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Original Scientific Paper

Nitrilotriacetato Complexes of Lanthanides — A Thermochemical Study

N. Ivičić, B. Kužnar, and Vl. Simeon*

Institute for Medical Research, Yugoslav Academy of Sciences and Arts, Zagreb, Croatia, Yugoslavia

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The heats of formation of mono- and bis-nitrilotriacetato complexes of trivalent lanthanide ions were measured calorimetrically at 20° C in 0.1 M KNO₃. From the experimental heat data and the formation constants determined by others under similar experimental conditions the entropy changes on coordination were calculated. A support is given for the opinion that, in essentially electrostatic complexes, the complex formation enthalpies and entropies are mutually correlated because of the displacement of solvent molecules in complex formation.

Nitrilotriacetato complexes of tripositive lanthanide ions have been subject of the investigations by Moeller and Ferrús¹ and Edelin de la Praudière and Staveley². There is a disagreement between these workers regarding the values to be ascribed to the heat of formation of lanthanide mono-NTA complexes, Staveley's calorimetric values having been considered as more reliable than those obtained by Moeller from temperature variation of respective stability constants. As far as we know, the heats of formation of lanthanide bis-NTA complexes have not yet been measured calorimetrically. Therefore, a study was undertaken in order to determine by direct calorimetry both heats of complex formation, *i. e.* ΔH_{01} and ΔH_{02} (these symbols denote cumulative heats of formation of mono- and bis-nitrilotriacetato complexes, respectively).

EXPERIMENTAL

Reagents

The reagents used were analytical grade chemicals and were used without further purification except KNO₃ which was recrystallized twice from hot water. The water was deionised and then distilled in an all-glass still.

Lanthanide stock solutions (*ca.* 0.02 M) have been prepared by dissolving respective sesquioxides (Johnson & Matthey's »Specpure«) in HNO₃ (1 : 1) and repeatedly evaporating to dryness to remove the excess of HNO₃ and finally adding KNO₃ up to 0.1 M. The final pH amounted to 4–5.5, except in the case of Yb (pH = 6.5) and Er (pH = 3.0). These solutions have been standardized by complexometric titration using potentiometric end-point indication³.

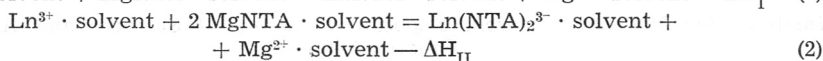
Magnesium nitrilotriacetate solution has been prepared in the following way: solid NTA was dissolved in a dilute solution of carbonate-free NaOH, an equivalent amount of carefully standardised MgCl₂ solution was added as well as KNO₃ (up to 0.1 M), and the pH was adjusted to 8.5. The equivalence of MgCl₂ addition was tested using Eriochrome Black T indicator. Finally, the solution was filtered off and

* The author to whom the correspondence concerning this paper should be addressed.

standardized by amperometric titration using Pb^{2+} as polarographically active reagent (titrate: ca. 4 mM $\text{Pb}(\text{NO}_3)_2$ in 0.1 M KCl , titrant: ca. 0.2 M MgNTA in 0.1 M KNO_3 ; $E = -0.60$ V vs. S. C. E.). Lead solution was standardised complexometrically³.

Calorimetric Procedure

The calorimeter and the general experimental patterns were described elsewhere⁴. Its accuracy and precision were tested using two standard reactions: neutralisation of HNO_3 with NaOH and the dissolution of tris-(hydroxymethyl)-amino-methane (THAM). Their heats were -13593 ± 20 cal mol⁻¹ and -7305 ± 10 cal mol⁻¹, respectively. The heats of complex formation have been determined by the »substitution method«:



The equilibrium constants K_{I} and K_{II} for reactions (1) and (2) were taken as $10^{5.02}$ and $10^{6.92}$ respectively in the most unfavorable case (*i. e.* for lanthanum), using the value of $10^{5.35}$ for $K_{\text{Mg}(\text{NTA})}$ according to Bohigian and Martell⁵.

