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Complexation of tris(β-diketonato)lanthanoids with monodentate and bidentate Lewis bases in chloroform

Yuko Hasegawa*, Akifumi Hirasawa, Setsuko Yajima

Department of Chemistry, Science University of Tokyo, Shinjuku, Tokyo 162-8601, Japan

Abstract

The enthalpy change and the equilibrium constants for the formation of adducts of tris(1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedionato)lanthanoids (LnA_3) with triphenylphosphine oxide (TPPO) and 1,10-phenanthroline (phen) in chloroform across the lanthanoid series have been determined by calorimetric titration and solvent extraction techniques. The formation constants with phen increase from the light to the middle lanthanoids, and the constants do not change from the middle to the heavy lanthanoids, while the constants of the second adducts with TPPO (LnA_3/TPPO=1:2) decrease with increasing atomic number, although those of the first (1:1) adducts do not change much. The enthalpy change in adduct formation with phen changes remarkably from endothermic to exothermic from light to heavy lanthanoids, while the enthalpy changes with TPPO do not vary much across the series. This suggests that, in adduct formation with phen, the match between the N–N distance in phen and the size of the lanthanoids(III), as well as dehydration from LnA_3, is a significant factor in determining the stability order of the adducts, while the degree of dehydration is significant for adduct formation with TPPO. © 1998 Published by Elsevier Science S.A.

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1. Introduction

There are many patterns in the variation of the stability constants of lanthanoid(III) complexes across the series, e.g. the stability constants of the complexes with aminopolycarboxylate ions increase while the constants of the adducts of tris(β-diketonato)lanthanoids with most monodentate ligands such as carboxylic acids in chloroform decrease with increasing lanthanoid atomic number. In order to determine the factors controlling the stability order, determination of the enthalpy change and the degree of dehydration in adduct formation, as well as the adduct formation constants of lanthanoid(III) chelates, would be useful.

2. Experimental details

2.1. Determination of adduct formation constants

A 0.1 M sodium perchlorate solution (1 M=1 mol dm^{-3}) containing 6×10^{-5} M lanthanoid(III) for phen and $(0.2–1)\times10^{-4}$ M for TPPO and an equal volume of chloroform containing 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (usually called 2-thenoyltrifluoroacetone, TTA) and/or a Lewis base (phen or TPPO) were shaken mechanically for 1 h in stoppered glass tubes. The lanthanoid(III) in the chloroform phase was then back-extracted with 0.1 M perchloric acid and the concentration was determined by inductively coupled plasma emission spectrometry (ICP/AES). The concentration remaining in the aqueous phase was evaluated as the balance between the initial concentration and the concentration in the organic phase at equilibrium. The concentration ratio between both phases was defined as the distribution ratio (D).

2.2. Calorimetric titration of LnA_3 with a Lewis base

A stock solution of TTA–chelate (LnA_3) was prepared by extracting lanthanoid(III) with TTA into chloroform. The stock solution was diluted with chloroform and the LnA_3 concentration was adjusted to around 1×10^{-3} M. The heat emitted was measured in a thermostatted bath at 25°C using an isoperibol calorimeter with a motorized buret (Tronac Model 450, USA), on injecting a chloroform

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*Corresponding author.

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solution of the Lewis base, phen or TPPO, into the LnA_3 solution at a constant rate.

2.3. Determination of the hydration number of the adducts

Europium(III) was extracted from the perchlorate solution into chloroform containing TTA and TPPO or phen. Various concentrations of TPPO were employed to change the proportion of the respective europium(III) species among the TTA chelate and the adducts. The concentration of water in the chloroform was determined by Karl–Fischer coulometric titration.

3. Results and discussion

3.1. Trends in the variation of the adduct formation constants of TTA chelates across the lanthanoid series

Fig. 1 shows the extraction enhancement of several lanthanoids(III) with adduct formation as a function of total concentration of phen or TPPO added to the glass tube. The degree of enhancement in the presence of phen is much larger than that of TPPO over the entire concentration range studied (the extraction constants of LnA_3 when lanthanoids(III) were extracted from 0.1 M $NaClO_4$ with TTA into $CHCl_3$ in the absence of phen or TPPO, $\log K_{ex}$, were 13.67 (La), 15.03 (Pr), 16.26 (Eu), 16.67 (Dy), 17.34 (Yb) and 17.30 (Lu)) [1]. The limiting slope of the plot of $\log D/[A^-]^3$ vs. log [phen] is unity for almost all lanthanoids, while the slope in the presence of TPPO seems to change from 2 to 0 depending on the TPPO concentration. Analyzing the data in Fig. 1 and other similar experimental data based on the mass balance of the relevant species, we determined the formation constants of the adducts with phen and TPPO. The solid curves were drawn using the formation constants obtained. The constants of the 1:2 adducts with TPPO decrease with increasing atomic number, as observed for adducts with most monodentate Lewis bases [1,2]. On the other hand, those of the adducts with phen increase with increasing atomic number. Such a trend is similar to the formation constants of the adducts with phen [3,4] and 2,2′-dipyridyl [3,5], as reported previously.

