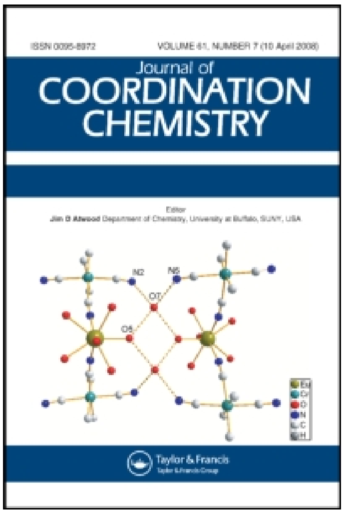

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COMPLEXATION THERMODYNAMICS OF LANTHANIDE IONS BY BENZENEPOLYCARBOXYLATE LIGANDS

G. R. Choppin[a]; E. N. Rizkalla[a]; T. A. El-ansi[a]; A. Dadgar[a]
[a] Department of Chemistry, Florida State University, Tallahassee, Florida

To cite this Article Choppin, G. R. , Rizkalla, E. N. , El-ansi, T. A. and Dadgar, A.(1994) 'COMPLEXATION THERMODYNAMICS OF LANTHANIDE IONS BY BENZENEPOLYCARBOXYLATE LIGANDS', Journal of Coordination Chemistry, 31: 4, 297 — 304

To link to this Article: DOI: 10.1080/00958979408024223

URL: http://dx.doi.org/10.1080/00958979408024223

J. Coord. Chem., 1994, Vol 31, pp. 297–304
Reprints available directly from the publisher
Photocopying permitted by license only

COMPLEXATION THERMODYNAMICS OF LANTHANIDE IONS BY BENZENEPOLYCARBOXYLATE LIGANDS

G.R. CHOPPIN*, E.N. RIZKALLA, T.A. EL-ANSI and A. DADGAR

Department of Chemistry, Florida State University, Tallahassee, Florida 32306-3006

(Received September 20, 1993; in final form December 3, 1993)

The complexation thermodynamics of lanthanide ions by 1,2,3-benzenetricarboxylate (hemimellitate), 1,2,4-benzenetricarboxylate (trimellitate) and 1,2,4,5-benzenetetracarboxylate (pyromellitate) ligands were studied using potentiometric, calorimetric and extraction techniques. The measurements were obtained at an ionic strength of 0.10 M ($NaClO_4$) and at 25°C. The results were compared to analogous values of benzoate, isophthalate and o-phthalate complexation. The apparent increased stability of these complexes above that expected for a typical bidentate complex is in fact merely a statistical factor. The ΔH_{101} and ΔS_{101} of these complexes reflect relatively strong dehydration of metal and ligand ions upon complex formation.

KEYWORDS: Lanthanide, benzenepolycarboxylate, complex formation

INTRODUCTION

The thermodynamic parameters, ΔG_{101}, ΔH_{101}, and ΔS_{101}, of formation of the 1:1 complexes between lanthanide cations and aromatic carboxylates such as benzoate, isophthalate and o-phthalate anions were reported earlier.[1,2] Even though complexation by the isophthalate anion must involve interaction between the metal and a single carboxylate group, the thermodynamic parameters are significantly more favorable than those for benzoate complex formation. It was proposed that such enhancement could be related to polarization of electronic charge from the unbound carboxylate group through the π-system of the phenyl group to the bonding carboxylate.

To further assess the role of the non-binding carboxylate groups on complexation, we have studied lanthanide complexation by hemimellitate (1,2,3-benzenetricarboxylate), trimellitate (1,2,4-benzenetricarboxylate) and pyromellitate (1,2,4,5-benzene-tetracarboxylate) ligands. The stereochemistry of these anions allow adjacent carboxylate groups to function as a bidentate ligand, leaving either one or two non-binding carboxylate groups.

---

* Author for correspondence.

