Complexation of the Lanthanides by Cryptand 2.2.2 † in Propylene Carbonate: an Electrochemical Determination of the Thermodynamic Parameters

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The complexation of the lanthanide ions by cryptand 2.2.2 in anhydrous propylene carbonate has been investigated by a competitive potentiometric method between 25 and 90 °C. The stability of the lanthanide cryptates increases from La^{III} (log K = 12.9) to Yb^{III} (log K = 17.6). All the complexes are enthalpy stabilized. The entropic term favours complexation at the beginning of the lanthanide series but rapidly becomes unfavourable, presumably because of a progressive rearrangement of the ligand. These complexation trends contrast significantly with results published previously and reflect the importance of the solvent in the complexation process.

Lanthanide complexes with various macrocyclic ligands have received increasing attention in recent years because of the many intriguing properties exhibited by these compounds.[1-3] For instance, bicyclic ligands such as cryptands 2.2.1 or 2.2.2 (see the Figure) form substitutionally inert complexes which are remarkably stable in aqueous solutions.[4] Furthermore these cryptands are able to stabilize the +2 oxidation state of Eu and Sm in water [4] and in methanol.[5] In an attempt to delineate further the properties of the lanthanide cryptates, several authors have measured the stability constants of these compounds. These measurements, however, are thwarted by many experimental difficulties. For instance, the slow kinetics of complexation and the ease of formation of the lanthanide hydroxides probably limit the reliability of the measurements in water.[6,7] Investigations in anhydrous solvents such as dimethyl sulphoxide,[8] methanol or propylene carbonate [5] are less hampered by experimental difficulties, although severe kinetic problems can exist. Indeed, up to 12 d are necessary to reach equilibrium during pH titrations of lanthanide 2.2.1 cryptates in anhydrous methanol.[5] The results obtained so far indicate that the stability of the lanthanide cryptates is barely affected by the contraction of the ionic radius of the metals and is nearly insensitive to changes in the cavity size of the ligands.

In view of the selectivity exhibited by some of the much simpler monocyclic crown ethers,[1-3] we were surprised by the lack of selectivity of the cryptands and decided to investigate the thermodynamics of the complexation of a few lanthanide ions by cryptand 2.2.2 in anhydrous propylene carbonate. The results reported in the present paper are the first thermodynamic data available for lanthanide cryptates and indicate that complexation selectivity can indeed be achieved with cryptand 2.2.2 in propylene carbonate.

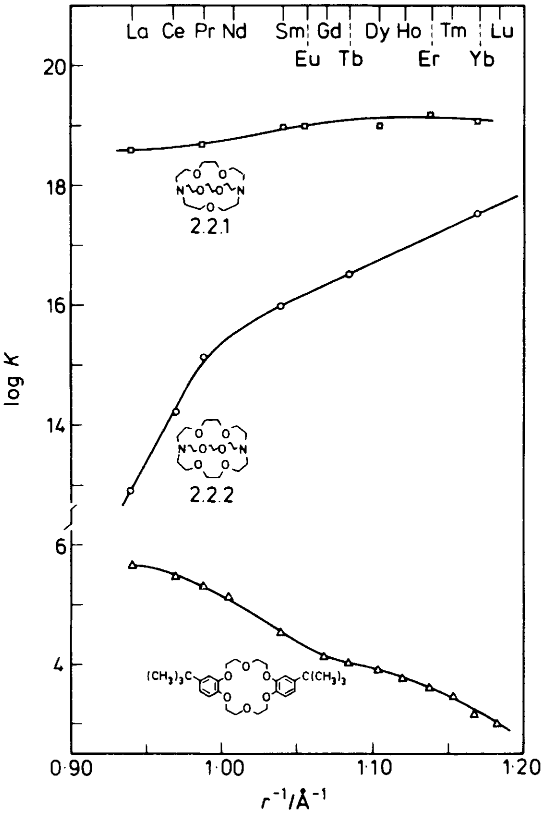

Figure. Complexation of the lanthanide ions in propylene carbonate by cryptand 2.2.1,[5] cryptand 2.2.2 (this work), and 4,4'-di-t-butyldibenzo-18-crown-6 (synthesis also gave the 4,5'-isomer)[2]

Experimental

Silver(I) was systematically used as auxiliary ion in a competitive potentiometric method as reported elsewhere.[2,3,9] The preparation of anhydrous lanthanide trifluoromethanesulphonates and purification of propylene carbonate follow previously described procedures.[2,3] All solutions were handled in an inert atmosphere dry-box. The kinetics of the competition reaction $AgL^+ + Ln^{3+} \rightleftharpoons LnL^{3+} + Ag^+$ (L = cryptand 2.2.2) were followed during 30 min at 25 °C, 15 min at 40 °C, and 10 min at higher temperatures. These periods of time were necessary to obtain a constant reading (less than 1 mV) of the potential of the silver electrode for more than 0.5 h. The potentiometric measurements were carried out at five temperatures between 25 and 90 °C, six competition

