Complexation of the Lanthanide Ions by 4,4′(5′)-Di-*tert*-butylbenzo-18-crown-6 in Propylene Carbonate and Stabilization of the Divalent Oxidation State of Samarium and Ytterbium

J. MASSAUX, J. F. DESREUX,* C. DELCHAMBRE, and G. DUYCKAERTS

The stability constants (β_{Ln}) of 1:1 complexes between all the trivalent lanthanide ions (except Eu^{3+}) and the macrocycle 4,4′(5′)-di-*tert*-butylbenzo-18-crown-6 in anhydrous propylene carbonate are determined by a potentiometric competitive method using lead as an auxiliary ion. The stability of the complexes steadily decreases through the lanthanide series (log $\beta_{La^{3+}}$ = 5.14 ± 0.05; log $\beta_{Lu^{3+}}$ = 2.51 ± 0.06) due to a better encapsulation of the larger ions into the cavity of the macrocycle. Solvation effects also appear to be significant. Because of their greater ionic radius and their smaller solvation, divalent samarium and ytterbium are more strongly coordinated by the macrocycle than the trivalent ions (log $\beta_{Sm^{2+}}$ = 7.60 ± 0.05; log $\beta_{Yb^{2+}}$ = 7.31 ± 0.10). This phenomenon results in a positive (anodic) shift of the III → II polarographic wave. The properties of the macrocycle contrast sharply with the behavior of classical noncyclic ligands.

Introduction

The solution behavior of the macrocyles has been the subject of diverse and detailed scrutiny.[1] The impetus behind these studies is understanding the factors which govern the complexation of various metal ions. Up to the present, the encapsulation of the lanthanide ions by a macrocycle has been much less explored than that of the alkali ions. A few reports deal with the preparation, crystallographic structure, or spectral properties of lanthanide polyoxa or polyaza complexes,[2–6] and only one research work[7] is devoted to the stability constants of some of these new lanthanide compounds. Our concern in this paper is to present quantitative data on the complexation of anhydrous lanthanide trifluoromethanesulfonates[8] by 4,4′(5′)-di-*tert*-butylbenzo-18-crown-6,[9] **1**, in propylene carbonate. To this end, stability constants were

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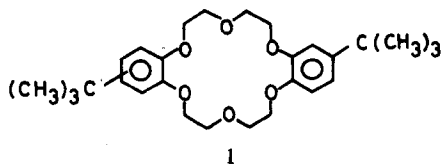
obtained by a potentiometric competitive method, a technique successfully applied to the study of many complexes in aqueous solution.[10]

An important second objective of the present work has been an investigation of the influence of ligand **1** on the electrochemical properties of the lanthanides which can exist in the 2+ oxidation state in solution, namely, Sm, Eu, and Yb. While this research was in progress, Gansow et al.[5] reported on the stabilization of Eu(II) in water by various cryptates.

Experimental Section

Preparative Methods. All solutions and reagents were stored and handled in a glovebox filled with an inert atmosphere, the water content of which was monitored by means of a dew point meter and was always below 20 ppm. Purification and dehydration of propylene carbonate, tetraethylammonium perchlorate, and $NaClO_4$ have been described previously.[11] Anhydrous lanthanide and lead trifluoromethanesulfonates were prepared as reported earlier,[8] and ligand **1** was synthesized according to Pedersen.[12]

All standard solutions were prepared by weighing the required amount of anhydrous salt and dissolving it in propylene carbonate. Appropriate dilutions were made just before use, the ionic strength being adjusted to 0.1 with tetraethylammonium perchlorate. The water content of the solutions as determined by K. Fischer titration was always below 10 ppm at the beginning of the measurements and never exceeded 40 ppm at the end of each series of measurements.

