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PH-metric and Theoretical Studies of The Complexation of 2-[α-(o-hydroxyphenyl)ethylidenehydrazino]-4,6-dimethylquinoline and 2-[α-(o-methoxyphenyl)methylidenehydrazino]-4,6-dimethylquinoline

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2-[α-(o-Hydroxyphenyl)ethylidenehydrazino]-4,6-dimethylquinoline (AHQ) and 2-[α-(*o*-methoxyphenyl)methylidenehydrazino]-4,6-dimethylquinoline (BHQ) have been synthesized and characterization is performed by elemental analysis and electronic, vibrational and mass spectra. The pK^H and log K were gritty in 75% solvent-water pH-metrically for BHQ ligand and at various temperatures for AHQ ligand. The dissociation and stability constants in the aqueous medium for BHQ ligand have been calculated by the relation of pK^H or log K with solvent parameters (D, ET, AN and DN). The isokinetic temperature was determined by using a linear regression analysis (LRA) of ΔH° *vs.* ΔS° for AHQ complexes. The thermodynamic parameters of AHQ compounds were analyzed into their electrostatic (el) and non-electrostatic (non) or cratic components. Full geometrical and structural optimizations of the ligands have been performed by a *DFT* study by using the hyperchem program.

Keywords: Quinolinyl hydrazones, Stability constants, Theoretical studies, Solvent and thermodynamic parameters

Introduction

Hydrazones are excellent chelating agents, which attracted special interest as well as their metal complexes because of their important applications including antimicrobial, antitumor and other biological applications[1-9]. The quinolone derivatives and their metal complexes play essential role in many fields[10]. The heterocycle compounds that have N atoms can carry a positive charge and act as a hydrogen bond acceptor or donor[11]. Many drugs in the market are prepared from quinolone derivatives[12]. They have pharmacological activities including antimicrobial, antioxidant, toxicity assessment[12], antiplasmodial, antimalarial[13], antituberculosis[14], anti-inflammatory[15] and anticancer properties[16]. This work is extension of studies on quinolone hydrazones[17-24]. The aim of the pH-metric studies is calculation of the dissociation constants of the ligands and the stability constants of their metal complexes in solution. However, these studies were performed under different experimental conditions *viz.*

Various mixed solvents, 75% (v/v) solvent-water; solvent = dioxane, isopropanol, ethanol and methanol) at 303K for BHQ ligand with some divalent 3d transition metal ions (Mn^{II}, Co^{II}, Ni^{II} and Cu^{II}), non transition 3d and 4d metal ions (Zn^{II} and Cd^{II}), trivalent 4f lanthanide metal ions (La^{III}, Ce^{III}, Sm^{III} and Ho^{III}) and 5f actinide metal ions (UO_2^{II}).

Various temperatures (283, 293, 303 and 313K) for AHQ ligand with Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}-ions.

Experimental

Materials

p-Toluidine, ethyl acetoacetate, phosphorus oxychloride, hydrazine hydrate, *o*-hydroxyacetophenone, *o*-anizaldehyde, hexamine, indicators, salts and solvents used

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in this investigation were of the highest purity available (Merck, BDH, Aldrich and Fluka).

Preparation of the hydrazones

2-Hydrazino-4,6-dimethylquinoline (HQ) is prepared as described in our previous publication[17]. To an ethanolic solution of 2-hydrazino-4,6-dimethylquinoline (HQ) (0.01 mol), *o*-anizaldehyde or *o*-hydroxyacetophenone (0.012 mol) was added. The mixture was heated under reflux for 1/2 hour. After cooling, the formed yellow compounds were filtered off, washed with ether and the ligands are crystallized by ethanol. The results of elemental analyses, % yield, colour and m.p °C are shown in Table 1. The resultant hydrazones are; 2-[α-(*o*-hydroxyphenyl) ethylidenehydrazino]-4,6-dimethylquinoline (AHQ) and 2-[α-(*o*-methoxyphenyl) methylidenehydrazino]-4,6-dimethylquinoline (BHQ). The results of elemental analyses (Table 1) are in best agreement with the proposed formulae.

Measurements

Physical measurements

IR spectra (4000-400 cm^{-1}) were verified on a BRUKER Vector 22 spectrometer (Germany) using KBr pellets. UV-Visible spectra were elucidated on a Jasco V-550 UV/VIS spectrophotometer. Mass spectra were examined at 70 eV on a gas chromatographic GCMSqp 1000-ex Shimadzu mass spectrometer.

Potentiometric measurements

WTW-D-8120 digital pH-meter fitted with a combined glass electrode was used to measure pH-reading of the titration of standard solutions of metal nitrates (0.001M) with ligands (0.003M). Solutions were adjusted to 0.05M ionic strength by addition of KNO_3, the total volume was made up to 30 mL and maintained at a constant temperature by circulated water through a sealed-jacketed cell.

Results and Discussion

Characterization of the ligands

The structures of the ligands have been determined by elemental analyses, IR, mass and UV-Vis spectra.

IR & Mass spectra of the ligands

The IR spectra of the hydrazones (AHQ & BHQ) (Table 1) showed very strong bands at *ca.* 1616 - 1614 and 3440 – 3175 cm^{-1} which are attributed to ν(C=N) and ν(NH), respectively[25-34]. On the other hand, the broad band centered at 2868 cm^{-1} is assignable to ν(OH---N) of the phenolic group of AHQ, ligand[35-37]. The mass spectrum of the BHQ ligand showed molecular ion and base peaks at *m/z* 305 and 172, respectively, which coincide with its formula weight.

Electronic spectra of the ligands

The electronic absorption spectra of the investigated ligands as well as the hydrazino compound; HQ ($5x10^{-5}$ mol. dm^{-3}) in dioxane involve three or two sets of bands in the region 239 – 418 nm (Table 2). On the basis of the high molar absorptivity ε_{max}, the highest energy bands at λ_1 (239 – 247 nm) are assigned to π - π* transitions of the quinoline ring[7], phenyl rings and/or azomethine groups. Also, the moderate energy bands at λ_2 (344 – 351 nm) may be composite bands due to charge transfer (CT) interactions[25-29]. Finally, the lower energy bands at λ_3 (329 - 418 nm) can be ascribed to the low intensity n - π* forbidden transitions. The π - π* transition (band at 247 nm) of the non condensed HQ compound is more intense by ≈ 2 – 4 times than the corresponding hydrazones. Also, this band shows a red shift (Table 2). The etheric hydrazone BHQ has the highest λ_{max} and ε_{max}. Therefore, the weak n - π* transition was hidden under the strong π - π* transitions.

Molecular orbital calculations

The calculated structural parameters are

TABLE 1. Analytical, physical data and selected IR absorption bands (cm^{-1}) of the ligands.

Compound (F.Wt) M.F.	Colour	% Yield	Elemental Analysis % Found / (Calcd)			m.p.°C	IR spectral bands (cm^{-1})		
			C	H	N		ν(C=N)	ν(OH---N)	ν(NH)
AHQ (305) $C_{19}H_{19}N_3O$	Yellowish-Orange	75	74.38 (74.75)	6.55 (6.20)	13.75 (13.77)	165	1616	2868	3440
BHQ (305) $C_{19}H_{19}N_3O$	Yellow	60	75.10 (74.75)	6.40 (6.20)	13.76 (13.77)	167	1614	-------	3175

presented in Table 3. The following remarks can be pointed out:

a) The dipole moment are higher for the ligands than that of HQ, which may be due to the rigid aromatic structure of BHQ and AHQ.

b) The shortening of the (N-N) bonds indicates electron delocalization as a result of condensation.

c) The length of the (C=NQ) bonds increases, indicating the weakens of the bonds as a result of condensation.

