** (or of a substituted derivative) indicate that the encaged cations still bind two $Cl^-$ ions (La) or a $Cl^-$ and a $H_2O$ molecule (Eu, Tb) [7].

Higher conversion efficiency might be achieved by appropriate structural modifications of cryptand **1** that would increase both the shielding of the enclosed ion and the yield of intramolecular energy transfer. To this end, the 2,2′-bipyridine 1,1′-dioxide ($bpyO_2$) and 2,2′-biisoquinoline 1,1′-dioxide ($biqiO_2$) units appeared to present attractive features. Indeed, they are known to easily form lanthanide complexes [8–13], and their O-sites may be expected to block the faces of the macrobicyclic structure towards $H_2O$ molecules. Furthermore, earlier work has shown that their $Eu^{III}$ complexes display a strong luminescence [10–13].

We, therefore, decided to replace one of the bpy units of cryptand **1** by a $bpyO_2$ or a $biqiO_2$ unit. We report here the synthesis of the sodium and europium cryptates of the corresponding macrobicyclic ligands **2** and **3** as well as some preliminary luminescence properties.

The $Eu^{III}$ cryptate **4**, with a macrobicyclic ligand incorporating $biqiO_2$, has already been reported and its photophysical properties studied [12]; long lifetimes as well as high

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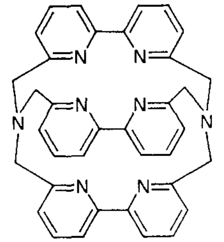
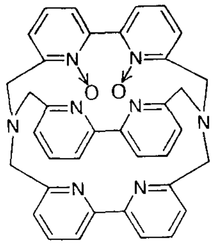
[1]) URA 422 of the CNRS.

UV-to-VIS-conversion efficiency were observed. The $Eu^{III}$ complex of a macrocycle containing two $bpyO_2$ groups has also been studied [13] [14]. The sodium cryptate of the [bpy · bpy · biqi] ligand corresponding to **3** has been described earlier [15].

**Sodium and Europium Complexes of Cryptands 1 and 2.** – *Syntheses.* Macrobicyclic molecules of type **1** are accessible *inter alia* by a stepwise procedure involving the synthesis of an intermediate macrocycle **5** [16] and its subsequent bridging. Such a sequence was followed for the preparation of **2** and **3**. Oxidation of 6,6′-bis(bromomethyl)-2,2′-bipyridine [1] (**6**) with 3-chloroperbenzoic acid ($3\text{-}ClC_6H_4CO_3H$) in $CHCl_3$ at



**1**



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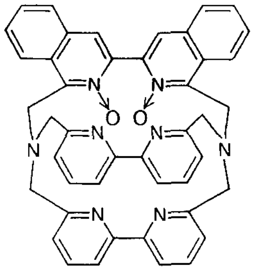
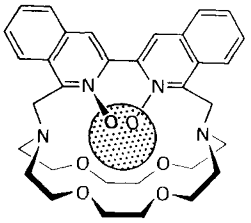
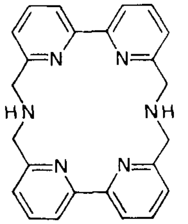


