Thermodynamic and Electrochemical Behaviour of Lanthanide Cryptates in *N,N*-Dimethylformamide

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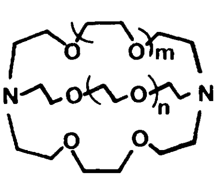
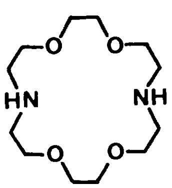
The stability of 222 (L^1), 221 (L^2), and 211 (L^3) cryptates of samarium(III), europium(III), and ytterbium(III) and the corresponding complexes with the related monocycle, 22 (L^4) have been determined in *N,N*-dimethylformamide by potentiometry using a competitive method with auxiliary alkali cations. Their electrochemical behaviour has also been investigated in the same solvent by polarography and cyclic voltammetry. The results clearly show the low stability of the trivalent cryptates. The electrochemical study of Ln^{3+} ions with increasing amounts of ligand shows two different behaviours: (*i*) with L^3, Ln^{3+} ions are complexed as shown by the decrease of the reduction waves of Ln^{3+} but no stabilization of Ln^{2+} ions is observed; (*ii*) with L^1, L^2, and L^4 the height of the reduction wave of Ln^{3+} is not affected by the ligand concentration and the reduction occurs according to the scheme: $Ln^{3+} + e^- \rightleftharpoons Ln^{2+} + L \longrightarrow [Ln(L)]^{2+}$. The differences δ between the redox potentials of the free and the complexed lanthanide(III) cations show an important stabilization of the divalent cryptates. Their stability constants have been calculated from the values of δ and the stability constants of the trivalent complexes. While no particular ligand or cation selectivity is observed for the trivalent cryptates, this is not so for the reduced lanthanides which form the strongest complexes with L^1. The results are interpreted by size and solvation considerations.

Lanthanide cryptates have been the subject of great interest during the past decade; their physicochemical properties have been intensively investigated, both in the solid state and in solution.[1,2] In particular, their inclusive nature has been shown by *X*-ray crystallography[3–5] and the luminescence properties of Eu^{3+} and Tb^{3+} cryptates have been studied.[1,6] The thermodynamic and electrochemical properties of some of these cryptates have also been investigated in various solvents.[7–18] The present paper reports the stabilities of some lanthanide cryptates in *N,N*-dimethylformamide (dmf), following our recent studies with methanol (MeOH)[11] and propylene carbonate (pc)[11,14,15] as solvents. Our results are the first to be obtained in dmf on the complexation of the three lanthanide(III) cations, Sm^{3+}, Eu^{3+}, and Yb^{3+}, by the three cryptands 222 (L^1), 221 (L^2), and 211 (L^3), and the related monocycle 22 (L^4).



222: m = n = 1 (L^1)
221: m = 1; n = 0 (L^2)
211: m = n = 0 (L^3)



22 (L^4)

Their electrochemical behaviour has also been investigated in dmf in order to provide evidence for the possible stabilization of the lanthanide(II) cations upon complexation, as already observed in water and methanol.[9,11] Our results are compared to some partial results in the same solvent, mainly devoted to Eu^{3+} and L^1, which were published by other authors during our present work.[16–18] Moreover, a reduction mechanism for lanthanide(III) cations in the presence of cryptands is also proposed. The measured redox potentials of the uncomplexed lanthanide cations and of the cryptates, and the stability constants determined for the lanthanide(III) cryptates allowed us to calculate the stability constants of the corresponding lanthanide(II) cryptates. Stability of lanthanide(III) and lanthanide(II) cryptates is discussed in terms of relative sizes of ligands and cations and solvent effects.

Experimental

The solvent dimethylformamide (dmf) (Fluka) was purified by the method previously described.[19]

The ligands L^1, L^2, L^3, and L^4 (Kryptofix, Merck) were used as provided.

The lanthanide(III) trifluoromethanesulphonates (Ln^{3+} = Sm^{3+}, Eu^{3+}, and Yb^{3+}) were prepared according to the procedure described by Massaux and Duyckaerts[20] and dried under vacuum at 60 °C for 24 h. The other metallic salts were $Na(ClO_4)$ and $K(ClO_4)$ (Merck) and $Ag(ClO_4)\cdot H_2O$ (Fluka) which were all dried under vacuum at 100 °C and 40 °C respectively.

