that they now consist of the n(NH_2) fragment orbital interacting with the π-CH_2 (σ-bonding) orbital. This is a four-electron interaction, and its net result is destabilization. Thus, torsion about the N-C bond gradually decreases the stabilizing effect of hyperconjugation and at the same time increases the repulsive four-electron interaction between the nitrogen lone pair and the π-CH_2 orbital.

Conclusion

We have tested experimental criteria for the definition of negative hyperconjugation in neutral molecular model systems. These criteria are as follows: (a) the stabilization energy (total energy); (b) changes in geometry (bond lengths and angles); and (c) charge transfer. We find the first two criteria to be useful in the definition of hyperconjugation, and the third one, transfer of charge, we find to be of lesser importance.

Analysis of the MO's of hyperconjugated and nonhyperconjugated conformations of **6**, **7**, and **8** provides an insight into the phenomenon: the VB concept of hyperconjugation, as expressed in **2a** and **2b**, is translated into the HOMO orbital. The effects of hyperconjugation in neutral systems such as these can be expected as long as (a) X is sufficiently electronegative and (b) the changes in HOMO dominate the behavior of the molecule.

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An Electrochemical Investigation of the Effect of Macrocycle Ring Size on the Binding of Di- and Trivalent Lanthanide Cations by 12-Crown-4, 15-Crown-5, 4-*tert*-Butylbenzo-15-crown-5, and Dibenzo-30-crown-10 in Propylene Carbonate

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Abstract: The complexation in anhydrous propylene carbonate of the lanthanide ions by various macrocyclic polyethers featuring from four to ten oxygen atoms has been investigated by a competitive potentiometric technique with lead(II) or thallium(I) as auxiliary ions. The stability of the complexes appears to depend primarily on the relative sizes of the metal ions and of the internal cavity of each macrocycle. It depends also on the rigidity of the ligands and is influenced by solvation effects. The small ligands 12-crown-4 (**1**) and 15-crwon-5 (**2**) exhibit a similar behavior: they form 1:2 lanthanide complexes, the stability of which decreases with decreasing ionic radius despite the higher charge density of the metal ions. The presence of an electron-withdrawing phenyl group, as in 4-*tert*-butylbenzo-15-crown-5 (**3**), leads to a strong reduction of the stability constants. A maximum stability of 1:1 complexes of **3** is found at Nd(III) while a marked minimum is observed at Gd(III) in the complexation curve of dibenzo-30-crown-10 (**5**). Divalent samarium and ytterbium are more strongly coordinated than the corresponding trivalent ions by the crown ethers **1**–**5**. The larger divalent ions fit better into the internal cavity of **5** and they form stable 1:2 sandwich complexes with **1** and **3**. The properties of the complexes described in the present work are completely different from those reported so far in the case of noncyclic ligands.

The advantages of using macrocyclic compounds as ligands of the alkali-metal ions are now well documented.[1-2] Much less attention has been focused on the complexes formed between the lanthanide ions and the macrocycles, although it has been demonstrated in several recent reports that the crown ethers[3] and the cryptates[4,5] can also bind the lanthanides by sequestering them within their internal cavity. In a previous communication,[6] we discussed the complexation of the lanthanide cations by 4,4'-(5')-di-*tert*-butylbenzo-18-crown-6 in anhydrous propylene carbonate. The stability constants of 1:1 complexes were found to decrease regularly through the lanthanide series. A similar behavior was noted[7] in the case of 18-crown-6 in partially hydrated methanol. The opposite trend has been reported for all the more familiar, noncyclic complexing agents such as the polyaminopolycarboxylic acids or the β-diketones.[8] Another intriguing feature of the complexing properties of 4,4'(5')-di-*tert*-butylbenzo-18-crown-6 is its ability to bind more strongly divalent samarium and ytterbium than the corresponding trivalent ions.[6] The stabilization of the +2 oxidation state of europium in aqueous solution by various cryptates has also been observed recently.[5] These stabilization effects contrast significantly with the properties of the noncyclic ligands which always complex better with the trivalent lanthanides.[8]

Except for the data cited above, no measurements of the stability constants of crown ether complexes of di- and trivalent lanthanides have been carried out. The aim of the present research work is to rectify this situation. We investigated the complexation of the lanthanide ions in anhydrous propylene carbonate by the small ligand 12-crown-4 (**1**), by the medium size cycle 15-crown-5 (**2**) and its substituted derivative 4-*tert*-butylbenzo-15-crown-5 (**3**),

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and finally by the very large macrocycle dibenzo-30-crown-10 (**5**) (see Figures 1–4 for the structure of the ligands). This systematic study should provide clues to the relationship between the structure of the crown ethers and their unusual complexation behavior toward lanthanide ions of varying size.

