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# Lanthanide Complexes of 5-Nitrophenol and its 1,3-Xylyl Crown Derivatives, 15-Crown-4 and 18-Crown-5, in Aqueous Solution

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## Abstract

The stabilities of the one–one complexes of some lanthanide ions with *p*-nitrophenolate and its 1,3-xylyl crown derivatives, 15-crown-4 (**I**) and 18-crown-5 (**II**), have been determined in aqueous solution at 25 °C by potentiometric measurements of the hydrogen ion concentration. Both the two cyclic ligands form complexes which are stronger than those of the *p*-nitrophenol, indicating that the ethereal chains are involved in the complex formation. A consideration of the stability constants as a function of the atomic number of the lanthanides obtained for the two cyclic ligands **I** and **II** suggests that in these coordination systems the phenoxide oxygen atom is the primary binding site while the ethereal oxygen atoms act as secondary binding sites with the metal ion probably located outside the cavity of the macroring.

## Introduction

A literature survey reveals that over the last fifteen years many papers concerning the preparation and characterization of solid state lanthanide–crown ether coordination compounds have been published [1]. The formation of such complexes is not surprising if we consider the similarities either of the coordination bonds and ionic radii between lanthanide and alkaline or alkaline-earth ions for which a variety of crown complexes is well known [2].

The interactions between crown ethers and the ions of the s-block elements have been extensively studied both in water and in non-aqueous solvents [2, 3], whereas a few reports exist about the complexation equilibria of the lanthanide(III) ions with these ligands and they refer to the non-aqueous solvents propylene carbonate, methanol and acetonitrile [4]. The solvating properties of the water molecules together with the relatively weak ion–dipole interactions occurring with neutral polyethers may account for the unfavourable energetics in the coordination reactions between rare earth ions and these ligands in aqueous solutions [3, 5]. It is well known that the Ln(III) ions preferentially interact with hard bases such as fluoride or charged oxygen donors. On the other hand, it was also proved that the interaction between these cations and the ethereal oxygens occurs in water when one or more charged oxygen donors are also present in the ligand, as in the oxa- and polyoxacarboxylates [6, 7]. Probably in these systems the charged groups bring about sufficient desolvation so that the ethereal groups can interact either in the inner or in the outer coordination sphere. The stability of lanthanide macrocyclic complexes in methanol or methanol/water remarkably increases when two ethereal oxygens of 15-crown-5 [4a] and 18-crown-6 [8] are replaced by –NH groups. When all oxygen atoms are substituted by –NH in 18-crown-6 to give hexaaza18-crown-6, the lanthanum(III) complex of this ligand results and is quite stable even in water [9].

The data available on the complexation reactions of the lanthanides with macrocyclic polyethers in solvents of poorer solvating ability than water [4] seem to indicate that among the various factors that determine the complex stabilities, the number of coordination sites of the ligands and the interactions with the solvent are more important than other factors such as the fit between the cation and the ligand cavity sizes and the variation of charge density along the lanthanide series.

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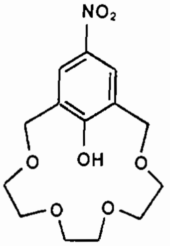
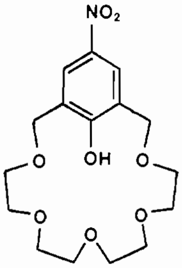
We thought that macrocyclic polyether derivatives containing a convergent charged oxygen donor would be competitive against the water molecules and at the same time could provide some information on the effect of the ring size in the complexation with lanthanides in aqueous solution.

Quite promising ligands, from this point of view, are **I** (5-nitro-2-hydroxy-1,3-xylyl-15-crown-4) and **II** (5-nitro-2-hydroxy-1,3-xylyl-18-crown-5) [10]. They bear a ionizable phenolic group, which can probably act as primary binding site, and a macrocyclic polyoxygenated array acting as secondary binding site. Besides, the presence of a *p*-nitro group in the 1,3-xylyl subunit increases the acidity of the phenolic group so that the complexation reactions could be studied in a pH range where the hydrolysis of the metal ions may be reasonably neglected. Finally, an examination of the CPK space-filling models suggests that **I** and **II** could assume a conformation wherein the cavity formed by the ethereal and phenolic oxygens is comparable with that of simple 15-crown-5 and 18-crown-6, respectively.



