

Stability Constants of Lanthanide Complexes with Some Related Organic Ligands

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Summary: The stability constants of the complexes formed between trivalent ions and related carboxyphenylhydrazo- β -diketones ligands are reported at 30°C and at constant ionic strength (0.1M KNO₃) in 75% dioxane-water.

The affinity of different ligands for complexation with lanthanide ions reaches its highest value with ortho-carboxyphenylhydrazo-benzoylacetone; the lowest affinity is attained in the case of m-carboxyphenylhydrazodiethyl malonate ligands.

The relation between the overall stability constants " β_2 " of chelate compounds and both the atomic number of the lanthanide and Σ pKa's of the ligands were investigated.

Introduction

Previous investigators have studied complex formation between trivalent lanthanide ions and a variety of organic ligands as malonate¹, dicarboxylate², acetylacetone³, and other β -diketones^{4, 5}. Little has been reported about the product of coupling between diazonium salt of anthranilic acid and β -diketones. Some authors, however, have studied the chelation between similar ligands and transition elements⁶⁻⁹.

In view of the limited scope of measurements, it was decided to study stability trends within complete series of lanthanide ions and a number of these related ligands.

Experimental

A-Reagents

Stock solutions of the desired concentrations of lanthanide were prepared as mentioned previously¹⁰. Also other reagents such as organic ligands, potassium hydroxide etc., were prepared as described previously^{7,10}. The pH-Value of the solution is measured with pH-meter Model-25 China type fitted with glass and calomel electrodes at 30°C and constant ionic strength ($\mu = 0.1$). The PH-meter was calibrated using standard BDH buffer solutions. All titrations were carried out twice to insure an agreement between the pH-readings within ± 0.02 unit.

Standardization of potassium hydroxide solution was performed by titration against a standard solution of potassium hydrogen phthalate.

The organic ligands were synthesized by coupling diazonium salt of 2 or 3-carboxy aniline with suitable β -diketones. After several crystallizations from suitable solvents, the pure product was obtained. These ligands are: ortho-carboxyphenylhydrazoacetylacetone⁶ (o-CPHAA), ortho-carboxyphenylhydrazobenzoylacetone⁷ (o-CPHBA), Orthocarboxyphenylhydrazodiethylmalonate⁸ (o-CPHDEM), and meta-carboxyphenylhydrazodiethylmalonate⁷ (m-CPHDEM).

Calculation

The calculation of stability constants requires a knowledge of the acid dissociation constants of the ligands. This was previously done by a direct algebraic method¹¹. The stability constants of the formed complexes between organic ligands and lanthanide ions were calculated as described previously^{10,12}. One of the commonest difficulties arises from a special property of unknown substances which behave almost as though only 2:1 complex is being formed even at the start of the titration. In such cases β_2 (overall stability) is the only constant obtainable, and it can be easily calculated from the following equation¹².

$$\log \beta_2 = \log n - \log (2-n) - 2 \log [L^-]$$

After subjecting the data to the least-square analysis, the standard error limits of the individual run was calculated.

Results and Discussion

The logarithms of the overall stability constants ($\log \beta_2$) for the complexes of the organic ligands and lanthanide ions are given in Table (2).

Table 1: Dissociation Constants of the Ligands in 75% Dioxane-water at T = 30°C and $\mu = 0.1$ M using KNO_3 .

Ligand	ρKa_1	ρKa_2
o-CPHAA	6.08 ± 0.02	13.90 ± 0.04
o-CPHBA	5.59 ± 0.02	13.68 ± 0.02
o-CPHDEM	5.98 ± 0.01	13.72 ± 0.04
m-CPHDEM	6.40 ± 0.02	11.89 ± 0.04
Acetylacetone(AA) ¹³	12.70	
Benzoylacetone(BA)	12.85	

The data representing the relation between $\log \beta_2$ of the different complexes and atomic number of the lanthanide elements are represented in figure (1).

