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Macrocyclic Effect in Lanthanoid Complexes with 12-, 15-, 18-, and 21-Membered Crown Ethers[1,2]

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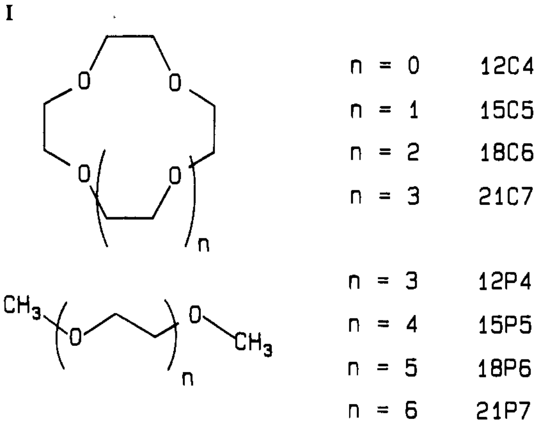
The complexation of lanthanoid trifluoromethanesulfonates by several linear and cyclic polyethers containing from four to seven oxygen atoms has been investigated in anhydrous propylene carbonate at 298.2 K. Stability constants have been measured by a competitive potentiometric method with silver(I) as the auxiliary cation and at 0.1 M ionic strength adjusted with tetraethylammonium perchlorate. For coronates, there is a gradual shift of the maximum of stability from the complexes of the lighter lanthanoid ions with 18-crown-6 ether to the 15-crown-5 adducts with the heavier ions. Both 1:1 and 1:2 complexes were observed with 12-crown-4 and 15-crown-5 ethers. The lanthanoid podates are less stable than the coronates, and no 1:2 complexes could be evidenced. Their stability usually increases with the number of donor atoms, with a few exceptions. The magnitude of the macrocyclic effect has been calculated from the measured stability constants and from literature data. It is approximately constant for 12-crown-4 ($\Delta(\log \beta_1) \simeq 1.0 \pm 0.3$), 18-crown-6 ether (3.1 ± 0.2), and 21-crown-7 ether (0.9 ± 0.2). For 15-crown-5 ether, it increases from 1.3 ± 0.1 for La to 2.3 ± 0.1 for Sm, 3.3 ± 0.2 for Tb, and 3.8 ± 0.1 for Lu. These data are discussed in terms of the fit between the ionic radius and the ligand cavity and in terms of the structural changes occurring along the series.

Introduction

Natural macrocyclic complexes play an important role in phenomena essential to life. The recognition of this fact led to the design of synthetic ionophores able to model natural processes (supramolecular chemistry).[3] Crown ethers belong to this class of compounds, providing, for instance, selective complexation of alkali-metal and alkaline-earth-metal cations, hence shedding light on the transport of these cations through biological membranes.[3,4] Trivalent 4f elements, Ln(III), also react with synthetic ionophores to yield complexes of the guest-host type,[5] in which the metal ion is partly or totally protected from further interaction with both solvent molecules and anions. We have recently reviewed the properties of these derivatives, including their use as analytical probes.[6]

In addition to the charge density of the metal, the complexation of 4f trivalent ions by macrocyclic ligands strongly depends on steric and structural effects, such as the fit between the ionic diameter and the dimension of the ligand cavity and the ligand flexibility. Solution studies on complexes with coronands featuring four, five, six, and ten oxygen atoms, namely 12-crown-4 (12C4),[7] 15-crown-5 (15C5), 18-crown-6 (18C6), 30-crown-10 (30C10), and their benzo or *tert*-butylbenzo derivatives have been previously published.[9-12] The plots of the stability constants vs the reciprocal of ionic radii, $1/r_i$, reflect the interplay between the abovementioned factors. There is no general trend: some curves go through an extremum, while others decrease monotonously with $1/r_i$. These studies leave two questions open. The first pertains to the magnitude of the macrocyclic effect, i.e. the additional stability gained upon complexation with a cyclic ligand, as compared to the complexation with an open-chain ligand having the same number of donor atoms (podand). Indeed, experimental stability constants have been measured only for one system, namely the 15C5 and 15P5[13] complexes.[12] The second question concerns the existence of 1:2 complexes with 15C5, reported in one study[12] but not in the other one.[11]

Chart I



In this communication, we bring experimental evidences to contribute to answering these two questions. The stability constants of lanthanoid trifluoromethanesulfonates $Ln(trif)_3$ complexes with 21-crown-7-ether (21C7), 12-podand-4 (12P4), 18-podand-6 (18P6), and 21-podand-7 (21P7) were determined at 25 °C by a competitive potentiometric method. We have also reinvestigated the 15C5 complexes and present additional data on 12C4, 18C6, and 15P5 complexes.