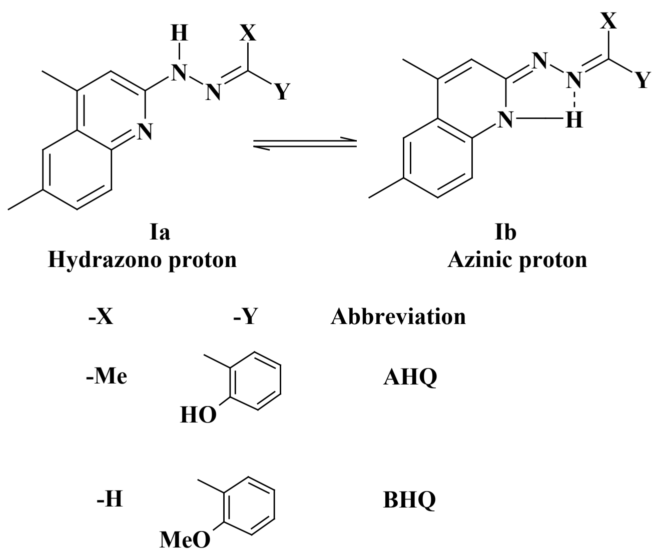
d) The formation of hydrazones is endothermic. The stability of ligands is higher than that of HQ.

e) The ligands are favorite to coordinate to metal ion, due to the small value of ΔE of ligands[38].

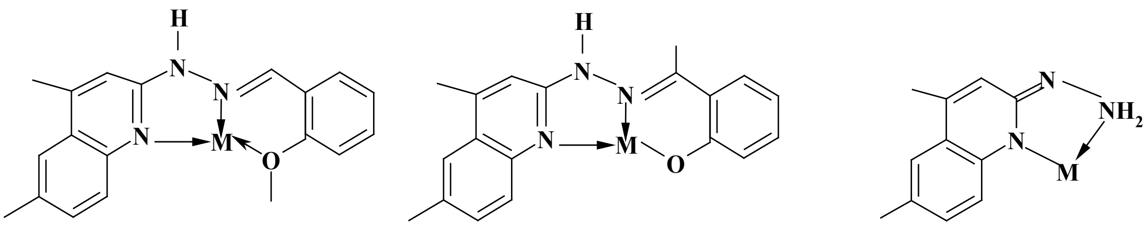
TABLE 2. Electronic spectral data* of the ligands in dioxane.

Ligand	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3
HQ	247	59634	----	----	329	13401
BHQ	241	28697	351	38076	----	----
AHQ	239	23901	344	22063	418	3929
Assignment	π - π*		π - π* + CT		n - π*	

* λ_{max} in (nm) and ε in (cm mol / L)$^{-1}$.



Scheme 1. H-bonding and tautomeric forms of the hydrazone ligands.



HQ (NN-donor) **BHQ** (NNO-donor) **AHQ** (NNO-donor)

(one 5-membered chelate ring) (one 5- and one 6- membered chelate rings)

Scheme 2. Chelating ability of the ligands.

pH-metric studies

Choice of the ligands

The ligands (phenolic: AHQ and etheric: BHQ) were selected to examine and investigate the effect of the following: (i) nature of the donor atoms, (ii) steric effects (BHQ), and (iii) rigidity of the structure produced by the presence of the benzene ring (AHQ and BHQ). This could be illustrated as shown in Schemes 1, 2.

Dissociation constants

Representative pH-metric titration curves of the free and complexed BHQ ligand at 303K in 75% (v/v) dioxane-water are presented in Fig. 1. All ligands dissociate just one proton, which is weakly ionized. The dissociated proton is that either of the phenolic group (AHQ) or belongs to the–NH at the quinoline ring or in the side chain (BHQ). Also, representative calculations of the dissociation constants (pK^{H}'s) of the investigated BHQ ligand according to Albert- Serjeant method[39] are plotted graphically in Fig. 2. The inhibition of the second dissociation in AHQ is due to ionization of the phenolic proton firstly, which increases the electron density and results in a more stable structure. Such behavior was observed in our previous studies[40-42].

Stability constants

The Irving-Rossotti[43] relations have been used to calculate the parameter ñ (average number of ligand ions attached / one metal ion) and pL (the free ligand exponent). The following Irving-Rossotti relations were used;

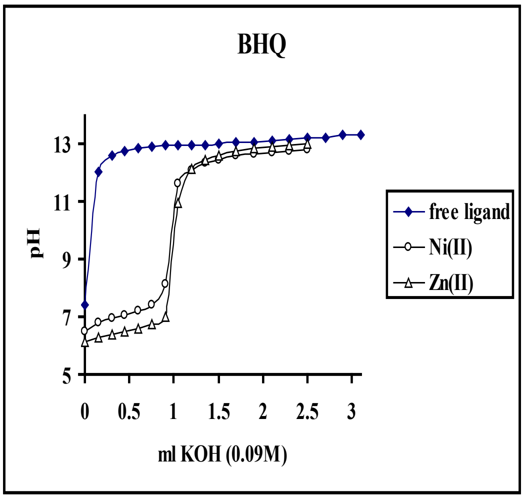


Fig. 1. pH-Metric titration curves of BHQ (3 x 10^{-3} M) in presence and absence of metal ions (1.5 x 10^{-3} M) in 75% (v/v) dioxane-water at 303K and Vo = 30 ml.

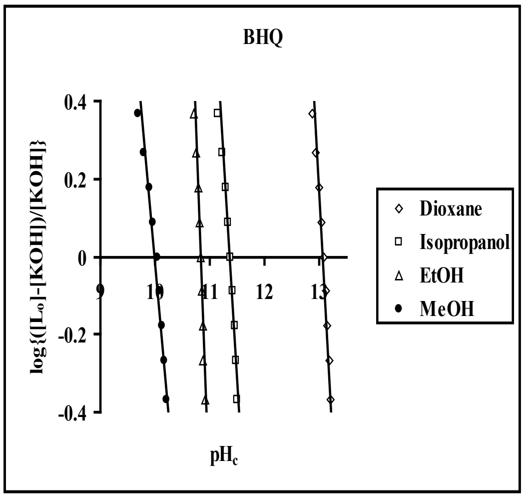


Fig. 2. Evaluation of the pK^{H}'s of BHQ in 75% (v/v) solvent-water at 303K.

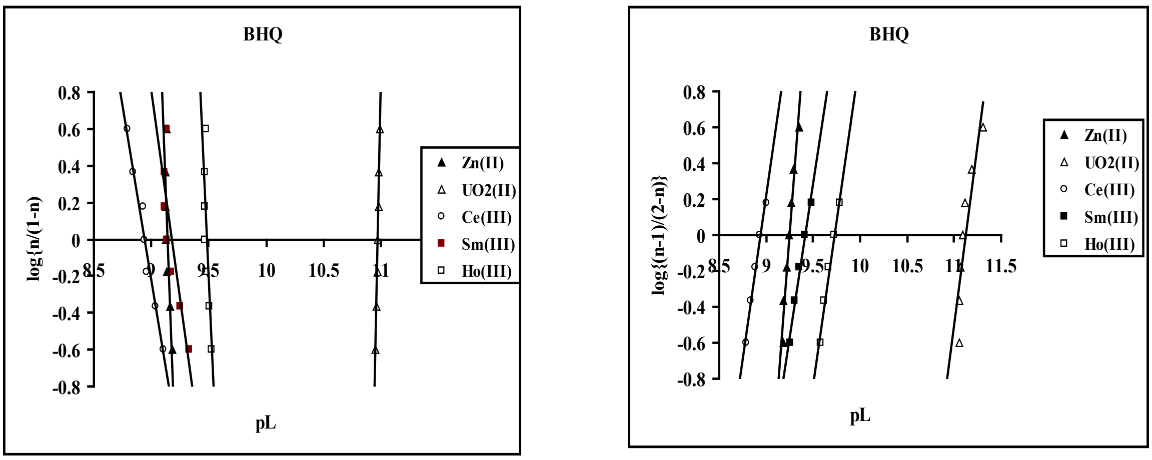


Fig. 3. Evaluation of the stability constants of the BHQ-complexes in 75% (v/v) dioxane-water at 303K.

