

Metal Chelates of Hydrazone Ligand Chelating Tendencies of 2-Carboxyphenylhydrazoacetanilide (2-Cphaaa) Ligand

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Abstract

The chelating properties, of hydrazone ligand 2-carboxyphenylhydrazoacetanilide (2-CPHAAA) (H_2L) have been studied. A series of binary complexes, of H_2L with the metal ions Cd(II), Cu(II), Co(II), $UO_2(VI)$ and Th(IV) were prepared. The binary Cu (II) complexes of 2-CPHAAA was reacted with the ligands 1,10-phenanthroline (1,10-phen) and 2-amino-4-methyl-pyridine (2 AMP) to form mixed ligand complexes. The structures of all complexes, were elucidated by elemental analyses, conductance, IR, electronic absorption spectra, magnetic moment, 1H NMR and TG-DSC measurements.

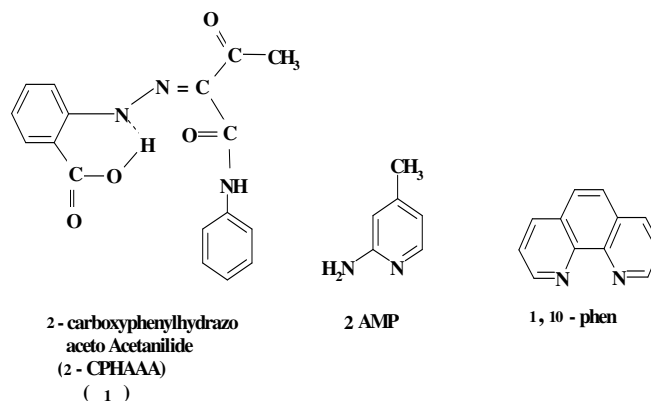
The metal-ligand stability constants of the Cu(II), Ni(II), Co(II), Zn(II), Mn(II), Cd(II), $UO_2(VI)$, Th(IV), Sm(III) and Er(III) chelates of 2-CPHAAA were determined in 75% (v/v) dioxane water medium at 10, 20, 30 and 40 °C and $\mu = 0.10 M KNO_3$. The thermodynamic parameters for the proton-ligand 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 electrostatic (el) and non electrostatic (non) components. The values of ΔH non show a linear variation with the hardness and softness (E_n) of the metal ion. The ternary complexes of 2-CPHAAA complexes of the Th(IV) and $UO_2(VI)$ with 2AMP or 1,10-phen ligands were studied in 75% (v/v) dioxane water solvents.

Key words: Binary complexes, mixed ligands, stability of complexes and thermodynamic parameters.

Introduction

In the preceding papers [1-3] we have reported on the complex equilibria of 2-carboxyphenylhydrazoacetanilide (2-CPHAAA) (structure I) and 2-carboxyphenylhydrazo paramethoxyacetanilide (2-CPH-P-OCH₃-AAA) with proton, some of transition¹ and lanthanide ions² in 75% (v/v) dioxane-water and 0.1 M KNO_3 . The study revealed that the ligands behave as dianionic tridentate (NOO)-donor. The coordination sites as obtained from infrared were carboxylate oxygen, ketonic oxygen and hydrazo nitrogen. In the present report, the chelating ability of 2-CPHAAA has been measured through the isolation of solid complexes and investigation through elemental analysis, IR, UV-visible, 1H NMR spectra and TG, -DSC measurements. The thermodynamic parameters were determined and discussed through the separation into their electrostatic (el) and non-electrostatic or cratic components.

The mixed-ligand complexes of copper (II), Ni(II), Co(II), Fe(III), $UO_2(IV)$ and Th(VI) were prepared by mixing equimolar amount 2CPHAAA with 2-amino-4-methylpyridine (2-AMP) or 1,10 phenanthroline(1,10-phen) In addition the mixed complexes were investigated in 75% (v/v) dioxane water solvents.



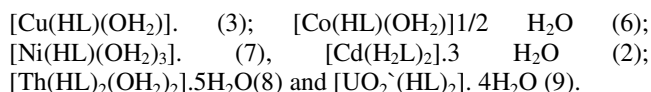
Material and Methods

The organic ligand 2-CPHAAA was prepared as described previously [1-2]. For starting materials, purification of solvents and procedure see reference³. Conductance and magnetic moment as well as recording parameters for infrared, UV-visible and 1H NMR spectra and TG-DSC measurements are described in⁴.

Preparation of Metal Complexes: The binary and ternary complexes were prepared in the presence of LiOH. H_2O as deprotonating agent.

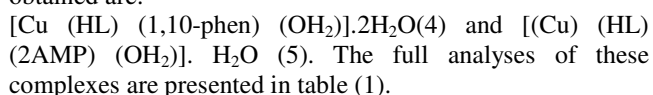
Preparation of binary complexes: A mixture as 1:1: 1 M^{n+} : H_2L : LiOH. H_2O in 75% (v/v) methanol – water was refluxed

for 3hr with constant stirring to ensure the complete formation of the metal complexes. The precipitated solid complexes were filtered, washed several times with 1:1 aqueous methanol to remove any traces of unreacted materials. Finally the complexes washed with diethylether and dried in a vacuum desiccator over anhydrous calcium chloride. The complexes obtained by this method are:



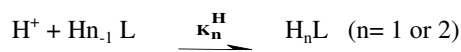
Preparation of ternary complexes: Molar ratio of Cu(II); 2CPHAAA : 2AMP or 1,10-phen : LiOH = 1:1:1 was refluxed in 50% methanol water for 5h with constant stirring to ensure the complete formation of the metal complexes.

The precipitated solid complexes were filtered, washed several times with 50% (v/v) methanol -water to remove any traces of unreacted starting materials. Finally, the mixed ligand complexes were washed with diethyl ether and dried under vacuum over anhydrous CaCl₂. The complexes obtained are:



Results and Discussion

The potentiometric titration curves of 2-CHAAA ligand in absence and presence of different metal cations using 75% (v/v) dioxane-water as solvent and 0.10 M KNO₃ is shown in figure 1. The curves shows long buffer region between a= 0 and a=1 (a = number of moles of base added per mol.of ligand followed by strong inflection at a= 1 due to the complete neutralization of carboxylic group of the ligand (K₁^H) The second buffer region occurs at higher pH without any inflection point which indicates that dissociation of hydrazo proton is not clear. The diprotic nature of this ligand is substantiated from the titration curves of the ligand in presence of various metal ions, where two protons librated. For the general protonation equilibrium



The constant K_n^H , were determined from hydrogen concentration of ligand solution for each increment of base added. The values of these constants were calculated using the general relationship:

$$\text{Log}K_n^H = \text{Log} \frac{(1-a-m-n)(C_L - [H^+] + [OH^-])}{(a+m+n)(C_L + [H^+] - [OH^-])} + pH \quad (1)$$

