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Thermodynamic Properties of Rare Earth Complexes

XIII. Free Energy, Enthalpy, and Entropy Changes for the Formation of Rare Earth(III)—Iminodiacetate Complexes

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The changes in free energy, enthalpy, and entropy for the formation of the complexes MA_r^{3-2r} ($r = 1-3$), MHA^{2+}, and MH_2A^{3+} have been determined. M denotes a lanthanoid (Pr, Eu, Ho, or Lu) and H_2A iminodiacetic acid. Stability constants for the complexes ScA^+, ScA_2^-, $ScHA^{2+}$, and ScH_2A^{3+} have also been determined. All measurements have been performed at 25°C in a medium with ionic strength 1.0 M using sodium perchlorate as the neutral salt.

The stoichiometric composition and the stability constants for the various complexes formed in the europium(III)-iminodiacetate system were described in a previous communication (part X in this series [1]). This investigation has been extended to include both free energy, enthalpy, and entropy data for the formation of the corresponding praseodymium, europium, holmium, and lutetium complexes. Free energy data have also been determined for some scandium iminodiacetate complexes. This choice of central ions has been made in order to investigate how the maximum number of coordinated ligands and the various thermodynamic quantities for the complex formation reactions are influenced by the size of the central ion. It has also been of interest to investigate how the thermodynamic properties are affected by a change of the donor atoms in various dicarboxylates (see part IX in this series [2]). Such a comparison between different ligands is facilitated if more than one central ion is investigated.

All measurements were performed at 25.0°C in a medium with ionic strength 1.0 M using sodium perchlorate as the neutral salt. The stability constants were determined by a potentiometric standard method, *viz.* emf-measurements of the hydrogen ion concentration. The enthalpy changes were obtained by calorimetric titrations.

The symbols not defined below are given in Ref. 2.

NOTATION

Q = the heat change after each addition of T-solution (*cf.* below).
Q_{corr} = the above heat change corrected for heats of dilution.
v = the total volume of added T-solution.
V_0 = the initial volume of S-solution (*cf.* below).
ΔG°_{pqr}, ΔH°_{pqr}, ΔS°_{pqr} = the over-all changes in free energy, enthalpy, and entropy for the formation of one mole complex according to the reaction

$$pM^{3+} + qH^+ + rA^{2-} \rightarrow M_pH_qA_r^{3p+q-2r}$$

CALCULATIONS

The calculation of the stability constants β_{pqr} has been described before.[1,2] It was assumed that the same species are predominant as those previously found in the europium system (for the scandium system, *vide infra* p. 3210).

The enthalpy changes have been calculated by using the least-squares program „LETAGROP KALLE".[3] The entropy changes were calculated by use of the relation $\Delta S^\circ_{pqr} = (\Delta H^\circ_{pqr} - \Delta G^\circ_{pqr})/T$.

EXPERIMENTAL

Chemicals. The rare earth(III) perchlorates, iminodiacetic acid, and sodium perchlorate were prepared and analyzed as described previously.[1,4]

Potentiometric measurements. The experimental technique was the same as described before.[1] Tables of the experimental emf data can be obtained from the authors.

Table 1. Composition of the various S- and T-solutions in the calorimetric titrations. Series 1 – 4 represent the proton system. $C_{M(T)} = 0$ in all cases.

Series	Metal	$C_{H(S)}$/mM	$C_{M(S)}$/mM	$C_{A(S)}$/mM	$C_{H(T)}$/mM	$C_{A(T)}$/mM	V_0/ml
1	–	210.4	0	105.2	584	0	100.0
2	–	100.6	0	100.5	584	0	100.0
3	–	7.59	0	15.09	58.4	0	100.0
4	Pr	0.58	11.74	5.09	16.2	157.8	93.0
5	Pr	0.33	11.93	2.59	16.5	157.8	91.5
6	Pr	0.13	24.26	0	101.0	200.1	90.0
7	Pr	0.13	24.26	0	151.6	150.6	90.0
8	Pr	16.68	35.21	6.42	511.2	199.1	93.0
9	Eu	1.00	14.35	5.09	16.7	157.9	93.0
10	Eu	0.74	14.59	2.59	16.2	157.8	91.5
11	Eu	0.69	21.18	0	101.9	200.2	90.0
12	Eu	0.69	21.18	0	151.4	150.6	90.0
13	Eu	17.83	41.0	6.42	511.2	199.1	93.0
14	Ho	2.00	13.08	5.09	16.2	157.8	93.0
15	Ho	1.77	13.30	2.59	16.5	157.8	91.5
16	Ho	2.18	19.32	0	101.0	200.1	90.0
17	Ho	2.18	19.32	0	151.6	150.6	90.0
18	Ho	19.69	28.04	6.42	511.2	199.1	93.0
19	Lu	1.40	12.25	5.09	16.2	157.8	93.0
20	Lu	1.17	12.45	2.59	16.5	157.8	91.5
21	Lu	1.30	18.09	0	101.0	200.1	90.0
22	Lu	1.30	18.09	0	151.6	150.6	90.0
23	Lu	18.37	26.25	6.42	511.2	199.1	93.0

