

**Metal complexes of triazine - Schiff bases:
Spectroscopic and thermodynamic studies of complexation of
some divalent metal ions with 3-(α -acetylethylidenehydrazino)-
5,6-diphenyl-1,2,4-triazine**

M. MASHALY^{a*} H. A. BAYOUMI^b and A. TAHA^a

^a*Faculty of Education, Ain Shams University, Roxy, Cairo and*

^b*University College for Girls, Ain Shams University, Heliopolis, Cairo, Egypt*

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Metal complexes of some divalent metal ions (Co, Ni, Cu and Zn) with 3-(α -acetylethylidenehydrazino)-5,6-diphenyl-1,2,4-triazine (AHDT) as a Schiff-base have been investigated potentiometrically and spectrophotometrically and found to have the stoichiometric formulae 1:1 and 1:2 (M:L). The formation constants of the proton-ligand and metal-ligand complexes have been determined potentiometrically at different temperatures (10, 20, 30, 40 and 50 °C) at an ionic strength of 0.1 M KNO₃ in 75% (v/v) dioxane-water solution. The standard thermodynamic parameters, viz. ΔG° , ΔH° , and ΔS° , for the proton-ligand and the stepwise metal-ligand complexes have been evaluated.

Key words: thermodynamic parameters; Schiff-base; metal(II)-complexes; cobalt(II)-complexes; nickel(II)-complexes; copper(II)-complexes; Zn(II)-complexes; formation constant; potentiometry and spectroscopy.

Numerous compounds containing the 1,2,4-triazine 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 colored complexes with different metal ions, and can be used as analytical reagents for their determinations.⁴⁻⁹ In a preceding communication,⁹ the complex formation of copper(II)-ions with 3-(α -phenylethylidenehydrazino)-5,6-diphenyl-1,2,4-triazine, which contains nitrogen donor atoms, was investigated using UV/VIS and IR spectroscopy, as well as electrochemical methods. It is believed that ligands containing different donor atoms, like the O-N type, form more stable complexes than either the O-O or N-N types.¹⁰ Therefore, we extended our investigations to a new ketonic Schiff-base of triazine which contains the O-N ligand system, viz. 3-(α -acetylethylidenehydrazino)-5,6-diphenyl-1,2,4-triazine (AHDT), which forms stable colored complexes with transition metal ions.

The aim of this work was to study the complex formation of AHDT with

* Author to whom correspondence should be addressed

Co(II), Ni(II), Cu(II), and Zn(II) in mixed dioxane-water solutions.

EXPERIMENTAL

3-Hydrazino-5,6 diphenyl-1,2,4-triazine (**I**) was prepared as described elsewhere.¹¹ A mixture of compound **I** (0.015 mol) and biacetyl was refluxed for 30 min in absolute ethanol (50 ml) and left overnight. The solid compound was obtained by dilution with cold water. The resultant solid was filtered off and recrystallized from an aqueous ethanolic solution giving the corresponding Schiff base, 3-(α -acetylenehydrazino)-5,6-diphenyl-1,2,4-triazine (AHDT).

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 standardized using EDTA titrations.¹² Dioxane was freshly distilled over sodium metal and LiAlH₄. Acetate buffer solutions were prepared using the recommended methods.¹² All chemicals used were of analytical grade.

Electronic absorption spectra of the free ligand and its complexes in 75% (v/v) dioxane-water mixtures, were recorded using a Jasco model V-550 UV/VIS spectrophotometer. The pH-metric titrations in 75% (v/v) dioxane-water of the free ligand and its mixtures with metal ions were carried out as described earlier⁹ using a digital WTW pH-meter 520 with a conventional pH-electrode. The compositions of the complexes in solutions were determined by means of the mole ratio and continuous variation methods.^{13,14} The pH-titration curves for the free and complexed AHDT are shown in Fig. 8. Between $a = 0$ and $a = 1$ and in presence of different metal ions, only one proton dissociated (a moles of base added per mole of ligand present). This suggests that under these conditions the ligand behaves as a monoprotic species with the dissociation of the hydrazo (-NH) proton). The acid dissociation constant, K^H , was calculated using the relationship:

$$\log K^H = \log \frac{aC_L - [H^+] + [OH^-]}{(1-a)C_L + [H^+] - [OH^-]} + \text{pH} + 0.28 \quad (1)$$

where C_L is the total concentration of the ligand. Since the ionic product, pK_w , of water in 75% dioxane-water medium is approximately 18.7,¹⁵ both the hydrogen ion and hydroxyl ion concentration terms in Eq. (1) are negligible in the region of dissociation. The correction for the pH values in 75% dioxane-water was taken as 0.28.¹⁶ Figure 8 shows the titration curves of the free AHDT (3×10^{-3} M) ligand in the absence and presence of different metal ions (1×10^{-3} M), namely: Co(II), Ni(II), Cu(II), and Zn(II), against 0.09 M KOH (also in 75% dioxane-water). The curves show distinct inflection points at $m = 1$ and 2 (m = number of moles of base added per mole of metal ion) indicating the stepwise formation of the ML and ML₂ complexes.

The values of the first formation constants K_1 ($M + L \xrightleftharpoons{K_1} ML$) were calculated using the expression given by Irving and Rossotti:¹⁵

$$\log \frac{\bar{n}}{1 - \bar{n}} = \log K_1 + \text{pL}$$

(\bar{n} = number of ligand bound per metal ion and L is the free ligand concentration).