From the measured heats ΔH_{I} and ΔH_{II} the complex formation heats are obtained using relations

$$\Delta H_{01} = \Delta H_{\text{I}} + \Delta H_{\text{MgNTA}} \quad (1a)$$

$$\Delta H_{02} = \Delta H_{\text{II}} + 2 \Delta H_{\text{MgNTA}} \quad (2a)$$

The heat of formation of MgNTA , ΔH_{MgNTA} , was taken from Staveley's paper².

The compositions of titrate and titrant solutions (S and T, respectively) were as follows:



in the experiments for the determination of ΔH_{I} and



in ΔH_{II} experiments. In the heat-of-dilution experiments the S solutions contained 0.1 M KNO_3 their pH being adjusted to approximately the same value as the respective lanthanide solution used in the main experiment. The volume of solution S was 80.0 ml throughout the experiments and the addition of T solution was (1.426 ± 0.001) ml.

The initial temperature in any calorimetric run was $20.0 \pm 0.01^\circ \text{C}$.

RESULTS

The measured heats of substitution are shown in Table I together with relevant experimental data. From the stability constants reported by Moeller and Ferrús¹ (determined also at 20°C in 0.1 M KNO_3) and from the present enthalpy data, ΔS_{01} and ΔS_{02} values were calculated. The cumulative ΔG , ΔH , and ΔS values are collected in Table II. By taking into account that both in Moeller's and in our work the solute concentrations were sufficiently low in comparison with KNO_3 concentration it was assumed that all the thermodynamic quantities quoted in Table II are reasonably good approximations to respective standard quantities (the standard state being defined as a hypothetical ideal molar solution in 0.1 M KNO_3 solvent).

The precision of the present enthalpy data can be assessed by inspecting the range of data quoted in Table II. The mean range for ΔH_{01} amounts to

TABLE I

Heats of Formation of $\text{Ln}(\text{NTA})$ and $\text{Ln}(\text{NTA})_2^{3-}$ from Ln^{3+} and $\text{Mg}(\text{NTA})^-$
at 20°C in 0.1 M KNO_3

Ln^{3+}	q_{I} (cal)	n_{I} (mmol NTA)	$-\Delta H_{\text{I}}$ (kcal mol^{-1})	q_{II} (cal)	n_{II} (mmol Ln^{3+})	$-\Delta H_{\text{II}}$ (kcal mol^{-1})
La	0.821 ₅	0.2630	3.12 ₄	0.863 ₄	0.0900	9.59 ₃
	0.831 ₄		3.16 ₁	0.859 ₅		9.55 ₀
	0.820 ₃		3.11 ₉			
Ce	1.288 ₂	0.3452	3.73 ₂	0.897 ₈	0.07850	11.43 ₇
	1.290 ₃		3.73 ₈	0.902 ₄		11.49 ₆
Pr	1.132 ₀	0.2630	4.30 ₄	1.138 ₆	0.09400	12.11 ₃
	1.131 ₇		4.30 ₃	1.148 ₁		12.21 ₄
Nd	1.081 ₃	0.2630	4.11 ₁	1.252 ₂	0.09715	12.88 ₉
	1.090 ₃		4.14 ₆	1.256 ₁		12.92 ₉
Sm	1.186 ₂	0.2630	4.51 ₀	1.396 ₆	0.09880	14.13 ₆
	1.185 ₈		4.50 ₉	1.399 ₅		14.16 ₅
Eu	1.137 ₈	0.2630	4.32 ₆	1.405 ₁	0.09300	15.10 ₉
	1.133 ₀		4.30 ₈	1.402 ₆		15.08 ₂
Gd	1.040 ₅	0.2630	3.95 ₆	1.508 ₅	0.09835	15.33 ₃
	1.034 ₇		3.93 ₄	1.512 ₆		15.38 ₀
Tb	0.870 ₇	0.2630	3.31 ₁	1.410 ₅	0.09850	14.32 ₀
	0.868 ₂		3.30 ₁	1.408 ₄		14.30 ₄
Dy	1.088 ₄	0.3452	3.15 ₃	1.404 ₄	0.1015	13.83 ₂
	1.084 ₃		3.14 ₁	1.408		13.87 ₆
Ho	1.132 ₂	0.3452	3.28 ₀	1.310 ₂	0.09750	13.43 ₃
	1.117 ₂		3.23 ₆	1.304 ₇		13.38 ₂
Er	1.088 ₀	0.3452	3.15 ₂	1.203 ₉	0.09975	12.06 ₉
	1.090 ₀		3.15 ₈	1.206 ₀		12.09 ₀
Tm	1.120 ₀	0.3452	3.24 ₅	1.089 ₀	0.1024	10.63 ₅
	1.121 ₆		3.24 ₉	1.093 ₀		10.67 ₄
Yb	1.299 ₀	0.3452	3.76 ₃	0.999 ₈	0.1020	9.80 ₂
	1.287 ₂		3.72 ₉	0.998 ₁		9.78 ₄
Lu	1.294 ₂	0.3452	3.74 ₉	0.941 ₈	0.09775	9.63 ₅
	1.293 ₅		3.74 ₇	0.942 ₁		9.63 ₃

