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Spectrophotometric Study of the Complexation of Some Lanthanide (III) Ions with a Series of 18-Crowns-6 in DMSO Solution Using Murexide as a Metallochromic Indicator

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Abstract

The complexation of La(III), Ce(III), Pr(III) and Er(III) with 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DCY18C6) and dibenzopyridino-18-crown-6 (DBPY18C6) has been studied in dimethylsulfoxide (DMSO) by means of a competitive spectrophotometric method using murexide as a metal ion indicator. The formation constants of the 1 : 1 complexes were found to vary in the order La(III) > Ce(III) > Pr(III) > Er(III). It was found that the structure influences the formation and stability of the resulting complexes. The effects of various parameters on complexation are discussed. The order of the stability constants of each lanthanide ion with these macrocycles are 18C6 > DC18C6 > DB18C6 > DBPY18C6.

Introduction

Most of the solution studies carried out with synthetic macrocyclic ligands such as crown ethers [1] and cryptands [2] have centered on the complexing abilities of these ligands with metal cations [3, 4]. There is a continued interest in studying macrocyclic complexes of lanthanides [5–7] due to their potential applications in fundamental and applied science [5]. Studies on lanthanide complexes have produced technological developments and industrial applications [8]. Macrocyclic complexes of paramagnetic lanthanide metal ions have found extensive biomedical applications as contrast enhancing agents in magnetic resonance imaging [9–12], as NMR shift reagents for biological systems [13] and as catalysts for the cleavage of RNA [14, 15]. Complexes of radioisotopes are used in diagnostic imaging and radioimmunotherapy[16] and as bioconjugates for monoclonal antibody radioisotope labeling [17]. Macrocyclic ligands are also used as effective lanthanide chelators [18, 19] and in the separation of lanthanides [3, 20, 21]. Competitive equilibrium methods, have been used in measuring stability constants, to avoid the necessity for direct determination of “free” metal, particularly in systems where the metal concentration can be prohibitively low.

In recent years, some researchers have developed a competitive spectrophotometeric method for the complexation study of metal ions with crown ethers and cryptands [22–25], using murexide as a suitable metallochromic indicator. A literature survey shows less attention for the complexation of both murexide [22] and 18-crowns-6 with lanthanide(III) ions [3, 22–27]. In this paper we report a spectrophotometric study of the complexation of La(III), Ce(III), Pr(III) and Er(III) with some macrocyclic polyethers 18-crown-6 (18C6, **I**), dibenzo-18-crown-6 (DB18C6, **II**), dicyclohexano-18-crown-6 (DCY18C6, **III**) and dibenzopyridino-18-crown-6 (DBPY18C6, **IV**) (Figure 1).

Experimental

Reagent grade nitrate salts of lanthanum, cerium, and prasedymium, erbium chloride and murexide (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Macrocycles 18C6, DB18C6, DCY18C6, DBPY18C6 were purchased from Merck. Reagent grade dimethylsulfoxide (DMSO, from Merck) was also used.

All spectra were recorded on a Cecil 3000 spectrophotometer which was connected to a personal computer. In a typical experiment, 2–2.8 mL of murexide in DMSO (3.0×10^{-5}–4.0×10^{-5} M) was placed in the spectrophotomer cell, thermostated to 25 °C, then a known amount of the metal solution (10 μl of 1.0×10^{-3} M) was added in a stepwise manner using a calibrated microsyringe. The spectra of the solution after attainment of equilibrium was recorded. Addition of the metal ion solution was continued until the desired metal to murexide mole ratio was achieved. The same procedure was used when the formation of crown complexes were evaluated. So, the solution of both ligands (3.0×10^{-5}–4×10^{-5} M) of murexide as coloured ligand

