Coordination Properties of a Polyamine Cryptand with Two Different Binding Moieties. A Case of a pH-Modulated Antenna Device Based on a New Eu(III) Cryptate Complex

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Protonation and alkali- and alkaline-earth-metal coordination by the dipyridine-containing cryptand L have been studied by means of potentiometric and spectroscopic (UV−vis, ^{1}H NMR) measurements in aqueous solutions. This ligand is constituted by an aliphatic polyamine chain and a coordinating cleft, delimited by two dipyridine units, where the metal ion is lodged. The resulting complexes are characterized by an unusually high stability. The polyamine chain is not involved, or weakly involved, in metal coordination, and facile protonation can occur on the nitrogen atoms of this moiety. Similar coordination features are found in the Eu(III) complex. A fluorescence emission study reveals that the Eu(III) cryptate shows the characteristic visible emission of the metal, due to the intramolecular energy transfer to the metal ion mainly from the lower energy triplet state of the cryptand. On the other hand, the emission intensity is modulated by pH, giving a maximum at neutral pH and decreasing at both acidic and alkaline pH values.

Introduction

In the past few years there has been considerable interest in the development of new polyamine macrobicyclic receptors. Macropolycyclic polyamines containing appropriate binding sites and cavities of suitable size and shape may be designed to form selective inclusion complexes in aqueous solution. Actually, the molecular topology of the host molecule can be synthetically modulated to bind many different chemical species from inorganic or organic cations[1−9] to anionic species.[9−15] An interesting perspective is the use of cryptands as selective complexing agents, able, at the same time, to signal the coordination of the bound substrate. To this purpose, incorporation of dipyridine into macrocyclic structures allows within the same ligand the special complexation feature of cryptands, e.g., high selectivity in metal coordination, to be combined with the versatile photoactivity exhibited by the metal complexes of this heterocycle. Actually, the photophysical properties of the Eu(III), Tb(III), and Ru(II) complexes with dipyridine-containing cryptands, such as L1 (Chart 1), have been extensively studied in the past few years.[16−18]

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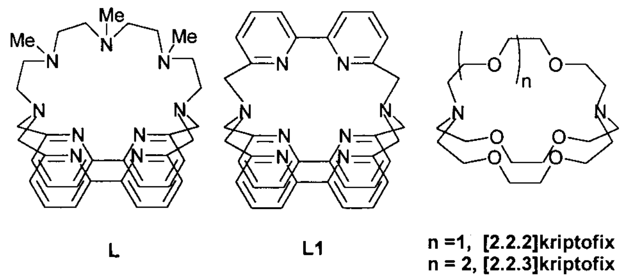
Chart 1



L

L1

n = 1, [2.2.2]kriptofix
n = 2, [2.2.3]kriptofix

Recently we have reported the synthesis of a new cryptand, L, containing two dipyridine chromophore units.[19]

The most significant difference from previously reported dipyridine-containing cryptands is the insertion of a polyamine chain connecting the two heteroaromatic units. We hoped that the insertion of a flexible polyamine chain would allow the kinetic inertness usually presented by metal complexes with this class of ligands to be overcome. Furthermore, aliphatic amines are more basic than heteroaromatic ones. This fact, in principle, would allow protonated complexes in aqueous solution, whose photophysical properties could be pH-modulated, to be achieved.

With the purpose to verify the potential use of this ligand as a selective receptor and potential luminescent sensor for metals, we have investigated its coordination properties toward alkali- and alkaline-earth-metal cations and Eu(III).

Results and Discussion

Synthesis of Metal Complexes. As most of the dipyridine-containing cryptands, L was obtained as a sodium cryptate complex, $[NaL]^+$, by means of a template synthesis involving this alkali-metal ion as templating agent.[19] In many cases the kinetic inertness of the resulting cryptate complexes precludes the analysis of the coordination behavior of the ligands. In the case of ligand L1, the inertness of the sodium cryptate complex was overcome by transmetalation of the Na^+ with Ag^+ followed by precipitation of Ag_2S to obtain the free cryptand.[17a] In the present case, simple treatment of the $[NaL]^+$ complex with $HClO_4$ leads to prompt removal of the Na^+ ion from the macrocyclic cavity, affording the ligand in its protonated form, $[H_5L](ClO_4)_5$, in almost quantitative yield. Such a different behavior with respect to L1 is probably related to the presence of a pentaamine chain, which increases the ligand flexibility, thus allowing easier access to the uncomplexed cryptand. The $[H_5L](ClO_4)_5$ salt can be used as a versatile precursor for the synthesis of different metal complexes as well as to carry out a solution study on ligand protonation and metal complexation. Simple addition of $MClO_4$ (M = alkali metal) or $M(ClO_4)_2$ (M = alkaline-earth metal) to an aqueous solution of $[H_5L](ClO_4)_5$ at alkaline pH, followed by extraction with chloroform and precipitation with cyclohexane, leads to the isolation of the alkali- or alkaline-earth-metal complexes as their perchlorate salts. The ESI mass spectra of these compounds show the characteristic peaks of the $[ML]^+$ and $[ML]^{2+}$ complexes and the absence of the peak of the free cryptand, suggesting a high stability of these adducts, probably due to the encapsulation of the metals inside the cavity.

