CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Observations on the Rare Earths. LXXIV. The Enthalpy and Entropy of Formation of the 1:1 and 1:2 Chelates of Nitrilotriacetic Acid with Tripositive Cations[1a]

BY THERALD MOELLER AND RICARDO FERRÚS[1b]

Received August 1, 1961

Enthalpy changes in the formation of 1:1 and 1:2 nitrilotriacetic acid (H_3NTA) chelates of the tripositive rare earth metal ions have been evaluated by the temperature coefficient method for aqueous solutions of ionic strength 0.10 (KNO_3). Corresponding entropy changes have been calculated from the enthalpy changes and stability constants at 25°. Values of enthalpy and entropy changes for the formation of $Ca(NTA)^-$ and $Cu(NTA)^-$ have been obtained also. The importance of the configurational entropy in accounting for trends in the stabilities of the rare earth metal chelates again is apparent.

In a previous paper,[1a] variations in the enthalpy and entropy of formation of N-hydroxyethylethylenediaminetriacetic acid (H_3HEDTA) chelates of the tripositive rare earth metal ions were examined in the light of possible steric hindrance as the size of the metal ion changes.[2] Contrary to the conclusions drawn previously for the ethylenediaminetetraacetic acid (H_4EDTA) chelates,[2,3] however, these variations are better correlated with a gradual weakening of the bond between the metal ion and a donor carboxyl group as cation radius decreases than with complete rupture of such a bond at a particular place in the series. It has been proposed[1] that the configurational entropies of these complex ions are important factors in correlating their stabilities.

These assumptions can be tested by carrying out comparable studies with chelating agents of carefully chosen structures. Such an agent is nitrilotriacetic acid, a quadridentate donor that gives both 1:1[4] and 1:2[5] complexes of moderate stability with these cations. The present study is concerned with a detailed evaluation of the stabilities of these chelates over a sufficiently broad temperature range to permit calculation of the thermodynamic functions essential to these considerations.

The equilibria

$$Ln^{3+} + X^{3-} \rightleftarrows LnX$$
$$LnX + X^{3-} \rightleftarrows LnX_2^{3-}$$

where Ln^{3+} represents yttrium or a rare earth metal ion and X^{3-} the nitrilotriacetate ion, are described, respectively, by the formation constants

$$K_{Ln/LnX} = [LnX]/[Ln^{3+}][X^{3-}] \qquad (1)$$

and

$$K_{LnX/LnX_2} = [LnX_2^{3-}]/[LnX][X^{3-}] \qquad (2)$$

These constants were determined by a variation of the potentiometric technique already described.[1] For this procedure,[6] the necessary equilibria that were investigated are

$$CuX^- + H_3tren^{3+} + Ln^{3+} \rightleftarrows Cutren^{2+} + LnX + 3H^+ \qquad (I)$$
$$CuX^- + H_3tren^{3+} + Ca^{2+} \rightleftarrows Cutren^{2+} + CaX^- + 3H^+ \qquad (III)$$
$$CuX^- + H_3tren^{3+} + LnX \rightleftarrows Cutren^{2+} + LnX_2^{3-} + 3H^+ \qquad (IV)$$
$$Ca^{2+} + H_3X \rightleftarrows CaX^- + 3H^+ \qquad (V)$$

The formation constant $K_{Ca/CaX}$ for the ion CaX^- was calculated directly from data for Equilibrium V. From this and the measured constants for equilibria I, III, and IV, $K_{Ln/LnX}$ and $K_{LnX/LnX}$ then were calculated as

$$K_{Ln/LnX} = K_I K_{Ca/CaX}/K_{III} \qquad (3)$$
$$K_{LnX/LnX_2} = K_{IV} K_{Ca/CaX}/K_{III} \qquad (4)$$

---

(1) (a) For the preceding communication in this series, see T. Moeller and R. Ferrús, *J. Inorg. & Nuclear Chem.*, in press (1961). (b) Facultad de Ciencias, Universidad de Valencia, Spain.

(2) E. J. Wheelwright, F. H. Spedding, and G. Schwarzenbach, *J. Am. Chem. Soc.*, **75**, 4196 (1953).

(3) R. H. Betts and O. F. Dahlinger, *Can. J. Chem.*, **37**, 91 (1959).

(4) (a) G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1492 (1951); (b) G. Schwarzenbach and R. Gut, *ibid.*, **39**, 1589 (1956).

(5) G. Anderegg, *ibid.*, **43**, 825 (1960).

(6) The notation employed here is the same as that used for comparable situations in the HEDTA study. Continuing consultation of Reference 1 will be helpful in following this treatment.

