

Thermodynamics and Nuclear Magnetic Resonance Studies of Lanthanide Complexation by Ethylenediamine-*NN'*-diacetate-*NN'*-di-3-propionate

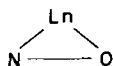
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Abstract

The proton NMR spectra of ethylenediamine-*NN'*-diacetate-*NN'*-di-3-propionate and its complexes with alkaline earth and diamagnetic lanthanide ions are described. Quartet splittings of the methylenic protons of the acetate groups upon complexation with metal ions of high charge density is indicative of long-lived metal–nitrogen bonds and short-lived metal–oxygen bonds. The observation of two AB quartets for the acetate protons complexed to trivalent ions was attributed to an unsymmetrical distribution of the acetate arms around the central ion. For Mg^{2+} complex, the two acetate arms are equivalently disposed and the two quartets collapse into one. For the other alkaline earths, a singlet is observed, indicating that the metal–nitrogen bond lifetime is also short. The spectra of the propionate protons are consistent of either an ABCD (LuENDPDA and YENDPDA) or an AA'BB' (MgENDPDA) spectral pattern. The thermodynamic data support these conclusions and show that substitution of $C_2H_4CO_2^-$ groups for $CH_2CO_2^-$ groups decreases the stability of the complex. This results from weakening of the metal–nitrogen interaction due to the expansion of the



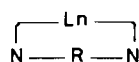
ring.

Introduction

Lanthanide ions form relatively strong complexes with a variety of polyaminopolycarboxylic acids. The complexation stability increases as the number of the amine and/or of the carboxylate donor groups increases. Generally, in these ligands the carboxylate groups are associated with the nitrogen atoms as $-CH_2COO^-$ (acetate). The nitrogen atoms are separated most commonly by $-C_2H_4-$ group. Recently, we have shown that increasing the length of the alkyl

group separating the nitrogen atoms decreases the stability of the lanthanide complexes [1]. In this paper we report on the effect on complexation stability of substituting $-C_2H_4CO_2^-$ (propionate) for $-CH_2CO_2^-$ groups in such ligands.

NMR patterns of the protons of the carboxylate arms (e.g., the $-CH_2CO_2^-$ of EDTA) are sensitive to the lifetime of the lanthanide–nitrogen bonds [2]. As the cationic radii decreases from La(III) through Lu(III), the resulting increase in charge density increases the lifetime of the Ln–N bonding which is reflected in a transition from a broad singlet (or poorly resolved AB quartet) for LaEDTA⁻ to a well resolved AB quartet for LuEDTA⁻. This splitting pattern has been used to gain insight in the bonding and structural aspects of several lanthanide polyaminopolycarboxylates [3, 4]. The decrease in the Ln–N bond lifetime as the alkyl chain separating the nitrogen donors increases observed in such a study is presumably related to the decreased stability of the complexes. The larger chelate ring in the



structure would account for these effects. The lanthanide-ethylenediamine-*NN'*-diacetate-*NN'*-di-3-propionate (ENDPDA) complexes were studied by PMR to ascertain whether lengthening the chelate rings involving the $-C_2H_4CO_2^-$ arms would similarly decrease the Ln–N bond lifetimes.

The PMR studies were combined with potentiometric and calorimetric determination of the thermodynamic (ΔG_{101} , ΔH_{101} and ΔS_{101}) changes for the complexation. The entropy changes in the lanthanide polyaminopolycarboxylate complexation have been shown to correlate linearly with the number of carboxylate groups [5] when the latter are acetate species. Moreover, the slope of the correlation had the value of the entropy change for complexation by an acetate anion. Based on this, the enthalpy of complexation was corrected by $n\Delta H_{Ac}$ (where n = number of binding acetate groups and ΔH_{Ac} = enthalpy change for formation of $LnAc^{2+}$). The

residual enthalpy $\delta\Delta H$ ($\delta\Delta H = \Delta H_{101} - n\Delta H_{Ac}$) correlated directly with the $\Sigma pK_{a(N)}$ *i.e.*, the basicity constants of the nitrogen donor sites for a series of ligands of the general structure $(C_2H_4N)_n-(CH_2CO_2^-)_m$. However, as the length of the alkyl chain separating the nitrogen donor atoms increases, the correlation fails indicating a decreased Ln–N interaction. The thermodynamic data of this study allows a similar analysis of the effect of increasing the alkyl chain of the carboxylate arms.

Experimental

Reagents

Stock solutions of the lanthanide perchlorate salts were prepared and standardized as described previously [6]. ENDPDA from Sigma Products Co. was recrystallized twice from ethanol–water solutions. For the NMR measurements, stoichiometric amounts of lanthanide and ENDPDA solutions were mixed and taken to dryness, then redissolved in D_2O . This process was repeated several times to eliminate H_2O before dilution to the proper volume with D_2O (and NaOD if necessary to adjust the pD). The exact molarity of these solutions were checked by complexometric titration using EDTA and xylenol orange. The NaOD solution was prepared by dissolving sodium metal in D_2O . PMR spectra of Na^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} solutions of ENDPDA were measured as well as those of the La^{3+} , Lu^{3+} and Y^{3+} complexes.

