

Stability Constants of Lanthanide Complexes with some Structurally Related Organic Ligands

By

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ABSTRACT

The stability constants of the complexes formed between trivalent lanthanide ions and related carboxyphenylhydrazo-B-diketones ligands are reported, at 30 °C and at constant ionic strength (0.1 KNO₃), in 75 % dioxane-water. The affinity of different ligands for complexation with lanthanide ions reaches its highest value with ortho-carboxyphenylhydrazo-benzoylacetone, while the lowest affinity is attained in the case of m-carboxyphenylhydrazo-diethyl malonate ligand. The relation between the overall stability constants "B₂" of chelate compounds and both the atomic number of the lanthanide elements and $\sum pK_1 + pK_2$ of the ligands were investigated.

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Introduction

Previous investigators have studied complex formation between trivalent lanthanides and simple dicarboxylate ligands such as malonate⁽¹⁾ and maleate⁽²⁾. Grenthe and Co-workers^(3,4) have studied lanthanide complexation by more complicated dicarboxylate as oxydiacetate and ethylenedioxydiacetate as well as the thio and imino analogues of these ligands. Choppin and Co-workers⁽⁵⁾ have extended these studies to the benzene—1, 2—dioxydiacetate, Squaric and Eronic acids⁽⁶⁾, and some amino carboxylate⁽⁷⁾. Many studies of the complex formation of lanthanide ions with several B-diketones are cited in literature⁽⁸⁻¹²⁾. Little has been reported about the coupling between diazonium salt of anthranilic acid and B-diketones. Some authors, have studied the chelation between similar ligands and transition elements⁽¹³⁻¹⁷⁾.

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

Ortho carboxyphenylhydrazo acetylacetone (o-CPHAA);
Ortho carboxyphenylhydrazobenzoylacetone (o-CPHBA);
Ortho carboxyphenylhydrazodiethylmalonate (o-CPHDEM); and meta carboxyphenylhydrazodiethylmalonate (m-CPHDEM).

Experimental

The organic ligands used in this investigation were synthesized by coupling the diazonium salt of anthranilic acid with acetylacetone, benzoylacetone, and diethylmalonate in sodium acetate medium. The yellow crude materials were crystalized several times from ethanol. The formulae and the structure of the ligands were confirmed by elemental analysis and IR spectra.

Stock solutions of the desired concentrations of the lanthanide ions were prepared by dissolving known amounts of metal oxides (99.9 % B.D.H.) in hot nitric acid, then evaporate the solutions till dryness. The resulting nitrates was dissolved to the appropriate volume using bidistilled water. The acidity of each of these solutions was checked. The exact concentration of metal ions was determined by titration with EDTA solution, using xylenol orange as indicator.

Standard potassium hydroxide solution was prepared by dissolving a concentrated-carbonate free-potassium hydroxide solution in boiled bidistilled water. The solution of potassium hydroxide in 75 % dioxane-water was standerized against potassium hydrogen phthalate.

pH measurements were carried out using a Beckman Model SSR-2 Expandomatic pH-meter fitted with combined electrode. In all measurements the correction of pH in 75 % dioxane was considered as 0.28⁽¹⁸⁾.

Apparatus

The titration vessel was a 100 ml beaker jacketed for circulation of water at 30 ± 0.1 °C. A three-hole plug allowing insertion of electrode, inlet and outlet purified nitrogen. The general procedure of titration was as follows : 50 ml of a mixture of 5×10^{-3} M ligand and 2.5×10^{-3} M metal ion in 75 % dioxane, and potassium nitrate (to keep the ionic strength constant at 0.1), was titrated against potassium hydroxide (also dissolved in 75 % dioxane). The pH of the solution was read after each addition of 0.05 ml base. Sufficient time was given after each addition for the attainment of equilibrium. All titrations were repeated at least two times and agreement between the pH-readings of different titrations was usually within ± 0.02 . The solutions were continuously stirred by bubbling nitrogen through them. Before and after each titration the pH-meter was checked against standard buffers of known pH.

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 method⁽¹⁹⁾. Bjerrum's method⁽²⁰⁾ was, also, adopted to calculate the stability constants of the complexes formed.

Results and Discussion

The acid dissociation constants of the ligands, and the logarithms of the overall stability constants ($\text{Log } B_2$) for the complexes of the organic ligands and lanthanide ions are given in tables (1) and (2).