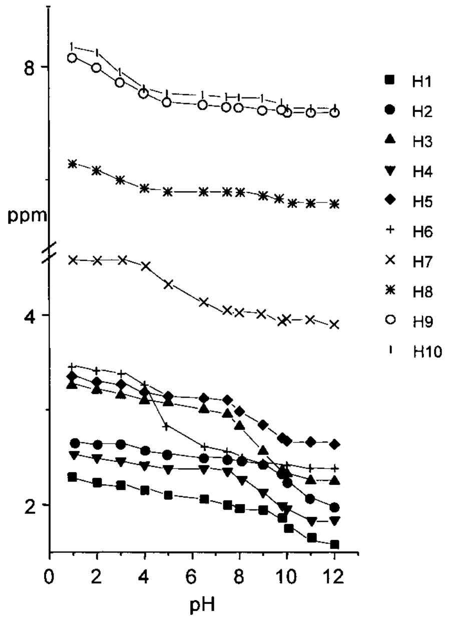


Figure 1. Experimental ^1H chemical shifts of L as a function of pH.

Table 1. Protonation Constants of L Determined in NMe_4NO_3 (0.1 M) at 298.1 K

$L + H^+ \rightleftarrows HL^+$	10.39(2)	$H_3L^{3+} + H^+ \rightleftarrows H_4L^{4+}$	3.67(5)
$HL^+ + H^+ \rightleftarrows H_2L^{2+}$	9.34(3)	$H_4L^{4+} + H^+ \rightleftarrows H_5L^{5+}$	2.0(1)
$H_2L^{2+} + H^+ \rightleftarrows H_3L^{3+}$	6.72(3)		

As usually found in lanthanide complexes, Eu(III) complexation is extremely slow at room temperature (see below). The protonated complex $[EuCl_3H_2L](ClO_4)_2 \cdot 4H_2O$ can be obtained by prolonged heating (24 h) of an aqueous solution containing $[NaL]ClO_4$ or $[H_5L](ClO_4)_5$ and $EuCl_3$ in a 1:1 molar ratio at pH 3. The crystal structure of this complex has been previously communicated.[20]

Ligand Protonation. The protonation constants of L were determined by means of potentiometric measurements in aqueous solution and are reported in Table 1. L can bind up to four protons in the pH range investigated by potentiometric measurements (2.5−10.5). A fifth protonation step was monitored at a strongly acidic pH value ($\log K = 2.0$) by means of spectrophotometric measurements. L shows a marked grouping of the protonation constants, the difference between the third and the fourth protonation constant being ca. 3.1 log units. This behavior is common in macrocyclic polyamines, and has been explained in terms of minimization of the electrostatic repulsion between the charged ammonium functions.[21] Dipyridine nitrogens, however, are characterized by far lower basicity than amine nitrogens, and therefore, it is expected that at least the first protonation steps take place on the polyamine chain.[21] To gain further insight into the stepwise protonation of L, we recorded ^1H NMR spectra of L in aqueous solutions at different pH values. Figure 1 shows the ^1H chemical shifts of the L signals as a function of pH. The ^1H NMR spectrum at pH 12 displays two singlets at 1.80 and 1.93 ppm (the methyl group H1 and H4), four triplets at 2.05, 2.33, 2.40, and 2.58 ppm (the protons of the ethylenic chains, H3, H2, H6, and H5, respectively), a quartet at 3.92 ppm (the benzylic protons H7), and a doublet and a multiplet at 6.95 and 7.82 ppm (the dipyridine nitrogen H8, H9, and H10). These spectral features are in accord with a

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Coord. Chem. Rev. **1993**, *125*, 75 and references therein. (c) Sabbatini, N.; Guardigli, M.; Lehn J.-M. *Coord. Chem. Rev.* **1993**, *123*, 201. (d) Balzani, V.; Credi, A.; Venturi, M. *Coord. Chem. Rev.* **1998**, *171*, 3 and references therein.

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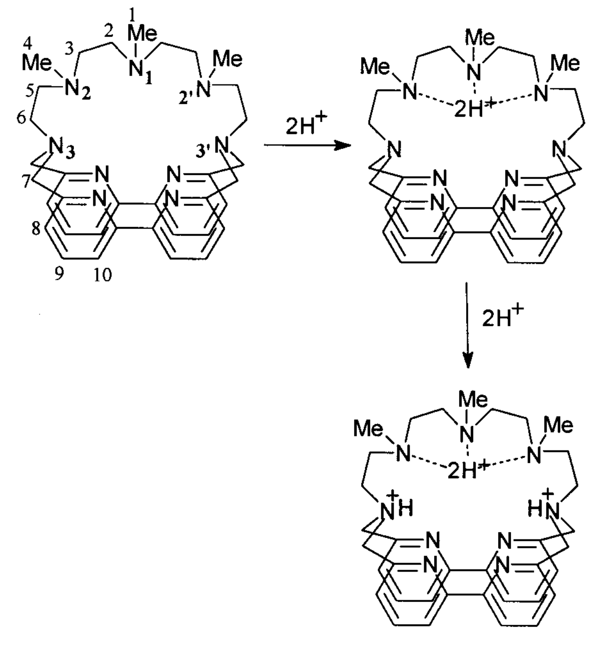
Scheme 1



C_{2v} time-averaged symmetry in aqueous solution, which is maintained throughout all the pH range investigated. As shown in Figure 1, in the pH range 12−7, where the first two protons bind to the ligand, the signal of hydrogens H1 and H2, in the α-position with respect to N1, and those of H3, H4, and H5, in the α-position with respect to N1, N2, and N2′, exhibit a marked downfield shift. Minor shifts are observed for the other signals.