EXPERIMENTAL

Reagents and solutions

Stock solutions of the lanthanide perchlorates were prepared and standardized as described previously.[1] The pH of the solutions was adjusted to ca. 3.5 with perchloric acid. Hemi-, tri- and pyromellitic acids (Aldrich ≥98%) were recrystallized from water, dissolved in 1 M sodium hydroxide and titrated to determine the exact molarity of the stock solution. All solutions were adjusted to 0.10 M ionic strength with $NaClO_4$.

Isotopes ^{152}Eu and ^{154}Eu were obtained from Oak Ridge National Laboratory. A stock solution was prepared by fuming the sample to dryness three times with concentrated $HClO_4$, followed by a final dissolution in 0.10 M $HClO_4$. The radiochemical purity of the tracer was confirmed by comparison of its gamma ray spectrum (obtained with a Ge(Li) detector and a Canberra Series 80 multichannel analyzer) to that of the standard spectrum.

Bis(2-ethylhexyl)phosphoric acid, HDEHP (Pfaltz and Bauer) was purified according to the procedure of Peppard, *et. al.*[3]

Procedures

The potentiometric measurements were performed with a radiometer titration system consisting of a digital pH meter model PHM 84 fitted with a combined glass-calomel electrode, ABU-80 auto-burette and TTA-80 titration assembly. The electrode was calibrated with standard buffers (Fisher) of pH 4.01 and 7.00. The hydrogen ion activity was converted to concentration by using 0.782 as the activity coefficient.[4]

The acid protonation constants of the ligands were obtained by titrating the sodium salt solutions with standard $HClO_4$. The stability constants were obtained by pH titration of the metal solution (50.0 ml of *ca.* 0.2–0.3 mM) with the ligand buffer solution (0.01–0.03 M). All measurements were obtained at 0.10 M ($NaClO_4$) ionic strength.

The trimellitate complexes of the lanthanides were too insoluble to obtain potentiometric or calorimetric data. Consequently, stability constants were obtained from tracer solvent extraction experiments. The measurements were performed with 5.0 ml of the buffered ligand at the desired pH and an equal volume of a toluene solution of HDEHP. The mixture was spiked with 10^5 cpm of the tracer, sealed and equilibrated at constant temperature for several hours. Aliquots of the separated phases were counted using a NaI(Tl) well counter to a present standard deviation of 1% for the count rate. The measurements were repeated over a range of ligand concentrations for each pH. The heats of protonation of the free ligands were measured with an adiabatic calorimeter designed in this laboratory[5] and interfaced to a PC[6] to perform the stepwise calorimetric titration, to control the calibration heater, the Peltier heating/cooling device and a Radiometer ABU-80 autoburette and to acquire the temperature data from the calorimeter thermistor.

Lanthanide solutions of *ca.* 6–10 mM (50.0 ml, $I = 0.10$ M ($NaClO_4$)) in the calorimeter cup were titrated with buffer solutions of the ligands at 25 °C. The heats of dilution were obtained for each system by substituting 0.10 M $NaClO_4$ solution, first for the titrant, and, subsequently, for the titrand.

RESULTS

The protonation constants and the thermodynamic parameters of protonation of the trimellitate (Tm), hemimellitate (Hm) and pyromellitate (Pm) anions are listed in Table 1. The value of the fourth protonation of the pyromellitate anion is not reported since it is too small (< 2) to be obtained with accuracy in our titrations. This constant, as well as the protonation constants for the trimellitate (Tm) ligand, were taken from the literature.[7]

The values of the stability constants for the general reactions ($L = Hm^{3-}$ or Pm^{4-}),

$$Ln^{3+} + L^{z-} \rightleftharpoons LnL^{3-z}; \beta_{101} = [LnL]/[Ln][L] \qquad (1)$$

and

$$Ln^{3+} + HL^{1-z} \rightleftharpoons LnHL^{4-z}; \beta_{11} = [LnHL]/[Ln][HL] \qquad (2)$$

were calculated using the mass balance equations for the total metal, total ligand and total hydrogen ion concentrations. The equations were solved for the different values of β using a standard non-linear least squares fitting program which minimized the values of $([H^+]_{calc} - [H^+]_{exp})^2$ for each reading.[8]

