Metal Complexes of Triazine Schiff Bases
Spectroscopic and Thermodynamic Studies of Complexation of Some Divalent Metal Ions with
3-[2-(1-Acetylethylidene)hydrazino]-5,6-diphenyl-1,2,4-triazine

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Metal complexes of some divalent metal ions (Co, Ni, Cu, and Zn) with 3-[2-(1-acetylethylidene)-hydrazino]-5,6-diphenyl-1,2,4-triazine (AHDT) as a Schiff base have been investigated potentiometrically and spectrophotometrically and found to have stoichiometric formulae 1 1 and 1 2 n(M) n(L). Formation constants of the proton—ligand and metal—ligand complexes have been determined potentiometrically at different temperatures (10—50 °C) and 0.1 mol dm^{-3} ionic strength (KNO$_3$) in 75 vol. % dioxane—water solution. The standard thermodynamic parameters, viz. $\Delta G°$, $\Delta H°$, and $\Delta S°$, terms for the proton—ligand and the stepwise metal—ligand complexes have been evaluated. Thermodynamic functions have been analyzed in terms of the electrostatic (el) and non-electrostatic (cratic, c) components. $\Delta H_c°$ was found to be linearly correlated with the acceptor number of the metal ion (AN_M), whereas $\Delta H_{el}°$ was linearly correlated with the ionic radii of the metal ion. UV VIS and IR spectroscopy have been used to characterize the free ligand AHDT and the compositions, structures, formation constants, and analytical applications of its complexes with Cu(II), Ni(II), and Co(II) ions. The formation constant values obtained from spectrophotometric studies are found to be consistent with those obtained from potentiometric studies.

Numerous compounds containing 1,2,4-triazines moiety are well known in natural materials and show interesting biological and antiviral properties [1—3]. Many derivatives of 1,2,4-triazine compounds form coloured complexes with different metal ions and can be used as analytical reagents for their determinations [4—9]. In the preceding communication [9] complex formation of copper(II) ion with 3-(2-phenylethylidene)hydrazino-5,6-diphenyl-1,2,4-triazine, which contains nitrogen donor atoms, was investigated using UV VIS and IR spectroscopy, and electrochemical methods. It is believed that ligands containing different donor atoms like O—N type form more stable complexes than either O—O or N—N types [10]. Therefore we are extending our investigations to a new ketonic Schiff base of triazine which contains O—N ligand system, viz. 3-[2-(1-acetylethylidene)hydrazino]-5,6-diphenyl-1,2,4-triazine (AHDT) which forms stable coloured complexes with transition metal ions.

This work aims to study the complex formation of AHDT with Co(II), Ni(II), Cu(II), and Zn(II) in mixed dioxane—water solutions using spectroscopic and potentiometric methods to throw some light on their compositions, structures, and analytical applications. Thermodynamic parameters are computed and analyzed in order to investigate the bond character between the metal and ligand.

The main characteristic IR vibrational bands of the free ligand AHDT at 3329 cm^{-1}, 1643 cm^{-1}, and 1581 cm^{-1} could be assigned to NH, C=O, and C=N stretching frequencies, respectively [9, 11, 12]. The shift of $\tilde{\nu}(\nu(C=O))$ and $\tilde{\nu}(\nu(NH))$ to lower frequencies than expected might be due to the formation of a strong hydrogen bond between the oxygen of the carbonyl group and the hydrogen of the NH group [12] (structure A in Scheme 1).

The electronic absorption spectra of AHDT in 75 vol. % dioxane—water solution within the region 200—600 nm display two absorption bands (Fig. 1) (λ_{max}, 286 nm and 246 nm having molar absorptivities $\varepsilon = 1.8 \times 10^4$ dm^3 mol^{-1} cm^{-1} and 2.1×10^4 dm^3 mol^{-1} cm^{-1}, respectively). The first band is due to an enhanced $n \to \pi^*$ transition (R band) [6—9],

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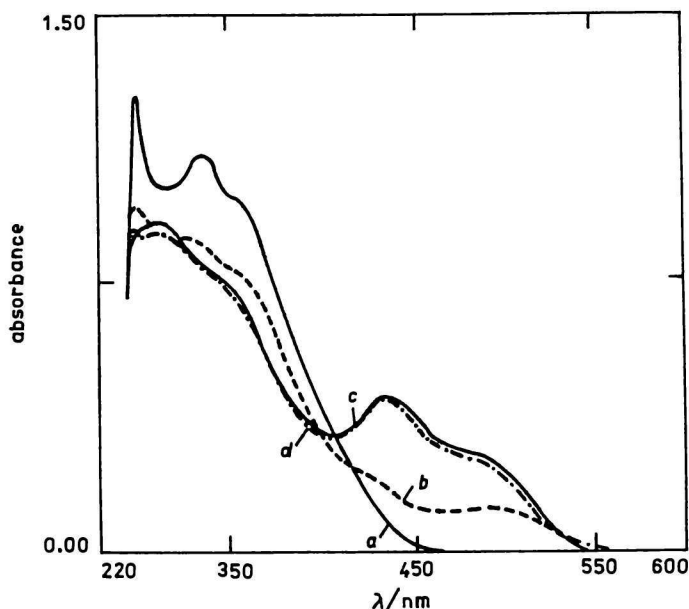*The author to whom the correspondence should be addressed.
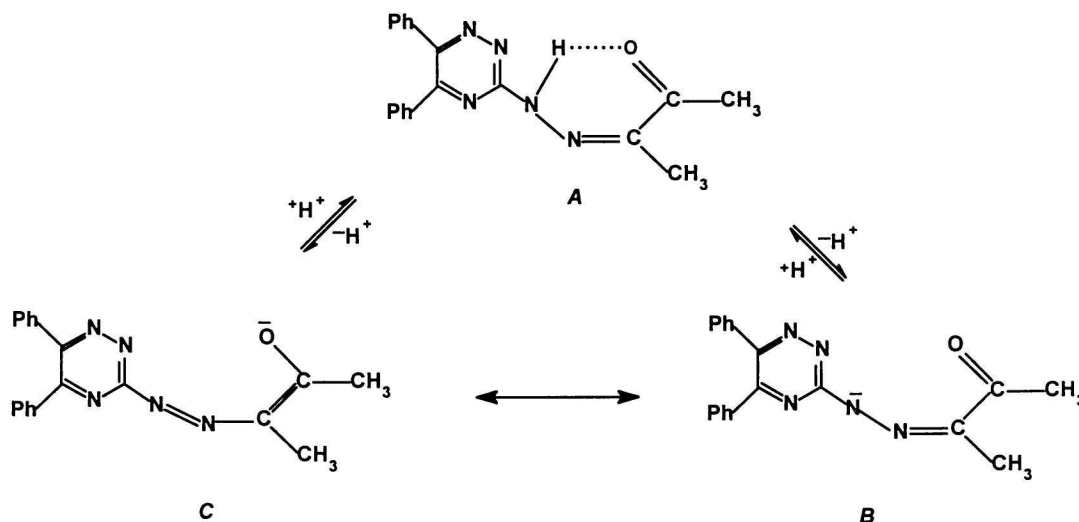
Scheme 1