Potentiometric Method. Potentiometric measurements were carried out at (25 ± 0.1) °C with a Fluke 8800A digital multimeter (input impedance 10^6 MΩ). The polarographic and potentiometric cells used in this work have been described elsewhere.[11]

For the measurements, a solution of lead trifluoromethanesulfonate was introduced into the cell, and the amalgam pool electrode was then prepared by electrolysis at constant potential. A high stability of this electrode was easily achievable provided the water content of the solutions was below 40 ppm, a condition which was always met in this research. By recording the potential at various stages of the electrolysis, we calculated the standard potential of the electrode, E_0. A solution of the crown ligand **1** was then added, and the potential E_1 shifted toward cathodic (negative) potentials as expected from eq 1, where L denotes ligand **1** and where brackets represent concen-

$$E_1 = E_0 + \frac{RT}{2F} \ln \frac{[Pb^{2+}]_1}{[Pb(Hg)]} = E_0 + \frac{RT}{2F} \ln \frac{[Pb^{2+}]_{tot}}{[Pb(Hg)]} - \frac{RT}{2F} \ln (1 + \beta_{Pb}[L]_1) \quad (1)$$

trations. The concentrations of the free species $[Pb]_1$ and $[L]_1$ were easily derived from the above equation. Aliquots of lanthanide (Ln) trifluoromethanesulfonate solutions were then added to the potentiometric cell, and the potential of the working electrode became more positive, indicating that the exchange reaction

$$PbL^{2+} + Ln^{3+} \rightleftharpoons LnL^{3+} + Pb^{2+} \quad (2)$$
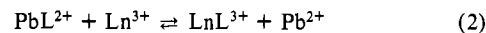
took place. Equilibrium was reached within a few minutes, and the potential E_2 was recorded. As this potential is related to the con-

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Table I. Stability Constants of the Trivalent Lanthanide Complexes with 4,4'(5')-Di-*tert*-butylbenzo-18-crown-6 at 25 °C in Propylene Carbonate ($\mu = 0.1$)[a]

Ln	$r,$[b] Å	$\log \beta_{Ln}$[c]	Ln	$r,$[b] Å	$\log \beta_{Ln}$[c]
La	1.061	5.14 ± 0.05	Dy	0.908	3.40 ± 0.07
Ce	1.034	4.95 ± 0.03	Ho	0.894	3.29 ± 0.15
Pr	1.013	4.79 ± 0.05	Er	0.881	3.16 ± 0.05
Nd	0.995	4.58 ± 0.06	Tm	0.869	2.94 ± 0.09
Sm	0.964	4.00 ± 0.04	Yb	0.858	2.57 ± 0.09
Gd	0.938	3.62 ± 0.13	Lu	0.848	2.51 ± 0.06
Tb	0.923	3.50 ± 0.08			

[a] Log $\beta_{Pb} = 9.74 \pm 0.04$; log $\beta_{Na} = 5.36 \pm 0.04$. See text.
[b] Ionic radius taken from D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954). [c] Mean values and standard deviations. See Experimental Section.

centration of uncomplexed lead according to eq 1, it is readily shown that

$$E_2 - E_1 = \frac{RT}{2F} \ln \frac{[Pb^{2+}]_2}{[Pb^{2+}]_1} = \frac{RT}{2F} \ln \frac{1 + \beta_{Pb}[L]_1}{1 + \beta_{Pb}[L]_2} = \frac{RT}{2F} \ln \frac{[L]_1}{[L]_2} \quad (3)$$

The concentrations $[L]_2$ and $[Pb^{2+}]_2$ were deduced from eq 3, and the formation constant of the lanthanide–macrocycle adduct β_{Ln} was then computed. All measurements were carried out with solutions containing lead and ligand 1, respectively 1 and 2 mM, and an excess of lanthanide which ranged from 3 to 10 mM. Mention should be made here that, in the above equations, activities are assumed to be equal to concentrations, a fair assumption considering the low concentration range of the reagents. Another pitfall in the data treatment is the neglect of the incomplete dissociation of the lanthanide salts in propylene carbonate. Lanthanide perchlorates and trifluoromethanesulfonates were found to behave identically in various aprotic solvents,[8] but the extent of their dissociation is unknown. It is assumed here that the dissociation of all lanthanide salts is insensitive to the metal ionic radius.

For all the lanthanide ions two measurements were performed with three additions of a solution of anhydrous rare earth salt in each case. The standard deviations σ were calculated from the six available values of each stability constant.