**I**



**II**

In this paper we report a study of the complex formation equilibria of the ligands **I** and **II** with lanthanide(III) ions. In order to elucidate possible synergistic effects between the phenoxy oxygen and the macrocyclic polyethereal ring, we have also studied the complexation reactions of some lanthanides with *p*-nitrophenol under the same experimental conditions. Stability constants were obtained by a potentiometric competitive method in aqueous solution at 25 °C and ionic strength 0.1 M.

## Experimental

### *Reagents*

The ligands **I** and **II** were prepared according to the reported method [10]. Their purity was checked both by elemental analysis and by potentiometric titration of a weighed amount of the ligands with standard NaOH. In their protonated form the two crown phenols are sparingly soluble. At 25 °C the concentration of the saturated solutions of **I** and **II** was around 4 and 8 mM, respectively. The *p*-nitrophenol (Baker analyzed) was recrystallized from chloroform [11]. Stock solutions of the ligands were prepared from weighed amounts of the substances. Potentiometric checks were always carried out.

Stock solutions of the various rare earth perchlorates were prepared by dissolving the appropriate oxide (99.9% pure) in a small excess of perchloric acid. The metal ion concentrations were checked by EDTA complexometric titrations using xylenol orange [12].

Tetraethylammonium hydroxide solutions of appropriate concentration were obtained by dilution of a Janssen solution (20% by weight), then titrated with standard perchloric acid.

Tetraethylammonium perchlorate (Fluka Purum) was twice crystallized from ethanol [11]. Both tetraethylammonium hydroxide and perchlorate were used to avoid possible complexation reactions between alkali metal ions and macrocyclic ligands.

All solutions were prepared with deionized, bidistilled and freshly boiled water.

### *Apparatus*

All measurements were performed at 25.0 ± 0.1 °C. Tetraethylammonium perchlorate was used to adjust to 0.1 M the concentration of perchlorate ion in the solutions. The potentiometric measurements were made using hydrogen as auxiliary ion [13]. They were carried out with a Metrohm model 654 pH-Meter in conjunction with a Metrohm EA109 glass electrode and a double junction Ag/AgCl reference electrode (Metrohm EA440). The set-up and calibration of the apparatus were carried out by procedures similar to those described in ref. 14. The e.m.f. of the titration cell was described by $E = E^0 - 59.16 \log[\mathrm{H}^+] + E_j$. The cell constant ($E^0$) and the liquid junction potential ($E_j$) were determined by titrating a known excess of perchloric acid in a solution containing known concentrations of both ligand, $C^0{}_\mathrm{L}$, and metal ion, $C^0{}_\mathrm{M}$, with $(\mathrm{NEt_4})\mathrm{OH}$. Successive additions of standard base were then made allowing the complexation of lanthanide ions by the ligands to be followed. When the protonation constant of the phenols had to be determined, a starting solution containing the ligand alone was employed. The metal concentrations in the titrations concerning the crown–phenols complexation varied from 1 to 8 mM. With *p*-nitrophenol, higher concentrations were used, from 10 to 30 mM.

The calculation of stability constants from the potentiometric data was performed by using the computer program Superquad [15]. The best fit of the experimental data was obtained when only the ML complex was taken into account.