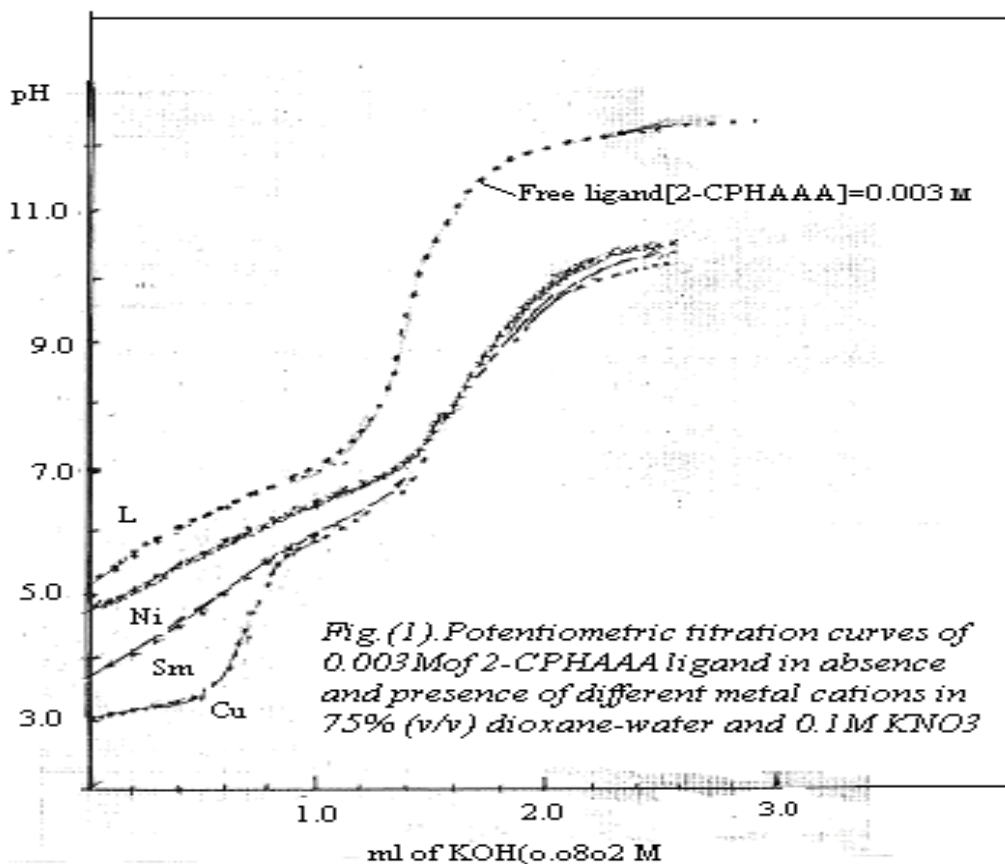


Table-1
Analytical and physical data of organic ligand: H₂L and its metal complexes

Compound	F.W	color	M.P (°C)	Yield	Elemental analysis , found (calc.) %			
					C	H	N	Metal
(1) C ₁₇ H ₁₅ N ₃ O ₄	325.32	Yellow	220	80	62.30 (62.76)	4.90 (4.65)	12.90 (12.92)	- -
(2) [Cd(H ₂ L) ₂].3H ₂ O C ₃₄ H ₃₄ N ₆ O ₁₁ Cd	815.08	Yellow	>250	73	49.90 (50.10)	4.60 (4.20)	10.10 (10.31)	13.83 (13.79)
(3) [Cu(HL)(OH ₂) C ₁₇ H ₁₅ N ₃ O ₅ Cu	404.87	Green	>250	59	50.60 (50.43)	3.70 (3.73)	10.10 (10.38)	15.87 (15.69)
(4) [Cu(HL)(1,10-phen)(OH ₂).2H ₂ O C ₂₉ H ₂₇ N ₅ O ₇ Cu	621.11	Pale green	>250	67	55.80 (56.08)	4.50 (4.38)	11.50 (11.28)	10.16 (10.23)
(5) [Cu(HL)(OH)(2-AMP)(OH ₂) ₂].H ₂ O C ₂₂ H ₂₅ N ₅ O ₇ Cu	535.01	Green	>250	63	49.40 (49.39)	4.80 (4.71)	12.90 (13.09)	11.92 (11.88)
(6) [Co(HL)(OH ₂) ₂].1/2 H ₂ O C ₁₇ H ₁₆ N ₃ O ₅ 1/2Co	409.26	Brown	>250	74	49.80 (49.89)	3.90 (3.94)	9.90 (10.27)	14.21 (14.40)
(7) [Ni(HL)(OH ₂) ₃] C ₁₇ H ₁₉ N ₃ O ₇ Ni	436.04	Pale green	>250	84	46.80 (46.83)	4.60 (4.39)	9.70 (9.64)	13.21 (13.46)
(8) [Th(HL) ₂ (OH ₂) ₂].5H ₂ O C ₃₄ H ₄₂ N ₆ O ₁₅ Th	1006.77	Yellow	>250	69	40.80 (40.56)	4.50 (4.20)	8.50 (8.35)	23.12 (23.05)
(9) [UO ₂ (H ₂ L) ₂].4H ₂ O C ₂₄ H ₃₆ N ₆ O ₁₄ U	990.72	Yellow	>250	64	41.20 (41.22)	3.80 (3.66)	8.30 (8.48)	- -

Table-2
Protonation constant and thermodynamic parameters of: 2CPHAAA ligand
In 75% (v/v) dioxane – water at different temperatures and ionic strength = 0.1 M KNO₃

Ligand	Symbol of Proton constant	Temperature				ΔG	ΔH	ΔS
		10 °C	20 °C	30 °C	40 °C			
	pK ₁ ^H	6.77	6.43	6.30	5.88	8.74	9.24	1.70
2-CPHAAA	pK ₂ ^H	12.42	12.22	11.94	11.14	16.63	16.49	-0.50

Table-3
Stability constants of 2 CPHAAA ligand – metal chelates at different temperatures,
[μ = 0.1 M KNO₃; 75 (v/v) dioxane– water]

Cation	Log K ₁				Log K ₂			
	10°C	20°C	30°C	40°C	10°C	20°C	30°C	40°C
Cu ²⁺	14.72	14.53	14.44	13.79	9.18	9.08	8.92	8.2
Ni ²⁺	10.84	10.53	10.28	9.46	8.60	8.14	8.22	7.79
Co ²⁺	10.71	10.37	10.19	9.31	7.99	7.82	7.63	7.29
Zn ²⁺	10.84	10.51	10.30	9.37	8.46	8.11	8.05	7.13
Mn ²⁺	10.36	10.11	9.90	9.01	6.84	6.43	6.34	5.62
Cd ²⁺	10.69	10.34	10.17	9.30	6.71	6.50	6.32	5.71
UO ₂ ²⁺	14.79	14.72	14.40	13.97	8.22	7.95	7.75	6.99
Th ⁴⁺	15.10	14.73	14.63	14.14	11.16	10.94	10.76	10.36
Sm ³⁺	12.87	12.58	12.33	11.73	9.33	9.29	9.21	9.11
Er ³⁺	12.49	12.19	11.94	11.32	9.43	9.32	9.05	8.42

Where m is the ligand basicity. The correction of pH values in 75% (v/v) dioxin- water was taken⁵ as 0.28. Since the ionic product of the water, pK_w in 75% (v/v) dioxine- water medium is approximately⁶ 18.7, both of the hydrogen and hydroxyl concentration term in equation 1 are negligible in the region of proton dissociations. The values of pK_1 and pK_2 for 2-CPHAAA ligand at different temperatures are presented in table 2.

The variation of pK_1^H and pK_2^H with $1/T$ was checked using linear regression method and always gave straight lines of correlation coefficient (r) equals to 0.990-0.999. This indicates that raising of the temperature increase the acidity of the ligand.

The linear change of pK_1^H or pK_2^H with $1/T$ permits the calculation of the enthalpies of protonation by use of Vant Hoff equation:

$$\frac{d\text{Log}K}{dT} = \frac{\Delta H}{2.303 RT^2}$$

The values of ΔH are calculated in each case by least – squares fit of the data to the relation:

$$\text{Log}K = \left(\frac{-\Delta H}{2.303RT}\right) + \text{constant} \quad (2)$$

The free energy ΔG and entropy ΔS are calculated from known relationships:

$$-\Delta G = 2.303 RT \text{Log} K \quad (3)$$

$$\text{and } \Delta S = \left(\frac{\Delta H - \Delta G}{T}\right) \quad (4)$$

The summary of protonation constants at different temperatures as well as the thermodynamic parameters for the ligand is coupled in table 2. The effect of –HN-N- β - diketone grouping on the dissociation of the carboxylate proton is apparent when this groups is absent e.g benzoic acid in which its pK^H equal⁷ 6.50.