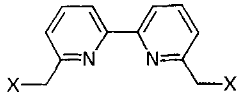
**3**



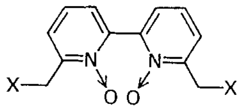
**4**



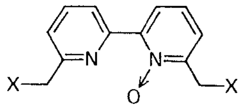
**5**



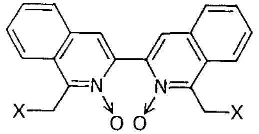
**6** X = Br



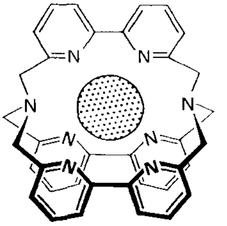
**7** X = Br



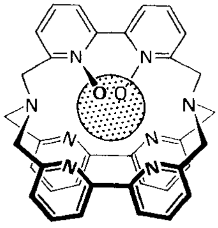
**8** X = Br



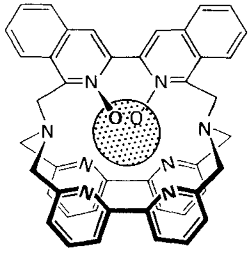
**9** X = Br



$[M^{n+} \subset \mathbf{1}]$



$[M^{n+} \subset \mathbf{2}]$
$(M^{n+} = Na^+, Eu^{3+})$



$[M^{n+} \subset \mathbf{3}]$

room temperature gave the corresponding *N,N'*-dioxide **7** (69% yield) together with some mono-oxide **8**. Condensation of **7** with macrocycle **5** in presence of $Na_2CO_3$ in MeCN [1] gave the NaBr complex of the macrobicyclic *N,N'*-dioxide **2** ($[Na^+ \subset \mathbf{2}]Br^-$), which was purified by column chromatography (58% yield). Similarly, a condensation of 1,1'-bis(bromomethyl)-3,3'-biisoquinoline 2,2'-dioxide [12] (**9**) with macrocycle **5** in presence of $Na_2CO_3$ in MeCN gave the NaBr complex of the macrobicyclic *N,N'*-dioxide **3** ($[Na^+ \subset \mathbf{3}]Br^-$), which was also purified by column chromatography (42% yield).

The $Eu^{3+}$ complexes of **2** and **3** were prepared by treatment of the corresponding $Na^+$ complexes with $EuCl_3$ in MeOH. Spectral and analytical data for all compounds obtained are in agreement with the proposed structures. The $^1$H-NMR spectra of **6–8** display characteristic variations between the oxidized and non-oxidized forms, the aromatic peaks of the former are broader and closer together than those of the latter.

*Structure and Properties of the Sodium and Europium Cryptates of Macrobicycles* **2** *and* **3**. The composition and spectral properties of the $Na^+$ and $Eu^{3+}$ complexes of the macrobicyclic ligands **2** and **3** agree with the formulation of these compounds as the cryptates $[Na^+ \subset L]Br^-$ and $[Eu^{3+} \subset L]3Cl^-$(L = **2** or **3**), respectively, in which the cation is contained in the intramolecular cavity, as in the case of the complexes of related ligands [1–4] [12] [15]. Such cryptate structures have been confirmed by X-ray crystallography for the $La^{III}$, $Eu^{III}$, and $Tb^{III}$ complexes with the parent **1** as ligands [7] (for a related case, see

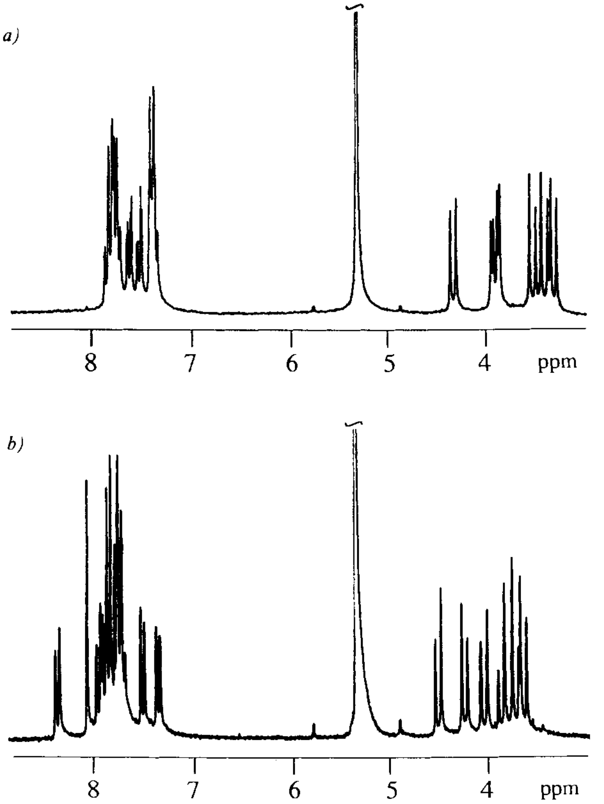


Fig. 1. *200-MHz $^1$H-NMR spectra ($CD_2Cl_2$, 20°) of the NaBr cryptates* a) *of ligand [bpy · bpy · bpy$O_2$]* **2** *and* b) *of ligand [bpy · bpy · biqi$O_2$]* **3**. Solvent at 5.35 ppm.

[17]) as well as for the cryptate **4** ($\mathrm{Na}^+$) containing a $\mathrm{biqiO}_2$ unit [18]. Finally, the crystal structure of the cryptate $[\mathrm{Eu}^{3+} \subset \mathbf{3}]\ 3\mathrm{Cl}^-$ has been determined recently [19].

The IR spectra show a marked decrease in the N–O stretching vibration from the $\mathrm{Na}^+$ to the $\mathrm{Eu}^{3+}$ cryptates of **2** ($\Delta\nu = 33\ \mathrm{cm}^{-1}$, from 1255 to 1222 $\mathrm{cm}^{-1}$), reflecting the tight binding of the $\mathrm{Eu}^{3+}$ ion to the $\mathrm{bpyO}_2$ site of the ligand. Similar effects have been reported for lanthanide complexes of the parent $\mathrm{bpyO}_2$ ligand and attributed to a decrease in $\pi$ character of the NO bond upon coordination of the cation to the O-atom [9].