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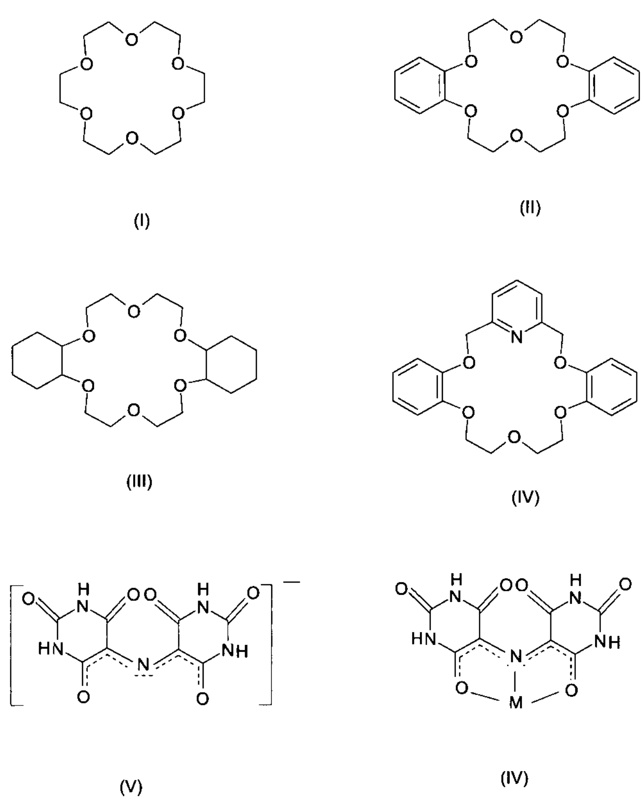

Figure 1. The structure of ligands.

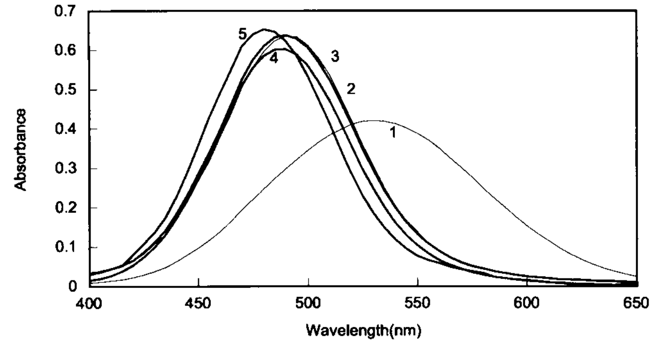

Figure 2. Visible spectra of 4.0 × 10^{-5} M murexide (1), and its complexes with (2) La(III), (3) Ce(III), (4) Pr(III), and (5) Er(III) in DMSO.

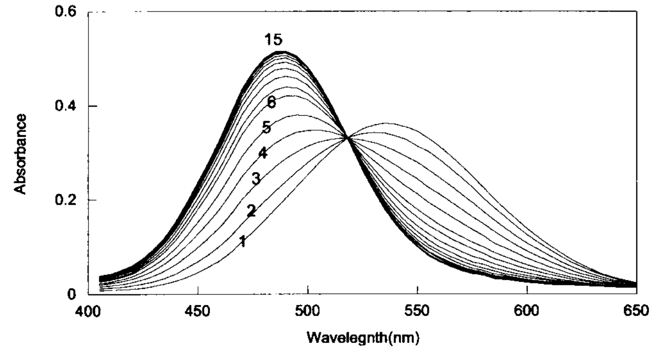

Figure 3. Visible spectra for titration of murexide (3.4 × 10^{-5} M) with Pr(III) ion in DMSO in the presence of DCY18C6 (3.4 × 10^{-3} M) at 25 °C. Respective Pr(III)/murexide mole ratios in different solutions are 1, 0.0; 2, 0.14; 3, 0.29; 4, 0.43; 5, 0.57; 6, 0.71; 7, 0.86; 8, 1.0; 9, 1.14; 10, 1.28; 11, 1.43; 12, 1.57; 13, 1.71; 14, 1.85; 15, 2.0.

and (2.0 × 10^{-3}–5.0 × 10^{-3} M) of crown), were titrated with a concentrated metal ion solution (1.0 × 10^{-3} M).