These spectral features indicate that the first two protonation steps mainly involve the nitrogens N1, N2, and N2′, and therefore, in the $[H_2L]^{2+}$ species the two protons are localized on the triamine chain N2−N1−N2′ (Scheme 1).

The higher basicity of these methylated nitrogens with respect to N3 and N3′ may be related to the electron-withdrawing effect exerted by the heteroaromatic units, which reduces the basicity of the adjacent benzylic amine groups. However, binding of the third and fourth protons in the pH region 7.5−3.5 gives rise to a marked downfield shift of the resonances H6 and H7, indicating that these protonation steps take place on the benzylic nitrogens. The most interesting finding of this study is the scarce tendency of the dipyridine nitrogens to protonate. Up to pH 3.5 signals of the dipyridine moieties do not shift appreciably. Only below pH 3.5, where the $[H_5L]^{5+}$ species is formed, the H8, H9, and H10 resonances experience a downfield shift, indicating that the fifth protonation step occurs on the heteroaromatic nitrogens. To better ascertain the role of the heteroaromatic nitrogens in the process of proton binding, we have recorded UV−vis spectra at different pH values. Figure 2a shows the spectra of the cryptand at different pH values. Figure 2b displays the titration curve obtained by monitoring the electronic absorption at 306 nm. The spectrum of ligand L in its unprotonated form displays a band with a maximum at 296 nm (spectrum a in Figure 2a). A marked change of these spectral features is observed at strongly acidic pH values (spectrum c), with a red shift of the absorption band (λ_{max} = 306 nm) and an increase of the molar absorbance. On the other hand, it is well-known that protonation of 4,4′-dipyridine leads to a red shift, accomplished by an increase of the molar absorption coefficient, of its absorption band. On this basis, the appearance of a new red-shifted band at 306 nm in the L spectrum can be ascribed to protonation of the dipyridine nitrogens. According to Figure 2b, this occurs in the fifth protonation step, in agreement with the protonation pattern deduced from the ^{1}H NMR measurements. An intriguing aspect is the smaller, but significant, red shift observed in the pH range 9−10.5, where the monoprotonated $[HL]^+$ species is prevalent in solution (Figure 2b). Such a red shift disappears with the formation of the $[H_2L]^{2+}$ and $[H_3L]^{3+}$ species. According to the ^{1}H NMR measurements, this red shift cannot be ascribed to direct protonation of the dipyridine nitrogens. Taking into account that in $[HL]^+$ the acidic proton is located on the N2′−N1−N2 moiety of the flexible aliphatic polyamine chain, a tentative explanation could reside in the formation of hydrogen bonds between the protonated amine groups and the heteroaromatic nitrogens. In the di- and triprotonated $[H_2L]^{2+}$ and $[H_3L]^{3+}$ species the electrostatic repulsion between the protons, gathered on the N1−N2−N3 moiety, would increase the rigidity of the aliphatic polyamine chain, preventing the interaction with the heteroaromatic nitrogens.

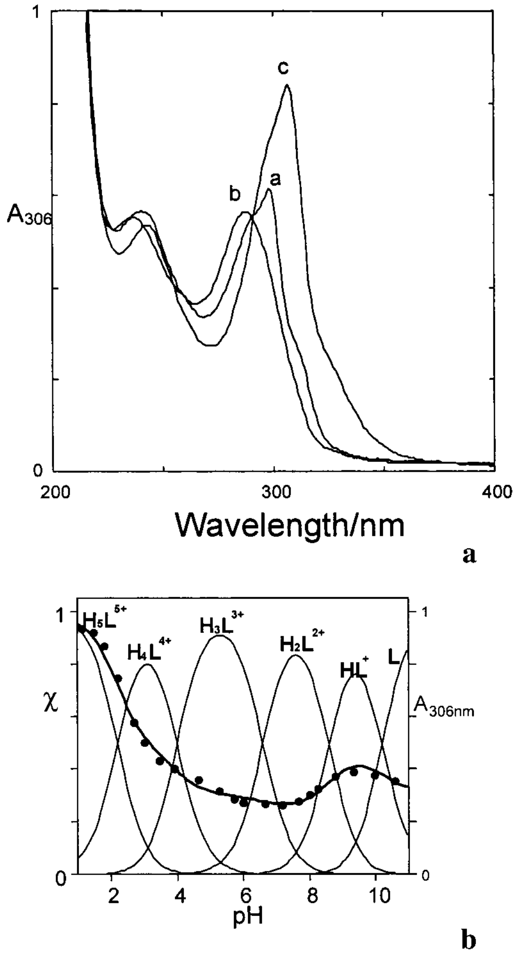


Figure 2. (a) Absorption spectra of the compound L in aqueous solutions at pH 11.5 (spectrum a, free amine L), pH 7.2 (spectrum b), and pH 1 (spectrum c, H_5L^{5+} species). (b) Absorbance monitored at 306 nm (●) and calculated molar fractions (χ) of the protonated species of L (—) as a function of pH.

Alkali- and Alkaline-Earth-Metal Complexation. Although complexation of alkali and alkaline-earth metals by cryptands in aqueous solution has been widely investigated in the past 20 years, most of the studies concern ligands containing oxygen atoms, due to high affinity of this donor toward hard metal ions.[1−3,22] This class of macrocycles may offer particular

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[22] Cox, B. G.; Schneider, H. *Coordination and Transport Properties of Macrocyclic Compounds in Solution*; Elsevier Science Publishers B.V.: Amsterdam, The Netherlands, 1992.