A new method was used for the preparation of the lanthanide(III) cryptates, with trifluoromethanesulphonate (triflate) as anion, as follows. A solution of ligand (1.1 mmol) in acetonitrile (10 cm^3) was added to a solution of lanthanide triflate (1 mmol) in methanol (10 cm^3) previously dried using trimethylorthoformate (Jansen Chemical) as previously described.[9] The mixture was refluxed for 0.5 h at 40 °C. The white crystals which precipitated were filtered off and washed with hexane and dichloromethane and dried under vacuum at 40 °C for 48 h. The triflate complexes thus obtained are slightly hygroscopic but are easier to dry than the corresponding perchlorates.

Tetraethylammonium perchlorate (teap) (Fluka) was used as supporting electrolyte after recrystallization from methanol.[21]

Table 1. Stability constants (log K) of Sm^{3+}, Eu^{3+}, and Yb^{3+} cryptates in dmf (I = 0.1 mol dm^{-3} teap)

	Ligand			
Cation	L^1	L^2	L^3	L^4
Sm^{3+}	2.7 ± 0.2	2.9 ± 0.2	4.06 ± 0.01	⩽2
Eu^{3+}	2.9 ± 0.1	3.2 ± 0.1	4.69 ± 0.01	⩽2
Yb^{3+}	2.9 ± 0.1	3.3 ± 0.2	4.52 ± 0.05	⩽2
Na^+	5.7 ± 0.2 (6.1)*		4.4 ± 0.1 (5.2)*	⩽2
K^+		6.1 ± 0.2 (6.6)*		⩽2

* Value from ref. 25.

Stability Constants.—These were determined at 25 °C by competitive potentiometry using Na^+ or K^+ as the auxiliary cation. The following electrochemical cell was employed:

$$\begin{array}{l|l||l||l|l} \text{Glass} & 0.1\ \text{mol dm}^{-3}\ \text{teap},\ \text{Ln(CF}_3\text{SO}_3)_3, & 0.1\ \text{mol dm}^{-3} & 0.09\ \text{mol dm}^{-3}\ \text{teap} & \\ \text{electrode} & \text{Na(ClO}_4)\ \text{or K(ClO}_4) & \text{teap} & 0.01\ \text{mol dm}^{-3}\ \text{Ag(ClO}_4) & \text{Ag(s)} \end{array}$$

The competition reactions were monitored by Na^+ or K^+ selective glass electrodes (Tacussel PNaV and PKV). In all cases the reference electrode was a silver electrode (Metrohm). The response of the working electrodes, checked by adding increasing amounts of a $Na(ClO_4)$ or $K(ClO_4)$ 0.01 mol dm^{-3} solution in dmf to a solution of lanthanide(III) triflate in dmf ($c_{Ln} = 10^{-3}$ mol dm^{-3}), was generally linear in the concentration range 10^{-5} to 10^{-3} mol dm^{-3} and nearly Nernstian. When c_{Na} or c_K was about 3 c_{Ln}, increasing amounts of ligand were added. The corresponding potential changes were treated by the program MINIQUAD.[22] The values of the stability constants for the alkali cryptates necessary for the calculations were first determined from solutions without lanthanide cations. The program HALTAFALL[23] was used in order to simulate the reactions and to determine the optimal experimental conditions.

Electrochemical Measurements.—These were performed with a multipurpose PRG4 device (Solea Tacussel) on a dropping mercury electrode (as working electrode) (m = 1.43 mg s^{-1}; h = 30 cm). The reference electrode was a saturated calomel electrode (s.c.e.) connected to the electrolysis cell by a bridge filled with 0.1 mol dm^{-3} teap in dmf. Studies carried out on a gold rotating disk electrode (EDI type, Solea Tacussel) were made on a computerized electrochemical device Dacfamov (Microtec: CNRS, Toulouse, France) connected to an Apple II computer.