TABLE 3. Structural parameters and bond length of the compounds by *DFT* calculation.

No.	Heat of formation	Dipole moment	HOMO Energy, [EV]	LUMO Energy, [EV]	ΔE_{gap}	global electro-philicity index (ω)	Electro-negativity (χ)	global softness (S)	global hardness (η)	C=N(Q)	N-N
HQ	-313808.8	0.9842	11.86395	13.84353	1.97958	83.4615	-12.8537	0.50516	0.98979	1.596	1.826
AHQ	-518082.3	3.633	12.09375	13.97758	1.88383	90.2038	-13.0357	0.53083	0.94192	1.664	1.733
BHQ	-518101.3	2.63	12.22082	14.04869	1.82787	94.3841	-13.1348	0.54709	0.91394	1.657	1.672

TABLE 4. Stability constants and (K_1/K_2) for the complexes in 75% (v/v) dioxane-water at 303K.

Complex	AHQ				BHQ			
	$logK_1$	$logK_2$	$log\beta_2$	K_1/K_2	$logK_1$	$logK_2$	$log\beta_2$	K_1/K_2
pK^H	12.16	--------	--------	--------	13.12	--------	--------	--------
Mn(II)	9.35	8.77	18.12	3.80	9.83	8.79	18.62	10.96
Co(II)	10.98	10.00	20.98	9.55	8.53	8.55	17.08	0.96
Ni(II)	10.01	9.33	19.34	4.79	8.60	8.50	17.10	1.26
Cu(II)	11.43	9.06	20.49	234.42	10.70	--------	--------	--------
Zn(II)	9.99	9.68	19.67	2.04	9.15	9.25	18.40	0.79
Cd(II)	9.50	9.17	18.67	2.14	8.51	8.21	16.72	2.00
UO_2(II)	11.09	11.15	22.24	0.87	10.97	11.13	22.10	0.69
La(III)	9.04	9.09	18.13	0.89	8.34	8.35	16.69	0.98
Ce(III)	9.27	9.30	18.57	0.93	8.95	8.23	17.18	5.25
Sm(III)	9.51	9.62	19.13	0.78	9.18	9.29	18.47	0.78
Ho(III)	9.73	9.84	19.57	0.78	9.49	9.62	19.11	0.74

$$\text{Log}\ (\tilde{n} / 1 - \tilde{n}) = logK_1 - pL \qquad \tilde{n} < 1.0$$

$$\text{Log}\ (\tilde{n} - 1 / 2 - \tilde{n}) = logK_2 - pL \qquad 1.0 < \tilde{n} < 2.0$$

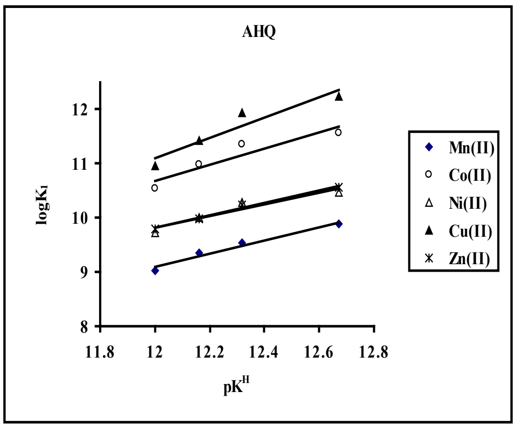
Also, representative graph of calculations of ñ and pL are given in Fig. 3. The data of stability constants were collected and summarized in Table 4. The degree of metal-ligand formation ñ is at the rang 0.1 – 1.9, suggesting that the higher species in solution is 1: 2; M: L.

Potentiometric titration curves

The titration curves (Fig. 1) give the following remarks:

(i) All ligands dissociate just one proton between a = 0.00 and a = 1.0 in presence and absence of different metal ions (a = number of moles of KOH / mole of ligand). This suggests that all ligands act as monoprotic (monobasic) species; HL towards the metal ions in solution.

(ii) For most transition metal ions (3d and 4d), two inflections (weak→sharp) at m = 1.0 and m =



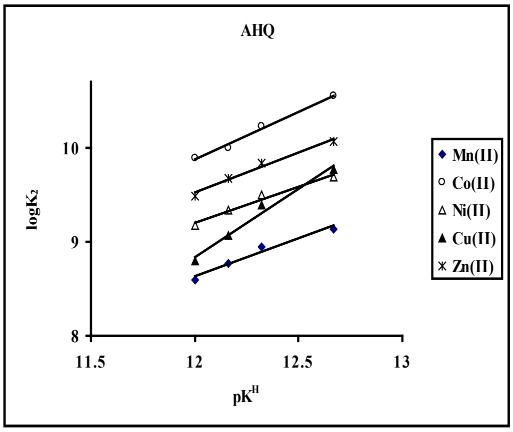


Fig. 4. LogK vs. pK^H for the AHQ–complexes at different temperatures in 75% (v/v) dioxane–water.

2.0 were detected (m = number of moles of KOH / mole of metal ion). The two inflections correspond to the stepwise formation of mono- and bis- chelates, respectively as shown by the following equilibria:

$$M^{+n} + HL + OH^- \rightleftharpoons ML^{+n-1} + H_2O \quad (m = 1.0)$$

$$ML^{+n-1} + HL + OH^- \rightleftharpoons ML_2^{+n-2} + H_2O \ (m = 2.0)$$

$$M^{+n} + 2\ HL + 2\ OH^- \rightleftharpoons ML_2^{+n-2} + 2\ H_2O$$

In general, this behaviour is consistent with the values of K_1 / K_2 (Table 4).

(iii) The above feature was not observed with most 4f lanthanides and UO_2^{II}, where only one overlapping buffer region between m = 0.0 to m = 3.0 (Fig. 1) was obtained, due to the formation of bis chelates directly as well as hydroxo complexes. This could be represented by the following equilibra:

Also, this is consistent with the lower values of K_1 / K_2 (Table 4).

