

interaction exists between the CO ligand and boron center which is analogous to that seen in metal carbonyl systems. Likewise, on going from the strongly back-bonding CO ligand to the weakly back-bonding PMe_3 ligand, PE results in conjunction with calculations show the same kind of inductive shifts observed in strictly metal systems.

Experimental Section

The compounds used in this study were prepared as previously described.^{2,3,21} The He I (21.2-eV) and Ne I (16.8-eV) photoelectron spectra were recorded by using a spectrometer whose configuration has also been described previously.^{1b,13} The instrument was initially calibrated by using a 50/50 mixture of Xe/Ar gas and in all cases achieved a resolution of 45 meV or better relative to Xe (fwhm). Individual band positions were determined by using Ar (15.76 and 15.93 eV) and a band

resulting from a trace amount of H_2O (12.62 eV). All samples were air-stable solids at room temperature, and it was necessary to heat them in order to produce sufficient vapor pressure to obtain a spectrum. The minimal temperature necessary to achieve sublimation was used, these temperatures being 88 °C for Ic, 91 °C for Id, 94 °C for Ie, 86 °C for IIIa, 120 °C for IIIb, and 81 °C for IV. In all cases, the samples sublimed cleanly with no evidence of decomposition being seen, i.e. production of CO.

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Supplementary Material Available: Tables and figures showing the results of MO calculations on Ic-e with related discussion (7 pages). Ordering information is given on any current masthead page.

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Thermodynamics of Complexation of Lanthanides by Dicarboxylate Ligands

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Thermodynamic parameters of complexation of lanthanide cations by succinate, glutarate, adipate, and *trans*-1,4-cyclohexanedicarboxylate (CHDCA) ligands have been measured with potentiometric and calorimetric techniques. When analogous data for oxalate and malonate complexing are included, the complex stability decreases sharply as the ring size increases from 5 to 7; however, for 7-9-membered rings, there is little difference in stability. The negative entropy contribution associated with expansion in ring size has been attributed to an increasing loss in the configurational entropy in the alkyl chain. The more positive entropy for the Sm-CHDCA complex compared to that of Sm-adipate is attributed to the favorable boat configuration for chelation with CHDCA.

Introduction

The strongly ionic nature of the bonding of lanthanide cations in complexes leads to variable coordination numbers and geometries that reflect steric and electrostatic interactions between metal, donor atoms, and solvent. Such properties allow lanthanide cations to accommodate a wider range of chelate rings than metals requiring orbital overlap with a fixed coordination geometry. The relation of stability and chelate ring size has been investigated for complexation of lanthanides by amino polycarboxylates. For the ligands $(-\text{O}_2\text{CCH}_2)_2\text{N}(\text{CH}_2)_n\text{N}(\text{CH}_2\text{CO}_2^-)_2$ where $n = 2$ (EDTA) 3, (TMDTA) and 4 (TMEDTA), the stability as measured by the formation equilibrium (stability) constant decreased by slightly more than 2 log units for each unit increase in the N-Ln-N chelate ring size.¹ This decreased stability was associated with more positive values for both the enthalpies and entropies of formation. The data were interpreted in terms of much weaker Ln-N interaction with increasing ring size.²

To expand the investigation of stability and chelate ring size, we have studied the thermodynamics of complexation of lanthanides by a series of alkanedicarboxylates. The ligands investigated were succinate $(\text{CH}_2\text{CO}_2^-)_2$, glutarate $\text{H}_2\text{C}(\text{CH}_2\text{CO}_2^-)_2$, adipate $(\text{C}_2\text{H}_4\text{CO}_2^-)_2$, and *trans*-1,4-cyclohexanedicarboxylate (CHDCA).

Experimental Section

Reagents and Solutions. Stock solutions of lanthanide perchlorates were prepared and standardized as previously described.³ The pH of the metal solutions for potentiometric measurements was adjusted to approximately 3.5 with perchloric acid. The pH for the solutions used in

the calorimetric measurements was slightly higher (4.5-5.0). Stock solutions of the ligands were prepared by using analytical grade reagents, and the molarity of these solutions was determined by potentiometric titrations. The ionic strength of all solutions was adjusted to 0.10 M with sodium perchlorate as the inert electrolyte.