Results and Discussion

Stability Constants.—The results are summarized in Table 1 as the logarithms of the stability constants, log K, corresponding to the arithmetic mean of n individual experiments with $2 \leqslant n \leqslant 5$. The standard deviation σ_{n-1} is also given. Equilibrium was reached very quickly in all cases. The choice of the auxiliary cation involved in the competition reactions was guided by the low stability constant values expected for the lanthanide cryptates from the electrochemical measurements (see below). Thus the Na^+ cation, which has a size adapted to the L^2 cavity and forms the strongest complex with this ligand,[24] was used in systems involving the ligands L^3 and L^1. For similar reasons, K^+, which is well adapted to L^1, was used with ligand L^2. The stability constants of the corresponding alkali cryptates are also given in Table 1. Our values are consistent with those previously determined by Cox *et al.*[25] although a little lower. Only an upper limit (log $K \leqslant 2$) is given in the case of the monocycle L^4, as neither Na^+ or K^+ forms complexes strong enough for the observation of significant changes in the cation concentrations during the titrations. This limit should also be valid for the L^4–lanthanide complexes since lanthanide cryptates are generally less stable in dmf than the corresponding alkali cryptates (Table 1).

Table 2. Polarographic data on the reduction of lanthanide(III) ions in dmf (I = 0.1 mol dm^{-3} teap)

Metal	$E_{\frac{1}{2}}(Ln^{3+/2+})$ (V *vs.* s.c.e.)	Slope, log $\frac{i}{i_d - i}$ (mV)	Rate constant 10^2k_s (cm^{-1} s)	$E_{\frac{1}{2}}$ $(Ln^{2+/0})$ (V *vs.* s.c.e.)
Sm	−1.88 ± 0.01	57 ± 2	2.5 ± 0.3	−2.05 ± 0.01
Eu	−0.71 ± 0.01	71 ± 2	2.4 ± 0.3	−2.11 ± 0.01
Yb	−1.43 ± 0.01	56 ± 2	3.5 ± 0.5	−2.15 ± 0.01

As expected, the stability constants of lanthanide(III) cryptates in dmf are not very high. They are lower than those determined in various other solvents, namely water,[7] methanol,[11] pc,[11,15] and dimethyl sulphoxide (dmso).[12] In general, the stability order decreases according to the following sequence: pc ⩾ MeOH ⩾ H_2O ⩾ dmso ⩾ dmf. This order is in agreement with the solvating properties of the solvents, as estimated by their Gutmann donor number (d.n.),[26] except for dmso and dmf: the lanthanide complexes should be stronger in dmf (d.n. = 26.6) than in dmso (d.n. = 29.8) as is the case, for instance, for alkali cryptates.[25]

The lack of metal-ion selectivity observed in dmf as in water and dmso can be partly attributed to strong interactions between these strongly solvating solvents and the lanthanide cations. On the other hand, L^3 forms the strongest complexes in dmf, despite its low number of donor atoms. This was also observed in dmso.[12] In water, no particular ligand selectivity was observed and $[Ln(L^2)]^{3+}$ are the most stable complexes in pc.[7,15]

As already observed in pc, lanthanide(III) cations exhibit a small macrobicyclic effect in dmf, as illustrated by the difference in the stability between L^1 and L^4 cryptates.

Electrochemical Behaviour.—Lanthanide(III) *triflates.* The polarographic reduction of Sm^{III}, Eu^{III}, and Yb^{III} triflates occurs in two steps: the first is monoelectronic and reversible, or quasi-reversible, as shown from the slope of the log plot (Table 2); the second is an irreversible two-electron charge transfer corresponding to the reduction of Ln^{2+} to the metal. These results are in agreement with previous studies.[27–30] Cyclic voltammetry carried out on the first reduction step confirms the quasi-reversible behaviour of the first charge transfer.

From the evolution of the peak potential difference, $E_{pc} - E_{pa}$, with the potential sweep rate, the heterogeneous charge-transfer rate constant was calculated, using the method developed by Nicholson[31] for quasi-reversible charge transfers (Table 2).

