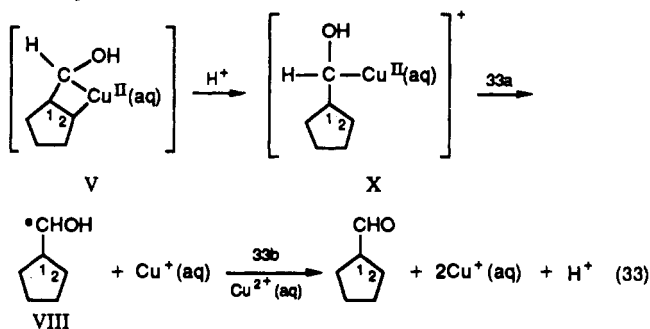


bonds.^{10,17} Thus, reaction 32 does not lead to the formation of the final products observed. Alternatively intermediate V might decompose via reaction 33. Intermediate X formed in the latter



reaction is identical with intermediate VII formed in reaction 31. The decomposition of this intermediate is expected to yield the observed final products as discussed above. The only difference

between the final products of reaction 33 and reaction 31 is that according to reaction 33 one of the hydrogen atoms bound to carbon 2 originates from the solvent. As the hydrogen bound to carbon 1 is enolic, it exchanges rapidly with the solvent. Therefore, according to a mechanism involving reaction 33 it is predicted that when the experiments are carried out in D₂O the product will be labeled by two deuterium atoms. This prediction is in full accord with the experimental results (Table III).

Thus, the results are in accord only with a scheme involving reaction 29 followed by reaction 33, and it is suggested that this is the mechanism of the processes observed.

Concluding Remarks

The results obtained in this study indicate that the detailed mechanism of the oxidation of 2-hydroxycyclohexyl free radicals by copper ions in aqueous solutions involves the reactions summed up in Scheme I. These results point out that the mechanism of the catalytic oxidation of cyclohexene by persulfate in the presence of copper ions is totally different from that previously proposed.²

This study also points out the applicability of the pulse-radiolysis technique to the study of the detailed mechanisms of complex catalytic processes of this type.

Acknowledgment. We wish to thank Professors J. H. Espenson and R. Breslow for helpful discussions and D. Carmi, Y. Nahon, Y. Nehemia, and S. Cohen for their technical assistance. This study was supported by the U.S.-Israel Binational Science Foundation (BSF), Jerusalem, Israel, and the Israel Atomic Energy Committee. D.M. expresses his thanks to Mrs. Irene Evens for her continuous interest and support.

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Thermodynamics of Chloro Complexation of Lanthanide(III) Ions in *N,N*-Dimethylformamide

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The chloro complexation of a series of Ln^{III} ions (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) has been studied by calorimetry in *N,N*-dimethylformamide (DMF) containing 0.2 mol dm⁻³ (C₂H₅)₄NClO₄ as a constant ionic medium at 25 °C. The formation of [LnCl]²⁺, [LnCl₂]⁺, [LnCl₃], and [LnCl₄]⁻ complexes is revealed for all the metal systems except that of La^{III}. The [LaCl₄]⁻ complex hardly forms. The large and positive enthalpy and entropy values show the favorable formation of inner-sphere chloro complexes for all the lanthanide(III) systems. The Δ*H*₁^o and Δ*S*₁^o values decrease with the atomic number *Z* for La^{III}, Ce^{III}, Pr^{III}, and Nd^{III}, while the values gradually increase with *Z* for Sm^{III}-Er^{III}. With respect to Tm^{III}, Yb^{III}, and Lu^{III}, the Δ*H*₁^o and Δ*S*₁^o values are particularly large and similar. The variation of Δ*H*₁^o and Δ*S*₁^o values along *Z* suggests that coordination energies and geometries of Ln³⁺ solvates vary significantly with decreasing ionic radii. It is proposed that an equilibrium [Ln(DMF)₈]³⁺ + DMF = [Ln(DMF)₉]³⁺ is established, which shifts to the right in the order La > Ce > Pr > Nd.

Introduction

Much attention has been paid to the complexation of lanthanide(III) ions in aqueous solution, but somewhat less has been devoted to complexation in nonaqueous solution. Lanthanide(III) ions yield outer-sphere halogeno complexes in aqueous solution¹⁻⁵ but inner-sphere chloro complexes in dimethylacetamide (DMA),⁶⁻⁸ methanol,⁹ and propylene carbonate.¹⁰ However, the

thermodynamic parameters thus far obtained in such nonaqueous solvents are not very reliable, and we believe that the thermodynamics of complexation of lanthanide(III) ions has not been established in nonaqueous solvents.