The $^1$H-NMR data of $[\mathrm{Na}^+ \subset \mathbf{2}]\mathrm{Br}^-$ and $[\mathrm{Na}^+ \subset \mathbf{3}]\mathrm{Br}^-$ (*Fig. 1*) indicate that these complexes are more rigid than those of the non-oxidized parent ligand **1**, the torsional motions being hindered by the two O-atoms, as was also found for **4** ($\mathrm{Li}^+$) [12]. In the case of $[\mathrm{Na}^+ \subset \mathbf{1}]\mathrm{Br}^-$ torsional motions around the *N,N'*-bridgehead axis of the trisbipyridine cryptate render the $\mathrm{CH}_2$ protons equivalent [1]. The $^1$H-NMR spectra of $[\mathrm{Eu}^{3+} \subset \mathbf{2}]3\mathrm{Cl}^-$ and $[\mathrm{Eu}^{3+} \subset \mathbf{3}]3\mathrm{Cl}^-$ (*Fig. 2*) show the highly characteristic effects of lanthanide ions, such as $\mathrm{Eu}^{3+}$, which strongly perturb NMR signals [20], and indicate a tighter binding of $\mathrm{Eu}^{3+}$ by the *N*-oxide sites of **2** and **3** than in the cryptate of **1**; one may indeed expect a strong complexation of the triply charged lanthanides by the highly polar and chelating bipyridine *N,N'*-dioxide unit (see IR data above).

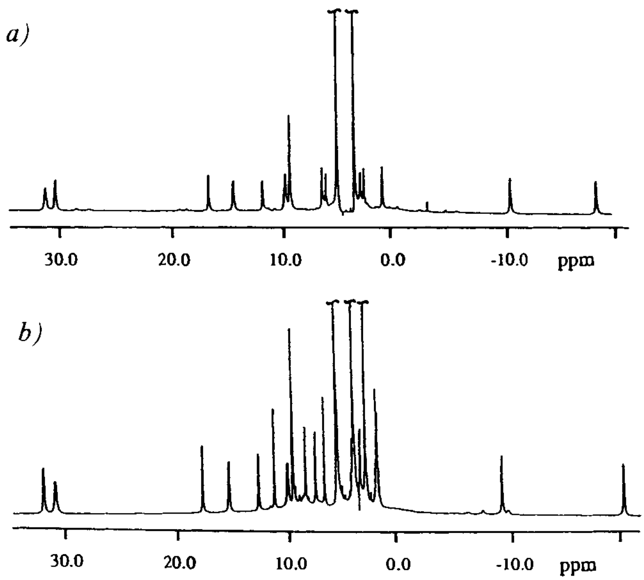


Fig. 2. *200-MHz $^1$H-NMR spectra ($\mathrm{CD_3OD}$, 20°) of the $\mathrm{EuCl}_3$ cryptates* a) *of ligand [bpy·bpy·bpyO$_2$]* **2** *and* b) *of ligand [bpy·bpy·biqiO$_2$]* **3**. Solvent at 3.35 and 4.90 ppm.