Lanthanide(III) *triflates in the presence of the cryptand L^3.* Upon addition of increasing amounts of the cryptand L^3, the reduction current of the Ln^{3+} reduction waves decreases without any change in the respective potentials. The polarographic limiting current becomes nil as the ligand:metal ratio ranges between 3 and 10, depending upon the cation. Such behaviour is consistent with the stability constants of L^3 cryptates determined in the present work (Table 1). In the presence of L^3, added in excess, no clear reduction wave, only an ill defined,

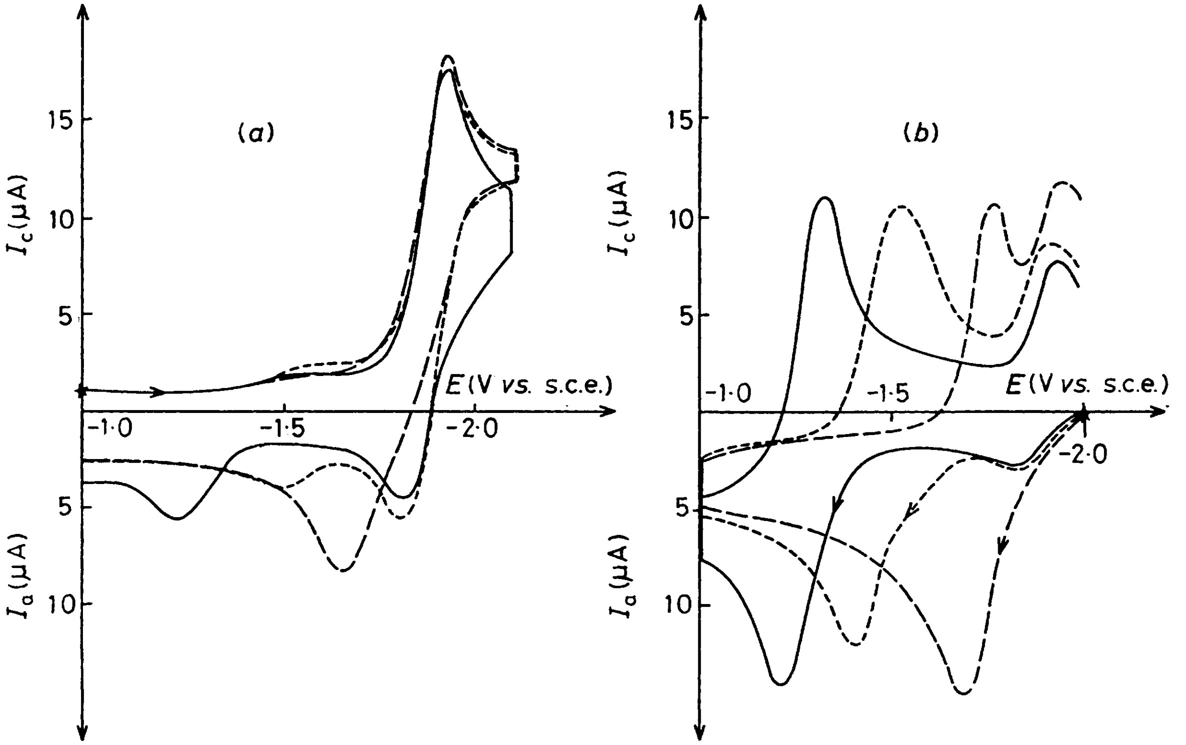


Figure. Cyclic voltammetry of samarium(III) in the presence of cryptands in dmf (I = 0.1 mol dm^{-3} teap) at 10 V s^{-1}; (———) c_{Sm} = 9.06 × 10^{-4} and c_{L^1} = 8.86 × 10^{-4}; (— — —) c_{Sm} = 8.20 × 10^{-4} and c_{L^2} = 1.02 × 10^{-3}; (— — —) c_{Sm} = 9.54 × 10^{-4} and c_{L^4} = 9.30 × 10^{-4} mol dm^{-3}. (*a*) Initial scan: cathodic, from −1.0 to −2.1 V *vs.* s.c.e. (*b*) Initial scan: anodic, from −2.0 to −1.0 V *vs.* s.c.e.