Results and discussion

Murexide, the ammonium salt of purpuric acid (5-[hexahydroxy-2,4,6-trioxo-5-pyrimidinyl)imino]-2,4,6-(1H,3H,5H) pyrimidinetrione, monoammonium salt, **V** (Figure 1) has been used for many years as a suitable complexing agent for a large number of metal ions over a wide range of experimental conditions [28–30]. The electronic absorption spectra of 4.0 × 10^{-5} M murexide and its complexes with lanthanide(III) ions (La(III), Ce(III), Pr(III) and Er(III)) used in DMSO solution are shown in Figure 2. The spectral behavior of the complexes is quite unique in all cases, consisting of strong shifts (40–50 nm) towards shorter wavelengths; the reasons for such strong and ion-specific blue shifts are discussed elsewhere [31].

The absorption spectra of murexide in DMSO upon titration with increasing amount of the different metal ions used in the absence and presence of the crown (18C6, DB18C6, DCY18C6, DBPY18C6) were also obtained. Sample spectra for murexide-Pr in the presence of DCY18C6 are shown in Figure 3. The stoichiometry of the murexide complexes of these lanthanide ions were examined by the mole-ratio method and supported by a computer fitting program. In all cases the stoichiometry was 1 : 1 and the existence of a well-defined isosbestic point in the resulting spectra (Figure 3) further emphasizes the simple 1 : 1 complexation equilibria of lanthanide- murexide (Figure 4) and Er-murexide in the presence of the macrocycles in DMSO solution (Figure 5) [32–34].

The formation constants of the 1 : 1 complexes between the metal ions used and murexide (Mu, as colored ligand) and crown (as buffer ligand) in DMSO solution were determined by absorbance measurements at the λ_{max} of the metal ion-murexide complex, a solution in which constant concentrations of both ligands were titrated with a concentrated metal ion solution using a pre-calibrated syringe. Attainment of equilibrium was checked by observation of

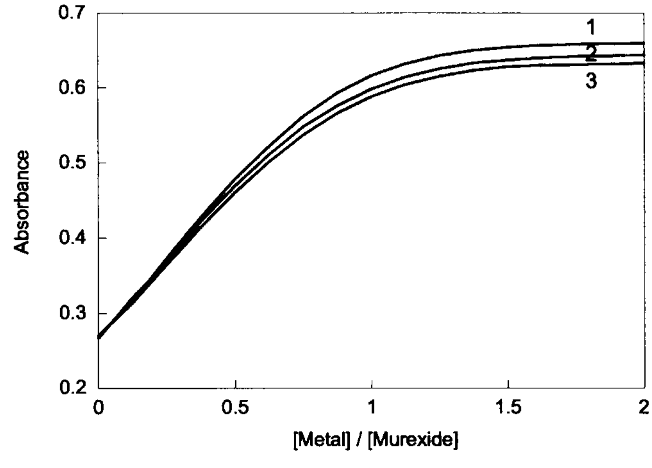

Figure 4. Absorbance – mole ratio plots for murexide complexes with (1) La (III), (2) Ce (III), and (3) Pr (III) in DMSO solutions at 25 °C.

