Solvent Effects on Thermodynamic and Electrochemical Parameters: Lanthanide Cryptates in Acetonitrile†

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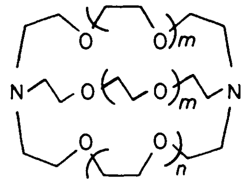
Complexation of the three reducible lanthanide(III) cations Sm^{3+}, Eu^{3+}, and Yb^{3+}, by the cryptands 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane [222 (L^1)], 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane [221 (L^2)], 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]icosane [211 (L^3)], and the related monocycle 1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane [22 (L^4)], has been investigated in acetonitrile, at different temperatures by a competitive potentiometric method with Ag^+ as auxiliary cation. The results show that the high stability of lanthanide(III) cryptates and of the corresponding complexes with L^4 is of enthalpic origin. The electrochemical behaviour of these cryptates and of the corresponding complexes of the crown ether 1,4,7,10,13,16-hexaoxacyclo-octadecane [18C6 (L^5)] has also been studied in the same solvent by polarography and cyclic voltammetry. The lanthanides(III) and their complexes are reduced in two well separated steps, except for L^3 cryptates. The $Eu^{3+/2+}$ couple and all $[LnL]^{3+/2+}$ couples behave reversibly. The effect of chloride anion has been studied and the formation of stable mixed-ligand complexes has been demonstrated. The differences between the redox potentials of the uncomplexed and of the complexed cations do not show a systematic stabilization of the bivalent cryptates with all ligands. Stabilities of europium(II) cryptates have been calculated from the latter values and from the stability constants of the corresponding trivalent cryptates. Predominance of solvent effects is evidenced for lanthanide(III) cryptates, whereas size effects are dominant for lanthanide(II) complexes as demonstrated by an important macrobicyclic effect.

The increasing importance of lanthanides in many industrial fields and their potential applications as sensors in biological systems imply the specific production of these elements and the constant improvement of separation processes. In this context it is not surprising that the physicochemical properties of lanthanide cations and of their complexes, especially cryptates, have been intensively investigated during the last decade both in the solid state and in solution.[1,2]

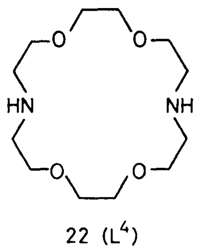
The search for complexation selectivities in the lanthanide series and for stabilization of unstable oxidation states has been the main concern of several studies in different solvents.[3–14] Our previous works in water,[7] methanol,[7] and *N*,*N*-dimethylformamide (dmf)[12] have shown that the bivalent oxidation states of samarium, europium, and ytterbium are stabilized by complexation with cryptands. As this stabilization was not systematically observed in propylene carbonate,[11] these studies were extended to acetonitrile, a solvent of solvating properties close to those of propylene carbonate.

The present paper reports the thermodynamic and electrochemical behaviour of the three reducible lanthanide(III) cations samarium, europium, and ytterbium, and of their complexes with cryptands 222 (L^1), 221 (L^2), and 211 (L^3) and the related monocycle 22 (L^4). The study was also extended for comparison purposes to the crown ether 18C6 (L^5), which has the same size and the same number of heteroatoms as L^4.

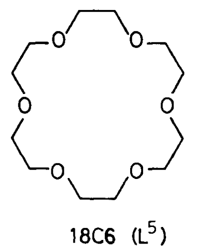
Up to now only scarce and contradictory electrochemical results were available in acetonitrile.[13,14] Our work, which settles the electrochemical behaviour of lanthanide cryptates in this solvent and emphasizes the effects of water and chloride anions, enables the determination of the stability of both tri- and bi-valent forms of these complexes in acetonitrile for the first time. The results provide us with more information in order to interpret solvent and size effects upon the stabilization



222 $m = n = 1$ (L^1)
221 $m = 1, n = 0$ (L^2)
211 $m = 0, n = 1$ (L^3)



22 (L^4)



18C6 (L^5)

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† *Non-S.I. unit employed:* cal = 4.184 J.

Table 1. Stability of trivalent lanthanide cryptates in acetonitrile at 25 °C and $I = 0.1$ mol dm^{-3} (NEt_4ClO_4); values are log $\beta \pm 2\sigma_{n-1}$, where σ_{n-1} = standard deviation on the arithmetic mean of n experiments ($2 \leqslant n \leqslant 5$)

Cation	L^1	L^2	L^3	L^4
Sm^{3+}	11.0 ± 0.1	11.6 ± 0.1	9.8 ± 0.2	9.9 ± 0.2
	(10.9 ± 0.1)[a]			
Eu^{3+}	11.4 ± 0.2	11.3 ± 0.1	9.1 ± 0.2	9.7 ± 0.2
	(10.9 ± 0.1)[a]			
Yb^{3+}	10.6 ± 0.2	11.6 ± 0.1	9.5 ± 0.2	⩾10.6
	(10.8 ± 0.1)[a]			
Ag^+	8.9	11.1	7.6	7.6
	8.9—9.3[b]	11.2[b]	7.7—7.8	

[a] Determined from a competition with K^+, log β for $[KL^1]^+ = 11.4$. [b] From ref. 19.