The coordination geometries of hydrated lanthanide(III) ions in solution have been explored by using various techniques such as X-ray and neutron diffraction and EXAFS.¹¹⁻¹⁹ It is widely

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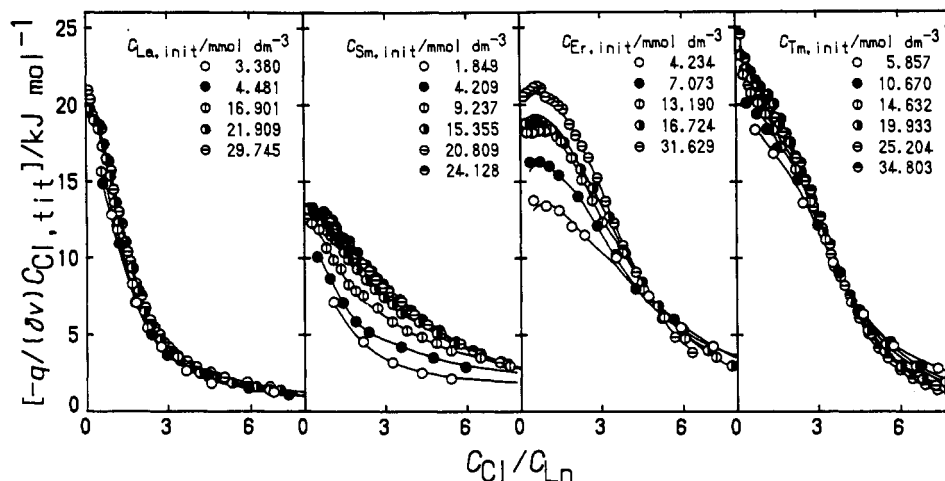


Figure 1. Calorimetric titration curves for the Ln³⁺-Cl⁻ (Ln = La, Sm, Er, Tm) systems obtained in *N,N*-dimethylformamide containing 0.2 mol dm⁻³ (C₂H₅)₄NClO₄ at 25 °C. Concentrations of the Ln(III) ions in initial test solutions, C_{Ln,init}/(mmol dm⁻³), are given. The solid lines are calculated by using constants in Table I.

accepted that there is nine-coordination for the light Ln^{III} ions (La–Nd), eight-coordination for the heavy Ln^{III} ions (Tb–Lu), and an equilibrium between eight- and nine-coordination for the intermediates (Sm–Gd). In water containing large excess HCl, Steele and Wertz showed the presence of eight-coordinate pseudocubic [GdCl₂(H₂O)₆]⁺, [NdCl(H₂O)₇]²⁺, and [NdCl₂(H₂O)₆]⁺ species.^{20,21} Indeed, [LnCl(H₂O)₇]Cl₂ (Ln = La, Pr) and [LnCl₂(H₂O)₆]Cl (Ln = Sm, Gd, Lu) have been isolated as crystal.²² However, such information in nonaqueous solvents is scarce. Complexation and preferential solvation of lanthanide ions have been studied in some aqueous organic solvents by NMR²³ and ultrasonic absorption measurements.^{24,25}

It is known that formation constants of lanthanide(III) complexes are not remarkably different due to shielded 4f orbitals. However, as the ionic radius decreases gradually from La^{III} (116.0 pm, Shannon²⁶) to Lu^{III} (97.7 pm), there may be significant differences in the structure also in the energies of solvation along the series. The same applies also for reaction enthalpies and entropies, and therefore, direct enthalpy measurements may provide more detailed insight into the thermodynamics of complexation of lanthanide(III) ions. Because the thermodynamics of the complexation of Ln^{III} ions is little known in nonaqueous solution, an accumulation of reliable thermodynamic data is valuable. Here we aimed at revealing the thermodynamics of the chloro complexation of Ln^{III} ions in DMF by precise titration calorimetry developed in our laboratory.²⁷

Experimental Section

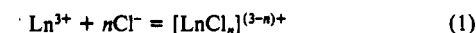
Reagents. The DMF solvates of the lanthanide(III) perchlorates were prepared by dissolving the hydrates in DMF and then by repeated recrystallizations from DMF. The hydrates of the lanthanide(III) perchlorates were prepared from the lanthanide oxides (99.9%) and perchloric acid, except for the hydrate of cerium(III) perchlorate, which was prepared from cerium carbonate and perchloric acid containing H₂O₂ to avoid oxidation to Ce(IV). All the DMF solvates were so hygroscopic that these crystals were treated in a drybox over P₂O₅ and dried in vacuo. The number of DMF molecules *n* in the Ln(ClO₄)₃·*n*DMF complexes ranged from 8.1 to 8.5 according to the EDTA titrations. The solvate crystals involve practically no water molecules according to the elemental analyses. Erbium(III), ytterbium(III), and lutetium(III) perchlorates are too hygroscopic to obtain crystals, and thus we prepared DMF stock solutions of these compounds.

Tetraethylammonium perchlorate was prepared from tetraethylammonium bromide and perchloric acid and recrystallized four times from water. Tetraethylammonium chloride of reagent grade was used without further purification. These salts were dried in vacuo at 100 °C before use. *N,N*-Dimethylformamide was dried for several weeks over 4A molecular sieves, distilled under reduced pressure (at 30 °C, 400 Pa), and stored with molecular sieves in a dark bottle with a P₂O₅ drying tube. The residual water was less than 200 ppm by the Karl Fischer test.

Measurements. Calorimetric measurements were carried out by using a fully automatic calorimetry system in a room thermostated at 25 ± 0.2 °C. All metal(III) perchlorate solutions contained 0.2 mol dm⁻³ (C₂H₅)₄NClO₄ as an ionic medium. Ln(ClO₄)₃ solutions were titrated with a 2.0 mol dm⁻³ (C₂H₅)₄NCl solution. A metal(III) perchlorate solution (40 cm³) was placed in a stainless steel vessel, the inside wall of which was coated with Teflon. The vessel, filled with dry argon gas and isolated from moisture with a P₂O₅ drying tube, was inserted into an aluminum block thermostated at 25.0 ± 0.0001 °C in an air bath. Portions of the (C₂H₅)₄NCl solution were added to this solution from an autoburet (APB-118, Kyoto Electronics). The metal concentration in the initial solutions was varied over the range 3–30 mmol dm⁻³ for all the metal systems examined. Heats of complexation at each titration point were measured with a certainty of ±0.02 J and corrected for heat of dilution of the titrant. The heat of dilution, determined in advance by separate experiments, was very small.