Whereas the $^1$H-NMR spectrum (room temperature) of $[\mathrm{Na}^+ \subset \mathbf{1}]\mathrm{Br}^-$ [1] shows a single peak at 3.85 ppm for the $\mathrm{CH}_2$ protons, the spectrum of $[\mathrm{Na}^+ \subset \mathbf{2}]\mathrm{Br}^-$ presents three well defined *AB* systems for the bpy–C*H*$_2$N and bpyO$_2$–C*H*$_2$N protons at 3.31 and 4.33 ppm ($J = 11.7$ Hz), 3.40 and 3.90 ppm ($J = 13.2$ Hz), and 3.52 and 3.89 ppm ($J = 12.5$ Hz). Similarly, the $^1$H-NMR spectrum of $[\mathrm{Na}^+ \subset \mathbf{3}]\mathrm{Br}^-$ shows three well defined *AB* systems for the bpy–C*H*$_2$N and biqiO$_2$–C*H*$_2$N protons at 3.60 and 4.01 ppm ($J = 12.8$ Hz), 3.69 and 3.83 ppm ($J = 12.6$ Hz), and 4.20 and 4.48 ppm ($J = 11.9$ Hz). The $^1$H-NMR signals of $[\mathrm{Eu}^{3+} \subset \mathbf{2}]3\mathrm{Cl}^-$ and $[\mathrm{Eu}^{3+} \subset \mathbf{3}]3\mathrm{Cl}^-$ in $\mathrm{CD_3OD}$ (*Fig. 2*) are strongly shifted with respect to those of the corresponding sodium cryptates (*Fig. 1*). The signals are spread over a very wide range of chemical shifts from *ca.* –20 to +32 ppm, whereas the corresponding domain was 0 to 8.5 ppm for the $\mathrm{Eu}^{3+}$ cryptate of **1**. Neglecting splittings due to spin-spin coupling, one may expect, for a rigid cryptate $[\mathrm{Eu}^{3+} \subset \mathbf{2}]$, a maximum number of 15 signals of different chemical shifts (6 for the 3 $\mathrm{CH}_2$ groups and 9 for 3 different pyridine units). The two resonances at very high field (*ca.* −10 and −20 ppm) might be due to the 4 H of the $CH_2$ groups of the bridges from the *N*-oxide moieties; the other $CH_2$ groups would then give signals above 0 ppm, noting that in the $Eu^{3+}$ complex of **1**, the $CH_2$ signal is found at 0.5 ppm [2]. Similar considerations hold also for $[Eu^{3+} \subset \mathbf{3}]$.

*Luminescence Properties of* $[Eu^{+3} \subset \mathbf{2}]3Cl^-$ *and* $[Eu^{3+} \subset \mathbf{3}]3Cl^-$. Preliminary measurements were performed on the strong red emission observed for the $Eu^{III}$ cryptates of **2** and **3** in dilute (*ca.* $10^{-6}$ M) aqueous solution at room temperature (see *Fig. 3*). It is seen that for the complexes of **2** and **3**, the emission around 610 nm is much more dominant than in the spectrum of $[Eu^{3+} \subset \mathbf{1}]$ (*Fig. 3a*, see [2]). Its intensity is similar to that obtained with solutions of the complex of **1** that are 10–15 times more concentrated. Furthermore, measurements performed in $D_2O$ and in $H_2O$ gave a comparable emission intensity, indicating that with ligands **2** and **3**, the included cation is better protected from interaction with water than in the case of **1**, where the emission quantum yield was found to be appreciably higher in $D_2O$ than in $H_2O$. A detailed photophysical study of the cryptates $[Eu^{3+} \subset \mathbf{2}]3Cl^-$ and $[Eu^{3+} \subset \mathbf{3}]3Cl^-$ is underway in order to characterize quantitatively the remarkable emission properties of these new complexes [21]. However, despite their preliminary nature, the present observations already show that these complexes present a significant gain in light-conversion efficiency over earlier europium cryptates [2–6], a feature of much interest for the development of highly sensitive luminescent labels.

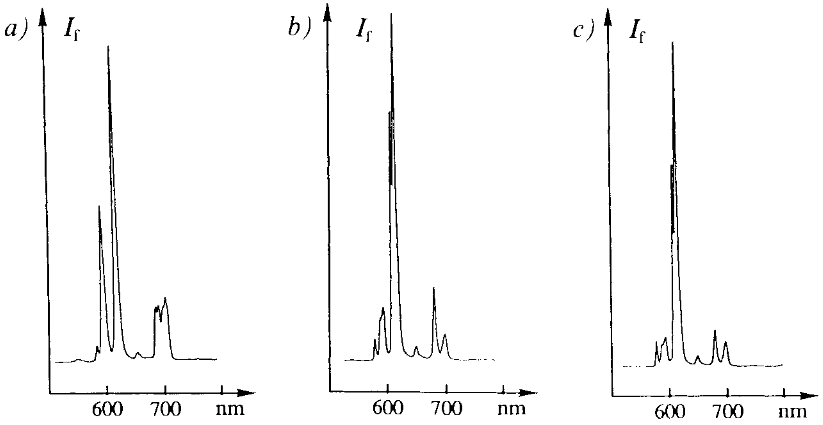


Fig. 3. *Luminescence spectra of the europium cryptates* a) $[Eu^{3+} \subset \mathbf{1}]3Cl^-$, b) $[Eu^{3+} \subset \mathbf{2}]3Cl^-$, *and* c) $[Eu^{3+} \subset \mathbf{3}]3Cl^-$ *in aqueous solution.* Concentrations and excitation wavelengths: *a)* $1.70 \cdot 10^{-5}$ M, 314.7 nm; *b)* $1.09 \cdot 10^{-6}$ M, 313.0 nm; *c)* $1.73 \cdot 10^{-6}$ M, 311.5 nm.