This expression can be solved graphically from a plot of $\log \bar{n}/(1-\bar{n})$ versus pL, which results in a straight line whose intercept with the pL axis is taken as the value of $\log K_1$. The values of \bar{n} and L are calculated from the titration curves of the ligand-metal mixture using the following expression:

$$[L] = \frac{[L_0] - [KOH] - [H^+]}{\frac{[H^+]}{K^H}}$$

$$\bar{n} = \frac{[L_0] - Q[L]}{[M_0]}$$

where,

$$Q = \frac{[H^+]}{K^H} + 1$$

and $[L_0]$ and $[M_0]$ are the total concentration of the free ligand and the free metal, respectively.

The values of the second formation constant K_2 ($ML + L \xrightleftharpoons{K_2} ML_2$) were calculated using the following relationship:

$$\log \frac{\bar{n} - 1}{2 - \bar{n}} = \log K_2 + pL$$

A plot of $\log (\bar{n}-1)/(2-\bar{n})$ versus pL gives a straight line whose intercept with the pL axis gives the value of $\log K_2$. The values of $\log K_1$ and $\log K_2$ were refined using the method of least squares.

At a fixed ligand concentration, the absorbance was found to be pH dependent (Fig. 3) with a slight blue shift in the absorption maxima at high alkali concentration ($-\log [H^+] = 9 - 12$). The results were analysed according to the modified limiting absorbance method¹⁷ for the calculation of the dissociation constants of AHDT in 75% dioxane-water and 0.1 M of KNO_3 using the following equation:

$$A = A_L - \frac{[H^+](A - A_{HL})}{K^H}$$

where A , A_L and A_{HL} denote the absorption of the mixture, anionic and neutral ligand species, respectively. The value of $\log K^H$ obtained at 25 °C was found to be 11.95 ± 0.05 compared to 12.02 ± 0.03 obtained potentiometrically at 20 °C.

The variations of pK^H , $\log K_1$ and $\log K_2$ versus $1/T$ give straight lines which enabled us to calculate the thermodynamic parameters: ΔG° , ΔH° and ΔS° of the complex formation by Vant Hoff equation and other known relationships.¹⁸

RESULTS AND DISCUSSION

The electronic absorption spectra of AHDT in 75% dioxane-water solution displays two absorption bands within the 200–600 nm region (see Fig. 1) (λ_{\max} , 286 and 246 nm having molar absorptivities $\epsilon = 1.8 \times 10^4$ and 2.1×10^4 L mol⁻¹ cm⁻¹, respectively).

The absorption spectra of AHDT at different pH-values exhibit two isosbestic points at about 292 and 334 nm (see Fig. 2). This reveals that at least three distinct species in equilibrium exist in a solution of AHDT 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 the increased extent of chain conjugation,¹⁹ compared with species B. Furthermore, comparison of species B and C, Scheme 1, shows that the tautomer C, which include an enolic OH group, might be formed in strong alkaline medium (\approx pH 13) and this tautomer also includes $-N=N-$ group which has $\lambda_{\max} > 350$

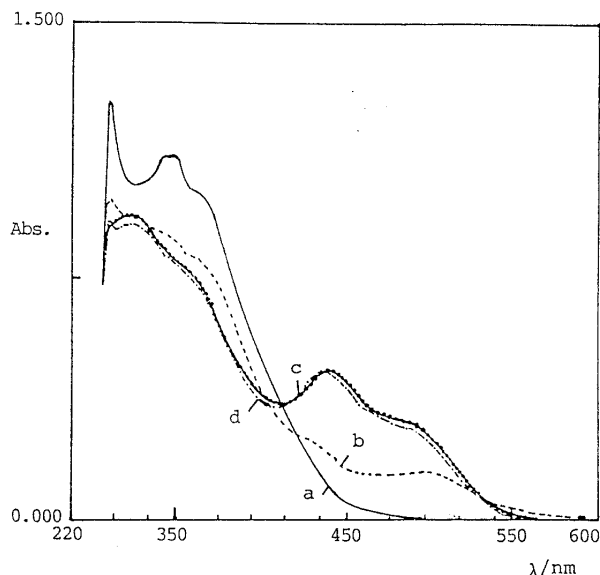
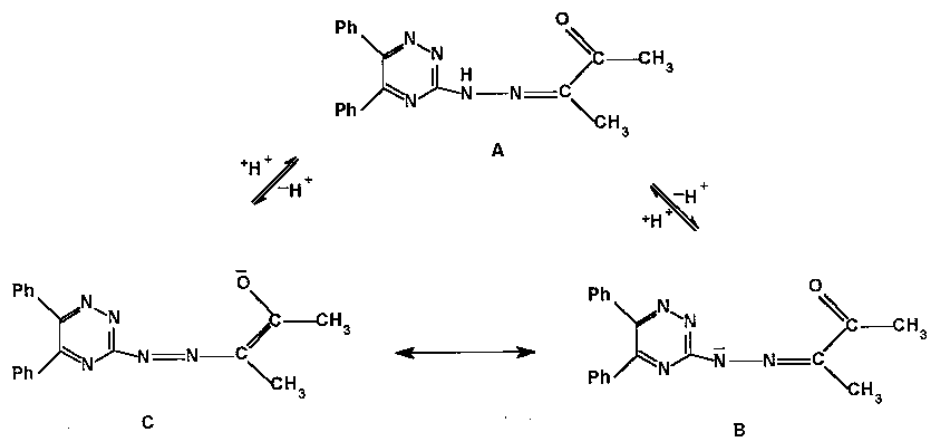


Fig. 1. Absorption spectra of AHDТ, 6×10^{-5} M solution in 75% (v/v) dioxane-water, 25 °C and pH 5.0 a); a mixture of AHDТ with 3×10^{-5} M Cu(II) at pH 5.0 b); a mixture of AHDТ with 3×10^{-5} M Co(II) at pH 8.0 c); and a mixture of AHDТ with 3×10^{-5} M Ni(II) at pH 8.0 d).

nm (see Fig. 2).²⁰ Consequently, the dissociated proton under our conditions might be present mainly in the hydrazo form.