Potentiometric and Calorimetric Measurement. Potentiometric (pH) data were obtained by titrating the metal solutions (50.0 mL) with partially neutralized ligand solutions. The pH, after each addition of titrant, was recorded with a Radiometer assembly consisting of a digital pH meter Model PHM 84 fitted with a combined glass-calomel electrode, an ABU 80 autoburette, and a TTA-80 titration assembly. The electrode was calibrated with standard "BuffAR" solutions of pH 4.01 and 7.00. All measurements were made at 25 °C under nitrogen gas. Since concentration quotients of the stability constants are calculated, the measured hydrogen ion activity as determined from the pH was corrected to hydrogen ion concentrations in the 0.10 M ionic medium by use of 0.782 for the activity coefficient.⁴

The heats of complexation were determined by titrating the partially neutralized ligand solution into the metal solution and using an adiabatic calorimeter fitted with a Radiometer ABU 80 autoburette and interfaced to an Ohio Scientific microcomputer.⁵ A thermistor detected the changes in temperature upon titrant addition. In a typical run, 50.0 mL of the metal solution was titrated with increments of the ligand solution. All the heats measured were corrected for dilution and deprotonation of the ligand. These corrections were determined in separate blank measurements.

Results

Protonation constants of CHDCA were determined by potentiometric titration with standard base (NaOH). Literature values of the acid constants were available for the other ligands.⁶

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Table I. Thermodynamics of Stepwise Protonation of Succinate, Glutarate, Adipate, and CHDCA Ligands ($I = 0.10$ M (NaClO₄); $T = 298$ K)

species		pK_a^a	ΔH , kJ mol ⁻¹	ΔS , J K ⁻¹ mol ⁻¹
oxalate	HL	3.82 ± 0.04 ⁶	6.28 ± 0.21 ⁷	94 ± 1
	H ₂ L	4.86 ± 0.14 ⁶	10.54 ± 0.42 ⁷	128 ± 3
malonate	HL	5.28 ± 0.05 ⁸	3.85 ± 0.13 ⁷	114 ± 1
	H ₂ L	7.93 ± 0.10 ⁸	2.64 ± 0.40 ⁷	160 ± 2
succinate	HL	5.24 ± 0.04 ⁶	-0.18 ± 0.15	100 ± 1
	H ₂ L	9.24 ± 0.06 ⁶	-5.97 ± 0.30	157 ± 2
glutarate	HL	5.03 ± 0.03 ⁶	1.34 ± 0.15	101 ± 1
	H ₂ L	9.16 ± 0.05 ⁶	4.29 ± 0.30	190 ± 1
adipate	HL	5.03 ± 0.03 ⁶	1.24 ± 0.15	101 ± 1
	H ₂ L	9.29 ± 0.06 ⁶	6.95 ± 0.30	201 ± 2
CHDCA	HL	5.70 ± 0.04	2.73 ± 0.05	118 ± 1
	H ₂ L	10.35 ± 0.10	5.35 ± 0.10	216 ± 2

^aThe HL values are for the reaction $H + L = HL$; the H₂L values are for $H + HL = H_2L$. $\Delta H_{HL} = \Delta H_{011}$ and $\Delta H_{H_2L} = \Delta H_{021}$.