Results

Potentiometric Measurements. Lead is used in the present research work as an auxiliary metal ion for a potentiometric determination of the stability constants of the lanthanide complexes with ligand 1 by a competitive method. This ion exhibits a partially irreversible dc polarographic wave in propylene carbonate (PC).[8] The pool amalgam electrode obtained by electrolysis of lead follows the Nernst law with a slope $\partial E / \partial$ log ([$Pb^{2+}(PC)$]/[Pb(Hg)]) of 29.3 ± 0.6 mV and an E_0 value of −394 ± 2 mV (referenced to the ferrocene–ferricinium couple). This electrode is thus suitable for a potentiometric investigation of the exchange reaction between the lead and lanthanide complexes with macrocycle 1. It is noteworthy that either a dropping or a hanging mercury drop electrode using lead as an auxiliary ion would not be convenient for a complexometric study by polarography or cyclic voltammetry. The latter technique was very recently proposed by Yee et al.,[13] but it requires the use of a fully reversible indicating electrode, a condition which is often difficult to meet in nonaqueous solvents. As already pointed out many years ago,[10] potentiometry affords entry to a broad variety of auxiliary metal ions. A potentiometric titration technique was recently applied to the determination of the stability constants of Tl+, Ag+, and Pb+ cryptates in aprotic solvents.[14]

By means of eq 1, a stability constant log $\beta_{Pb} = 9.74 \pm 0.04$ is obtained for the complex between lead and macrocycle 1.

(13) E. L. Yee, J. Tabib, and M. J. Weaver, *J. Electroanal. Chem. Interfacial Electrochem.*, **96**, 241 (1979).
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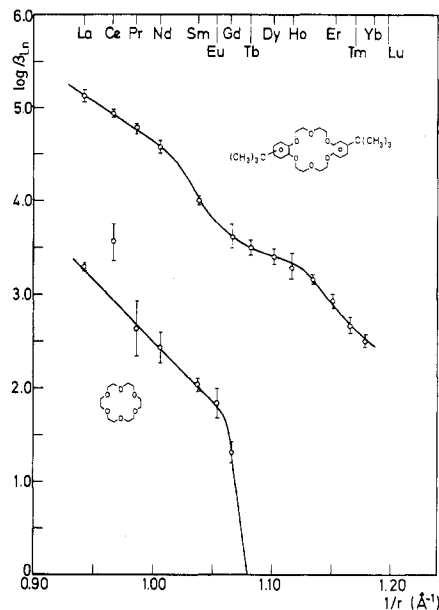

Figure 1. Dependence of the stability constants of anhydrous lanthanide complexes with 4,4'(5')-di-*tert*-butylbenzo-18-crown-6 in propylene carbonate on the inverse of the ionic radius of the encapsulated ions. The data reported for 18-crown-6 are taken from ref 7 and were obtained by calorimetric titrations in hydrated methanol.

The validity of the potentiometric method applied here was assessed by determining the stability constant of the sodium adduct with 1, first, by competition with lead and, second, with a sodium amalgam pool electrode.[11] The values obtained

log $\beta_{Na} = 5.41 \pm 0.06$ (competitive reaction)

log $\beta_{Na} = 5.36 \pm 0.04$ (amalgam electrode)

are in very good agreement.

The stability constants β_{Ln} of the lanthanide complexes with 4,4'(5')-di-*tert*-butylbenzo-18-crown-6 in anhydrous propylene carbonate are collected in Table I. The dependence of these constants with $1/r$, the inverse of the ionic radius of the metal ions[15] is reproduced in Figure 1. No data are given for europium(III) as this ion is reduced to the divalent state by the lead amalgam. For comparison purposes, the stability constants of the lanthanide adducts with 18-crown-6 in methanol in the presence of water are also plotted against $1/r$ in Figure 1. These data were obtained by Izatt et al.[7] by calorimetric titrations. It is pertinent to note that the stability constants listed in Table I are too high to be deduced from calorimetric titration data.