Fig. 1. Absorption spectra of AHDT, 6×10^{-5} mol dm^{-3} solution in 75 vol. % dioxane—water, 25 °C and pH 5.0 (*a*); a mixture of AHDT with 3×10^{-5} mol dm^{-3} Cu(II) at pH 5.0 (*b*); a mixture of AHDT with 3×10^{-5} mol dm^{-3} Co(II) at pH 8.0 (*c*); a mixture of AHDT with 3×10^{-5} mol dm^{-3} Ni(II) at pH 8.0 (*d*).

while the second band could be attributed to an enhanced $\pi \rightarrow \pi^*$ transition over the whole conjugated system (K band) [13].

The absorption spectra of AHDT at different pH values exhibit two isosbestic points at about 292 nm and 334 nm (Fig. 2). This reveals that the solution of AHDT contains at least two distinct species in an equilibrium depending on the pH of the medium (Scheme 1). Species C is present at high pH values and has a bathochromic shift as a result of increasing the extent of chain conjugation [14], compared with species B. Furthermore, comparison of species B and C shows that tautomer C which includes deprotonized form of enolic OH group might be formed in a strong

alkaline medium ($\approx$ pH 13) and this tautomer includes a —N=N— group which has $\lambda_{max} > 350$ nm (Fig. 2) [15]; consequently the dissociated proton under our work conditions might be present mainly in the hydrazo form.

The dissociation constant (pK^H) of the free ligand AHDT has been determined spectrophotometrically by applying a modified limiting absorbance method [16] and equals 11.95 ± 0.05.

Upon mixing a solution of the ligand with the metal ions, namely Co(II), Ni(II), and Cu(II), new visible bands (Fig. 1) were observed and the colour changed to an orange-red in case of Co(II) and Ni(II) and to wine red for Cu(II). This persuaded us to in-
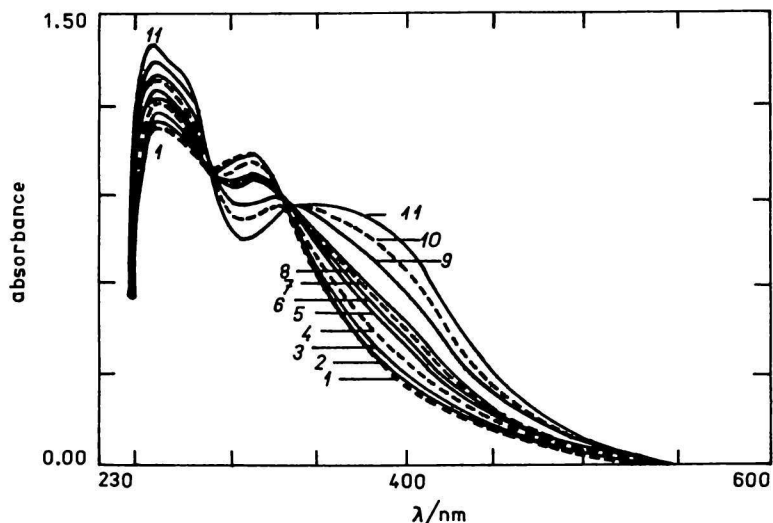
Fig. 2. The UV VIS spectra of 6×10^{-5} mol dm^{-3} AHDT in 75 vol. % dioxane—water at different pH values (adjusted by HCl and KOH solutions), $\mu = 0.10$ mol dm^{-3} KNO$_3$. pH: *1.* 8.0; *2.* 8.5; *3.* 9.0; *4.* 9.5; *5.* 10.0; *6.* 11.0; *7.* 11.7; *8.* 12.2; *9.* 12.7; *10.* 13.0; *11.* 13.3.

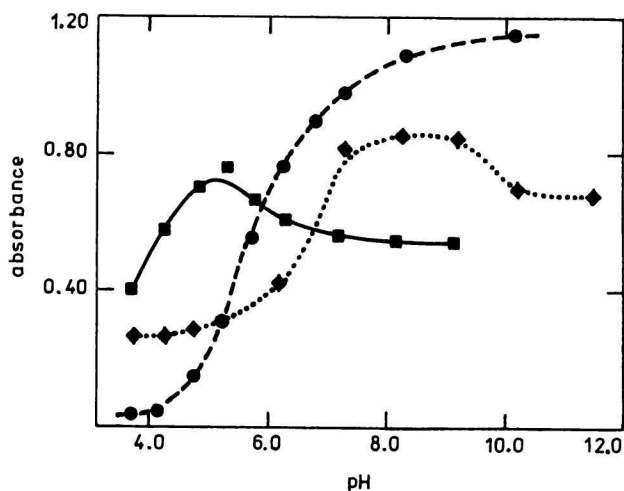**Fig. 3.** The pH *vs.* absorbance dependence of the mixtures of 3×10^{-4} mol dm^{-3} AHDT with 1×10^{-4} mol dm^{-3} Cu(II) (■, $\lambda = 480$ nm), Ni(II) (●, $\lambda = 475$ nm), and Co(II) (♦, $\lambda = 450$ nm) in 75 vol. % dioxane—water solution, $\mu = 0.10$ mol dm^{-3} (KNO$_3$) with reference ligand.