Table 2. Stability Constants of the Complexes with L Determined in NMe_4NO_3 (0.1 M) at 298.1 K

	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$M + L \rightleftarrows ML$[a]	3.4(1)	7.0(1)	3.6(1)	4.1(1)	8.54(7)	8.89(4)	6.56(7)
$ML + H \rightleftarrows MLH$	9.5(1)	9.4(1)	9.8(1)	9.9(1)	8.44(8)	8.48(4)	7.9(1)
$MLH + H \rightleftarrows MLH_2$	9.3(1)	8.0(1)	9.3(1)	9.1(1)	7.79(8)	7.29(4)	8.60(7)
$MLH_2 + H \rightleftarrows MLH_3$		5.2(1)			5.46(8)	5.59(3)	6.00(5)

[a] Charges omitted for clarity.

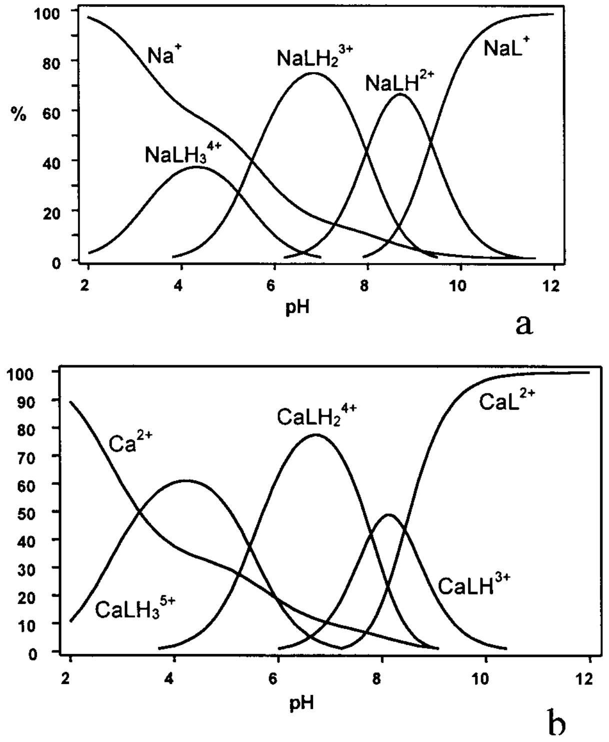

Figure 3. Distribution diagrams for the systems Na/L (a) and Ca/L (b) ([L] = [M] = 1×10^{-3} mol dm^{-3} (M = Na or Ca), NMe_4NO_3 (0.1 M), 298.1 K).

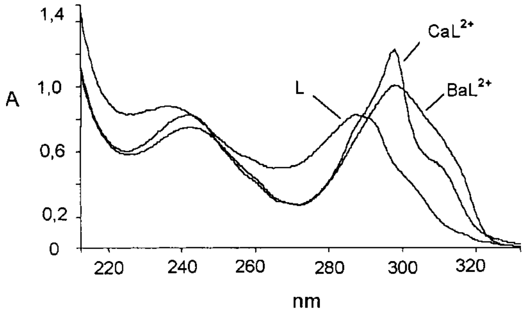

Figure 4. Absorption spectra of the compound L and its Ca^{2+} and Ba^{2+} complexes.

selectivity patterns, mostly due to a dimensional match between the metal ion and the cryptand cavity. Only a few data are available on the stability in aqueous solutions of complexes of alkali and alkaline-earth metals with cryptands containing only nitrogen donors,[23] because of the low stability of the adducts and/or the kinetic slowness of the process of metal complexation. No data on the complex stability with dipyridine-containing macrobicycles, such as L1, are available in the literature. The particular molecular architecture of the present cryptand, which contains a rigid and rather hydrophobic pocket, defined by the two dipyridine units, and, at the same time, a more flexible aliphatic polyamine chain could allow the problems related to the complex kinetic inertness to be overcome and, therefore, prompted us to carry out a potentiometric study on the complexation of alkali (Li^+, Na^+, and K^+) and alkaline-earth (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) metals by L. Surprisingly, we found that ligand L displays a good binding ability toward these metals, with a marked selectivity toward Na^+, among alkali metals, and Ca^{2+} and Sr^{2+} among alkaline-earth metals. Table 2 lists the species formed and the corresponding stability constants. At first glance, the stability of the complexes seems to be of the same order of magnitude with respect to the corresponding complexes with polyoxacryptand [2.2.2]kriptofix and somewhat higher than those with [2.2.3]kriptofix (Chart 1), whose cavity dimension can be compared with the L one. On the other hand, both [2.2.2]kriptofix and [2.2.3]kriptofix display a different selectivity pattern with respect to L, with a marked selectivity for K^+ with respect to Na^+ and for Ba^{2+} among alkaline-earth metals (for instance, log $K = 4.57$, 8.26, and 9.7 for the Ca^{2+}, Sr^{2+}, and Ba^{2+} complexes with [2.2.2]-kriptofix and log $K = 1.98$, 3.39, and 6.02 for the Ca^{2+}, Sr^{2+}, and Ba^{2+} complexes with [2.2.3]kriptofix).[1a,22] This comparison may suggest that the selectivity displayed by our ligand cannot be simply related to the overall dimension of the tridimensional cavity. A peculiar characteristic of the L complexes is the high tendency to protonate in aqueous solution. All complexes form mono- and diprotonated species and, in the case of Na^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}, also triprotonated species. The protonation constants are remarkably high and similar to those of the free ligand. As a consequence, protonated species of the complexes are formed at acidic pH values, as shown in Figure 3 for Na^+ and Ca^{2+}. This behavior is usually ascribed to protonation of nitrogens not involved or weakly involved in metal coordination. The protonation constants are also by far higher than that of 2,2′-dipyridine (log $K = 4.37$).[24] These observations point out that protonation occurs on amine groups of the aliphatic chain, which probably give rise only to weak interactions with the metal. On the other hand, UV spectra recorded on solutions containing the metal complexes show that the dipyridine units are indeed involved in metal coordination. As already observed in the case of proton binding by dipyridine (see above), metal coordination by this heteroaromatic unit leads to a marked change in the absorption spectrum of the ligand, with the appearance of new red-shifted bands at ca. 300 nm, as shown in Figure 4 for the Ca^{2+} and Ba^{2+} complexes. The involvement of the dipyridine units in metal binding is also confirmed by the comparison of the ^1H NMR spectra of L and its metal complexes, which generally show marked downfield displacement of the signals of the aromatic protons H8, H9, and H10 (0.2−0.3 ppm) and of the benzylic protons H7 (ca 0.2 ppm). Minor shifts, of less than 0.1 ppm, are observed for the resonances of the methyl groups and of the ethylenic chains. To shed further light on the coordination environment of the