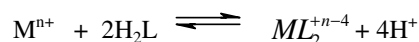
The thermodynamic parameters of the dissociation process of the ligand are given in table 2. Inspection of these values reveals that the values ΔH (ΔH_1 and ΔH_2) are positive, indicating that the dissociation is accompanied by absorption of heat and the processes is endothermic. Such positive value due to the breakage of the covalent bond present on the ligand. The thermodynamic parameters described the dissociation of the protons from carboxalate (ΔG_1 , ΔH_1 , ΔS_1) and hydrazo groups (ΔG_2 , ΔH_2 , ΔS_2) show the order $\Delta G_1 < \Delta G_2$

This order indicates that after the elimination of the carboxylate proton, the charge density on the species increases and this retards the dissociation of hydrazo proton. This is supported by the order obtained for the enthalpies and entropies $\Delta H_1 < \Delta H_2$, $\Delta S_1 < \Delta S_2$

The negative values of ΔS make the dissociation process non.- spontaneous and ΔG positive. This negative value of

entropy arise from the fact that the degree of the orientation and partial immobilization of dioxane and water molecules by H^+ , the neutral and anionic species is larger in dioxane - water mixture than in pure water.

Interaction Of 2-Cphaaa And Metal Ions: The titration curves of 3:1 2CPHAAA: metal ions indicate the diprotic nature of the ligand. Always two protons liberate by the metal cation. The curve show inflection point at $m = 4$ (m =number of moles of base added per mol of metal) due to the formation of bis chelates



The values of the stability constants at different temperateness were calculated as described in [3] and included in table 3.

The conventional thermodynamic functions accompanying complex formation were calculated and have been divided into electrostatic (el) and non-electrostatic (non) parts using the methods suggested by Gurney⁹, Anderegg⁹, Degisher and Nancalles¹⁰ and modified by Murakami and Yoshing¹¹

$$\Delta G = nRT \ln M + RC(a + e^{T/\theta}) \quad (5)$$

$$\Delta H = RC \left[a + (1 - T/\theta)e^{T/\theta} \right] \quad (6)$$

$$\Delta S = -nRT \ln M + R(C/\theta)e^{T/\theta} \quad (7)$$

Where θ is a temperature characteristic of the solvent¹². According to the definition, the separated thermodynamic parts are summarized in table 4.

Table 4 Non electrostatic (non) and electrostatic (el) thermodynamic function accompanying the complex formation:

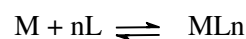


Table-4

	non	el
ΔG	$nRT \ln M + RCa$	$RCe^{T/\theta}$
ΔH	RCa	$RC(1 - T/\theta)e^{T/\theta}$
ΔS	$-nR \ln M$	$-(RC/\theta)e^{T/\theta}$

The values of the free parameters C and a to calculate each component in table 4 can be determined from equation 5 and 6 or 7 when the values of ΔS , ΔG and ΔH are known, the calculated values are given in table 5

Mixed Ligand Chelates of Uranyl and Thorium Metal Ions:

The nature of mixed complexes of $UO_2(VI)$ and $Th(IV)$ cations using 2AMP as primary ligand and 2CPHAAA as secondary one are carried out by PH –metry. The protonation constants pK_1^H and pK_2^H of the dihydro 2AMP were determined by titration of 30 ml of 0.003 M 2AMP in 75% (v/v) dioxane-water and 0.1 M KNO_3 against 0.06M HNO_3 . The values of constants obtained at 30⁰ C are 2.27 and 5.84 for pK_1^H and pK_2^H respectively.

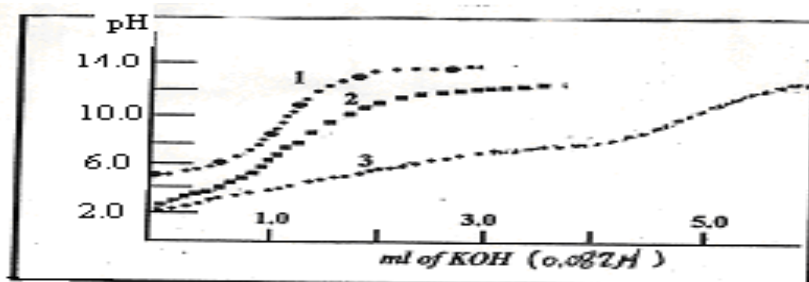


Figure-2

Potentiometric titration of 2-CPHAAA and 2-amino-4-methyl pyridine at ionic strength $\mu = 0.10\text{M-KNO}_3$, $T = 30^\circ\text{C}$ and 75% (v/v) dioacase-water in presence of $\text{UO}_2(\text{II})$ ions

- 1- 1:3 motar ratio of $\text{UO}_2(\text{II})$ (0.001M) to 2-CPHAAA(0.003M)
- 2- 1:3 molar ratio of $\text{UO}_2(\text{II})$ (0.001M) to 2-amino-4-methylpyridine (0.003M).
- 3- 1:1:1 motar ratio of $\text{UO}_2(\text{II})$ (0.003M) to 2-CPHAAA (0.003M) and 2-amino-4-methyl pyridine (0.003M)

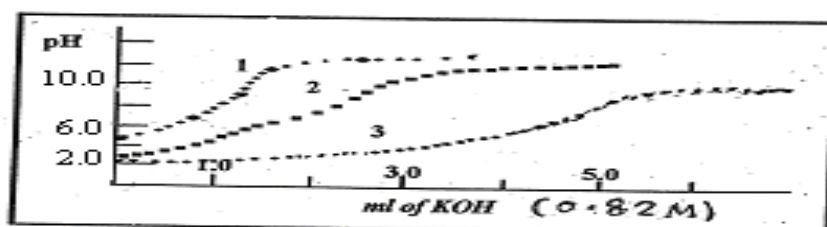


Figure-3

Potentiometric titration of 2-CPHAAA and 2-amino-4-methyl pyridine at ionic strength $\mu = 0.10\text{M KNO}_3$, $T = 30^\circ\text{C}$ and 75% (v/v) dioxane-water in presence of $\text{Th}(\text{IV})$ ions

- 1- 1:3 motar ratio of $\text{Th}(\text{IV})$ (0.001M) to 2-CPHAAA(0.003M)
- 2- 1:3 molar ratio of $\text{Th}(\text{IV})$ (0.001M) to 2-amino-4-methylpyridine (0.003M).
- 3- 1:1:1 motar ratio of $\text{Th}(\text{IV})$ (0.003M) to 2-CPHAAA (0.003M) and 2-amino-4-methyl pyridine (0.003M)

Titration procedures involved potentiometric titration of the following carbonate free solutions: 1:1:1 M: L : A (L = 2CPAAA; A = 2 AMP and M = Th^{4+} or UO_2^{2+}) = $[\text{H}_2\text{A}] = 0.003\text{ M} + [\text{H}_2\text{L}] = 0.003\text{ M} + [\text{Th}^{4+}]$ or $[\text{UO}_2^{2+}] = 0.003\text{M} + [\text{HNO}_3] = 0.006\text{ M}$

The titration curves are plotted in figure 2 and 3. The absence of any kind of precipitation during the course of the titration indicates that complex more resistant to hydrolysis is produced when the two ligands are mixed. The lowering of the original pH for 1 : 1 : 1 titration curve compared to MA and ML curves followed by inflection point at $m=4$ supported the formation of mixed complexes. Another evidence comes from each system UO_2LA or ThLA curves does not coincide with either ML or MA curve. The mixed complex formation should be, therefore takes place by simultaneous and not by stepwise equilibrium and both the ligands attached simultaneously to $\text{UO}_2(\text{VI})$ or $\text{Th}(\text{IV})$. The long buffer region between $m=0$ and $m=4$ followed by inflection point at $m=4$ in MLA curve indicate the following equilibrium:



and for UO_2^{2+}

$$K_{MLA} = \frac{[\text{MLA}]^{2-}}{[\text{H}_2\text{L}][\text{H}_2\text{A}][\text{UO}_2^{2+}]} \quad (8)$$

and for Th^{4+}

$$K_{MLA} = \frac{[\text{MLA}]}{[\text{H}_2\text{L}][\text{H}_2\text{A}][\text{Th}^{4+}]} \quad (9)$$

H_2L represents the primary ligand 2AMP and H_2A the secondary ligand 2CPHAAA.