When a solution of the ligand is mixed with solution of metal ions, namely, Co(II), Ni(II) and Cu(II), new visible bands (see Fig. 1) were observed. The color changes depending on the metal ion, orange-red in the cases of Co(II) and Ni(II), and wine red for Cu(II). The spectra of the Cu(II)-AHDТ mixture are characterized by two bands at 480 nm and at 412 nm in the pH region 3.5–5.0. Increasing the pH



Scheme 1.

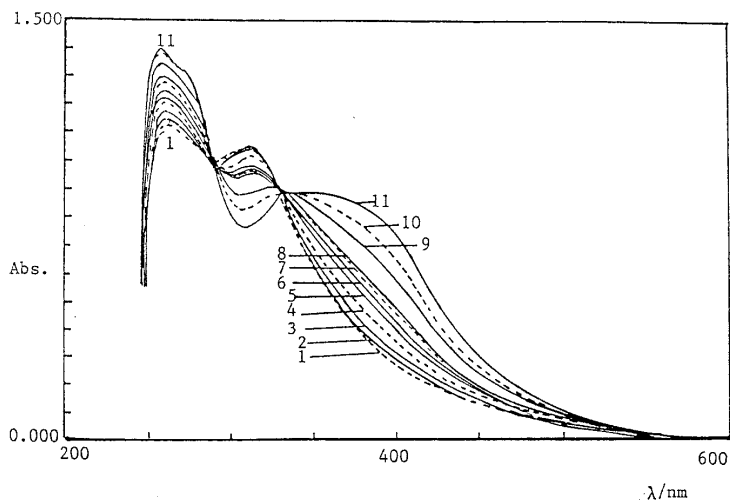


Fig. 2. UV/VIS spectra of 6×10^{-5} M AHDT in 75% dioxane-water at different pH values (adjusted with HCl and KOH solutions), $I = 0.10$ M KNO_3 , Curve 1, pH 8.0; 2, 8.5; 3, 9.0; 4, 9.5; 5, 10.0; 6, 11.0; 7, 11.7; 8, 12.2; 9, 12.7; 10, 13.0; 11, 13.3.

of the mixture to the range 6.0–9.0 leads to a decrease in the intensity of the band located at 480 nm and an increase in the intensity of the band at 412 nm. In the case of the Ni(II)-AHDT mixture, there is also two bands, observed at 475 nm and 410 nm in the pH range 3.5–10. Increasing the value of the pH leads to a gradual increase

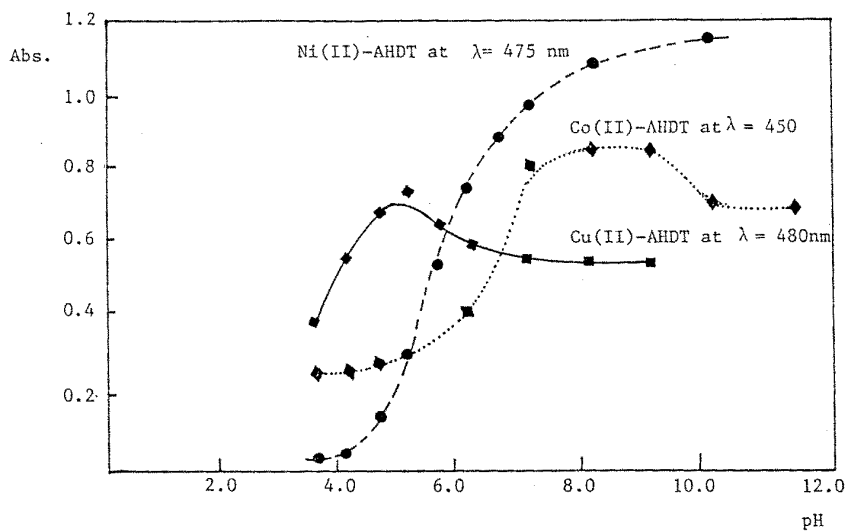


Fig. 3. Absorbance *versus* pH of mixtures of [AHDT], 3×10^{-4} M with 1×10^{-4} M of Cu(II), Ni(II) and Co(II) in 75% dioxane-water solution and $I = 0.10$ M KNO_3 with ligand as the reference.

in their absorbance. The electronic absorption spectra of the Co(II)-AHDТ mixture are also characterized by two bands, at 450 nm and 385 nm in the region 3.5–8.0. Above pH 8.0, the absorbance for the first band starts to decrease while the intensity of the absorbance of the second band increases. It was found that the intensities of the observed peaks are dependent on the pH value of the medium in the range 2–12. Figure 3 shows the optimum pH-range for complex formation, which was found to be 5.0 for the Cu(II)-complexes and 8.0 for both the Co(II)- and Ni(II)-complexes.