We found an appreciable ionic medium effect when the concentration of (C₂H₅)₄NClO₄ was varied over the range 0.1–0.4 mol dm⁻³, suggesting that lanthanide(III) ions form solvent-separated ion pairs with ClO₄⁻ ions in such solutions. Therefore, the thermodynamic parameters obtained in this work inevitably involve the contribution of ion pairing. However, the ionic medium effect is not large, and besides, the extent of ion pairing may be practically kept constant for all the lanthanide(III) ions in solution containing the same concentration of (C₂H₅)₄NClO₄.

Data Analysis. The formation of only mononuclear complexes is assumed, and the overall formation of the [LnCl_{*n*}]^{(3-*n*)+} complex can be defined as in eqs 1 and 2. A heat *q_i* measured at the *i*th titration point



$$\beta_n = [\text{LnCl}_n]^{(3-n)+} / [\text{Ln}^{3+}][\text{Cl}^-]^n \quad (2)$$

is expressed by the formation constant β_n and overall enthalpy $\Delta H_{\beta_n}^\circ$ as in eq 3, where *V_i* denotes the volume of the test solution. The concen-

$$q_i = -(V_i \sum \beta_n (\Delta H_{\beta_n}^\circ) [\text{Ln}^{3+}]_i [\text{Cl}^-]_i^n - V_{i-1} \sum \beta_n (\Delta H_{\beta_n}^\circ) [\text{Ln}^{3+}]_{i-1} [\text{Cl}^-]_{i-1}^n) \quad (3)$$

trations of free Ln³⁺ and Cl⁻ ions are related to their total concentrations, C_{Ln,*i*} and C_{Cl,*i*}, respectively, according to the mass-balance equations (4) and (5). Formation constants and enthalpies were obtained simultaneously by minimizing $U = \sum (q_{i,\text{obsd}} - q_{i,\text{calcd}})^2$.

$$C_{\text{Ln},i} = [\text{Ln}^{3+}]_i + \sum \beta_n [\text{Ln}^{3+}]_i [\text{Cl}^-]_i^n \quad (4)$$

$$C_{\text{Cl},i} = [\text{Cl}^-]_i + \sum n \beta_n [\text{Ln}^{3+}]_i [\text{Cl}^-]_i^n \quad (5)$$

Results

Typical titration curves are shown in Figure 1. The heat of reaction *q_i* measured at each titration point is normalized as

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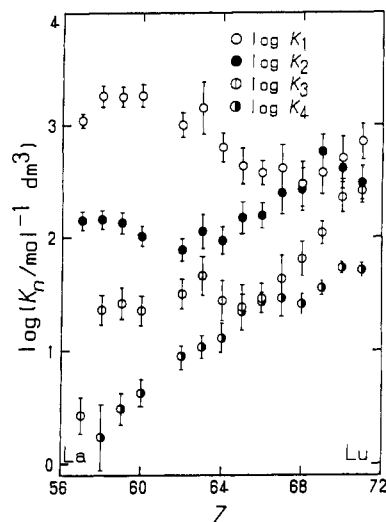


Figure 2. Variation of $\log(K_n/(\text{mol}^{-1} \text{dm}^3))$ along Z in N,N -dimethylformamide containing $0.2 \text{ mol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{NClO}_4$ at 25°C .

$-q_i/(\delta v_i)C_{\text{Cl,tit}}$, where δv_i and $C_{\text{Cl,tit}}$ stand for the volume of the added titrant and the concentration of the chloride ion in the titrant, respectively, and the term is plotted against $C_{\text{Cl,tit}}/C_{\text{Ln},i}$ in solution (i is omitted in the figure). The titration curves thus plotted showed different profiles depending on the metal system. For all the metal systems examined, reaction heats are endothermic throughout titration. It was found that the extent of endothermicity decreased in the order $\text{La}^{\text{III}} > \text{Ce}^{\text{III}} > \text{Pr}^{\text{III}} > \text{Nd}^{\text{III}}$, i.e. the order of decreasing ionic radii. On the contrary, with respect to the intermediates $\text{Sm}^{\text{III}}\text{--}\text{Er}^{\text{III}}$, the extent of endothermicity is gradually enhanced with the atomic number Z . Also, reaction heats depended strongly on the metal concentration. The titration curves of Tm^{III} , Yb^{III} , and Lu^{III} are very similar, but interestingly, the profile is markedly different from that of Er^{III} , as seen in Figure 1.