Experimental Section

Materials. As described earlier,[6,9] all solutions were manipulated under nitrogen in a recirculating atmosphere drybox. The ligands 12-crown-4 and 15-crown-5 (Aldrich) were purified by distillation under vacuum; 4-*tert*-butylbenzo-15-crown-5 and dibenzo-30-crown-10 (Parish Chemical Co.) were used after recrystallization and drying. The purity of each compound was checked by elemental analysis and by vapor-phase osmometry. Further details on the preparation of solutions for electrochemical measurements are given elsewhere.[6,9]

Procedure and Calculations. The stability constants β_n of the lanthanide (Ln^{3+}) complexes with a macrocycle L were determined in anhydrous propylene carbonate at 25 °C (ionic strength adjusted to 0.1 with tetraethylammonium perchlorate) by a competitive potentiometric method,[6] using either Pb(II) or Tl(I) as auxiliary ions (Me^{n+}). The equilibrium position of the reaction

$$MeL^{n+} + Ln^{3+} \rightleftarrows LnL^{3+} + Me^{n+}$$

was altered by the addition of various aliquots of lanthanide trifluoromethanesulfonate solutions.[10] The new equilibrium positions were determined by measuring the potential of an amalgam Tl(I) or Pb(II) mercury electrode against a $Ag|AgClO_4$ reference electrode.[6] Most often, lead was the best auxiliary ion. However, if the presence of lanthanide complexes of 1:1 and 1:2 stoichiometries was suspected, two series of potentiometric measurements were carried out: in one of these, Pb(II) was the auxiliary ion, while in the other one, Tl(I) was used for that purpose. Lead macrocyclic complexes are exceedingly stable and under our experimental conditions $[Ln]_{tot} < 3.5 - 2.5([L]_{tot} + [Pb]_{tot})$, where $[Ln]_{tot}$ ranges from 10 to 30 mM and LnL and PbL_2 were the main species in solution. On the other hand, the stability of the Tl(I) complexes is either lower than or comparable to the stability of the lanthanide complexes. Relatively high concentrations of the LnL_2 species (30 to 70% of $[Ln]_{tot}$) could then be reached in the conditions $[L]_{tot} < 3 - 2.5([Ln]_{tot} + [Tl]_{tot})$, where $[L]_{tot}$ ranges from 20 to 50 mM. The combined experimental data (15–25 points) were interpreted by a non-linear best-fit procedure based on the Simplex approach.[12] The difference between the experimental and the computed potentials did not exceed 4–7 mV in the worst cases.

The values of the stability constants of the Tl(I) and Pb(II) complexes are necessary for the interpretation of the measurements mentioned above. These values were determined with a pool amalgam mercury electrode obtained by electrolysis of Tl(I) or Pb(II).[6,9] All the Pb(II) and Tl(I) electrochemical systems investigated here were found to follow Nernst's law within the limits of the experimental errors. The stability constants of 1:1 and 1:2 complexes were deduced by the method proposed by DeFord and Hume.[13]

The polarographic measurements were performed as described elsewhere.[9] The stability of 1:1 and 1:2 complexes of divalent samarium and ytterbium was computed by DeFord and Hume's method.[13] A determination of the stability of the Eu(II) and Eu(III) complexes could not be achieved in propylene carbonate by potentiometry or by polarography either because of the reduction by the Pb(II) or Tl(I) amalgams or because the III → II polargraphic wave of complexed europium is displaced beyond the oxidation wave of mercury.[6]

Results and Discussion

Lead(II) and Thallium(I) Complexes. Lead(II) and thallium(I) are known to be involved in stable complexes with various crown ethers in water or in methanol–water mixtures[14] and they form mercury amalgam electrodes which follow Nernst's law. Pb(II) and Tl(I) were thus selected as auxiliary ions for the potentiometric determination of the stability of the lanthanide complexes with ligands **1–5**. The stability constants of the Pb(II) and Tl(I) crown ether adducts were obtained directly by potentiometry and are presented in Table I. The mathematical treatment proposed by DeFord and Hume[13] was applied to the calculation of these stability constants. If complexes of stoichiometry 1:1 and 1:2 were present in solution, β_1 was obtained by this method by an extrapolation while β_2 was computed from the value of a slope. Consequently, the error is usually larger on the values of the stability constants of 1:1 complexes. This is particularly true in the case of 15-crown-5. The 1:2 lead complex formed by this ligand is exceedingly stable; the concentration in uncomplexed Pb(II) was thus very low in our experimental conditions and the potential of the amalgam electrode was sometimes unstable. In this particular case, no value of β_1 could be obtained with sufficient accuracy. It was verified that neglecting the PbL species in the computation of the stability constants of the lanthanide complexes had a negligible effect on the values of these constants since the 1:2 lead complex appears to be much more stable than the 1:1 complex and since the calculations were performed simultaneously on the data obtained with the lead and thallium amalgams.