Table 2 presents a sample set of potentiometric data for the complexation of Gd^{3+} by pyromellitate ligand. The experimental data were tested for the presence of $Ln(Pm)^-$, $Ln(Pm)_2{}^{5-}$, $LnH(Pm)^0$, $LnH(Pm)_2{}^{4-}$, and $Ln_2(Pm)^{2+}$ complexes. The analysis indicated that $Ln(Pm)^-$ and $LnH(Pm)^0$ complexes were the only species formed in significant amounts as the calculated constants for $Ln(Pm)_2{}^{5-}$, $LnH(Pm)_2{}^{4-}$, and $Ln_2(Pm)^{2+}$ had unacceptable magnitudes for their standard deviations and the distribution of the residuals. Similarly, in the case of hemimellitate, only $Ln(Hm)^0$ and $LnH(Hm)^+$ species were indicated by the data analysis.

The absence of polynuclear species under the present experimental conditions is affirmed by the agreement (see Table 4) between the β_{101} values obtained from pH measurements and those calculated from extraction data for Eu(III) with these ligands at the tracer level (the treatment of extraction data to calculate stability constants is described elsewhere[9]).

Table 1 Thermodynamic Parameters for the Stepwise Protonation of Tri-, Hemi- and Pyromellitate Ligands T = 298 K; I = 0.10 M ($NaClO_4$)

Equilibrium quotient	log β	ΔH kJ mol^{-1}	ΔS J $K^{-1}mol^{-1}$
		a) Trimellitate	
[HL]/[H][L]	5.01[7]	4.0[7]	109
$[H_2L]/[H][HL]$	3.71[7]	0.4[7]	72
$[H_3L]/[H][H_2L]$	2.4[7]	5.2[7]	63
		b) Hemimellitate	
[HL]/[H][L]	5.49 ± 0.02	3.3 ± 0.2	116 ± 1
$[H_2L]/[H][HL]$	3.92 ± 0.01	7.1 ± 0.2	99 ± 1
$[H_3L]/[H][H_2L]$	2.62[7]	4.4[7]	70
		c) Pyromellitate	
[HL]/[H][L]	5.25 ± 0.03	4.5 ± 0.2	116 ± 1
$[H_2L]/[H][HL]$	4.18 ± 0.01	1.3 ± 0.1	84 ± 1
$[H_3L]/[H][H_2L]$	2.63 ± 0.03	6.8 ± 0.2	73 ± 1

Table 2 Potentiometric Titration Data for Gd-Pyromellitate* T = 298 K; I = 0.10 M ($NaClO_4$)

$V_{titrant}$	pH	$10^6[L^{4-}]$ M	$10^4[Gd^{3+}]$ M	$\bar{n}$
0.05	4.588	0.243	3.051	0.023
0.10	4.472	0.415	2.986	0.043
0.20	4.331	0.659	2.875	0.077
0.30	4.242	0.837	2.780	0.105
0.40	4.180	0.979	2.696	0.130
0.50	4.131	1.099	2.622	0.153
0.60	4.093	1.205	2.554	0.173
0.70	4.061	1.301	2.491	0.192
0.80	4.034	1.389	2.433	0.209
0.90	4.010	1.472	2.379	0.225
1.00	3.990	1.550	2.328	0.240
1.20	3.956	1.659	2.234	0.268
1.40	3.928	1.831	2.150	0.292
1.60	3.905	1.960	2.073	0.315
1.80	3.886	2.083	2.003	0.336
2.10	3.862	2.262	1.907	0.364
2.40	3.842	2.435	1.821	0.390

*Experimental conditions: ***Cup solution:*** C_M = 0.3126 mM; pH = 4.800, volume = 50.0 ml. ***Titrant:*** C_L = 9.531 mM, C_H = 18.072 mM, ***Calculated constants:*** log β_{101} = 4.78 ± 0.01; log β_{11} = 3.80 ± 0.01.