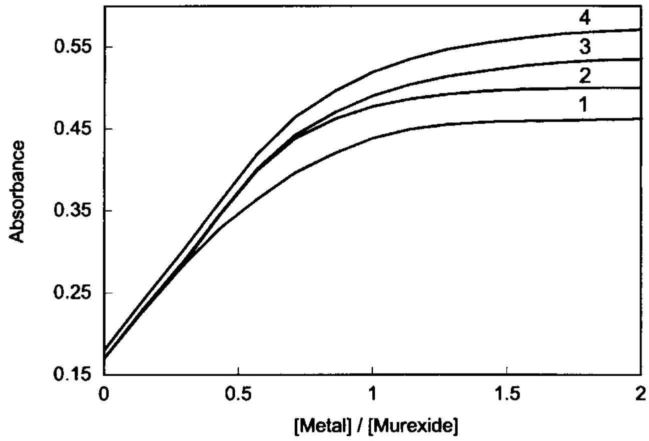

Figure 5. Absorbance – mole ratio plots for murexide – Er (III) complexes in the presence of macrocycles: (1) DB18C6, (2) DBPY18C6, (3) DCY18C6 and (4) 18C6 in DMSO at 25 °C.

no further change in the spectra after several hours. Sample absorbance-mole ratio plots in the absence and presence of crown are shown in Figures 4 and 5.

When a lanthanide (III) ion: M^{3+}, reacts with murexide and crown to form 1 : 1 complexes, the corresponding formation constants can be written as

$$\mathrm{M} + \mathrm{Mu} \rightleftharpoons \mathrm{MMu} \quad \mathrm{K_{Mmu}} = [\mathrm{MMu}]/[\mathrm{M}][\mathrm{Mu}] \tag{1}$$

$$\begin{aligned}\mathrm{M} + \mathrm{Crown} \rightleftharpoons \mathrm{MCrown} \quad & \mathrm{K_{MCrown}} \\ &= [\mathrm{MCrown}]/[\mathrm{M}][\mathrm{Crown}]\end{aligned} \tag{2}$$

(charges are omitted for simplicity). Mass balance equations and the observed absorbance, A_{obs}, are given as

$$\mathrm{C_{Mu}} = [\mathrm{Mu}] + [\mathrm{Mmu}] \tag{3}$$

$$\mathrm{C_{Crown}} = [\mathrm{Crown}] + [\mathrm{MCrown}] \tag{4}$$

$$\mathrm{C_M} = [\mathrm{M}] + [\mathrm{MMu}] + [\mathrm{MCrown}] \tag{5}$$

$$A_{\mathrm{obs}} = \varepsilon_{\mathrm{Mu}}[\mathrm{Mu}] + \varepsilon_{\mathrm{MMu}}[\mathrm{MMu}], \tag{6}$$

where C and ε are the analytical concentration and molar absorptivity of the species indicated, respectively. The mass balance equations can be solved in order to obtain an equation for the free metal ion concentration, [M], as follows

$$\begin{aligned}\mathrm{K_{MMu}K_{MCrown}}[\mathrm{M}]^3 &+ \{\mathrm{K_{MMu}K_{MCrown}}(\mathrm{C_M}-\mathrm{C_{Mu}}-\mathrm{C_{Crown}}) \\ &- \mathrm{K_{MMu}}-\mathrm{K_{MCrown}}\}[\mathrm{M}]^2 \\ &- \{\mathrm{K_{MCrown}}(\mathrm{C_M}-\mathrm{C_{Crown}}) \\ &+ \mathrm{K_{MMu}}(\mathrm{C_{Mu}}-\mathrm{C_M}) - 1\}[\mathrm{M}] \\ &- \mathrm{C_M} = 0.\end{aligned} \tag{7}$$

For evaluation of the formation constants from the absorbance vs. $\mathrm{C_M/C_{Mu}}$ mole ratio data, a non-linear least-squares curve fitting program KINFIT was used [35]. The program is based on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique [36] or the Powell procedure [37]. Adjustable parameters are the formation constants $\mathrm{K_{MMu}}$ and $\mathrm{K_{MCrown}}$ and the molar absorptivities $\varepsilon_{\mathrm{Mu}}$ and $\varepsilon_{\mathrm{MMu}}$. The free metal ion concentration was calculated from (7) by means of a Newton–Raphson procedure [38]. Once the value of [M] had been obtained, the concentrations of all other species involved were calculated from the mass balance Equations (3)–(5), using the estimated values of the formation constants and molar absorptivities of the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between the calculated and observed values of absorbance for all experimental points was minimized. The output of the program KINFIT comprises refined parameters, the sum-of-squares and the standard deviation of the data.

