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Lanthanide Complex Formation with a Hexaaza Macrocyclic Ligand, 1,4,7,10,13,16-Hexaazacyclooctadecane ($A_6$18-Crown-6)*

WALENTY SZCZEPANIAK, BERNARD JUSKOWIAK and WANDA CISZEWSKA

Laboratory of Instrumental Analysis, Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

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Abstract

Stability constants of lanthanide complexes with 1,4,7,10,13,16-hexaazacyclooctadecane ($A_6$18C6) in aqueous 0.1 M NaCl medium have been determined at 20 °C by an out-of-cell potentiometric titration method. Lanthanide complexes with $A_6$18C6 are more stable than those of the macrocyclic polyethers and bicyclic cryptands. No appreciable metal ion specificity is observed, but with increasing atomic number of the lanthanides, the stability increases similarly to that observed for diazapolyoxa-macrocycles. The unusually high stability of the lanthanide $A_6$18C6 complexes is discussed in terms of the formation of partial bonds between the lanthanide ion and nitrogen donors and the inertness of the Ln–hexaaza-18-membered system.

Introduction

In coordination chemistry, the lanthanides in general prefer oxygen donor atoms rather than nitrogen [1]. The bonding of lanthanide complexes is mainly electrostatic with possibly a slight covalent modification due to the influence of inner-shell f-orbitals. Thus, the bonding is similar to that of main group metal ions but different from those of transition metal ions, which involve a high proportion of covalent character.

However, recent reports dealing with the coordination properties of aza-containing macrocyclic ligands suggest the importance of the covalent character of the nitrogen–lanthanide interaction. It was ascertained that the trivalent lanthanides act as excellent templating agents in the formation of polyaza-macrocyclic systems. A variety of complexes containing the hexaaza-18-membered ring were obtained with all the lanthanides [2–6]. These cationic complexes do not undergo metal exchange; their unusual inertness is also shown in the presence of typical lanthanide precipitating reagents, *e.g.* F^-, OH^- or $C_2O_4^{2-}$ [5].

Our study dealing with the ion-pair extraction of the lanthanide complexes with the macrocyclic ligand hexaazacyclooctadecane ($A_6$18C6) showed also the remarkable inertness of some complexes in strong alkaline medium. On this basis the selective extraction–spectrophotometric determination of lighter lanthanides in the presence of heavier ones was proposed [7]. There are, however, some doubts concerning the role of stability of the complexes for good extractability of lanthanide ions. The value of the stability constant for the lanthanum–$A_6$18C6 complex ($\log \beta = 5.7$) reported by Kodama *et al.* [8] seems to be too low because quantitative extraction even at pH 11 is observed. In order to ascertain whether the good extractability of lanthanides is due to higher stability of Ln–$A_6$18C6 complexes than reported, we carried out the determination of the stability constants by the pH titration method. The results should also provide evidence as to whether the extraction selectivity is due to differences between stability constants for particular lanthanide complexes.

Experimental

Materials and Standard Solutions

The ligand 1,4,7,10,13,16-hexaazacyclooctadecane ($A_6$18C6) was obtained from the Parish Chemical Co. as its $3H_2SO_4$ adduct and was used without further purification. The stock solution of the ligand (1×10^{-2} M) was prepared by dissolution of an appropriate weighed amount in 2×10^{-2} M NaOH. The standard lanthanide solutions, having a concentration of about 0.01 M, were prepared by dissolution of metal oxides in HCl and were standardized by EDTA complexometric titrations using xylenol orange as indicator. The carbonate-free sodium hydroxide solution (0.05 M) was prepared by diluting a 30% NaOH aqueous solution from Merck (Suprapur).

Potentiometric Titration

All titrations were carried out at a constant ionic strength of 0.10 M NaCl. The use of $NaClO_4$ or Et_4NClO_4 gave the same results. Boiled water was used for all experiments. A model OP 208

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*Abbreviated as $A_6$18C6 throughout.

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Radelkis (Hungary) pH-meter in conjunction with a Radelkis OP 0808 combination pH-electrode (containing 0.2 M NaCl saturated AgCl) was employed to monitor the pH (±0.001 pH unit). The water-jacketed titration vessel with a 50 ml capacity, equipped with a Teflon five-hole cover was always kept at 20.0 ± 0.1 °C by using a constant temperature circulating bath. Prior to each experiment, the pH-meter was standardized at pH 4.00 and 9.22 ± 0.02 pH unit.

The solutions (20 ml) of the ligand (3.4×10^{-4} M), containing an additional amount of standardized HCl (added to keep the ligand in the hexa-protonated form), were titrated with 0.05 M NaOH delivered from a 10-ml OP 930 dispenser (Radelkis) with a reading accuracy of 0.001 ml. The solutions were covered with Ar gas and magnetically stirred. A 5-min equilibration time was required after each addition of the titrant. The titration data obtained with the ligand were analysed using the ES3TM computer program of Rigano *et al.* [9].