Experimental Section

Propylene Carbonate (PC). Special care has been devoted to the purification and desiccation of the solvent.[14] Between 300 and 800 mL of PC (Fluka, distilled in glass) was stirred for 10-14 h with $KMnO_4$ (Merck, p.a., 1.2 g/100 mL), filtered to remove MnO_2, refluxed for 4 h at 120 °C, filtered, and rapidly distilled under vacuum ($(2-3) \times 10^{-2}$ mmHg), yielding a colorless liquid. The core fraction was further purified by chromatography (acidic Al_2O_3, 45 g/100 mL), heated for 10-14 h at 40-50 °C under vacuum (10^{-1} mmHg), and fractionated in a predried distillation apparatus (10^{-2} mmHg; 30-cm Vigreux column). The collected fractions were stored in a glovebox and checked for their UV spectrum and water content (Karl Fischer titration, Mettler DL18 apparatus). The fractions used for potentiometric measurements had an absorbance at 220 nm smaller than 0.4 (1-cm cell; cf. Figure F1, sup-

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(1) Complexes of Lanthanoid Salts with Macrocyclic Ligands. 36. For part 35, see ref 2. Abstracted from the Ph.D. Thesis of F. P. Presented, in part at the 18th Rare Earth Research Conference, Lake Geneva WI, Sept 12-16, 1988; paper P4-30.

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(7) The crown ether nomenclature was coined by Pedersen.[8] See ref 6 for an explanation regarding the abbreviations used. Systematic names: 1,4,7,10-tetraoxacyclododecane (12C4); 1,4,7,10,13-pentaoxacyclopentadecane (15C5); 1,4,7,10,13,16-hexaoxacyclooctadecane (18C6); 1,4,7,10,13,16,19,22,25,28-decaoxacyclotridecane (30C10).

(8) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

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(13) Systematic names of the podands: 2,5,8,11-tetraoxadodecane (12P4), 2,5,8,11,14-pentaoxapentadecane (15P5), 2,5,8,11,14,17-hexaoxaoctadecane (18P6), 2,5,8,11,14,17,20-heptaoxaheneicosane (21P7).

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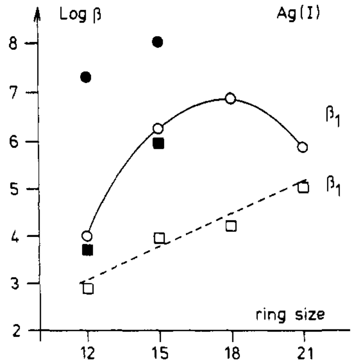

Figure 1. Stability constants (log β_i) of silver(I) coronates and podates, in propylene carbonate at 298.2 K and μ = 0.1 (TEAP), vs the ring or chain size: coronates, ○ (β_1) and ● (β_2); podates, □ (β_1) and ■ (β_2), this work.

plementary material) and contained between 10 and 20 ppm of water.

Lanthanide Trifluoromethanesulfonates, Ln(trif)$_3$. Approximately 1 g (5.4 mmol Ln) of pure lanthanide (Ln) oxide (Apache Chemicals, 99.9%, Ln = Nd, Er, Yb; Research Chemicals 99.99%, other Ln's) was dispersed in 16 mL of H_2O. A solution of 2.4 g (16 mmol) of triflic acid (Fluka, purum) in 1.5 mL of H_2O was added dropwise under stirring. The resulting mixture was heated for 4 h at 80 °C and filtered to remove the unreacted oxide, the resulting solution evaporated under vacuum giving a solid that was dried for several days in a desiccator over KOH and $CaCl_2$ (10^{-1} mmHg). Dehydration of the triflates was achieved by stepwise heating under high vacuum (10–30 days; final temperature 60–80 °C, final vacuum 5×10^{-6} mmHg). Care must be exercised to avoid decomposition of the salts. The final products contained, on average, 0.2–0.5 molecule of H_2O/Ln(III) ion. They were stored in sealed ampules.

Other Salts. Silver perchlorate (Fluka, puriss) was dried 24 h at 40 °C and 24 h at 60–70 °C under vacuum (2×10^{-2} mmHg). Potentiometric titrations with KCl indicated a water content smaller than 0.01 molecule of H_2O/Ag(I) ion. Tetraethylammonium perchlorate (TEAP; Fluka purum) was purified according to ref 11 and dried under vacuum similarly to $AgClO_4$ or under high vacuum, at room temperature (1 week). *Caution*! anhydrous $AgClO_4$ and $(Et_4N)ClO_4$ are highly explosive! Avoid any contact with grease and overheating.