The stoichiometry of the complexes under investigation were determined by means of the mole ratio and continuous variation methods.^{13,14} The absorption spectra of the Cu(II)-AHDТ complexes as a function of ligand concentrations are shown in Fig. 4 (as a representative example). The spectra reflect that the absorbance maximum at about 412 nm increases rapidly, while the maxima at ≈ 480 nm increases slightly with increasing ligand/metal ratio until it reaches a 1:1. On exceeding the ratio 1:1, a slight increase in the peak was found at 412 nm and a rapid increase in

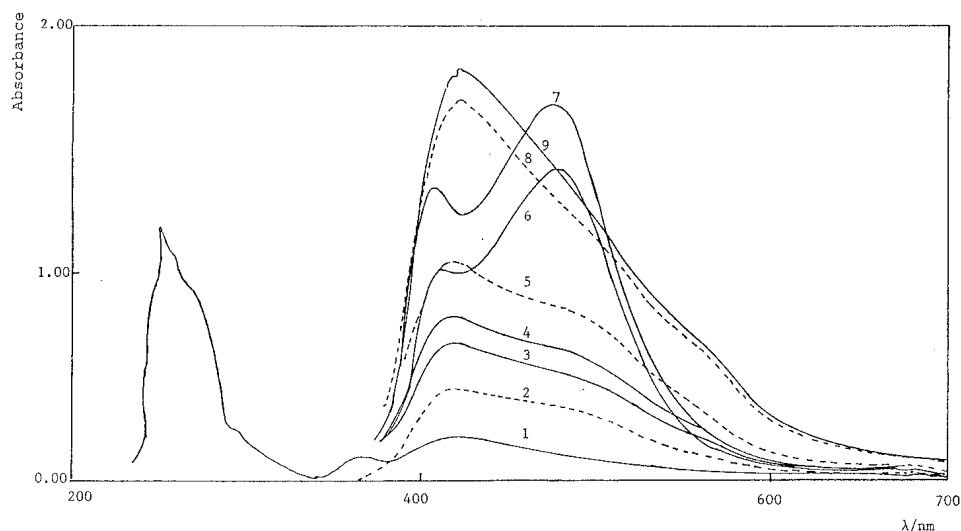


Fig. 4. Electronic absorption spectra of Cu(II)-AHDТ complexes in 75% (v/v) dioxane-water at pH 5.0 with ligand as the reference; [Cu(II)] 3.5×10^{-4} M (constant concentration) with various concentration of [AHDТ]: 1, 1×10^{-4} M; 2, 2×10^{-4} M; 3, 3×10^{-4} M; 4, 3.5×10^{-4} M; 5, 4.5×10^{-4} M; 6, 5.5×10^{-4} M; 7, 7×10^{-4} M; 8, 9×10^{-4} M; 9, 1×10^{-3} M.

the peak at ≈ 480 nm until the ratio reaches 2:1. On exceeding the ratio 2:1 the two peaks overlapped forming a single peak with a maximum at ≈ 420 nm and a steady increase in the absorbance was observed. This means that the predominant species formed are 1:1 and 1:2 (M:L).

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 (M:L), as shown in Figs. 5 and 6.

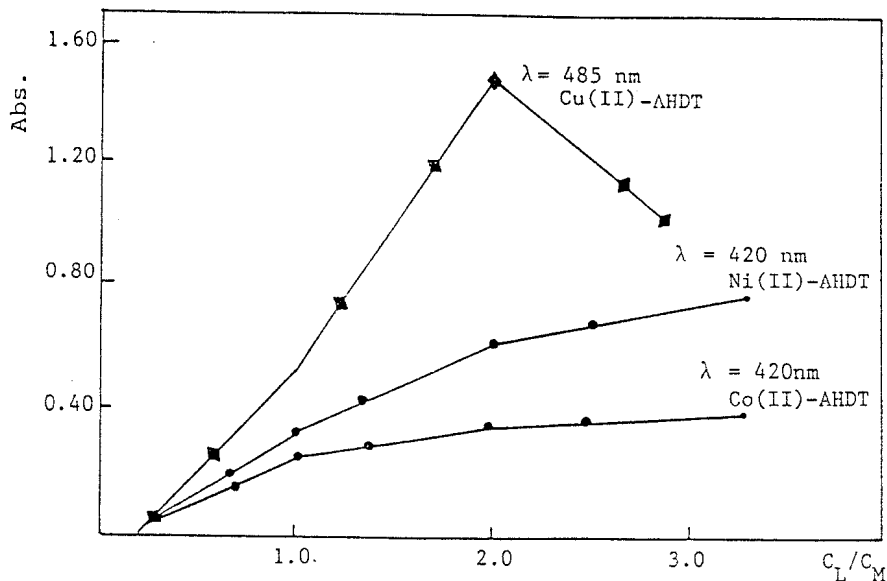


Fig. 5. Mole ratio method for Cu(II)-, Ni(II)- and Co(II)-AHDT complexes in 75% dioxane-water (v/v), $I = 0.10$ M KNO_3 using ligand as the reference: a) $[\text{Cu(II)}] 3.5 \times 10^{-4}$ and $[\text{AHDT}] 1 \times 10^{-5} - 1 \times 10^{-3}$ M at pH 5.0; b) $[\text{Ni(II)}] 6 \times 10^{-5}$ M and $[\text{AHDT}] 2 \times 10^{-5} - 2 \times 10^{-4}$ M at pH 8.0; c) $[\text{Co(II)}] 6 \times 10^{-5}$ M and $[\text{AHDT}] 2 \times 10^{-5} - 2 \times 10^{-4}$ M at pH 8.0.