Measurements

The lanthanide cation–ENDPDA stability constants were determined by potentiometric titration of 50.0 ml aliquots of *ca.* 1 mM ligand solution in the presence of equimolar amounts of the different lanthanide ions using CO_2 -free potassium hydroxide (0.10 M) as the titrant. The ionic strength was adjusted to either 0.10 M or 0.50 M in the stock solutions by adding the appropriate amount of sodium perchlorate. All measurements were obtained at 25 °C using a Radiometer PHM 84 pH-meter fitted with a combined glass–calomel electrode. The ENDPDA protonation constants were obtained by similar titration at constant ionic strength using standard base.

Enthalpy data were obtained using a calorimeter interfaced with an Ohio Scientific computer [7]. Titration of the tetrasodium salt of ENDPDA (50.0 ml of 5 mM) in the calorimeter cup by perchloric acid (0.10 M) gave the heats of protonation. The heats of formation of ENDPDA complexes were determined by titration of the ligand buffer into metal solutions (50.0 ml *ca.* 5 mM) under the same conditions of ionic strength and temperature as that used in the potentiometric study. The measurements were

repeated several times in different buffer regions to allow for the formation of significant fractions of either LnL^- and $LnHL^0$ species. This allowed refinement of the computed constants. Each enthalpy titration datum was corrected for the corresponding heat of dilution of both the metal ion and the ligand anion (as determined in separate blank titrations). Both potentiometric and calorimetric titrations were repeated at least twice for each metal.

The proton magnetic resonance measurements were conducted using the pulsed Fourier transform mode with a deuterium lock on the Bruker 270 MHz spectrometer of the Florida State University NMR Laboratory. The spectra of the lanthanide solutions were recorded at 0, ambient and 85 °C temperatures, whereas the alkaline earth solutions were investigated at ambient temperature only. In all measurements, equimolar amounts of metal and ligand were used. For the alkaline earth solutions, the pD value was adjusted between 9–10 while for the lanthanide solutions, the pD value ranged between 7–8. The chemical shifts were recorded relative to sodium-2,2-dimethyl-2-silapentane-5-sulphonate (DSS) as an external standard.

Results

The protonation titration curves showed three buffer zones with well-defined inflection points at two and at three moles of base added per mole of ligand. Accordingly, the values of the first two protonation constants were determined directly at the appropriate half-titration values. The third and fourth protonation constants were obtained by a curve fitting iterative procedure to minimize the residuals in \bar{n}_H values calculated from the experimental parameters and the fitted constants. The pK values obtained at 0.10 M ionic strength are in good agreement with those reported previously by Martell *et al.* [8]. The protonation enthalpies were calculated using the LINX program of this laboratory [9]. The thermodynamic values of protonation are given in Table I.

The numerical analysis of the titration curves obtained for solution of equimolar metal to ligand mixtures were carried out using standard mass balance equations for the total ligand, C_L ; total metal, C_M ; and total hydrogen ion, C_H ; concentrations:

$$C_L = A[L] + B[ML] \quad (1)$$

$$C_M = [M] + B[ML] \quad (2)$$

$$C_H = C[L] + D[ML] \quad (3)$$

where

TABLE I. Thermodynamics of Protonation of ENDPDA ($T = 298$ K)

Reaction	pK_a	$-\Delta H$ (kJ mol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	I (M)
$H^+ + L^{4-} \rightleftharpoons HL^{3-}$	9.99 ± 0.02	28.26 ± 0.7	96 ± 2	0.1
	10.01 ± 0.02	31.64 ± 0.7	85 ± 2	0.5
$H^+ + HL^{3-} \rightleftharpoons H_2L^{2-}$	6.02 ± 0.01	13.12 ± 0.2	71 ± 1	0.1
	6.09 ± 0.01	15.51 ± 0.4	65 ± 2	0.5
$H^+ + H_2L^{2-} \rightleftharpoons H_3L^-$	3.68 ± 0.02	3.30 ± 0.1	59 ± 1	0.1
	3.84 ± 0.02	6.12 ± 0.1	53 ± 1	0.5
$H^+ + H_3L^- \rightleftharpoons H_4L$	2.69 ± 0.03	2.55 ± 0.1	43 ± 1	0.1
	3.02 ± 0.03	7.21 ± 0.3	34 ± 1	0.5

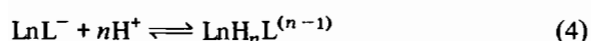
$$A = \sum_{i=0}^4 [H^+]^i \beta_{0i1}$$

$$B = \sum_{i=0}^n [H^+]^i \beta_i^H$$

$$C = \sum_{i=1}^4 i[H^+]^i \beta_{0i1}$$

$$D = \sum_{i=1}^4 i[H^+]^i \beta_i^H$$

The β_{0i1} is the overall acid protonation constant for the H_iL species, n is the number of protonated complexes and β_i^H represents the equilibrium constant for the reaction:



Equations (1–3) can be solved for the formation constant of the species LnL^- by fitting the general equation:

$$\beta_{101} = \frac{(BC - AD)(CC_L - AC_H)}{(BC_H - DC_L)(ABC_H + BCC_M - ADC_M - BCC_L)} \quad (5)$$

Best fit is obtained by the use of β_i^H values which give the least deviation for the β_{101} value over the entire titration curve. Table II presents a typical data set for the determination of the stability constants; the last column lists the value of $\log \beta_{101}$ calculated at each titration point.