Polarographic Measurements. On the addition of macrocycle 1 to a solution of samarium(III), europium(III), or ytterbium(III) trifluoromethanesulfonate in propylene carbonate, the III → II reduction polarographic wave exhibited by each of these ions is shifted toward the positive (anodic) potentials. These shifts clearly indicate that the divalent ions are better encapsulated by ligand 1 than the trivalent ions. The III → II polarographic wave of complexed europium appears to be displaced beyond the oxidation wave shown by mercury in the presence of a macrocycle.[11] No further study of the reduction of Eu^{3+} was thus carried out. In the case of samarium and ytterbium, an analysis of the III → II wave shape obtained from a dc polarographic plot of $[(i_d - i)/i]$ against the applied potential is consistent with a reversible one-electron reduction. The number of exchanged electrons was also determined by coulometry ($n = 0.97$ for Sm^{3+}, $n = 1.04$ for

(15) Plots of the dependence of log β_{Ln} on the atomic number Z or on the ionic radius r would bring out the same information. See ref 16.

Yb^{3+}). Furthermore, the reduction waves are controlled by diffusion: the electrode process is characterized by a zero intercept and a straight-line dependence of the diffusion current on concentration and on $h^{2/3}t^{1/6}$ where h is the height of the mercury column after correction for back-pressure and t is the fixed drop time. The diffusion coefficients were calculated from Ilkovic's equation as $D = 7.3 \times 10^{-7}$ cm^2 s^{-1} for the samarium(III) adduct with **1** and as $D = 6.9 \times 10^{-7}$ cm^2 s^{-1} for the corresponding adduct of ytterbium(III). The positive shifts of both polarographic waves are independent of the concentration of excess macrocycle; the divalent and trivalent ions are thus involved in complexes of the same stoichiometry. The interpretation of the potentiometric data leads to the conclusion that the stoichiometry is 1:1 in keeping with the composition of solid lanthanide complexes with ligands related to **1**[2-4] and with the thermodynamic data reported by Izatt et al.[7] Equations 1–3 as given above were established by assuming that only 1:1 adducts are formed in solution.

From the shift of the III → II polarographic waves it is easily deduced that

$$\log \beta_{Sm^{2+}}/\beta_{Sm^{3+}} = 3.63 \pm 0.03$$

$$\log \beta_{Sm^{2+}} = 7.60 \pm 0.05$$

$$\log \beta_{Yb^{2+}}/\beta_{Yb^{3+}} = 4.63 \pm 0.05$$

$$\log \beta_{Yb^{2+}} = 7.31 \pm 0.10$$

The II → 0 polarographic wave exhibited by each lanthanide ion is shifted toward negative potentials upon complexation by ligand **1**. These waves are highly irreversible and our attempt to interpret their shape did not prove useful.

Discussion

Complexes of the Trivalent Lanthanides. The stability constants of the lanthanide adducts with ligand **1** in propylene carbonate are compared in Figure 1 with data obtained by Izatt et al.[7] for the complexes with 18-crown-6 in methanol. Both complexing agents are 18-membered macrocycles of comparable dimension, the radius of their internal cavity is estimated to range from 1.3 to 1.6 Å.[12] The lanthanide ions are thus too small to fit exactly into the internal cavity of these ligands. The largest metal ion, namely, La^{3+}, is consequently the best encapsulated, and the stability constant β_{Ln} decreases along the lanthanide series when the ionic radius decreases. Moreover, the smallest (heaviest) lanthanides, like Lu^{3+}, are expected to coordinate more strongly with propylene carbonate, and accordingly, the encapsulation by a large macrocycle such as **1** should be further reduced due to the competition between the ligand and the solvent for the complexation of the metal ion. It is noteworthy that the polyoxa macrocycles of the 18-crown-6 type are the only ligands known to date which complex less the small lanthanides despite their higher charge density. A reversed trend in the complexation has always been noted for more classical ligands although a small decrease in stability is sometimes observed for the heavy lanthanides, for instance, in the case of DTPA.[16] The selectivity of cycle **1** ($\Delta \log \beta = 2.6$ from La^{3+} to Lu^{3+}) is comparable to the one achieved in water with isobutyric acid, a ligand currently used for lanthanide separations.[16] EDTA, however, is a more selective complexing agent.