vestigate the optimum conditions of the formation of these complexes. It was found that the intensities for the observed peaks are dependent upon the pH values of the medium in the range 2—12. Fig. 3 shows the optimum pH range of the complex formation which was found to be 5.0 for the Cu(II) complexes and 8.0 for both Co(II) and Ni(II) complexes.

Stoichiometry of the complexes under investigation was determined by means of the mole ratio and continuous variation methods [17, 18]. Fig. 4 shows the absorption spectra of Cu(II)—AHDT complexes as a function of the ligand concentration (as a representa-

tive example). The spectrum reflects that the maximum absorbance at about 430 nm increased rapidly, while the maximum at $\approx$ 480 nm increased slightly until a 1 1 metal/ligand mole ratio was reached. On exceeding the ratio 1 1, a slight increase was found for the peak at 430 nm and a rapid increase for the peak at $\approx$ 480 nm until the mole ratio reached 1 2. On exceeding the 1 2 mole ratio the two peaks overlapped forming a single peak with a maximum at $\approx$ 420 nm and a steady increase in the absorbance was observed. This means that the predominate species formed were 1 1 and 1 2, n(M) n(L), respectively.

Analysis of the data at various wavelengths proved that Cu(II), Co(II), and Ni(II) ions form two main complex species with stoichiometric ratios of 1 1 and 1 2 n(M) n(L) as shown in Figs. 5 and 6.

Spectrophotometric data were used to calculate the formation constants of the 1 : 1 Co(II)—, Ni(II)—, and Cu(II)—AHDT complexes by applying the limiting absorbance method [16]. The log K_1 values were calculated and found to be 7.32 ± 0.04, 7.93 ± 0.06, and 8.80 ± 0.08, respectively. Thus the trend for the complex stability follows the order: Cu(II), Ni(II), Co(II). This order agrees with the conclusions of *Irving* and *Williams* [19].

Under the optimum conditions, using a constant concentration of AHDT (1×10^{-3} mol dm^{-3}) and varying Cu(II), Co(II), and Ni(II) concentrations in water—dioxane solutions, it was found that the system obeys Beer's law with numerical values of standard deviations of 0.002, 0.006, and 0.003, respectively within the metal concentration range 1×10^{-5}—4×10^{-4} mol dm^{-3} for Cu(II) and 1×10^{-5}—2×10^{-4} mol dm^{-3} for Co(II) and Ni(II) complexes. The molar absorptivity (ε) values at 500 nm for Cu(II), Co(II), and Ni(II) complexes were 6.6×10^3 dm^3 mol^{-1} cm^{-1},
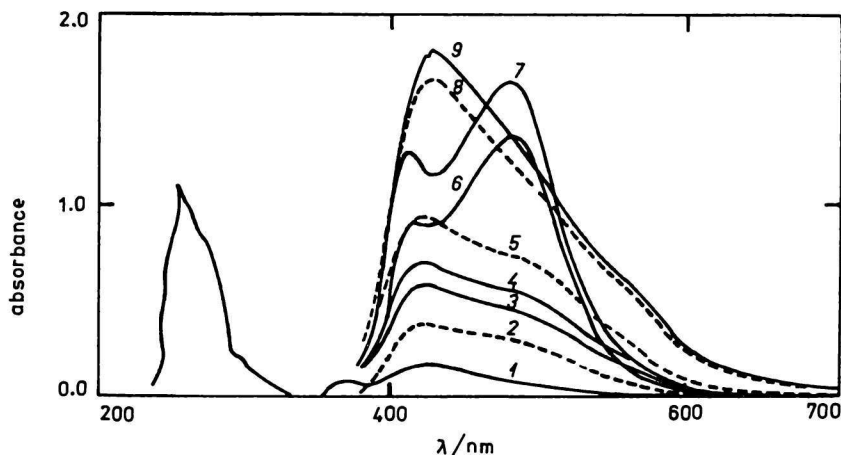
Fig. 4. Electronic absorption spectra of Cu(II)—AHDT complexes in 75 vol. % dioxane—water at pH 5.0 with reference ligand, [Cu(II)] $= 3.5 \times 10^{-4}$ mol dm^{-3}, [AHDT]: *1.* 1×10^{-4} mol dm^{-3}; *2.* 2×10^{-4} mol dm^{-3}; *3.* 3×10^{-4} mol dm^{-3}; *4.* 3.5×10^{-4} mol dm^{-3}; *5.* 4.5×10^{-4} mol dm^{-3}; *6.* 5.5×10^{-4} mol dm^{-3}; *7.* 7×10^{-4} mol dm^{-3}; *8.* 9×10^{-4} mol dm^{-3}; *9.* 1×10^{-3} mol dm^{-3}.
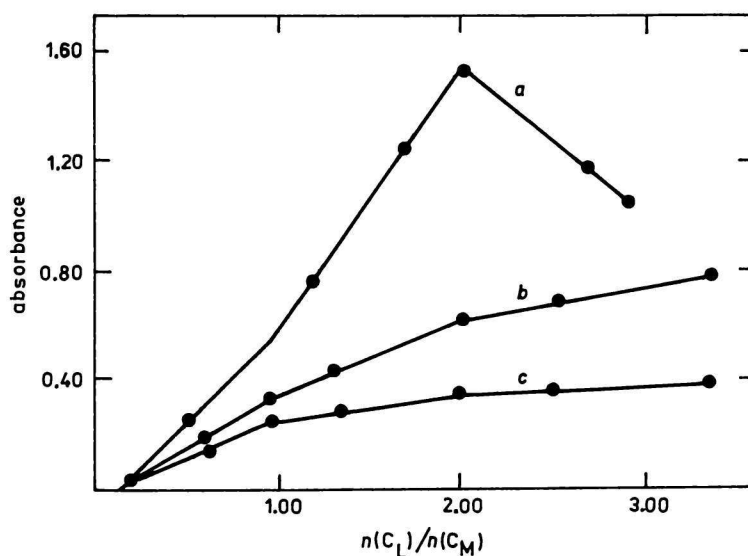

