Complexation of Lanthanides by Linear Polyethers in Propylene Carbonate: A 'Crown-like' Behaviour

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The stability of lanthanide complexes with tetraglyme (2,5,8,11,14-pentaoxapentadecane) in anhydrous propylene carbonate have been determined by a competitive potentiometric method using lead as an auxiliary ion. The stability sequence exhibited by the linear polyether is very similar to sequences previously reported for 15-membered crown ethers. Furthermore, tetraglyme displays a higher affinity for the divalent Sm^{II} and Yb^{II} ions than for the corresponding trivalent ions. Long-chain linear polyethers thus exhibit the co-ordination properties of the corresponding crown ligands although the macrocyclic effect of the former is less pronounced. Smaller glymes do not stabilize the +2 oxidation state of the lanthanides.

The co-ordination chemistry of the lanthanides is dominated by complexes with linear polydentate ligands.[1] The stability of these derivatives depends primarily on the charge density of the metal ions and increases with decreasing ionic radius. By contrast, complexation of the lanthanides by macrocyclic polyethers depends primarily upon steric factors such as the fit between the size of the metal ions and the dimensions of the internal cavity of the ligands.[2] Thus, crown ethers provide a cage which can be engineered to accommodate the lighter lanthanides or divalent Eu, Sm, and Yb despite the lower charge density of these ions.[2–5] For instance, selecting 18-crown-6 (1,4,7,10,13,16-hexaoxacyclo-octadecane), whose cavity size is commensurate with that of La^{III}, leads to a decreasing stability along the lanthanide series because the metal ions are less and less able to fill the internal cavity of the ligand. Also, macrocycles featuring from four to ten oxygen atoms in their internal cavity exhibit a higher affinity for the divalent ions Sm^{II} and Yb^{II} than for the corresponding trivalent species. This last result is rather surprising since stabilization of the +2 oxidation state of the lanthanides does not appear to arise solely from size relationship effects. The exact origin of the greater affinity of the crown ethers for Sm^{II} and Yb^{II} had thus to be left to speculation in a number of cases.[4]

It is against this background that we attempted to delineate further the unusual size selective properties of the macrocycles by investigating the complexation of lanthanides with open-chain polyethers. These ligands exhibit a 'crown-like' behaviour in the solid[2] and are excellent probes for assessing the importance of a cyclic structure in complexation with lanthanides. All measurements were conducted in propylene carbonate, an aprotic solvent that proved very useful for electrochemical studies[3,4] and which exhibits medium donor properties similar to those of acetonitrile.

Experimental

All polyethers (Aldrich Co.) were treated with lithium aluminium hydride and fractionally distilled under vacuum as described elsewhere.[6] All solutions and reagents were stored and handled in a glove-box filled with an inert recirculating atmosphere that was continuously monitored for its water content.

The stability constants of the lanthanide complexes with tetraglyme were determined in anhydrous propylene carbonate at 25 °C by a competitive potentiometric method as reported elsewhere.[3,6] The ionic strength was adjusted to 0.1 mol dm^{-3} with tetraethylammonium perchlorate and Pb^{II} was selected as the auxiliary ion. A lead amalgam electrode and a $Ag-AgClO_4$ reference electrode were used to follow the variations in concentration of Pb^{II} ions placed in competition with a lanthanide for the linear polyether. From 7 to 15 competition experiments were carried out for each lanthanide and the total lead, lanthanide, and ligand concentrations were varied in the limits 0.7—5, 5—15, and 5—17 mmol dm^{-3} respectively.

The complexation of divalent samarium and ytterbium was investigated by cyclic voltammetry and by polarography as reported previously.[3,4] The ligand:metal concentration ratio ranged from 3 to 15 and the polarographic waves were found to meet the criteria for thermodynamic reversibility.

Results and Discussion

Our most comprehensive study of the complexation of lanthanides by linear polyethers was carried out with tetraglyme (2,5,8,11,14-pentaoxapentadecane), L^1, because this ligand is the open-chain analogue of 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane), L^2, a macrocycle that forms stable lanthanide complexes in propylene carbonate.[4] Furthermore, the crystal structures of several lanthanide nitrate complexes with the corresponding diol, tetraethylene glycol (3,6,9-trioxaundecane-1,11-diol) have been published recently.[7,8] Finally, an analysis of the yield from the synthesis of lanthanide nitrate complexes with L^1 led Hirashima *et al.*[9] to suggest that the stability of these compounds might decrease when the ionic radius of the metals decreases.