Table 2. Thermodynamic parameters[a] for the complexation of Ln^{3+} and Ag^+ by some mono- and bi-cyclic ligands

Cation		L^1	L^3	L^4
Sm^{3+}	$-\Delta G$	15.0 ± 0.3	13.4 ± 0.4	13.5 ± 0.3
	$-\Delta H$	25 ± 5	12 ± 3	25 ± 2
	ΔS	−33 ± 17	3 ± 10	−39 ± 5
Eu^{3+}	$-\Delta G$	15.5 ± 0.1	12.4 ± 0.4	13.5 ± 0.3
	$-\Delta H$	24 ± 6	6 ± 2	26 ± 1
	ΔS	−26 ± 20	21 ± 6	−42 ± 4
Yb^{3+}	$-\Delta G$	14.4 ± 0.1	13.0 ± 0.4	⩾14.5
	$-\Delta H$	24 ± 5	2.8 ± 4	
	ΔS	−32 ± 16	34 ± 1	
Ag^+	$-\Delta G$	12.1 ± 0.1	10.5 ± 0.1	10.4 ± 0.1
	$-\Delta H$	12 ± 2[b]	8.6 ± 0.1	21 ± 0.1
	ΔS	0.2 ± 5	6 ± 1	−34 ± 4

[a] ΔG and ΔH are expressed in kcal mol^{-1}, ΔS in cal K^{-1} mol^{-1}. Precision: 95% confidence interval (±2σ). [b] $\Delta H = -12.78$ kcal mol^{-1} from calorimetric measurements.[20]

of low oxidation states of lanthanides and upon the stability of tri- and bi-valent lanthanide cryptates.

Experimental

Thermodynamic and electrochemical measurements were carried out in anhydrous acetonitrile. The solvent (Merck, Uvasol) was dried over molecular sieves (4 Å) and stored under argon.

The ligands L^1—L^4 (Kryptofix Merck) and the crown ether L^5 (Aldrich) were used as provided.

The lanthanide(III) trifluoromethanesulphonates (triflates) were prepared according to the procedure described by Massaux and Duyckaerts[15] and dried under vacuum at 60 °C for 24 h. The other metallic salts were lanthanide(III) chlorides (Strem Chemicals), $AgClO_4 \cdot H_2O$ (Fluka), and $KClO_4$ (Merck) which were all dried under vacuum and stored under argon.

The synthesis of lanthanide(III) cryptates with chloride or triflate as anion was previously described.[11,16]

Tetraethylammonium perchlorate (Fluka), used as supporting electrolyte, and tetraethylammonium chloride (Fluka), used as chloride source, were recrystallized in methanol[17] and dried under vacuum.

Electrochemical measurements were performed with a multipurpose PRG4 device (Solea Tacussel), at a dropping mercury electrode ($m = 2.015$ mg s^{-1}, $h = 40$ cm). The reference electrode was a saturated calomel electrode (s.c.e.) electrically connected to the electrolysis cell by a bridge filled with 0.1 mol dm^{-3} NEt_4ClO_4 in acetonitrite and the auxiliary electrode was a platinum wire. Cyclic voltammetry at low sweep rates at a hanging mercury drop electrode was performed with a computerized electrochemical device, Dacfamov (Microtec-CNRS, Toulouse, France) connected to an APPLE II computer.

The stability of trivalent lanthanide cryptates (log β or ΔG) was determined by potentiometry at 25 °C. Competitive experiments involving Ag^+ cation were carried out, as previously described.[9] Silver-rod electrodes (Metrohm) connected to a Tacussel Isis 20 000 millivolt meter were used as measuring and reference electrodes. Similar experiments were also performed at 20, 30, and 35 °C. Measurements were numerically treated by the program MINIQUAD[18] after determination of the stability constants of the corresponding silver cryptates[8] by direct potentiometry under the same experimental conditions. Stability constants relative to L^1 cryptates were checked by an alternative method involving K^+ as auxiliary cation, as these complexes and $[KL^1]^+$ have similar stabilities. In this case the measuring electrode was a K^+-selective glass electrode (Tacussel) and the value of β for $[KL^1]^+$ was determined by competition with Ag^+.