Fig. 5. Mole ratio method for Cu(II)—, Ni(II)—, and Co(II)—AHDT complexes in 75 vol. % dioxane—water, $\mu = 0.10$ mol dm^{-3} (KNO$_3$) using reference ligand. *a)* [Cu(II)] $= 3.5 \times 10^{-4}$ mol dm^{-3} and [AHDT] $= 1 \times 10^{-4}$—1×10^{-3} mol dm^{-3} at pH 5.0 and $\lambda = 485$ nm; *b)* [Ni(II)] $= 6 \times 10^{-5}$ mol dm^{-3} and [AHDT] $= 2 \times 10^{-5}$—2×10^{-4} mol dm^{-3} at pH 8.0 and $\lambda = 420$ nm; *c)* [Co(II)] $= 6 \times 10^{-5}$ mol dm^{-3} and [AHDT] $= 2 \times 10^{-5}$—2×10^{-4} mol dm^{-3} at pH 8.0 and $\lambda = 420$ nm.

8.0×10^3 dm^3 mol^{-1} cm^{-1}, and 1.4×10^4 dm^3 mol^{-1} cm^{-1}, respectively, indicating that AHDT can be readily utilized as a sensitive reagent for microanalytical determination of copper(II), cobalt(II), and nickel(II) (Fig. 7).

The pH-metric titration curves of the free AHDT $(3 \times 10^{-3}$ mol dm$^{-3})$ ligand in the absence and presence of different metal ions $(1 \times 10^{-3}$ mol dm$^{-3})$, namely Co(II), Ni(II), Cu(II), and Zn(II) show distinct inflection points at $m = 1$ and 2 ($m =$ number of moles of base added per mol of the metal ion), indicating the stepwise formation of [ML] and [ML$_2$] complex species, respectively, as shown in Fig. 8. This

conclusion is in harmony with spectrophotometric results. The titration curve of the free ligand is greatly different from those of its mixtures with metal ions due to the complex formation.

The dissociation constant values of the free ligand were calculated at different temperatures and collected in Table 1. The structure of AHDT shows a monobasic ligand with the value of p$K^{H} = 11.80$ at 30 °C which agrees well with the value obtained from spectrophotometric studies. Ligands containing the Ar—NH—N=CR$_2$ group are normally ionized in moderately alkaline media, and have pK^{H} values in the range 6—9 [20, 21]. The high basicity of the AHDT
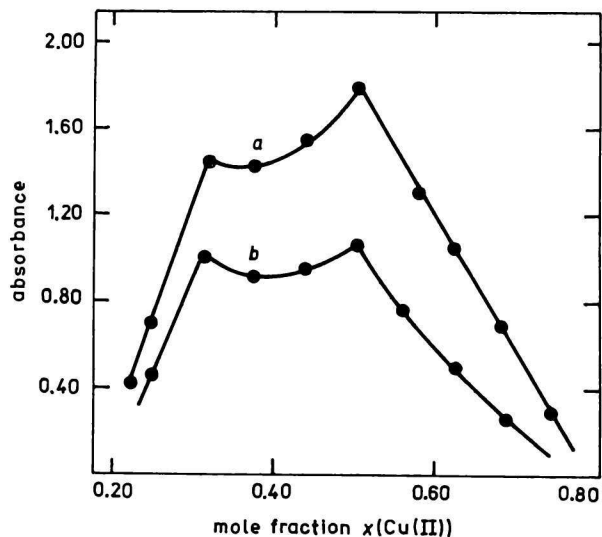
Fig. 6. Continuous variation method for Cu(II)—AHDT complex in 75 vol. % dioxane—water, total molar concentration $= 1 \times 10^{-3}$ mol dm^{-3} at $\lambda = 480$ nm (*a*) and $\lambda = 520$ nm (*b*).
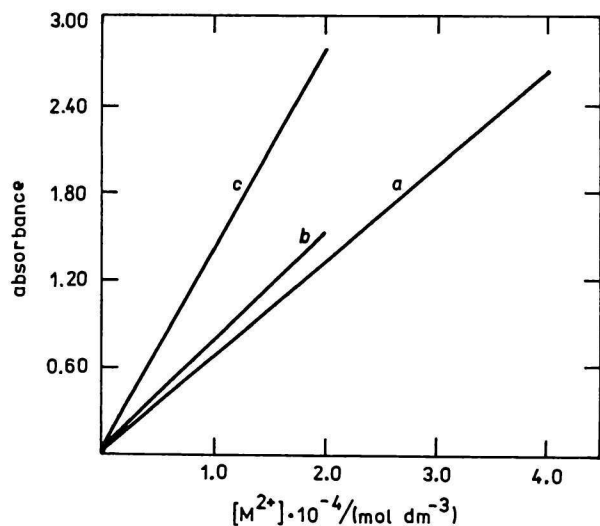

Fig. 7. Validity of Beer's law for the complexes of 1×10^{-3} mol dm^{-3} AHDT in 75 vol. % dioxane—water with Cu(II), Co(II), and Ni(II) of various concentrations, $\mu = 0.10$ mol dm^{-3} (KNO$_3$) using reference ligand at $\lambda = 500$ nm. *a*) Cu(II)—AHDT at pH 5.0; *b*) Co(II)—AHDT at pH 8.0; *c*) Ni(II)—AHDT at pH 8.0.

