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The thermodynamics of complexation of transition and lanthanide ions by 3-(α-carboxymethylaminobenzylidenehydrazino)-5,6-diphenyl-1,2,4 triazine (HipHt)

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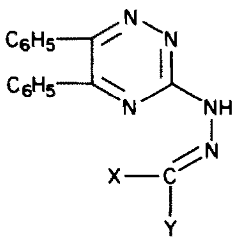
Abstract

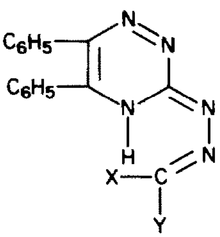
The metal–ligand stability constants of the Ni(II), Co(II), Zn(II), Mn(II), Cd(II), Fe(III), UO_2(II) and Ln(III) chelates of HipHT were determined in 75% (v/v) dioxane–water medium at 10, 20 and 30°C and $\mu = 0.1$ M (KNO_3). The thermodynamic parameters for the proton–ligand and metal–ligand stability constants were obtained by the temperature coefficient method. The thermodynamic functions ΔG and ΔH of the complexes were analyzed in terms of the electrostatic (el) and non-electrostatic (non) components. The values of ΔH_{non} and ΔH_{el} show a linear variation with the hardness and softness $E_n^{\#}$ of the metal ion and with the heat of hydration ΔH_h of the metal ion, respectively. HipHT behaves as a diprotic tridentate (NNO) donor towards the metal ions, as inferred from the infrared spectra of its metal chelates.

INTRODUCTION

In previous papers [1–4], the chelating abilities of a series of substituted 5,6-diphenyl-1,2,4 triazine ligands (structures **I** and **II**) were studied with transition, post-transition and lanthanide metal ions.



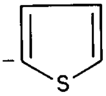
(I)



(II)

* Corresponding author.

BHT: $X = C_6H_5$–; $Y = $ –CO–C_6H_5
BAHT: $X = $ –CH_3; $Y = $ –CH_2–CO–C_6H_5
DBMHT: $X = C_6H_5$–; $Y = $ –CH_2–CO–C_6H_5

TTAHT: X =  $Y = $ –CH_2–CO–CF_3

TFAHT: $X = $ –CH_3; $Y = $ –CH_2–CO–CF_3
HiPHT: $X = $ –C_6H_5; $Y = $ –NH–CH_2–COOH

BHT is a monobasic bidentate ligand, the carbonyl oxygen and azomethine nitrogen being the coordination sites [1]. The introduction of a β-diketone group alters the mode of coordination and the protic nature of the ligands [2, 3]. In both BAHT and DBMHT the ligands behave as monobasic bidentate ON donors, with dissociation of the enolic OH proton. Under the extreme conditions of refluxing with the metal ion [3], two gram-equivalents of hydrogen are lost, probably those of the hydrazo and enolic groups. Also, the presence of a strong withdrawing group, as in TTAHT and TFAHT (–CF_3), makes these ligands behave as diprotic bidentate (ON) donors towards different metal ions [2, 3].

The thermodynamic parameters (free energies, enthalpies and entropies) of complexation of lanthanide ions by bis(5,6-diphenyl-1,2,4 triazin-3-yl-hydrazinocarbonyl) (DPTHC) [4] have been determined in 75% (v/v) dioxane–water solvent and 0.10 M KNO_3. The data obtained support the interpretation of an expanded solvation sphere through the lanthanide series.

Many of the organic substances that can affect the biological and ecological behavior of the lanthanide and actinide ions have aromatic carboxylate binding sites. Continuing our studies on the thermodynamic parameters of this important class of ligands, we report here the chelating tendencies of 3-(α-carboxymethylaminobenzylidenehydrazino)-5,5-diphenyl-1,2,4 triazine (HipHT) towards transition, post-transition and lanthanide metal ions. The ligand (HipHT) is the condensation product of hippuric (Hip) acid with 3-hydrazino-5,6-diphenyl-1,2,4 triazine.