## Results and Discussion

A set of pH titration curves for the system lutetium(III)–I is shown in Fig. 1. Curve a refers to a titration of the ligand alone; curves b and c are titration plots of similar amounts of the ligand in the presence of the metal ion in different concentrations. Their lowering with respect to the one referring to the ligand alone is indicative of complexation equilibria involving the metal ion. Curve d is a calculated plot describing the hydrolysis of the metal ion when its concentration is 10 mM. For the formation constant of the $Lu(OH)^{2+}$ species a value of $\log K = 5.83$ was used [16]. As can be seen, $Lu^{3+}$ is hydrolyzed at pH values approximately one unity and a half higher than those characteristic of the complexation equilibria. This fact allows us to rule out the formation of hydroxylic and/or mixed complexes in this system. A point was reached during the titrations in the presence of metal ion when formation of insoluble species was observed. The measurements herein considered relate to solutions in which precipitation had certainly not yet begun (experimental values of the curves b and c only for 'mole base/mole ligand' $< 0.6$ in Fig. 1).

The titration and complexation curves obtained for the systems lutetium(III)–II and lutetium(III)–*p*-nitrophenol are quite similar to those above seen for I (the *p*-nitrophenol curves are lowered to a smaller extent). Moreover, since an analogous behaviour was shown by the other lanthanides, the set of data reported in Fig. 1 may be regarded as qualitatively representative of all the systems examined.

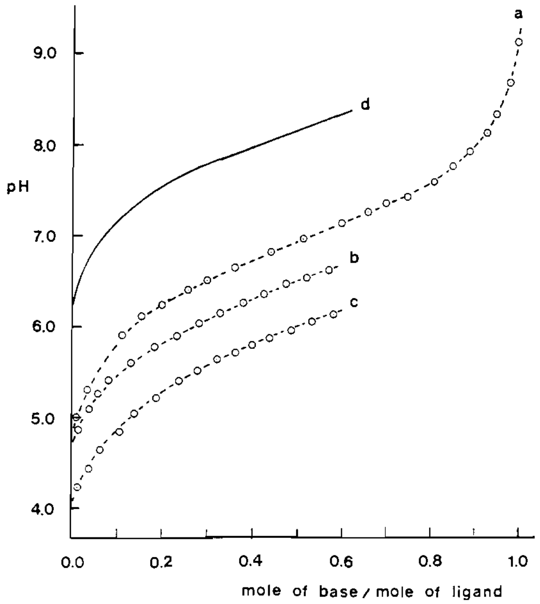


Fig. 1. Titration curves of the ligand I and Lu(III)–I solutions: a, $C^0_M = 0.0$, $C^0_L = 3.30$ mM; b, $C^0_M = 2.86$ mM, $C^0_L = 2.85$ mM; c, $C^0_M = 0.50$ mM, $C^0_L = 2.15$ mM. The dashed curves were calculated from the constants in Table 1. d, Hydrolysis curve of a solution of $Lu^{3+} = 10.0$ mM calculated from the constants reported in ref. 16. The pH for this curve are reported as function of the ratio 'mole of base/mole of metal ion'.

Some of the insoluble species were isolated and submitted to elemental analysis which indicates the stoichiometries $ML_2(ClO_4)\cdot 3H_2O$ for M = Eu, Yb, L = II, and $ML_2(HL)_2\cdot ClO_4\cdot 2H_2O$ for M = Eu, Pr, L = I. The formation of insoluble products was also observed during the titrations in lanthanide(III)–*p*-nitrophenolate systems. In these cases hydroxo species can be formed on account of the higher pH reached owing to the lower stability of the complexes and the higher metal ion concentrations. As a consequence of the formation of solid products at low concentrations of all ligands considered, the stability constants, *K*, only for the species of stoichiometry ML could be calculated. All the values of log *K* are reported in Table 1 together with the protonation constants obtained for the three anionic ligands. These last are compared with the values available in the literature [10, 17]. Taking into account the different experimental conditions and measurement techniques, our values for I and II are in fairly good agreement with the values reported by other authors [10]. The protonation constant relative to the *p*-nitrophenol is practically coincident with that previously obtained in the same experimental conditions [17]. The comparison of the $pK_a$ values of the three ligands indicates that the ethereal chains do not

