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Bond Strengths and Reproportionation Constants of Mixed Ligand Complexes of Lanthanones

La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III), Y(III)—Nitrilotriacetic acid—Tropolone

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1:1:1 mixed ligand complexes of lanthanones with nitrilotriacetic acid (*NTA*) and 2-hydroxy-2,4,6-cycloheptatrien-1-one (tropolone; *TR*) have been studied potentiometrically in 50% (*v*/*v*) aq. dioxane medium at $\mu \simeq 0.1M$-$NaClO_4$ at 30 ± 1 °C. For these systems, complexation of primary ligand (*NTA*) with lanthanones is complete before complexation with *TR* takes place. The formation constants have been calculated by a weighted least squares method. The results show that *NTA* and *TR* are incompatible ligands towards lanthanones and hence the mixed ligand complexes formed have lower stability than either of the parent complexes.

Komplexbildungskonstanten von Lanthaniden mit gemischten Liganden

Es wurden 1:1:1-Komplexe von Lanthaniden [*Ln*(III)] mit Nitrilotriessigsäure (*NTA*) und 2-Hydroxy-2,4,6-cycloheptatrien-1-on (Tropolon; *TR*) als gemischte Liganden potentiometrisch in 50% (*v*/*v*) wäßr. Dioxan bei $\mu \cong 0.1M$-$NaClO_4$ und 30 ± 1 °C untersucht. Die Komplexbildungskonstanten wurden mittels einer gewichteten Fehlerquadrat-Methode berechnet. Es zeigte sich, daß *NTA* und *TR* inkompatible Liganden gegenüber *Ln*(III) sind und die gemischten Komplexe somit eine geringere Stabilität als die jeweiligen einfachen Komplexe haben.

Introduction

Lanthanones are generally considered to have coordination number six or more in solution. In case of 1:1 complexes of lanthanones with nitrilotriacetic acid (*NTA*), the ligand can occupy four coordinating

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sites of the metal ion, leaving some coordinating sites vacant. A bidentate ligand like 2-hydroxy-2,4,6-cycloheptatrien-1-one (tropolone; *TR*) could therefore fill two of the vacant sites to give mixed chelates. For the present study *NTA* has been chosen as the primary ligand, because it forms very stable 1:1 complexes with lanthanones, which are neutral, thus minimizing the electrostatic repulsion towards the other incoming ligand. Also the (*Ln*—*NTA*) species have large stability constants and the possibility of ligand exchange is negligible, i.e. the reaction:

$$(Ln\text{—}NTA) + TR \rightleftharpoons (Ln\text{—}TR) + NTA$$

does not occur, as *TR* forms much less stable complexes with lanthanones as compared to *NTA*.

Experimental

All the metal ion solutions were prepared from A.R. lanthanone nitrate samples, obtained from Indian Rare Earth Ltd. and standardised complexometrically, using xylenol-orange as indicator. The solution of *TR* (Aldrich) was prepared in freshly distilled dioxane. *NTA* (Riedel) was dissolved in 3 equivalents of NaOH solution and was used as trisodium salt. Chemically pure sodium perchlorate was used to keep the ionic strength constant ($\mu \simeq 0.1\,M$). A standardised $0.05\,M$ solution of tetramethyl ammonium hydroxide (*TMAH*) in 50% dioxane (aqueous) was used as titrant. Dioxane was purified by refluxing with sodium wire for 24 h. and was freshly distilled over sodium before use. Presaturated nitrogen (with 50% aq. dioxane) was passed through the solutions during titration.

The titrations were carried out at 30 ± 1 °C with a Beckman pH-meter, SS-2 model, in conjugation with a glass and calomel electrode assembly (0-14 pH range).

The pH-meter was standardised with potassium hydrogen phthalate and phosphate buffers.

The following solutions (total volume = 19.7 ml, due to contraction on mixing dioxane with water) were titrated potentiometrically against $0.05\,M$ *TMAH* solution:

(I) 3.0 ml $HClO_4$ ($0.02\,M$) + 0.5 ml $NaNO_3$ ($0.02\,M$) + 1.0 ml $NaClO_4$ ($2\,M$) + 5.5 ml H_2O + 10.0 ml dioxane.