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† 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

Table. Stability constants (log K), free energies ΔG, enthalpies ΔH, and entropies ΔS for the complexation of some lanthanides by cryptand 2.2.2 in propylene carbonate

Lanthanide	log K[a]	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1}\text{ mol}^{-1}$	$\Delta G/\text{kJ mol}^{-1}$
La^{3+}	(12.91)[b]	-54.5 ± 8.9	64 ± 26	-73.6 ± 8.9
Ce^{3+}	(14.20)[b]	-76.5 ± 9.4	15 ± 9	-81.0 ± 9.4
Pr^{3+}	15.88 ± 0.15	-94.5 ± 3.5	-28 ± 10	-86.3 ± 3.5
Sm^{3+}	15.99 ± 0.15	-96.3 ± 2.6	-17 ± 8	-91.2 ± 2.6
	16.39 ± 0.13[c]	-96.2 ± 5.7[c]	-9 ± 7[c]	-93.5 ± 4.2[c]
Tb^{3+}	16.58 ± 0.10	-104.3 ± 4.6	-31 ± 14	-95.1 ± 4.6
Yb^{3+}	17.56 ± 0.22	-106.6 ± 9.7	-24 ± 9	-99.4 ± 9.7

[a] At 25 °C, ionic strength = 0.1 mol dm^{-3}. [b] Extrapolated from higher temperatures (see text). [c] Ionic strength = 0.9 mol dm^{-3}.

experiments being carried out at each temperature. The thermodynamic parameters ΔH and ΔS were then deduced from a plot of log K against $1/T$. The ionic strength was adjusted to 0.1 or 0.9 mol dm^{-3} with tetraethylammonium perchlorate and the total concentrations of ligand, silver perchlorate, and lanthanide trifluoromethanesulphonates ranged from 20 to 60, 10 to 20, and 20 to 70 mmol dm^{-3} respectively.

Results and Discussion

The first step when planning potentiometric competition experiments is the selection of an auxiliary ion. Silver(I) was preferred to Tl^{I} or Pb^{II} because the complexes of the former with cryptand 2.2.2 are too weak and the exchange reaction with the latter is too slow. The kinetics of exchange between the silver(I) cryptate and the lanthanides are also fairly slow around 25 °C and no equilibrium could be reached in the case of the lanthanium(III) and cerium(III) ions. However, the kinetics are considerably accelerated at higher temperatures. These results contrast with a recent report by Schwing-Weill and co-workers[5] who mentioned that the exchange reaction between AgL^+ (L = cryptand 2.2.1) and the lanthanide ions is fast at room temperature. The thermodynamic parameters for the complexation of Ag^{I} by cryptand 2.2.2 were deduced from the variation of the stability constants with $1/T$. The values obtained [log $K(25\ °\text{C}) = 16.73 \pm 0.05$; $\Delta H = -104 \pm 3\ \text{kJ mol}^{-1}$, $\Delta S = -29 \pm 8\ \text{J K}^{-1}\ \text{mol}^{-1}$, and $\Delta G(25\ °\text{C}) = =95.5 \pm 0.3\ \text{kJ mol}^{-1}$] are in good agreement with those previously published by Gutknecht *et al.*[10]

The values of the thermodynamic functions for the complexation of a few lanthanide ions by cryptand 2.2.2 in propylene carbonate are collected in the Table and the dependence of the stability constants upon the reciprocal of the ionic radius r is presented in the Figure together with similar results obtained for cryptand 2.2.1[5] and for 4,4′-di-t-butyldibenzo-18-crown-6.[2,*] Obtaining thermodynamic functions by an analysis of the influence of temperature on the stability of complexes is not the most reliable method and the data listed in the Table may be subject to serious errors. However, measuring ΔH calorimetrically would be difficult because of the very slow kinetics of complexation at room temperature. Another pitfall in our data collection and treatment could be the neglect of the association between the complexed or uncomplexed cations and the perchlorate or trifluoromethanesulphonate anions. It should be noted however that the perchlorates of the lanthanide cryptates of 2.2.2 were found to be 3 : 1 electrolytes in acetonitrile.[11] Furthermore, changing the ionic strength from 0.1 to 0.9 mol dm^{-3} has little influence (see the Table) on the thermodynamics of complexation of Sm^{III}.

As illustrated in the Figure, cryptand 2.2.1 displays a greater affinity for the lanthanide ions than does cryptand 2.2.2. The cavity size of cryptand 2.2.1 (radius[12] = 1.10 Å) is commensurate with the size of the lanthanide ions[13] and this ligand possesses significantly better ligating properties than cryptand 2.2.2 which is too large (radius[11] = 1.40 Å) to accommodate comfortably the lanthanides.