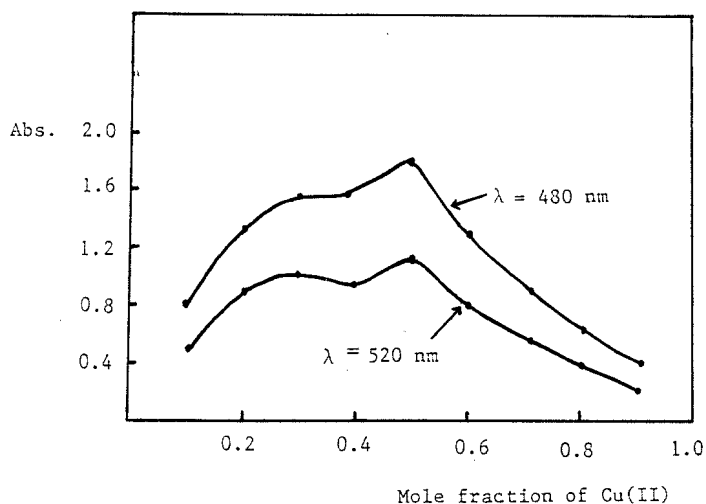


Fig. 6. Continuous variation method for Cu(II)-AHDT complex, in 75% dioxane-water, total molar concn. = 1×10^{-3} M.

The spectrophotometric data were used to calculate the formation of the 1:1 Co(II)- Ni(II)- and Cu(II)-AHDT complexes by applying the limiting absorbance

method.¹⁶ Log K_1 values at 25 °C 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 reached by Irving and William.²¹

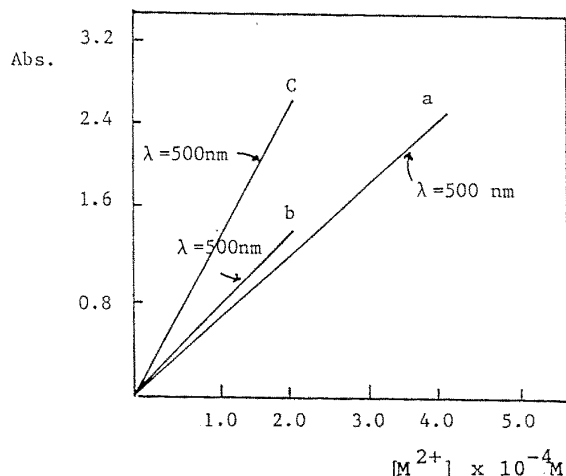


Fig. 7. Validity of Beer's law of 1×10^{-3} M AHDT in 75% (v/v) dioxane-water and various concn. of Cu(II), Co(II) and Ni(II), $I = 0.10$ M KNO_3 using ligand as the reference: a) Cu(II)-AHDT at pH 5.0; b) Co(II)-AHDT at pH 8.0; c) Ni(II)-AHDT at pH 8.0.

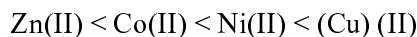
Under the optimum conditions, using a constant concentration of AHDT (1×10^{-3} M) and varying the Cu(II), Co(II) and Ni(II) concentrations in aqueous-dioxane solutions, it was found that the system obeys Beer's law with standard deviations of 0.002, 0.006 and 0.003, respectively, within the metal concentration range 1×10^{-5} – 4×10^{-4} for Cu(II)- and 1×10^{-5} – 2×10^{-4} for Co(II)- and Ni(II)- complexes. The molar absorptivity (ϵ) values at 500 nm for the Cu(II), Co(II) and Ni(II) complexes were 6.6×10^3 , 8.0×10^3 and 1.4×10^4 L mol⁻¹ cm⁻¹, respectively, indicating that AHDT can be readily utilized as a sensitive reagent for the microanalytical determination of copper(II), cobalt(II) and nickel(II) (see Fig. 7).

pH-Metric titration curves of the free AHDT (3×10^{-3} M) ligand in the absence and presence of different metal ions (1×10^{-3} M), namely: Co(II), Ni(II), Cu(II) and Zn(II), showed the stepwise formation of the [ML] and [ML₂] complex species, as shown in Fig. 8. This conclusion is in harmony with the 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 are summarized in Table I. The structure of AHDT, as shown in structure 1 and Scheme 1, shows a monobasic ligand with a pK^H value of 11.80 at 30 °C, which agrees well with the value obtained from the spectrophotometric studies. Ligands containing the group Ar–NH–N=CR₂ are normally ionized in moderately alkaline media, and have pK^H values ranging from 6 – 9.²²⁻²³

The high basicity of AHDТ ligand suggests that the proton of the hydrazo group forms a strong hydrogen bond with the oxygen atom of the carbonyl group, as indicated by the IR spectrum of the free ligand, to produce a six membered ring, and so it is less ionizable.²⁴

The formation constant values of the stepwise complex formation at different temperatures and their thermodynamic parameters are summarized in Table I. These values indicate that the complex formation constants of different metal ions with AHDТ increase in the following order:



This order agrees with that obtained from spectrophotometric data, which is again consistent with the order obtained by William and Irving.²¹

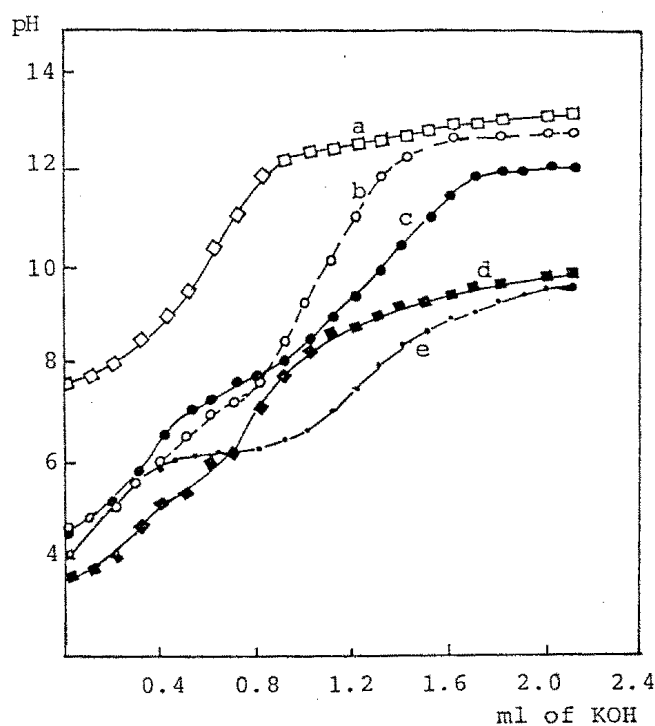


Fig. 8. Potentiometric titration curves of 30 ml of a solution containing 3×10^{-3} M AHDТ a) and in the presence of 1×10^{-3} M of metal ions (b Co(II); c Ni(II); d Cu(II), and e Zn(II)) in 75% (v/v) di-oxane-water at 30 °C, $I = 0.10$ M and adding 0.090 M KOH.