TABLE 1. Stability constants, log *K*, for the 1:1 association of hydrogen ion and some lanthanide(III) ions with the anionic ligands 5-nitro-2-oxy-1,3-xylyl-15-crown-4 (I), 5-nitro-2-oxy-1,3-xylyl-18-crown-5 (II) and *p*-nitrophenolate in water at 25 °C; $I = 0.1$ M $(NEt_4)ClO_4$. Errors are expressed as three times the standard deviations

| Cation | log *K* |  | *p*-Nitrophenolate |
|---|---|---|---|
|  | I | II |  |
| $H^+$ | 6.92 ± 0.02 | 6.78 ± 0.01 | 6.91 ± 0.01 |
|  | 6.8[a] | 6.6[a] | 6.9[b] |
| $La^{3+}$ | 2.70 ± 0.03 | 3.06 ± 0.01 | 1.0 ± 0.1 |
| $Ce^{3+}$ | 2.97 ± 0.02 |  | 1.1[c] |
| $Pr^{3+}$ | 3.00 ± 0.02 |  | 1.30 ± 0.04 |
| $Nd^{3+}$ | 2.98 ± 0.01 | 3.27 ± 0.01 |  |
| $Sm^{3+}$ | 3.23 ± 0.01 |  | 1.48 ± 0.05 |
| $Eu^{3+}$ | 3.28 ± 0.01 | 3.17 ± 0.01 |  |
| $Gd^{3+}$ | 3.18 ± 0.01 | 3.03 ± 0.01 | 1.64 ± 0.01 |
| $Tb^{3+}$ | 3.25 ± 0.01 |  |  |
| $Dy^{3+}$ | 3.22 ± 0.01 | 3.05 ± 0.01 |  |
| $Er^{3+}$ | 3.11 ± 0.01 | 2.79 ± 0.03 | 1.35 ± 0.04 |
| $Yb^{3+}$ | 3.07 ± 0.01 |  |  |
| $Lu^{3+}$ | 3.05 ± 0.02 | 2.74 ± 0.01 | 1.46 ± 0.04 |

[a] Ref. 10. [b] Ref. 17. [c] Ref. 19.

significantly influence the acidity of the phenolic group.

A limited amount of information regarding the interactions of the lanthanide ions with phenols is available in the literature. The formation constant of the one–one complex of lanthanum(III) with phenol ($pK_a = 9.78$), and *o*-nitrophenol ($pK_a = 7.06$), are $\log K = 1.51$ and 2.20, respectively [18]. These values, which are higher than those determined for *p*-nitrophenol, can be explained for phenol with its higher basicity, and with the possible formation of chelate rings by *o*-nitrophenol [18]. The value of $\log K = 1.1$ reported for Ce(III)–*p*-nitrophenol [19] falls in the trend of the values which we have obtained for some other lanthanides.

A first examination of the data in Table 1 indicates that the cyclic ligands **I** and **II** form complexes which are stronger than those of *p*-nitrophenol. This increase in stability must be attributed to the presence of the ethereal chain in the ligands. Moreover, it should be noticed that both the number of donor oxygen atoms and the dimensions of the cavities slightly influence the complex stabilities. In fact the differences in stability between the complexes of **I** and **II** are small, and the $\log K$ values for both ligands do not change very much along the lanthanide series. All the values of the stability constants fall approximately in the range of $\Delta \log K = 0.6$. All these considerations are well visualized in Fig. 2 where the $\log K$ values are reported as a function of the atomic number, $Z$.