Table 1
Dissociation constants of the ligands

in 75 % dioxane [T=30°C; \mathcal{M} =0.1 M (KNO₃)]

Ligand	pK_{a1} (a)	pK_{a2} (b)
o-CPHAA	6.08	13.90
o-CPHBA	5.59	13.68
o-CPHDEM	5.98	13.72
m-CPHDEM	5.40	11.89
Acetylacetone (AA) ⁽²¹⁾	12.70	
Benzoylacetone (BA) ⁽²¹⁾	12.85	

(a): ± 0.01

(b): ± 0.01

The error limits were calculated, subjecting the data to the least square analysis. The values of $\log B_2$, pK_{an} and σ were calculated from 12 measurements. The data representing the relation between " $\log B_2$ " of the different complexes and atomic number of the lanthanide elements were subjected to the same data processing treatment and represented in Figure (1).

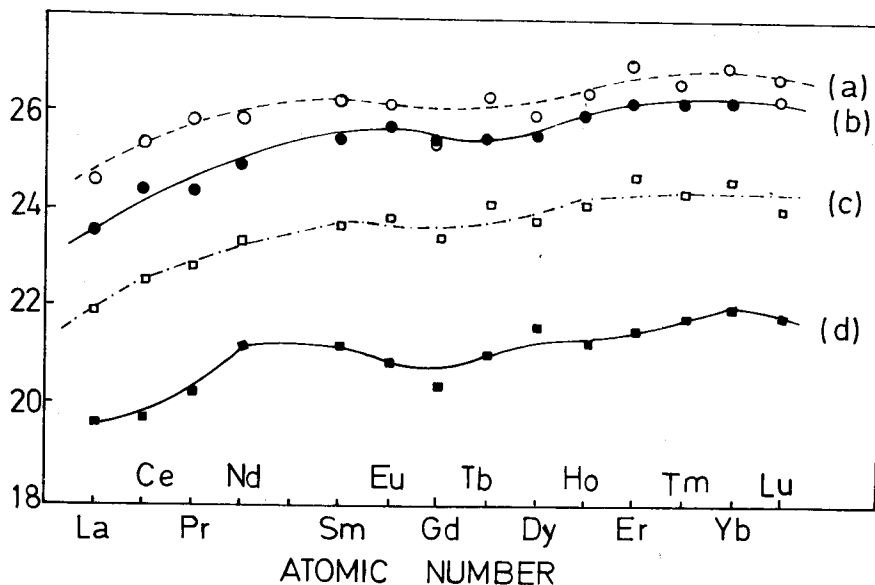


Fig. 1: The relationship between atomic number and " $\log B_2$ " for trivalent lanthanides with o-CPHAA (curve b); o-CPHBA (a); o-CPHDEM (c); and m-CPHDEM (d).

Table 2
 Stability constants of lanthanide complexation by
 o-CPHAA; o-CPHBA; o-CPHDEM and m-CPHDEM
 [T= 30°C, $\mu=0.1$ 75 % dioxane-water]

	<i>o</i> -CPHAA Log B ₂	<i>o</i> -CPHBA Log B ₂	<i>o</i> -CPHDEM Log B ₂	<i>m</i> -CPHDEM Log B ₂
La	23.62 ± 0.04	24.65 ± 0.03	21.97 ± 0.04	19.57 ± 0.02
Ce	24.36 ± 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	25.24 ± 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	25.06 ± 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	24.74 ± 0.04	21.47 ± 0.05
Tm	26.26 ± 0.05	26.26 ± 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	26.26 ± 0.04	24.00 ± 0.04	21.75 ± 0.05

It was expected that a linear relationship will be obtained when "Log B₂" 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, the first representing light lanthanide elements (La — Eu), shows a linear increase of the stability with increasing atomic number. The second part, representing heavy lanthanide elements (Gd—Lu) shows a break (almost a constant stability) around Gadolinium (Gd - break). A

small increase in stability of the complexes 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 hydration of cations upon complexation⁽²¹⁾. 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^(5,22), tropolone, N-hydroxy-ethylenediamine triacetic acid⁽²³⁾, and benzoylacetone⁽²⁴⁾. This similarity in behaviour of the studied ligands with other ones may be due to the presence of more than one type of coordination site in these ligands. There is, also 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 Log B₂ values of selected lanthanide complexes and $\sum pK_1 + pK_2$ 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 attributable to the aromatic ring giving a rigidity to the complex unsimilar to 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 hydration upon complex formation for all cations.