EXPERIMENTAL

Preparation of the solid ligand

HipHT was obtained by mixing 100 ml of a 0.01 M ethanolic solution of 3-hydrazino-5,6-diphenyl-1,2,4 triazine with 100 ml of a hot 0.01 M solution of hippuric acid in DMF. The reaction mixture was refluxed for 4 h, cooled and poured into ice. The solid obtained was filtered and crystallized from

TABLE 1

Analytical data for HipHT and its metal complexes

Species and formula	C in % Calc. (Found)	H in % Calc. (Found)	N in % Calc. (Found)	M in % Calc. (Found)	Conductance [a] in $ohm^{-1}\,cm^2\,mol^{-1}$
HipHT, $C_{24}H_{20}N_6O_2$	67.93 (67.82)	4.72 (4.69)	19.81 (19.72)		
$Cu_2(C_{24}H_{18}N_6O_2)(NO_3)_2(H_2O)$	41.67 (41.70)	2.89 (2.70)	16.21 (16.11)	18.39 (18.29)	4.4
$Ni_2(C_{24}H_{18}N_6O_2)(NO_3)_2(H_2O)_3$	40.14 (40.50)	3.35 (3.20)	15.61 (15.41)	16.37 (16.17)	8.5
$Fe[(C_{24}H_{18}N_6O_2)(H_2O)_3]$	54.15 (54.20)	4.51 (4.40)	15.79 (15.69)	10.50 (10.35)	10.1
$Fe(C_{24}H_{18}N_6O_2)(NO_3)(H_2O)_2$	50.01 (49.53)	3.82 (3.96)	17.03 (17.00)	9.71 (9.50)	18.2
$Er(C_{24}H_{18}N_6O_2)(NO_3)(H_2O)_5$	38.85 (39.10)	3.78 (3.82)	13.22 (13.01)	22.56 (22.21)	22.2

[a] 10^{-3} M complex in DMF.

ethanol to give HipHT. The elemental analyses of C, H, and N are given in Table 1.

The solid complexes of HipHT with divalent and trivalent metal ions were prepared following the procedures described previously [4, 5]. The elemental analysis results for C, H, N and metal are given in Table 1.

Reagents, materials and procedures

The metal nitrates, the purification of the solvents, the working procedures, infrared spectra and conductance measurements were essentially the same as described previously [4].

RESULTS

The potentiometric titration curves of HipHT in the absence and presence of some metal ions are shown in Fig. 1. One proton dissociates between $a = 0$ and $a = 1$ where a represents the moles of base added per mole of ligand present. At higher pH values, one additional proton dissociates, as indicated by the metal–ligand titration curves. For the general protonation equilibrium

$$H^+ + H_{n-1}L \rightleftarrows H_nL \ (n = 1 \text{ or } 2)$$

the constants K_n^H were determined as described previously [5]. The results obtained for K_1^H (–COOH proton) and K_2^H (–NH proton) are given in Table 2.

The titration curves of HipHT in the presence of lanthanide metal ions show one long buffer region and an inflection point at $m = 5.0$ (m is the moles of base added per mole of metal ion), due to the formation of

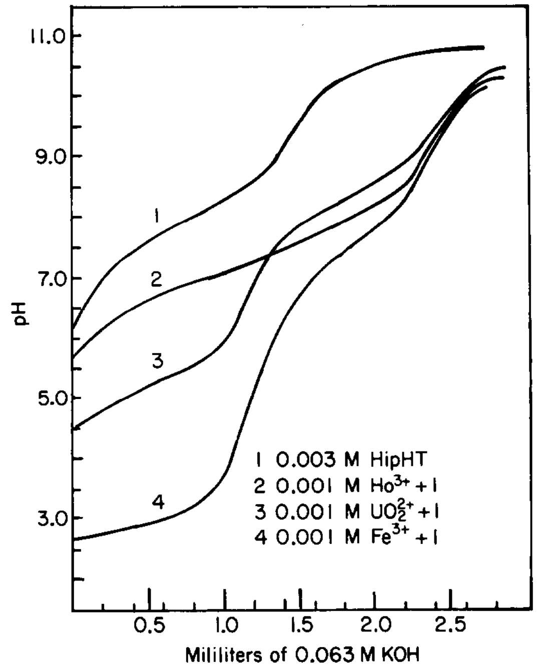


Fig. 1. Potentiometric titration curves of HipHT and its metal complexes.