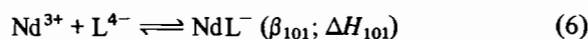
The treatment of the calorimetric titration data to calculate enthalpies of complexation has been described previously [10] and was modified to allow for formation of $LnHL$. A typical set of data is shown in Table III. Column 3 in this table lists the corrected

TABLE II. Potentiometric Titration Data for Ho-ENDPDA^a. $I = 0.10$ M (NaClO₄); $T = 298$ K

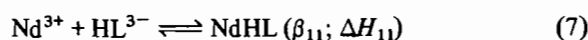
V_{titrant} (ml)	pH	$10^{14} [L^{4-}]$ (M)	$10^4 [Ho^{3+}]$ (M)	\bar{n}_H	$\log \beta_{101}$
0.50	3.209	1.364	5.435	1.541	13.83
0.55	3.229	1.498	5.181	1.475	13.83
0.60	3.249	1.642	4.935	1.408	13.83
0.65	3.270	1.805	4.685	1.340	13.83
0.70	3.290	1.971	4.455	1.271	13.84
0.75	3.312	2.169	4.212	1.202	13.83
0.80	3.334	2.382	3.979	1.132	13.85
0.85	3.357	2.622	3.747	1.062	13.86
0.90	3.381	2.893	3.517	0.992	13.87
0.95	3.406	3.200	3.289	0.922	13.88
1.00	3.432	3.546	3.067	0.851	13.90
1.05	3.464	4.014	2.812	0.783	13.90
1.10	3.497	4.549	2.569	0.715	13.91
1.15	3.535	5.236	2.314	0.648	13.91
1.20	3.578	6.115	2.055	0.583	13.90
1.25	3.627	7.262	1.794	0.518	13.88
1.30	3.688	8.939	1.515	0.456	13.84
1.35	3.750	10.965	1.276	0.390	13.83

^aExperimental conditions. Cup solution: $C_M = 1.196$ mM, $C_L = 1.197$ mM, pH = 3.007, Volume = 50.0 ml. Titrant: $C_{KOH} = 0.1151$ M. Calculated constants: $\log \beta_{101} = 13.86 \pm 0.04$, $\log \beta_{111} = 16.36 \pm 0.05$.

heats at each titration point. This corrected heat is associated with the formation of the amount of NdL^- in column 7 and of $NdHL$ in column 8 according to the reactions:



and



A summary of all the thermodynamic parameters determined at both 0.10 M and 0.50 M ionic strength is provided in Tables IV and V. The reported error limits are the propagated errors calculated from the

TABLE III. Calorimetric Titration Data for Nd–ENDPDA^a. $I = 0.10$ M (NaClO₄), $T = 298$ K

V_{titrant} (ml)	$-\Sigma Q_{\text{obs}}^a$ (mJ)	$-\Sigma Q_{\text{corr}}^c$ (mJ)	[Nd ³⁺] (mM)	10^{14} [L ⁴⁻] (M)	10^4 [H ⁺] (M)	10^2 [NdL ⁻] (mmol)	10^2 [NdHL] (mmol)
0.5	90.1	21.4	4.511	0.784	0.503	0.391	0.127
1.0	179.5	67.9	4.366	1.407	0.782	0.685	0.346
1.5	267.7	124.4	4.225	1.986	0.977	0.945	0.596
2.0	354.2	184.8	4.087	2.553	1.124	1.187	0.861
2.5	440.8	248.6	3.952	3.124	1.238	1.418	1.134
3.0	527.0	314.3	3.820	3.709	1.330	1.643	1.410
3.5	611.5	379.9	3.691	4.312	1.404	1.863	1.689
4.0	695.5	446.0	3.565	4.939	1.465	2.080	1.967
4.5	779.5	512.9	3.442	5.595	1.515	2.290	2.245
5.0	861.9	578.7	3.321	6.283	1.556	2.511	2.523
5.5	943.5	644.2	3.203	7.007	1.590	2.725	2.798
6.0	1025.0	709.7	3.087	7.771	1.618	2.939	3.072
6.5	1103.6	772.5	2.974	8.580	1.641	3.154	3.343
7.0	1179.4	832.6	2.863	9.437	1.660	3.370	3.611
7.5	1251.4	888.9	2.754	10.349	1.675	3.586	3.877

^aExperimental conditions. Cup solution: [Nd³⁺] = 4.660 mM, $C_{\text{H}} = 1.748 \times 10^{-6}$ M, Volume = 50.0 ml. Titrant: $C_{\text{L}} = 10.376$ mM, $C_{\text{H}} = 7.504$ mM. Computed enthalpies. $\text{Nd}^{3+} + \text{L}^{4-} \rightleftharpoons \text{NdL}^-$; $\Delta H_{101} = -3.00 \pm 0.33$ kJ mol⁻¹; $\text{Nd}^{3+} + \text{HL}^{3-} \rightleftharpoons \text{NdHL}$; $\Delta H_{11} = +25.82 \pm 0.49$ kJ mol⁻¹. ^bHeat observed and corrected for dilution. ^cHeat corrected for ligand deprotonation.