Experimental

Solutions.—Nitrilotriacetic acid (Geigy Chel 300) was purified by double recrystallization from distilled water, washed with absolute ethanol, and dried *in vacuo*. It was pure within the limits of acidimetric titration. A 0.00813 M solution of the acid was prepared by direct weighing. A 0.01006 M solution of its dipotassium salt was obtained by preparing an acid solution, adding potassium hydroxide to the potentiometric end-point,[7] and diluting appropriately. A *ca.* 0.01 M K[Cu(NTA)] solution was prepared by dissolving a weighed quantity of nitrilotriacetic acid in an equivalent amount of 0.1 M copper(II) nitrate solution, adding 0.1 M potassium hydroxide solution to pH 6.5, and diluting with water. The preparation of *ca.* 0.01 M calcium nitrate, 0.01 M tren·3HNO$_3$, 1.00 M potassium nitrate, and 0.005 M rare earth metal nitrate solutions has been described previously.[1]

Experimental Procedure.—Only those aspects of the procedure that differ significantly from the N-hydroxyethylethylenediaminetriacetic acid study[1] need be emphasized.

(1) K_{I}.–Solutions were prepared by mixing 10 ml. of 0.01007 M tren·3HNO$_3$, 10 ml. of 0.01008 M K[Cu(NTA)], 9 ml. of 1.00 M KNO$_3$, a volume of 0.005 M Ln(NO$_3$)$_3$ equivalent to 10 ml. of 0.01007 M solution, and 50 ml. of water. Equilibrium was established instantaneously after addition of a given volume of 0.1 M potassium hydroxide solution. The stabilities of the complexes Cu(NTA)$^-$ and Ln(NTA) are such that in solutions where equilibrium I is established a certain quantity of copper(II) ion remains free. The accuracy of measuring K_{I} is decreased by the presence of large concentrations of copper(II) ion.[4a,8] This concentration increases with increase in the ratio $K_{\text{Ln/LnX}}/K_{\text{Cu/CuX}}$. From La to Dy, the stability of the 1:1 NTA chelate is small enough to permit evaluation of log K_{I} values that differ from the average by no more than +0.02, when pH readings are made in the buffer region between a = 1 and a = 2. This is not possible for the heavier ions in the series. However, with these the difficulty was overcome by working above a = 2 since the concentration of copper(II) ion decreases rapidly with increasing pH. In every case, five pH readings were taken at intervals of 0.2a. The highest a value was reached with lutetium (buffer region, a = 1.75–2.55). The pH$_0$ ranged from 4.32 for the first reading at 40° for the lutetium solution to 5.43 for the last reading at 15° for the lanthanum solution.

(2) K_{III}.—Solutions were prepared from 10 ml. of 0.01011 M tren·3HNO$_3$, 10 ml. of 0.01008 M K[Cu(NTA)], 8 ml. of 1.00 M KNO$_3$, 50 ml. of 0.01076 M Ca(NO$_3$)$_2$, and 25 ml. of water. Five pH readings were taken between a = 0.96 and 1.76. Extreme pH$_0$ values were 5.57 and 6.28.

(3) $K_{\text{H/HX}}$.—The formation constant of the first proton complex of NTA was determined using solutions prepared from 10 ml. of 1.00 M KNO$_3$, 25 ml. of 0.00813 M H$_3$NTA, and 65 ml. of water. Five pH readings were made at each temperature between a = 2.38 and 2.77. Extreme pH$_0$ values were 9.28 and 10.24.

(4) $K_{\text{Ca/CaX}}$.—Solutions were prepared from 8 ml. of 1.00 M KNO$_3$, 25 ml. of 0.00813 M H$_3$NTA, 50 ml. of 0.01076 M Ca(NO$_3$)$_2$, and 10 ml. of water. Five pH readings were taken in the buffer region a = 2.28–2.68, with pH$_0$ values in the range 4.97–6.00.

(5) K_{IV}.—Solutions were prepared by mixing 10 ml. of 0.01007 M tren·3NHO$_3$, 10 ml. of 0.01008 M K[Cu(NTA)], 9 ml. of 1.00 M KNO$_3$, 10 ml. of 0.0100 M K$_2$HNTA, a volume of 0.005 M Ln(NO$_3$)$_3$ equivalent to 10 ml. of 0.01007 M solution, and such a volume of water that at the midpoint of the titration with 0.1 M KOH the total volume was 100.0 ml. Equilibrium was established instantaneously after the addition of each increment of alkali. Five pH readings at 0.2a intervals were taken in the range a = 2–3. Values of pH$_0$ ranged from 4.97 for the first reading at 40° for the lutetium solution to 6.44 for the last reading at 15° for the lanthanum solution.