Ligands. Polyethers 12C4, 12P4, 15C5, 15P5 (Fluka, purum), 18P6, 21P7 (Riedel-De-Haën), and 21C7 (Parish Chemical Co.) were heated under vacuum at 50–70 °C and distilled under vacuum in a predried apparatus (10^{-1}–10^{-2} mmHg). The purity of 15C5 was checked by gas chromatography, mass spectrometry (chemical ionization with NH_3), and ^1H NMR spectroscopy. Crown ether 18C6 was purified by recrystallization of its adduct with CH_3CN.[15]

Potentiometric Measurements. Solutions were prepared under controlled atmosphere (KSE glovebox; <10 ppm of water). The Ln content was checked by ICP-AES (Perkin-Elmer 6500, Ventron standards), and the water concentration was measured before and after the measurements (Karl Fischer titration; 20–40 ppm of H_2O). Titrations were carried out in the glovebox at (25 ± 0.2) °C with a Metrohm E632 potentiometer, using the following setup:

$$\mathrm{Ag/AgClO_4}\ (C_{Ag}),\ \mathrm{Ln(III)}\ (C_{Ln}),$$
$$\mathrm{TEAP\ 0.1\ M\ \|\ TEAP\ 0.1\ M/TEAP\ 0.09\ M,\ AgClO_4\ 0.01\ M/Ag}$$

For the measurements, 20 mL of ca. 10^{-3} M Ln(trif)$_3$ in PC containing 0.1 M TEAP were introduced into the cell; 1 mL of 0.02 M $AgClO_4$ was added by 0.05-mL increments, and the potential was read. These values were fitted to the Nernst equation (program ENZFITTER;[16] IBM PS/2-60 computer with mathematical coprocessor) in order to determine the reference potential $E°$ (typical values 138–142 mV). The ligand solution (0.8–1.5 mL; 0.05–0.1 M) was then added by 0.025–0.05-mL increments. Refer to Figure F2 (supplementary material) for a typical titration curve. Calculations were performed with the SUPERQUAD[17] program using unit weights (mainframe computer version for a VAX 8550 or IBM PS/2 version). Several chemical models were tested in each case in order to ascertain the number of complex species (especially 1:1 and 1:2) in equilibrium. The data reported in the tables are averages of two to four titration curves. Calculations using MINIQUAD[18] led to values differing by 0.1–0.3 logarithmic unit.

Table I. Stability Constants of the 1:1 and 1:2 Silver and Lanthanide Coronates, in Anhydrous Propylene Carbonate at 298.2 K and μ = 0.1 (TEAP)

L	M	log β_1 (±σ)	log β_2 (±σ)	L	M	log β_1 (±σ)
12C4	Ag	3.98 ± 0.01	7.29 ± 0.01	18C6	Sm	8.23 ± 0.09
15C5		6.24 ± 0.04	8.01 ± 0.06		Eu	8.07 ± 0.15
18C6		6.86 ± 0.01	*a*		Tb	7.99 ± 0.06
21C7		5.79 ± 0.01	*a*		Lu	7.20 ± 0.06
12C4	Dy	5.13 ± 0.01	6.30 ± 0.06	21C7	La	7.61 ± 0.15
	Er	4.85 ± 0.02	*b*		Pr	7.30 ± 0.08
15C5	La	6.38 ± 0.01	10.91 ± 0.01		Nd	7.55 ± 0.09
	Pr	6.97 ± 0.03	10.28 ± 0.03		Sm	7.46 ± 0.17
	Sm	7.34 ± 0.05	9.28 ± 0.11		Eu	7.14 ± 0.07
	Tb	7.10 ± 0.03	*b*		Tb	6.59 ± 0.03
	Er	7.50 ± 0.06	*b*		Ho	6.51 ± 0.03
	Yb	7.25 ± 0.03	8.78 ± 0.17		Er	6.10 ± 0.03
	Lu	7.50 ± 0.04	*b*		Tm	6.25 ± 0.02
					Lu	5.78 ± 0.03

[a] No 1:2 complex. [b] 1:2 complex not detected.