For a comparison with the behaviour of the simple crown ethers containing five or six oxygen atoms towards the lanthanide(III) ions, the only available data are those obtained in non-aqueous solutions [4] and particularly the ones from propylene carbonate, which are more numerous and homogeneous [4a, b, g]. Noticeable differences between the two coordinating systems can be pointed out. In propylene carbonate the complexes of 18-crown-6 are more stable than those of 15-crown-5 ($\Delta \log K \simeq 2$) [4a]. The monobenzosubstituted of 15-crown-5 and dibenzosubstituted of 18-crown-6 behave in a similar manner [4d]. Moreover these ligands, with respect to **I** and **II**, exhibit a higher selectivity between the lighter and heavier lanthanides. Lastly the complex stability for all these ligands decreases, more or less regularly, with the decrease of the ionic radius. This behaviour may result from a complicated contribution of both favourable (electrostatic metal–ligand interactions) and unfavourable (desolvation of the metal ions) factors. These factors also depend on the more or less favourable ratio 'ionic radius/cavity dimension'. This latter ratio was thought to be responsible for the usual decreasing stability with $Z$ of the lanthanide(III) complexes with all crown ethers of the type 15-crown-5 and 18-crown-6 in propylene carbonate: in fact the cavity dimensions become less suitable to ionic radius as $Z$ increases.

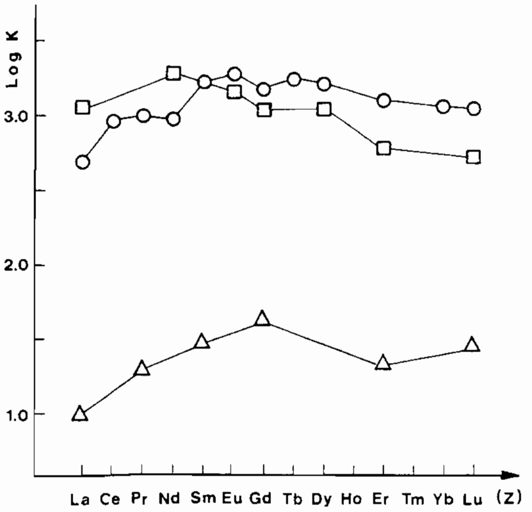


Fig. 2. Log $K$ as a function of the atomic number of some lanthanide(III) complexes with the anionic macrocyclic polyethers **I** (○), **II** (□) and *p*-nitrophenolate (△) in water at 25 °C, $I = 0.1$ M with $(NEt_4)ClO_4$.

It is reasonable to suppose that on changing from simple crown ethers to their derivatives bearing an intraannular functional group, some important differences in the macrocycle ring conformation are to be expected. For instance, the crystal structure of ligand **II** shows an angle of 47° between the aromatic ring plane and the mean plane of the macrocyclic ring atoms, and in its complexes with the ammonium ion this angle is increased to 58° [10]. Analogous conformations were found in the solid complexes of some lanthanides with the similar ligands 1,3-methoxyaryl-15-crown-4 [20] and 1,3-methoxyaryl-18-crown-5 [21]. It is possible that the interactions between the metal ions and the phenoxy oxygen, which acts as primary binding site, are insufficient to destroy completely the cation solvation sphere. The stiffness introduced by the presence of the 1,3-xylyl subunit in the ligands probably gives rise to conformational and/or steric conditions which do not help the complete desolvation process. Consequently the metal ion cannot occupy the center of the cavity and encapsulation is not achieved. If so, the ethereal oxygen atoms cannot be directly bonded to the metal ion: probably they act via hydrogen bonds with residual coordinated water molecules. This hypothesis seems to be supported by our results. In fact the metal–ligand interactions, though strengthened by the presence of the ethereal ring, could be fairly independent from the better or worse fit of the metal ion with the cavity of the ligand.

Despite the small differences between the stabilities of the complexes of the two ligands, they present a different trend when the atomic number is increased. The trend of $\log K$ for **I** is nearly parallel to that of *p*-nitrophenol and compares well with the behaviour in water of some charged ligands such as acetate and propionate [22]. The decrease in stability displayed by complexes with **II** from Nd(III) to Lu(III) is more similar, even if less marked, to the behaviour already mentioned of the crown ethers with five or six oxygen atoms in propylene carbonate [4].

We can therefore conclude that the driving force of the complexation is the interaction between the charged donor group of the ligands and the metal ions: for the complexes of **I** the extra contribution to stability probably originates from hydrogen bonds only, whereas for **II**, also a possible partial effect of the larger and more flexible cavity cannot be excluded.

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