(II) 3.0 ml $HClO_4$ ($0.02\,M$) + 0.5 ml $NaNO_3$ ($0.02\,M$) + 1.0 ml $NaClO_4$ ($2\,M$) + 5.5 ml H_2O + 0.5 ml *TR* ($0.02\,M$) + 9.5 ml dioxane.

(III) 3.0 ml $HClO_4$ ($0.02\,M$) + 0.5 ml $NaNO_3$ ($0.02\,M$) + 1.0 ml $NaClO_4$ ($2\,M$) + 0.5 ml *NTA* ($0.02\,M$) + 5.0 ml H_2O + 10.0 ml dioxane.

(IV) 3.0 ml $HClO_4$ ($0.02\,M$) + 1.0 ml $NaClO_4$ ($2\,M$) + 0.5 ml *NTA* ($0.02\,M$) + 0.5 ml metal ($0.02\,M$) + 5.0 ml H_2O + 10.0 ml dioxane.

(V) 3.0 ml $HClO_4$ ($0.02\,M$) + 1.0 ml $NaClO_4$ ($2\,M$) + 0.5 ml metal ($0.02\,M$) + 0.5 ml *NTA* ($0.02\,M$) + 0.5 ml *TR* ($0.02\,M$) + 5.0 ml H_2O + 9.5 ml dioxane.

Results and Discussion

Formation Constants

NTA reacts with lanthanones at lower pH which is evident from the titration curve of solution (IV). Also the titration curves of solutions (IV) and (V) for [*Ln*—*NTA*] and [*Ln*—*NTA*—*TR*] overlap each other in the lower pH range indicating that *TR* does not combine with metal ion in this pH range. At higher pH, one observes a divergence of the curves of solutions (IV) and (V), showing the coordination of *TR* with the species [*Ln*—*NTA*]. The reaction may be represented as:

$$Ln + NTA \rightleftharpoons [Ln\text{—}NTA]$$

$$[Ln\text{—}NTA] + TR \overset{K_{MAL}}{\rightleftharpoons} [Ln\text{—}NTA\text{—}TR].$$

The formation constant of the mixed species may be given by:

$$K_{MAL} = \beta_{1,1} = \frac{[Ln\text{—}NTA\text{—}TR]}{[Ln\text{—}NTA]\,[TR]}$$

where K_{MAL} denotes $K_{Ln\text{—}NTA\text{—}TR}$.

The proton-ligand stability constant for tropolone was found to be 7.5. The stability constants for *NTA*[1] and *TR*[2] complexes of lanthanones have been re-determined under the present conditions and are in good agreement with earlier reported values. From the titration curves of solutions (I), (II), and (V), $\bar{n}$ and pL values of the mixed complexes were determined at various pH values by the method of *Irving* and *Rossotti*[3]. From the values of n and pL, stability constants were computed on an IBM 360 computer using a weighted least squares program of *Sullivan et al.*[4]. This program assigns a weight W_i, to each residual U_i, and uses matrix algebra to solve the set of equations

$$\partial S / \partial \beta_n = 0$$

where $S = \sum_i W_i U_i^2$ and β_n is the nth overall formation constant. The residuals are defined as:

$$U_i = \sum_n (\bar{n}_i - n)\, \beta_n\, [P_i]^n$$

β_n values were again calculated by attaching to them approriate weight factors computed from the first set of β_n and the cycle was repeated till a change of less than one part per thousand was obtained in each β_n. This determines a set of β_n minimizing the functions A and S, $S_{\min}$ having the same significance as χ^2, with k degrees of freedom[5] ($S_{\min} = \chi^2$).

Reproportionation Constant

The constant which correlates the relative stability of the mixed ligand complex with the parent complexes formed with the same ligands, is termed as reproportionation constant. The correlation between the formation constant and the reproportionation constant is given by the following relation:

$$\beta_{j,i} = K_d \beta_{m,0}^{j/m} \beta_{0,m}^{i/m} \qquad (m = i + j)$$

where K_d is the reproportionation constant, which gives a measure of the compatibility of different ligands in the inner sphere of a given metal ion. If the ligands are not compatible, then the mixed complex formed will be less stable than the parent complexes. In such cases the reproportionation constant should be smaller than unity. In case of compatibility of the ligands, this constant is larger than unity[6]. The results of the present study are summarized in Table 1.

