Thermodynamics of complexation of isatin-3-thiosemicarbazone (HIT) and other related derivatives with some metal ions

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Proton-ligand formation constants of isatin-3-thiosemicarbazone (HIT) ; *N*-acetylisatin-3-thiosemicarbazone (HAIT) and 5-(*p*-nitrobenzoyl)-1,2,4-triazino[5,6-*b*]indole-3-thione (HBITr) ligands and their corresponding metal-ligand formation constants with Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, UO_2^{2+} and Th^{4+} ions were determined pH-metrically at 10, 20, 30 and 40 ºC in 75 %(v/v) ethanol–water. The thermodynamic parameters (ΔG, ΔH and ΔS) were also evaluated. It was found that both log K_1 and $-\Delta H_1$, for HIT and HAIT-complexes are somewhat larger than log K_2 and $-\Delta H_2$, indicating a change in the dentate character of these ligands from tridentate (ONN-donors) in 1:1 chelates to bidentate (ON-donors) in 1:2; M:L chelates. In contrast, the values of log K_2 and $-\Delta H_2$ for HBITr-complexes are somewhat larger than log K_1 and $-\Delta H_1$, indicating a strong *trans*-effect for the second coordination. The dissociation process is non-spontaneous, endothermic and entropically unfavourable while the complexation process is spontaneous, exothermic and entropically favourable. The thermodynamic parameters were separated into their electrostatic (el) and non-electrostatic (non) constituents.
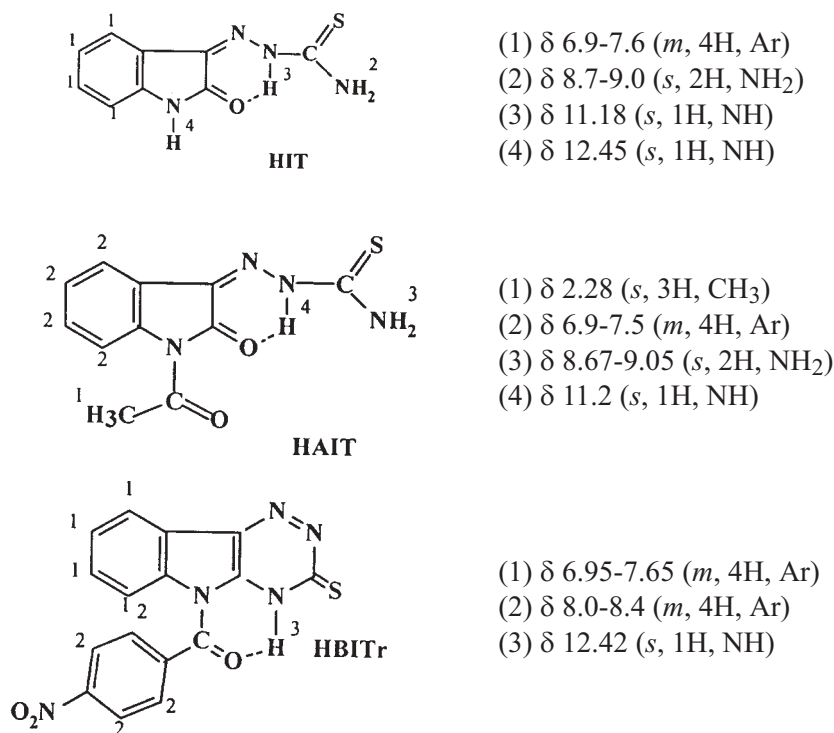
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INTRODUCTION

The antifungal activities of thiosemicarbazones and their corresponding metal chelates is substitution dependent with the chemical nature of the segment attached to the thione (C=S) carbon atom having the greatest effect.[1–6] Similarly, substitution in the ring system of Schiff bases derived from compounds containing carbonyl (C=O) groups attached to *N*-heterocyclic ring systems, thiosemicarbazides and their corresponding metal chelates highly affects the biological activity of these compounds.[1]

In this study, three different Schiff bases derived from isatin and thiosemicarbazide were used (Scheme 1). Isatins possess diverse biological activities.[2] Sulphur-containing substituted hydrazones also possess a wide spectrum of biological acitivites,[3–6] and, in many cases, coordination of these compounds to a transition metal

ion enhances their activities.[6] These findings stimulated our interest to study the effects of temperature, nature of the central metal ion, medium and structure of the ligands on the stability of Schiff base complexes derived from isatin and thiosemicarbazide; isatin-3-thiosemicarbazone (HIT), *N*-acetylisatin-3-thiosemicarbazone (HAIT) and 5-(*p*-nitrobenzoyl)-1,2,4-triazino [5,6-*b*]indole-3-thione (HBITr).