The dissociation constants of the ligands and their stepwise formation constants with metal ions at 303 K in 75% dioxane-water are summarized in Table 4. Inspection of the data discloses the following:

a) $(K_1/K_2) > 1.0$ for most complexes particularly 3d and 4d–complexes. This is due to the coulombic attractions between M^{2+} and L^-, which are higher than those between ML^+ and L^-, in addition to some steric hindrance for the second coordination.

b) $(K_1/K_2) < 1.0$ for UO_2^{II} and most lanthanide(III) complexes, suggesting their higher favorite for the second coordination, which is regular with their higher coordination numbers (8 – 10).

c) (K_1/K_2) has unusual high value for Cu^{II}-AHQ chelates, suggesting either a high steric hindrance for the second coordination or a change in the dentate character from tridentate in 1:1 to bidentate in 1:2; M:L chelates. The latter is dependable with the greater tendency of Cu^{II} ions to form tetra- coordinated square planar species.

d) The unexpected high stability constants of MnII- chelates (Table 4), suggest either a high selectivity of such class of hydrazones (containing the quinoline moiety) for MnII ions or an oxidation took place. However, such behavior is not observed with other hydrazones[42, 44].

e) The high stability of LnIII-AHQ chelates; (Ln = La, Ce, Sm and Ho) is consistent with the high affinity of lanthanides for O- donors especially phenolic[45] and carboxylate[46, 47].

f) For all complexes, $\log\beta_2$ for AHQ is greater than that for BHQ. This is due to the presence of a bulky Me group on the donor O-atom (BHQ), which causes the steric hindrance. In case of Co^{II} and Ni^{II}– complexes, BHQ shows reverse order. On the other hand, AHQ and BHQ exchange their positions in case of Mn^{II}-chelates.

g) The higher stability of Cu^{II}-complexes compared to that of Ni^{II}-complexes is due to Jahn-Teller distortion in addition to the shorter Cu–N bonds than Ni–N bonds which increases the antibonding overlap[48]. On the other hand, the small stability of Cd^{II}-complexes is consistent with their CFSE = 0; Cd^{II} is d^{10}-system.

h) The unusual high stability of Co^{II}- AHQ chelate (Table 4) may be attributed to the oxidation of $Co^{2+} \rightarrow Co^{3+}$.

i) For lanthanide(III) and UO_2^{II}–complexes, $\log\beta_2$ has the order;

TABLE 5. Comparison of $\log K_1$ for some *o*-hydroxyacetophenone hydrazones.

Complex	$\log K_1$ in 75%(v/v) dioxane-water at 303K			
	AHQ (Quinoline) Our Study	AHP_m (Pyrimidine) [18]	AHP_z (Pyridazine) [19]	AHT (Triazine) [25]
Co(II)	10.98	9.37	11.92	12.26
Ni(II)	10.01	9.21	11.85	12.32
Cu(II)	11.43	11.87	12.35	12.44
Zn(II)	9.99	8.85	10.19	11.03

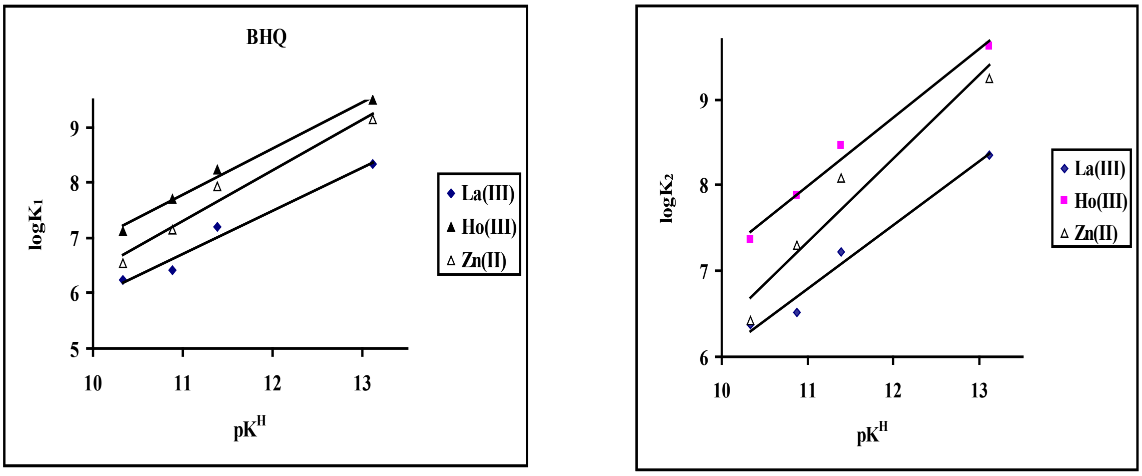


Fig. 5. LogK vs. pK^H for the BHQ–complexes in 75% (v/v) solvent–water.

TABLE 6. $LogK_1$(str)* for some hydrazone–complexes in 75 % (v/v) dioxane-water at 303K.

Complex	$logK_1$			$logK_1$(str) = $logK_1$ (hydrazone chelates) - $logK_1$ (HQ chelates).	
	HQ	AHQ	BHQ	AHQ	BHQ
Co(II)	7.65	10.98	8.53	3.33	0.88
Ni(II)	7.13	10.01	8.60	2.88	1.47
Cu(II)	11.01	11.43	10.70	0.42	-0.31
Zn(II)	7.53	9.99	9.15	2.46	1.62

UO_2^{II} > Ho^{III} > Sm^{III} > Ce^{III} > La^{III}

The relatively high stability of UO_2^{II}–complexes is due to the bonded O–atoms which increase the electrostatic attraction between the U^{VI} and the coordinated ligands, which in turn compensate the steric hindrance offered by oxygen of UO_2^{II} cation.

The order of Ln^{III}-complexes is consistent with the increase of ionic size Ho^{III}; (0.89 A°) La^{III}; (1.06 A°) i.e. this order is linearly correlated with either 1/r or z^2/r (ionic potential of the Ln^{III}-ions), where r is the ionic radii of Ln^{III}–ions.

Hardness / softness

According to the previous work in our laboratory, a significant comparison of the formation constant ($logK_1$) must be made for some similar hydrazones bearing the triazine[49], pyridazine[41], pyrimidine[42] and quinoline rings (our study) under the same experimental conditions as shown in Table 5. Inspection of the data gives that the order of stability for most metal ions is as follows;

Triazine >Pyridazine > Quinoline > Pyrimidine

This order confirm that the N-atom of the ring shares in chelation, where the electron density on the that ring increases in this order.

Chelate effect

The investigated ligands; BHQ and AHQ act as tridentate (NNO- donors) and form two chelate rings and as shown in Scheme 2. In general, the formation of two chelate rings and also the resonance within chelate rings lead to increasing stability of the formed chelates (Scheme 2). The effect of such chelate ring size can be illustrated by comparing $logK_1$ for HQ-chelates, which can form one 5- membered chelate ring with $logK_1$ for the hydrazone chelates, which can procedure two chelate rings (Scheme 2 and Table 6). The data showed that $logK_1$(str) is positive and ranges from 0.42 – 3.33, (an exception Cu^{II}-BHQ).

Effect of the reaction medium

In order to provide an explanation of the dependence of pK^H and logK (or $\Delta G°$) on the solvent parameters, the pK^H's of the BHQ ligand and logK of its chelates were resolved pH-metrically in 75% (v/v) solvent (dioxane, isopropanol, ethanol and methanol) -water at 303K. The results are listed in Table 7. Inspection of the data tells that:

(i) As the polarity of the medium increases, the pK^H and logK values decrease.

(ii) The following order showed the decreasing of stability of the chelates in 75% solvent-water.

Dioxane > Isopropanol > Ethanol > Methanol

This order means that the basicity of the ligand (pK^H) decreases by increasing the polarity of the medium and the coordinating ability of the solvent.

According to Gergely and Kiss[50], dioxane molecules progressively break-down the H–bonded of H_2O, while alcohols can form H–bonded associations with H_2O. Thus, it is predictable that the extent of H–bonding in alcohols is greater than that in dioxane.