14 cal mol⁻¹ and for ΔH_{02} to 38 cal mol⁻¹; hence the respective standard deviations (calculated according to Davies⁶) should be about ± 10 cal mol⁻¹ and ± 30 cal mol⁻¹, respectively. To estimate the absolute accuracy of the present data precisely is very difficult as is generally the case in such involved chemical systems where a number of side reactions can occur. Therefore in our experiments special attention was paid to the standardisation of lanthanide and Mg(NTA) solutions, their titres being precise to better than ± 0.2 per cent, and to the initial and final pH values in both complexation and dilution experiments. In this way, it is hoped, most analytical errors as well as those

TABLE II

Thermodynamic Data for the Formation of $\text{Ln}(\text{NTA})$ and $\text{Ln}(\text{NTA})_2^{3-}$ Complexes from Ln^{3+} and NTA^{3-} at 20°C in 0.1 M KNO_3

Ln^{3+}	$-\Delta G_{01}^0$ (cal mol $^{-1}$)	$\Delta H_{01}^0 \pm R/2^*$ (cal mol $^{-1}$)	ΔS_{01}^0 (cal K $^{-1}$ mol $^{-1}$)	$-\Delta G_{02}^0$ (cal mol $^{-1}$)	$\Delta H_{02}^0 \pm R/2^*$ (cal mol $^{-1}$)	ΔS_{02}^0 (cal K $^{-1}$ mol $^{-1}$)
La	13910	+ 935 \pm 16	50.6	23640	- 1432 \pm 22	75.7
Ce	14530	+ 335 \pm 3	50.7	25100	- 3327 \pm 30	74.3
Pr	14850	- 234 \pm 1	49.9	25880	- 4023 \pm 50	74.5
Nd	15090	- 59 \pm 17	51.3	26510	- 4769 \pm 20	74.2
Sm	15440	- 440 \pm 1	51.2	27580	- 6010 \pm 15	73.6
Eu	15410	- 247 \pm 9	51.7	27850	- 6956 \pm 14	71.3
Gd	15480	+ 125 \pm 11	53.2	28010	- 7219 \pm 21	70.9
Tb	15530	+ 764 \pm 5	55.6	28210	- 6172 \pm 8	75.2
Dy	15710	+ 923 \pm 6	56.7	28430	- 5714 \pm 22	77.5
Ho	15900	+ 812 \pm 22	57.0	28520	- 5270 \pm 28	79.3
Er	16100	+ 915 \pm 3	58.0	28560	- 3940 \pm 10	84.0
Tm	16370	+ 823 \pm 2	58.6	28770	- 2515 \pm 20	89.6
Yb	16590	+ 324 \pm 17	57.7	29110	- 1653 \pm 9	93.7
Lu	16730	+ 322 \pm 1	58.2	29390	- 1497 \pm 2	95.2

* R denotes the range of the observed values.

originating from side reactions (such as ligand protonation, metal-ion or complex hydrolysis) are considerably reduced. The formation enthalpies determined in this work fall between those quoted by Moeller and Ferrús¹ and De La Praudière and Staveley² being somewhat nearer to those by the latter authors.