Fig. 8. Potentiometric titration curves of a solution containing 3×10^{-3} mol dm^{-3} AHDT (30 cm^3) (*a*) and in the presence of 1×10^{-3} mol dm^{-3} metal ions: Co(II) (*b*); Ni(II) (*c*); Cu(II) (*d*); Zn(II) (*e*) in 75 vol. % dioxane—water at 30 °C, $\mu = 0.10$ mol dm^{-3}, adding 0.090 mol dm^{-3} KOH.

tion constants of different metal ions with AHDT increase in the following order: Zn(II), Co(II), Ni(II), Cu(II).

This order agrees with that obtained from spectrophotometric data which is again consistent with *Irving* and *Williams* series [19]. A number of interpretations are given for the above order among which are the ionization potential, ionic radius, and the electronegativity of the metal ion. The greater stability of Cu(II) complex is due to the Jahn—Teller effect. Furthermore, the order largely reflects the change of the heats of complex formations across the series, which arises from a combination of the influences of both the polarizing ability of the metal ion and the crystal field stabilization energies.

Unexpected small differences between $\log K_1$ and $\log K_2$ of the formed complexes (Table 1) reveal that the second chelate ligand anion favours the formation of a more symmetrical ML$_2$ complex species and offsets the expected steric hindrance of the bulky ligand molecules.

Distribution of the species as a function of pH was calculated using known expressions [23]. Fig. 9 shows that the mole ratio of ML$^+$ increases rapidly and attains a maximum value at pH values 5.70, 5.80, 6.50, and 6.90 for Cu(II), Ni(II), Co(II), and Zn(II), respectively, then it decreases, while free M(II) and ML$_2$ change monotonically with pH.

The standard thermodynamic parameters, *viz.* ΔG°, ΔH°, and ΔS° values of AHDT and its metal complexes at 30 °C were calculated from Arrhenius

ligand suggests that the proton of the hydrazo group forms a strong hydrogen bond with the oxygen atom of the carbonyl group, as previously indicated from the IR spectra of the free ligand, to produce a six-membered ring, so it is less ionizable [22].

The formation constant values of the stepwise complex formation at different temperatures and their thermodynamic parameters are summarized in Table 1. These values indicate that the complex forma-
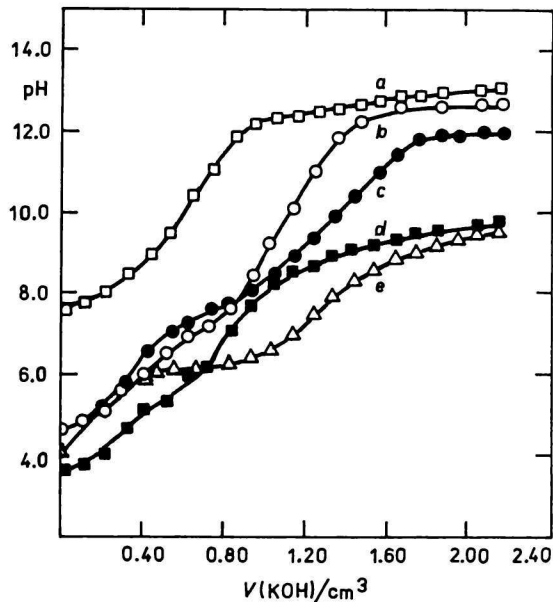
Table 1. Stepwise Formation Constants and Thermodynamic Parameters $\Delta G^\circ/(\text{kJ mol}^{-1})$, $\Delta H^\circ/(\text{kJ mol}^{-1})$, and $\Delta S^\circ/(\text{J mol}^{-1}\ \text{K}^{-1})$ of AHDT with Co(II), Ni(II), Cu(II), and Zn(II) Ions ($\mu = 0.10\ \text{mol dm}^{-3}$ KNO$_3$; 75 vol. % Dioxane—Water)