(1) δ 6.9-7.6 (*m*, 4H, Ar)
(2) δ 8.7-9.0 (*s*, 2H, NH$_2$)
(3) δ 11.18 (*s*, 1H, NH)
(4) δ 12.45 (*s*, 1H, NH)

HIT

(1) δ 2.28 (*s*, 3H, CH$_3$)
(2) δ 6.9-7.5 (*m*, 4H, Ar)
(3) δ 8.67-9.05 (*s*, 2H, NH$_2$)
(4) δ 11.2 (*s*, 1H, NH)

HAIT

(1) δ 6.95-7.65 (*m*, 4H, Ar)
(2) δ 8.0-8.4 (*m*, 4H, Ar)
(3) δ 12.42 (*s*, 1H, NH)

HBITr

^{1}H NMR of HIT, HAIT and HBITr ligands in DMSO, δ$_{TMS}$

Scheme 1.

EXPERIMENTAL

All chemicals, metal salts and solvents were either Aldrich or BDH products.

Analyses and physical measurements

Electronic spectra were recorded at room temperature on Jasco V.550 UV/Vis spectrophotometer. IR spectra, as KBr discs, were recorded on a Perkin-Elmer 437 IR spectrometer (200 – 4000 cm^{-1}). ^{1}H-NMR spectra in DMSO-d$_6$ were recorded on a Varian FT – 290.90 MHz spectrometer using TMS as an internal standard. Mass spectra were recorded at 70 eV and 300 ºC on a Hewlett Packard MS 5988 Mass spectrometer. Microanalyses for carbon, hydrogen, nitrogen and sulphur were carried out at the Microanalytical Centers, Cairo and Ain Shams Universities, Cairo, Egypt.

Potentiometric measurements

Appropriate aliquots of standard solutions of metal nitrates (0.001 M) and ligands (0.003 M) in 75 % (v/v) ethanol–water medium were titrated potentiometrically with 0.07 M KOH. The pH val-

ues were recorded on a WTW-D-8120 Weilheim digital pH-meter fitted with a combined glass-calomel electrode with an accuracy of ±0.01 units. The ionic strength of the medium was kept virtually constant at 0.05 M with KNO_3 as background electrolyte. The temperature was maintained constant by use of double-jacketed cells with water circulated from a constant-temperature bath. Purified nitrogen gas was bubbled through the solution before and during the titrations. Multiple titrations were carried out for each system. The pH-meter readings were corrected.[7]

Preparation and characterization of the organic ligands

HIT, HAIT and HBITr ligands (Scheme 1) were prepared according to the method cited in the literature.[8,9] The structures of the ligands were elucidated by IR, mass, ^{1}H-NMR and electronic (UV-Vis) spectroscopy, as well as microanalytical analyses. The results of the elemental analyses, % yield, m.p. ºC, and colour are given in Table I.

TABLE I. Analaytical and physical data of HIT, HAIT and HBITr ligands.

Compound M.F. (M.Wt)	Elemental analyses, %Found (Calcd.)				Colour	% Yield	M.p./ºC
	C	H	N	S			
HIT $C_9H_8N_4OS$ 220.26	48.79 (49.08)	3.44 (3.66)	25.31 (25.44)	14.44 (14.56)	Yellow	82	239–241
HAIT $C_{11}H_{10}N_4O_2S$ 262.29	50.23 (50.37)	3.80 (3.84)	21.15 (21.36)	11.90 (12.23)	Yellow	78	24496>245
HBITr $C_{16}H_9N_5O_3S$ 351.35	54.52 (54.70)	2.54 (2.58)	19.70 (19.93)	8.89 (9.13)	Lemon yellow	62	205

The mass spectra showed molecular ion peaks at m/z: 220, 262 and 351 corresponding to the molecular weights of the HIT, HAIT and HBITr ligands, respectively. Also, the base peaks were observed at m/z: 69, 192 and 65, respectively. In all mass spectra, no meta-stable ions were observed.

The electronic absorption spectra (UV-Vis) of the organic ligands in 75 % (v/v) ethanol–water displayed three bands: (i) λ_1 (361.5 – 355 nm) is associated with intramolecular charge transfer interaction involving the whole molecule; (ii) λ_2 (268 – 281.5 nm) is due to the low energy n-π* transitions of the carbonyl, thione and azomethine groups and (iii) λ_3 (247.5–251.5 nm) can be ascribed to the moderate energy π-π* transitions of both the aromatic and indole rings.