Table 3. Redox potentials of the cryptates studied in dmf (I = 0.1 mol dm^{-3} teap). Values of log K_{red}/K_{ox} (±0.3) are given in parentheses

	$E°$(V *vs.* s.c.e.)*			
Cations	$Ln^{3+/2+}$	$[Ln(L^1)]^{3+/2+}$	$[Ln(L^2)]^{3+/2+}$	$[Ln(L^4)]^{3+/2+}$
Sm^{3+}	−1.86	−1.25	−1.45	−1.73
		(10.5)	(7.1)	(2.2)
Eu^{3+}	−0.68	0.01	−0.25	−0.49
		(11.9)	(7.4)	(3.3)
Yb^{3+}	−1.41	−0.75	−0.95	−1.13
		(11.4)	(7.9)	(4.8)

* $E° = \frac{1}{2}(E_{pa} + E_{pc})$: confidence interval within ±0.01 V.

Table 4. Stability (as log K) of lanthanide-(II) and -(III) cryptates in dmf (I = 0.1 mol dm^{-3} teap). [Confidence interval within 0.1—0.2 for lanthanide(III) cryptates (see Table 1) and within 0.4—0.5 for lanthanide(II) cryptates]

	Cryptands		
Cations	L^1	L^2	L^4
Sm^{3+}	2.7	2.9	⩽2
Sm^{2+}	13.2	10.0	⩽4.2
Eu^{3+}	2.9	3.2	⩽2
Eu^{2+}	14.8	10.6	⩽5.3
Yb^{3+}	2.9	3.3	⩽2
Yb^{2+}	14.3	11.2	⩽6.8

spread out wave, is observed around −2 V *vs.* s.c.e. for samarium and ytterbium cryptates, while hardly any signal is detected for europium cryptate. This behaviour clearly indicates that the divalent lanthanides are not stabilized at all by L^3.

Lanthanides(III) *triflates in the presence of L^1, L^2, and L^4 cryptands.* (*i*) *Polarographic study.* Addition of L^1, L^2, and L^4 cryptands has no effect on the height and shape of the first reduction wave of lanthanide(III). It was possible to confirm that the added ligand remains mainly uncomplexed, as shown by the characteristic oxidation wave of mercury around 0 V *vs.* s.c.e. in the presence of cryptands. Oxidation of the dropping mercury electrode in the presence of free cryptands had been previously studied[32] and led to a powerful analytical method of measuring the free ligand concentrations in solutions. The results show that only a very small part of the cryptand is complexed, indicating the low stability of lanthanide(III) cryptates in dmf (log $K \leqslant 3$). The only effect of the addition of cryptand to lanthanide(III) solutions is an anodic potential shift, the magnitude of which depends on the ligand concentration. This is typical of an electrochemical–chemical (e.c.) mechanism. It may be speculated that the chemical reaction following the charge transfer is in fact the complexation of the reduced lanthanide(II) by the cryptand. This is confirmed hereafter by cyclic voltammetry. Identical electrochemical results were obtained when solid cryptates were employed as solutes.

(*ii*) *Cyclic voltammetry.* When performing a cathodic, followed by an anodic sweep, for a metal to ligand ratio of 1, the peak potentials of the metal are not affected by the presence of cryptands. Nevertheless the peak current ratio, $I_{pa}:I_{pc}$, which is very small at low sweep rates (v = 2 V s^{-1}), rises to unity when the sweep rate is increased up to 50 V s^{-1}. The evolution of this parameter is consistent with an electrochemical–chemical reduction (e.c. mechanism) of the lanthanide(III) in the presence of cryptands, the chemical step being the complexation of the lanthanide(II) cation by the cryptand. As shown in the Figure (*a*), a second peak corresponding to the oxidation of the $[Ln(L)]^{2+}$ cryptate is observed on the anodic scan of the cycle. In order to study the redox behaviour of the corresponding cryptates a second set of cyclic voltammetric studies were carried out, performing an anodic sweep followed by a cathodic one; thus an accumulation of cryptate was allowed on the electrode before the potential scan started [Figure (*b*)]. It was then possible to determine the redox potentials of the lanthanide(III) cryptates (Table 3). The values of the peak current ratio $I_{pc}:I_{pa}$ are close to unity at high sweep rates. Indeed the evolution of the cryptate peaks with sweep rate clearly indicates that oxidation of the cryptates occurs *via* an e.c. mechanism, the chemical step being the decomplexation of the unstable $[\mathrm{Ln(L)}]^{3+}$ cryptate. This behaviour is not surprising considering the low stability of the $[\mathrm{Ln(L)}]^{3+}$ cryptates.