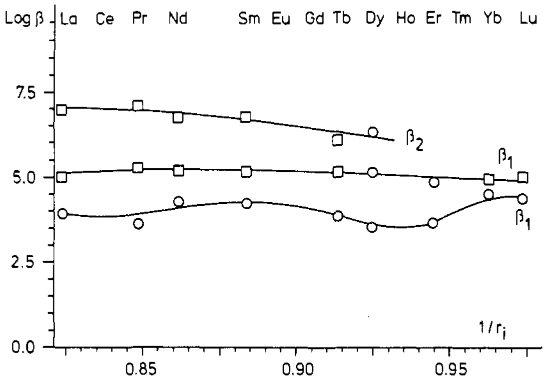

Figure 2. Stability constants (log β_i) of Ln(III) complexes with 12C4 and 12P4, in propylene carbonate at 298.2 K and μ = 0.1 (TEAP), vs the reciprocal of the ionic radius (CN = 9). Top two curves: 12C4 coronates, (□) data from ref 10, (○) this work. Bottom curve: 12P4 podates, (○) this work.

Stability Constants of the Coronates

Silver(I) is known to be involved in stable complexes with crown ethers in various solvents. Since these complexes have a stability comparable to that of the lanthanide coronates, we have selected Ag(I) as auxiliary cation for the potentiometric determination of the stability of the rare earth adducts. The stability constants of the silver coronates are reported in Table I and Figure 1. With 12C4 and 15C5, both 1:1 and 1:2 complexes are detected. The stability of the 1:1 coronates increases markedly in going from 12C4 to 15C5 and reaches a maximum for 18C6. In this complex, the fit between the ionic diameter and the ligand cavity diameter is ideal, being around 1. The stability of the 21C7 coronate is lower by 1 order of magnitude. Considering both 1:1 and 1:2 complexes, however, the 15C5 ligand appears as the best complexing crown ether for Ag(I). Data on 12C4 and 21C7 coronates have not yet been reported, but our values are in good agreement with literature data for 18C6 (log β_1 = 7.05[19] or 7.10[11]) and 15C5 (log β_1 = 5.67[11]). This latter value was obtained under experimental conditions that prevented the observation of the 1:2 complex.

Turning now to lanthanide coronates, the data for 12C4 complexes listed in Table I fit very well within the series of stability constants reported by Massaux and Desreux (Figure 2).[10] These authors have detected 1:2 complexes down to Tb(III). According to the presently reported measurements, 1:2 coronates are also

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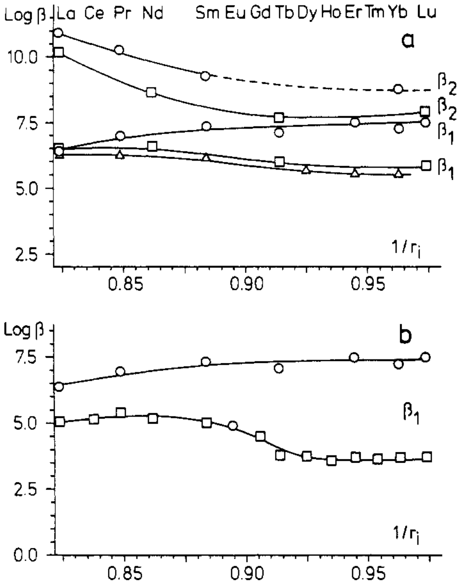

Figure 3. Stability constants (log β_i) of 15C5 and 15P5 complexes, in propylene carbonate at 298.2 K and μ = 0.1 (TEAP), vs the reciprocal of the ionic radius (CN = 9). (a) 15C5 coronates: (□) data from ref 10, (△) data from ref 11, (○) this work. (b) log β_1 values: top, 15C5 coronates, this work; bottom, 15P5 podates, (□) data from ref 12, (○) this work.

observed for Dy(III). The difference between log β_2 and log β_1 is decreasing along the Ln series and from Dy(III) on, log β_2 is too close to log β_1 to observe the 1:2 coronates with the chosen ligand and metal concentrations. In fact, 1:2 complexes have been isolated for the entire La–Lu series and characterized in solution by NMR spectroscopy.[20]