In each metal system, the data were analyzed by assuming the formation of various sets of mononuclear complexes, as has been done previously in the case of other metal-halide systems,^{28,29} and the best set was revealed by a nonlinear least-squares calculation. In all the metal systems except that of La^{III} , set (1, 2, 3, 4), assuming the formation of $[\text{LnCl}_2]^{2+}$, $[\text{LnCl}_2]^+$, $[\text{LnCl}_3]$, and $[\text{LnCl}_4]^-$, is proposed. For La^{III} , the formation of $[\text{LaCl}_4]^-$ is almost negligible, and set (1, 2, 3) is plausible as a final choice. The formation of $[\text{LnCl}_2]^{2+}$ is rejected in all the metal systems examined. The formation constants and reaction enthalpies and entropies are summarized in Table I. As seen in Figure 1, the solid lines, calculated by using the constants in Table I, reproduce well the experimental points.

Formation Constants. In Figure 2, the stepwise formation constants are compared. The $\log K_4$ value gradually increases with Z from 0.24 for Ce^{III} to ca. 1.7 for Yb^{III} and Lu^{III} . It is also obvious that the K_n values vary in the order $K_1 > K_2 > K_3 > K_4$ for light lanthanides, but $K_1 \approx K_2 \approx K_3$ for heavy lanthanides. The species distributions calculated by using the formation constants show that the formation of $[\text{LaCl}_2]^{2+}$ and $[\text{LaCl}_2]^+$ occurs extensively but the formation of $[\text{LaCl}_3]$ does not under the experimental conditions examined. For Ce^{III} , Pr^{III} , and Nd^{III} , the $[\text{LnCl}_3]$ complex extensively forms as do $[\text{LnCl}_2]^{2+}$ and $[\text{LnCl}_2]^+$, but the formation of $[\text{LnCl}_4]^-$ is still weak. With intermediates $\text{Sm}^{\text{III}}\text{--}\text{Er}^{\text{III}}$, the formation of $[\text{LnCl}_2]^{2+}$ is gradually suppressed, while that of $[\text{LnCl}_4]^-$ is gradually enhanced as Z increases. With heavy lanthanides Tm^{III} , Yb^{III} , and Lu^{III} , the formation of $[\text{LnCl}_4]^-$ occurs extensively in all the metal systems.

Reaction Enthalpies and Entropies. In Figures 3 and 4, respectively, the ΔH_n° and $T\Delta S_n^\circ$ ($n = 1, 2$) values for the stepwise reactions $\text{Ln}^{3+} + \text{Cl}^- \rightarrow [\text{LnCl}]^{2+}$ and $[\text{LnCl}]^{2+} + \text{Cl}^- \rightarrow [\text{LnCl}_2]^+$

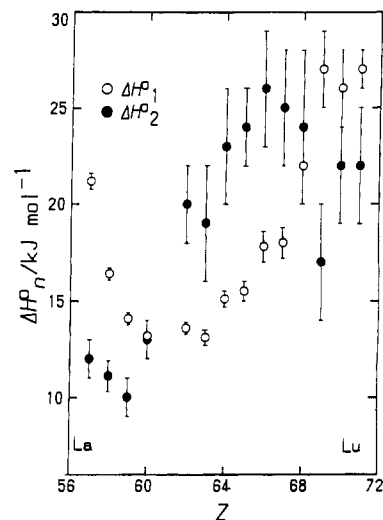


Figure 3. Variation of ΔH_n° ($n = 1, 2$) along Z in N,N -dimethylformamide containing $0.2 \text{ mol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{NClO}_4$ at 25°C . The limit of error bar refers to 3σ .

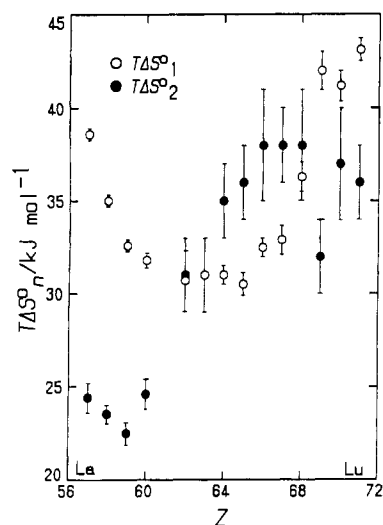


Figure 4. Variation of $T\Delta S_n^\circ$ ($n = 1, 2$) along Z in N,N -dimethylformamide containing $0.2 \text{ mol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{NClO}_4$ at 25°C . The limit of error bar refers to 3σ .

are compared. The ΔH_1° values, all large and positive (endothermic), evidently show that all the Ln^{3+} ions are strongly solvated in DMF and the rupture of metal-DMF bonds takes place upon complexation. Evidence of liberation of solvent molecules is also provided by large and positive $T\Delta S_1^\circ$ values.

The ΔH_1° values decrease remarkably in the order $\text{La}^{\text{III}} > \text{Ce}^{\text{III}} > \text{Pr}^{\text{III}} > \text{Nd}^{\text{III}}$ and then gradually increase in the order $\text{Sm}^{\text{III}} \approx \text{Eu}^{\text{III}} < \text{Gd}^{\text{III}} < \text{Tb}^{\text{III}} < \text{Dy}^{\text{III}} < \text{Ho}^{\text{III}} < \text{Er}^{\text{III}}$. The large and similar values are observed for Tm^{III} , Yb^{III} , and Lu^{III} . The variation of $T\Delta S_1^\circ$ along the Ln^{III} series is similar to that of ΔH_1° ; i.e., $T\Delta S_1^\circ$ compensates ΔH_1° . However, this compensation is not perfect. Indeed, in Figure 5 a linear $\Delta H_1^\circ\text{--}T\Delta S_1^\circ$ relationship is observed for light lanthanides $\text{La}^{\text{III}}\text{--}\text{Nd}^{\text{III}}$, while a distinct relationship applies for intermediates $\text{Sm}^{\text{III}}\text{--}\text{Ho}^{\text{III}}$. Er^{III} is located at the medium position between Ho^{III} and Tm^{III} , and heavy lanthanides Tm^{III} , Yb^{III} , and Lu^{III} occupy a specific region in the figure.