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(23) To our knowledge, the stability data on alkali-metal coordination by polyamine cryptands are very limited and concern lithium-selective small azacages; see ref 8.

(24) Smith, R. M.; Martell, A. E. *NIST Critical Stability Constants Database*, version 2; National Institute of Standards and Technology: Washington, DC, 1995.

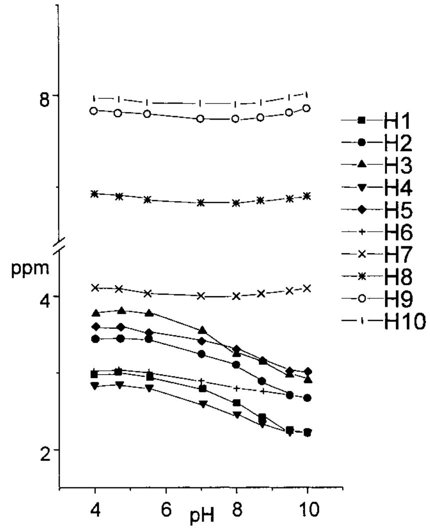

Figure 5. Experimental ^{1}H chemical shifts of the Ca^{2+} complex with L at different pH values.

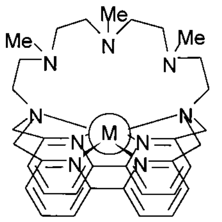

Figure 6. Proposed structure for the alkali- and alkaline-earth-metal complexes with L. Eventual weak interactions with the methylated nitrogens are not represented.

metals in the $[ML]^{2+}$ complexes as well as in their protonated species, we decided to perform ^{1}H NMR spectra at different pH values. Figure 5 gives the pH dependence of the ^{1}H signals for the Ca^{2+} complex. The most interesting finding is the fact that protonation of the complex, which takes place in the pH range 9−4 (Figure 3b), gives rise to marked downfield shifts of the resonances of the methyl group H1 and H4 and of the methylenic protons H2, H3, and H5. The signals of the dipyridine protons as well as those of the benzylic protons H7, adjacent to N3, are not affected by proton binding. Similar patterns have been obtained for the other metal complexes.

These data suggest that complex protonation takes place on the methylated nitrogens N1, N2, and N2′, while the heteroaromatic nitrogens and the benzylic amine group nitrogens N3 and N3′ are coordinated to the metal (Figure 6), in a fashion similar to that found in the crystal structure of the diprotonated Eu(III) complex (see below).

Therefore, ligand L displays two binding moieties with different coordination characteristics, i.e., the methylated triamine chain, which shows high affinity for protons and the hydrophobic "pocket" defined by the two dipyridine units and by the benzylic amine groups, which is the preferred binding site for alkali and alkaline-earth metals. The rigidity of the dipyridine units, accomplished by the presence of the triamine bridge between N3 and N3′, would give rise to a preorganized binding cleft where the metal ions can be lodged, achieving, at the same time, an optimal arrangement of the donors around the metals. From this point of view, the dimensional match between the metal ions and this coordinative pocket may account for the high selectivity exhibited by L in metal coordination.

Eu(III) Complexation in Aqueous Solutions. Eu(III) complexation by cryptands containing cromophoric units, such as dipyridine, has been the subject of several studies, due to the potential use of the complexes as luminescent labels in floroimmunoassay.[17a,b,d,f,18c,d] Encapsulation of Eu(III) inside the cryptand cavity allows the drawback of the extremely low absorption coefficient of the uncomplexed metal to be overcome. Cryptands are capable not only of efficiently binding to the metal, but also of protecting it from the solvent, especially in aqueous solution where coordinated water is an efficient quencher of the emission. As discussed above, L contains a coordinative cleft as a potential binding site for metals. However, the most significant difference from previously reported cryptands, such as L1, is the presence of an aliphatic polyamine chain which can easily bind protons in aqueous solutions. In principle, these structural features make L an appropriate ligand for simultaneous Eu(III) and H^+ binding. Indeed, the diprotonated complex $[EuCl_3H_2L](ClO_4)_2{\cdot}4H_2O$ crystallizes from aqueous solutions at acidic pH values containing L and Eu(III). The crystal structure of this complex showed the metal encapsulated inside the ligand cavity (Figure 7) coordinated by the heteroaromatic nitrogens and the two benzylic N1 and N4 amine groups.[20] The methylated nitrogens N7, N8, and N9 are not coordinated, and bind two acidic protons. The Eu(III) completes its coordination environment by binding three chloride anions. Lodging of Eu(III) in the coordinating cleft delimited by the dipyridine units leaves free binding sites at the metal, available for the coordination of exogenous species, such as chloride anions in the $[EuCl_3H_2L](ClO_4)_2{\cdot}4H_2O$ solid complex. Water molecules may reasonably replace these anions in aqueous solutions in the absence of chloride.