The radius of the internal cavity of 15C5 is estimated to be 0.85–1.1 Å, that is ca. 0.25 Å larger than the 12C4 cavity radius. This is still insufficient to encapsulate the Ln(III) ions, and 1:2 complexes are again observed (Figure 3a). However, the measured log β_2 values decrease with increasing atomic number, whereas log β_1 tends to increase. The concentration of the 1:2 coronate is therefore quite small in the heavier lanthanide solutions, which may explain the nonconvergence of the mathematical treatment for Tb, Er, and Lu when a two-complex model is provided. Isolation of the 1:2 complexes from acetonitrile solution has been reported down to Eu(III) with perchlorate as counteranion[21] and down to Gd with hexafluorophosphate.[22] The constants we report are somewhat at variance with the data already published in the literature. Almasio et al.[11] have only observed 1:1 complexes for the entire Ln(III) series and for Ag(I); these authors have, however, operated under slightly different experimental conditions, which did not allow them to detect the 1:2 complexes. On the other hand, Massaux and Desreux[10] report the formation of both 1:1 and 1:2 complexes for all the Ln(III) cations they investigated (La, Nd, Tb, Lu), but the log β_i values they found are smaller by up to 1.7 logarithmic units. We note that the larger the log β, the smaller the discrepancy. This might eventually be traced back to the use of different auxiliary cations, namely Tl(I) and Pb(II). The 15C5 coronates with this latter have a particularly large stability (log β_2 = 16.55) and the potential of the amalgam electrode was somewhat unstable.[10,23] The water content of the solutions may also play an important role. We have shown, for instance, that the stability constant of the 18C6 coronate with Sm(III) decreases by 0.85 logarithmic unit when the water content of the solution is increased from 50 to 280 ppm.[24]

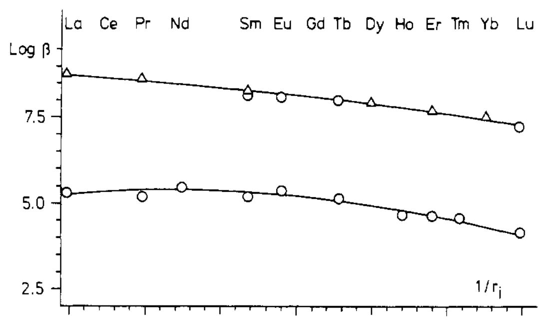

Figure 4. Stability constants (log β_1) of 18C6 and 18P6 complexes, in propylene carbonate at 298.2 K and μ = 0.1 (TEAP), vs the reciprocal of the ionic radius (CN = 9): top, 18C6 coronates, (△) data from ref 11, (○) this work; bottom, 18P6 podates, this work.

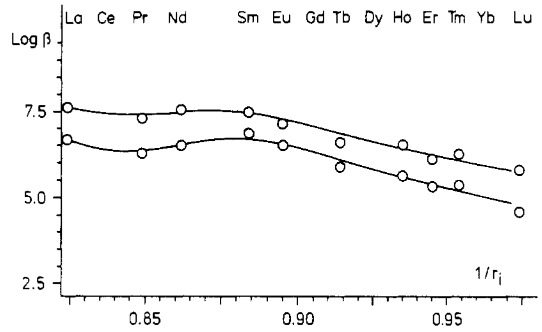

Figure 5. Stability constants (log β_1) of 21C7 and 21P7 complexes, in propylene carbonate at 298.2 K and μ = 0.1 (TEAP), vs the reciprocal of the ionic radius (CN = 9): top, 21C7 coronates, this work; bottom, 21P7 podates, this work.

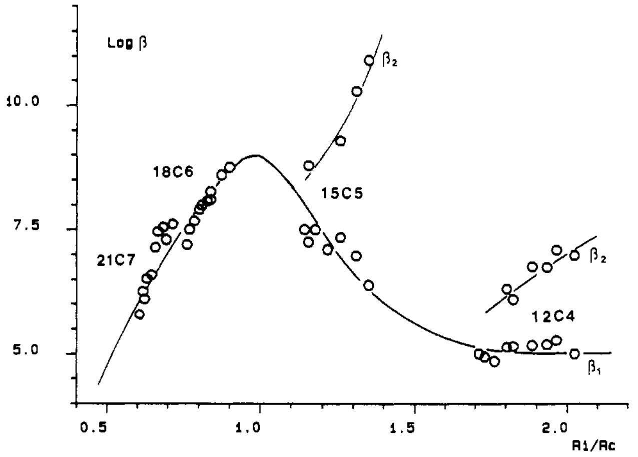

Figure 6. Stability constants (log β_i) of Ln(III) coronates vs the ratio ionic radius (CN = 9) to cavity radius, r_i/r_c.

The data for the 18C6 coronates of Sm, Eu, Tb, and Lu are in close agreement with the stability constants reported by Almasio et al.[11] for Sm and five other Ln(III) ions (Figure 4). They confirm the monotonous decrease of log β_1 down the lanthanide series. As expected, the stability of the lanthanide complexes with the 21C7 ether is smaller than that of the 18C6 coronates. The general trend of the log β_1 vs $1/r_i$ curve is however slightly different (cf. Figure 5). The stability of the 21C7 adducts is more or less constant up to Sm and then decreases more sharply than for the 18C6 complexes. As a result, the stability difference with 18C6 coronates, which amounts to 1.6 logarithmic units for La, first decreases to 0.6 unit for Sm and then increases again to ca. 1.6 units toward the end of the series.