3.2. Hydration number of EuA_3 adducts

When europium(III) was extracted into chloroform with TTA in the presence of a Lewis base, the water content in the chloroform decreased with increasing Lewis base concentration. The data were analyzed based on the mass balance of water as well as that of europium(III) in the chloroform. The results show that on adduct formation with phen all water molecules hydrated to EuA_3 were released, while on formation of the 1:1 adduct with TPPO, two water molecules from EuA_3, and on second adduct formation, almost all hydrated molecules, were released, as reported for the hydration number of the adduct of EuA_3 with TOPO in benzene [6].

3.3. Trends in the variation of the enthalpy change in adduct formation of TTA chelates across the lanthanoid series

Fig. 2a shows the heat change as a function of the concentration of phen added to the sample solution containing lanthanoid(III)–TTA chelate in the reaction cup. The heat emitted on the injection of phen solution is endothermic for light lanthanoids, while for heavy lanth-

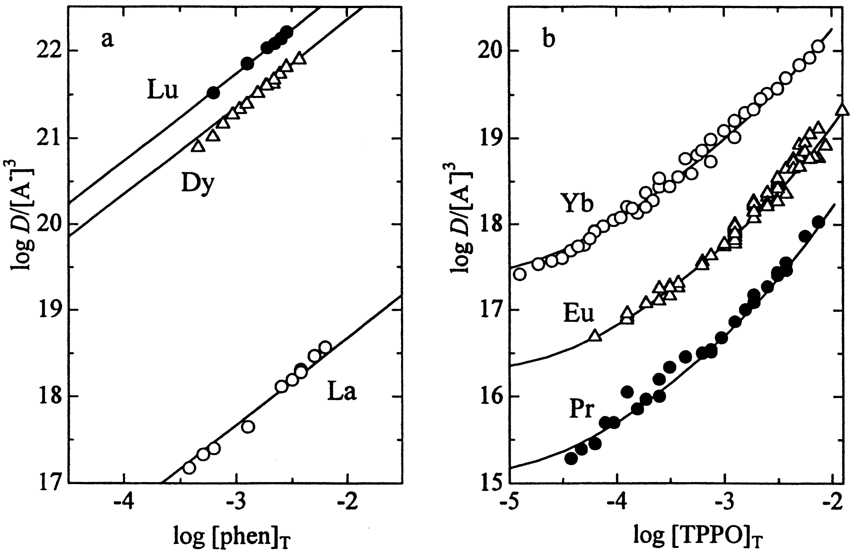

Fig. 1. Distribution ratio of several lanthanoids(III) between 0.1 M $NaClO_4$ and $CHCl_3$ containing TTA and phen (a) or TPPO (b) as a function of the Lewis base concentration.

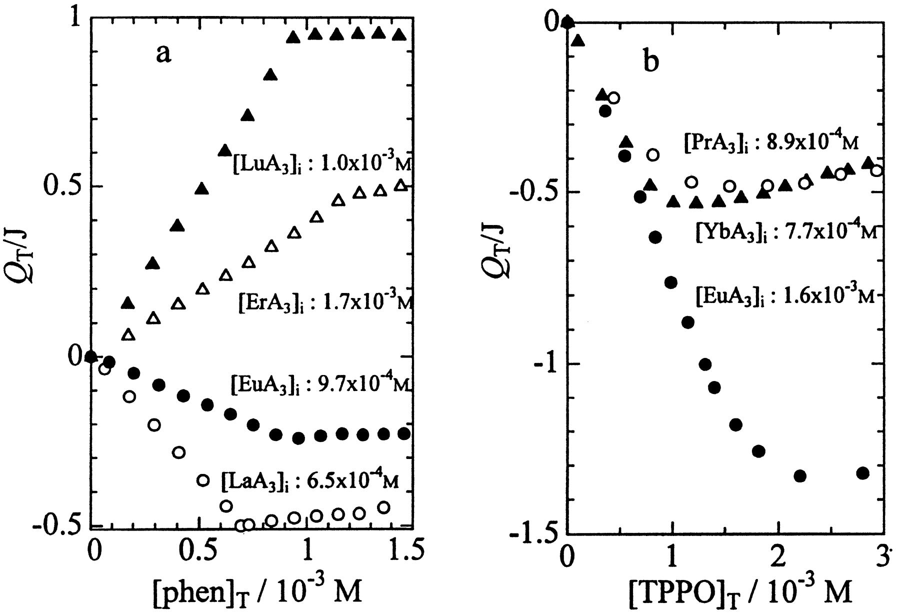

Fig. 2. The heat emitted on adduct formation of LnA_3 with phen (a) and TPPO (b) as a function of the Lewis base concentration.

anoids it is exothermic. On the addition of phen, when the concentration is over equivalent to that of LnA_3, the heat change is remarkably small. On the other hand, the heat emitted on the injection of TPPO solution is always endothermic until the concentration approaches the equivalence of the LnA_3 concentration and then it may be exothermic, as shown in Fig. 2b. The calorimetric titration data were analyzed and all thermodynamic parameters obtained are given in Fig. 3 as a function of lanthanoid atomic number.