Calorimetric measurements. The calorimeter used was of the type described in Ref. 5. The precision and the accuracy of the calorimeter were tested by electrical calibrations and by a determination of the heat of neutralization of sodium hydroxide, respectively. Details of the procedures are given in Refs. 5 and 6. The results agreed with those found previously.[5,6] (The experimental value for the heat of neutralization corrected to infinite dilution was equal to -55.81 ± 0.06 kJ/mol.)

The inner reaction vessel contained about 120 ml. It was initially filled with a solution S, whose volume (V_0) varied between 90.0 and 100.0 ml. Successive additions of 3.00 ml of a solution T were then made from a calibrated piston burette. The corresponding heat changes, Q, were obtained as described earlier.[5,6] The heats of dilution of the various T-solutions were also determined while those of the S-solutions are known to be negligible.[7] The corrected heat changes, Q_{corr}, were then used in the least-squares computation. The analytical composition of the various S- and T-solutions are given in Table 1.

RESULTS

Determination of stability constants. The least-squares refined stability constants with their estimated errors, given as three standard deviations, are represented in Table 2. The standard deviation, *sig y*, in the error-carrying variable C_H/C_A (*cf.* Ref. 1, p. 1403) has also been included.

Table 2. The stability constants obtained from the potentiometric measurements. The errors are given as three standard deviations. *Sig y* is the error in the error-carrying variable C_H/C_A. The number of experimental points is denoted N.

Metal Constant	Pr	Eu	Ho	Lu	Sc
$\beta_{101} \times 10^{-6} \times M$	1.186 ± 0.036	2.87 ± 0.09	4.39 ± 0.13	11.59 ± 0.22	7000 ± 1900
$\beta_{102} \times 10^{-10} \times M^2$	4.71 ± 0.18	45.5 ± 1.9	92.8 ± 3.6	749 ± 17	$(1.15 \pm 0.34) \times 10^6$
$\beta_{103} \times 10^{-13} \times M^3$	5.91 ± 0.41	612 ± 44	1922 ± 120	1411 ± 75	–
$\beta_{111} \times 10^{-10} \times M^2$	5.51 ± 0.17	6.52 ± 0.17	4.75 ± 0.16	3.99 ± 0.10	38.6 ± 4.9
$\beta_{121} \times 10^{-12} \times M^3$	7.46 ± 0.58	8.10 ± 0.65	6.75 ± 0.68	5.10 ± 0.45	30 ± 30
$(sig\ y) \times 10^3$	2.54	2.12	2.59	2.11	4.39
N	103	91	98	102	28

The values of the stability constants and particularly their standard deviations depend on the weighting scheme used in the least-squares refinement. All the experimental points have been assigned a weight of one in these calculations, and the experimental material has thus been weighted by the distribution of experimental points. In order to make comparisons between different lanthanoids it is advantageous to choose this distribution as similar as possible between the various systems. The stability constants of the europium system were recalculated by using only the titration series 10, 13, 14, and 19. These series have stoichiometric compositions, which are rather similar to those used in the three other systems investigated. The recalculated values of the europium constants have been included in Table 2. They differ only slightly from the values published previously (Ref. 1, p. 1403).

Table 3. The heats of dilution. In all the cases the S-solutions consisted of 1.00 M $NaClO_4$. $C_M = 0$ in all T-solutions.

(a) T: $C_H = 0.584$ M, $C_A = 0$, $V_0 = 100.0$ ml.
v/ml, Q/J: *3.00*, −0.50; *6.00*, −0.48; *9.00*, −0.47; *9.00*, −0.47; *12.00*, −0.46; *15.00*, −0.43; *18.00*, −0.41.

(b) T: $C_H = 0.0584$ M, $C_A = 0$. $V_0 = 100.0$ ml.
v/ml, Q/J: *3.00*, −0.10; *6.00*, −0.11; *9.00*, −0.13; *12.00*, −0.13.

(c) T: $C_H = 0.0167$ M, $C_A = 0.1579$ M. $V_0 = 90.0$ ml.
v/ml, Q/J: *3.00*, −0.11; *6.00*, −0.03; *9.00*, −0.02; *12.00*, −0.01; *15.00*, −0.01; *18.00*, −0.03; *21.00*, −0.03; *24.00*, −0.02; *27.00*, −0.02.