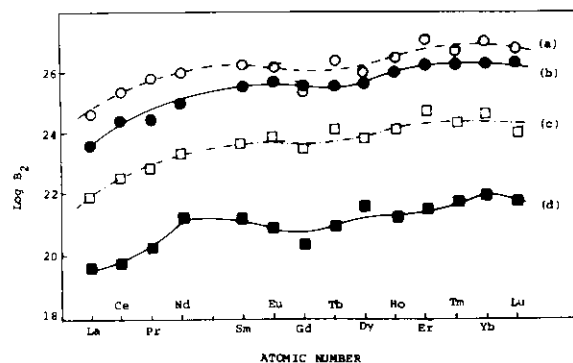


Fig 1: The relationship between atomic number and " $\text{Log } \beta_2$ " for trivalent lanthanides with o-CPHAA (curve b), o-CPHBA(a); o-CPHDEM (c) and m-CPHDEM (d).

It was expected that a linear relationship will be obtained when " $\text{Log } \beta_2$ " is plotted against the atomic number of the lanthanide if the nature of the bond between the organic ligands and the lanthanide ions were purely ionic.

The curves show two characteristic parts (1) representing light lanthanide elements (La–Eu), show a linear increase of the stability with increasing atomic number and (2) representing heavy lanthanide elements (Gd–Lu), show a buffer zone (almost a constant stability) around the gadolinium area. A small increase in the stability of the complexes

Table 2: Stability constants of Lanthanide Complexation by o-CPHAA; o-CPHBA, o-CPHDEM and m-CPHDEM at ionic strength $\mu = 0.1$ M using KNO_3 T = 30° in 75% dioxane water

	o-CPHAA Log β_2	o-CPHBA Log β_2	o-CPHDEM Log β_2	m-CPHDEM Log β_2
La	23.62 ± 0.04	24.65 ± 0.03	21.97 ± 0.04	19.57 ± 0.02
Ce	24.38 ± 0.04	25.38 ± 0.04	22.57 ± 0.03	19.70 ± 0.06
Pr	24.44 ± 0.05	25.82 ± 0.03	22.86 ± 0.04	20.29 ± 0.06
Nd	25.08 ± 0.05	26.01 ± 0.02	23.37 ± 0.04	21.26 ± 0.03
Sm	25.53 ± 0.01	26.24 ± 0.02	23.67 ± 0.04	21.26 ± 0.03
Eu	25.75 ± 0.05	26.18 ± 0.02	23.93 ± 0.04	20.89 ± 0.03
Gd	25.50 ± 0.05	25.46 ± 0.03	23.46 ± 0.05	20.40 ± 0.04
Tb	25.49 ± 0.05	26.41 ± 0.02	24.12 ± 0.03	21.04 ± 0.06
Dy	25.57 ± 0.06	25.01 ± 0.03	23.84 ± 0.04	21.63 ± 0.05
Ho	26.00 ± 0.05	26.47 ± 0.02	24.09 ± 0.04	21.31 ± 0.04
Er	26.26 ± 0.05	27.04 ± 0.03	24.47 ± 0.04	21.47 ± 0.05
Tm	26.26 ± 0.05	26.62 ± 0.03	24.28 ± 0.03	21.75 ± 0.05
Yb	26.26 ± 0.05	26.98 ± 0.02	24.64 ± 0.05	22.08 ± 0.05
Lu	26.26 ± 0.04	26.66 ± 0.03	24.00 ± 0.04	21.75 ± 0.05

for different cases is observed till lutetium, a behaviour that cannot be explained by the electrostatic bond theory. This behaviour may be attributed to some sort of different degrees of dehydration of cations upon complexation¹³. The above mentioned deviation from linearity is not peculiar; on the contrary, it seems to be common for most rare earth complexes with different chelating agents such as acetylaceton^{5,14}, tropolone, N-hydroxyethylenediamine triacetic acid¹⁵, and benzeoylacetone¹⁶. This similarity in the behaviour of the studied ligands with other ligands may be due to the presence of more than one type of coordination site in these ligands. There is also a possibility of change in the number of points of attachments before and after gadolinium since they contain oxygen and nitrogen as coordination sites.