Table I. Stability Constants of the Lead(II) and Thallium(I) Complexes with Crown Ethers in Anhydrous Propylene Carbonate at 25 °C ($\mu = 0.1$)

	Pb(II)		Tl(I)	
ligands[a]	log β_1	log β_2	log β_1	log β_2
1	7.68 ± 0.09	11.70 ± 0.08	3.71 ± 0.06	
2	*b*	16.55 ± 0.19	5.29 ± 0.02	6.74 ± 0.02
3	7.85 ± 0.03	14.39 ± 0.05	4.13 ± 0.06	6.35 ± 0.03
4	9.74 ± 0.04[c]		4.98 ± 0.02	
5	11.45 ± 0.09		5.35 ± 0.02	

[a] Structures of the ligands are presented in Figures 1–4. [b] No data of sufficient accuracy are available, see text. [c] Taken from ref 6.

With an examination of the results shown in Table I, it can be seen that Pb(II) and to a smaller degree Tl(I) form very stable adducts with all the macrocycles investigated in the present work. The high stability of the macrocyclic complexes with these metal ions has already been reported by Izatt et al.[14] and is attributed to the polarizability of these ions and to the covalent character of the bonds they form.

The stability of the thallium complexes with ligands **1–5** is of comparable magnitude in propylene carbonate (see Table I) and in acetonitrile[15] but is much higher than that in protic solvants such as water or methanol.[14] This should be expected since the donor number of acetonitrile is near that of propylene carbonate[16] while protic solvents strongly interact with both the ligands and the metal ions. However, it is pertinent to note that Hofmanová et al.[15] do not mention the formation of a 1:2 Tl(I) benzo-15-crown-5 complex in acetonitrile despite the fact that such complexes with various 15-membered cycles have been isolated in the solid state.[17] On the contrary, 1:2 adducts could not be prepared with dibenzo-18-crown-6 (**4**), in keeping with the data listed in Table I. These data can be rationalized in terms of the relative magnitudes of the internal cavity of each cycle and of the ionic radius of the encapsulated ion. Because of its relatively large internal cavity (ring cavity radius 1.34–1.43 Å), cycle **4** can partially encapsulate the Tl(I) ion (ionic radius 1.50 Å for a coordination number of six[18]) that is thus involved in 1:1 complexes only. On the contrary, cycles **2** and **3** are too small to accommodate even partially the Tl(I) ion and 1:2 adducts of the sandwich type are easily formed. The same stoichiometry was expected in the case of 12-crown-4, (**1**), but no sandwich complex was found

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[9] Massaux, J.; Desreux, J. F.; Duyckaerts, G. *J. Chem. Soc., Dalton Trans.* **1980**, 865–868.

[10] The trifluoromethanesulfonate anion is noncoordinating, see ref 11a and the following: Seminara, A.; Rizzarelli, E. *Inorg. Chim. Acta* **1980**, *40*, 249–256. It is assumed in the present paper that either lanthanide perchlorates and trifluoromethanesulfonates are totally dissociated or the extent of their dissociation is approximately constant throughout the lanthanide series.

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Table II. Stability Constants of the Lanthanide Complexes with 12-Crown-4 (1) and 15-Crown-5 (2) in Anhydrous Propylene Carbonate at 25 °C ($\mu = 0.1$)

Ln-(III)	1		2	
	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$
La	5.00 ± 0.12	6.98 ± 0.15	6.49 ± 0.14	10.18 ± 0.11
Pr	5.27 ± 0.08	7.09 ± 0.10		
Nd	5.19 ± 0.09	6.74 ± 0.12	6.55 ± 0.13	8.65 ± 0.20
Sm	5.17 ± 0.10	6.76 ± 0.14		
Tb	5.15 ± 0.13	6.09 ± 0.20	5.96 ± 0.14	7.66 ± 0.19
Yb	4.94 ± 0.09	*a*		
Lu	5.00 ± 0.11	*a*	5.83 ± 0.16	7.89 ± 0.22

[a] No significant concentrations of 1:2 complexes, see text.

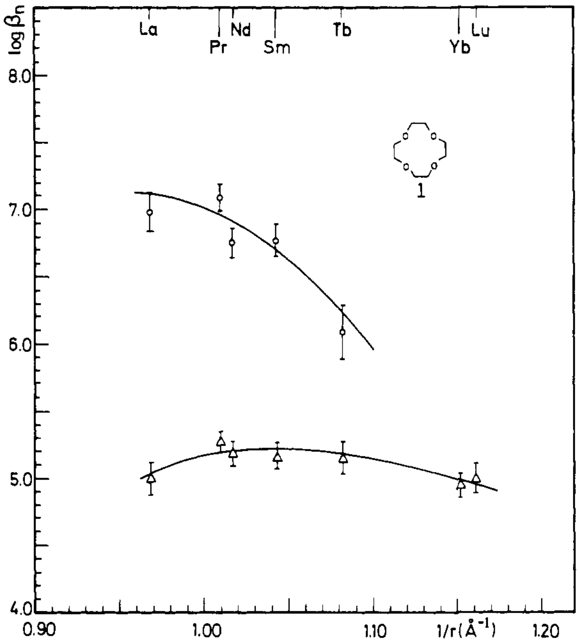

Figure 1. Plots of the stability constants of 1:1 and the 1:2 lanthanide complexes (lower and upper curves, respectively) formed by 12-crown-4 in anhydrous propylene carbonate against the reciprocal of the radius of the metal ions.

under our experimental conditions ($[L]_{tot} < 1.7[Tl]_{tot}$). The lower stability of the adducts with **1** is in agreement with the smaller number of potential coordination sites of this ligand. Likewise, the stability of the complexes increases through the substituted cycles **3**, **4**, and **5**. This phenomenon can also be accounted for by an increasing number of donor atoms, although cycle **5** most probably adopts a nonplanar sterically hindered "wrap around" structure[19] that is less stable than would be anticipated by simply relying on the large number of oxygen atoms of this crown ether.