The stability constant is calculated according to the method described by Candike and Martell¹³. The calculated values are presented in table (6).

$$\Delta\text{Log}K\text{values} = [\text{Log}K_{MLA}^M - (\text{Log}K_{ML}^M + \text{Log}K_{MA}^M)]$$

They are positive and equals 2.40 and 6.76 for UO_2^{2+} and Th^{4+} complexes respectively. The values of $\Delta\text{Log} K$ depend on the geometry of the complex and the denticity of the ligands. In the present study the $\Delta\text{Log} K$ values are relatively higher which indicates a greater stabilization of the mixed ligand complexes. The higher denticity on the ligand could account for such stabilization. The ligand 2CPHAAA

contains several coordination sites (behave as tridentate NOO-donar through oxygen of carboxylate and ketonic groups and azomethine nitrogen). This beside 2AMP ligand which acts as bidentate NN-donor

The parameter "percentage relative stabilization (% R.S.)" has been introduced and defined as

$$\%R.S. = \left(\frac{\text{Log}K_{MLA}^{MA} - \text{Log}K_{ML}^M}{\text{Log}K_{ML}^M} \right) \times 100$$

This value is 43.10 and 73.90 for UO_2^{2+} and Th^{4+} complexes respectively. These higher values indicate greater stabilization of the ternary complexes which could be tentatively be explained on the basis of cooperative effect¹⁴ between the primary and secondary ligands. The possibilities of the stereoselectivity, indirect cooperative effect and intra – molecular covalent bond formation being ruled out and hydrophobic interaction takes place and consequently greater stabilization of the mixed complexes results.

Complexes in solution state: Table 5 report the data on thermodynamic parameters ΔG_n , ΔH_n and ΔS_n (n=1,2). The data of all complex systems show negative values of enthalpy, while entropy values are positive or negative. These indicate that in systems of negative enthalpy and positive entropy values are enthalpy or entropy controlled, while for complex of negative enthalpy and entropy, the enthalpy contribution has the major deriving force.

The values of the stability constants of the complexes under investigation decrease with a rise of temperature, indicating that the formation equilibria are exothermic in nature. This is also borne out by the fact that ΔG and ΔH are both negative. The ΔG_n values in any solution examined varied as usual, in the sequence - $\Delta G_1 > -\Delta G_2$. The values of ΔH_n generally varied in the sequence - $\Delta H_1 > -\Delta H_2$ while the entropy order is as follows $\Delta S_1 > \Delta S_2$. Therefore, the decrease in ΔS_n with n increase is responsible for the decrease in ΔG_n with the increase in n.

Table-5
Thermodynamic parameters, non-electrostatic (non) and electrostatic (el),
Thermodynamic quantities and T* associated with the reaction of metal ions with 2-CPHAAA.
In 75% dioxane – water [$\mu = 0.1 \text{ M KNO}_3$, $V_o=30 \text{ ml}$, $[L_o]=0.003 \text{ M}$, $[M_o] = 0.001 \text{ M}$]

Cation	$-\Delta G_1$	ΔH_1	ΔS_1	c	a	$\Delta G_{1\text{non}}$	$-\Delta G_{1\text{el}}$	$\Delta H_{1\text{non}}$	$\Delta H_{1\text{el}}$	ΔS_1
	K cal / mol					K cal / mol		K cal / mol		
Cu^{2+}	20.04	10.56	101	-2798.1	-0.103	2.992	23.229	0.574	9.985	108.98
Ni^{2+}	14.27	15.68	98.9	-2743.10	-1.080	8.309	22.772	5.891	9.789	106.83
Co^{2+}	14.15	11.75	85.5	-2399.80	-0.668	5.603	19.923	3.185	8.564	93.465
Zn^{2+}	14.30	17.06	103.50	-2862.50	-1.203	9.262	23.764	6.844	10.215	111.49
Mn^{2+}	13.74	10.53	80.10	-2261.70	-0.547	4.876	18.776	2.458	8.071	88.085
Cd^{2+}	14.11	15.60	98.10	-2722.70	-1.087	8.301	22.603	5.883	9.716	106.04
UO_2^{2+}	19.98	9.94	98.8	-2740.50	-0.029	2.578	22.751	0.160	9.779	106.73
Th^{4+}	20.30	10.90	103	-2849	-0.129	3.150	23.651	0.733	10.167	110.96
Sm^{3+}	17.11	12.97	99.30	-2754.10	-0.574	5.559	22.863	3.141	9.828	107.26
Er^{3+}	16.37	13.32	98.70	-2721	-0.667	6.027	22.589	3.609	9.710	105.97
	ΔG_2	ΔH_2	ΔS_2	c	a	$\Delta G_{2\text{non}}$	$-\Delta G_{2\text{el}}$			
	Kcal/mol					cal/mol.K			Kcal/mol	
Cu^{2+}	12.37	13.17	84.30	-2369.30	-1.001	7.132	19.669	4.714	8.455	92.277
Ni^{2+}	11.45	9.32	68.60	-1965.10	-0.590	4.725	16.314	2.307	7.012	76.533
Co^{2+}	10.59	8.04	61.70	-1783.70	-0.472	4.092	14.808	1.674	6.365	69.47
Zn^{2+}	11.17	15.17	86.90	-2437.10	-1.336	8.890	20.232	6.472	8.697	94.617
Mn^{2+}	8.80	13.89	74.90	-2127.80	-1.489	8.714	17.664	6.296	7.593	82.87
Cd^{2+}	8.77	11.43	66.60	-1916.80	-1.205	7.007	15.913	4.589	6.8403	74.652
UO_2^{2+}	14.14	10.75	82.20	-2314.20	-0.541	4.909	19.212	2.491	8.258	90.131
Th^{4+}	14.93	9.10	79.30	-2241.40	-0.247	3.519	18.607	1.101	7.998	87.293
Sm^{3+}	12.79	2.02	48.90	-1460	-1.099	-0.772	12.120	-3.190	5.210	56.862
Er^{3+}	12.56	11.57	79.60	-2249.80	-0.792	5.959	18.677	3.541	8.028	87.623

Table-6
Stability constants of single and mixed chelates and other related parameters

Metal ion	Primary Ligand (H ₂ A)	LogK ^M _{MA}	Secondary Ligand(H ₂ L)	Logk ^M _{ML}	LogK _{MLA} Δ logk %R.S}
UO ₂ ²⁺	2AMP	3.34	2-CPHAAA	14.72	21.06
					2.40
					43.10
Th ⁴⁺	2AMP	4.02	2-CPHAAA	14.73	25.61
					6.76
					73.90

The decreased values of ΔH_n and ΔS_n with increase of n might be expected if stronger metal-ligand bonds within an aquametal ion-weakens when a part of the water molecules within the aquametal ion is replaced with a ligand which has an atom or atoms, with stronger donor property than water¹⁵. Thus we can accept that the Ln-OH₂ bonds within the mono complex are weaker than those within the aquametal ion. Therefore when the second ligand molecule bonded to the mono complex, the energy(enthalpy)to expel water molecules (the ligand is tridentate OON-donor) from the coordination sphere of the mono complex may be less than that of aquametal ion consequently the stepwise enthalpy of formation of these complexes became less negative than the mono complex.