Enthalpies of complexation were computed by fitting the observed heat changes (Q_c), after correction for dilution and deprotonation, to the equation:

$$Q_c = \Sigma Q_{HnL} + Q_{LnL} + Q_{LnHL} (n = 1 \text{ to } 4)$$

$$= \Sigma(\Delta X_{HnL})\Delta H_{Onl} + (\Delta X_{LnL})\Delta H + (\Delta X_{LnHL})\Delta H_{11} \qquad (3)$$

where ΔX is the change in the number of moles formed between successive titration aliquots. The residual error, E, is minimized by:

$$E = \sum_{i=1}^{N} [Q_{i,calc} - Q_{i,c}]^2 \qquad (4)$$

The calculations were performed using a non-linear SIMPLEX program (DELTAH) written in this laboratory. Table 3 presents a sample set of calorimetric titration data for Sm^{3+} ion with a buffered solution of pyromellitate. All pyromellitate titrations were conducted in the pH range 3.5 to 4.5 in which a significant fraction of $LnH(Pm)^0$ complex is formed (the ratio [LnL]/[LnHL] varied from *ca.* 0.9 to 0.2). This allowed determination of the enthalpies of formation for both species. Titrations which involved solutions of pH greater than 4.5 resulted in precipitation, presumably of $NaLn(Pm)\cdot XH_2O$ or $Ln_4(Pm)_3\cdot XH_2O$. Precipitation in La^{3+} and Pr^{3+} systems occurred at lower pH values and prevented measurement of complexation enthalpies. The hemimellitate complexes were more soluble, thereby allowing measurements in a pH range in which only the $Ln(Hm)^0$ species formed.

Table 4 lists the stability constants determined from potentiometric data. The standard deviations of the individual titrations for log β_{101} and log β_{11} were 0.002–0.008 and 0.003–0.017, respectively. Also, listed in Table 4 are the values of

Table 3 Calorimetric Titration Data of Sm-Pyromellitate* T = 298 K; I = 0.10 M ($NaClO_4$)

Titrant ml	$-\Sigma Q_{cor}$# mJ	$-\Sigma Q_{calc}$ mJ	$10^3[Sm^{3+}]$ M	$10^7[L^{4-}]$ M	$10^4[H^+]$ M	$\bar{n}$
0.5	66.3	65.6	5.987	1.055	0.750	0.014
1.0	127.1	124.9	5.837	1.581	1.207	0.028
1.5	181.7	181.0	5.702	1.974	1.571	0.041
2.0	238.0	235.6	5.572	2.307	1.876	0.054
2.5	289.7	288.2	5.446	2.607	2.138	0.067
3.0	341.4	339.4	5.324	2.889	2.366	0.079
3.5	390.2	389.4	5.206	3.160	2.566	0.091
4.0	442.0	438.3	5.092	3.426	2.742	0.102
4.5	492.7	486.2	4.981	3.689	2.897	0.114
5.0	539.0	533.2	4.874	3.951	3.035	0.125
5.5	580.1	579.5	4.769	4.216	3.157	0.136
6.0	628.6	625.0	4.667	4.483	3.265	0.147
6.5	677.3	669.8	4.568	4.754	3.361	0.157
7.0	720.6	714.0	4.471	5.030	3.446	0.168

*Experimental conditions: ***Cup solution:*** $[Sm^{3+}]$ = 6.126 mM; pH = 5.58. ***Titrant:*** C_L = 9.105 mM; C_H = 12.394 mM. **Computed constants:** ΔH_{101} = 16.7 ± 0.3 kJ mol^{-1}, ΔH_{11} = 9.0 ± 0.1 kJ mol^{-1}.
#ΣQ_{cor} is the observed heat corrected for dilution.