Despite large uncertainties, it is obvious that the variation of ΔH_2° shows a significantly different feature from that of ΔH_1° and the enthalpy crossover occurs; i.e., $\Delta H_1^\circ > \Delta H_2^\circ$ for $\text{La}^{\text{III}}\text{--}\text{Pr}^{\text{III}}$, $\Delta H_1^\circ < \Delta H_2^\circ$ for $\text{Sm}^{\text{III}}\text{--}\text{Ho}^{\text{III}}$, and again $\Delta H_1^\circ > \Delta H_2^\circ$ for $\text{Tm}^{\text{III}}\text{--}\text{Lu}^{\text{III}}$. A similar entropy crossover takes place; i.e., $\Delta S_1^\circ > \Delta S_2^\circ$ for $\text{La}^{\text{III}}\text{--}\text{Nd}^{\text{III}}$, $\Delta S_1^\circ < \Delta S_2^\circ$ for $\text{Gd}^{\text{III}}\text{--}\text{Er}^{\text{III}}$, and again $\Delta S_1^\circ > \Delta S_2^\circ$ for $\text{Tm}^{\text{III}}\text{--}\text{Lu}^{\text{III}}$. This suggests that the number of liberated solvent molecules upon complexation of $[\text{LnCl}_2]^+$ varies significantly depending on the metal system. The

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Table I. Stepwise Formation Constants $\log(K_n/(\text{mol}^{-1} \text{dm}^3))$ and Reaction Enthalpies $\Delta H_n^\circ/(\text{kJ mol}^{-1})$ and Entropies $\Delta S_n^\circ/(\text{J K}^{-1} \text{mol}^{-1})$ for the Reaction $[\text{LnCl}_{n-1}]^{(4-n)+} + \text{Cl}^- \rightleftharpoons [\text{LnCl}_n]^{(3-n)+}$ and Overall Thermodynamic Parameters for the Formation of $[\text{LnCl}_4]^-$, $\log(\beta_4/(\text{mol dm}^{-3}))$, $\Delta H_{\beta_4}^\circ/(\text{kJ mol}^{-1})$, and $\Delta S_{\beta_4}^\circ/(\text{J K}^{-1} \text{mol}^{-1})$, in *N,N*-Dimethylformamide at 25 °C^a