The IR spectra of the three ligands, HIT, HAIT and HBITr, showed strong bands at 1703, 1680 and 1695 cm^{-1}, respectively, belonging to ν(C=O). Also, a medium band at 1250 cm^{-1} belongs to ν(C=S) in the case of HIT and HAIT and a strong band at 1265 cm^{-1} in the case of HBITr. All ligands showed broad bands at 3160–3170 cm^{-1} ascribed to ν(NH). In addition, the IR spectra showed two bands at 3410 and 3330 cm^{-1} ascribed to ν_{as} and ν_s of the NH_2 group in the case of the HIT and HAIT ligands. In the case of the HBITr ligand, the bands at 1532 and 1310 cm^{-1} belong to ν_{as} and ν_s of the NO_2 group.[10]

Finally, the chemical shift (δ ppm) data extracted from the ^{1}H-NMR spectra of the organic ligands in DMSO-d_6 are summarized in Scheme 1. These data together with the data derived from the elemental analyses, IR, mass and electronic spectra confirmed the structure given for these ligands.

RESULTS AND DISCUSSION

Dissociation and formation constants

The potentiometric titration curves of HAIT-as an example- in the presence or absence of the studied metal ions are shown in Fig. 1. Similar curves were also obtained in
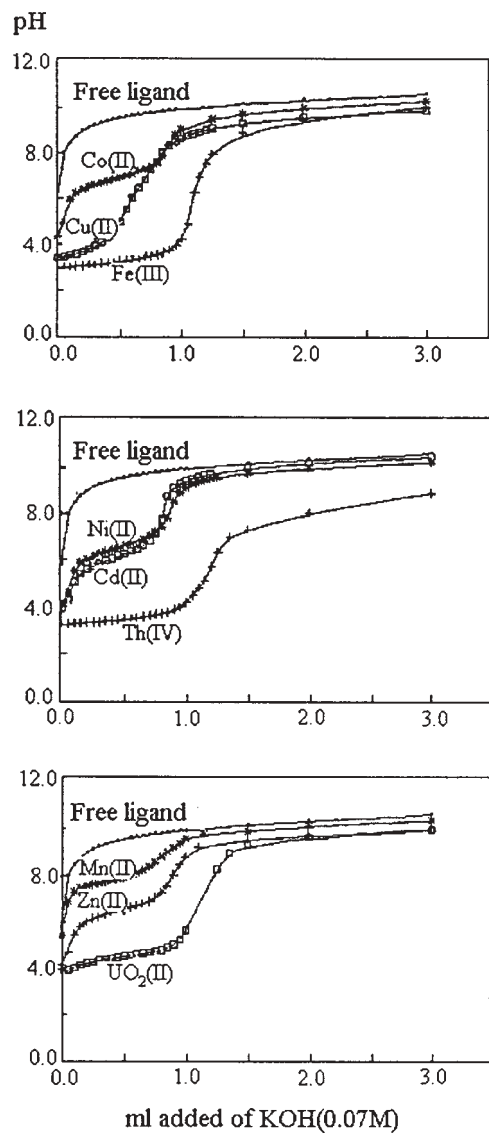
Fig. 1. Potentiometric titration curves for 3×10^{-3} M HAIT ligand in the absence and presence of 1×10^{-3} M metal ions in 75 % (v/v) ethanol-water at 30 °C, V_o = 30 mL and μ = 0.05 M (KNO$_3$).

the case of the HIT and HBITr ligands. The values of the dissociation constants of the free ligands, pK^Hs, were determined by the Albert – Serjeant method,[11] while the formation constants of their metal complexes were determined by the Irving-Rossotti method.[12] For all ligands, only one proton dissociates between a = 0.0 and a = 1.0 (a = number of moles of base / mole of ligand), suggesting that they behave as mono-protic species (HL). The values of the pK^Hs, formation constants, as well as the thermodynamic parameters in 75 % ethanol-water are given in Tables II–IV.

The pK^H values suggest that the proton dissociates from the NH group adjacent to the thione (C=S) group rather than from the NH proton of the isatin moiety in position-1, which may dissociate at higher pH values. However, similar conclusion for similar ligands was obtained by Hassan *et al.*[13,14] The pK^H value obtained for HIT, 9.55, in 75 % (v/v) ethanol-water at 30 ºC is close to that reported in the literature[13] for the same ligand under similar experimental conditions (*ca.* 9.30 in 60 % ethanol–water, corrected for the difference in the mole fraction of the solvent). The order of basicity, pK^Hs, is as follows; HIT > HAIT > HBITr. The increase in acidity or decrease in the basicity is due to the electron-withdrawing property (-I-effect) of the acetyl and *p*-nitrobenzoyl groups of the HAIT and HBITr ligands, respectively.