Table 4 Stability Constants for the Complexation of Lanthanide Ions by Tri-, Hemi- and Pyromellitate Ligands T = 298 K; I = 0.10 M ($NaClO_4$)

Ion	Trimellitate	Hemimellitate		Pyromellitate	
	$\log \beta_{101}$	$\log \beta_{101}{}^a$	$\log \beta_{11}{}^b$	$\log \beta_{101}{}^c$	$\log \beta_{11}{}^d$
La^{3+}		4.81	2.59	4.32	3.61
Pr^{3+}		5.01	2.59	4.72	3.72
Nd^{3+}		5.01	2.62	4.73	3.76
Sm^{3+}		5.08	2.75	4.81	3.74
Eu^{3+}		5.08	2.85	4.86	3.86
Eu^{3+}	4.38	5.08		4.95	
Gd^{3+}		5.05	2.94	4.78	3.80
Tb^{3+}		4.92	2.77	4.75	3.77
Dy^{3+}		4.92	2.81	4.69	3.72
Ho^{3+}		4.84	2.80	4.65	3.69
Er^{3+}		4.82	2.84	4.60	3.67
Tm^{3+}		4.81	2.88	4.58	3.67
Yb^{3+}		4.80	2.88	4.59	3.65
Lu^{3+}		4.80	2.93	4.60	3.64
Y^{3+}		4.76	2.81	4.57	3.62

[a]± 0.02; [b] ± 0.06; [c] ± 0.03; [d] ± 0.03 and [e]From extraction data, ± 0.05.

Eu(III) complexation as determined from the tracer experiments. For each ligand, four measurements were performed at pH values 4.89, 5.08, 5.27, and 5.48 and the constants obtained were the same, within experimental uncertainties, at these pH values.

Table 5 provides the thermodynamic parameters for the complexation by hemi- and pyromellitate ligands. The standard deviation of the calorimetric titrations was less than 0.4 kJ mol^{1-}. The errors in Table 5, however, reflect the agreement between repetitive runs.

Table 5 Thermodynamic Parameters for the Complexation of Lanthanide Ions by Hemi- and Pyromellitate Ligands T = 298 K; I = 0.10 M ($NaClO_4$)

Ion		Hemimellitate			Pyromellitate	
	$\Delta H_{101}{}^{a}$ kJ mol^{-1}	$\Delta S_{101}{}^{b}$ J K^{-1}mol^{-1}	$\Delta H_{101}{}^{c}$ kJ mol^{-1}	$\Delta S_{101}{}^{d}$ J K^{-1}mol^{-1}	$\Delta H_{11}{}^{e}$ kJ mol^{-1}	$\Delta S_{11}{}^{f}$ J K^{-1}mol^{-1}
La^{3+}	14.2	140	–	–	–	–
Pr^{3+}	14.0	143	–	–	–	–
Nd^{3+}	15.5	148	10.1	124	7.5	97
Sm^{3+}	17.9	157	16.7	148	9.0	102
Eu^{3+}	16.8	154	17.0	150	8.3	102
Gd^{3+}	17.6	156	22.7	168	9.0	103
Tb^{3+}	20.3	162	24.2	172	9.1	103
Dy^{3+}	21.4	166	27.2	181	14.1	119
Ho^{3+}	21.6	165	28.8	181	13.1	115
Er^{3+}	22.3	167	27.7	181	14.0	117
Tm^{3+}	20.2	160	25.4	173	15.5	122
Yb^{3+}	19.2	156	25.7	174	14.5	119
Lu^{3+}	19.5	157	21.0	159	14.3	118
Y^{3+}	18.5	153	20.2	155	15.3	121

[a] ± 0.2; kJ mol^{-1}; [b] ± 1 J K^{-1}mol^{-1}; [c] ± 1.6 kJ mol^{-1}; [d] ± 5 J K^{-1}mol^{-1}; [e] ± 1.0 kJ mol^{-1}; [f] ± 3 J K^{-1}mol^{-1}.