In non-aqueous solvents, macrocyclic complexes are most often enthalpy stabilized ($\Delta H < 0$) and entropy destabilized ($\Delta S < 0$).[14] The same trend has been reported for lanthanide complexes with non-cyclic ligands such as ethylenediamine in acetonitrile.[15] The sign of the entropy changes is attributed to a decrease of the internal entropy of the ligand which would dominate the gain in translational entropy due to the release of solvent molecules. The lanthanide cryptates with 2.2.2 in propylene carbonate are enthalpy stabilized; the enthalpy variation is the dominant quantity in determining the magnitude of log K and becomes more negative when the ionic radius of the metal ions decreases. Furthermore, the complexes are entropy stabilized at the beginning of the lanthanide series but the entropy changes become rapidly unfavourable, a trend which is taken as real despite the large errors inherent in the method used here. An increasingly negative enthalpy was expected because the smaller size and higher electron density of the heavier lanthanides favour the electrostatic ligand–metal ion interactions.[15] The enthalpic stabilization takes place despite the poor fit between the cavity size of the ligand and the ionic radius of the metal ions and probably requires a progressive rearrangement of the ligand. This hypothesis is supported by crystallographic analyses[12] of alkali-metal ion cryptates with 2.2.2 which indicate that the ligand has to undergo a torsion around its main symmetry axis in order to reduce its cavity size. Similar conformational changes have also been noted in solid cryptates of 2.2.2 with La^{III},[16] Sm^{III},[17] and Eu^{III}.[11] Furthermore, the analysis[18] of the n.m.r. spectra of paramagnetic lanthanide cryptates of 2.2.2 in D_2O clearly indicates that the structure of these compounds changes with the ionic radius of the encapsulated ions. Entropy variations might also be accounted for by a structural modification of the 2.2.2 cryptates. If the macrocycle undergoes relatively modest conformational rearrangements at the beginning of the lanthanide series, the entropic term would favour complexation since the dominant effect would then be the release of co-ordinated solvent molecules. However, the lanthanide contraction would rapidly bring about more drastic conformational changes and add a negative contribution to the entropy. It is noteworthy that positive values of ΔS are not unknown, for instance, in the case of the sodium and potassium complexes with cryptand 2.2.1 in acetonitrile.[12]

The stability data reported in the present work contrast

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[*] 2,14-Di-t-butyl-6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*]-[1,4,7,10,13,16]hexaoxacyclo-octadecine.

significantly with results obtained in the case of other cryptands and/or other solvents. In dimethyl sulphoxide [8] and in water,[6] all lanthanide cryptates were found to have approximately the same stability irrespective of the cavity size and of the ionic radius of the metals. Dimethyl sulphoxide and water are considerably more solvating than propylene carbonate and molecules of these solvents most probably remain co-ordinated to the lanthanide ions despite their encapsulation by the cryptands. All thermodynamic parameters are then likely to be very different from those reported in the present work. In methanol, however, a selective complexation has been found in the case of the cryptates with 2.2.1. Schwing-Weill and co-workers [5] have indeed reported that YbL^{3+} is 3.7 orders of magnitude more stable than LaL^{3+} (L = cryptand 2.2.1). Surprisingly, the stability of the complexes of 2.2.1 in propylene carbonate [5] is nearly independent of the charge density of the ions (see the Figure). The origin of this intriguing difference between the 2.2.2 and 2.2.1 cryptands is unclear at this stage.

Another aspect of particular interest in the chemistry of lanthanide macrocyclic complexes is the stabilization of the +2 oxidation state of Sm and Yb. Monocyclic ligands such as 4,4′-di-t-butyldibenzo-18-crown-6 in propylene carbonate [2] exhibit stability sequences that are the opposite of the complexation trend of cryptand 2.2.2 (see the Figure): the stability decreases with the ionic radius, presumably because the lanthanide ions are less and less able to fill the internal cavity of these polyethers. The larger bivalent samarium and ytterbium ions are then better co-ordinated in the macrocyclic cavity despite their lower charge density. The polarographic reduction waves of the samarium(III) and ytterbium(III) cryptates are highly irreversible in propylene carbonate and this cannot be analysed quantitatively following the method described previously.[2,3] However, the displacements of the reduction waves of $Sm^{III,II}$ and $Yb^{III,II}$ toward negative potentials upon complexation clearly indicate that cryptand 2.2.2 does not display a higher affinity for the bivalent ions. Similar conclusions have already been reached by Schwing-Weill and co-workers [5] and are entirely in keeping with the complexation trend shown in the Figure: the larger ions are the less strongly complexed. Finally, it is pertinent to note that cryptand 2.2.2 and the 18-crown-6 derivatives have internal cavities of about the same size although they are of course three- and two-dimensional respectively. Cavity-size effects, however, seem to prevail only in the case of the crown ethers which surprisingly would thus be less prone to molecular rearrangements than cryptand 2.2.2, at least in propylene carbonate.

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