Solvation effects account for the data reproduced in Figure 1. Izatt et al.[7] performed their complexometric studies in methanol in the presence of 7–9 mol of water/mol of metal. The presence of water and the protic character of the solvent give rise to a significant reduction of the stability constants

because of solvation effects. Furthermore, Izatt et al.[7] tentatively ascribed the sudden decrease of the complexation after gadolinium to a possible change in the coordination number of the encapsulated ion. In the anhydrous and aprotic system investigated here, the dependence of log β_{Ln} on the inverse of the ionic radius is not too far from linearity. It thus seems that the data of Izatt et al.[7] could be better rationalized in terms of a solvent (methanol and water)–macrocycle competition which would favor the solvent at the end of the lanthanide series. Another aspect of interest is that ligand **1**, when involved in the complexation of small ions, is probably less prone than 18-crown-6 to undergo a rearrangement to a nonplanar conformation of reduced cavity size because of the rigidity brought about by the two phenyl moieties.[3] On the basis of the data presented in Figure 1, solvation appears to prevail over the structural effects of substituents since ligand **1**, in contrast to 18-crown-6, is able to complex all the lanthanides.

The influence of the solvent is also reflected in a comparison of the stability constants of the sodium and the lanthanide adducts with **1** in propylene carbonate. Despite an ionic radius comparable to the one of neodymium, sodium forms a complex which is ten times more stable, a difference which probably arises from the lower charge of this ion and consequently from its smaller solvation. It is also interesting to note that Pb^{2+} is involved in a very stable complex with macrocyle **1**, presumably because of the partially covalent bonds formed by this metal.[17]

Finally, it is tempting to associate the dependence of log β_{Ln} with $1/r$ (Figure 1) with the synthesis of solid stoichiometric complexes of dibenzo-18-crown-6. King and Heckley[2] failed to obtain pure adducts between hydrated (Sm–Lu)(NO$_3$)$_3$ and this ligand. On the other hand Cassol et al.[4] reported on the preparation of complexes between the complete series of lanthanide nitrates or thiocyanates and dibenzo-18-crown-6. Further studies with the same ligand in anhydrous medium[3] supported the findings of King and Heckley.[2] The results presented here were obtained under anhydrous conditions and in the presence of a noncoordinating anion.[8] A direct comparison with the synthesis work[2-4] should thus be accepted with reservation as the nitrate and thiocyanate ions are well-known to be complexing agents of the lanthanides. However, it is pertinent to note that although all the lanthanides are complexed by ligand **1**, the stability of the adducts decreases faster between Nd^{3+} and Sm^{3+}.

Complexes of Divalent Lanthanides. Divalent samarium and ytterbium form adducts with ligand **1** which are respectively 3.6 and 4.6 orders of magnitude more stable than the corresponding trivalent ions. To our knowledge, it is the first time that the stabilization of Sm^{2+} and Yb^{2+} by complexation is observed. This effect can be attributed to the larger size of the divalent ions (Sm^{2+}, $r = 1.11$ Å; Yb^{2+}, $r = 0.93$ Å[16]), which are better accommodated in the internal cavity of cycle **1**, and, also, to the smaller solvation of the ions due to their smaller charge. All known noncyclic ligands coordinate better with the trivalent lanthanide ions simply because of stronger electrostatic interactions. Solvation effects are particularly apparent if the stability constants of Yb^{2+} and Tb^{3+} are compared. Both ions have approximately the same ionic radius, but Yb^{2+} is involved in a much more stable complex with **1**, a difference which most probably originates in the smaller solvation of this ion. Gansow et al.[5] recently reported that various cryptates form lanthanide adducts stable in water for an extended period of time and which are able to complex better Eu^{2+} than Eu^{3+}. As detailed above, europium solutions

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were not accessible to experiment. However, it is anticipated that the stability constant of the Eu^{2+} adduct with macrocycle **1** should be near to the constant measured for Sm^{2+}. From a comparison with the data of Gansow et al.,[5] it appears that ligand **1** should be as effective as cryptate [2.2.1] for the stabilization of europium in the divalent oxidation state (the nature of the solvents being not taken into account).

Other macrocycles of suitable size should give rise to complexometric and stabilization effects similar to the ones described here. Polarographic and potentiometric investigations

of these new facets of the properties of macrocycles are now in progress.