bis-chelate as a higher complex type and to the neutralization of the –COOH group in the uncomplexed ligand molecule. The titration curves of HipHT in the presence of Ni(II), Co(II), Zn(II), Mn(II), Cd(II), UO_2(II) and Fe(III) show strong inflections at $m = 2$ due to the formation of 1:1 complexes (Fig. 1).

The stability constants of the 1:1 and 1:2 complexes were calculated as described elsewhere [6]. Examples of these calculations are plotted in Fig. 2. The values of the constants obtained are given in Table 2. The values of ΔH and ΔS given in Table 2 were calculated using the temperature coefficient and the Gibbs–Helmholtz equation as described previously [4].

DISCUSSION

The values of the two protonation constants of HipHT listed in Table 2 are consistent with the structure of this ligand. If the HipHT molecule is considered to consist of a 3-hydrazino-triazine group condensed with a hippuric acid molecule, then the second protonation constant pK_2^H is associated with the highly basic triazine nitrogen which is probably hydrogen-bonded to the hydrazo nitrogen most distant from the ring. This is evident from the infrared spectrum of HipHT which shows a broad band at 3120 cm^{-1} due to hydrogen-bonded NH groups. The value of pK_1^H is much lower than that of glycine (9.60 at $\mu = 0.1$, aqueous [7]), because in the former case protonation takes place on a secondary nitrogen which is

TABLE 2

Stability constants and thermodynamic parameters of HipHT–metal complexes

	$\log K_1$ [a]			$\log K_2$ [b]			$-\Delta G_1$ [c]	$-\Delta H_1$ [d]	$-\Delta S_1$ [e]	$-\Delta G_2$ [c]	$-\Delta H_2$ [f]	$-\Delta S_2$ [g]
	10°C	20°C	30°C	10°C	20°C	30°C						
H^+	8.72	8.40	8.11	11.95	11.25	10.52	47.07	50.00	9.6	61.17	115.52	179.5
Ni^{2+}	10.22	9.48	8.68				50.38	127.95	256.1			
Co^{2+}	10.82	10.13	9.37				54.39	118.74	212.6			
Zn^{2+}	10.79	10.01	9.43				54.77	100.88	150.6			
Mn^{2+}	7.03	6.45	6.01				34.90	83.72	161.1			
Cd^{2+}	13.01	12.49	11.96				69.41	86.02	54.4			
Fe^{3+}	17.22	16.59	15.86	10.16	9.36	8.86	92.05	111.46	64.0	51.42	106.82	128.8
	$\log K_3$									ΔG_3	ΔH_3	ΔS_3
	6.78	6.04	5.10							29.62	137.49	356.1
UO_2^{2+}	12.14	11.49	10.85	6.58	6.19	5.72	62.97	105.81	141.4	33.22	78.70	150.2
La^{3+}	6.76	6.25	5.72	5.62	5.08	4.87	33.22	85.23	171.5	28.28	61.76	110.5
Pr^{3+}	6.83	6.37	5.88	6.13	5.80	5.51	34.14	77.82	144.4	31.97	50.83	62.3
Nd^{3+}	6.80	6.38	6.06	6.11	5.80	5.52	35.19	60.75	84.5	32.05	48.37	54.0
Sm^{3+}	7.16	6.84	6.27	6.74	6.41	5.80	37.24	72.72	120.9	33.68	76.78	142.3
Eu^{3+}	7.52	6.93	6.60	6.91	6.39	6.12	38.28	75.65	123.4	35.52	64.98	97.1
Gd^{3+}	7.44	6.94	6.50	6.53	6.09	5.65	37.74	77.07	129.7	32.08	72.13	129.7
Tb^{3+}	7.30	6.89	6.40	6.46	5.79	5.39	37.15	73.68	120.5	31.30	87.95	187.0
Dy^{3+}	8.45	7.92	7.54	7.83	7.07	6.70	41.51	74.73	109.6	38.87	92.55	177.0
Ho^{3+}	8.85	8.42	7.98	7.09	6.59	6.00	46.32	71.30	82.4	34.81	89.20	179.5
Er^{3+}	8.06	7.58	7.25	6.84	6.56	5.91	42.09	66.53	80.8	34.31	75.86	137.2
Tm^{3+}	8.25	7.60	7.01	6.91	6.19	5.86	40.67	67.28	87.9	34.02	86.40	172.8
Yb^{3+}	8.39	8.08	7.53	6.76	6.38	6.00	43.72	70.25	87.5	34.81	62.30	90.8
Lu^{3+}	8.33	7.92	7.57	6.60	6.24	6.03	43.93	62.34	60.7	35.02	46.86	38.9