TABLE IV. Thermodynamic Parameters of the Complexation of Lanthanide Ions with ENDPDA. $I = 0.10$ M (NaClO₄), $T = 298$ K

Ln ³⁺	β_{101}	β_{111}	β_{11}	$-\Delta G_{101}$ (kJ mol ⁻¹)	$-\Delta G_{11}$ (kJ mol ⁻¹)	ΔH_{101} (kJ mol ⁻¹)	ΔH_{11} (kJ mol ⁻¹)	ΔS_{101} (JK ⁻¹ mol ⁻¹)	ΔS_{11} (JK ⁻¹ mol ⁻¹)
La	10.53 ± 0.02	14.88 ± 0.02	4.89 ± 0.03	60.08 ± 0.11	27.90 ± 0.17	-6.77 ± 0.60	29.13 ± 0.72	179 ± 2	191 ± 3
Pr	11.94 ± 0.01	15.98 ± 0.02	5.99 ± 0.03	68.12 ± 0.06	34.18 ± 0.17	-2.39 ± 0.83	21.92 ± 1.44	221 ± 3	188 ± 5
Nd	12.34 ± 0.01	16.15 ± 0.02	6.16 ± 0.03	70.41 ± 0.06	35.15 ± 0.17	-3.00 ± 0.33	25.82 ± 0.50	226 ± 1	205 ± 2
Sm	12.86 ± 0.01	16.15 ± 0.02	6.16 ± 0.03	73.37 ± 0.06	35.15 ± 0.17	1.85 ± 0.90	32.38 ± 1.60	252 ± 3	226 ± 5
Eu	13.04 ± 0.01	16.33 ± 0.01	6.34 ± 0.02	74.40 ± 0.06	36.17 ± 0.11	1.86 ± 0.78	31.85 ± 2.37	256 ± 3	228 ± 8
Gd	13.21 ± 0.01	16.22 ± 0.02	6.23 ± 0.03	75.37 ± 0.06	35.55 ± 0.17	4.09 ± 0.82	32.78 ± 2.85	267 ± 3	229 ± 10
Tb	13.50 ± 0.01	16.31 ± 0.03	6.32 ± 0.04	77.03 ± 0.06	36.06 ± 0.23	2.37 ± 0.60	31.86 ± 2.09	266 ± 2	228 ± 7
Dy	13.76 ± 0.01	16.31 ± 0.07	6.32 ± 0.07	78.51 ± 0.06	36.06 ± 0.40	1.19 ± 0.24	30.98 ± 2.17	267 ± 1	225 ± 7
Ho	13.84 ± 0.01	16.36 ± 0.05	6.37 ± 0.05	78.97 ± 0.06	36.34 ± 0.29	2.78 ± 0.30	33.38 ± 4.14	274 ± 1	234 ± 14
Er	14.13 ± 0.01	16.46 ± 0.16	6.47 ± 0.16	80.62 ± 0.06	36.92 ± 0.91	3.40 ± 0.54	30.07 ± 4.50	282 ± 2	225 ± 15
Tm	14.25 ± 0.01	16.65 ± 0.04	6.66 ± 0.04	81.30 ± 0.06	38.00 ± 0.23	3.74 ± 0.78	27.86 ± 3.09	285 ± 3	221 ± 10
Yb	14.52 ± 0.01	16.88 ± 0.05	6.69 ± 0.05	82.85 ± 0.06	38.17 ± 0.29	2.89 ± 1.11	25.02 ± 2.69	288 ± 3	212 ± 9
Lu	14.48 ± 0.02	16.78 ± 0.08	6.79 ± 0.08	82.62 ± 0.11	38.74 ± 0.46	3.25 ± 0.45	24.68 ± 2.40	288 ± 2	213 ± 8
Y	13.52 ± 0.01	16.28 ± 0.02	6.29 ± 0.03	77.14 ± 0.06	35.89 ± 0.17	6.81 ± 1.02	30.60 ± 3.80	282 ± 3	223 ± 13

deviations of both the stability and enthalpy parameters from several runs and represents 3σ .

Discussion

NMR Studies

The PMR spectra of the free ligand (*i.e.* of the Na⁺ solution) shown in Fig. 1a has two singlets at 3.26 and 2.81 ppm assigned to the protons of acetate carboxylate arms and to the protons of the ethylenic backbone, respectively. The spectrum of the protons of the propionate arms is expected to give rise to

either an A₂X₂ or A₂B₂ splitting patterns depending on the $J/\nu_0\delta$ value [11], where J is the coupling constant between the non-equivalent nuclei. The observed pattern is consistent with an A₂B₂ spectrum since asymmetric triplets are observed with a value of $J/\nu_0\delta$ of 0.08 at pH 7.3 which increases to 0.13 at pH *ca.* 10. The spectra of the metal chelates vary markedly with differences in the charge density of the metal ion. In the first group (Ca²⁺, Sr²⁺ and Ba²⁺ complexes), the spectra are very similar to that of the free ligand with a slight chemical shift. The absence of splitting of the acetate and propionate protons spectra is consistent with the formation of chelates

TABLE V. Thermodynamic Parameters of the Complexation of Lanthanide Ions with ENDPDA. $I = 0.50 \text{ M (NaClO}_4\text{)}$, $T = 298 \text{ K}$