As a whole, all the stability data reported for these unsubstituted coronates may be explained on the basis of a fairly simple model,

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[20] Desreux, J. F.; Duyckaerts, G. *Inorg. Chim. Acta* **1979**, *35*, L313.

[21] Bünzli, J.-C. G.; Oanh, H. T. T.; Gillet, B. *Inorg. Chim. Acta* **1981**, *53*, L219.

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[23] The ligand 15C5 was purified by distillation by both research groups. We have checked its purity by several methods (NMR, MS, IR, and GC).

[24] Pilloud, F. Ph.D. Thesis, University of Lausanne (1988).

[25] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Table II. Stability Constants (log $\beta_1 \pm \sigma$) of the 1:1 Silver and Lanthanide Podates, in Anhydrous Propylene Carbonate at 25 °C and $\mu = 0.1$ (TEAP)

M	log β_1			
	12P4	15P5	18P6	21P7
Ag	2.83 ± 0.01 3.73 ± 0.06[a]	3.93 ± 0.01 5.94 ± 0.13[a]	4.44 ± 0.01	5.02 ± 0.01
La	3.92 ± 0.05		5.30 ± 0.14	6.68 ± 0.03
Pr	3.64 ± 0.08		5.19 ± 0.10	6.27 ± 0.02
Nd	4.29 ± 0.12		5.46 ± 0.16	6.49 ± 0.03
Sm	4.25 ± 0.15		5.18 ± 0.17	6.84 ± 0.07
Eu		4.96 ± 0.02	5.36 ± 0.13	6.50 ± 0.04
Tb	3.90 ± 0.09		5.14 ± 0.04	5.87 ± 0.03
Dy	3.58 ± 0.12			
Ho			4.66 ± 0.10	5.62 ± 0.03
Er	3.70 ± 0.11		4.63 ± 0.03	5.31 ± 0.03
Tm			4.56 ± 0.08	5.34 ± 0.02
Yb	4.56 ± 0.17			
Lu	4.41 ± 0.17		4.14 ± 0.03	4.57 ± 0.03

[a] log β_2.

namely the fit between the cation ionic radius and the radius of the internal cavity of the macrocycle.[6] This is shown in Figure 6, in which the stability constants are plotted against this ratio r_i/r_c. The cavity radii r_c have been taken from known estimations.[6] The ionic radii change with the coordination number,[26] but since this latter is not known in solution, we have chosen r_i values corresponding to a coordination number of nine. Owing to the uncertainty on r_c values resulting from the flexibility of the ligands, this restriction does not affect significantly the shape of the curve depicted in Figure 6. As far as log β_1 values are concerned, the maximum stability is effectively observed when r_i/r_c is close to unity, which explains the larger stability of the 18C6 complexes with the lighter lanthanide ions. For heavier lanthanide ions, both 15C5 and 18C6 have approximately the same complexing strength. When 1:2 complexes are taken into account, however, the 15C5 ether is clearly the best ligand for Ln(III) ions, maybe because these may then achieve a more convenient coordination number, namely around 10–12 (taking the anion coordination into account).[6]

Stability Constants of the Podates

The data pertaining to Ag(I) and Ln(III) podates are reported in Table II and displayed in Figures 1–5. Silver complexes with a 1:2 stoichiometry could be observed with both 12P4 and 15P5 podands. The stability of the silver(I) podates increases regularly with the number of donor atoms, reflecting the ability of the open-chain ligands to wrap around the metal ion. As for the cyclic ethers, the best complexing agent is the 15-membered ligand.