In contrast, when water molecules within the mono complex in which water molecules combine relatively weakly with the metal ions are removed from the coordination sphere, a lower entropy gain may result compared with that for releasing water molecules from aquametal ion.

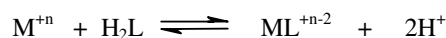
The tridentate (OON-donor abilities of 2-CPHAAA is confirmed from its higher negative enthalpy values of different complexes table 5. Digisher and Nancollas¹⁰ have permitted out that for systems involving nitrogen and carboxylate oxygen, the ΔH values reflected the change in the number and strength of the bonds made and broken during the reactions and have correlated the values of ΔH to the type of bonding between metal ion and the ligand molecule, and to structural feature of the complex-considering this and the fact that the crystal field produced by an oxygen containing ligand, i. e COOH or C=O are similar to those of water molecule¹⁶, ΔH will not be significantly affected by the displacement of water molecules. Thus, the higher negative values of the enthalpies of the complex system obtained here could be related to the coordination sites of nitrogen atom of hydrazo group.

The entropy changes associated with metal – chelate formation on the studied systems are relatively high and positive for 1:1 complexes table 5. In the case of bis – chelate positive values are obtained which could be attributed to a combination of (a) an increase in ΔS values owing to release of water of hydration (b) a decrease in entropy of translation on the formation of one chelate from two species (c) a

decrease in configuration entropy of the ligand on the complex formation. For reactions with charged donor group (the ligand behaves as dianion species i.e L²⁻) the entropy changes associated with (a) predominate because neutralization of charge on the metal ion cause great disorder.

In order to provide information on the nature of bonding in the complexes, the values of ΔG_n, ΔH_n and ΔS_n have been separated into their electrostatic (el) and non electrostatic (non) or cratic components. The separated ΔG_{el}, ΔG_{non}, ΔH_{el}, ΔH_{non} and ΔS_{el} (ΔS_{non} is constant and equals to 8 cal/mol.k) are calculated and given in table 5 for all complexes:

For the equilibrium involving mono complex formation which has been represented by the equation



ΔG_{non} values are more negative than ΔG_{el} value indicating that the electrostatic forces are weaker than non-electrostatic forces: The order is- ΔG_{non} > -ΔG_{el} and remains almost constant in all complexes table 5, indicating thereby that metal chelation reactions occurs by similar mechanism. The enthalpy that also support the above consideration i.e -ΔH_{non} > -ΔH_{el}. The ΔH_{non} value reflects the covalency of bonding and structural change on complexes¹⁰.

Regarding the covalency, the softer metal ion has a greater affinity for softer donor¹⁷. The quantity E_n[#] was introduced by Klopman¹⁸ as a measure of hardness and softness of metal ion in aqueous solution, A soft metal is characterized by a large negative value of E_n[#] and vice versa. In general the E_n[#] value above 2.0 ev (hard), 2 to - 2 ev intermediate and below - 2ev (soft) respectively. According to this soft metal such as Cd²⁺ (E_n[#] = -2.04ev), Cu²⁺ (E_n[#] = -0.55ev) border line, metals such as Ni²⁺, (E_n[#] = 0.29ev), Fe²⁺ (E_n[#] = 0.69ev), hard metals such as La³⁺ (E_n[#] = 4.5 ev), Co²⁺ (E_n[#] = 2.03ev). Values of ΔH_{non}(ΔH_{non1} + ΔH_{non2}}) are plotted against the quantity E_n[#] Figure 4. A linear correlation appears to exist, -ΔH_{non} increases with the softness or hardness of metal ion. A deviation of Co²⁺ from the line, in addition to Ln³⁺ (E_n[#] = 4.5 ev) does not fit the line in the figure. This could be related to the different nature of lanthanum complexes (mainly ionic) than d-block elements.}

Table-7
Characteristic IR bands (cm⁻¹)^a of organic ligands and H₂L and its metal complexes

Compound	ν (OH)	ν (NH) Hydrazone	ν (CH) aromatic	ν (CH) aliphatic	ν (C=O)	ν (C=N)	$\nu_{as}COO^-$	ν_sCOO^-	ν (M-O)	ν (M-N)	Additional bands
(1) H ₂ L (ligand)	3308 br	3255 br	3055 s	2967 m	1695 s 1664 s	1598 s	-	-	-	-	3182 br ν (NH) of acetanilide moiety.
(2)	-	3234 br	3075 m	2959 m	1661 s	1597 s	1484 s	1319 s	691 m 624 m	532 m	3380 br (lattice water), 3185 br ν (NH) of acetanilide moiety.
(3)	-	-	3083 m	2963 m	1675 s	1591 s	1448 s	1314 s	690 m 665 m 636 m	530 m	3523 br (coordinated water), 3186 br ν (NH) of acetanilide moiety.
(4)	-	-	3070 m	2966 m	1669 s	1593 s	1447 s	1311 s	690 m 663 m 636 m	561 m 530 m	3522 br (coordinated water), 3411 br (lattice water), 1574 s (coordinated C=N of 1,10-phen) 3184 br ν (NH) of acetanilide moiety.
(5)	-	-	3063 m	2962 m	1676 s	1591 s	1448 s	1314 s	690 m 666 m 637 m	560 m 530 m	3528 br (coordinated water), 3411 br (lattice water), 3176 br (coordinated NH ₂ group and ν (NH) of acetanilide moiety), 961 s (pyridine ring breathing mode).
(6)	-	-	3075 s	2967 m	1659 s	1590 s	1448 m	1310 s	690 m 660 m 624 m	538 m	3508 br (coordinated water), 3394 br (lattice water), 3183 br ν (NH) of acetanilide moiety.
(7)	-	-	3059 s	2961 m	1654 s	1593 s	1448 s	1313 s	693 m 663 m 624 m	560 m	3486 br (coordinated water), 3185m br ν (NH) acetanilide moiety).
(8)	-	-	3074 s	2964 m	1659 s	1584 s	1485 s	1356 s	693 m 665 m 621 m	533 m	3504 br (coordinated water), 3428 br (lattice water), 3187 br ν (NH) of acetanilide moiety.
(9)	-	3222 br	3067 s	2962 m	1659 s	1584 s	1485 s	1313 s	693 m 666 m	530 m	3391 br (coordinated water), 3180 br ν (NH) of acetanilide moiety, 931 s (antisymmetric ν (O=U=O))

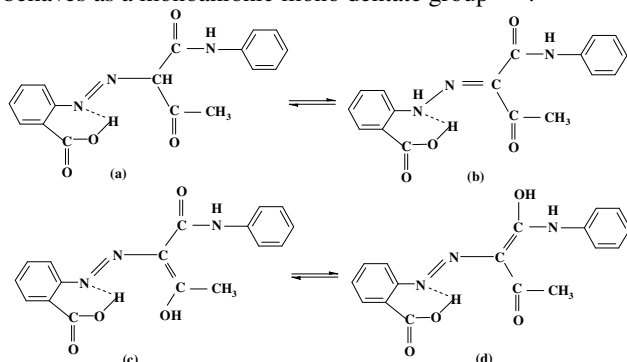
The values of ΔH_{ci} presented in table 5 are nearly constant. This is ascribed to the nearly constant ionic radius of these metals. As result of this the value of ΔH for a given complex system is mainly determined by the value of ΔH_{non}

Complexes in solid state: The ligand 2 CPHAAA (H₂L) has different tautomers as shown in scheme 1. The band at 3204 cm⁻¹ due to hydrazo group¹⁹⁻²¹ indicates that tautomer (b) in scheme 1 is the predominant one. The broad band observed at 3308 cm⁻¹ in the spectra of the free ligand table 7 is

assigned to ν (OH) of the carboxylic group. The broadness of such band is due to hydrogen bond formation.