	La ^{III}	Ce ^{III}	Pr ^{III}	Nd ^{III}	Sm ^{III}		La ^{III}	Ce ^{III}	Pr ^{III}	Nd ^{III}	Sm ^{III}
$\log K_1$	3.04 (0.06)	3.25 (0.09)	3.25 (0.09)	3.26 (0.1)	3.00 (0.11)	ΔH_4°		120 (73)	85 (22)	63 (17)	51 (10)
$\log K_2$	2.15 (0.08)	2.16 (0.08)	2.13 (0.09)	2.01 (0.09)	1.89 (0.1)	ΔS_1°	129 (1)	118 (1)	109 (1)	107 (1)	103 (1)
$\log K_3$	0.43 (0.16)	1.36 (0.13)	1.42 (0.14)	1.35 (0.13)	1.50 (0.13)	ΔS_2°	82 (3)	79 (2)	75 (2)	83 (2)	102 (6)
$\log K_4$		0.24 (0.29)	0.49 (0.14)	0.63 (0.12)	0.95 (0.09)	ΔS_3°	249 (62)	79 (11)	87 (16)	94 (19)	79 (21)
K_1/K_2	7.8	12.6	13.2	17.8	12.9	ΔS_4°			292 (72)	224 (56)	188 (34)
K_2/K_3		6.3	5.1	4.6	2.5	$\log \beta_4$		7.0 (0.3)	7.3 (0.3)	7.2 (0.2)	7.3 (0.2)
K_3/K_4			8.5	5.2	3.6	$\Delta H_{\beta_4}^\circ$					99 (6)
ΔH_1°	21.2 (0.4)	16.4 (0.2)	14.1 (0.3)	13.2 (0.2)	13.6 (0.3)	$\Delta S_{\beta_4}^\circ$					472 (22)
ΔH_2°	12.1 (1.1)	11.1 (0.7)	10.3 (1.1)	13.2 (1.2)	19.8 (2.5)	R^b	0.0178	0.0165	0.0145	0.0135	0.0162
ΔH_3°	72 (1.9)	16 (4)	18 (5)	20 (6)	15 (7)	N^c	95	174	136	143	158
	Eu ^{III}	Gd ^{III}	Tb ^{III}	Dy ^{III}	Ho ^{III}		Eu ^{III}	Gd ^{III}	Tb ^{III}	Dy ^{III}	Ho ^{III}
$\log K_1$	3.15 (0.23)	2.80 (0.13)	2.63 (0.16)	2.57 (0.11)	2.61 (0.21)	ΔH_4°	55 (11)	46 (15)	31 (15)	24 (10)	32 (11)
$\log K_2$	2.05 (0.15)	1.97 (0.12)	2.17 (0.14)	2.19 (0.11)	2.39 (0.19)	ΔS_1°	104 (3)	104 (1)	102 (2)	109 (1)	110 (2)
$\log K_3$	1.66 (0.17)	1.44 (0.18)	1.38 (0.20)	1.46 (0.13)	1.63 (0.21)	ΔS_2°	104 (6)	116 (7)	121 (6)	128 (8)	128 (6)
$\log K_4$	1.03 (0.10)	1.11 (0.13)	1.34 (0.15)	1.43 (0.08)	1.46 (0.16)	ΔS_3°	74 (19)	95 (30)	111 (34)	95 (30)	98 (26)
K_1/K_2	12.6	6.8	2.9	2.4	1.7	ΔS_4°	206 (35)	177 (50)	131 (49)	106 (32)	136 (35)
K_2/K_3	2.5	3.4	6.2	5.4	5.8	$\log \beta_4$	7.9 (0.3)	7.3 (0.2)	7.5 (0.2)	7.7 (0.1)	8.1 (0.2)
K_3/K_4	4.3	2.1	1.1	1.1	1.5	$\Delta H_{\beta_4}^\circ$	101 (8)	105 (9)	96 (6)	87 (2)	95 (5)
ΔH_1°	13.1 (0.4)	15.1 (0.4)	15.5 (0.5)	17.8 (0.8)	18.0 (0.8)	$\Delta S_{\beta_4}^\circ$	488 (27)	492 (30)	465 (22)	439 (9)	473 (18)
ΔH_2°	19.5 (2.6)	23.4 (3.0)	23.7 (2.4)	25.8 (3.1)	24.6 (2.9)	R^b	0.0188	0.0183	0.0159	0.0176	0.0189
ΔH_3°	13 (6)	20 (10)	25 (11)	20 (10)	20 (9)	N^c	109	154	115	113	119
	Er ^{III}	Tm ^{III}	Yb ^{III}	Lu ^{III}			Er ^{III}	Tm ^{III}	Yb ^{III}	Lu ^{III}	
$\log K_1$	2.47 (0.2)	2.57 (0.2)	2.70 (0.2)	2.82 (0.2)		ΔH_4°	35 (7)	20 (3)	31 (2)		23 (2)
$\log K_2$	2.42 (0.2)	2.76 (0.15)	2.61 (0.18)	2.48 (0.15)		ΔS_1°	122 (2)	141 (4)	138 (2)		144 (2)
$\log K_3$	1.81 (0.10)	2.04 (0.10)	2.35 (0.13)	2.41 (0.11)		ΔS_2°	127 (1)	109 (7)	125 (9)		121 (7)
$\log K_4$	1.41 (0.09)	1.55 (0.06)	1.73 (0.05)	1.71 (0.06)		ΔS_3°	106 (20)	108 (12)	92 (13)		104 (11)
K_1/K_2	1.1	0.7	1.2	2.3		ΔS_4°	145 (24)	98 (12)	137 (9)		109 (8)
K_2/K_3	4.1	5.3	1.8	1.2		$\log \beta_4$	8.1 (0.2)	8.9 (0.2)	9.4 (0.2)		9.5 (0.2)
K_3/K_4	2.5	3.1	4.2	5.0		$\Delta H_{\beta_4}^\circ$	103 (3)	85 (1)	93 (1)		89 (1)
ΔH_1°	22.2 (1.4)	27.4 (2.0)	25.8 (1.5)	26.8 (1.0)		$\Delta S_{\beta_4}^\circ$	500 (12)	456 (5)	493 (5)		479 (5)
ΔH_2°	24.2 (3.6)	16.6 (2.8)	22.4 (3.4)	21.9 (2.8)		R^b	0.0174	0.0201	0.0209		0.0194
ΔH_3°	21 (6)	21 (4)	14 (4)	17 (4)		N^c	127	159	190		194

^a Values in parentheses refer to three standard deviations. ^b The Hamilton *R* factor. ^c The number of calorimetric data points.

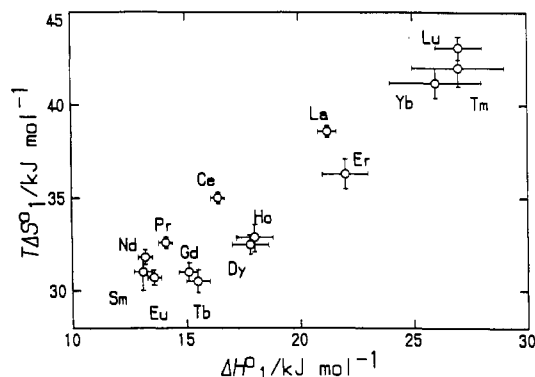


Figure 5. $\Delta H_4^\circ - T\Delta S_1^\circ$ plots for the reaction $\text{Ln}^{3+} + \text{Cl}^- \rightarrow [\text{LnCl}]^{2+}$ in DMF. The limit of error bar refers to 3σ .

stepwise ΔH_n° and ΔS_n° ($n = 3, 4$) values cannot be determined with accuracy due to weak and simultaneous formation of the complexes under the experimental conditions examined. It is observed that the overall $\Delta H_{\beta_4}^\circ$ and $\Delta S_{\beta_4}^\circ$ values for Sm^{III}–Lu^{III} are kept almost constant with the average values of 95.3 kJ mol⁻¹ and 476 J K⁻¹ mol⁻¹, respectively. The $\Delta S_{\beta_4}^\circ$ value is larger than that for the formation of $[\text{M}^{\text{II}}\text{Cl}_4]^{2-}$, which is tetrahedrally four-coordinated,^{30,31} suggesting that solvent molecules are extensively liberated from the primary coordination sphere of lanthanide ions.