The pH-metric titration curves in the case of Cu(II) showed a sharp inflection at $m = 1.0$ (m = number of moles of KOH added / mole of metal ion) corresponding to the formation of the 1:1 CuL^+ complex. This could be represented by the following equilibrium:

$$Cu^{2+} + HL + OH^- \rightleftharpoons CuL^+ + H_2O \qquad \text{(at } m = 1.0) \qquad (1)$$
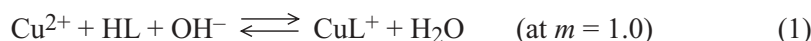
Such a feature was not observed with the other metal cations, where there was only one overlapping buffer region between $m = 0.0$ and $m = 2.0$ corresponding to the formation of bis-chelate ML_2 complexes. This could be represented by the equilibrium:

$$M^{n+} + 2HL + 2OH^- \rightleftharpoons ML_2^{+n-2} + 2H_2O \qquad \text{(at } m = 2.0) \qquad (2)$$
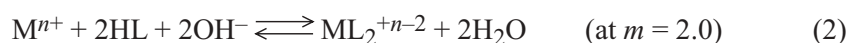
It should be mentioned that only $\log K_1$ was calculated for Mn(II), Zn(II), and Cd(II)-complexes due to precipitation of the metal hydroxide and since the maximum $\bar{n} < 1.0$.

As can be seen from Tables II–IV, the higher stability of the Fe(III) and Th(IV)-complexes is attributed to the higher charge on the these metal cations and on the basis of their higher ionization potential. Also, the higher stability of the UO_2(II)-complexes may be due to the bonded O-atoms, which increase the electrostatic attraction between the metal ion and the coordinated ligands and overcome any steric hindrance offered by the oxygen of the oxygenated UO_2^{2+} cation.[15] The greater stability of the Cu(II)-complexes, $3d^9$, is to be expected on the basis of the well-known Jahn-Teller effect. The order of the stability constants of the ligands is HIT > HAIT > HBITr which is the same as the order of basicity (pK^Hs). The variation of $\log K_1$ *vs.* pK^H is shown in Fig. 2, where a linear relation was obtained. This linearity reflects the similarity of the ionic nature of the metal- ligand interaction.[16]

Inspection of the data (Tables II–IV) reveals that $\log K_1$ for HIT and HAIT – complexes is somewhat larger than $\log K_2$. This is due to the fact that the interaction of a second bulky ligand molecule is usually weaker than the first ligand, *i.e.,* the ML_2 (1:2) species is not formed until complete formation of the ML (1:1) species. This can be ascribed to: (i) the increase in the Lewis acidity of the free metal ion (M^{+n}) as compared to the 1:1 chelated ion (ML^{+n-1}) and (ii) the steric hindrance caused by the addition of a second bulky ligand molecule on the ML^{+n-1} chelated ion. However, this is compatible with the values of ΔH for the HIT and HAIT-complexes, where $-\Delta H_1 > -\Delta H_2$, indicating a strong steric hindrance for the second coordination.

In contrast, the values of $\log K_2$ are somewhat larger than $\log K_1$ for the HBITr
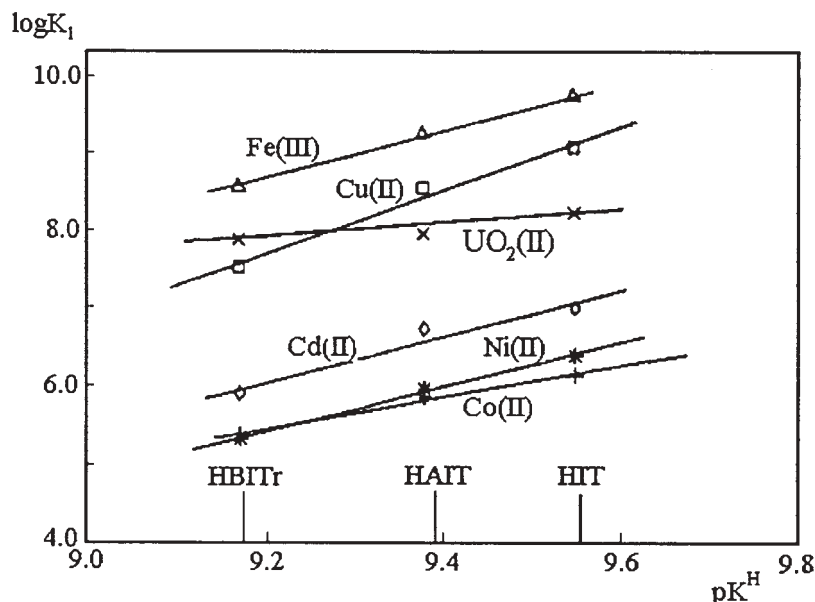
Fig. 2. Relationship between the values of the formation constants (log K_1) and the basicity of the ligands (pK^H).

complexes. This indicates a strong *trans*-effect for the second coordination.[17] This *trans*-effect was also supported by the thermodynamic data given in Table IV, where it was found that $-\Delta H_2 > -\Delta H_1$ for the HBITr-complexes which is related to the bond strengths in these complexes.