Values of the enthalpies (ΔH) and entropies (ΔS) of complexation were obtained from the temperature dependence of ΔG, respectively as the slope and the intercept of the least-squares linear plot log $\beta = f(1/T)$.

Results and Discussion

Stability of Trivalent Lanthanide Cryptates in Acetonitrile.— Stability constants of the 1:1 lanthanide(III) complexes are given in Table 1 together with those of Ag^+ necessary for the computation. The latter are in good agreement with those previously determined by Cox *et al.*[19] The low stability of $[AgL^5]^+$ (log $\beta < 2$) precluded the determination of the stability of the L^5 complexes. Values relative to L^1 cryptates, determined by two different competitive methods involving Ag^+ and K^+ (in parentheses), are in good agreement.

The results indicate that cryptands form very stable complexes with lanthanide(III) cations. Nevertheless no particular ion selectivity is observed with any of the ligands. On the other hand, for a given cation the stability order falls in the sequence $[LnL^2]^{3+} \geqslant [LnL^1]^{3+} > [LnL^4]^{3+} > [LnL^3]^{3+}$. The higher stability of L^2 cryptates could be due to the fact that the size of the L^2 cavity is best adapted for lanthanide cations. However the differences in stability between these complexes are low as illustrated by a very small macrobicyclic effect, between 1 and 1.5 log units from L^4 to L^1 complexes.

Table 2 gives the thermodynamic parameters ΔH and ΔS for the complexation of Ln^{III} and Ag^+ with L^1, L^3, and L^4, obtained from the temperature dependence of ΔG. Though less precise than calorimetry, this method leads nevertheless to reliable results as shown by the agreement between our value of ΔH for the formation of $[AgL^1]^+$ and the literature data (−12.78 kcal mol^{-1}) derived from calorimetric measurements.[20] Values of ΔH and ΔS for L^1 cryptates of samarium, europium, and ytterbium are of the same order of magnitude as those found for the corresponding complexes with lanthanum, praseodynium, and neodymium by calorimetry.[21] However the 'temperature dependence' method failed in the case of L^2 cryptates as no reliable results could be obtained.

The results confirm that lanthanide(III) cryptates are all enthalpically stabilized ($\Delta H < 0$) in acetonitrile, whereas the entropic term can be favourable or unfavourable according to the ligand: $\Delta S > 0$ with L^3 and <0 with both L^1 and L^4. Similar conclusions had been drawn previously in propylene carbonate.[8,9,21] The ΔH values are almost constant with L^1 and L^4 and the three lanthanides, whereas they are much lower with L^3 while decreasing from Sm^{3+} to Yb^{3+}. It is more difficult to describe a specific trend for ΔS because of the poor precision of these values: the negative values observed for L^1 and L^4

Table 3. Polarographic results of the reduction of Eu^{3+}, Sm^{3+}, and Yb^{3+} and their complexes in acetonitrile, $I = 0.1$ mol dm^{-3} (NEt_4ClO_4); irr. = irreversible

Compound	$E_{\frac{1}{2}}(La^{3+}$-$La^{2+})$/ V *vs.* s.c.e.	log $[I/(I_d - I)]$ (slope in mV)	$E_{p_c} - E_{p_a}$/ mv at 5 V s^{-1}	$\frac{1}{2}(E_{p_c} + E_{p_a})$/ V *vs.* s.c.e.	$E_{\frac{1}{2}}(La^{2+} - La^0)$/ V *vs.* s.c.e.
$Sm(CF_3SO_3)_3$	-1.04	73	irr.	irr.	-1.65
$[SmL^5][CF_3SO_3]_3$	-1.05	60	60	-1.02	-2.11
$[SmL^1][CF_3SO_3]_3$	-1.12	64	90	-1.08	
$[SmL^2][CF_3SO_3]_3$	-1.27	55	80	-1.25	
$[SmL^4][CF_3SO_3]_3$	-1.40	82	90	-1.38	-2.30
$[SmL^5]Cl_3$	-1.45	60	60	-1.45	-2.15
$[SmL^1]Cl_3$	-1.38	87	70	-1.36	
$[SmL^2]Cl_3$	-1.56		100	-1.56	
$[SmL^4]Cl_3$	-1.65	90	110	-1.64	-2.30
$Eu(CF_3SO_3)_3$	$+0.12$	62	130	$+0.13$	-1.75
$[EuL^5][CF_3SO_3]_3$	$+0.18$	57	110	$+0.21$	-2.11
$[EuL^1][CF_3SO_3]_3$	$+0.16$	59	60	$+0.18$	
$[EuL^2][CF_3SO_3]_3$	$+0.04$	57	60	-0.05	-1.90
$[EuL^4][CF_3SO_3]_3$	-0.20	60	100	-0.16	
$Yb(CF_3SO_3)_3$	-0.59	79	irr.	irr.	-1.75
$[YbL^5][CF_3SO_3]_3$	-0.50	65	70	-0.50	-2.14

complexes have been explained by a partial desolvation of the cation prior to complexation, the cavity of L^1 being large enough to accept the cation with some solvent molecules attached.[21] This would not be possible with the smaller L^3 ligand and complete desolvation should be necessary in this case leading to the observed positive entropic changes.