Ln^{3+}	β_{101}	β_{111}	β_{11}	$-\Delta G_{101}$ (kJ mol^{-1})	$-\Delta G_{11}$ (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔH_{11} (kJ mol^{-1})	ΔS_{101} (JK^{-1} mol^{-1})	ΔS_{11} (JK^{-1} mol^{-1})
La	10.19 ± 0.02	14.47 ± 0.04	4.46 ± 0.04	58.14 ± 0.11	25.45 ± 0.23	-8.05 ± 1.47	29.07 ± 1.02	168 ± 5	183 ± 4
Pr	10.96 ± 0.01	14.86 ± 0.02	4.85 ± 0.03	62.53 ± 0.06	27.67 ± 0.17	-3.79 ± 0.92	24.58 ± 0.81	197 ± 3	175 ± 3
Nd	11.09 ± 0.01	14.92 ± 0.03	4.91 ± 0.04	63.27 ± 0.06	28.01 ± 0.23	-3.05 ± 1.00	29.14 ± 0.88	202 ± 3	192 ± 3
Sm	11.54 ± 0.01	15.24 ± 0.03	5.23 ± 0.04	65.84 ± 0.06	29.84 ± 0.23	-0.63 ± 1.04	33.72 ± 0.98	219 ± 3	213 ± 3
Eu	11.73 ± 0.01	15.29 ± 0.04	5.28 ± 0.04	66.93 ± 0.06	30.13 ± 0.23	2.19 ± 1.60	38.94 ± 1.00	232 ± 5	232 ± 3
Gd	11.83 ± 0.01	15.45 ± 0.04	5.44 ± 0.04	67.50 ± 0.06	31.04 ± 0.23	2.27 ± 0.15	37.11 ± 0.87	234 ± 1	229 ± 3
Tb	12.14 ± 0.01	15.53 ± 0.06	5.52 ± 0.06	69.27 ± 0.06	31.49 ± 0.34	5.01 ± 1.15	40.79 ± 1.49	249 ± 4	243 ± 5
Dy	12.43 ± 0.01	15.75 ± 0.05	5.74 ± 0.05	70.92 ± 0.06	32.75 ± 0.29	4.74 ± 1.46	36.66 ± 1.29	254 ± 5	233 ± 4
Ho	12.63 ± 0.01	15.92 ± 0.08	5.91 ± 0.08	72.06 ± 0.06	33.72 ± 0.46	6.05 ± 0.40	38.49 ± 0.73	262 ± 1	242 ± 3
Er	12.80 ± 0.01	16.14 ± 0.06	6.13 ± 0.06	73.03 ± 0.06	34.98 ± 0.34	5.22 ± 0.29	34.90 ± 0.98	263 ± 1	234 ± 3
Tm	13.04 ± 0.01	16.37 ± 0.04	6.36 ± 0.04	74.40 ± 0.06	36.29 ± 0.23	4.82 ± 0.38	35.83 ± 0.94	266 ± 1	242 ± 3
Yb	13.08 ± 0.01	16.31 ± 0.09	6.30 ± 0.09	74.63 ± 0.06	35.95 ± 0.51	5.18 ± 1.33	36.37 ± 1.17	268 ± 4	243 ± 4
Lu	13.13 ± 0.01	16.26 ± 0.05	6.25 ± 0.05	74.91 ± 0.06	35.66 ± 0.29	6.67 ± 0.53	40.24 ± 1.44	274 ± 2	255 ± 5
Y	12.20 ± 0.02	15.67 ± 0.06	5.66 ± 0.06	69.61 ± 0.11	32.29 ± 0.34	6.80 ± 2.11	37.38 ± 0.84	256 ± 7	234 ± 3

of short M–N and M–O bond lifetimes [3]. With cations of higher charge density, the acetate singlet splits into two down-field AB quartets with baricenters of 3.49 and 3.51 ppm (Fig. 2b). The coupling constants are estimated to be 17.2 Hz and 16.1 Hz, respectively. Since the working pH for the lanthanide chelates was 7–8, these two quartets cannot be attributed to the presence of similar concentrations of LuL^- and LuHL species in solution (the ratio $[\text{LuL}^-]/[\text{LuHL}]$ is $>5 \times 10^4$). However, the observation of two AB quartets may be attributed to an unsymmetrical distribution of the acetate arms around the central ion. The presence of quartets of different baricenter and J_{AB} values for the acetate protons in HEDTA and MEDTA in their lanthanide complexes has been assigned to such an asymmetry in the structure of the ligand about the metal ion [3].

Based on this assignment of the acetate arms, the β -propionate segments should be present also in two different modes. The observed spectra show the presence of two multiplets (each of 7 lines) with a baricenter of 2.82 ppm. The intensity ratio of the two multiplets is 1:1 and each corresponds to four protons. Based on molecular models, we expect that the propionate protons would assume a gauche or skew conformation giving rise to overlapping ABCD spectral patterns. Earlier studies concerning the analysis of PMR spectra of the ortho disubstituted benzene [12] indicate the presence of 32 transitions associated with ABCD spectral patterns. A minimum requirement to solve for the four frequencies ν_{A} , ν_{B} , ν_{C} , and ν_{D} and the associated six coupling constants is the availability of 10 resonance lines for half of the spectral pattern. Under the circumstances, a satisfactory analysis of the ABCD pattern is not plausible. The spectrum of the backbone protons

overlaps the up-field half of the ABCD spectra and has an estimated chemical shift of 2.70 ppm.