(d) T: $C_H = 0.0167$ M, $C_A = 0.1579$ M. $V_0 = 90.0$ ml.
v/ml, Q/J: *1.50*, −0.07; *4.50*, −0.05.

(e) T: $C_H = 0.1019$ M, $C_A = 0.2002$ M. $V_0 = 90.0$ ml.
v/ml, Q/J: *3.00*, 0.20; *6.00*, 0.18; *9.00*, 0.16; *12.00*, 0.15; *15.00*, 0.12; *18.00*, 0.13; *21.00*, 0.13; *24.00*, 0.10; *27.00*, 0.08.

(f) T: $C_H = 0.1514$ M, $C_A = 0.1506$ M. $V_0 = 90.0$ ml.
v/ml, Q/J: *3.00*, 0.10; *6.00*, 0.12; *9.00*, 0.12; *12.00*, 0.12; *15.00*, 0.10; *18.00*, 0.09; *21.00*, 0.08.

(g) T: $C_H = 0.5112$ M, $C_A = 0.1991$ M. $V_0 = 90.0$ ml.
v/ml, Q/J: *3.00*, −1.62; *6.00*, −0.83; *9.00*, −0.61; *12.00*, −0.49; *15.00*, −0.42; *18.00*, −0.38; *21.00*, −0.35.

The stability constants for the scandium system have been calculated from three titrations series. A satisfactory description of the experimental data could only be obtained in the range $1.8 < -\log(h/\mathrm{M}) < 4.0$, presumably due to hydrolysis at lower hydrogen ion concentrations. The stability constants have a lower precision than those in the corresponding lanthanoid systems. This may be due to the presence of other species than those found in the lanthanoid systems, *e.g.* some hydroxo complexes. The fact that the data with high free ligand concentrations are rather uncertain makes it difficult to find out whether a complex ScA_3^{3-} is formed or not. The experimental material indicates that such a complex ought to be very weak if formed at all. (The $\bar{n}$ *versus* $[A^{2-}]$-curve shows a clear plateau at $\bar{n} = 2$ for $-5.0 < \log([A]/M) < -4.0$.)

Table 4. Corresponding values of v/ml, $(Q_{corr} \times 100)$/J and $(Q_{corr,calc} - Q_{corr,obs}) \times 100 \times J^{-1}$ from the calorimetric titrations.

Series 1: *3.00*, 586, −1; *6.00*, 568, −4; *9.00*, 534, −3; *12.00*, 483, −2; *15.00*, 425, −10.

Series 2: *3.00*, 597, −9; *6.00*, 594, −6; *9.00*, 587, 4; *12.00*, 591, 1; *15.00*, 580, 10; *18.00*, 567, 15.

Series 3: *3.00*, 627, 0; *6.00*, 629, −3; *9.00*, 629, −3; *12.00*, 626, 2.

Series 4: *3.00*, 186, −10; *6.00*, 239, −6; *9.00*, 293, 3; *12.00*, 334, −6; *15.00*, 353, 0; *18.00*, 323, −1; *21.00*, 208, 0; *24.00*, 96, −4.

Table 4. Continued.

Series 5: *3.00*, 178, −15; *6.00*, 209, −11; *9.00*, 268, 1; *12.00*, 315, −3.
15.00, 345, −3; *18.00*, 342, 5; *21.00*, 275, −1; *24.00*, 141, 4.

Series 6: *3.00*, 93, 4; *6.00*, 81, 11; *9.00*, 93, 5; *12.00*, 107, 8;
15.00, 121, 12; *18.00*, 140, 11; *21.00*, 154, 15;
24.00, 175, 10; *27.00*, 195, 3.

Series 7: *3.00*, −117, −2; *6.00*, −98, −5; *9.00*, −94, 1; *12.00*, −88, 3;
15.00, −84, 7; *18.00*, −79, 9; *21.00*, −74, 10.

Series 8: *3.00*, −24, −17; *6.00*, −17, −1; *9.00*, −16, 8; *12.00*, −10, 7;
15.00, −8, 8; *18.00*, −5, 7.

Series 9: *3.00*, 214, −16; *6.00*, 290, −16; *9.00*, 391, 3; *12.00*, 487, 11;
15.00, 572, −7; *18.00*, 632, −13; *21.00*, 659, −3;
24.00, 647, 3; *27.00*, 350, 16.