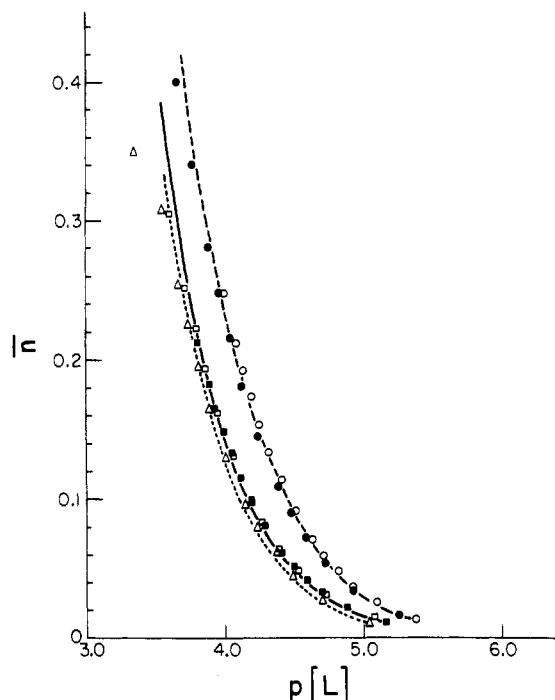


Figure 1. Fit of experimental points to \bar{n} curves calculated from the stability constants. Open and closed symbols represent duplicate titration data: $\circ, \bullet = \text{Sm} + \text{succinate}$; $\square, \blacksquare = \text{Sm} + \text{glutarate}$; $\triangle = \text{Sm} + \text{Adipate}$.

Although these values are not reported as determined in NaClO₄ media, in practice at 0.1 M ionic strength pK_a values are the same within experimental error in NaClO₄, KNO₃, etc. The heats of protonation of all the ligands were obtained by calorimetric titration of the partially neutralized solution using perchloric acid as titrant. The successive acid constants and the corresponding enthalpies and entropies of protonation are listed in Table I. The literature values for benzoic, oxalic, and malonic acids are included for reference in the subsequent discussion.

In the potentiometric study, the data were processed by a nonlinear curve-fitting (BETA) program written in this laboratory by W. Cacheris. The program allows for the presence of both normal and protonated species, and the fitting is based on the Newton-Raphson method using the SIMPLEX algorithm to min-

Table II. Thermodynamic Values for Lanthanide-Dicarboxylate Complexation ($I = 0.10$ M (NaClO₄); $T = 298$ K)

M	$\log \beta_{101}$	$-\Delta G_{101}$, kJ mol ⁻¹	ΔH_{101} , kJ mol ⁻¹	ΔS_{101} , J K ⁻¹ mol ⁻¹
Succinate				
La	3.09 ± 0.02	17.63 ± 0.11	11.50 ± 0.45	98 ± 2
Pr	3.36 ± 0.04	19.17 ± 0.23	12.75 ± 0.80	107 ± 3
Sm	3.50 ± 0.02	19.97 ± 0.11	13.46 ± 1.33	112 ± 4
Gd	3.42 ± 0.03	19.51 ± 0.17	12.71 ± 0.33	108 ± 1
Dy	3.33 ± 0.05	19.00 ± 0.29	16.64 ± 0.24	120 ± 1
Er	3.32 ± 0.04	18.94 ± 0.23	18.15 ± 0.27	124 ± 1
Lu	3.31 ± 0.04	18.89 ± 0.23	17.31 ± 0.21	121 ± 1
Glutarate				
La	2.99 ± 0.01	17.06 ± 0.06	12.37 ± 0.40	99 ± 1
Pr	3.17 ± 0.03	18.09 ± 0.17	14.36 ± 1.00	109 ± 3
Sm	3.24 ± 0.01	18.49 ± 0.06	14.13 ± 0.62	109 ± 2
Gd	3.19 ± 0.03	18.20 ± 0.17	16.88 ± 0.11	118 ± 1
Dy	3.13 ± 0.07	17.86 ± 0.40	18.10 ± 0.27	121 ± 1
Er	3.09 ± 0.04	17.63 ± 0.23	17.76 ± 1.01	119 ± 3
Lu	3.16 ± 0.01	18.03 ± 0.06	18.98 ± 1.40	124 ± 5
Adipate				
La	2.95 ± 0.02	16.83 ± 0.11	14.37 ± 0.74	105 ± 3
Pr	3.09 ± 0.03	17.63 ± 0.17	15.82 ± 0.18	112 ± 1
Sm	3.19 ± 0.03	18.20 ± 0.17	15.25 ± 0.14	112 ± 1
Gd	3.09 ± 0.04	17.63 ± 0.23	16.47 ± 0.38	114 ± 1
Dy	3.04 ± 0.05	17.34 ± 0.29	19.22 ± 1.20	123 ± 4
Er	3.05 ± 0.02	17.40 ± 0.11	19.26 ± 0.24	123 ± 1
Lu	3.09 ± 0.02	17.63 ± 0.11	18.37 ± 0.29	121 ± 1
CHDCA				
La	4.34 ± 0.04	24.76 ± 0.23	12.86 ± 0.20	126 ± 1
Pr	4.35 ± 0.05	24.83 ± 0.26	11.92 ± 0.41	123 ± 1
Nd	4.37 ± 0.04	24.93 ± 0.22	14.73 ± 0.20	133 ± 1
Sm	4.42 ± 0.01	25.23 ± 0.06	15.33 ± 0.98	136 ± 3
Eu	4.41 ± 0.02	25.13 ± 0.11	15.59 ± 0.94	137 ± 3
Gd	4.35 ± 0.04	24.83 ± 0.22	16.24 ± 0.22	138 ± 1
Tb	4.34 ± 0.05	24.76 ± 0.28	17.12 ± 0.13	141 ± 1
Dy	4.30 ± 0.01	24.53 ± 0.06	16.57 ± 0.30	138 ± 1
Ho	4.31 ± 0.05	24.56 ± 0.28	17.75 ± 0.10	142 ± 1
Er	4.29 ± 0.06	24.48 ± 0.33	19.57 ± 0.65	148 ± 2
Tm	4.33 ± 0.05	24.68 ± 0.28	19.02 ± 0.10	147 ± 1
Yb	4.34 ± 0.01	24.74 ± 0.06	20.95 ± 1.29	153 ± 4
Lu	4.35 ± 0.04	24.84 ± 0.22	22.15 ± 0.20	158 ± 1
Y	4.24 ± 0.04	24.16 ± 0.22	17.18 ± 0.20	141 ± 1
Oxalate ⁸				
Eu	5.30 ± 0.03	30.30 ± 0.17	13.60 ± 2.5	147 ± 8
Malonate ⁹				
Sm	4.53 ± 0.03	25.86 ± 0.17	13.77 ± 0.3	133 ± 1