All the resulting formation constants, evaluated from computer fitting of the absorbance-mole ratio data, are summarized in Table 1. A sample computer fit of the data is shown in Figure 6. Our assumption of 1 : 1 stoichiometry for the murexide and crown complexes with La(III), Ce(III), Pr(III) and Er(III) ions seems reasonable in the light of the fair agreement between observed and calculated absorbances. The formation constants obtained for the murexide-Prasedium complex in DMSO solution is in fair agreement with that reported in the literature [22].

The resulting data in Table 1 show that the sequence of stability of the murexide complexes with the cations La(III) > Ce(III) > Pr(III) > Er(III) in DMSO follows the effective ionic radii [39]. However, amongst these metal ions the La(III)-purpurate complex has the highest stability in DMSO solution and this is probably due to the proper size of lanthanum ion which could favor a suitable fit with the donating atoms of the murexide (bridging nitrogen atom and neighboring oxygen atoms, **V**, **VI**, Figure 1) [39].

As seen in Table 1 the stability of the La(III), Ce(III), Pr(III) and Er(III) complexes with the various 18-crowns-6 in DMSO increases in the order La(III)> Ce(III) >Pr(III) > Er(III). This increase in stability is fairly small when compared with the specificity displayed by the groups IIA ions. Since the best fit of metal ion to ligand cavity is a prime requisite for complex stability, La(III) with an ionic radius of 1.061 Å should fit nicely inside the cavities of 18-crowns with radii of 1.3-1.6 Å [33, 34]. The other cations with smaller ionic radii are too loose for the cavities of the 18-memebered ring. Therefore weaker complexes were expected. The fact that the trivalent lanthanide ions have radii comparable to $\mathrm{Na^+}$ and $\mathrm{Ca^{2+}}$ leads to the expectation that lanthanide ions would also form stable complexes with 18- crowns. There are at least two factors that may account for the lack of high stability constants in lanthanide complex formation. First, the radii decreases by only ca, 0.2 Å from La(III) to Er(III). This is much less than the differences in radii among the ions of groups IA and IIA. Second, using dimethylsulfoxide as the solvent removes difficulties associated with metal ion hydrolysis, but the solvent may specifically interact with metal complexes [22]. Extension of these ideas to lanthanide ions suggest

Table 1. Formation constants for Lanthanide (III) ions complexes with murexide and some 18-crowns-6 in DMSO solution at 25 °C.*

Cation	λ_{max}	log K_{MMu}	log K_{M18C6}	log $K_{MDB18C6}$	log $K_{MDCY18C6}$	log $K_{MDBPY18C6}$
La^{3+}	493	6.08 ± 0.08	2.22 ± 0.01	2.01 ± 0.01	2.03 ± 0.01	1.94 ± 0.01
Ce^{3+}	491	4.95 ± 0.05	2.20 ± 0.01	1.95 ± 0.01	2.00 ± 0.01	1.89 ± 0.01
Pr^{3+}	490	5.76 ± 0.03	1.90 ± 0.01	1.72 ± 0.01	1.76 ± 0.01	1.68 ± 0.01
Pr^{3+a}		5.45 ± 0.08				
Er^{3+}	482	5.70 ± 0.04	1.75 ± 0.01	1.49 ± 0.01	1.61 ± 0.01	1.62 ± 0.01

* λ_{max} of pure murexide in DMSO is 535 nm.

[a] Reference [22], $PrCl_3 \cdot 6H_2O$.

La^{3+}(1.061 Å), Ce^{3+}(1.034 Å), Pr^{3+}(1.013 Å), Er^{3+}(0.881 Å) [47, 48].