The carbonyl group of carboxylic was observed at 1695 cm⁻¹. In all complexes the band due to ν (OH) of the carboxylic group disappeared, indicating its deprotonation in the ligand during complexation. The participation of the carboxylate groups in complex formation is also confirmed by the disappearance of the band due to ν (C=O) of -COOH group and appearance of two new bands at 1447-1487 and 1310-

1356cm⁻¹. Table 7, assigned to $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ respectively. This indicates that the carboxylate group behaves as a monoanionic mono dentate group²²⁻²⁴.



Scheme-1

The stretching vibrations of carbonyl groups of the ligand is complicated due to the overlap between the carbonyl groups of both carboxylic and acetyl group which leads to a single band at 1695cm⁻¹, the band due to carbonyl group of acetanilide moiety was observed at 1664cm⁻¹. In all complexes a band was observed at 1664-1675 cm⁻¹ assigned to the overlap of the coordinated group of the acetyl group and the uncoordinated carbonyl group of the acetanilide moiety. The azomethine group was observed at 1598 cm⁻¹ in ligand spectra and was slightly affected in all complexes of 2CPHAAA ligand.

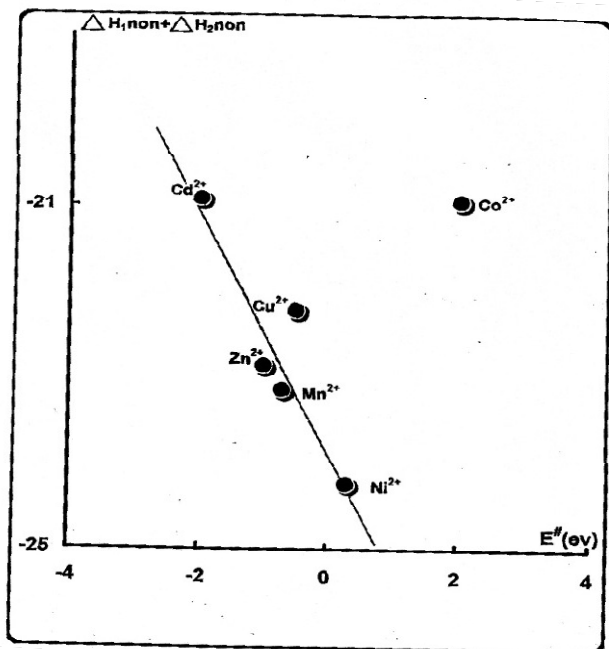


Figure-4

The relation between hardness and softness $E^\#$ (eV) of metal ion with $\Delta H_{1ion} + \Delta H_{2non}$ for 2-CPHAAA

The ligand (H₂L) showed IR bands at 3255 and 3182 cm⁻¹, due to $\nu(\text{NH})$ of hydrazone moiety and $\nu(\text{NH})$ of acetanilide moiety respectively. The band due to $\nu(\text{NH})$ of acetanilide moiety, was slightly shifted in all complexes except cadmium and uranyl complexes appears at 3234 and 3222cm⁻¹ respectively.

The IR spectra of the free ligand and its metal complexes indicated that the ligand behaves either as a monoanionic tridentate, through oxygen atoms of carboxylic or carbonyl groups and the nitrogen atom of NH group of hydrazone moiety or as a dianionic tridentate ligand, as the previous mode of coordination except the deprotonation of NH group of hydrazone moiety. The mixed -1,10-phen complexes (4) showed new band at 1574 cm⁻¹ would be due to the coordinated C=N groups of 1-10-phen²⁵⁻²⁸.

The mixed 2-amino-4-methylpyridine (2AMP) complexes (5) showed two new bands at 3176 and 961 cm⁻¹. The second band is assigned to the skeletal vibration of pyridine ring [29], breathing mode, while the first band is due to the coordinated NH₂ groups. The two new bands at 690cm⁻¹ and 561cm⁻¹ are assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ respectively. The $\nu(\text{OH})$ of the lattice water were observed at 3411 cm⁻¹, while the IR spectra of complexes display the absorption peaks of coordinated water at 3528 cm⁻¹.

The IR spectra of the uranyl complexes (19) show strong band at 931cm⁻¹ assigned to anti symmetric $\nu_{as}(\text{O}=\text{U}=\text{O})$ vibration

The assignment of the main signal in the ¹H NMR spectra of the free ligand and their diamagnetic complexes of cadmium ion are listed in table 8. The free ligand showed a signal at 14.92 ppm due to the carboxylic group proton. This signal disappeared in the complex [Cd(HL)₂].3H₂O (2). This indicates the deprotonation of the carboxylic group - COOH during the formation of the metal complexes. The signal due to the NH group of hydrazone moiety was observed at 13.73 ppm this signal was shifted down field in the spectrum of complex indicating the participation of this group in coordination to central metal ion. The signal of the NH group of acetanilide moiety in the free ligand was observed at δ 11.08 ppm (H) and slightly affected in complex (2) indicating the non involvement of this group in coordination to the central metal ion.

The free ligand also showed the signals due to the aromatic protons at δ 7.15-8.00 ppm which were slightly shifted upfield in the complexes. The signals due to aliphatic protons were observed at δ 1.92 ppm (3H) due to the CH₃ group. These protons were slightly shifted to 2.01 ppm in the complex. The lattice water molecules were observed at δ 3.40 ppm (6H) for cadmium complexes.

Table-8
¹H NMR data for organic ligand H₂L and its Diamagnetic Cadmium complexes

Compound	$\delta(\text{COOH})^a$	$\delta(\text{NH})$ hydrazone	$\delta(\text{CH})$ aromatic	$\delta(\text{CH})$ aliphatic	Additional signals
H ₂ L Free ligand	14.92 (H)	12.73 (H)	7.15 – 8.0 (9H)	1.92 (3 H)	δ 11.08 (H) proton of NH group of acetanilide moiety
(2)	-	15.26 (2H)	7.13-8.11(18 H)	2.01 (6 H)	δ 11.07 (2H) protons of NH group of acetanilide moiety δ 3.4 (6H) lattice water

Table-9
Molar conductance, Magnetic Moment and Electronic Spectral Data, cm⁻¹ for organic ligand H₂L and its metal complexes

Compound	Molar Conductance ^a (Ohm-1 cm ² mol ⁻¹)	μ_{eff}^b (B.M.)	$\Pi \longrightarrow n^*, n \longrightarrow n^*$ Charge transfer transitions	$d \longrightarrow d$ Transitions
H ₂ L Free ligand	-	-	333670 , 28612 , 25126	-
2	6.16	Diam	34483 , 28571 , 24630	-
3	4.85	1.97	34602 , 28531 , 23781	20325 , 17480
4	3.30	1.91	34188 , 28490 , 23952	19084 , 15106
5	7.95	1.78	34662 , 28612 , 23781	20555 , 14738
6	9.30	2.64	34423 , 28571 , 23502	20704 , 16892
7	9.60	2.89	33784 , 28612 , 23809	15314
8	19.30	Diam	34130 , 28531 , 24450	-
9	8.24	Diam	34130 , 28531 , 24125	-

a DMF solutions , 10⁻³ , at 28 °C

b Measurements were taken at 27 °C

From the results of both ¹HNMR and IR spectra, it is suggested that the modes of coordination of the free ligand are as follows:

The ligand behave as mono basic tridentate one , through the oxygen atom of the carboxylic group, the nitrogen atom of NH group of the hydron moiety and oxygen atom of the carbonyl groups of the acetyl moiety or dianionic ligand, as previous mode of coordination except the deprotonation of NH groups of the hydrazone moiety.