Since the ligands are insoluble in water and

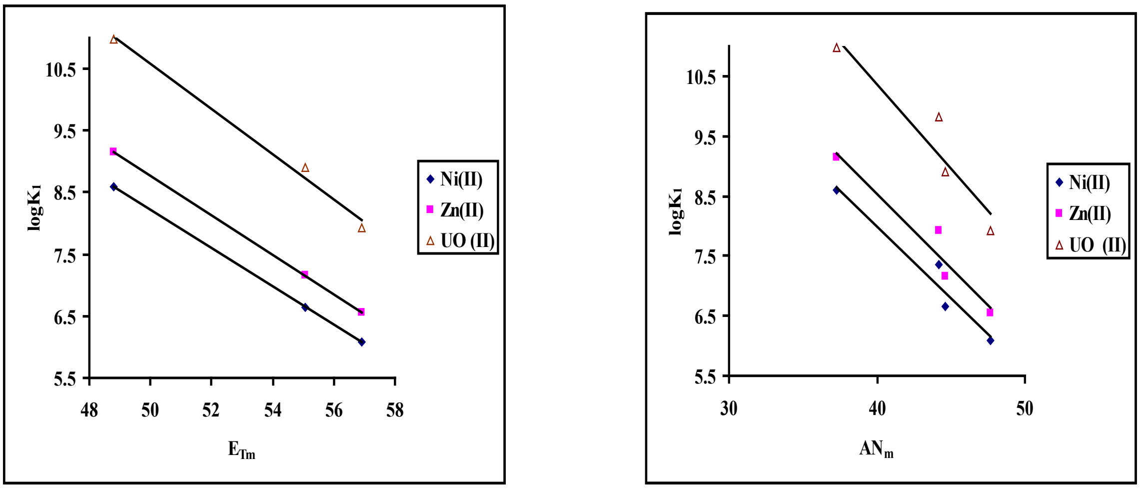


Fig. 6. LogK$_1$ vs. E$_{Tm}$ (A) and AN$_m$ (B) for BHQ-complexes in 75% (v/v) solvent–water.

TABLE 7. Stability constants of the BHQ-complexes in 75% (v/v) solvent-water at 303K and calculation of logK in aqueous medium by using the LRA.

Complex	Dioxane		Isopropanol		Ethanol		Methanol		H_2O		H_2O	
	E_{Tm}(48.8)		E_{Tm}(….)		E_{Tm}(55.05)		E_{Tm}(56.9)		Method A[a]		Method B[b]	
	AN_m(37.30)		AN_m(44.16)		AN_m(44.60)		AN_m(47.70)					
	$logK_1$	$logK_2$	$logK_1$	$logK_2$	$logK_1$	$logK_2$	$logK_1$	$logK_2$	$logK_1$	$logK_2$	$logK_1$	$logK_2$
Mn(II)	9.83	8.79	8.17	7.47	7.42	6.30	6.51	6.09	4.06	3.73	4.42	4.13
Co(II)	8.53	8.55	7.25	7.31	6.49	6.54	6.03	6.31	4.05	4.39	5.12	4.68
Ni(II)	8.60	8.50	7.35	7.33	6.65	6.45	6.09	5.88	4.19	3.85	4.45	4.22
Cu(II)	10.70	-------	9.93	-------	8.84	------	↓↓↓	------	-----	-----	7.36	-----
Zn(II)	9.15	9.25	7.92	8.08	7.16	7.30	6.55	6.42	4.59	4.42	4.90	4.76
Cd(II)	8.51	8.21	7.33	6.95	6.33	6.15	5.92	5.94	3.82	3.97	4.17	4.24
UO2(II)	10.97	11.13	9.83	9.50	8.91	8.59	7.92	7.99	5.77	5.50	6.20	5.87
La(III)	8.34	8.35	7.19	7.23	6.41	6.52	6.23	6.37	4.38	4.62	4.66	4.87
Ce(III)	8.95	8.23	7.59	7.76	7.07	7.03	6.64	6.68	4.81	4.46	5.02	5.78
Sm(III)	9.18	9.29	7.82	8.08	7.25	7.51	6.76	7.03	4.89	5.24	4.31	5.49
Ho(III)	9.49	9.62	8.23	8.46	7.70	7.88	7.13	7.36	5.35	5.63	5.57	5.89
pK^H	13.12±0.088		11.39±0.085		10.88±0.135		10.33±0.099		8.13		8.33	

[a]These values were obtained (at 63.1; E_{Tm}) by LRA of $logK_1$, $logK_2$ or pK^H *vs.* E_{Tm} of the 75% (v/v) solvent-water (r = 0.977 – 1.00).
[b]These values were obtained (at 54.8; AN_m) by LRA of $logK_1$, $logK_2$ or pK^H *vs.* AN_m of the 75% (v/v) solvent-water (r = 0.7099 - 0.970).

in an attempt to decide the dissociation constants (pK^H's) of the BHQ ligand and its stability constants ($logK_1$ and $logK_2$) in pure water, a LRA of pK^H, $logK_1$ or $logK_2$ *vs.* Reichardt (E_{Tm}), (Fig. 6; method A) and acceptor number (AN_m) (Fig. 6; method B) was constructed and analyzed (Table 7). In conclusion, the stability of the chelates increases by decreasing both the E_{Tm} and AN_m of the solvent.

Effect of temperature

In an attempt to calculate the thermodynamic parameters, the formation constants of the phenolic AHQ ligand with Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}-ions were calculated pH-metrically in 75% (v/v) dioxane-water at various temperatures *viz*. 283, 293, 303 and 313 K (Table 8).

The thermodynamic functions (Table 8) are calculated by using the well-known relations:

(i) $\Delta G° = -19.12\ T\ logK$ where ΔG^o is in J mol^{-1}.

(ii) $LogK = (-\Delta H° / 19.12\ T) + (\Delta S^o / 19.12)$.

Thus, on plotting logK *vs.* 1/T (Fig. 8), one gets a straight line whose slope = $-\Delta H° / 19.12$ and its intercept = $\Delta S^o / 19.12$. Inspection of the data (Table 8) gives the following:

(i) High positive values of ΔG° of the dissociation process indicate that it is non-spontaneous process. The large negative values of ΔG° of the formed complexes indicate that the complexation proceeds spontaneously[51].

(ii) Large negative value of ΔS° of the dissociation process refers that the ionization of the ligand is entropically unfavourable. Large positive values of ΔS° of the formed metal complexes[51] (an exception Cu^{II}-complex) indicate that the complexation process is entropically favourable and the mechanism of complexation is based upon replacement of H_2O by L^- according the following interaction:

$$[Ni(OH_2)_6]^{++} + 2HL \rightleftharpoons NiL_2 + 6H_2O + 2H^+$$

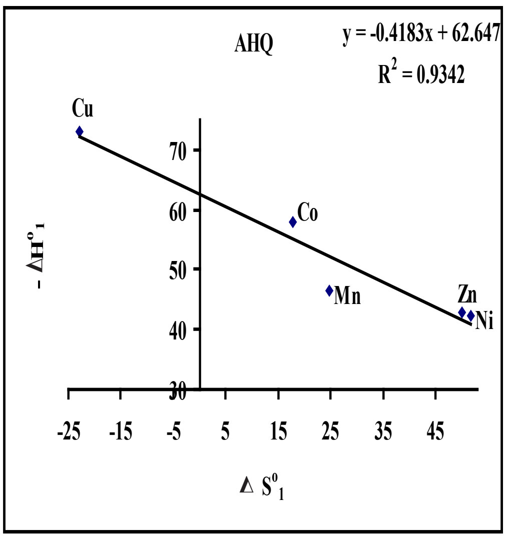
3 particles 7 particles

So that the above reaction proceeds with an increase of the entropy.

(iii) Large negative values of ΔH° for all metal chelates indicate that the complexation process is enthalpically favourable and it is exothermic process[51].

(iv) $\Delta S^o_1 << \Delta S^o_2$
i.e. more orderless upon the second coordination. This is due to a large number of water molecules is released upon the second coordination than the first coordination. Furthermore, this is caused by the transformation of the dentate character of AHQ ligand from tridentate in 1:1 to bidentate in 1:2; M:L chelates to relieve steric hindrances ($K_1/K_2 > 1.0$; Table 4).