Effect of temperature

The dissociation constants of the ligands (pK^Hs), as well as the stability constants of their complexes with Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, UO_2^{2+} and Th^{4+} ions in 75 % (v/v) ethanol/water were evaluated at 10, 20, 30 and 40 ºC. The slope of the plot (pK^H or log K *vs.* 1/T) was utilized to calculate the enthalpy change (ΔH) for the dissociation or complexation process, respectively. From the free energy change (ΔG) and the enthalpy change (ΔH), the entropy change (ΔS) can be calculated using the well-known relationships:

$$\Delta G = - RT \ln K \tag{3}$$

and

$$\Delta S = (\Delta H - \Delta G) / T \tag{4}$$

The data given in Tables II–IV reveal that: (i) The pK^H values of the free ligands decrease with increasing temperature indicating that the acidity of the ligands increases with increasing temperature, *i.e.,* a higher temperature favours the dissociation or ionization process. (ii) On the basis of (i), a positive value of ΔH would be expected indicating that the dis-

TABLE II. Thermodynamic functions and stepwise formation constants of 1:1 and 1:2 metal-HIT complexes at various temperatures in 75 % (v/v) ethanol–water

| Complex | HIT | | | | | | | | kJ mol⁻¹ | | | | J mol⁻¹ K⁻¹ | |
| | 10 °C | | 20 °C | | 30 °C | | 40 °C | | $-\Delta G_{30}$ | | $-\Delta H$ | | ΔS_{30} | |
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
Mn(II)	4.95	–	4.90	–	4.88	–	4.86	–	28.29	–	2.51	–	85.16	–
Fe(III)	9.73	9.62	9.70	9.60	9.66	9.58	9.64	9.58	55.95	55.49	2.17	1.92	177.51	176.80
Co(II)	6.12	5.62	6.09	5.58	6.06	5.54	6.00	5.50	35.10	32.09	13.58	4.43	71.04	91.30
Ni(II)	6.35	5.98	6.30	5.90	6.32	5.87	6.20	5.81	36.60	34.01	12.53	8.57	79.44	83.99
Cu(II)	9.08	–	9.04	–	9.00	–	8.95	–	52.15	–	6.69	–	150.05	–
Zn(II)	6.94	–	6.60	–	6.53	–	6.45	–	37.82	–	14.12	–	23.69	–
Cd(II)	6.97	–	6.94	–	6.92	–	6.87	–	40.11	–	11.28	–	95.15	–
Th(IV)	9.45	9.35	9.43	9.38	9.40	9.37	9.40	9.35	54.45	54.32	3.68	1.84	167.56	173.20
UO₂(II)	8.22	8.14	8.20	8.12	8.15	8.05	8.10	8.00	47.22	46.63	8.10	5.01	128.12	137.35
pK^H	9.75	–	9.64	–	9.55	–	9.43	–	−55.33	–	−18.26	–	−122.31	–

pK^H ± (0.04–0.06); $\log K_1$ ± (0.02–0.17); $\log K_2$ ± (0.02–0.19)

TABLE III. Thermodynamic functions and stepwise formation constants of 1:1 and 1:2 metal-HAIT complexes at various temperatures in 75 % (v/v) ethanol–water

| Complex | HAIT | | | | | | | | kJ mol^{-1} | | | | J mol^{-1} K^{-1} | |
| | 10 ºC | | 20 ºC | | 30 ºC | | 40 ºC | | $-\Delta G_{30}$ | | $-\Delta H$ | | ΔS_{30} | |
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
Mn(II)	5.17	–	5.15	–	5.11	–	5.03	–	29.58	–	2.88	–	88.13	–
Fe(III)	9.25	9.20	9.20	9.14	9.18	9.14	9.13	9.11	53.19	52.99	10.70	6.94	140.23	151.98
Co(II)	6.04	5.38	5.95	5.36	5.85	5.35	5.80	5.55	33.89	30.96	11.07	1.96	75.30	95.69
Ni(II)	6.18	5.80	6.08	5.71	6.06	5.67	6.01	5.62	35.10	32.84	10.20	7.23	82.19	84.83
Cu(II)	8.56	–	8.55	–	8.53	–	8.49	–	49.43	–	4.64	–	147.84	–
Zn(II)	6.48	–	6.30	–	6.22	–	6.31	–	36.02	–	13.96	–	72.83	–
Cd(II)	6.87	–	6.71	–	6.67	–	6.61	–	38.65	–	15.92	–	75.01	–
Th(IV)	9.01	9.05	8.96	9.01	8.93	8.96	8.88	8.89	51.73	51.90	7.65	7.06	145.50	147.96
UO$_2$(II)	8.05	7.93	8.01	7.89	7.99	7.87	8.01	7.89	46.30	45.59	3.59	1.92	140.94	144.12
pK^H	9.52	–	9.49	–	9.38	–	9.24	–	−54.36	–	−20.22	–	−112.66	–