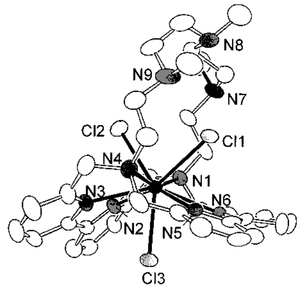

Figure 7. Crystal structure of the $[EuCl_3H_2L]^{2+}$ cation.

The luminescence spectrum of the Eu(III) cryptate in aqueous solution at pH 6.8, in the absence of chloride, shows the characteristic visible emission of the metal with a maximum at 617 nm, upon excitation at 306 nm. The emission from the metal upon excitation of the ligand was previously observed for many other Eu(III) cryptate complexes. The metal presents very low molar absorption coefficients, and thus the excitation light is almost exclusively absorbed by the ligand. The observed emission from Eu(III) can thus be explained by an intramolecular energy transfer to the metal ion mainly from the higher energy triplet state of the cryptand.

Keeping in mind that the three central nitrogen atoms of the polyamine chain show a high tendency to bind protons, we decided to study the influence of pH on the luminescence emission of the cryptate complex. Figure 8a gives the fluorescence emission spectra of the cryptate at different pH values, while Figure 8b gives the titration curve obtained by following the fluorescence emission at 617 nm.

Inspection of this figure shows that the intensity of the fluorescence emission exhibits a maximum at neutral pH, and undergoes a significant decrease at both acidic and alkaline pH values. pK_a values of 2.1, 4.2, 6.3, 8.7, and 10.5 for the Eu(III) complex were obtained by least-squares analysis of the titration

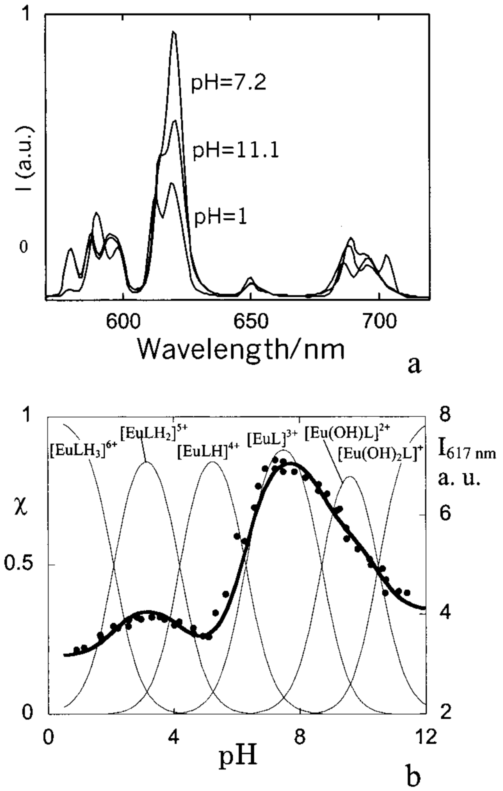

Figure 8. (a) Fluorescence emission spectra of the europium cryptate complex in aqueous solutions at pH 1, 7.2, and 11.1. (b) Luminescence emission (●) of the Eu(III) complex with L ($\lambda_{exc} = 260$ nm; $\lambda_{em} = 617$ nm, $[L] = [Eu^{3+}] = 5 \times 10^{-5}$ M, $T = 300$ K) and calculated molar fractions (χ) of the Eu(III) complexes (—) as a function of pH.

curve. The analysis of the coordination features of L toward alkali- and alkaline-earth-metal ions revealed that the triamine moiety N2′−N1−N2 is weakly involved in metal binding and can easily bind up to three protons in aqueous solutions. At the same time, the crystal structure of the Eu(III) complex shows that these three nitrogens do not bind to the metal. Therefore, it is reasonable that the first three constants correspond to protonation of the three not-coordinated amine groups of L to give the $[EuH_nL]^{(n+3)+}$ ($n = 1-3$) complexes at acidic pH values, while the last two may be attributed to the formation of the hydroxylated $[Eu(OH)L]^{2+}$ and $[Eu(OH)_2L]^+$ complexes at alkaline pH values. Protonation of the aliphatic polyamine chain N2′−N1−N2 prevents the interaction of the methylated amine groups with the metal. Therefore, the metal core is less protected from the solvent molecules. The free binding sites are occupied by water molecules, which can act as effective quenchers of the luminescence. This hypothesis is confirmed by the analysis of the lifetimes of the cryptate complex in water at neutral and acidic pH values, which are shown in Table 3 together with the corresponding emission quantum yields.

Applying the Horrocks and Sudnick equation[25] to the data in Table 3, it can be estimated that ca. two water molecules are coordinated to the metal at pH 2 and just one is coordinated at pH 6.8.[9] The increasing number of coordinated water molecules at acidic pH values leads to a decrease of the luminescence emission.