The above results are consistent with the following reduction mechanism for lanthanide(III) in the presence of cryptands (L).

$$\begin{array}{lcl} \mathrm{Ln}^{3+} & + e^- \rightleftharpoons & \mathrm{Ln}^{2+} \\ + & & + \\ \mathrm{L} & & \mathrm{L} \\ \uparrow & & \downarrow \\ [\mathrm{Ln(L)}]^{3+} & + e^- \rightleftharpoons & [\mathrm{Ln(L)}]^{2+} \end{array}$$

As evidenced from the results (Table 3), all the redox potentials of the $\mathrm{Ln^{III}}$–$\mathrm{Ln^{II}}$ cryptates, E°_c, are more anodic than the redox potentials of the corresponding, uncomplexed, ions, E°_m, thus indicating stabilization of the reduced lanthanides in the cryptates. In the reduction of a complexed metallic cation from one oxidation state to another without any change in stoicheiometry, it is possible to determine the ratio of the stability constants, K_{red} and K_{ox}, corresponding, respectively, to the bivalent and trivalent cryptates, according to the following expression derived from von Stackelberg's relationship.[33]

$$\delta = \log K_{red}/K_{ox} = (E^\circ_m - E^\circ_c)nF/RT$$

The high values of δ thus obtained (Table 3) reveal an important stabilization of the $[\mathrm{Ln(L)}]^{2+}$ cryptate. Our results with L^1 and L^2 cryptates of europium (for which δ is equal to 11.9 and 7.4 respectively) are consistent with previous results obtained by Tabib *et al.*[16] in the same medium: values of 11.04 and 7.1 can be calculated in these cases from the formal potential values given by these authors. Bessiere *et al.*[17] found a lower value of 9.4 in the presence of $\mathrm{NaNO_3}$ or $[\mathrm{NBu_4}]\mathrm{ClO_4}$ for the former complex. On the other hand stabilization of $[\mathrm{Ln(L)}]^{2+}$ complexes (Ln = Sm, Eu, or Yb and L = L^1 or L^2) has already been observed in other solvating media such as water and methanol,[9–11] as well as the stabilization of $[\mathrm{Eu(L^1)}]^{2+}$ in dmso and tmu.[17] In pc, which is a weaker donor solvent, no stabilization of the divalent cryptates occurred.[14]

The stability constants of the divalent lanthanide cryptates have been calculated in Table 4 using δ and log *K* values of the corresponding trivalent cryptates. These absolute values illustrate unambiguously that lanthanide(II) cryptates are much more stable in dmf that the corresponding lanthanide(III) cryptates. Surprisingly, it is noted that alkaline-earth cations, in particular $\mathrm{Ca^{2+}}$, to which $\mathrm{Eu^{2+}}$ is often compared because of their similar size, charge, and reactivity, form cryptates which are much less stable.[25] These results show that an important factor in the complexation stability and selectivity is the interaction of the solvent with the lanthanide ions, which is much less important for divalent than for trivalent lanthanides.

Whereas poor cation or ligand selectivities are found among trivalent cryptates, reduced lanthanides display a good cryptand specificity: divalent L^1 cryptates are about 3—4 log units more stable than the corresponding L^2 cryptates. The highest stabilization obtained with L^1 complexes, in dmf as in water, originates in the better fit achieved between divalent lanthanides and L^1 rather than L^2.

Further evidence of the importance of size effects among divalent lanthanide cryptates is the existence of a strong macrobicyclic effect, as measured by the difference $\Delta \log K$ in the stability constants of L^1 cryptates and homologous L^4 complexes: $\Delta \log K$, estimated from results in Table 4 [*e.g.* $9 \leqslant \Delta \log K \leqslant 11.2$ for samarium(II)] lie among the highest values ever observed, even higher than for alkali cryptates in water or in non-aqueous solvents.[34]

Further studies in other media exhibiting different solvating properties would contribute greatly to a thorough definition of thermodynamic and electrochemical behaviour of lanthanide cryptates.

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