(v) $-\Delta H^o_1 >> -\Delta H^o_2$
i.e. the bond strength from the ligand to the metal ion is stronger in the first coordination than that in the second coordination. Also, this provides another strong evidence of the



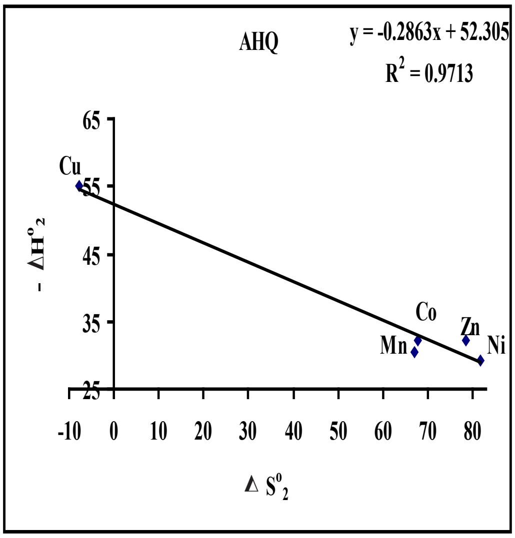


Fig. 8. ΔH° vs. ΔS° for AHQ-complexes in 75% (v/v) dioxane–water (Evaluation of Tiso).

TABLE 8. Stability constants and thermodynamic functions* of the AHQ-complexes in 75% (v/v) dioxane-water.

Complex	283K		293K		303K		313K		–ΔG°		–ΔH°		ΔS°	
	$logK_1$	$logK_2$	$logK_1$	$logK_2$	$logK_1$	$logK_2$	$logK_1$	$logK_2$	$-\Delta G°_1$	$-\Delta G°_2$	$-\Delta H°_1$	$-\Delta H°_2$	$\Delta S°_1$	$\Delta S°_2$
Mn(II)	9.88	9.14	9.54	8.95	9.35	8.77	9.03	8.60	53.78	50.47	46.40	30.49	24.76	67.05
Co(II)	11.57	10.55	11.36	10.23	10.98	10.00	10.55	9.89	63.25	57.88	57.97	32.26	17.71	67.91
Ni(II)	10.46	9.69	10.29	9.50	10.01	9.33	9.72	9.17	57.60	53.65	42.17	29.31	51.77	81.65
Cu(II)	12.24	9.77	11.95	9.39	11.43	9.06	10.97	8.80	66.26	52.66	73.09	54.97	-22.91	-7.78
Zn(II)	10.56	10.07	10.23	9.84	9.99	9.68	9.80	9.49	57.74	55.62	42.81	32.20	50.11	78.58
pK^H	12.67	-----	12.32	-----	12.16	-----	12.00	-----	- 69.96	-----	- 36.95	-----	- 110.79	-----

* ΔG° and ΔH° are in k J mol^{-1} while ΔS° is in J mol^{-1} K^{-1} (r = 0.9831 - 0.9999).

alteration of the dentate character of the AHQ ligand.

(vi) The values of $\Delta H^o = \Delta H^o_1 + \Delta H^o_2$ (Table 8) indicates that a tetrahedral geometry around Mn^{II}, Zn^{II} and Ni^{II}–ions, an octahedral environment around Co^{II}–ions and a square planar geometry around Cu^{II}–ions. The exothermicity has order:

$$D_{4h} >> O_h >> T_d$$

(Square planar) (Octahedron) (Tetrahedron)

Isokinetic ΔH° - ΔS° relationships

In an attempt to evaluate the isokinetic temperature (T_{iso}) i.e. the temperature at which the complexation reactions proceed at the same rate[52]. Using the LRA, the following relations for AHQ chelates in 75% (v/v) dioxane-water (Fig. 8) were obtained:

$\Delta H°_1 = 0.418\ \Delta S°_1 – 62.65$ $r^2 = 0.934$

$T_{1(iso)} = 418K$, $\Delta G^o_{1(iso)} = -62.65$ kJ/mol.

$\Delta H°_2 = 0.286\ \Delta S°_2 - 52.31$ $r^2 = 0.971$

$T_{2\ (iso)} = 286K$, $\Delta G^o_{2(iso)} = -52.31$kJ/mol.

Inspection of the relations reveals the following:

(i) $T_{1(iso)} >> T_{2(iso)}$ suggesting a change in the dentate character of AHQ ligand from tridentate (1 : 1) to bidentate (1 : 2; M : L), to relieve steric hindrances.

(ii) $T_{1(iso)} >> T_{exp}$ i.e. the 1st coordination is enthalpically controlled.

(iii) $T_{2(iso)} \approx T_{exp}$ i.e. the 2nd coordination is entropically and enthalpically controlled.

Electrostatic and cratic thermodynamic functions

The thermodynamic parameters (Table 8) were analyzed into their electrostatic (el) and non-electrostatic (non) or cratic components (Table 9) to get an insight into the extent of ionic and covalent nature of the formed complexes. Inspection of the data (Table 9) reveals the following;

(i) $\Delta H°_{el}$ has positive values, this is consistent with T = 298K > θ = 219K and results in an endothermic contribution to the total change of enthalpy;

$$\Delta H°_{el} = (T - \theta)\ \Delta S°_{el}.$$

TABLE 9. Electrostatic and cratic thermodynamic functions[a,b,c] of AHQ–chelates.

Complex	1st coordination						2nd coordination					
	$-\Delta G^o_{el}$	$-\Delta G^o_{cratic}$	ΔH^o_{el}	$-\Delta H^o_{cratic}$	ΔS^o_{el}	T*	$-\Delta G^o_{el}$	$-\Delta G^o_{cratic}$	ΔH^o_{el}	$-\Delta H^o_{cratic}$	ΔS^o_{el}	T*
Mn(II)	12.75	41.03	4.60	51.00	58.20	362	22.01	28.46	7.94	38.43	100.49	338
Co(II)	11.20	52.05	4.04	62.01	51.15	401	22.20	35.68	8.01	45.66	101.35	368
Ni(II)	18.66	38.94	6.73	48.90	85.21	355	25.20	28.45	9.09	38.40	115.09	338
Cu(II)	2.31	63.95	0.83	73.92	10.53	443	5.62	47.04	2.03	57.00	25.66	416
Zn(II)	18.30	39.44	6.60	49.41	83.55	357	24.53	31.09	8.85	41.05	112.02	349

[a] ΔG^o_x, ΔH^o_x are in k J mol^{-1} while ΔS^o_{el} is in J mol^{-1} K^{-1} (x = el or cratic).

[b] ΔS^o_{cratic} = constant = -33.44 J mol^{-1} K^{-1} (not included in the Table). [c] T* is in K.

(ii) $-\Delta G_1°_{non}$, $-\Delta H_1°_{non}$ >> $-\Delta G_2°_{non}$, $-\Delta H_2°_{non}$
(1st coordination) (2nd coordination)

This order suggests a higher degree of covalency in the 1:1 compared to the 1:2 complexes. Hence, the higher negative values of $\Delta H°_{non}$ would reflect the bond strength from ligand to metal ion which is stronger in the 1st coordination than the 2nd coordination.

(iii) $\Delta G°_{el}$ has negative comparable values and suggests that the complexation process is affected by the temperature and environment (Table 9).

Ligand field stabilization energy (LFSE)

N.B.: Calculation of the LFSE (Table 10) is based on the assumption that an O_h complex is formed in the solution.