## Experimental Part

*General.* All reagents were commercial and used without purification. $CHCl_3$ was filtered over basic aluminium oxide (*Merck 90*, act. I). MeCN and $CH_2Cl_2$ were distilled over $CaH_2$. Aluminium oxide: *Merck 90*, act. II–III. M.p.: uncorrected; digital melting-point apparatus, electrothermal. UV/VIS spectra: *Cary-13* spectrophotometer. Luminescence spectra: *Shimadzu-Rf-540* spectrophotometer. IR spectra: *Perkin-Elmer-597* spectrometer; KBr pellets. NMR spectra: *Bruker-SY 200* (200.1 ($^1$H) or 50.3 MHz ($^{13}$C)); $\delta$(H) in ppm rel. to residual protiated solvent $CDCl_3$ (7.26), $CD_2Cl_2$ (5.32), or $CD_3OD$ (3.30); $\delta$(C) in ppm rel. to the solvent $CDCl_3$ (77.03), $CD_2Cl_2$ (53.84), or $CD_3OD$ (49.02). MS: fast-atom bombardment (FAB), positive mode *ZAB-HF* in 4-nitrobenzyl alcohol (NBA) or trifluoromethanesulfonic acid (TSA) matrix unless otherwise specified. Elemental analyses were performed by the analytical service of the Institut de Chimie, Strasbourg.

*6,6′-Bis(bromomethyl)-2,2′-bipyridine 1,1′-Dioxide* (**7**). A stirred soln. of 6,6′-bis(bromomethyl)-2,2′-bipyridine (1.0 g, 2.9 mmol) in $CHCl_3$ (150 ml) was cooled to 0° (ice-bath). A soln. of 3-$ClC_6H_4CO_3H$ (55% aq.; 0.9 g, 2.9 mmol) in $CHCl_3$ (50 ml) was added. The mixture was allowed to warm to r.t., and at 10-h intervals, equal portions of 3-$ClC_6H_4CO_3H$ (4 × 0.9 g) in $CHCl_3$ (4 × 50 ml) were added within 2 days (TLC monitoring). Evaporation at 25° yielded **7**, which was washed thoroughly with $Et_2O$ and dried *in vacuo*. When an insufficient amount of 3-$ClC_6H_4CO_3H$ was added, **8** was also formed (see below). Recrystallization of crude **7** from hot $CHCl_3$ gave a white crystalline product: 780 mg (69%). M.p. 225–228° (dec.). TLC ($Al_2O_3$, 2% MeOH/$CHCl_3$): $R_f$ 0.47. UV/VIS ($CH_2Cl_2$): 325 (2700), 278 (12800). IR (KBr): 3067, 3084, 1391, 1386 (py); 1257 (N–O), 668 (C–Br). $^1$H-NMR ($CDCl_3$): 4.73 (*s*, 4 H, $CH_2$Br); 7.33 (*t*, *J* = 7.9, 2 H, pyO); 7.56 (*dd*, *J* = 7.9, 2.0, 2 H, pyO); 7.65 (*dd*, *J* = 7.9, 2.0, 2 H, pyO). FAB-MS (NBA/TSA): 375.1 ([*M* + H]$^+$). Anal. calc. for $C_{12}H_{10}Br_2N_2O_2$ (374.00): C 38.53, H 2.69, N 7.49; found: C 38.38, H 2.61, N 6.99.

*6,6′-Bis(bromomethyl)-2,2′-bipyridine 1-Oxide* (**8**). When the amount of 3-$ClC_6H_4CO_3H$ used was insufficient (see above), **8** was formed besides **7** and isolated by chromatography ($Al_2O_3$). M.p. 194°. $^1$H-NMR ($CDCl_3$): 4.63 (*s*, 2 H, C*H*$_2$Br-py); 4.75 (*s*, 2 H, C*H*$_2$Br-pyO); 7.35 (*t*, *J* = 7.8, 1 H, pyO); 7.52 (*d*, *J* = 8.0, 1 H, py); 7.60 (*dd*, *J* = 7.7, 1.1, 1 H, pyO); 7.82 (*t*, *J* = 7.8, 1 H, py); 8.22 (*dd*, *J* = 7.7, 1.2, 1 H, pyO); 8.81 (*d*, *J* = 7.7, 1 H, py). Anal. calc. for $C_{12}H_{10}Br_2N_2O$ (358.02): C 40.25, H 2.81, N 7.82; found: C 40.15, H 2.71, N 7.82.