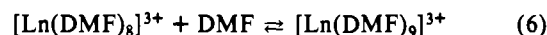
Discussion

In DMF, inner-sphere chloro complexes may predominantly form in all the Ln^{III} systems, as is evident from large and positive

ΔH_1° and ΔS_1° values for $\text{Ln}^{3+} + \text{Cl}^- \rightarrow [\text{LnCl}]^{2+}$, suggesting the liberation of solvating DMF molecules upon complexation. Such large and positive ΔH_1° and ΔS_1° values cannot be expected upon formation of outer-sphere complexes. Indeed, significantly smaller ΔH° and ΔS° values are observed for the Ln³⁺–Br⁻ systems in DMF.³²

Both Ln³⁺–DMF and Ln³⁺–Cl⁻ interactions may be enhanced with decreasing ionic radii of lanthanide ions. If the extent of enhancement of the Ln³⁺–DMF interaction is larger (or smaller), the ΔH_1° value will monotonically increase (or decrease) with *Z*. However, this is not so, and a decrease followed by an increase of ΔH_1° and ΔS_1° with *Z* in fact occurs. We believe that the ligand field stabilization energies (LFSE) do not play a key role in the variation of ΔH_1° and ΔS_1° among Ln^{III} complexes. Such an irregular variation of ΔH_1° and ΔS_1° may be due to varying coordination geometries of lanthanide(III) solvates; i.e., steric interactions in the primary coordination sphere may play a more important role.

Merbach et al.^{33,34} have obtained evidence by a ¹H NMR study that an equilibrium between eight- and nine-coordination as in eq 6 is established for La^{III}, Ce^{III}, Pr^{III}, and Nd^{III} in DMF, and



the equilibrium shifts to the right in the order La > Ce > Pr >

(32) Ishiguro, S.; Takahashi, R. Unpublished data. For example, the ΔH_1° and ΔS_1° values for the formation of $[\text{LaBr}]^{2+}$ are 4.8 kJ mol⁻¹ and 43 J K⁻¹ mol⁻¹, respectively, which are significantly small compared to the value of the chloro complexes. This is unexplainable in terms of the formation of inner-sphere bromo complex because the Ln–Br bond may be weaker than the Ln–Cl bond for hard lanthanide ions. This leads to the conclusion that outer-sphere complexes are mainly formed in the bromide systems.

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Nd. An observed ΔH_1° value, also ΔS_1° , for the formation of the monochloro complex thus changes depending on the equilibrium constant between the eight- and nine-coordination species. As both ΔH° and ΔS° values for eq 6 are negative,³⁵ the chloro complexation of $[\text{Ln}(\text{DMF})_9]^{3+}$ is more endothermic than that of $[\text{Ln}(\text{DMF})_8]^{3+}$. A systematic decrease in the ΔH_1° and ΔS_1° values in the sequence $\text{La} > \text{Ce} > \text{Pr} > \text{Nd}$ thus implies that the equilibrium in eq 6 is shifted to the right to a greater extent in the same order. This conclusion is consistent with that obtained by the ^1H NMR study.^{33,34} Consequently, it is plausible that, in DMF, the La^{3+} ion prefers $[\text{La}(\text{DMF})_9]^{3+}$ to $[\text{La}(\text{DMF})_8]^{3+}$, while the Nd^{3+} ion prefers $[\text{Nd}(\text{DMF})_8]^{3+}$.

Also according to Merbach, the sole eight-coordinated species $[\text{Ln}(\text{DMF})_8]^{3+}$ occurs for $\text{Sm}^{\text{III}}\text{--Lu}^{\text{III}}$. That the ΔS_1° values of $\text{Sm}^{\text{III}}\text{--Ho}^{\text{III}}$ ions are practically the same in the range $103\text{--}110 \text{ J K}^{-1} \text{ mol}^{-1}$ is consistent with the unvarying geometries of these solvate ions. The ΔH_1° value increases gradually with Z , which suggests that the metal–DMF bonds within $[\text{Ln}(\text{DMF})_8]^{3+}$ are enhanced monotonically as ionic radii of Ln^{III} ions decrease.