Table 1. *Formation and reproportionation constants of various mixed ligand complexes and $S_{\min}$ values*

Ln^{3+}	$\log \beta_{1,1}$	$S_{\min}$	$\log \beta_{0,1}$	$(\beta_{2,0})^{\frac{1}{2}}$ (NTA)	$(\beta_{0,2})^{\frac{1}{2}}$ (TR)	K_d
La^{3+}	4.46	0.45	6.31	4.205	3.435	0.31
Pr^{3+}	4.76	1.09	6.76	4.350	3.503	0.31
Nd^{3+}	5.01	1.23	6.84	4.444	3.528	0.32
Sm^{3+}	5.28	0.63	7.01	4.530	3.577	0.33
Gd^{3+}	5.34	0.42	7.13	4.563	3.609	0.32
Dy^{3+}	5.53	0.78	7.23	4.599	3.636	0.32
Yb^{3+}	5.89	0.96	7.76	4.661	3.760	0.33
Y^{3+}	5.43	0.79	7.18	4.661	3.622	0.33

Bond Strengths of Ln—NTA—TR Complexes

The strength of the individual M—X bonds in the complex MX_jY_i can be calculated from the formation constants of the mixed ligand complex and the parent complexes MX_j and MY_i using the following equation:

$$F_x = \frac{RT}{4j} \ln \beta_{j,i} \frac{\beta_{j,0}}{\beta_{0,i}} \tag{1}$$

Similarly, the M—Y bond strengths in the same complex is given by:

$$F_Y = \frac{RT}{4i} \ln \beta_{j,i} \frac{\beta_{0,i}}{\beta_{j,0}} \qquad (2)$$

The strengths of the metal ligand bonds in the parent complexes MX_m and MY_m can be calculated from their formation constants

$$F_X = \frac{RT}{2m} \ln \beta_{m,0}; \quad F_Y = \frac{RT}{2m} \ln \beta_{0,m} \qquad (3)$$

The differences in the free energies calculated from eqs. (1), (2), and (3) characterise the changes of the M—X and M—Y bond energies which occur in the mixed ligand complex formation[6]. The results of these investigations are given in Table 2 (values given in cal).

Table 2. *Bond strengths of complexes [cal]*

Ln^{3+}	$F_{X'}$ M-NTA (parent)	F_X M-NTA (mixed)	(F_X-$F_{X'}$)	$F_{Y'}$ M-TR (parent)	F_Y M-TR (mixed)	(F_Y-$F_{Y'}$)
La^{3+}	6106	2963	—3143	4103	114	—3989
Pr^{3+}	6563	2123	—3440	4238	138	—4100
Nd^{3+}	6822	3270	—3552	4300	190	—4110
Sm^{3+}	7087	3391	—3696	4418	256	—4162
Gd^{3+}	7191	3385	—3806	4495	304	—4191
Dy^{3+}	7308	3481	—3827	4565	332	—4233
Yb^{3+}	7506	3657	—3849	4883	418	—4465
Y^{3+}	7506	3382	—4124	4531	370	—4161

Results of the present investigations show that the mixed ligand complexes formed are less stable than either of the parent complexes, i.e. $\beta_{1,1}$ is less than $\beta_{1,0}$ or $\beta_{0,1}$. This can be explained on the basis that NTA and TR are incompatible ligands for forming mixed complexes with lanthanones, as the values of reproportionation constants for these systems are less than unity (Table 1). These values are quite close to one another, which clearly indicates that all the Ln^{3+} ions behave in the same manner towards the two ligands. In mixed ligand complexes formed by such incompatible ligands, the free energy and strengths of all the metal-ligand bonds decrease[7], which is evident from the data in

Table 2. If the geometrical structures and bond types of the parent complexes differ, then the corresponding mixed ligand complexes are less stable than either of the parent complexes[8].

The lower stability of the mixed complexes can also be explained from statistical considerations. The driving force for binding of the secondary ligand $[TR]^-$ with $[Ln—NTA]$ should be less than the binding force of $[TR]^-$ with $[Ln \cdot aq]^{3+}$. Further, the bulky *NTA* molecule is expected to produce a greater steric hindrance for $[TR]^-$ thereby decreasing $\beta_{1,1}$ considerably.

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