pK^H ±0.05; $\log K_1$ ± (0.02–0.16); $\log K_2$ ± (0.01–0.16)

sociation process is accompanied by the absorption of heat and it is endothermic. (iii) The large positive values of ΔG indicate that the dissociation process is non spontaneous. (iv) The large negative values of ΔS of the dissociation process indicate that the ionization of the ligands is entropically unfavourable. (v) The large positive values of ΔS of the complexation process indicate that the complex formation is entropically favourable and the mechanism of complexation is based on hydrogen ion (H^+) liberation and the release of water.[18] (vi) The negative values of both ΔG and ΔH of the complexation process indicate that the complexation process proceeds spontaneously and exothermically, respectively, *i.e.,* the complex formation is enthalpically favourable.

In general, the abnormal higher positive values of ΔS for all the complex systems are consistent with the hypothesis that a large number of water molecules are released upon complexation with the probability of a change of the coordination number.[18] This was supported by the values of ΔH, where it was found that $-\Delta H_1 > -\Delta H_2$ for the HIT and HAIT-complexes (Tables II, III). The lower negative values of ΔH_2 were taken as good evidence for a change in the dentate characters of the HIT and HAIT ligands from tridentate (ONN- donors) in the 1:1 complexes to bidentate (ON-donors) in the 1:2, M:L, complexes, whereby the steric hindrance in the 1:2 species is relieved. Similar observations were obtained by Evans *et al.*[19] In contrast, $-\Delta H_2 > -\Delta H_1$ for the HBITr-complexes which is taken as an additional evidence for the *trans*-effect[17] of the second coordination as mentioned previously.

The higher values of the thermodynamic functions for the Cu(II)-complexes is attributed to the $3d^9$-configuration of Cu(II) which undergoes Jahn-Teller distortion. On the other hand, the lower values for the Mn(II)-complexes may be attributed to the $3d^5$ – configuration of Mn(II) which probably exists as tetrahedral $[Mn(OH_2)_4]^{2+}$ in aqueous solutions.[20]

In order to provide information on the nature of the bonding in the formed complexes, the values of ΔG, ΔH and ΔS were separated into their electrostatic (el) and non-electrostatic (non) components[21] (Table V) according to the following equations:

$$\Delta G_{non} = nRT \ln M + Rca; \quad \Delta G_{el} = Rc \exp(T/\theta) \tag{5}$$

$$\Delta H_{non} = Rca; \quad \Delta H_{el} = Rc(1-T/\theta) \exp(T/\theta) \tag{6}$$

$$\Delta S_{non} = -nR \ln M; \quad \Delta S_{el} = (-Rc/\theta) \exp(T/\theta) \tag{7}$$

$$\Delta G = nRT \ln M + Rc(a + \exp(T/\theta)) \tag{8}$$

$$\Delta H = Rc[a + (1-T/\theta) \exp(T/\theta)] \tag{9}$$

$$\Delta S = -nR \ln M - (Rc/\theta) \exp(T/\theta) \tag{10}$$

Where θ is a temperature characteristic of the solvent ($= 219$ K); M is the number of moles contained in 1000 g of water ($= 55.5$); c and a are constants and can be calculated from the above equations.
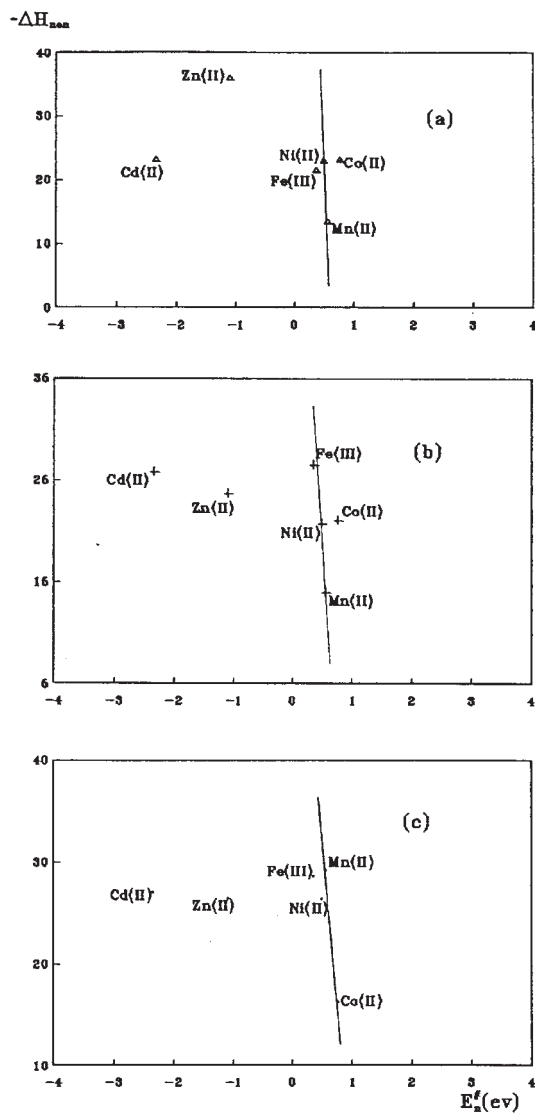
Fig. 3. Relationship between the hardness and softness, $E^{\#}_n$, of the metal ion and the non-electrostatic enthalpy change ΔH_{non}, of complex formation (a) HIT, (b) HAIT and (c) HBITr.