Generally speaking, the lanthanide podates are less stable than the corresponding coronates, and no 1:2 complexes have been evidenced. Moreover, the stability sequence is different from that observed with the coronands. As for Ag(I), the stability constants usually increase with the number of donor atoms, but this rule does not always hold. The 15P5 and 18P6 podates of the lighter rare earths (La–Sm) have approximately the same stability, as well as the 12P4 and 15P5 podates of the Tb–Er ions, and finally, the 12P4 podates of the heavier lanthanides (Tm–Lu) are more stable than the 15P5 podates. Within the series of podates, one notes different shapes of the curves log β vs $1/r_i$. For 12P4 complexes, it adopts a sinuslike behavior with two minima around Pr and Ho and two maxima around Sm and Yb. Since these complexes have a comparatively low stability, quantum effects may play a role in these small variations.[26] Only one stability constant was determined with the 15P5 podand, namely for Eu, which was not investigated previously. The log β value obtained (4.96 ± 0.02) fit very well into the data published by Barthélemy et al.[12] (Sm, 5.03 ± 0.06; Gd, 4.49 ± 0.06), so that we have not remeasured the other constants. The sharp drop in the 15P5 curve between Sm and Tb (Figure 3) is unusual in lanthanide chemistry[12] and may reflect a change in the structure of the complexes, possibly due to the repulsion of the two methyl groups. Indeed, crystal structure determinations on complexes of lanthanide nitrates with 18P6[27] and pentaethylene glycol[28] show the ligand forming a ring as in the corresponding coronates. When the ionic radius decreases, the ligand must contract, hence the possible steric conflict between the methyl groups. For longer podates, such as 18P6 and 21P7, the problem can be partly overcome by the adoption of a helixlike conformation, which explains the smaller drop observed between Eu and Lu in the plots of Figures 4 and 5. The decrease in stability with increasing atomic number is a trend opposite to what is usually observed in lanthanide coordination chemistry with classic ligands[12] and exemplifies the cyclic nature of the podates.

Table III. Macrocyclic Effect, Δ(log β_1), for Ag(I) and Ln(III) Complexes with Crown Ethers, in Anhydrous Propylene Carbonate at 298.2 K and $\mu = 0.1$ M (TEAP)

M	Δ(log β_1)			
	21C7 – 21P7	18C6 – 18P6[a]	15C5 – 15P5[b]	12C4 – 12P4[c]
Ag	0.75 ± 0.02	2.42 ± 0.02	2.31 ± 0.05	1.85 ± 0.02
La	0.93 ± 0.18	3.45 ± 0.24	1.33 ± 0.06	1.08 ± 0.17
Pr	1.03 ± 0.10	3.41 ± 0.20	1.57 ± 0.08	1.63 ± 0.16
Nd	1.06 ± 0.12			0.90 ± 0.21
Sm	0.62 ± 0.24	3.05 ± 0.26	2.31 ± 0.11	0.92 ± 0.25
Eu	0.64 ± 0.11	2.71 ± 0.48		
Tb	0.72 ± 0.10	2.85 ± 0.10	3.30 ± 0.18	1.25 ± 0.22
Dy				1.55 ± 0.13
Ho	0.89 ± 0.06			
Er	0.79 ± 0.06	3.04 ± 0.13	3.77 ± 0.12	1.15 ± 0.13
Tm	0.91 ± 0.04			
Yb			3.55 ± 0.16	0.38 ± 0.26
Lu	1.21 ± 0.06	3.06 ± 0.09	3.78 ± 0.10	0.59 ± 0.28

[a] Data for La, Pr, and Er coronates are taken from ref 11. [b] Data from ref 10 and 12, except that for Eu. [c] Data for 12C4 are taken from ref 10, except those for Dy and Er.

Macrocyclic Effect

The additional stability of the coronates with respect to the corresponding podates has been named the macrocyclic effect.[29] Its origin, enthalpic or entropic, remains unclear, although several explanations have been proposed, including solvation and counteranion effects, kinetic differences, and structural and steric effects. As already stated, few experimental data have been gathered to study the macrocyclic effect in lanthanide macrocyclic complexes, but for the investigation of Barthélemy et al.[12] on 15-membered ligands and the work of Loufouilou et al.[30] on the macrobicyclic effect in rare-earth cryptates. One difficulty in such studies is the choice of the podand, which should be as similar as possible to the coronand and, moreover, which should form complexes structurally similar to the corresponding coronates. In this respect, the investigated podands seem to be adequate, being identical with the coronands, but for one C-C bond and the terminal methyl groups introducing some steric repulsion between the two ends of the molecules. The structures of both the coronates and podates are not known in solution. Depending upon the counteranion, however, coronates may exist as $[LnLX_2]^+$ complexes.[6] We have performed conductometric measurements on solutions of trifluoromethanesulfonates with and without ligand. In all cases, the solutions behaved as 2:1 electrolytes.[24,31] Since the coordination ability of perchlorate anions, used as supporting electrolyte, is quite close to that of trifluoromethanesulfonate,[32] we assume that the investigated podates and coronates exist