The ΔH_1° and ΔS_1° values of Tm^{III} , Yb^{III} , and Lu^{III} systems are particularly large compared to those of the Tb^{III} , Dy^{III} , and Ho^{III} systems. Interestingly, the drastic change in the ΔH_1° and ΔS_1° values seems parallel to that for the solvent-exchange

mechanism. Indeed, the solvent-exchange mechanism of $[\text{Ln}(\text{DMF})_8]^{3+}$ in DMF is shown as an interchange mechanism for Tb^{III} , Dy^{III} , and Ho^{III} and as a dissociative one for Tm^{III} and Yb^{III} .³⁴ Thus a mechanistic crossover occurs at Er^{III} . It is also noteworthy that the solvent-exchange rate of Tm^{III} and Yb^{III} increases remarkably compared to that of $\text{Tb}^{\text{III}}\text{--Ho}^{\text{III}}$. This implies that the $[\text{Ln}(\text{DMF})_8]^{3+}$ ($\text{Ln} = \text{Tm}, \text{Yb}, \text{Lu}$) solvates involve $\text{Ln}^{3+}\text{--DMF}$ bonds that are extremely weak and labile. On the other hand, the large and positive ΔH_1° and ΔS_1° values show that the $[\text{Ln}(\text{DMF})_8]^{3+}$ solvates involve also $\text{Ln}^{3+}\text{--DMF}$ bonds of normal strength. These facts thus suggest that there exist two kinds of solvents, one bonded strongly and the other weakly, within $[\text{Ln}(\text{DMF})_8]^{3+}$ ($\text{Ln} = \text{Tm}, \text{Yb}, \text{Lu}$). A largely distorted geometry is thus plausible for $[\text{Ln}(\text{DMF})_8]^{3+}$ ($\text{Ln} = \text{Tm}, \text{Yb}, \text{Lu}$). It is also plausible that a simultaneous rupture of both strong and weak $\text{Ln}^{3+}\text{--DMF}$ bonds accompanies the chloro complexation of Tm^{III} , Yb^{III} , and Lu^{III} ions.

Although the ΔH_2° and ΔS_2° values involve large uncertainties, the values evidently depend on the lanthanide ion. Also, the $\Delta S_{\beta_4}^\circ$ values provide evidence of extensive desolvation of Ln^{3+} ions at higher stages of complexation. These facts suggest that a coordination geometry change occurs upon the chloro complexation of Ln^{III} ions.

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(35) With Nd^{III} , the values of $\Delta H^\circ = -14.9 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -69 \text{ J K}^{-1} \text{ mol}^{-1}$ have been obtained in DMF.³²

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Pressure Effects on the Self-Exchange Rates of Cobalt(III/II) Couples: Evidence for Adiabatic Electron Transfer in the Bis(1,4,7-trithiacyclononane) and Sepulchrate Complexes

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The pressure dependences of the logarithms of the self-exchange rate constants k for the title complexes in aqueous solution at 25°C are linear within experimental uncertainty and are characterized by the following parameters: for low-spin/low-spin $\text{Co}(\text{9JaneS}_3)_2^{3+/2+}$ at ionic strength $I = 0.1 \text{ mol L}^{-1}$ ($\text{CF}_3\text{SO}_3\text{K}$), $k = 9.5 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ at 0.1 MPa, and $\Delta V^\ddagger = -4.8 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$; for low-spin/high-spin $\text{Co}(\text{sep})^{3+/2+}$ at $I = 0.2 \text{ mol L}^{-1}$ (NaCl), $k = 5.0 \text{ L mol}^{-1} \text{ s}^{-1}$ at 0.1 MPa, and $\Delta V^\ddagger = -6.4 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$. The pressure dependence of k is accounted for in both cases by an adaptation of the Marcus–Hush theory if internal reorganization makes the usual small contribution (ca. $+1 \text{ cm}^3 \text{ mol}^{-1}$) to ΔV^\ddagger . The implication is that the title reactions are essentially fully adiabatic, despite the difference in spin type, and that the low-spin/high-spin $\text{Co}(\text{en})_3^{3+/2+}$ exchange, for which the pressure-dependent ΔV^\ddagger is some $13 \text{ cm}^3 \text{ mol}^{-1}$ more negative than predicted on the above basis (Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* 1990, 29, 385), is nonadiabatic.

Introduction

As Endicott and Ramasami¹ have remarked, there is growing evidence that, of the various outer-sphere electron-transfer (ET) reactions of metal complexes that have been studied in aqueous solution, the self-exchange reactions are relatively adiabatic. In the case of redox reactions involving the $\text{Fe}(\text{H}_2\text{O})_6^{3+/2+}$ couple, for example, it appears that the self-exchange reaction is essentially adiabatic even though its “cross-reactions” may not be.^{2–4} However, ET reactions of the numerous cobalt(III/II) couples for which the ground states of the Co^{III} and Co^{II} complexes are low- and high-spin (^1A and ^4T), respectively, are spin-forbidden in the sense that they are three-electron processes. It may therefore

be anticipated either that ET will involve the ground states of both the Co^{III} and the Co^{II} complexes and be nonadiabatic or that ET occurs adiabatically from a low-spin ^2E excited state of Co^{II} in (usually unfavorable) equilibrium with the ^4T ground state. In either case, the result should be slower ET and a much stronger acceleratory effect of pressure P on ET than are predicted from the adiabatic Marcus–Hush theory.^{5–7}

These expectations appear to be realized for the $\text{Co}(\text{en})_3^{3+/2+}$ self-exchange ($\text{en} = 1,2\text{-diaminoethane}$), for which the rate constant k is small ($8 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ at 65°C , 0.1 MPa, and ionic strength $I = 0.5 \text{ mol L}^{-1}$) and the pressure effect much larger than predicted from the Marcus–Hush theory for adiabatic ET between the ground states (limiting zero-pressure volume of activation $\Delta V_0^\ddagger = -20 \text{ cm}^3 \text{ mol}^{-1}$, vs. $-7 \text{ cm}^3 \text{ mol}^{-1}$ predicted).⁶ The

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