According to some authors,[22,23] electrostatic (el) or environment components represent long-range electrostatic forces depending on the environment and temperature; while non-electrostatic (non) or cratic components represent short-range or quantum-mechanical forces; insensitive to the environment and independent of temperature. Also, ΔH_{non} arises from changes in the ligand field stabilization (LFS) accompanying complex formation[22,23] and reflects the covalency in the bonding and the structural changes on complexation.[24] As seen from Table V, ΔH_{non} has high negative values while ΔH_{el} has positive values and, since ΔH_{non} reflects the covalent nature of the

TABLE IV. Thermodynamic functions and stepwise formation constants of 1:1 and 1:2 metal-HBITr complexes at various temperatures in 75 % (v/v) ethanol–water

| Complex | HBITr | | | | | | | | kJ mol^{-1} | | | | J mol^{-1} K^{-1} | |
| | 10 ºC | | 20 ºC | | 30 ºC | | 40 ºC | | $-\Delta G_{30}$ | | $-\Delta H$ | | ΔS_{30} | |
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
Mn(II)	5.41	–	5.16	–	5.11	–	5.05	–	29.63	–	24.65	–	16.46	–
Fe(III)	8.70	8.73	8.56	8.57	8.53	8.50	8.55	8.51	49.39	49.18	15.29	19.77	112.57	97.11
Co(II)	5.46	5.75	5.41	5.68	5.35	5.62	5.36	5.58	31.01	32.55	5.47	8.02	84.32	80.90
Ni(II)	5.54	5.85	5.35	5.65	5.30	5.57	5.18	5.45	30.71	32.26	20.06	21.81	35.18	34.43
Cu(II)	7.74	–	7.55	–	7.48	–	7.40	–	43.37	–	21.14	–	73.38	–
Zn(II)	6.57	–	6.41	–	6.36	–	6.26	–	36.81	–	17.55	–	63.52	–
Cd(II)	6.09	–	5.93	–	5.86	–	5.74	–	33.93	–	19.72	–	46.93	–
Th(IV)	9.85	9.96	9.66	9.77	9.56	9.72	9.42	9.63	55.41	56.33	24.82	19.10	100.79	122.89
UO$_2$(II)	8.19	8.30	7.95	8.05	7.84	7.92	7.70	7.76	45.42	45.88	27.04	31.34	60.63	48.05
pK^H	9.73	–	9.37	–	9.17	–	9.05	–	–53.11	–	–27.29	–	–85.24	–

pK^H ± (0.03–0.11); $\log K_1$ ± (0.02–0.12); $\log K_2$ ± (0.07–0.26)

TABLE V. Electrostatic (el) and non-electrostatic (non) thermodynamic functions*

Com-plex	HIT						HAIT						HBITr					
	$-\Delta G_{el}$	$-\Delta G_{non}$	$-\Delta H_{non}$	ΔH_{el}	ΔS_{el}	$r(\text{Å})$	$-\Delta G_{el}$	$-\Delta G_{non}$	$-\Delta H_{non}$	ΔH_{el}	ΔS_{el}	$r(\text{Å})$	$-\Delta G_{el}$	$-\Delta G_{non}$	$-\Delta H_{non}$	ΔH_{el}	ΔS_{el}	$r(\text{Å})$
Mn(II)	25.16	3.13	13.29	10.78	118.59	2.68	25.78	3.80	13.96	11.07	121.56	2.62	10.57	19.05	29.17	4.51	49.89	6.38
Fe(III)	44.71	11.24	21.35	19.18	210.94	1.51	36.81	16.38	26.49	15.80	173.66	1.83	30.96	18.43	28.58	13.29	146.00	2.18
Co(II)	22.15	12.95	23.07	9.49	104.47	3.05	23.07	10.82	20.98	9.90	108.73	2.93	24.95	6.06	16.17	10.70	117.75	2.71
Ni(II)	23.94	12.66	22.82	10.28	112.86	2.82	24.53	10.57	20.73	10.53	115.62	2.75	14.54	16.17	26.28	6.23	68.61	4.64
Cu(II)	38.90	13.25	23.40	16.71	183.48	1.74	38.44	10.99	21.14	16.51	181.27	1.76	22.65	20.73	30.88	9.74	106.81	2.98
Zn(II)	12.12	25.70	35.85	21.73	57.12	5.57	22.52	13.50	23.61	9.65	106.26	3.00	20.56	16.26	26.41	8.86	96.94	3.28
Cd(II)	27.24	12.87	22.98	11.70	128.58	2.48	22.98	15.67	25.78	9.86	108.44	2.94	17.05	16.88	27.04	7.31	80.35	3.96
Th(IV)	42.62	11.83	21.98	18.30	201.00	1.58	37.94	13.79	23.94	16.30	178.93	1.78	28.46	26.95	37.11	12.29	134.22	2.37
UO$_2$(II)	34.27	12.97	23.11	14.71	161.55	1.97	36.98	9.32	19.47	16.13	174.37	1.83	19.93	25.49	35.60	8.57	94.06	3.39