imize the residuals in the observed and calculated hydrogen ion concentrations for a particular set of fitted equilibrium constants. Under the present experimental conditions, only the LnL complexes were observed (\bar{n} , the average ligand bound per metal, = 0–0.5). The results are listed in Table II. The values for β_{101} are defined by ⁶

$$\beta_{101} = [\text{LnX}^+]/[\text{Ln}^{3+}][\text{X}^{2-}]$$

where [] = concentration in 0.10 M (NaClO₄) ionic medium. The reported error limits are based on the average deviation of the constants calculated from 3–4 different potentiometric sets of data from different buffer regions and represent 1 σ . The agreement between the experimental data and the curves calculated with the constants of Table II is shown in Figure 1.

Enthalpies of complexation were computed by fitting the observed heat changes, after correction for metal and ligand heats of dilution, Q_c , to the equation

$$Q_c = Q_{HL} + Q_{H_2L} + Q_{LnL} \\ = (\Delta n_{HL})\Delta H_{011} + (\Delta n_{H_2L})\Delta H_{021} + (\Delta n_{LnL})\Delta H_{101}$$

then

$$E = \sum_{i=1}^N [Q_{i,\text{calcd}} - Q_{i,\text{c}}]^2$$

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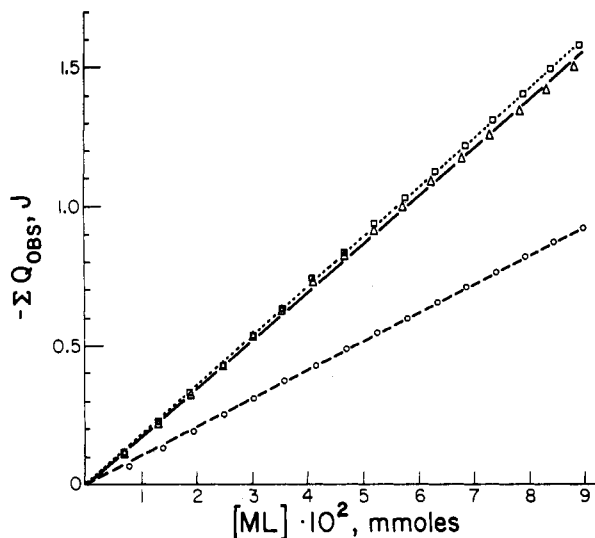


Figure 2. Fit of experimental points to $-\Sigma Q_{\text{obs}}$ curve calculated from the stability constants and formation enthalpies: ● = Gd + succinate; ▲ = Gd + glutarate; ■ = Gd + adipate.