The negative heat of the reaction;

$$Zn^{2+}_{(g)} + [MnL(H_2O)_n]^{2+} \rightleftharpoons Mn^{2+}_{(g)} + [ZnL(H_2O)_n]^{2+}$$

is defined as the transition series contraction energy, E_r, and this can be calculated from the following equation;

$$E_r = (\Delta H°_h + \Delta H°_C)^{Mn(II)} - (\Delta H°_h + \Delta H°_C)^{Zn(II)}$$

For convenience, $E_r = \Delta H°_r(Mn^{2+}) - \Delta H°_r(Zn^{2+})$

where $\Delta H°_r = \Delta H°_h + \Delta H°_C$; $\Delta H°_C$ is the heat of complex formation and $\Delta H°_h$ is the heat of hydration of the bivalent transition metal ions. The ligand field stabilization energy, ∂H, can be calculated by the following equation: $\partial H = \Delta H°_r(Mn^{2+}) - \{(n-5)/5\}E_r - \Delta H°_r(M^{2+})$

Inspection of the data given in Fig. 9 and Table 10, reveals that;

A. There is some agreement between E_r and ∂H values for each metal complex indicating the identical coordination as was supported by Irving–Rossotti relationship[43].

B. The LFSE, ∂H, followed the order;

Cu^{II} > Ni^{II} > Co^{II}

which is in good accordance to the Irving-Williams order for stability of the complexes.

Conclusions

In conclusion, the following remarks can be pointed out:

(i) The hydrazones act as monobasic (monoprotic) ligands (HL) towards the metal ions in solution as evidenced from the titration curves.

(ii) The maximum $\tilde{n}$ values were found to be ≈ 2, revealing that both ML and ML_2 species are formed in solution.

(iii) For most complexes; $\log K_1 > \log K_2$ indicating that the binding of a first ligand with the vacant sites of the metal ions are more available than for a second one.

(iv) Stable complexes will be formed with;

- Higher charges and small sizes of the metal ions i.e. higher polarizing power.
- Higher basicity of the ligands.
- Lower temperatures, this is consistent with the exothermic complexation.
- Less polar media. The strong coordinating ability of the solvents (polar solvents) retards the metal-ligand interaction.

(v) The dissociation of AHQ is endothermic, non-spontaneous and entropically unfavourable while its complexation is exothermic, spontaneous and entropically favourable.

(vi) The LFSE follows the order:

Co^{II} < Ni^{II} < Cu^{II}

TABLE 10 . Ligand field stabilization energy (LFSE) of the AHQ–chelates in 75% (v/v) dioxane-water.

Metal ion	$\Delta H°_h$(k J mol^{-1})	$\Delta H°_c$	$\Delta H°_r$	$\{(n-5)/5\}E_r$	∂H(k J mol^{-1})	%($-T\Delta S°_1$/ $\Delta G°_1$)	%($-T\Delta S°_2$/ $\Delta G°_2$)
$3d^5(Mn^{2+})$	2733.72	76.89	2810.61	0.00	----	13.72	39.59
$3d^7(Co^{2+})$	2913.46	90.23	3003.69	78	115.08	8.34	34.96
$3d^8(Ni^{2+})$	2992.88	71.48	3064.36	117	136.75	26.78	45.35
$3d^9(Cu^{2+})$	2996.64	128.06	3124.70	156	158.09	----	----
$3d^{10}(Zn^{2+})$	2930.60	75.01	3005.61	195 (E_r)	----	25.86	42.10

in accordance to Irving–Williams order.

(vii) The stability of the chelates in different media follows the order:

Methanol < Ethanol < Isopropanol < Dioxane

(Viii) For M^{II}-AHQ chelates: ΔH^o is the main driving force for 1:1 chelates, whereas both ΔH^o and ΔS^o are the driving forces for 1:2 chelates.

(ix) The structural features of the hydrazones have a considerable effect on the stability of their chelates.

References

1. El-Gammal, O.A., Mononuclear and binuclear complexes derived from hydrazone Schiff base NON donor ligand: Synthesis, structure, theoretical and biological studies., *Inorg. Chim. Acta,* **435**, 73-81 (2015).

2. Shebl, M., Coordination behavior of new bis(tridentate ONO, ONS and ONN) donor hydrazones towards some transition metal ions: Synthesis, spectral, thermal, antimicrobial and antitumor studies, *J. Mol. Struct.,* **1128**, 79-93 (2017).

3. Shebl, M. and Khalil, S.M.E., Synthesis, spectral, X-ray diffraction, antimicrobial studies, and DNA binding properties of binary and ternary complexes of pentadentate N_2O_3 carbohydrazone ligands, *Monatsh Chem*, **146**, 15–33 (2015).

4. Shebl, M., El-ghamry, M.A., Khalil, S.M.E. and Kishk, M.A.A., Mono- and binuclear copper(II) complexes of new hydrazone ligands derived from 4,6-diacetylresorcinol: Synthesis, spectral studies and antimicrobial activity, *Spectrochim. Acta A,***126**, 232–241 (2014)

5. Raja, D.S., Ramachandran, E., Bhuvanesh, N.S.P. and Natarajan, K., Synthesis, structure and *in vitro* pharmacological evaluation of a novel 2-oxo-1,2-dihydroquinoline-3-carbaldehyde (2′-methylbenzoyl) hydrazone bridged copper(II) coordination polymer, *Eur. J. Med. Chem.,* **64,** 148-159 (2013**).**

6. Yosef, H.A.A. and Ibrahim, N.M., Synthesis, Thermolysis, Photolysis and Antimicrobial Evaluation of some Novel Semicarbazones and Thiosemicarbazones Derived from 3-Methyl- -benzothiazolinone Hydrazone, *Egypt. J. Chem.* **59**(5), 867– 885 (2016).

7. Abd El-Karim, S.S., Gouhar, R.S., Haiba, M.E., El-Zahar, M.I., Awad, G.E.A. and Bagato, O., Synthesis of Novel Derivatives Bearing Heterocycles-Tetrahydronaphthalene Conjugates for Antimicrobial and Antiviral Evaluation, *Egypt. J. Chem*. **57**(4), 281-313 (2014).

8. Zaki, M.Y., Cytotoxicity of Novel Hydrazide-hydrazone Derivatives towards Tumor and Normal Cell Lines, *Egypt. J. Chem.* **56**(1), 25- 34 (2013).

9. Samy, F. and Taha, A., Synthesis, Spectroscopic, Biological and Theoretical Studies of Nano Complexes Derived from Triazine Hydrazone, *Egypt. J. Chem.,* **61**(5), 731 - 746 (2018).

10. El-Taweel, F.M.A., Elagamey, A.A. and Elmougy, Sh.M., Studies on Substituted Heteroarenes: New Synthesis of Substituted Pyrrole, Pyridine, Pyrazolo[4,3-*b*pyridine, Pyrano [3,2-*c*]quinoline, Benzo [*f*] chromene, Benzo[*h*] chromene, Chromeno [8,7-*h*]chromene, Chromeno[6,5-*f*] chromene and 2*H*-chromene Derivatives, *Egypt. J. Chem.,* **54**(6), 703-721 (2011).

11. Xu, H., Tang, H., Feng, H. and Li, Y., Design, synthesis and anticancer activity evaluation of novel C14 heterocycle substituted epi-triptolide, *Eur. J. Med. Chem.,* **73**, 46-55 (2014).

12. Thangaraja, M., Gengana, R.M., Ranjanb, B. and Muthusamyc,_R., Synthesis, molecular docking, antimicrobial, antioxidant and toxicity assessment of quinoline peptides, *J. Photochem. & Photobio., B: Bio.,* **178**, 287-295 (2018).

13. Hu, Y., Gao, C., Zhang, S., Xu, L., Xu, Z., Feng, L., Wu, X. and Zhao, F., Quinoline hybrids and their antiplasmodial and antimalarial activities, *Eur. J. Med. Chem.,* **139**, 22-47 (2017).