The unexpected small differences between $\log K_1$ and $\log K_2$ of the formed complexes (see Table I) reveal that the second chelate ligand anion favours the formation of the more symmetrical ML_2 complex species and offset the expected steric hindrance of the bulky ligand molecules.

TABLE I. Stepwise formation constants and thermodynamic parameters* ($\Delta G^\circ/\text{kcal mol}^{-1}$, $\Delta H^\circ/\text{kcal mol}^{-1}$ and $\Delta S^\circ/\text{kcal mol}^{-1} \text{ K}$ of AHDT) with Co(II), Ni(II), Cu(II), and Zn(II) ions ($I = 0.10 \text{ M KNO}_3$; 75% (v/v) dioxane-water solvent)

Cation	Symbol	$-\Delta G^\circ$	$-\Delta H^\circ$	ΔS°	10 °C	20 °C	30 °C	40 °C	50 °C
H ⁺	pK^{H}	-16.36	-8.74	-25.15	12.26	12.02	11.80	11.64	11.42
Co(II)	$\log K_1$	10.08	13.84	12.41	7.94	7.65	7.27	6.92	6.64
	$\log \beta$	18.47	26.78	27.43	14.63	14.02	13.32	12.66	12.09
Cu(II)	$\log K_1$	12.09	9.98	6.96	9.21	8.94	8.72	8.38	8.24
	$\log \beta$	21.87	21.14	2.41	16.85	16.26	15.77	15.17	14.81
Ni(II)	$\log K_1$	10.72	10.98	0.86	8.30	8.02	7.73	7.50	7.24
	$\log \beta$	19.87	21.70	6.04	15.41	14.87	14.33	13.85	13.31
Zn(II)	$\log K_1$	9.25	14.53	17.43	7.32	7.00	6.67	6.30	5.92
	$\log \beta$	16.94	22.78	19.27	13.22	12.72	12.22	11.63	11.02

* $\Delta G \pm (0.01-0.2)$; $\Delta H \pm (0.01-0.16)$; and $\Delta S \pm (0.01-0.27)$, **The values of $\log K_1 - \log K_2$ ranged between 0.82 and 1.67

The distribution of the species as a function of pH has been calculated using known expressions.²⁵ Figure 9 shows that the mole ratio of ML^+ increases rapidly and attains a maximum value at pH values of 5.70, 5.80, 6.50 and 6.90 for Cu(II), Ni(II), Co(II) and Zn(II), respectively, then decreases, while free M(II) and ML_2 change monotonically with pH.

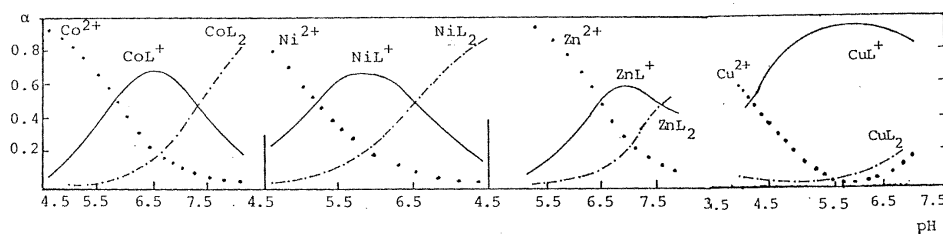
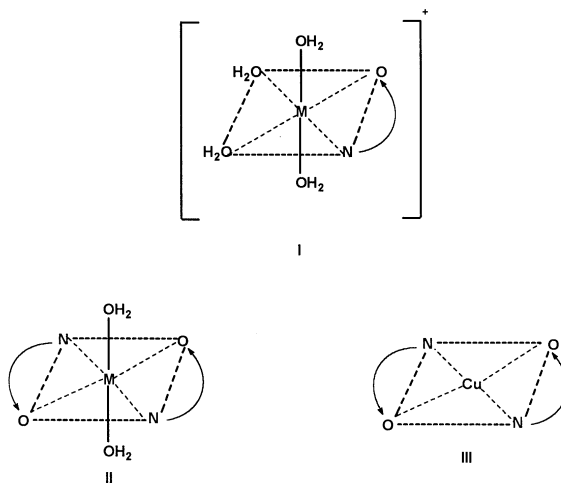


Fig. 9. Distribution diagram of the complex species as a function of pH for the Cu(II), Co(II), Ni(II) and Zn(II)-AHDT systems in 75% (v/v) dioxane-water solvent at 30 °C.