[a] $\log K_1 \pm (0.01–0.23)$. [b] $\log K_2 \pm (0.01–0.15)$. [c] $kJ\ mol^{-1}$. [d] $\Delta H_1 \pm (0.04–1.13)\ kJ\ mol^{-1}$. [e] $\Delta S_1 \pm (0.04–1.42)\ J\ mol^{-1}\ K^{-1}$. [f] $\Delta H_2 \pm (0.04–1.67)\ kJ\ mol^{-1}$. [g] $\Delta S_2 \pm (0.04–4.10)\ J\ mol\ K^{-1}$.

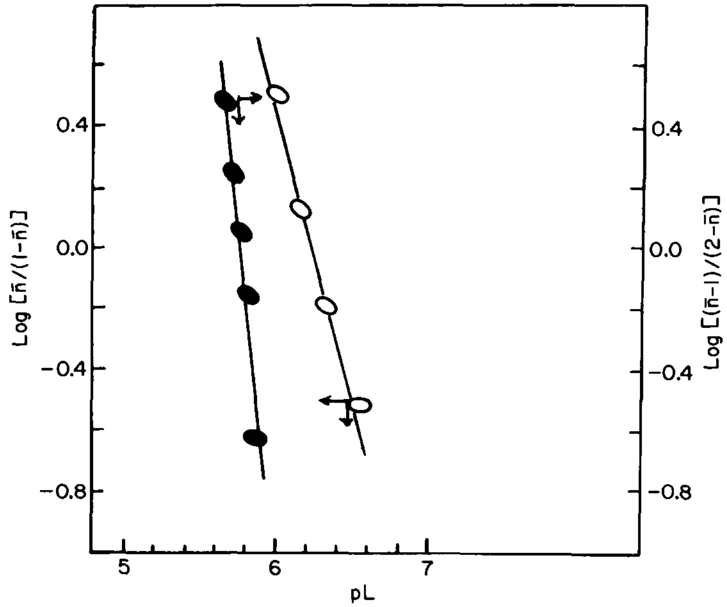
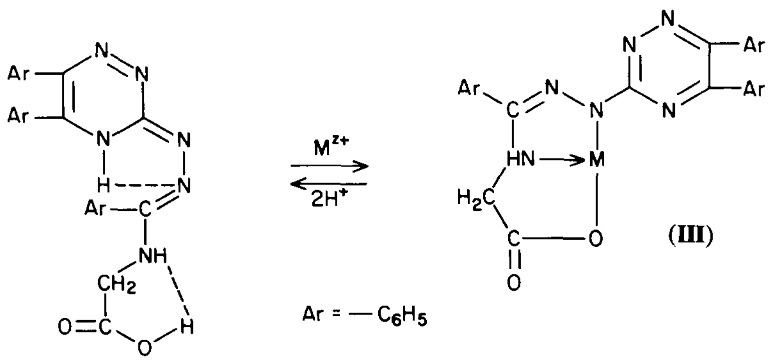