The stability constants, $K_{ML} = [ML]/[M][L]$, of the lanthanide complexes with L^1 were obtained by a potentiometric competition method using Pb^{II} as an auxiliary ion. Preliminary potentiometric determinations of the stability constant of the 1:1 complex formed between Pb^{II} and L^1 led to $\log K_{ML} = 7.31 \pm 0.08$. The stability of the lanthanide complexes with L^1 are listed in the Table and their dependence upon the ionic radius of the metals is reproduced in the Figure together with corresponding data previously obtained for L^2 and its t-butylbenzo analogue,[4] L^3. A distinctive feature of the Figure is the striking similarity between the stability sequence exhibited by L^1 and the sequences obtained with the 15-membered crown ethers: the highest affinity for the lanthanides is displayed for

Table. Stability constants, K_{ML}, of the lanthanide complexes with tetraglyme, L^1, in propylene carbonate (25 °C, 0.1 mol dm^{-3})*

Ln^{3+}	log K_{ML}
La^{3+}	5.05 ± 0.05
Ce^{3+}	5.15 ± 0.04
Pr^{3+}	5.40 ± 0.05
Nd^{3+}	5.17 ± 0.07
Sm^{3+}	5.03 ± 0.06
Gd^{3+}	4.49 ± 0.06
Tb^{3+}	3.80 ± 0.15
Dy^{3+}	3.75 ± 0.07
Ho^{3+}	3.60 ± 0.12
Er^{3+}	3.73 ± 0.06
Tm^{3+}	3.63 ± 0.11
Yb^{3+}	3.70 ± 0.13
Lu^{3+}	3.72 ± 0.06

* K_{ML} = [ML]/[L][M], where M = lanthanide ion and L = ligand.

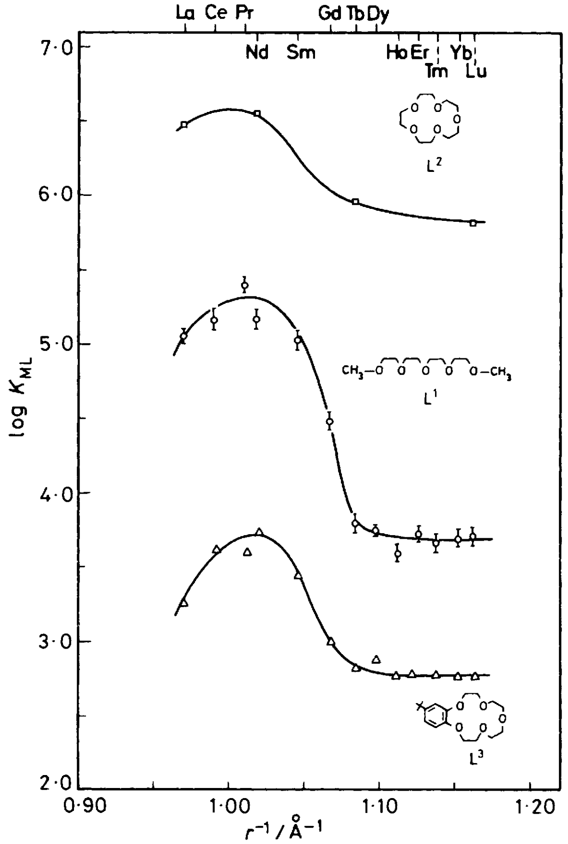

Figure. Complexation of lanthanide ions in anhydrous propylene carbonate by L^1 (this work), L^2 and L^3 (taken from ref. 4).

the Pr–Nd couple, the strength of complexation rapidly decreases from Sm to Dy and the heavier lanthanides are all complexed to the same extent. This complexation behaviour is most unusual in lanthanide chemistry[1] and probably reflects the fact that L^1 adopts a ring-like conformation in its complexes. In the solid, tetraethylene glycol is wrapped around La^{III} or Nd^{III} with its five oxygen atoms arranged at the corners of a quasi-regular hexagon, the vacant position being occupied by a nitrate ion. This conformation is very close to the structure exhibited by the 18-crown-6 lanthanide derivatives[5] but is not believed to predominate here since only non-co-ordinating anions such as perchlorate or trifluoromethanesulphonate ions were added to the propylene carbonate solutions. L^1 can probably pucker further so that all its heteroatoms are co-ordinated in an arrangement similar to the one of 15-crown-5 complexes[10] as indicated by the close analogy between all the stability sequences reproduced in the Figure.