Cation	Symbol	$-\Delta G^\circ$	$-\Delta H^\circ$	ΔS°	$\theta/{}^\circ$C				
					10	20	30	40	50
H$^+$	pK^{H}	−68.50	−36.59	−105.30	12.26	12.02	11.80	11.64	11.42
Co(II)	$\log K_1$	42.20	57.94	51.96	7.94	7.65	7.27	6.92	6.64
	$\log K_2$	35.13	54.13	62.72	6.69	6.37	6.05	5.74	5.45
	$\log(K_1 K_2)$	77.33	112.12	114.84	14.63	14.02	13.32	12.66	12.09
	$\log(K_1/K_2)$				1.25	1.28	1.22	1.18	1.19
Cu(II)	$\log K_1$	50.62	41.78	29.14	9.21	8.94	8.72	8.38	8.24
	$\log K_2$	40.95	46.56	18.50	7.64	7.32	7.05	6.79	6.57
	$\log(K_1 K_2)$	91.56	88.51	10.09	16.85	16.26	15.77	15.17	14.81
	$\log(K_1/K_2)$				1.57	1.62	1.67	1.59	1.67
Ni(II)	$\log K_1$	44.88	45.97	3.60	8.30	8.02	7.73	7.50	7.24
	$\log K_2$	38.31	44.88	21.68	7.11	6.85	6.60	6.35	6.07
	$\log(K_1 K_2)$	83.19	90.85	25.29	15.41	14.87	14.33	13.85	13.31
	$\log(K_1/K_2)$				1.19	1.17	1.13	1.15	1.17
Zn(II)	$\log K_1$	38.73	60.83	72.97	7.32	7.00	6.67	6.30	5.92
	$\log K_2$	32.24	34.54	7.62	5.90	5.72	5.55	5.33	5.10
	$\log(K_1 K_2)$	70.92	95.37	80.68	13.22	12.72	12.22	11.63	11.02
	$\log(K_1/K_2)$				1.42	1.28	1.12	0.97	0.82
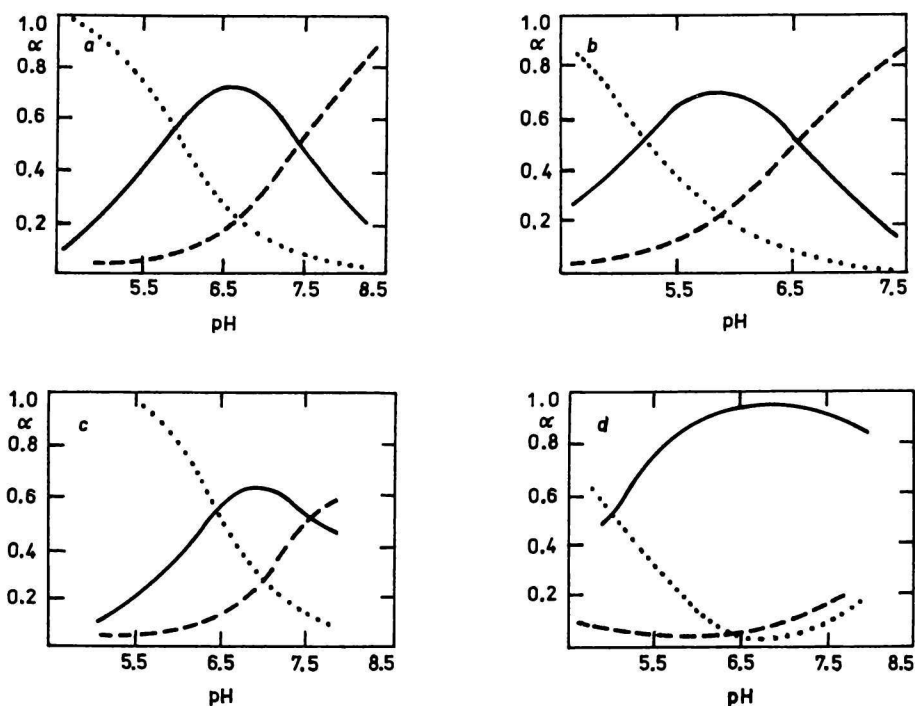
Fig. 9. Distribution diagram of complex species as a function of pH values for Cu(II)— (*a*), Co(II)— (*b*), Ni(II)— (*c*), and Zn(II)— AHDT (*d*) systems in 75 vol. % dioxane—water at 30 °C ($\cdots$ M^{2+}, —— ML$^+$, – – – ML$_2$).

plot and collected in Table 1. The positive values of ΔG° and ΔH° of the free ligand indicate that the deprotonation process of AHDT is nonspontaneous, endothermic and enhanced by increasing temperature. The high negative value of ΔS° is due to the

conversion of translational entropy of AHDT ligand which disfavours its deprotonation. Similar observations have been reported by *Abdel-Moez et al.* [24]. On the other hand, the high negative values of ΔG° and ΔH° associated with K_1 and K_2 (Table 1) of the com-

plex formation indicate that the complexation tends to proceed exothermally and spontaneously. Furthermore, the positive values of ΔS^o, favouring the complex formation, reveal that the loss of entropy accompanying the formation of metal-to-ligand bonds and the conversion of translational entropy of the free ligand are offset by the gain resulting from the liberation of solvent molecules from the metal ions [25].

The ΔH^o and ΔS^o values associated with K_1 are generally higher than that of K_2, again with the exception of Cu(II) complexes where $\Delta H_1^o < \Delta H_2^o$. This might be attributed to the geometrical change from "six-coordinate" for CuL$^+$ to "four-coordinate" for CuL$_2$ as a result of the Jahn—Teller effect [26]. The CuL$^+$ complex ion would attain six-coordinate sphere through coordination of the Cu(II) ion to one ligand anion and four water molecules (I), while the CuL$_2$ complex would be four-coordinated by linking two ligand anions (III) [27]. This interpretation was confirmed by the visible spectral data of Cu(II) ions in the presence of the AHDT ligand where the $d \rightarrow d$ transitions ($\lambda_{max} \approx 480$ nm) indicate that the geometrical shape of the higher species (CuL$_2$) is square-planar [27].

The other metal complexes, on the other hand, would retain their most probable octahedral structure in both 1 1 (I) and 1 2 n(M) n(L) complexes (II); water molecules would complete the coordina-

tion sphere [7, 27]. On the basis of this interpretation the plausible structures of the complexes under investigation are I—III. The ΔH^o values associated with the first step of complex formation increase in the order Zn(II), Co(II), Ni(II), Cu(II). This order agrees with the increase of the degree of covalency in the ligand-metal bonds [25]. Moreover, this order is opposite to that observed in the values of the formation constants of ML$^+$ species ($\log K_1$) (Table 1), as the latter values are dependent on the electrostatic forces, which is more pronounced in the case of this complex ion as compared to complex ML$_2$. This interpretation is confirmed also by the linearity of ΔS^o (Table 1) with the values of $1/r$, where r are the ionic radii of divalent metal ions ($\{\Delta S_1^o\} = 140.2 - 91.5 \times \{1/r\}$, c.c. = 0.999) with the exception of Cu(II) complexes. This indicates the predominant role of the electrostatic forces involved in the ion association processes, a fact which is in harmony with the Bjerrum original ion pair concept. Similar observations were reported by *Martell* [28] and *Stavely* and *Randall* [29].