The spectrum of the yttrium chelate is essentially similar to that of lutetium. However, for the lanthanum complex the inner quartet of the acetate protons as well as the up-field multiplet of the ABCD patterns have collapsed to broad singlets as shown in Fig. 2a.

For the magnesium complex, only one quartet equivalent to four protons is observed (Fig. 1b), indicating that the two acetate arms are equivalently placed around the metal ion. Consequently, the up-field multiplet is probably due to an AA'BB' spectral pattern for the equivalent propionate arms. A summary of all the observed chemical shifts is listed in Table VI.

The PMR spectra of the lanthanide chelates were investigated over the temperature range 0 to 85 °C. Decreasing the temperature was always accompanied by loss of resolution, particularly for the ABCD multiplets. However, the coupling constants, J_{AB} , for the acetate protons remained unchanged within experimental uncertainties. Such an effect has been observed with the lanthanide chelates of ethylenediaminetetra(methylenephosphonic) acid [15]. In those complexes, the loss of resolution with decreasing temperature was attributed to an equilibrium between different conformers for which the rate of transition between the conformers increased with temperature. In the present system, conformers associated with acetate/propionate exchange for in-plane and out-of-plane orientation may coexist. Such conformers would be likely to have relatively small energy barriers to interchange which would result in the observed temperature sensitivity.

In summary, the metal–nitrogen bond lifetimes of ENDPDA complexes increases with increasing the

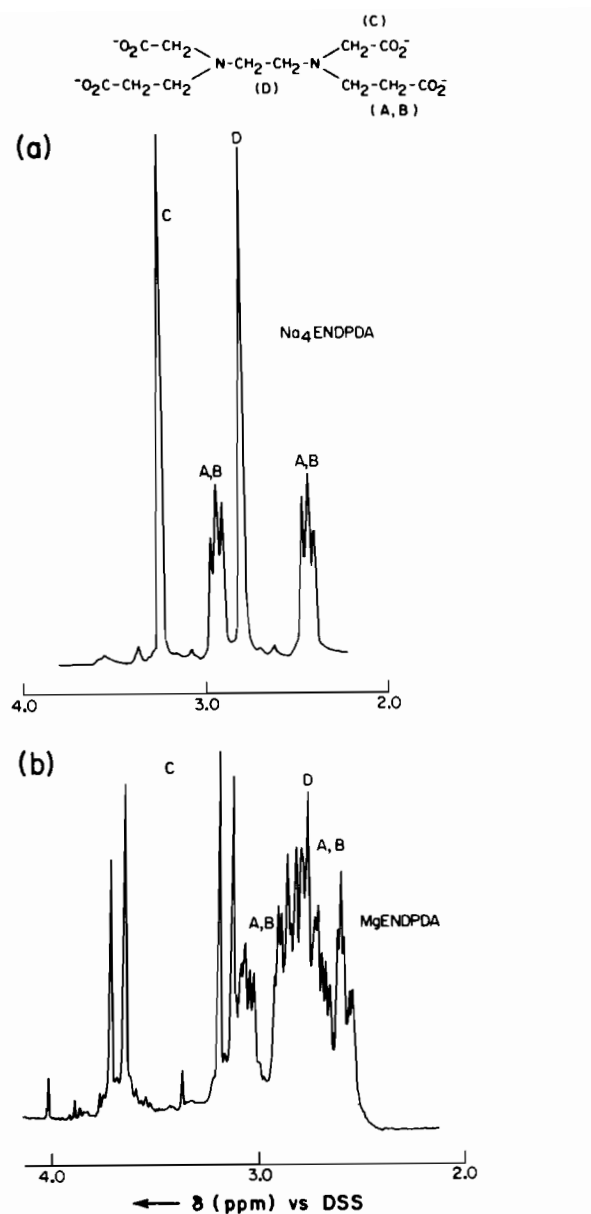


Fig. 1. Proton resonance spectra and assignments for (a) Na_4ENDPDA ; (b) MgENDPDA .

metal charge density, similar to the trend in EDTA complexes. However, the change from a singlet (short M–N lifetime) to a quartet (long M–N lifetime) pattern for the acetate protons requires higher metal ion charge density for the ENDPDA complexes. The loss of spectral resolution is even more sensitive to metal charge density for the propionate protons in the ENDPDA complexes than for the acetate protons. These effects reflect weaker metal-nitrogen interactions than in the EDTA complexes. Also, the chelate rings