The standard thermodynamic parameters, viz. the ΔG° , ΔH° and ΔS° values of AHDT at 30 °C and its metal complexes were calculated and are presented in Table I. The positive values of ΔG° and ΔH° of the free ligand indicate that the deprotonation process of AHDT is non-spontaneous, endothermic and enhanced by increasing temperature. The high negative value of ΔS° is due to the conversion of the translational entropy of the AHDT ligand which disfavor its deprotonation. Similar observations were been reported by Abel-Moez *et al.*²⁶ On the other hand, the high negative values of ΔG° and ΔH° associated with K_1 and K_2 (see Table I) of complex formation indicate that the complexations tend to proceed exothermally and spontaneously. Furthermore, the positive values of ΔS° , favouring complex

formation, reveal that the loss of entropy accompanying the formation of metal-to-ligand bonds and the conversion of the translational entropy of the free ligand are offset by the gain resulting from the liberation of solvent molecules from the metal ions.²⁷

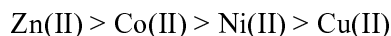


Formulae I–III.

The ΔH° and ΔS° values associated with K_1 are in general higher than those of K_2 , again with the exception of the Cu(II) complexes where $\Delta H_1^\circ < \Delta H_2^\circ$. This might be attributed to the geometrical change from "6-coordinate" for CuL^+ to "four-coordinate" for CuL_2 , as a result of the Jahn-Teller effect.²⁸ The CuL^+ complex ion would attain a 6-coordinate sphere through coordination of the Cu(II) ion to one ligand anion and four water molecules (see Formula I), while the CuL_2 complex would be 4-coordinate by linking two ligand anions²⁹ (see Formula III). This interpretation is confirmed by the visible spectral data of Cu(II) ions in the presence of AHDT ligand where the d-d transitions ($\lambda_{\text{max}} \approx 480 \text{ nm}$) indicate that the geometrical shape of the higher species (CuL_2) is square-planar.²⁹

The other metal complexes, on the other hand, retain their most probable octahedral structure in both 1:1 (Formula I) and 1:2 (metal:ligand) complexes (Formula II), water molecules completing the coordination sphere.^{7,29} On the basis of this interpretation the plausible structures of the complexes under investigation are given by Formulae I–III (see above).

The ΔH° values associated with the first step of complex formation increase in the following order.



This order agrees with the increase of the degree of covalency in the ligand-metal bonds.²⁷ Moreover, this order is opposite to that observed in the values of the

formation constants of the ML^+ species ($\log K_1$) (see Table I), as the latter values are dependent on the electrostatic forces which are more pronounced in the case of this complex ion as compared to the complex ML_2 . This interpretation is further confirmed by the linearity of ΔS° (see Table I) with the values of $1/r$, where r is the ionic radii of the divalent metal ions ($\Delta S_1^\circ = 140.2 - 91.5 \times 1/r$, *c.c.* = 0.999) with the exception of the Cu(II)-complexes. This fact indicates the predominant role of electrostatic forces in the ion association processes, which is in harmony with the Bjerrum original ion pair concept. Similar observations were reported by Martell³⁰ and Stavely.³¹

It is convenient to analyze any thermodynamic function ΔX° ($X = G^\circ, H^\circ$ and S°) into two parts: (a) ΔH_c° (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) ΔH_{cl}° , a temperature dependent part, owing to the interaction of the dipoles or ions with long range electrostatic forces of the solvent medium, whereby

$$\Delta X^\circ = \Delta X_{cl}^\circ + \Delta X_c^\circ$$

The separation of thermodynamic parameters into temperature dependent and temperature independent parts was first suggested by Gurney³² for proton ionization reactions and has been extended to metal complex formation by Andergg³³ and Nancollas.^{34,35} The nature of the temperature dependence ΔX_{cl}° can be approximated from the Born model.³⁶

The temperature dependent and temperature independent data, which were calculated as described earlier,³⁷ are summarized in Table II. The complex formation reactions of most metal ions with AHDT are found to be highly exothermic (see

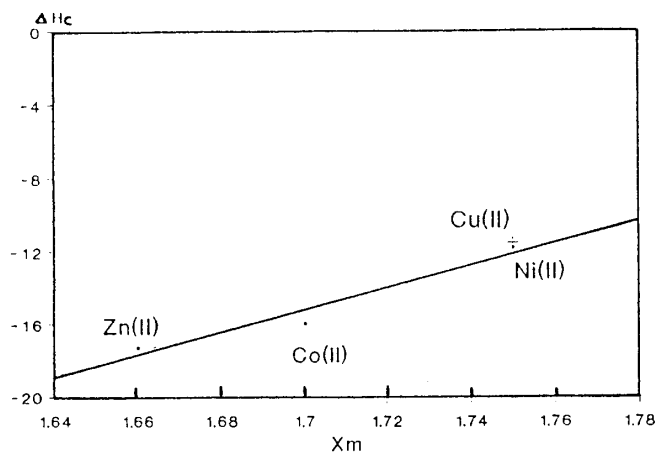


Fig. 10. Relation of χ_m (electronegativity of metal ion) with $\log K_1 K_2$ of AHDT a), and ΔH_c b) of Co(II), Ni(II), Cu(II) and Zn(II) complexes in 75% (v/v) dioxane-water solvent at 30 °C.