*{6,6′-[*N,N′:N,N′*-Bis(2,2′-bipyridine-6,6′-dimethyl)bis(aminomethyl)]-2,2′-bipyridine 1,1′-Dioxide}sodium Bromide* ([Na$^+$ ⊂ **2**]Br$^-$). Compound **7** (285 mg, 0.76 mmol) was added to a stirred, refluxing mixture of **5** [16] (300 mg, 0.76 mmol) and $Na_2CO_3$ (800 mg, 7.60 mmol) in freshly distilled MeCN (400 ml) under $N_2$. Vigorous stirring at reflux was continued for 24 h. The hot mixture was filtered and the filtrate evaporated at r.t. Chromatography ($Al_2O_3$, $CH_2Cl_2$/MeOH 9:1) yielded pure [Na$^+$ ⊂ **2**]Br$^-$ (unstable in $CHCl_3$). TLC ($Al_2O_3$, 10% MeOH/$CH_2Cl_2$): $R_f$ 0.39. Washing with $Et_2O$ gave white powder: 310 mg (58%). M.p. 210° (dec.). UV/VIS (EtOH): 288 (21000), 236 (34000). IR (KBr): 1577, 1575, 1397, 1384 (py); 1255 (N–O). $^1$H-NMR ($CD_2Cl_2$): 3.31 (*d*, *J* = 11.7, 1st *AB*, 2 H); 3.40 (*d*, *J* = 13.2, 2nd *AB*, 2 H); 3.52 (*d*, *J* = 12.7, 3rd *AB*, 2 H); 3.89 (*d*, *J* = 12.5, 3rd *AB*, 2 H); 3.90 (*d*, *J* = 12.9, 2nd *AB*, 2 H); 4.33 (*d*, *J* = 11.7, 1st *AB*, 2 H); 7.35–7.89 (*m*, 18 H). $^{13}$C-NMR ($CD_2Cl_2$): 61.3 (2*C*H$_2$–bpyO$_2$); 61.4 (4*C*H$_2$–bpy); 121.8, 122.6, 124.9, 125.0, 127.1, 129.5, 138.4, 138.7 (CH of bpy and bpyO$_2$); 156.9, 157.5 (C of bpyO$_2$); 158.2, 159.1 (C of bpy). FAB-MS (NBA): 629.2 ([*M* + Na]$^+$), 413.2 ([(bpy · bpy) + Na]$^+$). Anal. calc. for $C_{36}H_{30}N_8O_2 \cdot NaBr \cdot 3H_2O$ (763.60): C 56.62, H 4.75, N 14.67; found: C 56.87, H 4.92, N 14.12.

*{6,6′-[*N,N′:N,N′*-Bis(2,2′-bipyridine-6,6′-dimethyl)bis(aminomethyl)]-2,2′-bipyridine 1,1′-Dioxide}europium(III) Chloride* ([Eu$^{3+}$ ⊂ **2**]3Cl$^-$). $EuCl_3 \cdot 6H_2O$ (240 mg, 0.65 mmol) was added to a stirred soln. of [Na ⊂ **2**]Br$^-$ (310 mg, 0.44 mmol) in MeOH (100 ml) at reflux. Heating and vigorous stirring was continued for further 24 h under $N_2$. After cooling to r.t., $Et_2O$ (50 ml) was added, resulting in the formation of a white precipitate which was isolated after centrifugation: [Eu$^{3+}$ ⊂ **2**]3Cl$^-$ as white powder, 250 mg (66%). M.p. 258° (dec.). UV ($H_2O$): 320 (13700), 306 (19500), 250 (22400), 230 (29000). IR (KBr): 1577, 1574, 1405, 1390 (py); 1222 (N–O). Luminescence spectrum ($H_2O$, $c = 1.09 \cdot 10^{-6}$ M): $\lambda_{exc} = 313.0$, $\lambda_{em} = 579.0$, 595.0, 607.0, 611.3, 651.0, 683.5, 701.2. $^1$H-NMR ($CD_3OD$): br. signals at −18.6 (2 H), −10.7 (2 H), +0.7 (2 H), +2.4 (2 H), +2.7 (2 H), +5.9 (2 H), +6.3 (2 H), +9.1 (4 H), +9.6 (2 H), +11.6 (2 H), +14.2 (2 H), +16.5 (2 H), +30.3 (2 H), +31.2 (2 H). FAB-MS (NBA): 829.0 ([*M* + Eu + 2Cl]$^+$), 793.0 ([*M* + Eu + Cl]$^+$), 541.9 ([(bpy · bpy) + Eu + Cl]$^+$). Anal. calc. for $C_{36}H_{30}N_8O_2 \cdot EuCl_3 \cdot NaBr \cdot 3H_2O$ (1021.94): C 42.31, H 3.55, N 10.96; found: C 41.80, H 3.54, N 10.35.