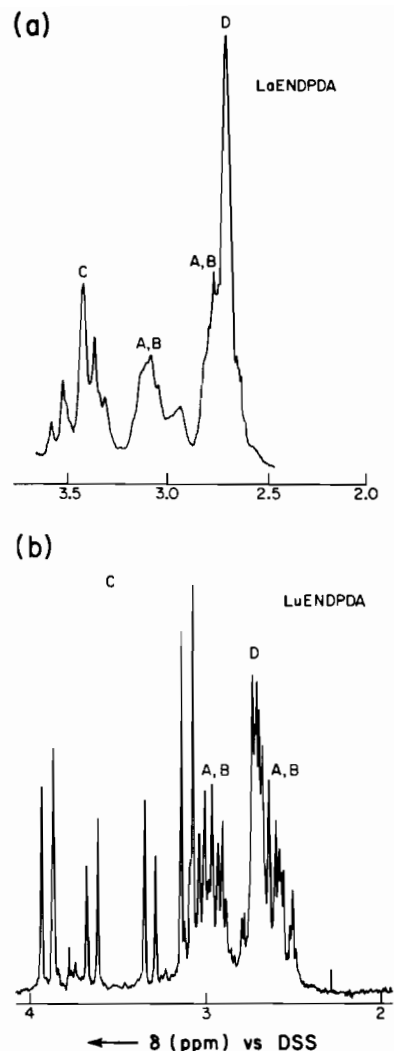
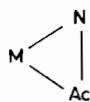


Fig. 2. Proton resonance spectra and assignments for diamagnetic lanthanide complexes with ENDPDA.



(5-membered) apparently are somewhat more stable than those of



(6-membered).

Thermodynamic Studies

The values of ΔG_{101} , ΔH_{101} , and ΔS_{101} for the formation of the LnENDPDA complexes are compared in Figs. 3–5. The stability of the LnENDPDA complexes are seen in Fig. 3 to be much less than that of

TABLE VI. Proton Chemical Shifts of ENDPDA and its Complexes with Alkaline Earths and Diamagnetic Lanthanide Ions

M^{2+}	Acetate (α)	Propionate $A_2B_2, AA'BB'$ or ABCD Baricenters (ppm) ^a	Backbone (β)
Na^+	3.26	2.71	2.81
Mg^{2+}	3.44 ($Q, J_{AB} = 18.8$ Hz)	2.80	2.78
Ca^{2+}	3.29	2.69	2.75
Sr^{2+}	3.31	2.75	2.76
Ba^{2+}	3.29	2.72	2.74
La^{3+}	3.41 (S_i)	~ 2.83	~ 2.70
	3.43 ($Q_o, J_{AB} = 17.2$ Hz)		
Y^{3+}	3.48 ($Q_i, J_{AB} = 16.1$ Hz)	2.81	2.72
	3.50 ($Q_o, J_{AB} = 18.6$ Hz)		
Lu^{3+}	3.49 ($Q_i, J_{AB} = 16.1$ Hz)	2.82	2.70
	3.51 ($Q_o, J_{AB} = 17.2$ Hz)		

^aRelative to DSS as an external standard; Q = quartet; S = singlet, i = inner and o = outer.

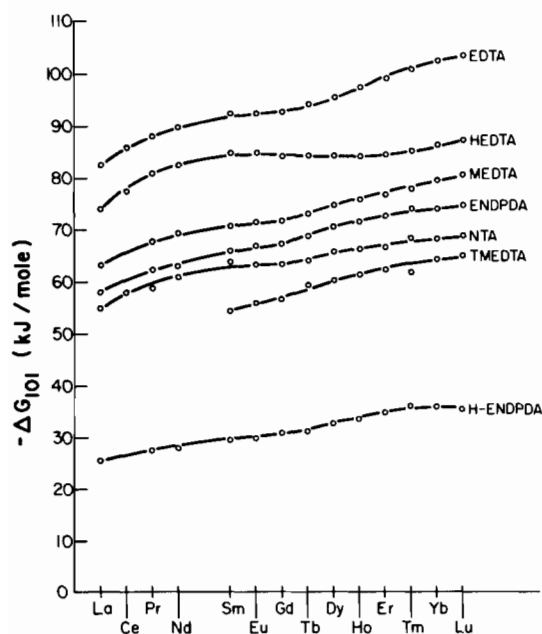


Fig. 3. The variation of the free energy of complexation across the lanthanide series for some aminopolycarboxylate ligands.

the LnEDTA complexes and between that of the LnMEDTA (2 N's and 3 Ac's) and LnNTA (1 N and 3 Ac's) complexes. However, the destabilizing effect of the two propionate arms in ENDPDA is not as great as that of substituting a propylene chain (in TMEDTA) for the ethylene chain between the nitrogens. Comparison of the data in Fig. 5 shows that the decreased stability of LnENDPDA relative to LnEDTA is not an entropy effect as the ΔS_{101} values

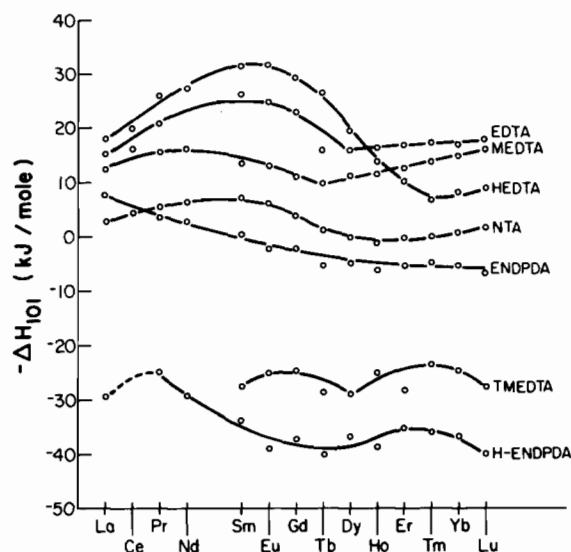


Fig. 4. The variation of the enthalpy of complexation across the lanthanide series for some aminopolycarboxylate ligands.