A similar line of arguments can be followed in the case of lead(II) (ionic radius 1.19 Å[18]), which forms more stable complexes than Tl(I) essentially because of its higher charge.

Lanthanide Complexes with 12-Crown-4 and 15-Crown-5. The stability constants of the complexes formed between 12-crown-4 (**1**) and a few lanthanide cations are collected in Table II and are plotted against the reciprocal of the ionic radius *r* of the complexed cations in Figure 1 (*r* values are those given by Shannon[18] for a coordination number of six). These data were obtained by a best-fit treatment of potentiometric measurements carried out with a Pb(II) and also with a Tl(I) amalgam electrode. The error function did not decrease in the case of Yb(III) and Lu(III) if 1:2 complexes were taken into account in addition to 1:1 complexes. It thus seems doubtful that stable complexes of 1:2 stoichiometry are formed by the smallest lanthanide ions in propylene carbonate under our experimental conditions.

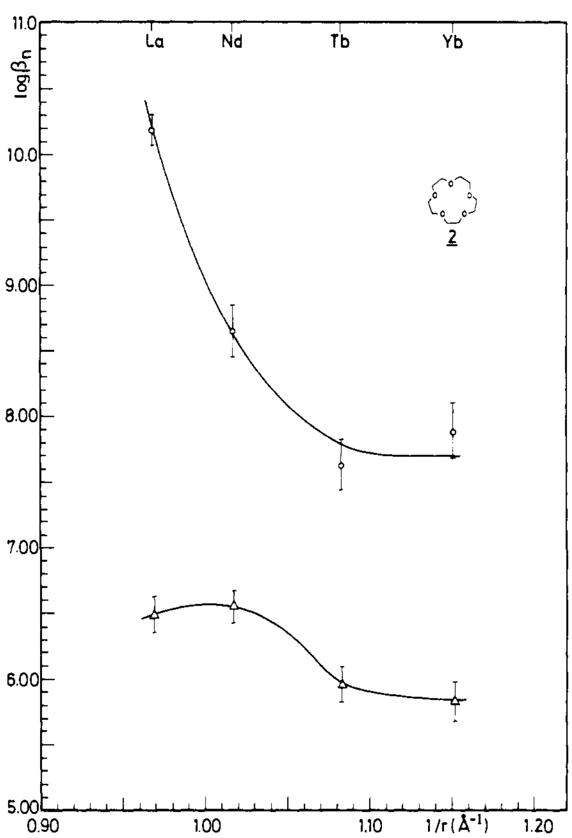

Figure 2. Plots of the stability constants of 1:1 and 1:2 lanthanide complexes (lower and upper curves, respectively) formed by 15-crown-5 in anhydrous propylene carbonate against the reciprocal of the radius of the metal ions.

Several studies have already been devoted to the complexes formed by cycle **1**, despite the fact that this ligand is much too small to encapsulate any of the lanthanide cations (radius of internal cavity 0.57 Å[20]). Adducts of different stoichiometries have been isolated. In the presence of a coordinating anion, for instance the nitrate group, 1:1 complexes were prepared while 1:2 complexes were obtained with all the lanthanide perchlorates.[21-22] NMR studies indicated that 1:2 complexes display a sandwich structure.[21] As appears in Figure 1, the stability of 1:1 complexes with **1** does not depend upon the ionic radius *r* of the complexed ion. A smaller radius and thus a higher charge density of the lanthanides brings about stronger electrostatic interactions with the cycle but also with propylene carbonate, a solvent with a high dipole moment (4.94 D). It appears from Figure 1 that these two effects cancel each other. On the other hand, the stability of the 1:2 sandwich complexes decreases with increasing atomic number. In addition to the competition between **1** and propylene carbonate for the solvation of the metal ions, a structural effect could also account for the rapid decrease in stability. The two cycles of sandwich complexes are brought closer together when *r* decreases and steric interactions are likely to become important at the end of the lanthanide series. Another factor might have to be considered, although its magnitude is difficult to assess in the case of metal ions which form essentially electrostatic noncovalent bonds. In the sodium chloride sandwich complex with **1**, the lone-pair electrons of each oxygen atom are directed toward the Na$^+$ ion.[20] Furthermore, all ethylene groups of each cycle are