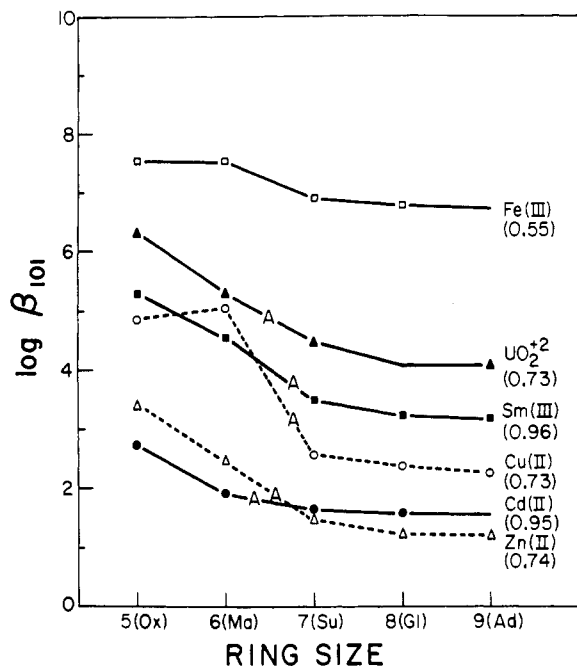


Figure 3. Correlation of $\log \beta_{101}$ with ring size for Sm(III) and other cations.^{6,10} The symbol A shows the value of β_{102} for the $M(\text{OAc})_2$ complexation (OAc = acetate).

where E is the residual error and Δn_x is the change of moles formed of the species x between one point and another. The latter were calculated by a nonlinear SIMPLEX program (DELTA-H). ΔH_{011} and ΔH_{021} are the stepwise protonation enthalpies (Table I). Table II presents the thermodynamic values with error limits that are calculated from the results of two different runs (3σ). The fits of the experimental data and the calculated curve are quite satisfactory (Figure 2). In the calorimetric titrations, \bar{n} was ≤ 0.4 .

Discussion

Few studies are reported in the literature⁶ that provide insight into the effects on the thermodynamic parameters of increasing the size of the chelate ring in metal-ligand reactions. Stability constants obtained in comparable media for the complexation of metals and the dicarboxylic acid ligands are available for several metals including Cd(II) (a soft acid), Zn(II) and Cd(II) (borderline acids), and UO_2^{2+} (a hard acid). These values for the 1:1 complexation, β_{101} , are shown in Figure 3 as a function of the chelate ring size. Values for Sm(III), also a hard acid and typical of the lanthanides, are included. No consistent difference is

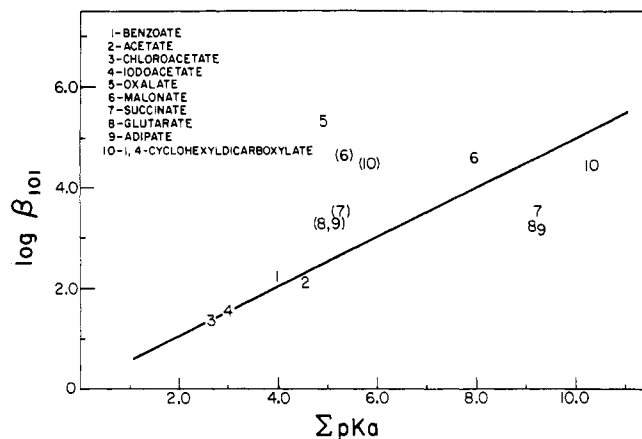


Figure 4. Correlation of $\log \beta_{101}$ with ΣpK_a for Sm(III) complexes at 25 °C and 0.10 M ionic strength.

observed in the patterns in Figure 3 between the hard and soft metals. The smaller cations seem to show less difference between five and six-membered rings while all the metals have much less variation in their stability constants for chelate rings with or greater than seven members. These data show no obvious effects of either coordination number or coordination geometry except, perhaps, for Cu(II) in the malonate complexation. For all the metals, the nonchelate diacetato complex (MAC_2) had a stability constant between those of the malonato and succinato complexes.