It is convenient to analyze any thermodynamic function ΔX^o ($X = G^o, H^o$, and S^o) into two parts: *a*) ΔX_c^o (cratic), a temperature-independent component intrinsic to the molecules or ions and arising out of short range or covalent forces insensitive to the environment, *b*) ΔX_{el}^o, a temperature-dependent part, owing to the interaction of the dipoles or ions with

I

II

III
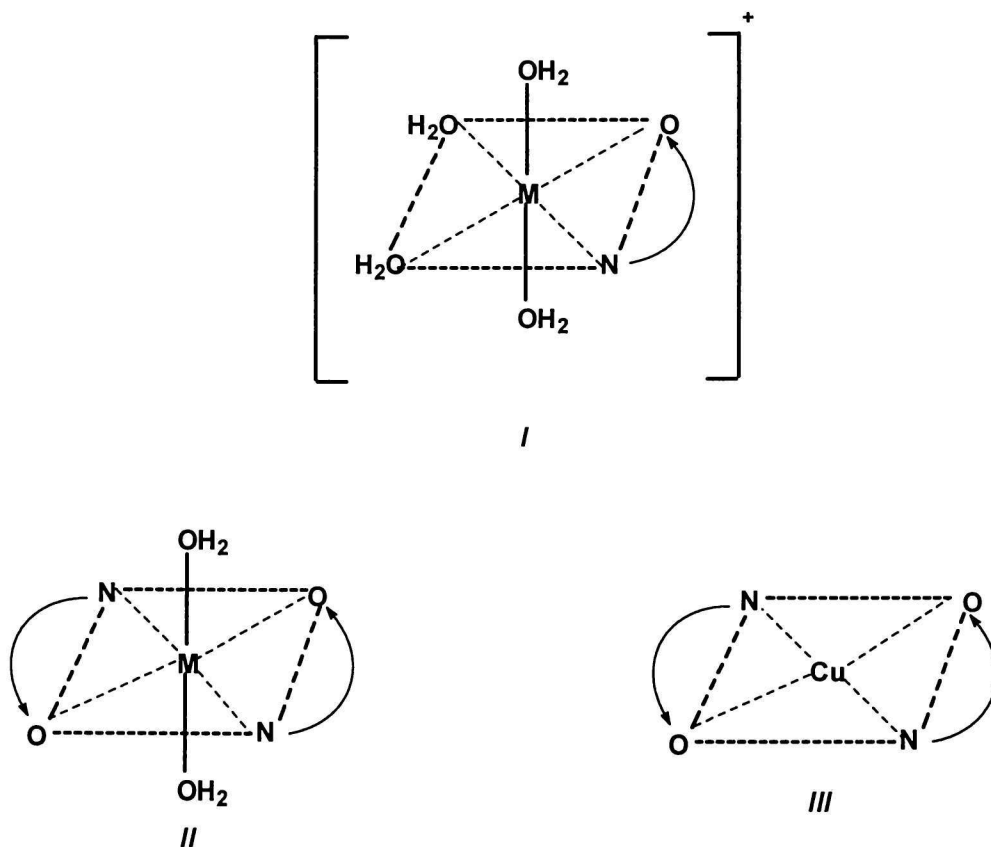
long-range electrostatic forces of the solvent medium; then

$$\Delta X^\circ = \Delta X^\circ_{el} + \Delta X^\circ_c$$

The separation of thermodynamic parameters into temperature-dependent and temperature-independent was first suggested by *Gurney* [30] for proton ionization reactions and has been extended to metal complexes formation by *Anderegg* [31] and *Nancollas* [32, 33]. The nature of temperature dependence ΔX°_{el} can be approximated from the *Born* model [34].

Table 2 summarizes the temperature-dependent and temperature-independent data which were calculated as described earlier [35]. The complex formation reactions of most metal ions with AHDT are found to be highly exothermic (Table 1) due to a higher stability constant values of these complexes. The ΔH°_c values reflect the covalency of the bonding and the structural changes on complexation [35]. Regarding the covalency, ΔH°_c increases according to the order Zn(II), Co(II), Ni(II), Cu(II).

This order is in a good agreement with the softness of the metal ions [36], except that of Zn(II) which has

a higher ΔH°_c than expected. Since $T > \theta$, ΔH°_{el} is positive and this temperature-dependent component results in an endothermic contribution to the total change of enthalpy (Table 2).

In the formation of bis-chelates of the AHDT ligand, the temperature-independent part of entropy changes, ΔS°_c becomes negative and reflects the loss of translational entropy of the ligand on complex formation as well as changes in rotational and vibrational motions which are normally small [35]. The observed entropy changes (ΔS°) are, however, positive due to the large positive contribution of the temperature-dependent part ΔS°_{el}, which reflects the release of bounded water molecules from the hydrated ions on complex formation. The increase of the value of ΔS° results in an increased endothermicity of ΔH°_{el} and hence a lower observed exothermic change in ΔH°

The plot of χ_m (electronegativity of metal ion) against the logarithm of the overall formation constant ($\log K_1 K_2$) (Fig. 10a) shows a linear relationship with the exception of the Cu(II) complexes. It may be inferred that the stability of the metal complexes increases with increasing the χ_m values and consequently the metal—ligand bond would be more

Table 2. Electrostatic (el) and Non-Electrostatic (c) Thermodynamic Quantities Associated with Reaction of Divalent Metal Ions with AHDT in 75 vol. % Dioxane—Water