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Table III. Stability Constants of the 1:1 Lanthanide Complexes with 4-*tert*-Butylbenzo-15-crown-5 (3) and with Dibenzo-30-crown-10 (5) in Anhydrous Propylene Carbonate at 25 °C ($\mu = 0.1$)

	$\log \beta_1$	
Ln(III)	3	5
La	3.26 ± 0.04[a]	4.29 ± 0.04
Ce	3.62 ± 0.04	4.10 ± 0.03
Pr	3.60 ± 0.08	4.12 ± 0.04
Nd	3.75 ± 0.04	4.10 ± 0.05
Sm	3.45 ± 0.04	3.75 ± 0.03
Gd	3.02 ± 0.05	3.53 ± 0.04
Tb	2.85 ± 0.05	4.07 ± 0.06
Dy	2.90 ± 0.12	
Ho	2.80 ± 0.08	
Er	2.82 ± 0.07	4.48 ± 0.05
Tm	2.81 ± 0.05	
Yb	2.80 ± 0.10	4.76 ± 0.04
Lu	2.80 ± 0.06	4.80 ± 0.05

[a] $\log \beta_2 = 5.91 \pm 0.08$, see text.

fully staggered. It has been postulated that the unusually high stability of the sodium 1:2 complex in propylene carbonate originates from this structural arrangement.[9] If the same orientation of the lone-pair electrons is to be maintained when the ionic radius of the lanthanides decreases, a gradual alteration of the conformation of **1** becomes necessary and should lead to a decrease in stability. The most notable fact about the behavior of **1** is that this crown ether shows a complexation trend which is opposite to the one exhibited by all noncyclic ligands: the overall stability decreases with decreasing ionic radius despite the higher charge density of the metal ions. Notwithstanding its small size, **1** thus shows a macrocyclic effect similar to the one observed with the much larger cycle **4**.[6]

As readily appears from a comparison of Figures 1 and 2, the ligands 15-crown-5 (**2**) and 12-crown-4 (**1**) exhibit a rather similar behavior. The decrease in overall stability displayed by complexes with **2** is ascribed to the structural effects already discussed above. The stability constants of these complexes are presented in Table II. For each lanthanide investigated, a significant improvement in the best-fit treatment was achieved if the presence of both 1:1 and 1:2 complexes was taken into account. The high stability of 1:2 adducts of the larger lanthanide ions with **2** is in keeping with an observation made by Bünzli et al.,[22a] who reported that the complex $Pr(ClO_4)_3(2)_2$ is the only species which can be synthesized even in the presence of an excess of the perchlorate salt. These complexes probably adopt a sandwich conformation similar to the one described for the sodium perchlorate adduct.[23] Both 1:1 and 1:2 complexes with **2** are one to four orders of magnitude more stable than corresponding complexes with **1**. This difference is mainly due to the greater number of coordinating sites of cycle **2**. This ligand is also larger than **1** (radius of internal cavity 0.86–0.92 Å) and could accommodate better the lanthanide cations when forming 1:1 adducts. However, it should be noted that since the exact value of the coordination number of a lanthanide ion complexed by **2** is unknown, it is difficult to estimate its radius. For a coordination number of seven, the smallest lanthanide ions, namely Yb^{3+} and Lu^{3+}, could be nearly completely encapsulated by ligand **2**. On the contrary, the largest metal ions would partially protrude out of the cycle as has been found in the case of the 1:1 sodium perchlorate complex.[23] Furthermore, the increased stability of 1:2 complexes with **2** could also be ascribed in part to the fact that this ligand is less rigid than **1** and can rearrange more easily so as to maintain the lone-pair electrons of its oxygen atoms oriented toward the encapsulated ion.

Lanthanide Complexes with 4-*tert*-Butylbenzo-15-crown-5 and 4,4′(5′)-Di-*tert*-butylbenzo-18-crown-6. An inspection of the data contained in Figures 2 and 3 readily leads to the conclusion that the presence of a phenyl substituent on the 15-membered cycle **2** has a strong depressing effect on the complexation. The stability constants of the lanthanide complexes formed by 4-*tert*-butylbenzo-15-crown-5 (**3**) are listed in Table III; they are several orders of magnitude lower than in the case of the unsubstituted cycle **2**. Moreover, La(III) is the only ion which forms a stable 1:2 complex ($\log \beta_2 = 5.91 \pm 0.08$) in our experimental conditions. The lower stability of the complexes with **3** is ascribed to the electron-withdrawing effect of the phenyl ring and thus to the lower basicity of the oxygen atoms. The substitution also causes a small decrease in cavity size and a greater rigidity of the ligand. It is noteworthy that the complexation curve of **3** exhibits a maximum at Nd(III) followed by a level portion that extends from Tb(III) to Lu(III). Such a curve is a rare but not totally unknown case in lanthanide chemistry. A small maximum is observed at Sm(III) for 1:1 acetate complexes in aqueous solution and at Eu(III) in the presence of benzene-1,2-dioxydiacetate,[24] a ligand which has some common structural features with crown **3**. This maximum probably originates from a delicate balance between the formation of a stable 1:2 complex with La(III); the solvation by propylene carbonate, which increases when the ionic radius of the metal ions decreases; and the encapsulation by the ligand, which follows the same trend.