For the ligand–lanthanide complexation, the 'out-of-cell' titrations [10] were applied in order to ensure the necessary equilibration time. Sets of about fourteen solutions containing in each 2×10^{-4} M Ln^{3+} plus 3.4×10^{-4} M ligand were prepared. Different quantities of 0.05 M NaOH were added to each solution to give a pH range of *ca.* 5–8. These tightly stoppered solutions were then left for 24 h under Ar gas to ensure the equilibration was achieved. Data points in the buffer region ($3 < a < 5$) were employed for the calculation of stability constants by the method based on the iterative procedure, where hydrolysis of lanthanides was considered [11].

The concentration of free ligand [L], average ligand number $\bar{n}$ and concentration of free metal [M] were calculated from eqns. (1) to (4) [12].

$$[L] = \frac{(6-a)C_L - [H] + [OH] + K_{OH}[M][OH]}{\beta_H} \qquad (1)$$

$$\bar{n} = \frac{C_L - [L]\alpha_{L(H)}}{C_M} \qquad (2)$$

$$\log \frac{\bar{n}}{1-\bar{n}} = \log \beta + \log \frac{[L]}{1 + K_{OH}[OH]} \qquad (3)$$

$$[M] = \frac{C_M}{1 + \beta[L] + K_{OH}[OH]} \qquad (4)$$

where

a = mole of base/mole of ligand.

$$\alpha_{L(H)} = 1 + K_1[H] + K_1K_2[H]^2 + \cdots + K_1 \cdots K_6[H]^6,$$

$$\beta_H = K_1[H] + 2K_1K_2[H]^2 + \cdots + 6K_1K_2 \cdots K_6[H]^6,$$

$$K_{OH} = \frac{[M(OH)]}{[M][OH]} \quad \text{and} \quad \beta = \frac{[ML]}{[M][L]}$$

The charges are omitted. The approximate values of [L], $\bar{n}$ and β were first calculated with the assumption that $[M] = C_M$, and then the more accurate value of [M] was calculated. The calculations were repeated until the desired value of $|\log \beta^i - \log \beta^{(i-1)}|$ was obtained.

Results and Discussion

The stepwise protonation constants for the macrocycle $A_6$18C6 are reported in Table I. As has already been observed for polyaza-macrocycles, these values constitute two groups [13, 14]. The cyclic amine exhibits high basicity in the first three steps and rather low basicity in the last three steps. For comparison, the protonation constants reported by Kodama *et al.* [8] are also listed and a good agreement of the first three constants is observed.

The complexation of lanthanides takes place above pH 6.5 (Fig. 1) and therefore differences in the values of the last three protonation constants have no essential effect on the determined values of the stability constants listed in Table II.

The remarkably high stability of the lanthanide–$A_6$18C6 complexes should be attributed to the presence of the nitrogen donors. The cyclic hexaether 18-crown-6 having O-donor atoms forms complexes only with light lanthanides and their stability constants in methanol range from $\log \beta$ = 3.3 (La) to 1.3 (Gd) [15]. The replacement of two

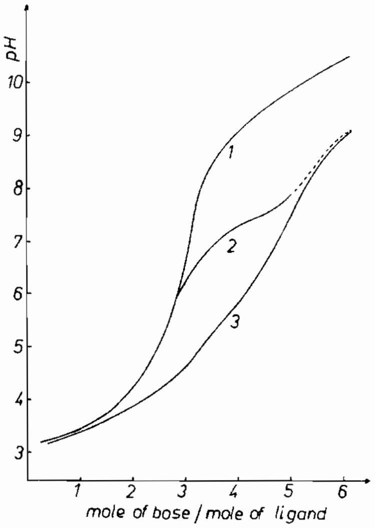

Fig. 1. Potentiometric titration curves of $A_6$18C6 (1), $A_6$18C6 + Pr (2) and back-titrated $A_6$18C6 + Pr (3). [L] = 3.4×10^{-4} M, $[Pr^{3+}] = 2 \times 10^{-4}$ M. Ionic strength = 0.1 M (NaCl); temperature = 20 °C.

TABLE I. Protonation Constants[a] of $A_6$18C6

log K_1	log K_2	log K_3	log K_4	log K_5	log K_6	Reference
10.42 ± 0.05	9.58 ± 0.05	8.51 ± 0.07	4.89 ± 0.10	*ca.* 3	2	This work
10.19	9.23	8.73	4.09	*ca.* 2	*ca.* 1	8

[a] $K_n = [LH_n][LH_{n-1}]^{-1}[H]^{-1}$.