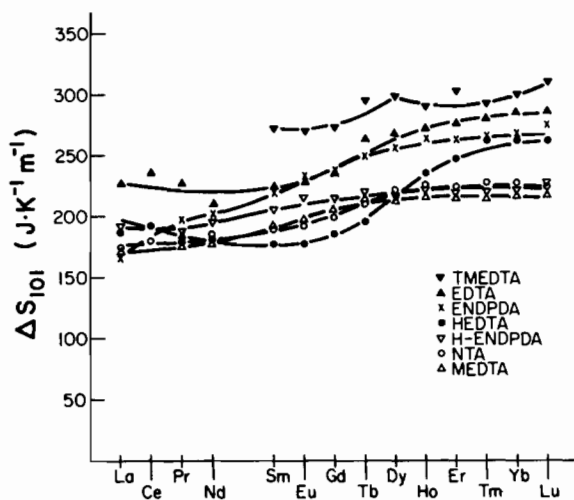


Fig. 5. The variation of the entropy of complexation across the lanthanide series for some aminopolycarboxylate ligands.

of these systems are similar. This similarity is in agreement with our earlier observation of the correlation between the ΔS_{101} values of lanthanide polyaminopolycarboxylate complexation and the number of the binding carboxylate groups [5]. This correlation suggested that the ΔS_{101} values (which are dominated by the dehydration accompanying complexation) are primarily related to the binding of the metal to the carboxylate groups and reaction of the metal with the nitrogen sites play essentially no role. With such a model, it is expected that increasing the length of the carboxylate arms would not change the complexation entropy as the metal propionate interaction should be very similar to metal acetate interaction. This model cannot be rigorously valid since

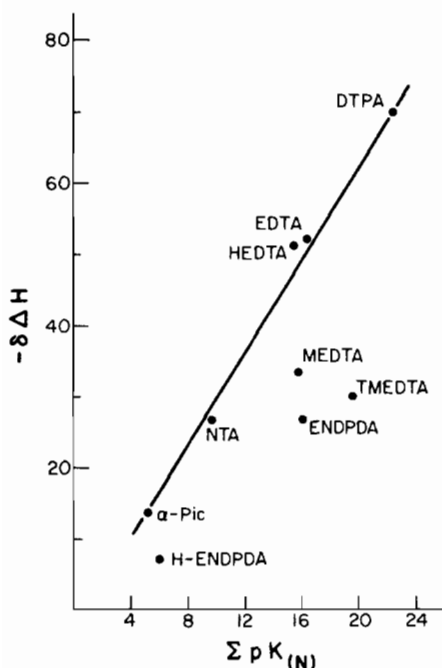


Fig. 6. The relation between the residual enthalpy ($\delta\Delta H = \Delta H_{101} - 6.5n$) and the total basicity of the nitrogen donor atoms of the ligands.

the relatively large ΔS_{101} values for the LnTMEDTA complexation (compared to the LnEDTA values) show that the entropy has some dependence on the Ln–N interaction. The LnTMEDTA values may represent a weaker



chelate ring with a smaller loss of configurational entropy than for the corresponding chelate ring in LnEDTA.

The weaker interaction in LnENDPDA relative to complexes involving ligands with four acetate arms is seen clearly in Fig. 4. If the same analysis as used previously [5] is followed, the enthalpy assigned to the lanthanide–nitrogen interaction can be calculated. Comparison of this value with the $\Sigma pK_{a(N)}$ of the two nitrogen donors (*i.e.*, $pK_{a1} + pK_{a2}$) in Fig. 6 reflects much weaker Ln–N interactions. This observation agrees well with the PMR data which supports a shortened Ln–N lifetime in ENDPDA complexes compared to that in EDTA.

The thermodynamic data for reaction 7 supports our interpretation of the LnENDPDA structures as reflecting interaction with all four carboxylate groups but much weakened Ln–N interaction. The ΔS_{11}

values are roughly similar to the ΔS_{101} values. The ΔS_{101} values have been correlated with the number of carboxylate groups [5] and to a first approximation, show no dependence on the Ln–N interaction. In LnHENDPDA, the proton is expected to be associated with a nitrogen donor, so all four carboxylate groups should be free for interaction with the lanthanide cation. The ΔH_{11} is, however, much more endothermic than the ΔH_{101} values. If we use the earlier treatment to calculate $\delta\Delta H$ (the enthalpy associated with the Ln–N interaction), we obtain a value of $+6.3 \text{ kJ mol}^{-1}$ for SmHENDPDA. This would be the enthalpy of interaction with the less basic nitrogen (*i.e.*, $pK_{a(N-2)} = 6.09$). As seen in Fig. 6, the $\delta\Delta H$ and $pK_{a(N-2)}$ values correlate fairly well and support the models presented for the LnENDPDA and LnHENDPDA structures in solution.

In summary, the thermodynamic data show that substitution of $\text{C}_2\text{H}_4\text{CO}_2^-$ groups for CH_2CO_2^- groups in polyaminopolycarboxylate ligands decreases the stability of the complex. This decreased stability seems to be due to a weakened metal–nitrogen interaction which is reflected in the NMR spectra as a shortened Ln–N bond lifetime.

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