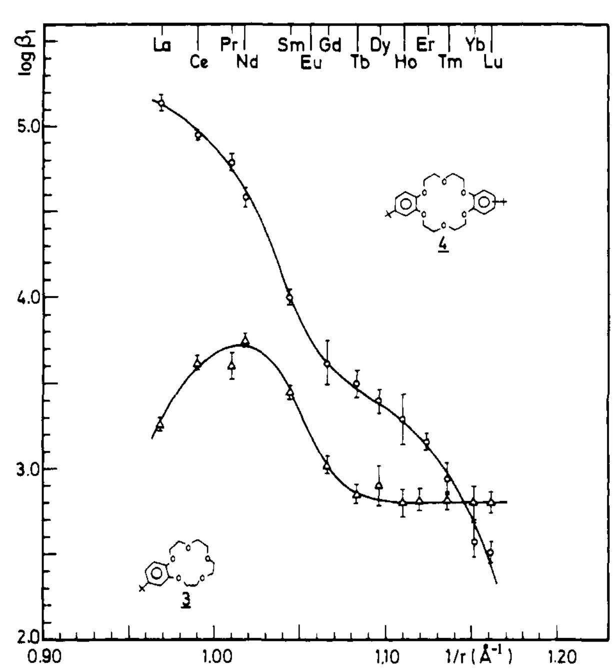

Figure 3. Plots of the stability constants of 1:1 lanthanide complexes formed by 4-*tert*-butylbenzo-15-crown-5 (lower curve) and 4,4′(5′)-di-*tert*-butylbenzo-18-crown-6 (upper curve, taken from ref 6) in anhydrous propylene carbonate against the reciprocal of the radius of the metal ions.

The dependence of the stability constants of 1:1 lanthanide complexes with 4,4′(5′)-di-*tert*-butylbenzo-18-crown-6 (**4**) upon the reciprocal of the ionic radius *r* is also plotted in Figure 3. As described elsewhere,[6] the stability of these complexes decreases regularly through the lanthanide series, presumably because the metal ions are less and less able to fill the large internal cavity of this ligand (radius 1.34–1.43 Å). Such behavior has never been observed with noncyclic ligands. As expected, cycle **4** forms more stable complexes than cycle **3** with the largest metal ions because of its greater number of coordinating sites. However, the reverse is found at the end of the lanthanide series, probably because the very poor fit between the size of the metal ions and of crown **4** becomes a more important factor than the number of coordinating sites.

Lanthanide Complexes with Dibenzo-30-crown-10. Adducts of 1:1 stoichiometry between all lanthanide perchlorates and dibenzo-30-crown-10 (**5**) have been isolated by Ciampolini and Nardi.[25] This very large ligand is highly flexible and can twist

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Table IV. Complexation of Divalent and Trivalent Samarium and Ytterbium by Macrocycles of Varying Size

	log β_n				log β_n			
ligand	n	Sm(II)	n	Sm(III)	n	Yb(II)	n	Yb(III)
1	2	8.4 ± 0.2[a]	1 2	5.17 ± 0.10 6.76 ± 0.14	2	8.3 ± 0.2[a]	1	4.94 ± 0.09
3	2	10.8 ± 0.1[a]	1	3.45 ± 0.04	2	8.4 ± 0.1[a]	1	2.80 ± 0.10
4[b]	1	7.60 ± 0.05	1	4.00 ± 0.04	1	7.31 ± 0.10	1	2.57 ± 0.09
5	1	8.3 ± 0.1	1	3.75 ± 0.03	1	7.5 ± 0.1	1	4.76 ± 0.04

[a] No data of sufficient accuracy are available for the 1:1 complexes, see text. [b] Data taken from ref 6.

around K^+ to form a cavity of smaller size (radius 1.45–1.53 Å[19a]). The same "wrap around" structure has also been reported for the sodium tetraphenylborate complex provided its synthesis is carried out in anhydrous medium.[19b] The formation of these complexes is characterized by a large negative entropy.[1,2] The stability constants of a few 1:1 lanthanide complexes with **5** in propylene carbonate are included in Table III and their dependence on the reciprocal of the ionic radius r is reproduced in Figure 4. The complexation properties of **5** are most unusual since a marked minimum in stability is observed at Gd(III). It is well known that the "gadolinium break", a small decrease in log β around Gd(III), has been observed for a large number of ligands which have no structural features in common.[8] However, the complexation curve presented in Figure 4 is unique in that it can be considered as a "gadolinium break" which extends over the entire lanthanide series.