TABLE II. Stability Constants of Lanthanide Complexes with $A_6$18C6 in Water at 20 °C

M	La	Ce	Pr	Nd	Sm	Eu	Gd
log β (ML)	9.1 ± 0.2	9.8 ± 0.1	10.0 ± 0.2	10.2 ± 0.1	10.1 ± 0.1	10.1 ± 0.2	9.8 ± 0.1
M	Tb	Dy	Ho	Er	Tm	Yb	Lu
log β (ML)	10.0 ± 0.3	10.1 ± 0.1	10.1 ± 0.1	10.0 ± 0.2	10.4 ± 0.2	11.2 ± 0.1	11.8 ± 0.3

O-donors by NH groups leads to an increase in the stability of the lanthanum–$A_2$18C6 complexes of approximately three orders of magnitude [16]. Thus, the presence of six N-donors in $A_6$18C6 has a more pronounced stabilizing effect and a further increase in the stability of lanthanide complexes is observed.

The difference ($\Delta \log \beta = 3.4$) between the stability constant of La–$A_6$18C6 reported by Kodama *et al.* [8] and that determined here can be explained by a slow complexation reaction. The reported value of $\log \beta = 5.7$ refers to the equilibration time of 1 min [8] which is not enough to complete complex formation. The slow complexation of lanthanides was also observed for other aza-containing macrocycles [17, 18].

The slow complexation of the lanthanides with $A_6$18C6 is accompanied by the slow dissociation of the complexes. The back-titration curve for the praseodymium–$A_6$18C6 system, shown in Fig. 1, illustrates the inertness of the complex. The inertness of Ln–$A_6$18C6 complexes to attack by hydroxide ions was observed during the extraction study [7]. The postulated earlier formation of extractable Ln(OH)$A_6$18C6 species [7] was not confirmed by the potentiometric study because data points above pH 7.5, where the mixed hydroxo complexes might form, had to be excluded from the calculation because of precipitation of hydroxides of lanthanides and/or lanthanide complexes. However, the existence of mixed hydroxo complexes in solution (reported for the more encapsulated lanthanide cryptates [19] and in the solid state for the Ln–hexaaza macrocyclic Schiff base [5, 6]) indicates the possibility of the formation of Ln(OH)–$A_6$18C6 complexes in more alkaline solutions.

The pattern of metal selectivity (Fig. 2) is similar to that observed for other aza-macrocyclic ligands (cryptand (2.2.1.), $A_2$15C5) and for classical ethylenediamine tetraacetic acid, but is the reverse of that observed for polyoxa-macrocycles of the 18-crown-6 type, where the decreasing stability of 18-C-6 lanthanide complexes is explained by competition between the solvent and the macrocycle (the smaller lanthanides are expected to coordinate more strongly with the solvent) [19]. For ligands of the EDTA type, the increase in lanthanide complex stability constants is attributed to the increase in the charge density of the metal ions. In the case of polyazamacrocycles, because of the presence of a macrocyclic ring with amine donors, both the charge density and the ionic radius of the lanthanide ions have to be considered in order to rationalize the strength of complex formation. The lanthanide

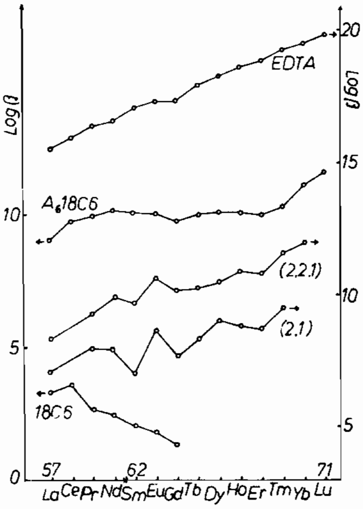

Fig. 2. Variation of stability constants with atomic numbers of the lanthanides. L = $A_6$18C6 in H_2O; EDTA in H_2O [12]; (2.2.1), (2.1) [18] and 18C6 [15] in methanol.

with the largest ionic radius fits better into the ligand cavity, but the lower charge density offsets this advantage. Further disadvantageous decrease in ionic radius is compensed by an increase in the charge density and the stability of the complexes from Pr to Er is nearly unchanged. The increase in stability constants from Tm to Lu, apart from a contribution by the charge density effect, is probably caused by additional ligand rearrangement which results in a partially folded macrocyclic ring conformation. Some support for the possibility of such an effect comes from the solid structure of the lutetium–hexaaza-macrocyclic Schiff base complex, where the Lu–macrocyclic moiety has a 'folded butterfly' structure [6]. In contrast, only a minor deviation from planarity was observed for the lanthanum [2] and samarium complexes [4].

It should be noted that hexaaza-macrocyclic Schiff base ligands represent the rigid (macrocyclic) system, while in the case of the flexible $A_6$18C6 ligand the folding effect should be more important. Unfortunately, there are no data concerning the structure of complexes of lanthanides with the $A_6$18C6 ligand.

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