Figure (2) represents the relation between $\text{Log } \beta_2$ values of selected lanthanide complexes and pK_a 's of the organic ligands. The correlation reflects the ionic nature of the metal-ligand interaction. Only benzoylacetone ligand fails to fit the linear correlation. This can be attributed to the aromatic ring giving a rigidity to the complex not present in the other systems. This behaviour leads to the conclusion that these ligands are structurally the same and consist of the same species and having similar degree of dehydration upon complex formation for all cations.

The order of the overall stability constants Table (2) of different ligands with lanthanide ions is as follows :-

$\text{o-CPHBA} > \text{o-CPHAA} > \text{o-CPHDEM} > \text{m-CPHDEM}$ while the order of summation of dissociation constants, $\sum \text{pK}_a$'s is as follows.

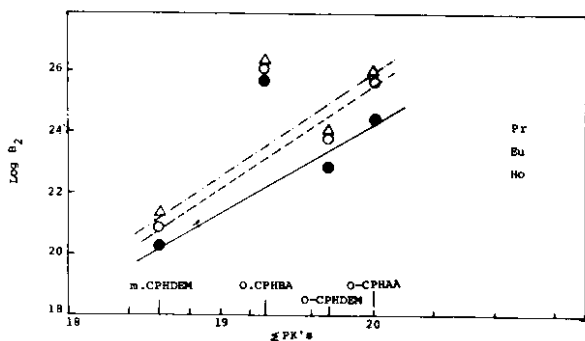


Fig. 2 Correlation of $\text{Log } \beta_2$ of the Pr(III), Eu(III) and HO(III) complexes and $\sum \text{pK}_a$'s of the ligands.

$\text{o-CPHAA} > \text{o-CPHDEM} >$

$\text{o-CPHBA} > \text{m-CPHDEM}$.

It is seen that the o-CPHDEM forms more stable than m-CPHDEM which is attributed to the higher basicity (i.e. $\sum \text{pK}_a$) of the ortho-type than that of the meta-type by 0.69 units. Moreover, the shifting of the carboxylate group to the meta position decreases the role of the sharing of that group in chelation which is reflected on the values of the stability constant.

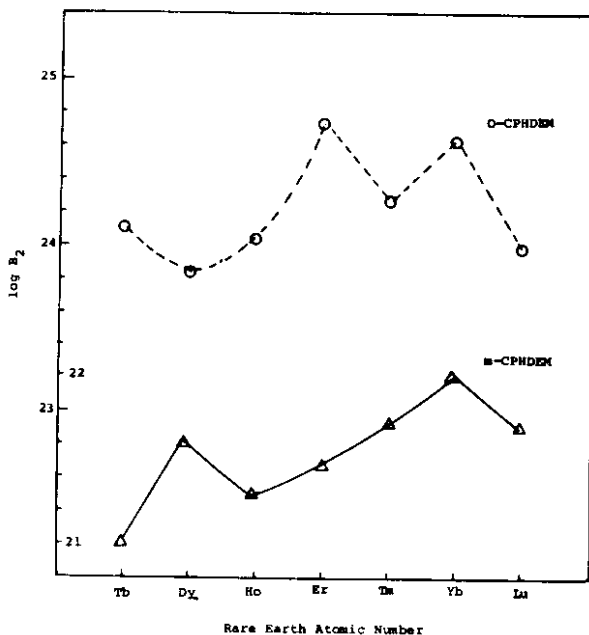


Fig. 3 Apparent odd-even effect in chelate stabilities noted with the heavier rare-earth malonate species.

A curious odd-even effect was observed from Tb to Lu, with $\text{Log } \beta_2$ in malonate ligands, figure (3). The difference in $\text{Log } \beta_2$ from Tb - Lu is outside the limits of experimental error. This lead to the conclusion that malonate ligands appear to be of value in the separation of rare earth mixtures by ion exchange elution techniques.

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