By analogy to the structural data reported for the sodium complex,[19b] it can be assumed that ligand **5** also adopts a "wrap around" conformation in the presence of the largest lanthanide cations. This nonplanar structure is highly strained and the large intraligand repulsions lead to a reduction in stability. Consequently, ligands **4** and **5** form lanthanide complexes of similar stability despite the much larger number of oxygen atoms of **5**. Moreover, a reduction of the radius of the encapsulated ions causes a further contraction of the internal cavity of **5**; intraligand repulsions become progressively stronger and the stability of the complexes decreases from La(III) to Gd(III). It seems likely that a structural change takes place after Gd(III) because **5** is no longer able to further reduce the size of its internal cavity. Preliminary calorimetric and temperature variation studies indicate that all lanthanide complexes of **5** are enthalpy stabilized and entropy destabilized in propylene carbonate. At the beginning of the lanthanide series (La^{3+}–Gd^{3+}), the formation entropies are nearly constant while the formation enthalpies become less exothermic, thus reflecting weaker interactions between the metal ions and ligand **5**. From Gd^{3+} to Yb^{3+}, both the formation enthalpy and the formation entropy become more negative, the enthalpic stabilization always being greater than the entropic destabilization. The strongly negative value of the entropy change measured for the Yb^{3+} complex (around −200 vs. −60 J(K mol)$^{-1}$ for the La^{3+} complex) might be taken as an indication of a structural change of the ligand and also of the accompanying coordination of molecules of solvent. Further studies aimed at interpreting these data are now in progress.

Complexation of Divalent Sm and Yb. In an earlier paper,[6] it was demonstrated that cycle **4** forms more stable complexes with Sm(II) and Yb(II) than with the corresponding trivalent ions. This very unusual property has been ascribed to the greater ionic radius of the divalent ions that are better able to fill the internal cavity of **4**. The opposite trend has been reported for all the noncyclic ligands which interact more strongly with the trivalent ions because of their higher charge density. Our earlier work[6] has now been extended to ligands **1**, **3**, and **5**. It was found that, whatever the size or the rigidity of their internal cavity, *all these cycles are able to stabilize the +2 oxidation state of samarium and ytterbium.*

The III → II reduction waves of samarium and ytterbium were investigated by polarography as described elsewhere.[6] These waves are shifted toward more positive potentials by the complexation by **1**, **3**, and **5** and are partially irreversible. On the contrary, the reduction waves measured in the presence of crown **4** were found to be fully reversible.[6] Corrections for the partial irreversibility of the reduction waves of complexed and uncomplexed samarium and ytterbium were performed by Gellings' method.[26] As mentioned elsewhere,[9] a comparison of stability constants of the sodium complexes determined by either potentiometry or polarography after correction leads to the conclusion that this method is reliable. In the present study, corrections amounting to 2–15 mV had to be made if the differences between the electrode potential in the presence of complexed and uncomplexed metal ions were of the order of 80–150 mV. For larger differences (150–300 mV), the corrections were in the range 5–20 mV. In the case of ligands **1** and **3**, the stability constants of 1:1 and 1:2 complexes were determined by the method proposed by DeFord and Hume.[13] The accuracy on log β_1 was usually so low that no value of this constant will be given. For comparison purposes, the stability constants of the complexes with di- and trivalent samarium and ytterbium are presented together in Table IV. In all cases, the +2 oxidation state is stabilized.

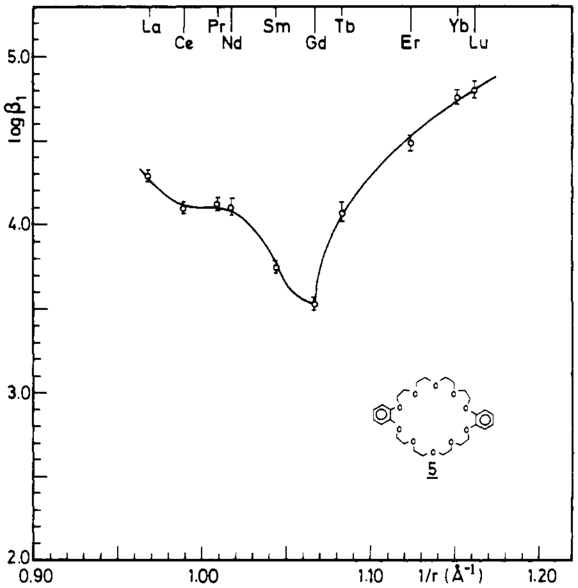

Figure 4. Plot of the stability constants of 1:1 lanthanide complexes formed by dibenzo-30-crown-10 in anhydrous propylene carbonate against the reciprocal of the radius of the metal ions.