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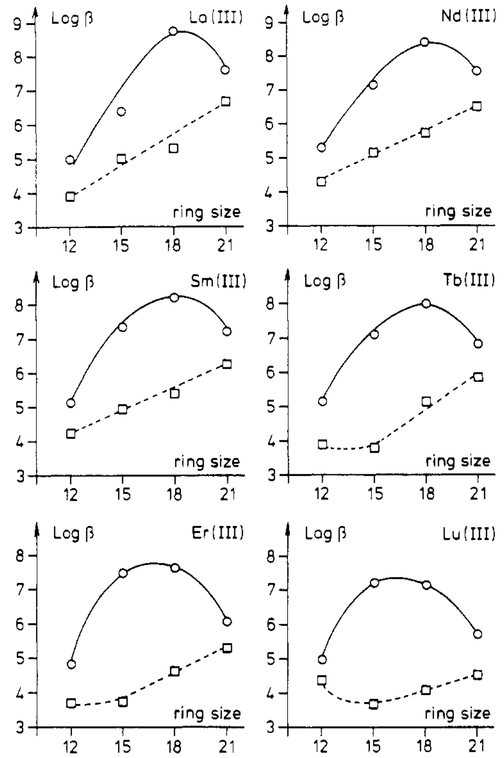

Figure 7. Stability constants of Ln(III) coronates and podates vs the ring or chain size: data for 15P5 podates, ref 12; data for 12C4 coronates (except for Er), ref 10; data for the La 18C6 coronate, ref 11; data for the Nd 15C5 and 18C6 podates, interpolated from ref 11 and our data.

predominantly as $[LnLX]^{2+}$ complexes. We cannot, however, exclude the presence of some $[LnLX_2]^+$ species, and small variations of the stability constants of the podates or coronates within the lanthanide series may arise from differences in the coordination of the counteranion.

Relevant data for the macrocyclic effect are reported in Table III; the variation along the series of complexes may be seen in Figures 2–5, whereas the dependence of this effect upon the ring or chain size is depicted in Figure 1 for Ag(I) and in Figure 7 for selected Ln(III) ions. The magnitude of the macrocyclic effect for the Ag(I) coronates follows the stability sequence of the latter, going through a maximum for 18C6. This is expected if the leading effect in the stability is the fit between the ionic radius and the cavity radius. In this respect, the strong macrocyclic effect in the 15C5 complex is somewhat surprising. The stability differences are, however, relatively small: in 99% methanol, the macrocyclic effect reported for 18C6 coronates amounts to $\Delta(\log \beta_1) = 3.3$, 3.8, and 4.5 for Na(I), K(I), and Ba(II), respectively.[33,34]

To a first approximation, the macrocyclic effect for the lanthanide complexes is constant, within experimental errors, for 12C4 ($\Delta(\log \beta_1) \simeq 1.0 \pm 0.3$), 18C6 ($3.1 \pm 0.2$), and 21C7 ($0.9 \pm 0.2$). For 15C5 coronates, the macrocyclic effect increases by a factor of 200 between La and Tb, and then remains almost constant, with a magnitude 5 times larger than that for the 18C6 adducts. The gradual shift of the maximum of stability from the 18C6 coronates with lighter Ln(III) ions to the 15C5 complexes with the heavier rare-earth metals is clearly illustrated in Figure 7. We interpret these data as reflecting two main influences on the $\Delta(\log \beta_1)$ values. The first one is the fit between the ionic radius and the ligand cavity, which is best for 18C6 complexes and for the 15C5 adducts with the heavier lanthanide ions. The relative constancy of the macrocyclic effect along the 18C6 series is due to the flexibility of the ligand, which adapts itself to the lanthanide contraction. The same explanation would hold for the 21C7 complexes, whereas the approximate constancy of the macrocyclic effect for the 12C4 coronates arises from the nonencapsulation of Ln(III) ions by this small crown ether. The second parameter is related to structural changes in the complexes with 15-membered ligands. We have already postulated that such a change occurs between Sm and Tb, resulting in less stable coronates. This contributes to the corresponding increase in $\Delta(\log \beta_1)$, whereas the increase at the beginning of the series is attributable to the increasing stability of the coronates. Here again, this may be thought of as arising from a structural effect since the cations are getting closer to encapsulation when the ionic radius decreases.

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Supplementary Material Available: Absorption spectrum of anhydrous propylene carbonate (Figure F1) and a typical titration curve for the system Sm/Ag/15C5 (Figure F2) (2 pages). Ordering information is given on any current masthead page.

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(33) We have chosen these comparison data because the complexes have a stability comparable to that of the lanthanide 18C6 coronates: $\log \beta_1 = 4.33$, 6.05, and 7.00 for Na(I), K(I), and Ba(II), respectively.[34]

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