*{1,1′-[*N,N′:N,N′*-Bis(2,2′-bipyridine-6,6′-dimethyl)bis(aminomethyl)]-3,3′-biisoquinoline 2,2′-Dioxide}sodium Bromide* ([Na$^+$ ⊂ **3**]Br$^-$). Compound **9** (270 mg, 0.58 mmol) was added to a stirred and refluxing mixture of **5** [16] (230 mg, 0.58 mmol) and $Na_2CO_3$ (620 mg, 5.80 mmol) in freshly distilled MeCN (400 ml) under $N_2$. Vigorous stirring at reflux was continued for 24 h. The hot mixture was filtered and the filtrate evaporated at r.t. Chromatography ($Al_2O_3$, $CH_2Cl_2$/MeOH 9:1) yielded pure [Na$^+$ ⊂ **3**]Br$^-$ (unstable in $CHCl_3$). TLC ($Al_2O_3$, 10% MeOH/$CH_2Cl_2$): $R_f$ 0.38. The product was washed with $Et_2O$: pale yellow powder, 340 mg (42%). M.p. 217° (dec.).

UV/VIS (MeOH): 323 (11000), 264 (65000), 236 (49000). IR (KBr): 1577, 1573, 1397, 1383 (py); 1254 (N–O). $^1$H-NMR ($CD_2Cl_2$): 3.60 (*d*, $J$ = 12.9, 2 H, 1st *AB*); 3.69 (*d*, $J$ = 12.5, 2 H, 2nd *AB*); 3.83 (*d*, $J$ = 12.7, 2 H, 2nd *AB*); 4.01 (*d*, $J$ = 12.7, 2 H, 1st *AB*); 4.20 (*d*, $J$ = 11.9, 2 H, 3rd *AB*); 4.48 (*d*, $J$ = 11.9, 2 H, 3rd *AB*); 7.35 (*d*, $J$ = 7.7, 2 H); 7.50 (*d*, $J$ = 7.5, 2 H); 7.68–7.97 (*m*, 14 H); 8.06 (*s*, 2 H); 8.37 (*d*, $J$ = 8.4, 2 H). $^{13}$C-NMR ($CD_2Cl_2$): 49.22 ($CH_2$–biqi$O_2$); 61.82, 61.92 ($CH_2$–bpy); 121.86, 122.60, 123.37, 124.77, 124.96, 125.77, 128.66, 129.43, 130.79, 138.43, 138.62 (CH of biqi$O_2$ and bpy); 128.70, 131.05, 142.29, 145.16 (C of biqi$O_2$); 157.06, 157.63, 158.32, 159.05 (C of bpy). FAB-MS (NBA/$CHCl_3$): 729.2 ([*M* + Na]$^+$). Anal. calc. for $C_{44}H_{40}N_8O_5 \cdot NaBr \cdot 3H_2O$ (863.71): C 61.18, H 4.66, N 12.97; found: C 61.84, H 4.66, N 12.44.

*{1,1'-[*N,N':N,N'*-Bis(2,2'-bipyridine-6,6'-dimethyl)bis(aminomethyl)]-3,3'-biisoquinoline 2,2'-Dioxide}europium(III) Chloride* ([Eu$^{3+}$ ⊂ **3**]3Cl$^-$). $EuCl_3 \cdot 6H_2O$ (260 mg, 0.71 mmol) was added to a stirred soln. of [Na$^+$ ⊂ **3**]Br$^-$ (300 mg, 0.37 mmol) in MeOH (100 ml) at reflux. Heating and stirring was continued for 24 h under $N_2$. After cooling to r.t., $Et_2O$ (60 ml) was added, resulting in the formation of a precipitate, which was isolated after centrifugation: [Eu$^{3+}$ ⊂ **3**]3Cl$^-$ as pale yellow powder, 314 mg (88 %). M.p. 268° (dec.). UV ($H_2O$): 358 (4000), 305 (24000), 268 (76000). IR (KBr): 1578, 1574 (py); 1255 (N–O). Luminescence spectrum ($H_2O$, $c = 1.73 \cdot 10^{-6}$ M): $\lambda_{exc}$ = 359.0, $\lambda_{em}$ = 579.7, 595.0, 607.0, 611.0, 651.7, 683.0, 701.0. $^1$H-NMR ($CD_3OD$): br. signals at –21.5 (2 H), –10.2 (2 H), +1.2 (4 H), +2.6 (2 H), +6.0 (2 H), +6.8 (2 H), +7.8 (2 H), +8.9 (4 H), +9.4 (2 H), +10.6 (2 H), +12.0 (2 H), +14.7 (2 H), +17.1 (2 H), +30.3 (2 H), +31.3 (2 H). FAB-MS (NBA/MeCN): 929.1 ([*M* + Eu + 2Cl]$^+$), 893.1 ([*M* + Eu + Cl]$^+$), 542.1 ([(bpy · bpy) + Eu + Cl]$^+$). Anal. calc. for $C_{44}H_{34}N_8O_2 \cdot EuCl_3 \cdot NaBr$ (1068.01): C 49.48, H 3.21, N 10.49; found: C 49.33, H 3.63, N 10.25.