The smallest crowns, **1** and **3**, form very stable 1:2 sandwich complexes with Sm(II) and Yb(II). These cations are too large to be accommodated in the cavity of **3** and, of course, of **1**. In view of the results described above, the formation of stable 1:2 complexes was thus expected but it was not anticipated that these complexes would be more stable than the adducts with the trivalent ions. The solvation by propylene carbonate is of course smaller when the charge of the cation is reduced, but a cavity effect should also be taken into account since the addition of a noncyclic ligand such as dimethyl sulfoxide to a solution of Yb(II) in propylene

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carbonate does not lead to the stabilization of the +2 oxidation state.[11b] It can be considered that the larger size of the +2 ions leads to smaller steric interactions between the two cycles of sandwich complexes and thus to an increased stability. Also, as mentioned above in the discussion of the stability of sandwich complexes with **1**, van Remoortere et al.[20] found that the 1:2 sodium adduct with this ligand adopts a particularly stable conformation in the solid state and the authors of the present work reported[9] that this complex is significantly more stable than the complexes formed by the other alkali-metal ions. For a coordination number of eight, the ionic radius of ytterbium increases from 0.98 to 1.14 Å when the metal is reduced from the trivalent to the divalent oxidation state;[18] the new ionic radius is then very near that of Na^+ (1.18 Å). The high stability of the Yb(II) sandwhich complex with **1** might thus be ascribed partially to the formation of an adduct with a conformational arrangement similar to the one of the sodium 1:2 complex.

One of the largest shifts toward the positive potentials (around 300 mV) has been obtained in the reduction of the samarium complex with the very large macrocycle **5**. The cation Yb(II) is also stabilized by this ligand but to a smaller degree. It can be assumed that the divalent ions are better able to fill the internal cavity of **5** when this ligand is in a "wrap around" conformation; these ions are thus complexed more strongly. Furthermore, intraligand repulsions are probably smaller for the Sm(II) complex than for the Yb(II) complex, and accordingly, the stability of the former is higher.

Concluding Remarks

The chemistry of the lanthanides has been thoroughly investigated[8] and the complexation of these metals by a variety of ligands has been shown to follow some common trends, namely that the stability of the complexes increases more or less regularly when the ionic radius decreases and that the divalent lanthanides are involved in less-stable complexes than the trivalent ions. Because of their peculiar structure, the macrocyclic lanthanide complexes exhibit an entirely different behavior which is often quite unexpected. The novel chemistry of the crown ethers, as described in the present paper, is a new addition to the already long list of exciting properties of the macrocycles.[1,2]

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Registry No. 1, 294-93-9; **2**, 33100-27-5; **3**, 15196-73-3; **5**, 17455-25-3; Pb, 7439-92-1; Tl, 7440-28-0; La, 7439-91-0; Ce, 7440-45-1; Pr, 7440-10-0; Nd, 7440-00-8; Sm, 7440-19-9; Gd, 7440-54-2; Tb, 7440-27-9; Dy, 7429-91-6; Ho, 7440-60-0; Er, 7440-52-0; Tm, 7440-30-4; Yb, 7440-64-4; Lu, 7439-94-3.

Liquid-Crystalline Solvents as Mechanistic Probes. 8. Dynamic Quenching of Pyrene Fluorescence by Pyrene in the Liquid-Crystalline and Isotropic Phases of a Cholesteric Solvent[1]

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Abstract: Rate constants and activation parameters for the quenching of pyrene fluorescence by pyrene have been determined in the cholesteric and isotropic phases of a 59.5/15.6/24.9 (w/w/w) mixture of cholesteryl oleate/cholesteryl nonanoate/cholesteryl chloride. From the small differences in the energies and entropies of activation (E_3(cholesteric) = 9.3 ± 0.3 kcal/mol and E_3(isotropic) = 7.0 ± 0.4 kcal/mol; $\Delta S^{\ddagger}$(cholesteric) = 5 ± 2 eu and $\Delta S^{\ddagger}$(isotropic) = −2 ± 3 eu), it is concluded that cholesteric solvent order has little effect on the quenching efficiency. The influence of solvent anisotropy on the efficiency of this process is compared to that observed with other reactions which are retarded or enhanced by solvent order.

Recently, we concluded from dynamic quenching data obtained in the cholesteric and isotropic phases of a 59.5/15.6/24.9 (w/w/w) mixture of cholesteryl oleate/cholesteryl nonanoate/cholesteryl chloride (CM) that the preferred orientation for the quenching of pyrene fluorescence by 5α-cholestan-3β-yldimethylamine (CA) is very specific and resembles closely the commonly accepted exciplex configuration.[2] In this study, we have employed similar techniques to probe the sensitivity of pyrene fluorescence quenching by pyrene (P) to liquid-crystalline order.

Previous studies have shown[3] that the preferred geometry for the pyrene excimer, Er, is the "sandwich"-like configuration which allows maximum overlap of the π orbitals of a pyrene singlet (^{1}P) and P. Both polarity and viscosity of isotropic solvents can influence the stablity of the excimer.[4] Theoretical calculations[5] suggest that altering solvent polarity changes the relative importance of charge-transfer ($[P_1{}^+P_2{}^-]$ and $[P_1{}^-P_2{}^+]$) and excitation resonance ($[P_1{}^*P_2]$ and $[P_1P_2{}^*]$) contributions, thus modifying the electronic nature of the complex. In contrast, high solvent viscosity increases excimer stability by inhibiting molecular motions which distort the complex from its preferred, symmetrical configuration to less symmetrical, nonparallel orientations.[4b,6] Thus,

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