The enthalpy change in 1:1 adduct formation with TPPO is endothermic, and that in 1:2 adduct formation is slightly exothermic.

The enthalpy change in adduct formation with phen varies remarkably from endothermic to exothermic from light to heavy lanthoids, although the adduct formation constants do not change from the middle to the heavy lanthanoids. Such phenomena may be related to dehydration from LnA_3 in adduct formation, because the dehydration is endothermic and the formation of new bonds may be exothermic. In addition, data show [7] that, in chloroform, the TTA chelates of light to middle lanthanoids(III) have around three hydrated molecules, while the hydration number in heavy lanthanoid(III)–TTA chelates is two. If all hydrated molecules are released from the lanthanoid chelate on adduct formation across the lanthanoid series, similarly as in the interaction between europium(III) chelates and phen, the more endothermic heat change for lighter lanthanoids is reasonable.

Apart from the effect of dehydration, the following

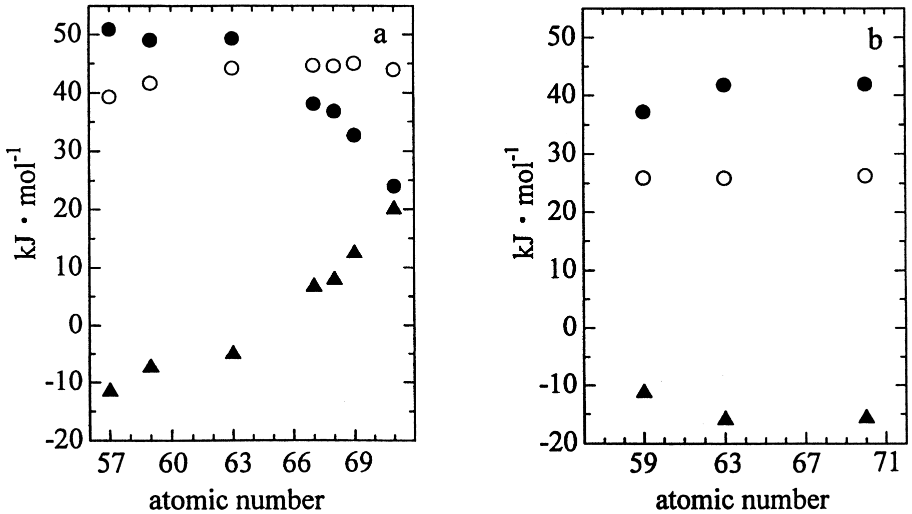

Fig. 3. Thermodynamic parameters in adduct formation of LnA_3 in chloroform with phen (a) and TPPO (b): (○) $-\Delta G_1$; (▲) $-\Delta H_1$; (●) $T\Delta S_1$.

explanation could also be reasonable: when phen combines more strongly with the heavier lanthanoids(III) due to better matching of the size to the distance between two N atoms in phen(=N–C=C–N=), the energy emitted due to the formation of the new bond may overcome the dehydration energy.

The large variation in enthalpy change in adduct formation with phen across the series may be due to both reasons.

The entropy change in phen adduct formation is smaller with increasing atomic number. Such a trend in the variation of the entropy changes across the series can also be explained in terms of the effects of dehydration as well as that of the match between the N–N distance in phen and the size of the lanthanoid(III).

A comparison of the thermodynamic parameters in adduct formation with phen (bidentate) and TPPO (monodentate) may be helpful in understanding the factors affecting the variation in adduct formation constants across the lanthanoid series, because the size effect would not be significant for the monodentate ligand. As seen from Fig. 3b, the enthalpy change as well as the entropy change in 1:1 adduct formation with TPPO does not seem to be much different across the lanthanoid series, differing from that with phen, although the variation of the free energy change from the middle to the heavy lanthanoids is similar between phen and TPPO adduct formation. Little variation in the entropy change in TPPO adduct formation across the lanthanoid series would suggest that the degree of dehydration is similar across the series. The different degree of dehydration with phen from that with TPPO could be due to differences in the basicity and geometry of these Lewis bases. The much larger decrease in the entropy change in adduct formation with phen than that with TPPO may also support that the phen adducts of the heavier lanthanoids are in better order owing to the formation of a more rigid structure. However, to obtain a clearer explanation, much more data such as the dehydration number of the adducts across the series is indispensable.

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