The results also show that the small macrobicyclic effect observed is only due to a less unfavourable entropic term, ΔS for L^1 cryptates being less negative than for L^4 complexes.

Electrochemical Behaviour in Acetonitrile.—Reduction of the lanthanide(III) *triflates.* The polarographic reduction of Sm^{3+}, Eu^{3+}, and Yb^{3+} occurred in two consecutive well defined diffusional waves. Nevertheless the second reduction wave of samarium was slightly perturbed by adsorption. The first reduction step is monoelectronic as checked by potentiostatic coulometry. The wave heights are in 1:2 ratio and proportional to the concentration of the metal salt over the range 10^{-4}—2×10^{-3} mol dm^{-3}. The diffusional nature of the corresponding limiting currents was checked using a chronoamperometric criterion developed for this purpose.[22] The logarithmic analysis of the different waves was done by plotting log $(I/I_d - I)$ *vs.* E. The resulting values as well as the main characteristics of the reduction processes, summarized in Table 3, are in good agreement with previous studies.[13,14,23]

By cyclic voltammetry only the first reduction of Eu^{3+} to Eu^{2+} is a quasi-reversible redox couple. Samarium and ytterbium behave as irreversible couples as the peak separation for the $Ln^{3+/2+}$ couple is rather high: the reduction peak of Yb^{3+} and the oxidation peak of the generated Yb^{2+} appeared at -0.93 and -0.55 V *vs.* s.c.e. (respectively at -1.21 and -0.84 V *vs.* s.c.e. for samarium).

Reduction of $[LnL^5]^{3+}$ *complexes in anhydrous acetonitrile.* In order to study the complexation of Ln^{3+} cations by L^5, increasing amounts of L^5 were added to solutions of the metal salts ($c_M = 10^{-3}$ mol dm^{-3}). As a similar behaviour was observed for the three cations, the case of ytterbium(III) will be described in detail. For different values of r ranging from 0.2 to 4.0 ($r = c_L/c_M$) the first reduction wave of Yb^{3+} at -0.59 V *vs.* s.c.e. was shifted to a more positive potential while keeping the same height, whereas the second reduction wave at -1.75 V *vs.* s.c.e. decreased with increasing r and disappeared as soon as $r > 1$. At the same time a new wave appeared at -2.14 V *vs.* s.c.e. the amplitude of which increased until $r = 1$. The corresponding half-wave potential was concentration independent and the limiting current was constant as soon as $r > 1$. This behaviour is typical of the formation of a stable 1:1 complex between L^5 and Yb^{3+}.

For $r > 1$, two well defined reduction waves were observed with heights in a 1:2 ratio and the corresponding limiting currents were diffusion controlled. These two steps correspond to the successive reduction of $[LnL^5]^{3+}$ to $[LnL^5]^{2+}$ and to the reduction of $[LnL^5]^{2+}$ to Ln^0 and the free ligand. The main characteristics of the reduction of the L^5 complexes are summarized in Table 3.

Unlike the redox behaviour of the uncomplexed lanthanides, the first reduction steps of these complexes are all approximately reversible as shown by the slope of the log plot and by cyclic voltammetry giving a peak potential separation $\Delta E = E_{p_c} - E_{p_a}$ close to 60 mV for samarium and ytterbium and equal to 110 mV for europium, at 5 V s^{-1}. Identical results were obtained when solid complexes $[LnL^5][CF_3SO_3]_3$ were employed as solutes.

The dissolution of $[SmL^5]Cl_3$ led also to two well defined reduction waves. The first step occurred at a more negative potential ($E_{\frac{1}{2}} = -1.45$ *vs.* s.c.e.) than for the complex with triflate as an anion ($E_{\frac{1}{2}} = -1.05$ V) whereas the second one remained unchanged. This potential shift shows a strong interaction between Sm^{3+} in the complex and chloride anions.