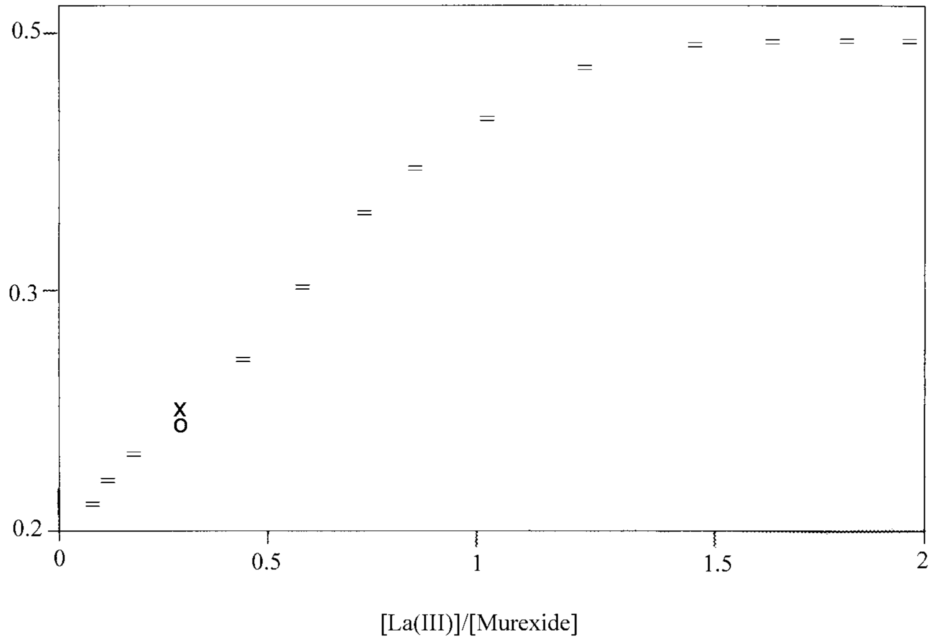

Figure 6. A sample of computer fit of absorbance vs. La(III)/murexide mole ratio plot in the presence of DBPY18C6 in DMSO solution at 25 °C: (×) experimental point; (○) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

that because of their higher charge and higher coordination number [41, 42], lanthanide complexes may interact significantly with the solvent. Comparison of the evaluated stability constants for different 18-crowns-6 with lanthanide ions given in Table 1, follows the order 18C6 > DC18C6 > DB18C6 > DBPY18C6. This sequence of order except for DBPY18C6 has been reported before only for potassium ion [44], transition metal ions [23], thallium ion [45] and alkali metal ions [40, 43]. Information about the complexation of DBPY18C6 is rare [26, 44]. The presence of three aromatic moieties in this macrocycle substantially reduced the affinity of the donor atoms towards the lanthanide ion. Introducing the pyridyl unit into the ring decreases both the flexibility and interaction of the macrocycle with lanthanide ions. This may be due to the pyridino nitrogen not being able to donate to the inner d orbital of lanthanide ion; on the other hand, these cations are so strongly solvated that considerably more energy must be expended in the desolvation step. The contribution of the solvent – complex and even solvent – ligand interactions on the stability of the resulting complexes cannot be ignored. Since the two main parameters for specificity and affinity of complexation of metal ions with these macrocycles are size and solvating power. Literature review [3, 23, 27, 40, 43, 45, 46] clearly shows, both two trends for complexation of 18-membered crowns with various metal ions group. These order are 18C6 > DCY18C6 > DB18C6 > DBPY18C6 for macrocycles and group IA > group IIA > lanthanide (III) ions. So this trend for similar ionic size cations is Na^+ [40, 43] > Ca^{2+} [46] > La^{3+} [this work] for all 18-membered crowns. The conclusion of this research shows that the 18-crowns-6 lack the specificity with lanthanide ions.

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