If we are to use the data in Table II to interpret the effect of increasing chelate ring size, we must ascertain the validity of assigning chelation to these complexes. Support for such assignment is found in the correlation of the $\log \beta_{101}$ values with the ligand acidity constants shown in Figure 4. The dicarboxylate complex data are plotted vs. $pK_{a(1)}$ (numbers in parentheses), with which they should correlate if complexation involves only one carboxylate, and vs. $\Sigma pK_{a(1+2)}$, which implies chelation. All of the alkanedicarboxylate ligands are more stable than would be predicted for the correlation line of the monocarboxylate ligands (i.e., with the $pK_{a(1)}$ values). This would indicate the presence of chelation in the dicarboxylate complexes. However, the $\log \beta_{101}$ values for the succinate, glutarate, adipate, and CHDCA complexations are below the correlation line for $\Sigma pK_{a(1+2)}$, which reflects less stabilization than expected simply from the basicity of the chelating ligand.

Chelation is expected to be reflected more in the formation entropies than in the corresponding enthalpies. The values in Table II show a rather small variation in ΔH_{101} (e.g. for Sm the values range from $+13.5 \pm 1.3 \text{ kJ mol}^{-1}$ for succinate to $15.3 \pm 1.0 \text{ kJ mol}^{-1}$ for CHDCA) while the values of ΔS_{101} differ more (e.g., for Sm from $147 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$ for oxalate to $109 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$ for glutarate). For the $\text{Sm}(\text{OAc})_2^+$ formation, data in 0.1 M ionic strength medium are lacking. From the data at 2.0 M ionic strength,⁶ we estimate the values in 0.1 M medium to be $\Delta H_2 \approx 1.4 \text{ kJ mol}^{-1}$ and $\Delta S_2 \approx 110 \text{ J K}^{-1} \text{ mol}^{-1}$. The agreement between the ΔS_2 value for $\text{Sm}(\text{OAc})_2^+$ formation and the values of ΔS_1 for the 1:1 complexation of Sm(III) with succinate, glutarate, and adipate again supports the presence of chelation in these systems. The ΔS_1 values of the dicarboxylate complexes include a negative contribution due to the loss of some configurational entropy in the chelated alkyl chain.

The differences in configurational entropy could be obscured by differences in the dehydration of the different ligands upon chelation. To minimize such differences in the contributions to the entropy values by the dehydration of the ligands, we have calculated the entropies for the reaction



The various deprotonated ligands can be expected to be more similar in hydration or, at least, have the same relative sequence as the metal chelates. The variations in ΔS_{101} and ΔS_{101}^* with increased chelate ring size are shown in Figure 5. The almost regular decrease in ΔS_{101}^* with increasing chain length presumably

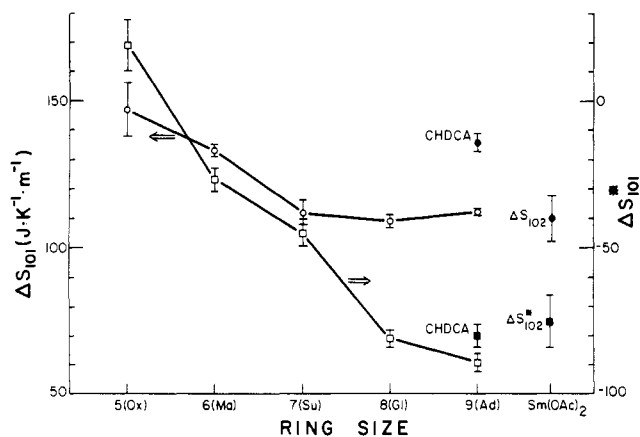


Figure 5. Variation of the entropies of complexation, ΔS_{101} and ΔS_{101}^* , of Sm(III) with various $(\text{CH}_2)_n(\text{CO}_2^-)_2$ ligands ($n = 0-4$). The values of ΔS_{102} and ΔS_{102}^* for the diacetate complexation are also included.