Fig. 2. Metal–ligand formation constants of Sm(III)–HipHT by the linear plot method.

deshielded by the inductive effect of the adjacent azomethine group. A similar trend in pK_1^H values has been observed for the closely related glutamic and benzoylglutamic acids ($pK_1^H = 9.60$ and 4.63 respectively at $\mu = 0.1$, aqueous [8]). The drop of 4.80 log units compares well with the difference $\Delta[pK_2^H(\text{HipHT}) - pK_1^H(\text{glycine})]$ if an allowance is made for the differences in the medium and the electron-withdrawing effects of the >C=O and >C=N groups.

The structure of HipHT allows a reasonable arrangement of three coordinate bonds around the metal ions, as indicated by the formula **III** (Scheme 1). This structure can be inferred from the change in the IR absorption bands of the free ligand and its metal complexes. The IR



Scheme 1.

spectrum of HipHT exhibits the ν(O–H) band for the –COOH group, and the ν(N–H), ν(C=O), ν(O–H) out-of-plane bands at 2900(b), 3120(b), 1620(m) and 1330 cm^{-1}, respectively. The band of ν(O–H) at 2900 cm^{-1} disappears in the spectra of all the complexes (Table 3), indicating the deprotonation of the –COOH group in the ligand during complexation. The participation of the carboxylate group in complex formation is also indicated in the spectra of the complexes by the disappearance of the bands due to the ν(C=O) and ν(C–OH) stretching modes, which are replaced by two bands at 1450–1500 and 1350–1370 cm^{-1} assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ respectively, and by the appearance of new bands at 610–650 cm^{-1}, assigned to ν(M–O).

Due to the overlap of the –NH stretching vibration with the –OH vibration of the coordinated water in the spectra of the complexes, no conclusions could be drawn regarding the nature of these bonds. The ν(C=N), ν(C–N) and ν(N–N) modes can be used to diagnose the nitrogen coordination, as follows. The spectrum of the ligand exhibits a medium band and a very strong band at 1575 and 1530 cm^{-1}, which can be assigned to ν(NH) and ν(C=N + C=C) respectively. In the spectra of the complexes, the first band disappears and the second is shifted to higher frequencies; this indicates that the secondary NH and azomethine groups are coordinated to the metal ions. The bands due to ν(C–N) (1035 and 1210 cm^{-1}) and ν(N–N) (930 cm^{-1}) in the spectrum of the ligand are shifted or disappear (Table 3) in the complexes, indicating their participation in chelate formation. The new bands observed in the 630 and 590 cm^{-1} regions are assigned to ν(M–N) and $\nu(M–N^-)$, with N and N^- being the nitrogen atoms of azomethine and secondary NH groups, or vice versa.

The tridentate (NNO) donor ability of HipHT is further confirmed from its higher negative enthalpy values for the different complexes. (Table 2). Degischer and Nancollas [9] have pointed out that for systems involving nitrogen and carboxylate oxygen, the ΔH values reflect the change in the number and strength of the bonds made and broken during the reactions, and have correlated the values of ΔH to the type of bonding between the metal ion and the ligand molecules, and to the structural features of the complex. Considering this and the fact that the crystal-fields produced by an oxygen-coordinating ligand, i.e. COOH, are similar to those of the water molecule [10], ΔH will not be significantly affected by the displacement of water molecules. Thus, the higher negative values of the enthalpies of all the complex systems obtained here could be related to the coordination sites of the nitrogen atom of the –C=N and –NH groups.