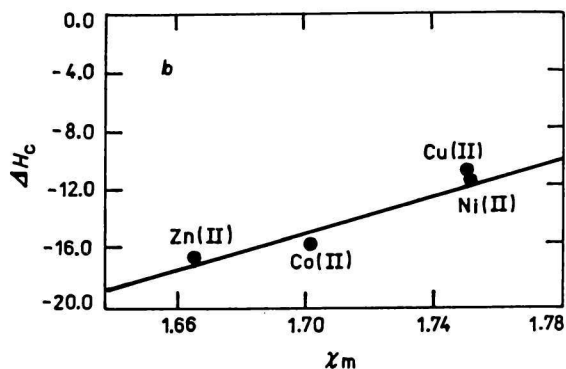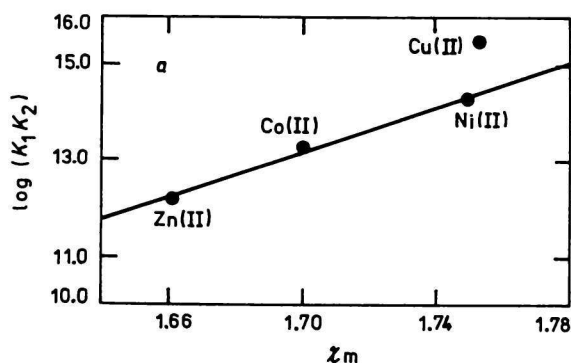| Cation	ΔG°/(kJ mol^{-1})		ΔH°/(kJ mol^{-1})		ΔS°/(J mol^{-1} K^{-1})	
	ΔG°_c	ΔG°_{el}	ΔH°_c	ΔH°_{el}	ΔS°_c	ΔS°_{el}
H$^+$	−83.02	14.53	−27.46	−9.13	−26.00	−131.21
Co(II)	−27.92	−14.28	−66.90	8.96	26.00	25.96
	−14.15	−20.97	−61.42	7.28	−52.00	114.72
Cu(II)	−40.53	−10.09	−48.15	6.36	26.00	3.14
	−28.05	−12.89	−52.54	5.99	−52.00	70.50
Ni(II)	−39.48	−5.40	−49.40	3.39	26.00	−22.40
	−24.83	−13.48	−53.17	8.47	−52.00	73.69
Zn(II)	−20.60	−18.13	−72.43	11.39	26.00	46.97
	−21.31	−10.93	−41.41	6.87	−52.00	59.62

Fig. 10. Relation of χ_m (electronegativity of metal ion) with $\log(K_1 K_2)$ of AHDT (*a*), and ΔH_c (*b*) of Co(II), Ni(II), Cu(II), and Zn(II) complexes in 75 vol. % dioxane—water at 30 °C.
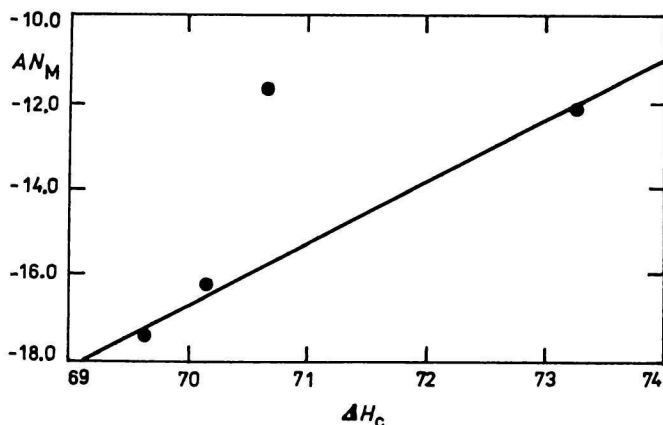
Fig. 11. Relation between the acceptor number of the metal ion (AN_M) and ΔH_c of Co(II), Ni(II), Cu(II), and Zn(II) complexes in 75 vol. % dioxane—water at 30 °C.

covalent. This interpretation is supported by the linear correlation between ΔH_c vs. χ_m (Fig. 10b). On the other hand, the covalency character of these complexes can be concluded from the linear correlation of ΔH_c vs. AN_M (Fig. 11) of the cations [37]. Similar conclusions were cited by *Van Uitert* [38] and *Selbin* [39].

EXPERIMENTAL

Stock solutions of Co(II), Ni(II), Cu(II), and Zn(II) metal ions were prepared by dissolving their nitrates in twice-distilled water and they were standardized using EDTA titrations [40]. Dioxane was freshly distilled over sodium metal and LiAlH$_4$. Acetate buffer solutions were prepared using the recommended methods [40]. All chemicals used were of anal. grade.

IR spectra of the ligand compound as KBr pellet were recorded using a Perkin—Elmer 598 spectrometer (200—4000 cm^{-1}). Electronic absorption spectra of the free ligand and its complexes in 75 vol. % dioxane—water mixtures were recorded using a Jasco model V-550 UV VIS spectrophotometer. The compositions of the complexes in solutions were determined by means of the mole ratio and continuous variation methods [17, 18]. The pH-metric titrations in 75 vol. % dioxane—water solutions of the free ligand and its mixtures with metal ions were carried out as described earlier [9] using a digital WTW pH-meter 520 with a conventional pH-electrode. Using equations of *Irving* and *Rossotti* [41] the curves were used to calculate the formation constants of the following equilibria

$$M^{2+} + HL \xrightleftharpoons{K_1} ML^+ + H^+$$

and

$$ML^+ + HL \xrightleftharpoons{K_2} ML_2 + H^+$$
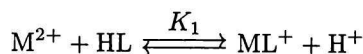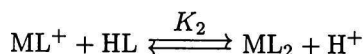
The variations of pK^H, $\log K_1$, and $\log K_2$ vs. $1/T$ gave straight lines which enabled us to calculate the thermodynamic parameters ΔG°, ΔH°, and ΔS° of the complex formation by the Vant Hoff equation and other known relationships [42].

3-[2-(1-Acetylethylidene)hydrazino]-5,6-diphenyl-1,2,4-triazine (AHDT)

3-Hydrazino-5,6-diphenyl-1,2,4-triazine [43] (3.95 g; 0.015 mol) and biacetyl (1.3 cm^3, 0.015 mol) were refluxed for 30 min in absolute ethanol (50 cm^3) and left to stand overnight. Dilution with cold water precipitated a solid material that was filtered off and recrystallized using aqueous ethanolic solution giving the corresponding Schiff base. For C$_{19}$H$_{17}$N$_5$O ($M_r = 331.38$) w_i(calc.): 68.87 % C, 5.17 % H, 21.13 % N; w_i(found): 68.43 % C, 5.24 % H, 21.26 % N.

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