reflects the increasing loss of configurational entropy in the alkyl chain. The ΔS_{101}^* value for SmCHDCA^+ formation is more positive than for the adipate complex, even though both form nine-membered rings. Presumably, the CHDCA is in the boat form, which gives a more favorable configuration for chelation. The ΔS_{101}^* for $\text{Sm}(\text{OAc})_2$ formation is comparable to the glu-

tarate complexation value. We would expect that the ΔS_{101}^* values would have a "cratic" contribution¹¹ compared to the diacetate reaction of about $-33 \text{ J K}^{-1} \text{ mol}^{-1}$. If this is added to the ΔS_{101}^* values, the ΔS_{102}^* for $\text{Sm}(\text{OAc})_2^+$ becomes comparable to ΔS_{101}^* for SmSu^+ ($-78 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$). Apparently, the loss of configurational entropy in the succinate complex is about equal to the cratic entropy to which the primary stabilizing effect of chelation has been attributed.¹²

In summary, the complexation of lanthanide cations by alkanedicarboxylate ligands seems best described in terms of chelation even when the ring has nine members. The complexation stability decreases sharply as the ring size increases from five to seven, after which it shows much less effect of increasing ring size. The loss of configurational entropy in the chelated alkyl chain is a significant factor in the decreasing stability. In the cyclohexane ligand, CHDCA, the loss of configurational entropy in the nine-membered ring is less than in the adipate chelate, which is also a nine-membered ring. Presumably, the boat conformation of the CHDCA ligand is present in the complex, reducing strain in the chelate ring.

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Coordination of Thiocyanate in Tetraamine and Diimine-Diamine Complexes of Copper(II)

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Complexes of the general formula $\text{CuL}(\text{SCN})_2$, where $\text{L} = N,N'$ -bis(2-aminoethyl)-1,2-ethanediamine, N,N' -bis(2-aminoethyl)-1,3-propanediamine, N,N' -bis(3-aminopropyl)-1,3-propanediamine, N,N' -bis(3-aminopropyl)-1,2-ethanediamine, (1SR,4RS,7RS,8SR,11SR,14SR)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, (1RS,4RS,7RS,8SR,11SR,14SR)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, (1SR,4SR,7SR,8SR,11SR,14SR)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, (1RS,4SR,7SR,8SR,11SR,14SR)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, (1SR,8RS)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, (1SR,8SR)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, or 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene, have been prepared and characterized. Their infrared spectra were used to establish the bond type $\text{Cu}-\text{SCN}$ or $\text{Cu}-\text{NCS}$. The dependence of the bond type on the structure of the coordinated quadridentate ligand in the complex is discussed.

Introduction

Metal-thiocyanato complexes have been extensively investigated in order to solve the interesting problem of whether the thiocyanato group is bonded to the metal through the nitrogen atom ($\text{M}-\text{NCS}$), through the sulfur atom ($\text{M}-\text{SCN}$), or through both by means of bridging ($\text{M}-\text{NCS}-\text{M}$).¹ It has been suggested by Pearson that S in SCN^- is soft and prefers to coordinate with soft acids (class b metals), whereas N in SCN^- is hard and coordinates with hard acids (class a metals).^{2,3} However, other factors such as the oxidation state of the metal, the nature of other ligands in the complex, and steric effects also influence the mode of coordination.⁴

In order to expand the knowledge in this area, we have initiated a systematic spectroscopic, thermodynamic, and kinetic study of inorganic linkage isomerism of this ambidentate ligand. This paper is concerned with the coordination of thiocyanate in some tetraamine and diimine-diamine complexes of copper(II). Copper(II) is on the borderline between hard and soft.⁵ The nature of the other ligands attached to it has a very great effect on the coordination behavior of the thiocyanate group. Ligand abbreviations used in this paper: 2,2,2-tet, N,N' -bis(2-aminoethyl)-1,2-ethanediamine; 2,3,2-tet, N,N' -bis(2-aminoethyl)-1,3-propanediamine; 3,3,3-tet, N,N' -bis(3-aminopropyl)-1,3-propanediamine; 3,2,3-tet, N,N' -bis(3-aminopropyl)-1,2-ethanediamine; tet a, *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetra-

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