DISCUSSION

The irregular dependence of either ΔH_{01} or ΔH_{02} on the atomic number (Z) of the central atom (or on the reciprocal ionic radius) is a well known fact in solution chemistry of lanthanides. Such plot of our ΔH and ΔS data is shown in Figs. 1 and 2. Even after the recalculation of ΔH_{02} values to the same initial state (crystalline isomorphous salts containing 9 molecules of water) according to Staveley *et al.*⁷ no improvement in the regularity is achieved, probably due to residual hydration (effective coordination number in bis-NTA complexes is most likely to be 8).

The important role of hydration in such systems, which has been pointed out earlier by the other workers (see *e. g.* ref. 7), can partly be elucidated by examining the ΔH — ΔS relationship:

On the grounds of a crude electrostatic picture $-\Delta H_{01}$ and $-\Delta H_{02}$ should linearly increase with the charge density of the central ion. This is almost never encountered and — for our particular case — the plot in Fig. 1 is also far from linearity. The points in this diagram can be crudely approximated by two lines having opposite slopes, the first comprising the points from La to Gd, the other the remaining (Gd—Ln) points. The slope of the first line is negative, *i. e.* qualitatively compatible with what would be expected

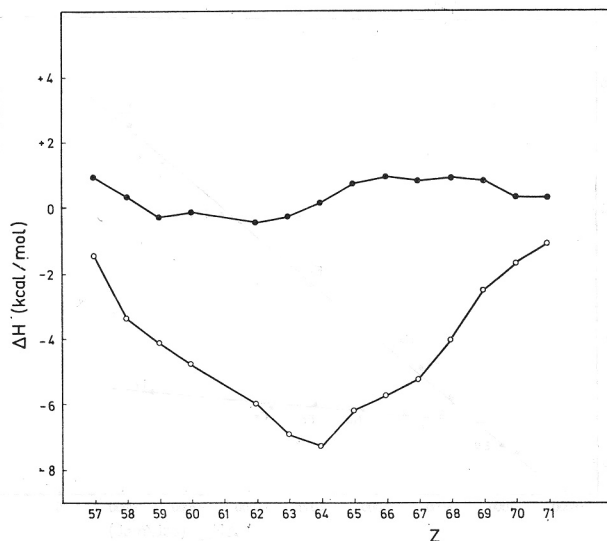


Fig. 1. Heats of formation of lanthanide mono- and bis-NTA complexes plotted against the atomic number; dots: ΔH_{01} , circles: ΔH_{02} .

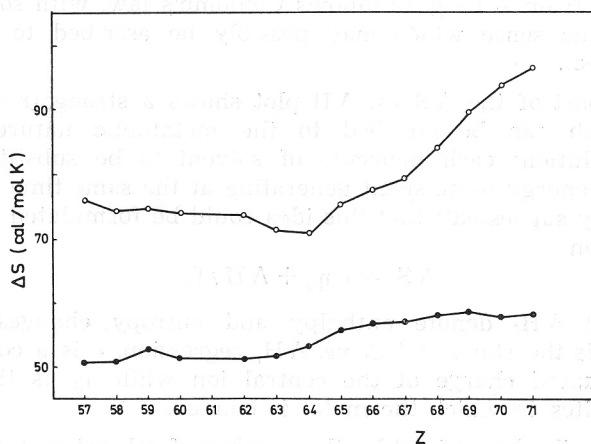


Fig. 2. Entropies of formation of lanthanide mono- and bis-NTA complexes; dots: ΔS_{01} , circles: ΔS_{02} .