The values of ΔG, ΔH and ΔS have been separated into their electrostatic (el) and non-electrostatic (non) or cratic components, as described in ref. 11, in order to provide information on the nature of the bonding in the complexes. The separated thermodynamic functions are shown in eqns. (1)–(3), below. The values of the parameters C and a are

TABLE 3

Some important infrared spectral bands of HipHT and its metal complexes in cm^{-1}

HipHT	Cu(II)–HipHT	Ni(II)–HipHT	Fe(II)–HipHT	Fe(III)–HipHT	Er(III)–HipHT	Assignment
	3500b	3550–3000sb			3500–3000sb	ν_{as} and ν_s of HOH and NH
3120b	3100w		3200b			
2900b	–	–	–	–	–	ν(OH) (–COOH)
		1990s			1990m	
1620s	–	–	–	–	–	ν(C=O)
1590w	–	1590w	–			ν(C=N); ν(C=C) and ν(N–H) in-
1575m	–	–	–	–	–	plane deformation
1530vs	1550vs	1540vs	1535sh	–	1540–1480sb	
	1500s	1450s	1440b	1470s		$\nu_{as}(COO^-)$
1440w		1410m		1430w	1430w	ν(–CH) deformation of $-CH_2-$
1360vs	1370vs	1360w	1365m	1350s	1370s	ν(C–C) phenyl; ν(N=N); $\nu_s(COO^-)$
1330vs		1310w	1330m	1320s	1300w	ν(C–OH) in-plane deformation
1250m	1250m		1230s	1205w	1210w	ν(C–C); ν(C–O) and ν(C–N)
1210m	1200vs					
1190s				1190m		
1180s				1180m		
	1080m	1080m	1110s	1095b	1120w	$\delta(H_2O)$
1035s	–	–	–	–	–	ν(C–N) and ν(–N–N)
1025s	–	–	–	–	–	
930w		910w	920w	920w	920w	
800w	790s	790w	800w	790s	–	ν(N–H) out-of-plane deformation
770vs	720vs	765s	770s		760m	ν(C–H) out-of-plane deformation
750s	–	–	–	–	–	ν(O–H) out-of-plane deformation
	610m	620w	610m	610m	650w	ν(M–O)
	550m	550w	590m	590m	630w	ν(M–N)
	430w	510w	500m	500m	590w	$\nu(M-N^-)$

Key: s, strong; m, medium; w, weak; b, broad; v, very; sh, shoulder.

TABLE 4

Non-electrostatic (non) and electrostatic (el) thermodynamic quantities associated with the reaction of bivalent and trivalent metal ions with HipHT in 75% (v/v) dioxane–water

Cation	$-\Delta H_1$/ (kJ mol^{-1})	$-\Delta S_1$/ (J mol^{-1} K^{-1})	C	a	ΔG_{non}/ (kJ mol^{-1})	ΔG_{el}/ (kJ mol^{-1})	ΔH_{non}/ (kJ mol^{-1})	ΔH_{el}/ (kJ mol^{-1})	ΔS_{el}/ (J mol^{-1} K^{-1})
Ni^{2+}	127.95	256.1	1358.0	−9.54	−117.85	47.18	−107.71	−20.28	−222.6
Co^{2+}	118.74	212.6	1092.7	−11.27	−112.53	37.96	−102.39	−16.32	−179.1
Zn^{2+}	100.88	150.6	714.6	−15.18	−100.33	24.82	−90.19	−10.67	−117.2
Mn^{2+}	83.72	161.1	778.4	−11.14	−82.24	27.04	−72.09	−11.62	−127.6
Cd^{2+}	86.02	54.4	127.6	−79.29	−94.26	4.43	−84.12	−1.91	−20.9
Fe^{3+}	111.46	64.0	186.3	−70.17	−118.83	6.47	−10.87	−2.78	−30.5
UO_2^{2+}	105.81	141.4	658.5	−17.53	−106.12	22.88	−95.97	−9.83	−108.0
Sm^{3+}	72.72	120.9	533.4	−14.60	−64.75	18.53	−64.75	−7.97	−87.5

calculated from eqns. (4) and (5) or (6) when the values of ΔS and ΔG or ΔH are known

$$\Delta G_{non} = nRT \ln M + RCa \qquad \Delta G_{el} = RC\, e^{T/\theta} \tag{1}$$

$$\Delta H_{non} = RCa \qquad \Delta H_{el} = RC(1 - T/\theta)\, e^{T/\theta} \tag{2}$$