For $[YbL^5]Cl_3$ three reduction waves appeared after dissolution of the salt. In order to explain this peculiar behaviour, increasing amounts of tetraethylammonium chloride were added to a solution of $[YbL^5][CF_3SO_3]_3$: three waves were definitely observed for three-fold excess of chloride with respect to the complex, at the same potential as after dissolution of $[YbL^5]Cl_3$, and only two waves for larger chloride excess (higher than ten-fold) (Figure 1). Under these conditions the reduction potential for the first wave was shifted to more negative potentials as shown by the linear plot $E_{\frac{1}{2}} = f(\log c_{Cl})$ (Figure 1). The corresponding slope of 128 mV is consistent with a variation $p - q$ of the chloride co-ordination from the oxidized to the reduced complex equal to 2, according to the Stackelberg equation[24,*]. As the second reduction wave at -2.2 V *vs.* s.c.e. was not well defined for an excess of chloride, it was not possible to state if there was any chloride co-ordination with Yb^{2+}. However the fact that two waves corresponding to the

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[*] The Stackelberg equation was applied to the reduction $[Ln^{III}LCl_p] + e \rightleftharpoons [Ln^{II}LCl_q] - (p - q)Cl$, where the charge of chloride is omitted for clarity. The relationship has the form: $\Delta E_{\frac{1}{2}} = 0.059 \log (\beta_{red}/\beta_{ox}) - (p - q)0.059 \log c_{Cl}$ where β denote the stability constants.

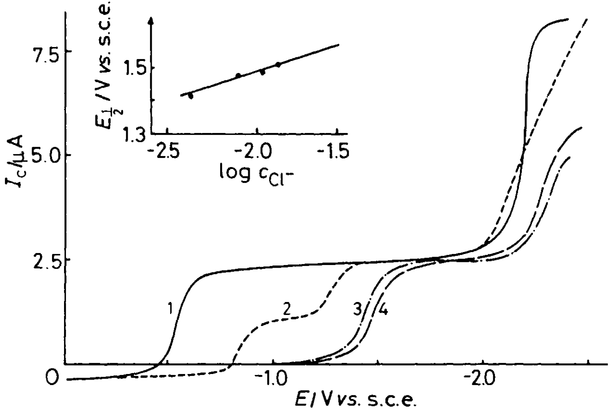

Figure 1. Polarograms of $[YbL^5][CF_3SO_3]_3$ (8.3×10^{-4} mol dm^{-3}) in the presence of variable amounts of chloride; $I = 0.1$ mol dm^{-3} (NEt_4ClO_4). $c_{Cl}/c_{Yb^{3+}} = 0$ (curve 1), 3 (2), 10 (3), and 20 (4)

Table 4. Effect of chloride anion upon the reduction potential of samarium(III) complexes in acetonitrile. Slopes of the lines $E_{\frac{1}{2}} = f(\log c_{Cl})$, corresponding $(p - q)$ and log β values ($\beta = [SmLCl_p]/[SmL][Cl]^p$)

Complex	Slope (mV)	$p - q$	log β
$[SmL^1]^{3+}$	−70	1	7.9
$[SmL^2]^{3+}$	−120	2	9.7
$[SmL^4]^{3+}$	−130	2	11.7

reduction of Yb^{3+} to Yb^{2+} were observed at lower chloride concentrations may be explained by assuming the presence of mixed-ligand complexes $[YbL^5Cl_n]$ of different stoicheiometries. A defined stoicheiometry was observed only for a large excess which was higher or equal to two-fold.

Reduction of the lanthanide(III) *cryptates.* Unlike with L^5, the *in situ* complexation of Ln^{3+} by cryptands L^1, L^2, and L^4 led to ill defined reduction waves. The redox behaviour was thus studied after dissolution of the solid cryptates. Two points should be noted: (*i*) the reduction curves of ytterbium(III) complexes and of all L^3 complexes were not interpretable; (*ii*) the study of europium complexes with chloride as an anion was impossible because reduction took place at about the same potential as the oxidation of the chloride anion at mercury.

The polarographic reduction of $[EuL][CF_3SO_3]_3$, $[SmL][CF_3SO_3]_3$, and $[SmL]Cl_3$ ($L = L^1, L^2$, or L^4) gave rise to two separate well defined reduction waves in a 1:2 ratio, corresponding to the reduction of complexed Ln^{3+} to complexed Ln^{2+}, followed by the two-electron reduction of the reduced complex to metal and free ligand. Cyclic voltammetry showed that the first reduction step was a reversible or a quasi-reversible reduction. The main characteristics are summarized in Table 3. From these results it is clear that the first reduction step of the complexes with chloride anions occurs at more negative potentials, about 250 mV, indicating a strong interaction between chloride anions and the complex $[LnL]^{3+}$. In order to explain this behaviour we studied the effect of increasing amounts of chloride anion on the redox behaviour of samarium(III) cryptates.