on the basis of the coulombic picture. It can be noted that this part of data shows no ΔH — ΔS correlation as can be seen in Fig. 3. The existence of this »constant-entropy region« can be explained by assuming the hydration numbers of both free metal ions and complex ions to remain constant, which is in accordance with the opinions expressed by others⁸. A similar pattern is also observed in the plots ΔS_{01} vs. ΔH_{01} and ΔS_{12} vs. ΔH_{12} . It can also be found with other ligands *e. g.* EDTA⁹ and CPDTA¹⁰ but there the correlation is less precise so the »constant-entropy region« falls inside the confidence limits of the regression lines. In the »constant entropy region« the

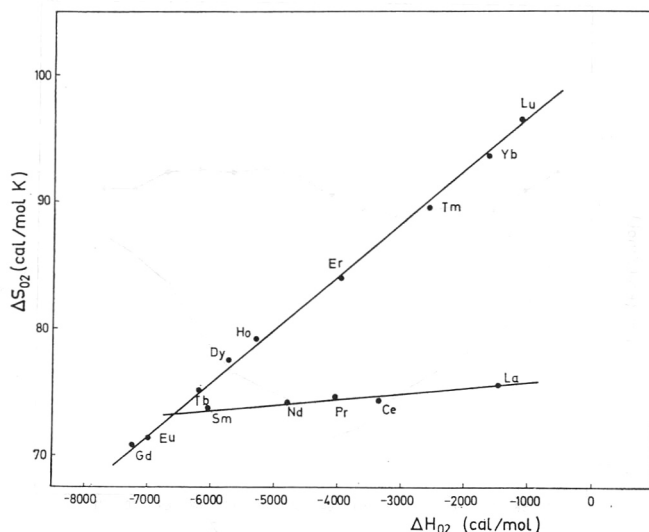


Fig. 3. The correlation of ΔS_{02} vs. ΔH_{02} for lanthanide nitrilotriacetato complexes.

dependence of ΔH on Z roughly follows Coulomb's law, with some deviations in the exothermic sense which may possibly be ascribed to a differential crystal-field effect.

The other part of the ΔS vs. ΔH plot shows a strong ($r = 0.999$) linear correlation which can be ascribed to the metathetic nature of complex formation in solution: each molecule of solvent to be substituted requires some amount of energy to be spent generating at the same time some entropy. We have recently suggested¹¹ that this idea could be formulated quantitatively by the expression

$$\Delta S_f = c \eta_L + \Delta H_f/T_c \quad (3)$$

where ΔS_f and ΔH_f denote enthalpy and entropy changes on complex formation, $1/T_c$ is the slope of ΔS_f vs. ΔH_f regression, c is a constant dependent on the squared charge of the central ion while η_L is the number of ligand's donor sites to which the metal is bonded.

ΔS_f is primarily determined by the number of solvent molecules displaced on coordination: c and η_L allow for the metal and ligand hydration numbers while ΔH_f is a measure of the strength of hydrate bonds.

From the data quoted in Table II, stepwise enthalpy and entropy changes for the formation of $\text{Ln}(\text{NTA})_2$ complexes can be computed. The $\Delta H_{1,2}$ values are more exothermic than $\Delta H_{0,1}$, the corresponding entropy changes being more positive which is in complete agreement with the explanation of enthalpy-entropy relationship since more water is expected to be released in forming the 1:1 complex than in the second step of stepwise formation of the 1:2 complex.

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IZVOD

Nitrilotriacetato-kompleksi lantanida — termokemijska studija

N. Ivičić, B. Kužnar i Vl. Simeon

Topline stvaranja mono- i bis-nitrilotriacetato-kompleksa trovaljanih iona iz niza lantanida izmjerene su kalorimetrijski kod 20° C u 0.1 M KNO₃. Iz tih podataka te iz literaturnih vrijednosti za konstante stabilnosti izračunate su entropije stvaranja kompleksa. Opažena je značajna međusobna korelacija entalpija i entropija stvaranja kompleksa koje se uzrokom smatra istiskivanje otapala u toku stvaranja kompleksa.

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