$$\Delta S_{non} = -nR \ln M \qquad \Delta S_{el} = -\frac{RC}{\theta}\, e^{T/\theta} \tag{3}$$

$$\Delta G = nRT \ln M + RC(a + e^{T/\theta}) \tag{4}$$

$$\Delta H = \left[RCa + \left(1 - \frac{T}{\theta}\right) e^{T/\theta}\right] \tag{5}$$

$$\Delta S = -nR \ln M - \frac{RC}{\theta}\, e^{T/\theta} \tag{6}$$

where θ is a temperature characteristic of the solvent ($\theta = 211.9$ K for water [12]). The values of the calculated thermodynamic parameters (el and non) are given in Table 4. The complex-formation reactions of many metal ions with HipHT are highly exothermic due to the higher stability values of these complexes. The ΔH_{non} values reflect the covalency of the bonding and the structural changes on complexation [9]. Regarding the covalency, the softer metal ions have a greater affinity for the softer donor [13]. In Fig. 3, values of ΔH_{non} are plotted against the quantity $E_n^{\#}$, introduced by Klopman [14] as a measure of the hardness and softness of a metal ion in solution. A soft metal is characterized by a large negative value of $E_n^{\#}$, and vice versa. As can be seen in Fig. 3, a linear correlation appears to exist between ΔH_{non} and $E_n^{\#}$: ΔH_{non} increases with the softness of the metal ion. The ΔH_{non}

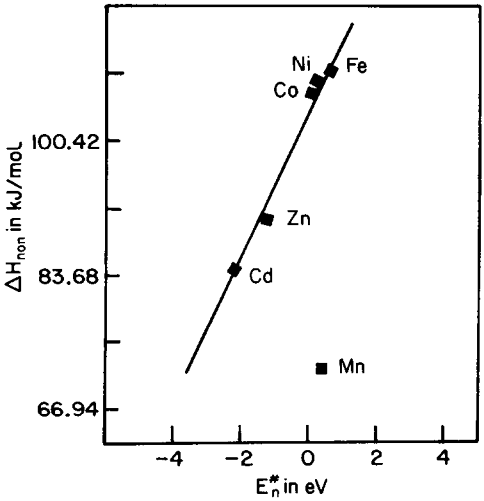


Fig. 3. Relationship between the non-electrostatic heat change ΔH_{non} on HipHT complex formation and the hardness or softness $E_n^{\#}$ of the metal ion.

values are in the order Mn(II) < Cd(II) < Zn(II) < Co(II) < Ni(II) < Fe(III), a result of the ligand field stabilization energy (lfs). According to some authors [15–18], the non-electrostatic enthalpy change arises from the changes in lfs accompanying complex formation.

It is generally accepted that the heat of hydration of a metal ion is closely related to its tendency to complex formation in aqueous solution, because the process involves the replacement of the metal–water bonds by metal–donor bonds. The heat change upon complex formation will be related to the difference between the strengths of the metal–donor bonds and hydration bonds. The heat change on complexation must be determined from the electrostatic and covalent interactions, together with a structural contribution and ligand field stabilization. It is of great interest to note that the electrostatic heats ΔH_{el} of formation of the HipHT complexes show a linear relation with the hydration heats ΔH_h of the corresponding metal ions, as seen in Fig. 4. This correlation of ΔH_{el} and ΔH_h suggests that most of the HipHT complexes are essentially similar in size and in the geometry of the coordination sphere of the corresponding hydrated ions.