Calculations

The constants K_{I}, K_{III}, $K_{\text{H/HX}}$, and $K_{\text{Ca/CaX}}$ can be calculated as was done for the HEDTA systems,[1b] using the same set of general material balance equations. Although these equations are not repeated here, they are referred to frequently in discussing the evaluation of constants involving the rare earth metal–NTA chelates, using the same numbering notation given previously.[1b]

Evaluation of K_{I}.—In eq. 8a, ϵ varied from 1.00 to 1.09. The coefficient of [M′] in eq. 8b was 1.00 and in eq. 8d zero. The terms γ and δ were always 1.00 and 3.00, respectively. In eq. 8c, the term $\alpha/K_{\text{M/MX}}$ ranged from 0.00 to 0.005, and in eq. 8e, both [OH] and the last term were negligible.

Evaluation of K_{III}.—For NTA (X), $K_{\text{Ca/CaX}}$ is not large enough to give a sufficiently flat buffer region when a solution containing equimolar quantities of H$_3$tren^{3+}, CuX$^-$, and Ca^{2+} is titrated with 0.1 M potassium hydroxide. Therefore, an excess of calcium ion was essential to give buffer systems for which equilibrium constants could be obtained with accuracy. As a consequence, in the material balance for Ca^{2+} (eq. 8b), the total concentration c was larger than 10^{-3} M. Inasmuch as ϵ' is infinitely large,[1] the coefficient of [M′] was 1.00 in eq. 8b and zero in eq. 8d. In eq. 8c, the coefficient of [MX] ranged from 1.18 for the first pH reading at 15° to 1.39 for the last reading at 40°. In eq. 8e, γ varied from 1.00 to 1.01, δ from 3.00 to 3.02, and the last term from 1.10 × 10^{-4} M (last reading at 15°) to 1.50 × 10^{-4} M (first reading at 40°).

Evaluation of K_{HX}.—This was done by use of eq. 12c.

Evaluation of $K_{\text{Ca/CaX}}$.—Only eq. 8b, 8c, and 8e apply. As was outlined above for K_{III}, addition of excess calcium ion was necessary. The coefficient of [M′] in eq. 8b was always 1.00. Inasmuch as

---

[7] G. Schwarzenbach, E. Kampitsch, and R. Steiner, *Helv. Chim. Acta*, **28**, 828 (1945).

[8] G. Schwarzenbach and E. Frietag, *ibid.*, **34**, 1503 (1951).

no copper(II) ion was present in solution, eq. 8c reduced to

$$[\mathrm{X}]_t = c = [\mathrm{M'X}] + \alpha[\mathrm{X}] \qquad (8c')$$

where α is given by eq. 9a. With due regard for the $p\mathrm{H}_c$ range in which $K_{\mathrm{Ca/CaX}}$ is measured and the pK values for the dissociation of the acid $\mathrm{H_3NTA}$,[9] eq. 9a may be reduced to

$$\alpha = [\mathrm{H}]K_{\mathrm{HX}} \qquad (9a')$$

This is then valid for all temperatures since $K_{\mathrm{H_2X}}$ and $K_{\mathrm{H_3X}}$ are small, and their change with changing temperature should have an insignificant effect. Finally, eq. 8e reduces to

$$[\mathrm{H}]_t = (3 - a)c = [\mathrm{H}] + [\mathrm{H}][\mathrm{X}]\,K_{\mathrm{HX}} \qquad (8e')$$

because all terms on the right side of eq. 9b are negligible compared with $[\mathrm{H}]K_{\mathrm{HX}}$.

Evaluation of K_{IV}.—Here a new type species $\mathrm{Ln(NTA)_2^{3-}}$, not previously considered in material balance equations,[1] is involved. These equations may be extended to cover evaluation of K_{IV} by adding $[\mathrm{M'X_2}]$ to eq. 8b, adding $2[\mathrm{M'X_2}]$ to eq. 8c, realizing that $[\mathrm{X}]_t$ is now 2×10^{-3} M, and writing $(4-a)c$ in eq. 8e instead of $(3-a)c$. The last of these results from the addition of $\mathrm{K_2H(NTA)}$, giving a total of four hydrogen ions. In the buffer region used, ϵ was always 1.00. The coefficient of [M′] was 1.00 in eq. 8b and zero in eq. 8d. The concentration of free rare earth metal ion, [M′], was always very small in eq. 8b but not always negligible. Where [M′] reached its maximum value (first reading with terbium at 15°), log K_{IV} was found to be −13.23 including [M′] and −13.25 neglecting it. The coefficient of [MX] in eq. 8c ranged from 1.01 for the first pH reading for terbium at 15° to 1.76 for the last reading for lanthanum at 40°. The coefficients γ and δ were always 1.00 and 3.00, respectively. The last term in eq. 8e ranged from 0.06×10^{-4} M for the first readings for terbium, dysprosium, holmium, and lutetium at 15° to 2.19×10^{-4} M for the last reading for lanthanum at 40°.