Addition of tetraethylammonium chloride to solutions of the complexes $[SmL][CF_3SO_3]_3$ shifted the first reduction wave of the complexes to more negative potentials. For a chloride:complex ratio of 3:1 the reduction of Sm^{3+} to Sm^{2+} was observed at the same potential as after the dissolution of the solid $[SmL]Cl_3$ complexes, confirming a strong interaction between the metal cation and the chloride anion. For a chloride:complex ratio ranging from 3 to 10:1 the potential was found to vary linearly with log c_{Cl}. According to the Stackelberg equation[24] it was then possible to determine the change in the number, $p - q$, of the chloride anion co-ordinated during the reduction of Sm^{3+} to Sm^{2+} from the slope of $E_{\frac{1}{2}} = f(c_{Cl})$. It was also possible to obtain the stability constant of the mixed-ligand complex (Table 4) corresponding to the equilibrium $[SmL]^{3+} + nCl \rightleftharpoons SmLCl_n^{(3-n)+}$. As the reduction wave of the complexed Sm^{2+} was not affected by the chloride concentration, it could be assumed that no chloride anion was co-ordinated to the reduced complex. The rather high values of the stability constants demonstrate the existence of stable mixed-ligand complexes in acetonitrile. The results emphasize the importance of the nature of the anions present in solution: small complexing anions such as Cl^-, F^-, or OH^- can interact strongly with lanthanide cryptates as already shown in other solvents such as water,[4] dimethyl sulphoxide (dmso),[8] and propylene carbonate.[11]

Effect of water content on the redox potentials of Ln^{3+} *and their complexes.* It was observed during this work that the redox potentials were very sensitive to the presence of water in acetonitrile. Thus, half-wave potentials of the complexed and uncomplexed cations were measured by polarography as a function of the water concentration. The addition of increasing amounts of water to solutions of lanthanide triflates in acetonitrile shifted the reduction waves towards more negative potentials without any change in their shape. The slope of the linear variation log $I/(I_d - I)$ *vs.* potential was independent of the water concentration. A plot of $E_{\frac{1}{2}}$ *vs.* log c_{water} is linear: the slopes depend on the salt and are much higher for uncomplexed lanthanides than for complexed ones (Figure 2). This result shows that the complexed lanthanide cation is more or less shielded against hydration by complexation. As was previously concluded in propylene carbonate, the water content must also be controlled when working in acetonitrile.

Stability of Lanthanide(II) *Cryptates in Acetonitrile.*—Stability constants of lanthanide(II) complexes in acetonitrile could be easily determined from those of the corresponding lanthanide(III) complexes (Table 1) and their redox potentials (Table 3), using Stackelberg's relationship applied to the reduction $[LnL_p]^{n+} + (n - m)e \rightleftharpoons [LnL_q]^{m+} + (p - q)L$. As in the present case there is no change in the stoicheiometry of the reduced and oxidized species, *i.e.* $p - q = 0$, this relationship is finally reduced to $\Delta E_{\frac{1}{2}} = [0.059/(n - m)] \log(\beta_{red}/\beta_{ox})$ where $\Delta E_{\frac{1}{2}} = E^c_{\frac{1}{2}} - E^{Ln}_{\frac{1}{2}}$, β_{red} and β_{ox} are the stability constants of the cryptates of Ln^{II} and Ln^{III} respectively, and $E^c_{\frac{1}{2}}$ and $E^{Ln}_{\frac{1}{2}}$ the half-wave potentials of the complexed and uncomplexed cations. In the present case, only the stability constants of europium(II) complexes could be calculated as the couple $Eu^{3+/2+}$ is the only reversible one (Table 5). Values of log (β_{red}/β_{ox}) could also be calculated from redox potentials observed by Tabib *et al.*[13] for $[EuL^1]^{3+/2+}$ and $[EuL^2]^{3+/2+}$ and were found equal to −0.11 and −3.0 respectively. These results are different from ours but are however in better agreement than the values calculated from Bessière *et al.*[14] which show a very strong stabilization of $[EuL^1]^{2+}$ [$\log(\beta_{red}/\beta_{ox}) = 5$].

The results show a good ligand specificity for lanthanide(II) cations in contrast to trivalent ones. This, in particular, leads to an important bicyclic effect as the difference in stability between L^1 and L^4 complexes amounts to 7.9 log units.