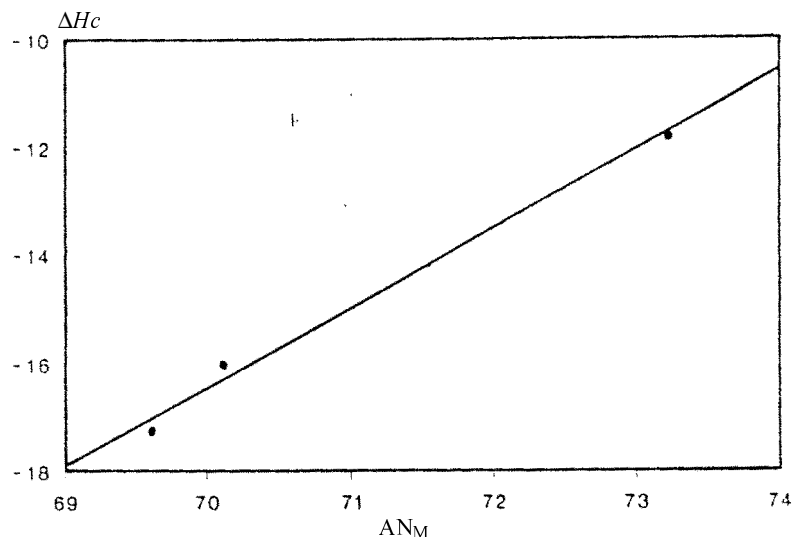
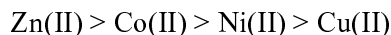


Fig. 11. Relation between the acceptor number of the metal ion (AN_M) and ΔH_c of Co(II), Ni(II), Cu(II) and Zn(II) complexes in 75% (v/v) dioxane-water solvent at 30 °C.

Table I) due to the higher stability values of these complexes. The ΔH_c^0 values reflect the covalency of the bonding and the structural changes on complexation.³⁷

Regarding the covalency, ΔH_c^0 increases in the following order:



This order is in good agreement with the softness of the metal ions,³⁸ except for Zn(II) which has a higher ΔH_c^0 than expected. Since $T > \theta$, ΔH_{cl}^0 is positive and this temperature dependent component of the enthalpy change results in an endothermic contribution to the total change of enthalpy (see Table II).

TABLE II. Electrostatic (el) and non-electrostatic (c) thermodynamic quantities associated with the reaction of divalent metal ions with AHDT in 75% (v/v) dioxane-water

Cation	ΔG^0		ΔH^0		ΔS^0	
	$\Delta G_c^1(\Delta G_c^2)$	$\Delta G_{cl}^1(\Delta G_{cl}^2)$	$\Delta H_c^1(\Delta H_c^2)$	$\Delta H_{cl}^1(\Delta H_{cl}^2)$	$\Delta S_c^1(\Delta S_c^2)$	$\Delta S_{cl}^1(\Delta S_{cl}^2)$
H ⁺	-19.83	3.47	-6.56	-2.18	-6.21	-31.43
Co(II)	-6.67 (-3.38)	-3.41 (-5.01)	-15.98 (-14.67)	2.14 (1.74)	6.21 (-12.42)	6.20 (27.40)
Cu(II)	-9.68 (-6.70)	-2.41 (-3.08)	-11.50 (-12.55)	1.52 (1.43)	6.21 (-12.42)	0.75 (16.84)
Ni(II)	-9.43 (-5.93)	-1.29 (-3.22)	-11.80 (-12.70)	0.81 (2.02)	6.21 (-12.42)	-5.35 (17.60)
Zn(II)	-4.92 (-5.09)	-4.33 (-2.61)	-17.30 (-9.89)	2.72 (1.64)	6.21 (-12.42)	11.22 (14.24)

*The values cited in paranthesis are for second formation constants

In the formation of bis-chelates of the AHDT ligand, the temperature independent part of the entropy change, ΔS_c^0 becomes negative and reflects the loss of translational entropy of the ligand on complex formation, as well as changes in the rotational and vibrational motion which are normally small.³⁷ The observed entropy changes (ΔS^0) are, however, positive due to the large positive contribution of the temperature dependent part ΔS_{el}^0 , which reflects the release of bound water molecules from the hydrated ions on complex formation. The increase of the value of ΔS^0 results in an increased endothermicity of ΔH_{el}^0 , and, hence, a lower observed exothermic change in ΔH^0 .

The plot of χ_m (electronegativity of the 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 increase with increasing χ_m values and, consequently, the metal-ligand bond would become more covalent. This interpretation is supported by the linear correlation between ΔH_c versus χ_m (see Fig. 10b). On the other hand, the covalent character of these complexes can be concluded from the linear correlation between ΔH_c and AN of the cations.³⁹ Similar conclusions were cited by Van Uiter⁴⁰ and Selbin.⁴¹

ИЗВОД

МЕТАЛНИ КОМПЛЕКСИ ТРИАЗИНА КАО ШИФОВЕ БАЗЕ: СПЕКТРОСКОПСКА И
ТЕРМОДИНАМИЧКА ПРОУЧАВАЊА КОМПЛЕКСИРАЊА НЕКИХ
ДВОВАЛЕНТНИХ ЈОНА МЕТАЛА СА
3-(α -АЦЕТИЛСТИЛИДЕНХИДРАЗИНО)-5,6-ДИФЕНИЛ-1,2,4-ТРИАЗИНОМ

M. MASHALY^a, H. A. BAYOUMI^b and A. TAHA^a

^aFaculty of Education, Ain Shams University, Roxy, Cairo and ^bUniversity College for Girls, Ain Shams University, Heliopolis, Cairo, Egypt

Потенциометријским и спектрофотометријским испитивањима комплекса двовалентних јона метала (Co, Ni, Cu и Zn) са 3-(α -ацетил-етилиденхидразином)-5,6-дифенил-1,2,4-триазином (AHDT) као Шифовом базом нађено је да имају стехиометријске формуле 1:1 и 1:2 (M:L). Потенциометријски су одређене константе стварања протон-лиганд и метал-лиганд комплекса при различитим температурама (10, 20, 30, 40 и 50 °C), при јонској јачини 0.1 M KNO₃ у 75% (v/v) раствору диоксан-вода. Израчунати су и стандардни термодинамички параметри (ΔG^0 , ΔH^0 и ΔS^0) за протон-лиганд и ступњевите метал-лиганд комплексе.

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