Evaluation of Formation Constants and Thermodynamic Functions.—The formation constant and the heat of formation of the copper(II)-NTA chelate were calculated by the procedure previously outlined.[1] Formation constants for the 1:1 and 1:2 rare earth metal–NTA chelates were calculated from eq. 3 and 4, above. Then, using

$$\Delta H_1 = \Delta H_{\mathrm{I}} + \Delta H_{\mathrm{Ca/CaX}} - \Delta H_{\mathrm{III}} \qquad (5)$$

$$\Delta H_2 = \Delta H_{\mathrm{IV}} + \Delta H_{\mathrm{Ca/CaX}} - \Delta H_{\mathrm{III}} \qquad (6)$$

enthalpies of formation of these chelates were obtained.[10] All terms on the right-hand sides of eq. 5 and 6 were obtained by least squares analysis, with uncertainties calculated to 95% confidence intervals. Entropies of formation at 25° were evaluated from formation constants and enthalpies at this temperature. Finally, partial molal entropies were related to experimental ΔS values as[3]

$$\bar{S}^\circ_{\mathrm{LnX}} = \Delta S^\circ_1 + \bar{S}^\circ_{\mathrm{Ln}} + \bar{S}^\circ_{\mathrm{X}} \qquad (7)$$

$$\bar{S}^\circ_{\mathrm{LnX_2}} = \Delta S^\circ_1 + \Delta S^\circ_2 + \bar{S}^\circ_{\mathrm{Ln}} + 2\bar{S}^\circ_{\mathrm{X}} \qquad (8)$$

using $\bar{S}^\circ_{\mathrm{Ln}}$ values calculated from Powell and Latimer's semiempirical equation.[11]

Results and Discussion

The formation constants for $\mathrm{H(NTA)^{2-}}$ and $\mathrm{CaNTA^-}$, the equilibrium constants for reactions I, III, and IV, and the corresponding enthalpy changes are summarized in Table I. Some comparisons with available published data for certain of these systems are in order. Schwarzenbach, Ackermann, and Ruckstuhl[9] reported log $K_{\mathrm{HX}} = 9.73$ and log $K_{\mathrm{Ca/CaX}} = 6.41$ at 20° and $\mu = 0.11$ (KCl). Agreement here is excellent for log K_{HX}. Use of the same log K_{HX} to calculate log $K_{\mathrm{Ca/CaX}}$ would have reduced the difference to 0.08, again demonstrating excellent agreement. The only value of log K_{I} available is −11.98 ± 0.03 for lanthanum at 20° in 0.1 M KCl.[4a] Using Anderegg's values[5] for $K_{\mathrm{LnX/LnX_2}}$, log $K_{\mathrm{Cu/Cutren}} = 19.08$,[5] log $\bar{K}_{\mathrm{H_3tren}} = 28.44$,[12] log $K_{\mathrm{Cu/CuX}} = 12.96$,[4a] and the relationship

$$K_{\mathrm{LnX/LnX_2}} = K_{\mathrm{Cu/Cutren}}K_{\mathrm{IV}}/\bar{K}_{\mathrm{H_3tren}}K_{\mathrm{Cu/CuX}} \qquad (9)$$

one can calculate for typical log K_{IV} values at 20°: Nd, −13.87; Sm, −13.22; Gd, −12.95; Dy, −12.92; Yb, −13.10; Y, −13.30. These agree well with the measured values summarized in Table I.

Formation constants calculated from the data in Table I are summarized in Table II. With due regard for differences between the experimental methods used, agreement both between log $K_{\mathrm{Ln/LnX}}$ at 20° and comparable values for certain of the ions obtained by polarographic evaluation of auxiliary metal ion concentrations in exchange equilibria[4b] and between log $K_{\mathrm{LnX/LnX_2}}$ at 20°

---

[9] G. Schwarzenbach, H. Ackermann, and P. Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).

[10] Here and in the discussion that follows, subscript 1 refers to the 1:1 chelate and subscript 2 to the 1:2 chelate.

[11] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1136 (1951).

[12] H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 1543 (1949).