Solvent Effects on the Redox Behaviour.—No anodic redox potential shift of the complexed $Ln^{3+/2+}$ couple with respect to the uncomplexed one is observed in acetonitrile except for L^5 and L^1 complexes. This result indicates that the stabilization of Ln^{2+} complexes, observed in water, MeOH, and dmf is not systematic in acetonitrile, as already found in propylene carbonate.[10] In order to interpret this behaviour, the formal

Table 5. Stability of europium(II) complexes in acetonitrile: values of log (β_{red}/β_{ox}) derived from voltamperometric data (Table 3) and of log β (95% confidence interval on log β within 0.4 and 0.5)

	Ligand			
	L^1	L^2	L^4	L^5
log (β_{red}/β_{ox})	1.5 -0.11^a 5^b	-2.0 -3.0^a	-4.1	2.0
log $\beta(EuL^{2+})$	12.9	9.3	5.0	

[a] From ref. 13. [b] From ref. 14.

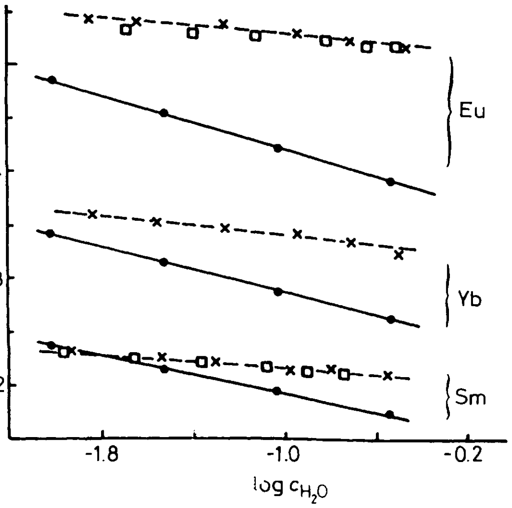

Figure 2. Effect of the water content upon the half-wave potentials of $Ln^{3+/2+}$ (●) and $[LnL]^{3+/2+}$ couples (□, L^1; ×, L^5)

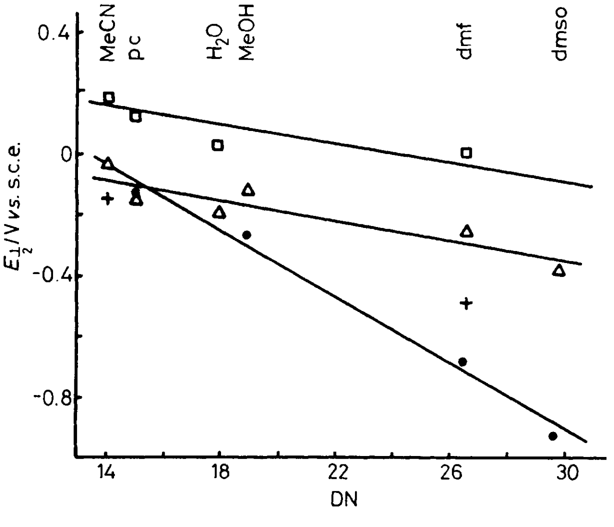

Figure 3. Redox potentials of $Eu^{3+/2+}$ (●) and $[EuL]^{3+/2+}$ couples in different solvents as a function of the donor number DN: □, L^1; △, L^2; +, L^4; pc = propylene carbonate

redox potentials of the complexed and uncomplexed $Ln^{3+/2+}$ couples in various solvents were plotted *vs.* Gutmann's donor numbers (DN) of the solvents.[25] The lack of information and/or reversibility of some couples, for instance ytterbium and samarium, limited the discussion to the europium systems (Figure 3). For the uncomplexed $Eu^{3+/2+}$ couple the linear variation of the redox potential with DN is in agreement with previous conclusions of Gutmann and Peychal-Heiling[26] and Tabib *et al.*[13] For L^1 and L^2 cryptates, parallel straight lines are observed, the slope of which is lower than for the uncomplexed cation. As this slope difference may be related to solvent-shielding effects by cryptation, the respective positions of these lines indicate that cryptation does not lead to a systematic stabilization of the bivalent oxidation state of lanthanide cations. The corresponding line for the L^1 europium complex lies above that for Eu^{3+} indicating stabilization of Eu^{2+} in all the solvents investigated. In contrast, the two lines intersect for the L^2 complex, thus confirming that stabilization of Eu^{2+} by cryptation takes place only in strongly solvating solvents (DN > 18). The same conclusion holds for L^4, as Eu^{2+} is stabilized by this ligand in dmf and destabilized in acetonitrile.