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Oxidation of the Ligand in Nitro Complexes of Ruthenium(III)

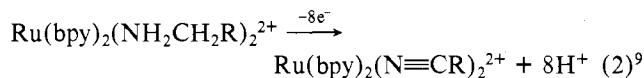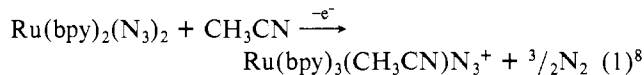F. RICHARD KEENE, DENNIS J. SALMON, JERRY L. WALSH, HECTOR D. ABRUÑA, and THOMAS J. MEYER*

Nitro complexes of bis(bipyridyl)ruthenium(III) are unstable with respect to oxidation of the coordinated nitro ligand. For the complexes $Ru(bpy)_2(L)NO_2^+$ (L = NH_3, py (pyridine), pyr (pyrazine), CH_3CN, PPh_3) and $Ru(bpy)_2(Cl)NO_2$, electrochemical oxidation to the ruthenium(III) state results in production of the corresponding nitrosyl and nitrato complexes in a 1:1 ratio. A two-electron oxidation of the nitro ligand to nitrate occurs, and the corresponding reduction is delocalized over two sites, one at the metal ($Ru^{III} \rightarrow Ru^{II}$) and one at the ligand ($RuNO^+ \rightarrow Ru\overset{.}{N}O$). For the chloro complex the rate of disappearance of $Ru^{III}(bpy)_2(Cl)NO_2^+$ is first order in Ru(III) and the rate constant, determined by monitoring the reaction by cyclic voltammetry, is 1.8×10^{-3} s^{-1} in acetonitrile at room temperature. For the pyridyl complex, variable scan-rate cyclic voltammetry experiments show the intervention of an intermediate past the initial oxidation step. A mechanism is suggested for the oxidation of coordinated nitrite which consists of an initial rearrangement of the nitro ligand from N bound to O bound. The O-bound isomer is a reactive intermediate which undergoes a bimolecular oxygen atom transfer reaction probably with the corresponding Ru^{II}–NO_2 complex to give the observed products. The acid–base properties of the $Ru(bpy)_2(py)NO_2^+$–$Ru(bpy)_2(py)NO^{3+}$ acid–base pair and formal reduction potentials for the chloro and pyridyl complexes as two-electron-acceptor, oxide ion donor oxidants have been determined. In basic solutions, oxidation of the nitro group becomes catalytic and the nitrato complex is the sole product of the oxidation.

Introduction

We are attempting to design 2,2′-bipyridyl complexes of ruthenium which can function as redox catalysts. As potential catalytic systems, the complexes are attractive because of the stability of the Ru–bpy chemical link, the availability of possible multiple electron donor or acceptor properties based either on metal[1,2] or ligand[3,4] redox sites, the existence of dimeric and oligomeric multimetallic complexes,[5] and the versatility of the background synthetic chemistry for making controlled chemical modifications.[5a,6] The complexes are also attractive from the kinetic point of view since they retain the same basic coordination number in a series of different oxidation states and, where known, the kinetic barriers to electron transfer are low as shown by electron-transfer self-exchange studies.[4a,7]

In earlier work it was shown that relatively facile oxidation of ligands coordinated to $(bpy)_2$ complexes of ruthenium can occur (eq 1 and 2). The reactions in eq 1 and 2 are known

$$Ru(bpy)_2(N_3)_2 + CH_3CN \xrightarrow{-e^-}$$
$$Ru(bpy)_3(CH_3CN)N_3^+ + {}^3/_2N_2 \quad (1)^8$$

$$Ru(bpy)_2(NH_2CH_2R)_2^{2+} \xrightarrow{-8e^-}$$
$$Ru(bpy)_2(N{\equiv}CR)_2^{2+} + 8H^+ \quad (2)^9$$

to occur by initial oxidation of Ru(II) to Ru(III). For the case where bound amines are oxidized (eq 2), the initial Ru(II) $\rightarrow$ Ru(III) step is followed by a series of net two-electron oxidative dehydrogenation steps at the bound amine ligands.

In this paper a third example is described where a bound ligand is oxidized following oxidation of Ru(II) to Ru(III). The chemistry involves oxidation of a bound nitro to a nitrato

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