TABLE I

EQUILIBRIUM CONSTANTS AND ENTHALPY CHANGES

$\mu = 0.10\ (KNO_3)$

Equilibrium	log K						ΔH kcal./mole
	15°	20°	25°	30°	35°	40°	
HX	9.86	9.80	9.75	9.70	9.62	9.58	−4.68 ± 0.22
CaX	6.59	6.56	6.57	6.57	6.53	6.53	−0.81 ± 0.22
III	−16.16	−15.92	−15.68	−15.49	−15.29	−15.09	17.56 ± 0.26
I—Y	−11.29	−11.02	−10.77	−10.52	−10.24	−10.02	21.06 ± 0.27
La	−12.37	−12.11	−11.89	−11.63	−11.37	−11.13	20.42 ± 0.34
Ce	−11.90	−11.65	−11.42	−11.19	−10.94	−10.71	19.62 ± 0.28
Pr	−11.64	−11.41	−11.18	−10.94	−10.72	−10.51	18.82 ± 0.20
Nd	−11.47	−11.23	−10.99	−10.76	−10.53	−10.33	19.05 ± 0.18
Sm	−11.22	−10.97	−10.72	−10.51	−10.28	−10.08	18.77 ± 0.19
Eu	−11.23	−10.99	−10.73	−10.52	−10.27	−10.07	19.30 ± 0.26
Gd	−11.18	−10.94	−10.71	−10.47	−10.23	−10.02	19.39 ± 0.23
Tb	−11.15	−10.90	−10.66	−10.41	−10.15	− 9.55	20.08 ± 0.28
Dy	−11.02	−10.77	−10.51	−10.27	− 9.99	− 9.78	20.62 ± 0.27
Ho	−10.88	−10.63	−10.35	−10.10	− 9.85	− 9.62	21.00 ± 0.23
Er	−10.72	−10.48	−10.22	− 9.97	− 9.70	− 9.47	20.88 ± 0.27
Tm	−10.54	−10.28	−10.03	− 9.78	− 9.53	− 9.32	20.27 ± 0.26
Yb	−10.36	−10.11	− 9.85	− 9.61	− 9.35	− 9.14	20.46 ± 0.31
Lu	−10.27	−10.01	− 9.76	− 9.51	− 9.26	− 9.04	20.35 ± 0.26
IV—Y	−13.66	−13.45	−13.30	−13.12	−12.96	−12.79	14.18 ± 0.27
La	−15.41	−15.23	−15.01	−14.81	−14.63	−14.46	15.94 ± 0.29
Ce	−14.81	−14.60	−14.41	−14.21	−14.04	−13.89	15.31 ± 0.30
Pr	−14.44	−14.26	−14.07	−13.91	−13.70	−13.56	14.65 ± 0.33
Nd	−14.16	−13.97	−13.78	−13.61	−13.43	−13.28	14.59 ± 0.23
Sm	−13.58	−13.43	−13.25	−13.09	−12.89	−12.75	14.00 ± 0.30
Eu	−13.39	−13.21	−13.07	−12.88	−12.72	−12.60	13.29 ± 0.30
Gd	−13.29	−13.14	−12.99	−12.83	−12.68	−12.53	12.57 ± 0.25
Tb	−13.22	−13.03	−12.87	−12.74	−12.55	−12.42	13.16 ± 0.28
Dy	−13.18	−13.00	−12.84	−12.69	−12.53	−12.41	12.76 ± 0.22
Ho	−13.23	−13.07	−12.90	−12.75	−12.59	−12.43	13.22 ± 0.21
Er	−13.39	−13.19	−12.99	−12.85	−12.66	−12.51	14.50 ± 0.28
Tm	−13.43	−13.23	−13.02	−12.84	−12.63	−12.46	16.01 ± 0.27
Yb	−13.39	−13.15	−12.96	−12.78	−12.55	−12.39	16.51 ± 0.35
Lu	−13.26	−13.04	−12.83	−12.62	−12.41	−12.21	17.26 ± 0.22

and comparable values for certain of the ions obtained by potentiometric study of reactions between Ln(NTA) and H_3NTA[5] is remarkably good. All of these approaches are reliable, therefore, and of comparable accuracy.

Thermodynamic functions for the formation of the various NTA chelates at 25° are summarized in Table III. The uncertainty of ± 0.03 in the $\Delta F°$ values reflects an uncertainty of ± 0.02 in log K_{I} and log K_{IV} (Table I). Such uncertainties are based upon departures from averages and do not in any way include systematic experimental errors. Uncertainties cited for the enthalpies of formation of the species Ln(NTA) and $Ln(NTA)_2^{3-}$ are those characterizing ΔH_{I} and ΔH_{IV}, respectively. When the values from Table III are to be used for correlations other than those within the lanthanide series, the uncertainties in log $K_{\mathrm{Ca/CaX}}$ and log K_{III} should be added to those introduced by log K_{I} and log K_{IV}, in terms of eq. 3 and 4, and the range of error in ΔH_{I} and ΔH_{IV} should be increased by the uncertainties in $\Delta H_{\mathrm{Ca/CaX}}$ and ΔH_{III}, according to eq. 5 and 6. This has been done to estimate the uncertainties in the thermodynamic functions related to the formation of $Cu(NTA)^-$.