In Fig. 5, the thermodynamic parameters of complexation of the lanthanides with HipHT ligand are plotted as a function of the ionic potential z^2/r (r is the cationic radius of the lanthanide element) of the lanthanide elements. On an electrostatic basis, the strength of the bonds between ion and ligand would be expected to be fairly closely related to cation size. This energy might be expected to increase almost uniformly (linearly) as the radius of the ion decreases through the series. This expected behavior is not observed for the lanthanide series shown in Fig. 5. The ΔG_n, ΔH_n and ΔS_n ($n = 1$ and 2) plots discontinuities in the middle of

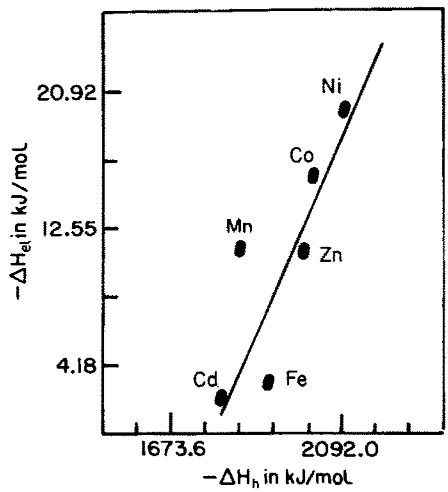


Fig. 4. Relationship between the electrostatic heat change ΔH_{el} on HipHT complex formation and the heat of hydration ΔH_h of the metal ion.

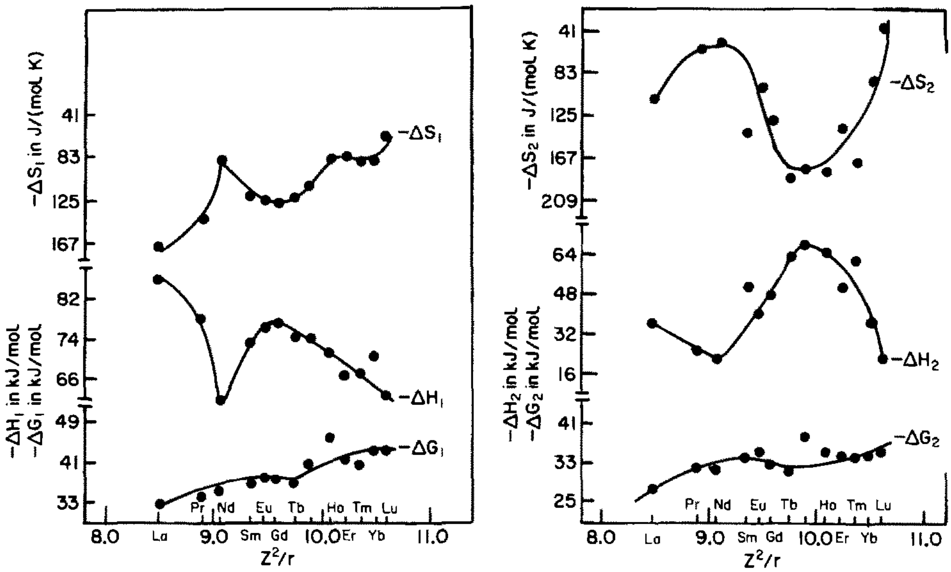


Fig. 5. Thermodynamic parameters ($-\Delta G_n$, $-\Delta H_n$ and $-\Delta S_n$, $n = 1$ or 2) on complexation between lanthanoid(III) and HipHT.

the series (the "gadolinium break"). This behavior has been attributed to a structural change in the hydration sphere of the lanthanide ions near the middle of the series [19–21]. In solution [22], the majority of the data supports a change in hydration number across the lanthanide series. The light lanthanides (La–Nd) form a series with a hydration number of nine (primary sphere) and a tricapped trigonal prism (TCTP) geometry, whereas the heavier elements (Tb–Lu) apparently form octahydrates with square anti-prismatic structures. For the hydrated ions in the middle of the series (Nd–Tb), there is either some type of transitional structure between these two geometries or else both hydrate structures exist in rapid equilibrium. These conclusions are supported [22] by data from X-ray and neutron diffraction, from fluoresence, Raman and visible spectroscopy, and from thermodynamic and exchange kinetics. They are also in agreement with data [22] on the apparent molal volumes, relative viscosities, molal heat capacities, heat of dilution, electrical conductance and entropies of hydration. Plots of these properties as a function of the lanthanide ionic radius showed the general pattern of an early minimum and a mid-series maximum (an "S-shape") from La to Lu.

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