Finally, the observed decrease of the luminescence at alkaline pH values can be related to the formation of the hydroxylated complexes $[Eu(OH)L]^{2+}$ and $[Eu(OH)_2L]^+$. Binding of hydroxide anions to Eu(III), in fact, usually gives rise to a quenching of the emission.

Table 3. Lifetimes and Luminescence Quantum Yields of the Eu(III) Cryptate

	H_2O	D_2O	pH	methanol	*d*-methanol	pH
τ/ms[a]	0.52	1.34	6.8	0.80	1.20	neutral
τ/ms[b]				0.92	1.20	neutral
Φ[c]	0.014	0.051	6.8	0.0092	0.016	neutral
τ/ms[a]	0.45	1.25	3.5	0.73	0.94	3.5[d]
Φ[c]	0.012	0.035	3.5	0.0054	0.0072	3.5[d]
τ/ms[a]	0.39	1.40	2.0			2[d]

[a] 300 K. [b] 77 K. [c] 300 K, based on the total light absorbed by the cryptand. [d] Calculated on the basis of the concentration of added acid.

Table 4. Rate Constants of the Processes Involving the Luminescence of the Cryptate Complex with L at Neutral pH

	water	methanol
k_r/s^{-1}	746	833
$k_{nr}(T)$/s^{-1}	≅0	≅0
k_{nr}(OH)/s^{-1}	1177	417

Table 3 also reports the lifetimes and luminescence quantum yields of the Eu(III) cryptate complex in methanol. The measured lifetimes at 77 K and quantum yields allow some typical rate constants to be calculated, i.e., the radiative rate constant, the nonradiative temperature-independent rate constant due to the coupling with the high-energy O−H oscillators, and the temperature-dependent decay rate constant, both in water and in methanol, which are reported in Table 4.

It is of interest that the quantum yield in aqueous solution at pH 6.8 ($\Phi = 0.014$ at 300 K), the radiative rate constant ($k_r = 746$ s^{-1}), the nonradiative temperature-independent rate constant ($k_{nr}(OH) = 1177$ s^{-1}), and the temperature-dependent decay rate constant ($k_{nr}(T) \cong 0$) are similar to those reported for other dipyridyl-containing europium cryptates[17a,b,d,f,18c,d] and somewhat lower than those found for $[EuL1]^{3+}$,[26] as expected considering the replacement of a dipyridyl chromophore unit of L1 by an aliphatic polyamine chain in L. The present complex, therefore, still remains an efficient luminescent system but, at the same time, displays a peculiar feature, which is the pH dependence of the luminescence intensity, with a maximum at neutral pH.

The increase of the emission with the formation of the cryptate complex in aqueous solutions can be used to study the kinetics of complex formation. Only the Eu(III) complex, in fact, displays luminescence emission. In a typical experiment equimolecular solutions of L and Eu(III) were mixed (both 4×10^{-5} M). At 25 °C, the encapsulation is very slow and ca. one month is necessary to reach an emission plateau, i.e., to obtain the complete complexation of the metal. The rate of complex formation increases with the temperature; for instance, at 60 °C the Eu(III) complex is completely formed in ca. one day, as clearly shown in Figure 9. Fitting of the data points in Figure 9, according to second-order kinetics, furnishes the rate constant value ($k = 2.2 \times 10^{-4}$ M^{-1} min^{-1} at 60°). Interestingly, the rate constants are practically independent of the solution pH in the pH range 2−10, suggesting that the rigidity of the cryptand framework is not much affected by its protonation degree.

Measurements carried out at different temperatures (ΔT range 25−60 °C) allowed an activation energy for the Eu(III) complex formation of 92 kJ mol^{-1} to be calculated, by means of an

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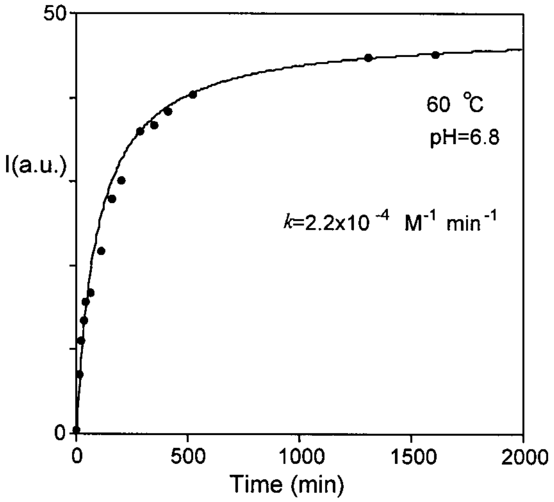
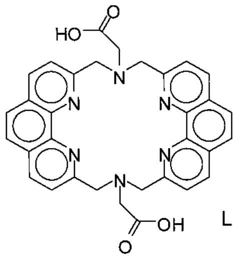


Figure 9. Time course luminescence emission at 617 nm (●) (λ_{exc} = 260 nm, [L] = [Eu^{3+}] = 4.55 × 10^{-5}, 60 °C, pH 6.8).

Chart 2



L2

Arrhenius plot. Previous examples of kinetic studies of Eu(III) complexation with dipyridine-containing macrocycles are rare. In the case of ligand L2 (Chart 2), however, Eu(III) complexation is much faster, the complete complexation occurring in 1 h at 22 °C.[27]

In our case the slowness of the process of complex formation is due to the macrobicyclic architecture of the ligand, together with the overall rigidity imposed by the two heteroaromatic units. By analogy with hemicarcerands,[28] it can be considered that in some way cryptand L possesses portals through which the europium could enter into the cavity. The large value of the activation energy may reflect the high energy barrier for the process of opening of the portals to permit the entry of europium inside the cavity. A mechanism involving the preliminary formation of an intermediate followed by a ligand rearrangement to give the final Eu(III) cryptate complex in the rate-determining step can also be proposed.