The stability of the lanthanide complexes with L^1 is of course much smaller than in the case of 15-crown-5 and no 1:2 complexes with L^1 were observed. The lanthanide derivatives of L^1 are however about an order of magnitude more stable than the complexes of L^3, an indication of the strong effect exerted by the phenyl substituent on the complexation.

The crown-like behaviour of L^1 is also apparent in the complexation of the divalent lanthanide ions since the III–II reduction waves of Sm and Yb are shifted toward positive potentials upon co-ordination. The divalent oxidation state of Sm and Yb is thus stabilized by complexation with a linear polyether but the anodic shifts are much smaller than in the case of the crown ethers.[3,4] The reduction wave of ytterbium is 64 mV more positive in the presence of L^1 and the stability constant of the Yb^{II} complex, log $K_{ML} = 4.8 \pm 0.1$, is thus about one order of magnitude larger than the stability constant of the corresponding Yb^{III} complex. The half-wave potential of the Sm^{III}–Sm^{II} couple becomes only 17 mV more positive on addition of the polyether ligand and the stabilization of the divalent oxidation state that takes place is considered to be too weak to allow an accurate determination of the stability constant of the Sm^{II} complex. Of particular relevance here is that potential shifts amounting to about 130 and 250 mV were recorded[4] for samarium and ytterbium co-ordinated to L^3.

In view of the results obtained with L^1, we undertook an electrochemical study of the reduction of Sm^{III} and Yb^{III} complexed by smaller linear polyethers such as triglyme (2,5,8,11-tetraoxadodecane) and monoglyme (2,5-dioxahexane). In both cases, the anodic shifts are smaller than 7 mV and independent of ligand concentration. Within the limits of error, the addition of small-chain polyethers does not seem to alter the relative stability of the divalent and trivalent Yb and Sm ions. By contrast, 12-crown-4, the cyclic analogue of triglyme, displays an unusual affinity for the divalent lanthanide ions.

In summary, we conclude that long-chain linear polyethers exhibit to some degree the co-ordination properties of the macrocycles. Ligands such as L^1 probably adopt a quasi-cyclic conformation because this structure is favoured by electrostatic interactions with the lanthanide ions and by steric constraints imposed by the ethylenic groups which tend to be fully staggered. Smaller polyethers are unable to form crown-like complexes but high-molecular-weight glymes or glycols should behave like L^1 although the formation of polymetallic complexes would probably also take place.[9]

Acknowledgements

J. F. D. and P. P. B. are grateful for support by the Fonds National de la Recherche Scientifique of Belgium.

References

1 T. Moeller, in 'Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Pergamon Press, Oxford, 1973, vol. 4, pp. 1—104.
2 J-C. G. Bünzli and D. Wessner, *Coord. Chem. Rev.*, 1984, **60**, 191 and refs. therein.
3 J. Massaux, J. F. Desreux, C. Delchambre, and G. Duyckaerts, *Inorg. Chem.*, 1980, **19**, 893.
4 J. Massaux and J. F. Desreux, *J. Am. Chem. Soc.*, 1980, **102**, 2278.

5 R. M. Izatt, J. D. Lamb, J. J. Christensen, and B. L. Haymore, *J. Am. Chem. Soc.*, 1977, **99**, 8344.

6 J. Massaux, J. F. Desreux, and G. Duyckaerts, *J. Chem. Soc., Dalton Trans.*, 1980, 865.

7 Y. Hirashima, T. Tsutsui, and J. Shiokawa, *Chem. Lett.*, 1981, 1501.

8 U. Casellato, G. Tomat, P. Di Bernardo, and R. Graziani, *Inorg. Chim. Acta*, 1982, **61**, 181.

9 Y. Hirashima, K. Kanetsuki, I. Yonezu, K. Kamakura, and J. Shiokawa, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 738.

10 T. J. Lee, H-R. Sheu, T. T. Chiu, and C. T. Chang, *Acta Crystallogr., Sect. C*, 1983, **39**, 1357.

Received 6th *January* 1986; *Paper* 6/030