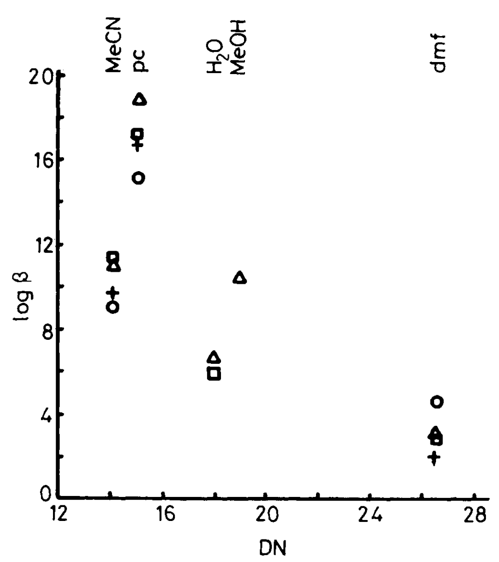

Figure 4. Stability of trivalent europium cryptates in different solvents: log β as a function of DN: □, L^1; △, L^2; ○, L^3; +, L^4

For samarium, the same evolution and conclusion can be drawn despite fewer values available.

Solvent and Size Effects on the Stability of Lanthanide-(II) *and -*(III) *Cryptates.*—Comparison of the present results in acetonitrile to other previous results in various solvents shows that the stability of trivalent lanthanide cryptates increases along the sequence dmf < dmso < H_2O < MeOH < MeCN ≪ propylene carbonate, which is nearly in agreement with the solvating properties of the solvents expressed as their Gutmann donor numbers.[25] For instance the difference in stability of the complexes in two very different solvents such as acetonitrile and dmf lies roughly between 5 and 8 log units; it is even higher from dmf to propylene carbonate (about 10—17 log units). However it can be clearly seen in Figure 4 relative to europium cryptates, given as an example, that the stability constants of lanthanide(III) cryptates in propylene carbonate are higher than those expected from the DN value of this solvent. This observation is in agreement with the conclusions of a recent calorimetric investigation, which shows that the higher stability of lanthanide cryptates in propylene carbonate is only due to a favourable entropic contribution resulting from a more important release of solvent molecules.[21]

On the other hand, comparing the stability of the different cryptates in a given solvent, L^2 forms the most stable complexes in poor solvating media (DN < 18) whereas the strongest complexes of L^3 are observed in strongly solvating ones (DN > 18). In intermediate media such as water, all cryptates have about the same stability. Despite the difficulty in estimating the ionic radii of trivalent cations because of their

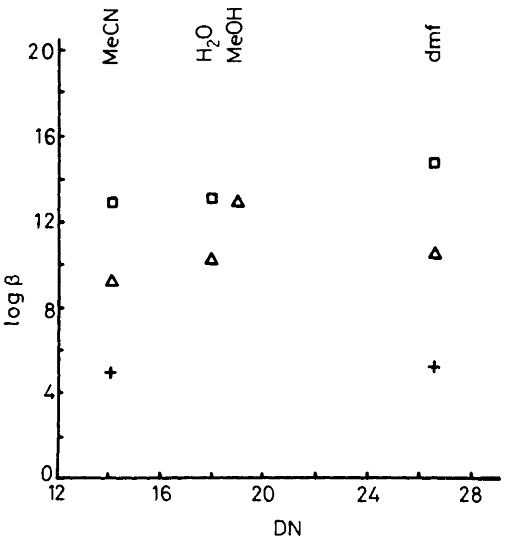

Figure 5. Stability of bivalent europium cryptates in different solvents: log β as a function of DN: □, L^1; △, L^2; +, L^4

variation with co-ordination number, it is quite clear that these results cannot be interpreted in terms of size effects only. They emphasize the role of the solvent on the stability of trivalent lanthanide cryptates. Strong interactions can take place between these highly charged cations and solvating solvents. Even with less solvating ones like propylene carbonate and acetonitrile, the cation interacts with the solvent as demonstrated by the equality of the enthalpy of transfer from propylene carbonate to acetonitrile of the uncomplexed cations and of the cryptates.[21]

By contrast, the stabilities of divalent lanthanide complexes are solvent independent: this is clearly shown by the plot log β *vs.* DN in the case of europium(II) (Figure 5). Similar trends could be obtained in the case of samarium and ytterbium despite fewer available values. This levelling effect can be explained by the shielding of the cation by the ligand. On the other hand, Sr^{2+}, which is often compared to Eu^{3+} on the basis of size considerations (the ionic radius of both cations is about 1.13 Å), forms cryptates of which the stability varies with the solvating properties of the solvents.[27] The main difference between the alkaline-earth-metal and lanthanide(II) complexes is the existence of a certain degree of covalency in the bonding of the latter. This factor could perhaps be invoked in the explanation of this levelling effect.

Our results show that the stability of trivalent lanthanide cryptates is mainly governed by charge effects, whereas predominant factors for bivalent lanthanide cryptates are size effects as demonstrated by the high macrobicyclic effect evidenced when going from L^4 to L^1.

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