Concluding Remarks

Cryptand L contains two distinct binding moieties, a rigid coordinating cleft, delimited by the two dipyridine moieties, and a less rigid polyamine chain. The presence of a rather flexible aliphatic chain accounts for the lack of kinetic inertness in alkali- or alkaline-earth-metal complexation. This polyamine moiety displays weak coordination ability toward metals and, at the same time, a high tendency to protonate. The dipyridine-containing cleft is the preferred binding site for alkali- and alkaline-earth-metal ions as well as for Eu(III). The different binding features of the two moieties lead to the formation of protonated complexes in aqueous solutions. This strongly affects the photophysical properties of the Eu(III) complex, which displays a maximum of luminescence at neutral pH. Protonation of the polyamine chain at acidic pH values and formation of hydroxylated Eu(III) at alkaline pH values causes a decrease of the emission, originating a novel pH-modulated “antenna effect”.

Experimental Section

Synthesis. Ligand L was prepared as already described.[19]

General Procedure for the Synthesis of the Alkali- and Alkaline-Earth-Metal Complexes. A 10^{-2} M aqueous solution (5 cm^3) of $MClO_4$ (M = Li, Na, or K) or $M(ClO_4)_2$ (M = Mg, Ca, Sr, or Ba) was added to a 10^{-2} M solution of L·$5HClO_4$ in water (5 cm^{-3}). The pH of the solution was adjusted to 11 by addition of NMe_4OH (1 M). The resulting solution was extracted with chloroform (5 × 10 cm^3). Addition of cyclohexane led to precipitation of the L complexes as perchlorate salts ($[ML]ClO_4$ or $[ML](ClO_4)_2$) in 40−60% yield. A complete list of the characterization data (elemental analysis, ^1H NMR and ESI mass spectra) is reported in the Supporting Information.

$[EuCl_3LH_2](ClO_4)_2 \cdot 4H_2O$. A solution of $EuCl_3 \cdot 6H_2O$ (36.6 mg, 0.1 mmol) in water (10 cm^3) was added to an aqueous solution (10 cm^{-3}) of $[NaL]ClO_4$ (70 mg, 0.1 mmol). The pH was adjusted to 3 with 1 M HCl, and the resulting solution was heated at reflux over a period of 24 h. After the solution was cooled to room temperature, $NaClO_4$ (5 g) was added. By slow evaporation of the solution, crystals of the complex suitable for X-ray analysis were obtained. Anal. Calcd for $C_{35}Cl_5EuH_{55}N_9O_{12}$: C, 37.43; H, 4.94; N, 11.22. Found: C, 37.4; H, 4.9; N, 11.3.

NMR Measurements. ^1H (300.07 MHz) and ^{13}C (75.46) NMR spectra in D_2O solutions at different pH values were recorded at 298.1 K with a Varian Unity 300 MHz spectrometer. $^1H-^1H$ and $^1H-^{13}C$ 2D correlation experiments were performed to assign the signals. Small amounts of 0.01 mol dm^{-3} NaOD or DCl solution were added to a solution of L to adjust the pD. The pH was calculated from the measured pD value using the relationship pH = pD − 0.40.[29]

Potentiometric Measurements. Equilibrium constants for protonation and complexation reactions with L were determined by pH-metric measurements at 298.1 ± 0.1 K, by using equipment and a procedure[30] which have already been described. Ligand and metal ion concentrations of 1 × 10^{-3} to 2 × 10^{-3} mol dm^{-3} were employed in the potentiometric measurements, varying the metal to ligand molar ratio from 0.5:1 to 2:1. Three titration experiments (about 100 data points each) were performed in the pH range 2.5−10.5. The computer program HYPERQUAD[31] was used to calculate equilibrium constants from emf data.

Spectrophotometric and Spectrofluorimetric Titrations. Absorption spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer and fluorescence emission spectra on a SPEX F111 Fluorolog spectrofluorimeter. The $[EuL]^{3+}$ complex used in the spectrophotometric titrations was obtained in aqueous solution by addition of Eu(III) to L in aqueous solution (1:1 molar ratio, 60°, 20 h at pH 7). $HClO_4$ and HTBA were used to adjust the pH that was measured on a Metrohm 713 pH meter. The pK_a values of the Eu(III) complex were obtained from the spectrofluorimetric titration curve taking into account that the total emission intensity at each pH value is given by $\sum_i c_i \chi_i$, where c_i is a constant proportional to the quantum yield and χ_i the molar fraction of the *i*th species. The c_i and χ_i values were calculated by least-squares

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fitting of the emission data collected at different pH values.[32] The pK_a values were then derived from the calculated χ_i. The fitting was carried out by using the emission intensity at 617 nm with an excitation wavelength of 260 nm. Absolute quantum yields were calculated by least-squares fitting of the integrals of the emission spectra at each pH value, using the fluorescence emission of $[Ru(bpy)_3]^{2+}$ as reference.

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Supporting Information Available: Characterization data for alkali- and alkaline-earth-metal complexes with L. This material is available free of charge via the Internet at http://pubs.acs.org.

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