Values for $\Delta S°_1 + \bar{S}°_{\mathrm{Ln}}$ and $\Delta S°_1 + \Delta S°_2 + \bar{S}°_{\mathrm{Ln}}$ are given in Table IV. These differ only by a constant quantity from the partial molal entropies of the chelates Ln(NTA) and $Ln(NTA)_2^{3-}$ and thus may be used to indicate trends in these partial molal quantities.[1,3,13] From the graphic representation given in Figure 1, it is apparent that entropy trends for the two types of chelates are roughly parallel from lanthanum through holmium but that for the last members of the series

---

(13) L. C. Thompson, Doctoral Dissertation, University of Illinois, 1960.

TABLE II

FORMATION CONSTANTS FOR NTA CHELATES

$\mu = 0.10$ (KNO_3)

Species	log $K_{M/MX}$					
	15°	20°	25°	30°	35°	40°
La(NTA)						
Ln = Y	11.46	11.46	11.48	11.54	11.56	11.60
La	10.38	10.37	10.36	10.43	10.43	10.49
Ce	10.85	10.83	10.83	10.87	10.86	10.91
Pr	11.11	11.07	11.07	11.12	11.08	11.11
Nd	11.28	11.25	11.26	11.30	11.27	11.29
Sm	11.53	11.51	11.53	11.55	11.52	11.54
Eu	11.52	11.49	11.52	11.54	11.53	11.55
Gd	11.57	11.54	11.54	11.59	11.57	11.60
Tb	11.60	11.58	11.59	11.65	11.65	11.67
Dy	11.73	11.71	11.74	11.79	11.81	11.84
Ho	11.87	11.85	11.90	11.96	11.95	12.00
Er	12.03	12.00	12.03	12.09	12.10	12.15
Tm	12.21	12.20	12.22	12.28	12.27	12.30
Yb	12.39	12.37	12.40	12.45	12.45	12.48
Lu	12.48	12.47	12.49	12.55	12.54	12.58
$Ln(NTA)_2^{3-}$						
Ln = Y	9.09	9.03	8.95	8.94	8.84	8.83
La	7.34	7.25	7.24	7.25	7.17	7.16
Ce	7.94	7.88	7.84	7.85	7.76	7.73
Pr	8.31	8.22	8.18	8.15	8.10	8.06
Nd	8.59	8.51	8.47	8.45	8.37	8.34
Sm	9.17	9.05	9.00	8.97	8.91	8.87
Eu	9.36	9.27	9.18	9.18	9.08	9.02
Gd	9.46	9.34	9.26	9.23	9.12	9.09
Tb	9.53	9.45	9.38	9.32	9.25	9.20
Dy	9.57	9.48	9.41	9.37	9.27	9.21
Ho	9.52	9.41	9.35	9.31	9.21	9.19
Er	9.36	9.29	9.26	9.21	9.14	9.11
Tm	9.32	9.25	9.23	9.22	9.17	9.16
Yb	9.36	9.33	9.29	9.28	9.25	9.23
Lu	9.49	9.44	9.42	9.44	9.39	9.41
$Cu(NTA)^-$	13.21	13.16	13.10	13.15	13.10	13.13

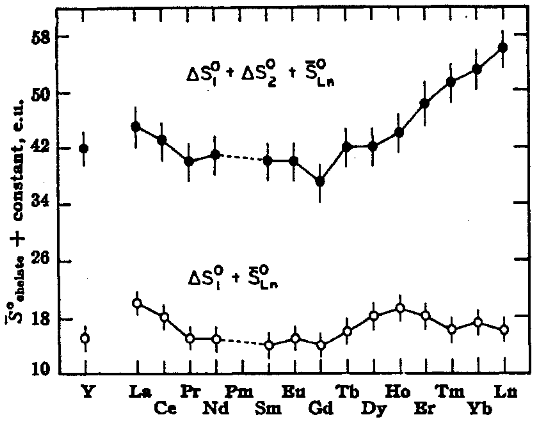

Fig. 1.—Partial molal entropies of NTA chelates.

the behaviors are substantially different. The steady increase in $\bar{S}^o_{LnX_2}$ beyond holmium can be ascribed to an increase in configurational entropy[1] among these complexes. As has been shown for the HEDTA chelates,[1] this is caused by increasing steric hindrance among the acetate groups as the size of the central cation decreases. That a small decrease characterizes the 1:1 chelates in this region reflects the greater influence of enhanced bond strength where excessive crowding of the ligands is reduced by the presence of fewer donor sites. These data and those previously reported[1a] suggest that (1) steric hindrance does indeed exist among donor groups, (2) steric hindrance is important only in the latter half of the lanthanide series, (3) the configurational entropy is large enough to be affected by differences in steric hindrance, and (4) the larger the number of donor groups the larger the effect of decreasing cation size on the configurational entropy of the chelate.