*ΔG (kJ/mol); ΔH (kJ/mol); ΔS (J/mol K)

formed complexes,[25] the expected degree of covalency exists in such systems. Also, $-\Delta G_{el} \gg -\Delta G_{non}$ for all complex systems except for the Zn(II)-HIT and Mn(II), Ni(II) and UO$_2$(II)-HBITr complexes, indicating that the complexation process is highly influenced by the temperature and environment (medium).

Regarding the covalency, a softer metal ion has a greater affinity for a softer donor.[26] In Fig. 3, the values of ΔH_{non} are plotted against the quantity $E^{\#}_n$, introduced by Klopman[27] as a measure of the softness of a metal ion in solution. A soft metal ion is characterized by a large negative value of $E^{\#}_n$ and *vice versa*. As can be seen from Fig. 3, a linear correlation with a number of scattered points (for the Zn(II) and Cd(II)-complexes) was obtained. In general, ΔH_{non} increases with the softness of the metal ion.

The metal-ligand interactions can be divided into two groups; (i) those of copper, nickel and cobalt which have high affinities for N-donor atoms and (ii) those of manganese, zinc and cadmium with intermediate affinities for both N and O-donor atoms.[28] This is consistent with the above linear correlation with some scattered points (Fig. 3).

In conclusion, the following remarks can be indicated:

(i) All ligands behave as monobasic (monoprotic) species (HL) towards the metal ions as evidenced from the titration curves.

(ii) The maximum $\bar{n}$ values were found to be ≈ 2, revealing that both ML and ML$_2$ species are formed in solution.

(iii) For the HIT and HAIT complexes, $\log K_1 > \log K_2$ indicating that the vacant sites of the metal ions are more freely available for the binding of the first ligand than for the second one.

(iv) More stable complexes, will be formed with:

– hard-hard or soft-soft interactions of the metal ions and the ligands.

– higher charges and small sizes of the metal ions.

– higher basicity of the ligands.

– lower temperatures. This is consistent with exothermic complexation.

(v) The dissociation process is non-spontaneous, endothermic and entropically unfavourable while the complexation (chelation) process is spontaneous, exothermic and entropically favourable.

И З В О Д

ТЕРМОДИНАМИКА КОМПЛЕКСИРАЊА ИЗАТИН-3-ТИОСЕМИКАРБАЗОНА (HIT) И
ДРУГИХ ОДГОВАРАЈУЋИХ ДЕРИВАТА СА ЈОНИМА НЕКИХ МЕТАЛА

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Проучаване су pH-метријски константе стабилности протон-лиганд за изатин-3-тио-семикарбазон (HIT), *N*-ацетилизатин-3-тиосемикарбазон (HAIT) и 5-(*p*-нитробензо-ил)-1,2,4-триазино [5,6-*b*]индол-3-тион (HBITr) као лиганде и њихове одговарајуће кон-

станте стабилности метал-лиганд са Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, UO_2^{2+} и Th^{4+} јонима у смеши 75 % етанол – вода на 10, 20, 30 и 40 ºC. Изведени су и одговарајући термодинамички параметри (ΔG, ΔH и ΔS). Нађено је да су и log K_1 и $-\Delta H_1$ за HIT и HAIT комплексе нешто већи од log K_2 и $-\Delta H_2$, указујући на промену у дентатном карактеру ових лиганада од тридентата (ONN-донори) у 1:1 хелатима у бидентате (ON-донори) у 1:2; M:L хелатима. Насупрот овоме, вредности log K_2 и $-\Delta H_2$ за HBITr комплексе су нешто већи од log K_1 и $-\Delta H_1$ указујући на јак *trans*-ефекат за другу координацију. Процес дисоцијације није спонтан, ендотерман је и ентропијски неповољан, док је процес комплексирања спонтан, егзотерман и ентропијски повољан. Термодинамички параметри су раздељени на њихове електростатичке и нееелектростатичке компоненте.

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