Series 10: *3.00*, 189, −11; *6.00*, 247, −17; *9.00*, 339, −6;
12.00, 447, 7; *15.00*, 536, 0; *18.00*, 609, −14;
21.00, 654, −11; *24.00*, 667, −3; *27.00*, 551, 17.

Series 11: *3.00*, 228, 8; *6.00*, 81, 7; *9.00*, 107, 10;
12.00, 140, 12; *15.00*, 171, 19; *18.00*, 214, 16;
21.00, 254, 14; *24.00*, 287, 15; *27.00*, 330, 0.

Series 12: *3.00*, −100, −5; *6.00*, −112, −7; *9.00*, −114, 2;
12.00, −108, 5; *15.00*, −100, 6; *18.00*, −94, 8;
21.00, −87, 8.

Series 13: *3.00*, −39, −18; *6.00*, −23, −8; *9.00*, −29, 10;
12.00, −20, 8; *15.00*, −20, 12; *18.00*, −13, 8.

Series 14: *3.00*, −5, −15; *6.00*, 77, −17; *9.00*, 223, −3;
12.00, 405, −3; *15.00*, 622, −10; *18.00*, 855, −3;
21.00, 1028, 2.

Series 15: *3.00*, −18, −11; *6.00*, 24, −14; *9.00*, 142, −10;
12.00, 308, 1; *15.00*, 501, −4; *18.00*, 732, −5;
21.00, 941, 9; *24.00*, 1052, 3; *27.00*, 521, −5.

Series 16: *3.00*, 502, 17; *6.00*, −42, 3; *9.00*, −37, 7;
12.00, −11, 14; *15.00*, 19, 25; *18.00*, 65, 26;
21.00, 125, 17; *24.00*, 175, 19.

Series 17: *3.00*, −49, −3; *6.00*, −107, −6; *9.00*, −120, −5;
12.00, −123, 0; *15.00*, −122, 5; *18.00*, −116, 5;
21.00, −116, 13.

Series 18: *3.00*, −25, −19; *6.00*, −20, −3; *9.00*, −24, 11;
12.00, −15, 7; *15.00*, −13, 8; *18.00*, −11, 9.

Series 19: *3.00*, 83, −12; *6.00*, 165, −10; *9.00*, 270, −1;
12.00, 351, −7; *15.00*, 623, −5; *18.00*, 869, 3;
21.00, 705, −9.

Series 20: *3.00*, 67, −12; *6.00*, 119, −14; *9.00*, 218, −5;
12.00, 312, −2; *15.00*, 408, −5; *18.00*, 816, 13;
21.00, 819, −5.

Series 21: *3.00*, 278, 3; *6.00*, 6, 2; *9.00*, 25, 9; *12.00*, 59, 13;
15.00, 91, 22; *18.00*, 135, 18; *21.00*, 173, 15; *24.00*, 205, 10.

Series 22: *3.00*, −137, −3; *6.00*, −177, −4; *9.00*, −182, 5; *12.00*, −174, 7;
15.00, −164, 9; *18.00*, −153, 9; *21.00*, −146, 12.

Series 23: *3.00*, −22, −20; *6.00*, −20, 0; *9.00*, −19, 8;
12.00, −10, 5; *15.00*, −10, 8; *18.00*, −11, 11.

Determination of enthalpy changes. The experimental Q-values are positive for exothermal and negative for endothermal reactions.

The various heats of dilution are given in Table 3. The experimental data for the protonation and metal complexation reactions in the various iminodiacetate systems are collected in Table 4. Values of the quantity

$$\Delta Q = Q_{\text{corr, calc}} - Q_{\text{corr, exp}}$$

have also been included in this table in order to show how well the experimental data can be described by the various molar enthalpy changes. These are given in Table 5 with their errors, estimated as three standard deviations. The least-squares refinements of the calorimetric data have been made by using the stability constants β_{pqr} given in Table 2.

The hydrogen ion concentration is rather low in the latter part of some of the calorimetric titrations. Hence, the reaction

$$H^+ + OH^- \rightarrow H_2O$$

must be considered. In the final least-squares computations this reaction has been included by using values of K_w and enthalpy of neutralization equal to 1.70×10^{-14} M^2 (*cf.* Ref. 8) and -56.11 kJ/mol (*cf.* Ref. 9), respectively. The corrections for the neutralization reaction are relatively small; at most cor-

Table 5. The enthalpy changes obtained from the calorimetric titrations and the corresponding entropy changes. The quantities ΔH° are divided by kJ × mol^{-1}; the quantities ΔS° are divided by J × mol^{-1} × K^{-1}. The errors are given as three standard deviations. *Sig Q* is equal to the standard deviation in the measured Q_{corr}-values.