The trends in enthalpy are essentially the same (Figure 2). Again steric hindrance causes some

TABLE III

THERMODYNAMIC FUNCTIONS FOR THE FORMATION OF NTA CHELATES IN AQUEOUS SOLUTION AT μ = 0.10 (KNO_3), 25°

Species	$\Delta F°$ kcal./mole	ΔH kcal./mole	$\Delta S°$ e.u.
$Ca(NTA)^-$	− 8.97 ± 0.03	−0.81 ± 0.22	27.4 ± 0.8
$Cu(NTA)^-$	−17.88 ± 0.08	−1.1 ± 1.1	56.3 ± 4.0
	$\Delta F°_1$	ΔH_1	$\Delta S°_1$
Ln(NTA)			
Ln = Y	−15.67 ± 0.03	2.69 ± 0.27	61.6 ± 1.0
La	−14.14 ± 0.03	2.05 ± 0.34	54.3 ± 1.2
Ce	−14.78 ± 0.03	1.25 ± 0.28	53.8 ± 1.0
Pr	−15.11 ± 0.03	0.45 ± 0.20	52.2 ± 0.8
Nd	−15.37 ± 0.03	0.68 ± 0.18	53.8 ± 0.7
Sm	−15.73 ± 0.03	0.40 ± 0.19	54.1 ± 0.7
Eu	−15.72 ± 0.03	0.93 ± 0.26	55.8 ± 1.0
Gd	−15.75 ± 0.03	1.02 ± 0.23	56.2 ± 0.9
Tb	−15.82 ± 0.03	1.71 ± 0.28	58.8 ± 1.0
Dy	−16.02 ± 0.03	2.25 ± 0.27	61.3 ± 1.0
Ho	−16.24 ± 0.03	2.63 ± 0.23	63.3 ± 0.9
Er	−16.42 ± 0.03	2.51 ± 0.27	63.5 ± 1.0
Tm	−16.68 ± 0.03	1.90 ± 0.26	62.3 ± 1.0
Yb	−16.92 ± 0.03	2.09 ± 0.31	63.7 ± 1.1
Lu	−17.04 ± 0.03	1.98 ± 0.26	63.8 ± 1.0
	$\Delta F°_2$	ΔH_2	$\Delta S°_2$
$Ln(NTA)_2^{3-}$			
Ln = Y	−12.31 ± 0.03	−4.19 ± 0.27	26.9 ± 1.0
La	− 9.88 ± 0.03	−2.43 ± 0.29	25.0 ± 1.1
Ce	−10.70 ± 0.03	−3.06 ± 0.30	25.6 ± 1.1
Pr	−11.16 ± 0.03	−3.72 ± 0.33	24.9 ± 1.2
Nd	−11.56 ± 0.03	−3.78 ± 0.23	26.1 ± 0.9
Sm	−12.28 ± 0.03	−4.37 ± 0.30	26.5 ± 1.1
Eu	−12.53 ± 0.03	−5.08 ± 0.30	25.0 ± 1.1
Gd	−12.64 ± 0.03	−5.80 ± 0.25	22.9 ± 0.9
Tb	−12.80 ± 0.03	−5.21 ± 0.28	25.4 ± 1.0
Dy	−12.84 ± 0.03	−5.61 ± 0.22	24.2 ± 0.8
Ho	−12.76 ± 0.03	−5.15 ± 0.21	25.5 ± 0.8
Er	−12.64 ± 0.03	−3.87 ± 0.28	29.4 ± 1.0
Tm	−12.60 ± 0.03	−2.36 ± 0.27	34.3 ± 1.0
Yb	−12.68 ± 0.03	−1.86 ± 0.35	36.3 ± 1.3
Lu	−12.85 ± 0.03	−1.11 ± 0.22	39.4 ± 0.8

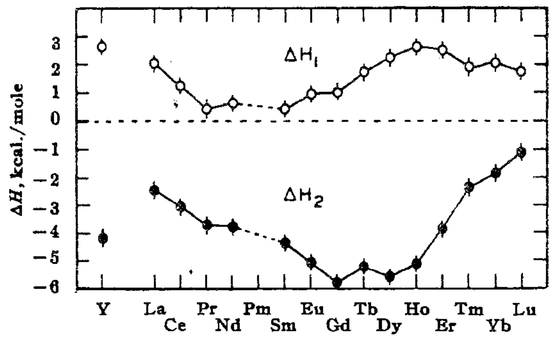

Fig. 2.—Enthalpy changes in formation of NTA chelates.

weakening of the donor–metal bonds in the 1:2 chelates and a parallel increase in ΔH_2. It is of interest that although the stabilities of the EDTA chelates appear to be governed by both entropy and enthalpy changes[14] the enthalpy contribution for the $Ln(NTA)_2^{3-}$ chelates is more important than the entropy contribution. Inasmuch as enthalpy is also significant for the HEDTA chelates,[1a] it is essential to consider both ΔH and ΔS in accounting for observed trends in stability.