## REFERENCES

[1] J.C. Rodriguez-Ubis, B. Alpha, D. Plancherel, J.-M. Lehn, *Helv. Chim. Acta* **1984,** *67,* 2264.
[2] B. Alpha, J.-M. Lehn, G. Mathis, *Angew. Chem.* **1987,** *99,* 259; *ibid. Int. Ed.* **1987,** *26,* 266.
[3] B. Alpha, V. Balzani, J.-M. Lehn, S. Perathoner, N. Sabbatini, *Angew. Chem.* **1987,** *99,* 1310; *ibid. Int. Ed.* **1987,** *26,* 1266.
[4] B. Alpha, thèse de doctorat-ès-sciences, Université Louis Pasteur, Strasbourg, 1987.
[5] N. Sabbatini, S. Perathoner, V. Balzani, B. Alpha, J.-M. Lehn, in 'Supramolecular Photochemistry', Ed. V. Balzani, Reidel, Dordrecht, 1987, p. 187; J.-M. Lehn, *ibid.*, p. 29.
[6] B. Alpha, R. Ballardini, V. Balzani, J.-M. Lehn, S. Perathoner, N. Sabbatini, *Photochem. Photobiol.* **1990,** *52,* 299.
[7] J. Guilhem, C. Pascard, B. Alpha, R. Deschenaux, J.-M. Lehn, to be published.
[8] A. R. Al-Karaghouli, R.O. Days, J.S. Wood, *Inorg. Chem.* **1978,** *17,* 3702.
[9] D.M. Mehs, S.K. Madan, *J. Inorg. Nucl. Chem.* **1968,** *30,* 3017.
[10] A. Musumeci, R.P. Bonomo, V. Cucinotta, A. Seminara, *Inorg. Chim. Acta* **1982,** *59,* 133; A. Seminara, A. Musumeci, *ibid.* **1984,** *95,* 291.
[11] M. Tan, N. Tang, Y. Shai, J. Bai, *New Front. Rare Earth Dev. Appl.* **1985,** *1,* 199.
[12] J.-M. Lehn, M. Pietraszkiewicz, J. Karpiuk, *Helv. Chim. Acta* **1990,** *73,* 106.
[13] M. Pietraszkiewicz, S. Pappalardo, P. Finocchiaro, A. Mamo, J. Karpiuk, *J. Chem. Soc., Chem. Commun.* **1989,** 1907; J.-M. Lehn, C.O. Roth, unpublished work.
[14] For another macrocycle containing the bpy$O_2$ unit, see H.E. Katz, *J. Org. Chem.* **1985,** *50,* 2086.
[15] B. Alpha, E. Anklam, R. Deschenaux, J.-M. Lehn, M. Pietraszkiewicz, *Helv. Chim. Acta* **1988,** *71,* 1042.
[16] G.R. Newkome, S. Pappalardo, V.K. Gupta, F.R. Fronczek, *J. Org. Chem.* **1983,** *48,* 4848.
[17] A. Caron, J. Guilhem, C. Riche, C. Pascard, B. Alpha, J.-M. Lehn, *Helv. Chim. Acta* **1985,** *68,* 1577.
[18] K. Suwińska, J. Lipkowski, unpublished work; J.-M. Lehn, J. Lipkowski, K. Suwińska, J. Karpiuk, M. Pietraszkiewicz, presented at the Polish School on 'Supramolecular Chemistry', Gdansk, August 20–31, 1990.
[19] J. Guilhem, C. Pascard, J.-M. Lehn, C.O. Roth, to be published.
[20] O.A. Gansow, D.J. Pruett, K.B. Triplett, *J. Am. Chem. Soc.* **1979,** *101,* 4408.
[21] L. Prodi, M. Maestri, V. Balzani, J.-M. Lehn, C.O. Roth, to be published.