DISCUSSION

Figure 1 shows the relationship between the value of log β_{101} for Sm^{3+} complexes with a number of alkyl and aryl carboxylate ligands and the sum of the acidity constants, ΣpK_a, for the carboxylate groups involved in binding. Such a linear dependence of the stability constant on the ligand basicity (as reflected by the protonation constants) is expected for systems involving hard acid-hard base interactions. The deviation of the values for the isophthalate, trimesitate (1,3,5-benzenetricarboxylate)[10], hemimellitate and pyromellitate complexes can be explained by considering the arrangement of the donor groups in these ligands. Isophthalate and trimesitate anions can bind the metal ion by only a single carboxylate group and thus have, respectively, two and three possible binding sites. To correct for the increased probability, log β_{101} should be reduced by 0.3 (*i.e.*, log 2) and 0.5 (*i.e.*, log 3) for the isophthalate and trimesitate complex formation. Similarly, tri-, hemi-, and pyromellitate anions can act as bidentate, chelating ligands which gives each ligand two sets of possible binding sites. Again, their values of log β_{101} should be corrected for this statistical enhancement by substracting *ca.* 0.3 log units. However, the corrected values for isophthalate, trimesitate and fumarate complex formation are somewhat above ($> 1\sigma$) the correlation line, possibly reflecting enhanced binding from charge polarization. The corrected values for tri-, hemi- and pyromellitate fit the correlation, indicating no significant effect due to charge polarization through the π system of these ligands.

It has been proposed that the enthalpy and entropy terms in lanthanide complex formation reflect primarily the effect of dehydration of the Ln(III) cations and the ligand anions.[11] To compensate for the latter, comparisons of these parameters can be based on the reaction:

$$Ln^{3+}{}_{(aq)} + H_nL_{(aq)} \rightleftharpoons LnL^{3-n}{}_{(aq)} + nH^{+}{}_{(aq)};\ \Delta H^{*}, \Delta S^{*}$$