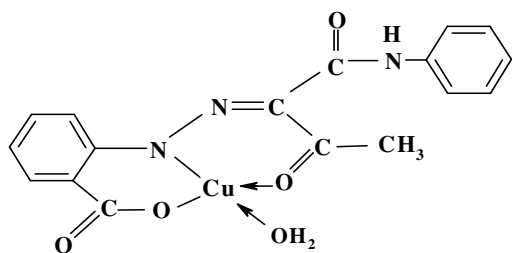
The conductance measurements (10⁻³M in DMF) indicate the complexes are non electrolyte. The UV-Visible spectra of the ligand and its complexes were carried out in 10⁻³ solutions. The values of band position (cm⁻¹) and the magnetic moment values are listed in table 9.

The UV-Visible spectra of the ligand showed bands at 33670, 28612 and 25126 cm⁻¹ assigned to $\Pi - \Pi^*$, $n - \Pi^*$ and charge transfer (CT) transitions within the molecules, respectively. The band of the free ligand were slightly blue shifted in all complexes, while new bands were observed in the visible region for Cu(II), Co(II) and Ni(II) complexes due to d-d transitions.

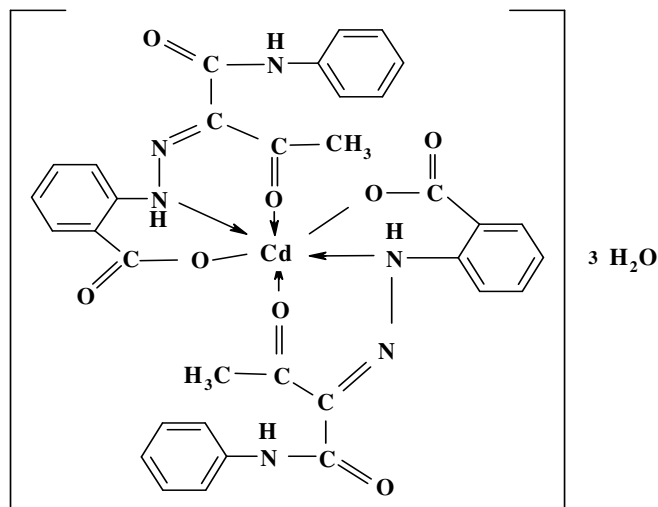
The magnetic moment μ_{eff} value, of the binary Cu(II) complexes (3) was 1.97 B.M. This value reveals the presence of one unpaired electron and shows no copper – copper interaction. The a absorption band observed in its visible region at 20325 and 17480cm⁻¹ are due to d –d transition in square planar Cu(II) complexes and are assigned to combination of $B_{1g} - E_g$ and $B_g - A_{1g}$ transitions³⁰. The proposed structure for this complex in the square planar geometry is shown in figure 5.

The mixed ligand complexes of Cu (II) with 1,10- phen. (4) and 2AMP (5) showed magnetic moment values, μ_{eff} in the range, 1.78-1.91 B.M These values correspond to one unpaired electron and this offer an evidence for mononuclear structure of the complexes.

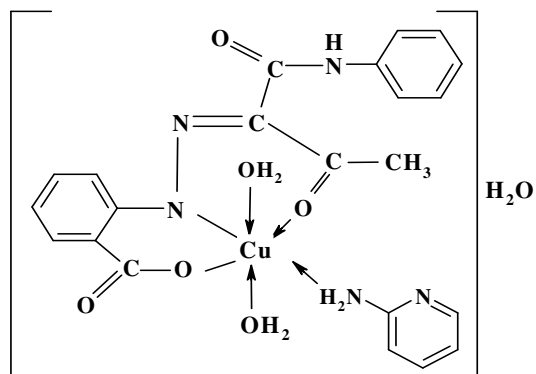
The mixed ligand complexes of Cu (II) exhibited two transitions bands in the region 19084 – 20555 and 14738–15196 cm⁻¹.The transitions including the mixed ligand complexes are similar in energies to those of binary complexes, and this indicated that the geometry of copper ion in the mixed complexes is distorted octahedral. The proposed structures of the mixed 1, 10 phen and 2AMP complexes are shown in figure.5.



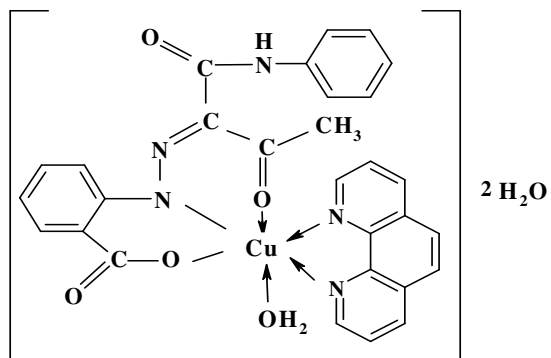
(3)



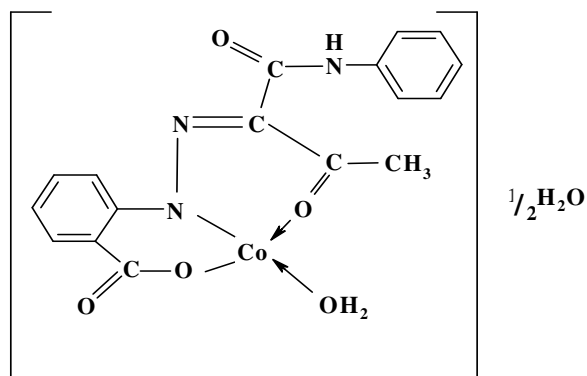
(2)



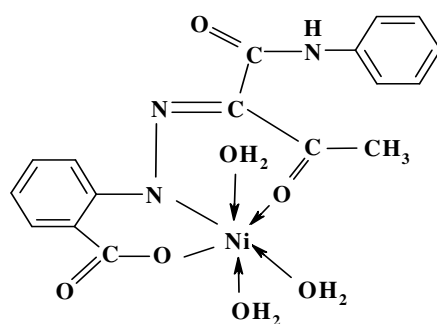
(5)



(4)



(6)



(7)

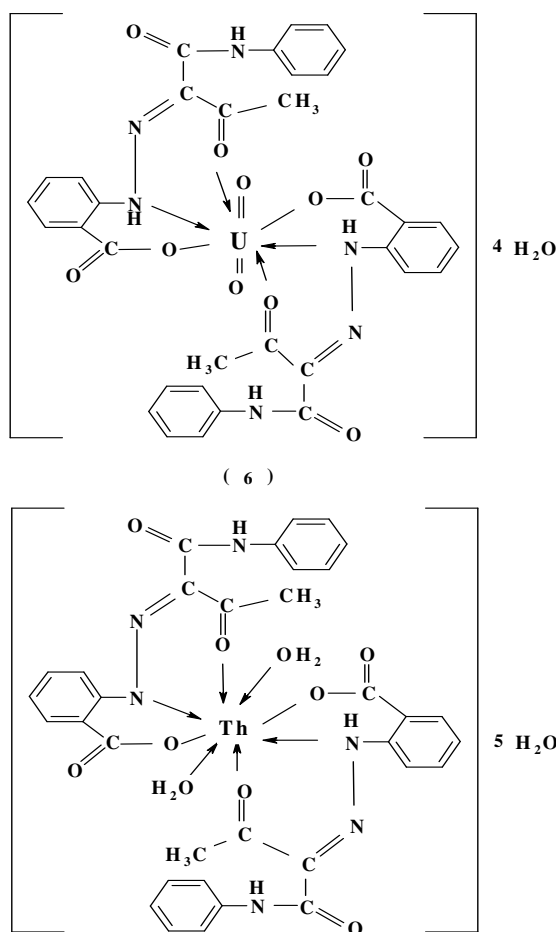


Figure-5
Suggested Structures of binary and ternary complexes

The binary Co(II) chelates have the room temperate magnetic moment value 1.78 B.M, as expected for a square – planar Co(II) complexes^{31,32}. The visible spectra exhibit peaks at 20704 and 16892 cm^{-1} , assigned to $A_{1g} - {}^2 E_g$ and $A_{1g} - {}^2 E_{2g}$ transitions respectively, and are compatible with a square – planar geometry figure 5.