Inasmuch as only concentration constants have been measured, ΔH and $\Delta S°$ values reported are not true thermodynamic values. However, constancy of activity coefficients has been assured through use of constant ionic strength in all meas-

---

(14) L. A. K. Staveley and T. Randall, *Discussions Faraday Soc.*, **26**, 157 (1958).

TABLE IV

VARIATION OF THE PARTIAL MOLAL ENTROPY OF NTA CHELATES WITH THE TRIPOSITIVE RARE EARTH METAL ION COMPLEXED

Ion	$\Delta S°_1 + \bar{S}°_{Ln}$[a]	$\Delta S°_1 + \Delta S°_2 + \bar{S}°_{Ln}$[b]
Y	15	42
La	20	45
Ce	18	43
Pr	15	40
Nd	15	41
Sm	14	40
Eu	15	40
Gd	14	37
Tb	16	42
Dy	18	42
Ho	19	44
Er	18	48
Tm	16	51
Yb	17	53
Lu	16	56

[a] Estimated uncertainty ± 2 e.u. [b] Estimated uncertainty ±3 e.u.

urements, and the concentration values thus reflect the same trends as the thermodynamic ones would. In comparing ΔH and $\Delta S°$ data for formation of the 1:1 and 1:2 chelates, effects due to the NTA^- group can be neglected since this group is common to the formation of both. However, for the 1:1 chelate a cation (Ln^{3+}) is converted to a neutral species, whereas for the 1:2 chelate, a neutral species is converted to an anion. This amounts to removal and addition of charge, respectively. If ion–water dipole interactions are important in these systems, it is then reasonable that ΔH_1 is always more positive than ΔH_2 and that $\Delta S°_1$ is always larger than $\Delta S°_2$.

Acknowledgment.—The granting of a Teaching Assistantship by the Chemistry Department of the University of Illinois is gratefully acknowledged by R.F.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

Thermodynamics of Association of Iron(III) Ion and Chloride Ion in Aqueous Solution[1]

BY SISTER M. JOHN MARK WOODS, O. P., PATRICK K. GALLAGHER, AND EDWARD L. KING

Received July 5, 1961

Electromotive force, spectrophotometric, and calorimetric measurements have allowed evaluation of certain thermodynamic quantities for the reaction $Fe^{+3} + Cl^- = FeCl^{+2}$. Electromotive force measurements and spectral data at 335 mμ, an absorption maximum for monochloroiron(III) ion, give values of $Q_1° = [FeCl^{+2}]/[Fe^{+3}][Cl^-]$ for a solvent of 1.0 M perchloric acid at 25° which agree well, 2.89 and 2.95 ± 0.09, respectively. Values of $\Delta H_1°$, obtained from the temperature coefficient $Q_1°$ for 1.0 M perchloric acid are +4.4 kcal./mole from electromotive force measurements and +4.1 kcal./mole from spectrophotometric measurements. The calorimetric study gave a value of $\Delta H_1° = 4.2$ kcal./mole for 1.0 M perchloric acid. The value of $\Delta S_1°$ derived from these quantities pertaining to 1.0 M perchloric acid is +16.6 cal. mole^{-1} deg.$^{-1}$, and electromotive force and calorimetric measurements yield a value of +16.1 cal. mole^{-1} deg.$^{-1}$, for $\Delta S_1°$ in 3.7 M perchloric acid as the medium; this value agrees closely with that for the analogous chromium(III)-chloride reaction, which suggests that iron(III) does not change coördination number in the reaction under consideration. Consideration has been given to medium effects which may accompany the concentration changes necessary in this study of a system showing slight association. In arriving at the conclusions stated in this summary, certain assumptions were necessary; these are given mild support by the general agreement of values obtained using the different experimental methods.

That the interaction of iron(III) ion and chloride ion is not simply an ion-atmosphere effect is indicated by the magnitude of the second-order rate constant for the spectral change which occurs when solutions containing iron(III) ion and chloride ion are brought together.[2] Readjustment of the ion-atmosphere around iron(III) ion occurring in chloride-containing media would

---

(1) This work, presented in part at the 136th National Meeting of the American Chemical Society at Atlantic City, New Jersey, September 1959, is based upon Ph.D. theses of Sr. M. J. M. Woods, O.P., 1960 (electromotive force and spectrophotometric studies), and Patrick K. Gallagher, 1959 (calorimetric studies). The work was supported by the United States Atomic Energy Commission (Contract AT (11-1)-64, Project 3) and the Research Committee of the Graduate School, University of Wisconsin.

(2) R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959); see also H. Wendt and H. Strehlow, *Z. Elektrochem.*, **64**, 131 (1960).