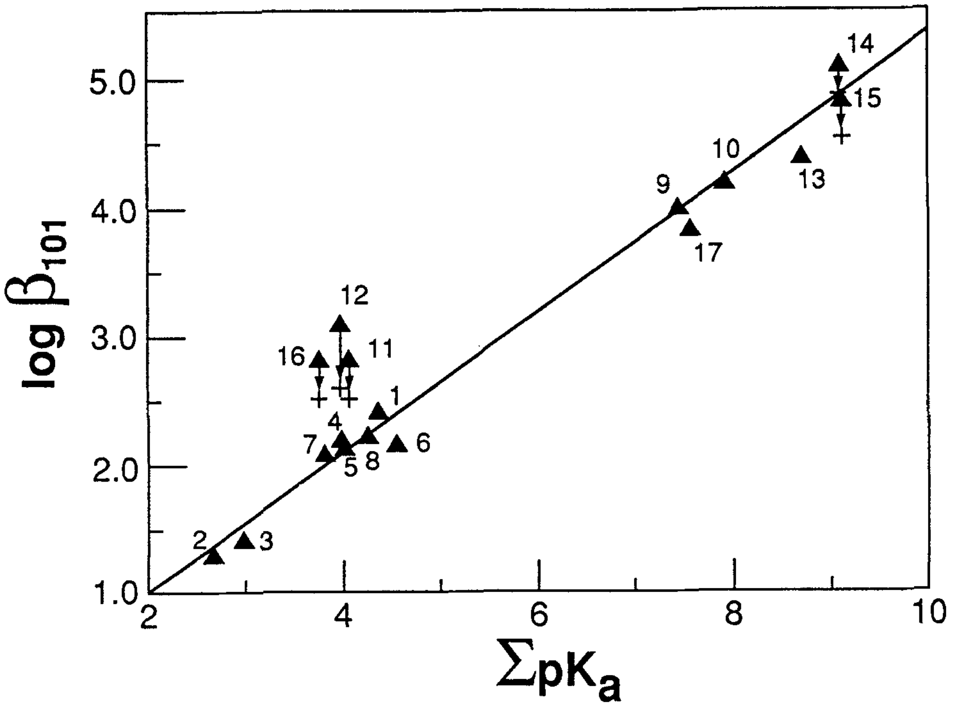

Figure 1 Correlation of log β_{101} with ΣpK_a for Sm(III) complexes at 25°C and 0.10 M ionic strength. The symbols (▲) and (+) represent the observed and corrected values of log β_{101}, respectively. In both cases, the values are plotted *vs.* the corrected values of ΣpK_a for the statistical enhancement: 1) acetate; 2) chloroacetate; 3) iodoacetate; 4) benzoate; 5) 3-hydroxybenzoate; 6) 4-hydroxybenzoate; 7) o-methoxy-benzoate; 8) p-methoxybenzoate; 9) phthalate; 10) malonate; 11) isophthalate; 12) trimesitate; 13) trimellitate; 14) hemimellitate; 15) pyromellitate; 16) fumarate and 17) maleate.

It is assumed that the protonation serves to dehydrate the anion in a similar fashion to reactions with metals. Using complex formation with Sm^{3+} for illustration, the order (and values) of the entropy change, ΔS^* ($J\ K^{-1} mol^{-1}$) of this reaction, for the aromatic carboxylate complexes under discussion is:

hemimellitate (– 58) < pyromellitate (– 52) < phthalate (– 46) << benzoate (– 6) < isophthalate (– 2)

The values for phthalate, hemi- and pyromellitate ligands are comparable to the values of ΔS^* for 1:1 complexes of Sm^{3+} with the aliphatic dicarboxylate ligand succinate which has the same size chelate ring.[11] These values confirm the monodentate nature of the benzoate and isophthalate complexes and the bidentate nature of that with hemi- and pyromellitate.

To summarize, the complexes of lanthanide cations by hemi- and pyromellitate ligands show enhancement in the stability constant above that expected for typical bidentate complex formation. This enhancement is principally due to a statistical increase in the probability of binding in these systems and differs from what would have been expected based upon previous results. Further data are still required to explain the variance. The values of ΔH_{101} and ΔS_{101} reflect the difference in the dehydration of the metal and ligand upon complexation.

Acknowledgement

The research was supported at F. S. U. by a grant from the USDOE-OBES Division of Chemical Sciences.

References

1. G. R. Choppin, P. A. Bertrand, Y. Hasegawa and E. N. Rizkalla, *Inorg. Chem.* **21**, 3722 (1982).
2. E. Pascual and G. R. Choppin, *Lan. Act. Res.* **1**, 57 (1985).
3. D. F. Peppard, G. W. Mason, J. L. Vaier and W. F. Driscoll, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
4. C. W. Davies, "*Ion Association*", Butterworths, London, 1962.
5. E. Orebaugh and G. R. Choppin, *J. Coord. Chem.* **5**, 123 (1976).
6. M. S. Caceci and G. R. Choppin, *Comput. Chem.* **6**, 161 (1982).
7. A. E. Martell and R. M. Smith, "*Critical Stability Constants*", Vol. 3, Plenum Press, New York, 1977.
8. E. Pascual, *Ph. D. Dissertation*, Florida State University, 1976.
9. G. R. Choppin, F. I. Khalili and E. N. Rizkalla, *J. Coord. Chem.* **26**, 243 (1992).
10. W. Bradly, *M. Sc. Thesis*, Florida State University, 1986.
11. G. R. Choppin, A. Dadgar and E. N. Rizkalla, *Inorg. Chem.* **25**, 3581 (1986).