	$-\Delta H^\circ_{011}$	$-\Delta H^\circ_{021}$	$-H^\circ_{031}$	ΔS°_{011}	ΔS°_{021}	ΔS°_{031}	*sig Q*/J
Protonation	35.64 ± 0.72	39.04 ± 0.72	43.22 ± 0.73	59	97	119	0.084

Metal	$-\Delta H^\circ_{101}$	$-\Delta H^\circ_{102}$	$-\Delta H^\circ_{103}$	$-\Delta H^\circ_{111}$	$-\Delta H^\circ_{121}$
Pr	3.63 ± 0.27	11.04 ± 0.35	20.97 ± 0.46	31.46 ± 0.78	46.04 ± 1.90
Eu	3.72 ± 0.39	16.51 ± 0.48	33.15 ± 0.54	30.82 ± 1.20	44.07 ± 2.33
Ho	−1.47 ± 0.40	6.15 ± 0.55	34.29 ± 0.62	28.59 ± 1.53	46.37 ± 3.88
Lu	0.55 ± 0.38	8.94 ± 0.43	32.36 ± 0.60	27.98 ± 1.90	49.48 ± 4.58

Metal	ΔS°_{101}	ΔS°_{102}	ΔS_{103}	ΔS°_{111}	ΔS°_{121}	*Sig Q*/J
Pr	104	167	194	100	92	0.080
Eu	111	168	191	104	99	0.115
Ho	132	208	197	108	90	0.121
Lu	133	217	200	109	77	0.107

responding to 0.13 J in an individual measurement and 0.16 kJ/mol in a computed enthalpy change.

An estimate of the possible influence of hydrolysis products on the enthalpy values has also been made. We have assumed that the only hydroxo complexes present are MOH^{2+} and $M_2(OH)_2^{4+}$. The stability constants used were the same as those for the corresponding yttrium complexes.[10] The enthalpy changes for the reactions

$$pM^{3+} + qH_2O \rightarrow M_p(OH)_q^{3p-q} + qH^+$$

have been estimated as 30 – 50 kJ/mol from the compilation made by Arnek.[11] A calculation of the influence of hydroxide complexation reactions to the measured Q-values showed that the contribution always was small, at most 0.01 J in an individual measurement. Hence, these hydroxo complexes have been neglected in the computations.

Some attempts were made to vary enthalpy values and stability constants simultaneously. The only quantities varied in these calculations were one of β_{pqr} and the corresponding ΔH°_{pqr}-value. In all cases except for the complex MH_2A^{3+} the results confirm the magnitude of the potentiometrically determined stability constants. No calculation was possible for MH_2A^{3+} because of the low concentrations of this species.

DISCUSSION

The variations in the thermodynamic functions ΔH° and ΔS° for the stepwise reactions

$$MA_r^{3-2r} + A^{2-} \rightarrow MA_{r+1}^{1-2r}$$

through the lanthanoid series seem to follow the patterns observed earlier for the diglycolate and dipicolinate systems.[7]

The ion HA^- acts as ligand in a similar way as the bimalonate ion [2] and the acetate ion.[13–15] This point was discussed briefly in part X of this series. The most basic atom in the iminodiacetate ligand is the nitrogen atom and the proton in the complex MHA ought to be bonded to this atom. Another piece of evidence for this is the enthalpy change for the reaction

$$MA^+ + H^+ \rightarrow MHA^{2+}$$

equal to approximately -28 kJ/mol. This quantity is of the same magnitude as the heat of protonation of A^{2-} (-35.6 kJ/mol) and much smaller than the heats of protonation of the carboxylate groups of HA^- and H_2A (equal to -4.4 and -4.2 kJ/mol, respectively). The ΔG°-values for the reaction

$$M^{3+} + H_2A \rightarrow MH_2A^{3+}$$

also vary in a manner similar to the acetate system.

The errors in the corresponding ΔH° and ΔS°-values are too large to warrant a comparison between the various lanthanoids.

The strength of the acid MHA^{2+} increases with increasing atomic number from 2.15×10^{-5} for Pr to 29.5×10^{-5} for Lu in much the same way as was

found previously in the lanthanoid malonate system (Ref. 2, p. 1399). The first dissociation constant of the acid MH_2A^{3+} remains on the other hand nearly constant throughout the lanthanoid series. This fact might be correlated with a large difference in distance between the metal ion and the two protons.

A comparison between the scandium system and the lanthanoid systems shows the same type of "steric hindrance" for the formation of a third complex for small central ions as was found previously in other dicarboxylate systems.[4,16] Already the second scandium complex is relatively weak compared to the first one, the ratio K_1/K_2 is equal to 43, as compared to 5.6 for lutecium.

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