The magnetic moment of the binary Ni(II) complex was found to be 2.89 B.M. suggest its octahedral structure [33]. The transition bands in the region 23809 and 15314 cm^{-1} assignable to ${}^3A_{2g} - T_{1g} (F)$ and ${}^3A_{2g} - {}^3T_{1g}(P)$ transitions respectively. The first transition band of the complex was overlapped by CT transition across the ligand molecules figure 5.

The binary complexes of Cd(II), Th(IV) and $\text{UO}_2(\text{VI})$ are diamagnetic and the electronic spectra of the complexes are dominated only by the ligand bands. The elemental analysis and ${}^1\text{H}$ N M R spectra showed that Cd(II) complex have octahedral configuration figure 5. The complexes of Th(IV)

and $\text{UO}_2 (\text{VI})$ have octa- coordination number and in a distorted dodecahedral geometry figure 5.

The results of TG – DSC analysis of the binary and mixed complexes are shown in table 10. The results shown good agreement with theoretical formula as suggested from analyses data. The complexes became anhydrous at 76–137 $^\circ\text{c}$.

The loss of crystal water molecules was accompanied by endothermic peak in DSC with ΔH 33.67 – 571.23 J/g. The coordinated water molecules were eliminated from complexes at relatively higher temperatures than the lattice water or outersphere water molecules. There are different routes in the removal of coordinated water molecules from the complexes, as follows:

1-Elimination of coordinated water molecules only in a separate steps as complexes (5) , (6) , (7) , (8) and (9) – The elimination of coordinated water molecules in this step (112–

240°C) was accompanied by endothermic peak 2-elimination of the coordinated water molecules was accompanied by the decomposition of the complex at 272 °c (ΔH 64.82 j/g) and lead to non – isoble complex.

The complexes start to decompose at relatively higher temperatures > 260 °c, and the organic ligand lose the gases CO_2 , CO, (CN) $_2$, HC \equiv CH, and $CH_3 - CH_3$.

Table-10
Thermal analyses data for organic ligand H₂L and its metal complexes

Compound	Temperature Range (°C)	% Loss in weight found (calc.)	DSC peak (°C)		ΔH (J/g)	Composition of the Residue	Probable composition of the Expelled Groups
			Endo	Exo			
(1) H ₂ L Free ligand	50-293 293-517	38.92(38.73) 75.49(75.31)	256 483	- -	93.17 107.33	C ₁₃ H ₁₃ N ₂ C ₄ H ₄ N ₂	One molecule of CO ₂ , two molecules of CO and one molecule of CN Half molecule of CH ₃ -CH ₃ and four molecules of HC \equiv CH
(2)	40-119 119-353	6.54(6.63) 44.69(44.42)	99 -	- 271	53.66 -13.36	[Cd(H ₂ L) ₂] [Cd(C ₁₁ H ₁₀ N ₂) ₂]	Three molecules of lattice water Two molecules of CO ₂ , four molecules of CO, two molecules of CN, half molecule of CH ₃ -CH ₃ and one molecule of HC \equiv CH
(3)	50-167 167-374	4.50(4.45) 52.37(52.12)	118 -	- 331	11.00 -53.85	[Cu(HL)] [Cu(C ₆ H ₆ N ₂) ₂]	One molecule of coordinated water One molecule of CO ₂ , two molecules of CO, one molecule of CN, half molecule of CH ₃ -CH ₃ and two molecule of HC \equiv CH
(4)	40-119 119-310 310-352	5.83(5.80) 29.20(28.98) 48.27(48.14)	103 - 239	- 272 -	122.00 -64.82 26.19	[Cu(HL)(1,10-phen)(OH ₂)] [Cu(C ₁₃ H ₁₃ N ₂ (1,10-phen))] [Cu(C ₄ H ₂ N ₂ (1,10-phen))]	Two molecules of lattice water One molecule of coordinated water, one molecule of CO ₂ , two molecules of CO and one molecule of CN Half molecule of CH ₃ -CH ₃ and four molecules of C \equiv N
(5)	40-109 109-240 240-474	3.74(3.67) 10.22(10.10) 63.93(63.76)	101 - 402	- 240 -	38.94 -79.24 16.84	[Cu(HL(2-Amp)(OH ₂) ₂)] [Cu(HL(2-Ampy))] [Cu(C ₆ H ₆ N ₂) ₂]	One molecule of lattice water Two molecules of coordinated water One molecule of CO ₂ , two molecules of CO, one molecule of CN, half molecule of CH ₃ -CH ₃ , two molecules of HC \equiv CH
(6)	35-87 87-185 185-414	2.26(2.20) 6.77(6.60) 53.94(53.75)	68 161 342	- - -	34.75 70.52 14.56	[Co(HL)(OH ₂)] [Co(HL)] [Co(C ₆ H ₆ N ₂) ₂]	Half molecules of lattice water One molecule of coordinated water One molecule of CO ₂ , two molecules of CO, one molecule of CN, half molecule of CH ₃ -CH ₃ , two molecules of HC \equiv CH
(7)	50-160 160-235 235-401	8.40(8.26) 12.44(12.39) 56.79(37.55)	160 224 349	- - -	78.38 3.52 15.34	[Ni(HL)(OH ₂)] [Ni(HL)] [Ni(C ₈ H ₆ N ₂) ₂]	Two molecule of coordinated water One molecule of coordinated water One molecule of CO ₂ , two molecules of CO, one molecule of CN, half molecule of CH ₃ -CH ₃ , two molecules of HC \equiv CH
(8)	35-127 127-262 262-405	8.76(8.94) 12.48(12.52) 37.79(37.55)	103 - -	- 236 385	61.56 30.17 184.45	[Th(HL) ₂ (OH ₂) ₂] [Th(HL) ₂] [Th(C ₁₃ H ₁₃ N ₂) ₂]	Five molecules of lattice water Two molecule of coordinated water Two molecule of CO ₂ , four molecules of CO, and two molecule of CN
(9)	40-123 123-343 343-568	7.14(7.27) 27.69(27.46) 56.98(56.73)	104 - 441	- 311 -	69.08 -68.92 3.90	[UO ₂ (H ₂ L) ₂] [UO ₂ (C ₁₄ H ₁₄ N ₃) ₂] [UO ₂ (C ₄ H ₃ N ₂) ₂]	Four molecules of lattice water Two molecules of CO ₂ , and four molecules of CO Two molecules of CN, one molecule of CH ₃ -CH ₃ and eight molecules of HC \equiv CH

Conclusions

This study reports the effects of temperature, metal ions, ligands on the stability of the chelates as well as their thermodynamic parameters. Generally the values of the stability constants of the complexes under investigation decrease with a rise of temperature, indicating that the formation equilibria are exothermic in nature. This is also borne out by the fact that ΔG and ΔH are both negative. The ΔG_n values in any solution examined varied as usual, in the sequence $-\Delta G_1 > -\Delta G_2$. The values of ΔH_n generally varied in the sequence $-\Delta H_1 > -\Delta H_2$ while the entropy order is as follows $\Delta S_1 > \Delta S_2$. Therefore, the decrease in ΔS_n with n increase is responsible for the decrease in ΔG_n with the increase of n . Value of ΔH non show linear variation with the hardness and the softness (E_n) of the metal ions. The tridentate OON-donor abilities of 2-CPHAAA is confirmed from its higher negative enthalpy values of different complexes. The most solid complexes have an octahedral geometry which is distorted in the mixed complexes.

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