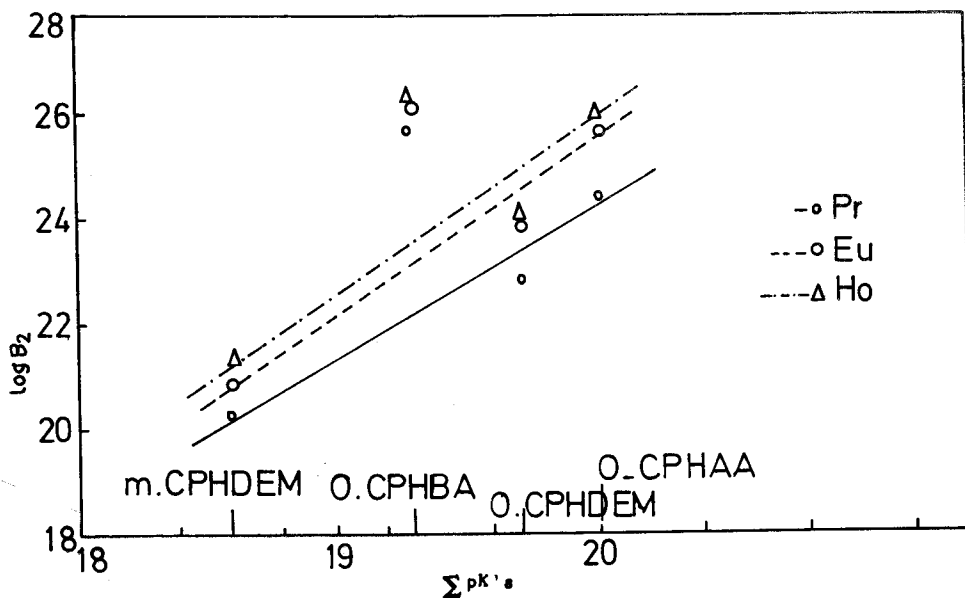
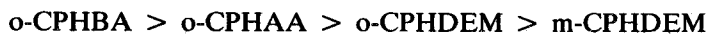
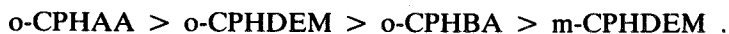


Fig. 2: Correlation of Log B₂ of the Pr (III), Eu (III); and Ho (III) complexes and $\sum pK$'s of the ligands.

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



while the order of summation of dissociation constants, $\sum pK_a$'s is as follows :



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

A curious odd-even effect was observed from Tb to Lu, with $\text{Log} B_2$ in malonate ligands, figure (3). The difference in $\text{Log} B_2$ from Tb — Lu is outside the limits of experimental error. This leads to a conclusion that malonate ligands appear to be of value in separation of rare earth mixtures by ion exchange techniques.

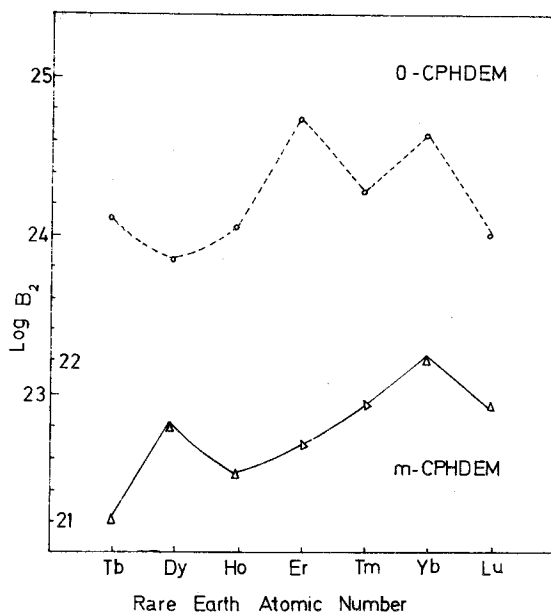


Fig. 3: Apparent odd-even effect in chelate stabilities noted with heavier rare-earth malonate species.

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ثوابت الاستقرار لمتراكبات اللنتانيدات مع بعض الليجانادات العضوية

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ملخص

قدرت ثوابت الاستقرار للمتراكبات المحضرة من تفاعل ايونات اللنتانيدات الثلاثية مع كربوكسي فينيل هيدرازو - بيتا - داي كيتونات ، عند ٣٠ م وتركيز ايوني ثابت (٠١ مولى نترات بوتاسيوم) في محلول ٧٥٪ ديوكسان - ماء .

وقد وصلت قابلية الليجانادات المختلفة لتكوين متراكبات مع اللنتانيدات نهاية عظمى مع ليجاند الارثو - كربوكسي فينيل هيدرازو بنزويل اسيتون ، بينما وصلت هذه القابلية نهاية صغرى مع ليجاند ميتا كربوكسي فينيل هيدرازو داي اثيل مالونيت .

وقد نوقشت العلاقة بين محصلة ثوابت الاستقرار (B₂) للمتراكبات وكلا من الاعداد الذرية للنتانيدات وثوابت الليجانادات .