14. Mandewale, M.C., Thorat, B., Nivid, Y., Jadhav, R., Nagarsekar, A. and Yamgar, R., Synthesis, structural studies and antituberculosis evaluation of new hydrazone derivatives of quinoline and their Zn(II) complexes, *J. Saudi Chem. Soc*., **22,** 218-228 (2018).

15. Sureshkumar, K., Maheshwaran, V., Rao, T.D., Themmila, K., Ponnuswamy, M.N., Kadhirvel, S. and Dhandayutham, S., Synthesis, characterization, crystal structure, in-vitro anti-inflammatory and molecular docking studies of 5-mercapto-1-substituted tetrazole incorporated quinoline derivative, *J. Mol. Struct.*, **1146**, 314-323 (2017).

16. Thirunavukkarasu, T., Sparkes, H.A. and Natarajan, K., Quinoline based Pd(II) complexes:

Synthesis, characterization and evaluation of DNA/protein binding, molecular docking and in vitro anticancer activity, *Inorg. Chim. Acta,* **482**, 229-239 (2018).

17. Seleem, H.S., El-Inany, G.A., Eid, M.F., Mousa, M.A. and Hanafy, F.I., Complexation of some Hydrazones Bearing the Quinoline Ring. Potentiometric Studies, *J. Braz. Chem. Soc.*, **17,** 723-729 (2006).

18. Seleem, H.S., El-Inany, G.A., Mousa, M.A. and Hanafy, F.I., Spectroscopic studies on 2-[2-(4-methylquinolin-2-yl)hydrazono]-1,2-diphenylethanone molecule and its metal complexes, *Spectrochim. Acta A*, **74**(4), 869-874 (2009).

19. Seleem, H.S**.**, El-Inany, G.A**.**, Mousa, M.A. and Hanafy, F.I**.**, Spectroscopic and pH-metric studies of the complexation of 3-[2-(4-methylquinolin-2-yl)hydrazono]butan-2-one oxime compound, *Spectrochim. Acta A,* **75**, 1446–1451 (2010).

20. Seleem, H.S., Mostafa, M. and Hanafy,_F.I., Stability of transition metal complexes involving three isomeric quinolyl hydrazones, *Spectrochim. Acta A*, **78**, 1560-1566 (2011).

21. Seleem, H.S., El-Inany, G.A., El-Shetary, B.A. and Mousa, M.**A.**, The ligational behavior of an isatinic quinolyl hydrazone towards copper(II)-ions, *Chem. Central J.*, **5**(2) (2011).

22. Seleem, H.S., El-Inany, G.A., El-Shetary, B.A., Mousa, M.**A.** and Hanafy, F.I., The ligational behavior of an isatinic quinolyl hydrazone towards copper(II)- ions, *Chem. Central J.*, **5**(20) (2011).

23. Seleem, H.S., Transition metal complexes of an isatinic quinolyl hydrazone, *Chem. Central J.*, **5**(35) (2011).

24. Seleem, H.S. and Mousa, M.A., Ligand substitution reactions of a phenolic quinolyl hydrazone; oxidovanadium (IV) complexes, *Chem. Central J.*, **5**(47) (2011).

25. El-Shafiy, H.F. and Shebl, M., Oxovanadium(IV), cerium(III), thorium(IV) and dioxouranium(VI) complexes of 1-ethyl-4-hydroxy-3-(nitroacetyl) quinolin-2(1H)-one: Synthesis, spectral, thermal, fluorescence, DFT calculations, antimicrobial and antitumor studies, *J. Mol. Struct.*, **1156,** 403-417 (2018).

26. Seleem, H.S., Ramadan, A.A.T., Taha, A., Eid, M.F. and Samy, F., The complexation of a novel squaricbis(thiosemicarbazone); 3,4-bis{[(aminothioxomethyl)-amino] azamethylene}cyclobut-ene-1,2-diol, *Spectrochim. Acta A*, **78**(3), 1097-1104 (2011).

27. Samy, F., Ramadan, A.A.T.,Taha, A. and Seleem., H.S., Cobalt(II) and Nickel(II) complexes of hydrazone ligand ({(1E)-1-Aza-2-pyrrol-2-ylvinyl}{5,6-diphenyl(1,2,4-triazin-3-yl)}amine): Synthesis, spectral, pH-metric, antimicrobial and *PM3* studies, *Asian J. Chem.,*. **28**(12), 2650-2660 (2016).

28. Shebl, M., Synthesis, spectroscopic characterization and antimicrobial activity of binuclear metal complexes of a new asymmetrical Schiff base ligand: DNA binding affinity of copper(II) complexes, *Spectrochim. Acta A,* **117**, 127-137 (2014).

29. Khalil, S.M.E., Shebl, M. and Al-Gohani, Fa.S., Zinc(II) Thiosemicarbazone Complex As a Ligand Towards Some Transition Metal Ions: Synthesis, Spectroscopic and Antimicrobial Studies**,** *Acta Chim. Slov.***, 57***,* 716–725 (2010).

30. Shebl, M., Synthesis and spectroscopic studies of binuclear metal complexes of a tetradentate N_2O_2 Schiff base ligand derived from 4,6-diacetylresorcinol and benzylamine, *Spectrochim. Acta A*, **70**, 850–859 (2008)

31. Shebl, M., Khalil, S.M.E., Ahmed, S.A. and Medien, H.A.A., Synthesis, spectroscopic characterization and antimicrobial activity of mono-, bi- and tri-nuclear metal complexes of a new Schiff base ligand, *J. Mol. Struct.,* **980**, 39–50 (2010).

32. Shebl, M., Khalil, S.M.E., Al-Gohani, F.S., Preparation, spectral characterization and antimicrobial activity of binary and ternary Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ce(III) and UO_2(VI) complexes of a thiocarbohydrazone ligand, *J. Mol. Struct.,* **980**, 78–87 (2010).

33. Khalil, S.M.E., Seleem, H.S., El-Shetary, B.A. and Shebl, M., mono- and bi-nuclear metal complexes of schiff-base hydrazone (ONN) derived from o-hydroxyacetophenone and 2-amino-4-hydrazino-6-methyl pyrimidine, *J. Coord. Chem.,* **55**(8), 883–899 (2002).

34. Shebl, M., Seleem, H.S. and El-Shetary, B.A., Ligational behavior of thiosemicarbazone, semicarbazone and thiocarbohydrazone ligands towards VO(IV), Ce(III), Th(IV) and UO_2(VI) ions: Synthesis, structural characterization and

biological studies, *Spectrochim. Acta A,* **75**, 428–436 (2010).

35. Seleem, H.S., El-Shetary, B.A. and Shebl, M., Synthesis and characterization of a novel series of metallothiocarbohydrazone polymers and their adducts**,** *Heteroatom Chem.,* **18**(1), 100-107 (2007).

36. Seleem, H.S., Emara, A.A. and Shebl, M.**,** The relationship between ligand structures and their Co^{II} and Ni^{II} complexes: Synthesis and characterization of novel dimeric Co^{II}/Co^{III} complexes of bis(thiosemicarbazone), *J. Coord. Chem.,* **58**(12), 1003–1019 (2005).

37. Seleem, H.S., El-Shetary, B.A., Khalil, S.M.E., Mostafa, M. and Shebl, M., Structural diversity in copper(II) complexes of bis(thiosemicarbazone) and bis(semicarbazone) ligands, *J. Coord. Chem.,* **58**(6), 479–493 (2005).

38. Shah, R., Ligational, potentiometric and floatation studies on Cu(II) complexes of hydrazones derived from p and o-vanillin condensed with diketo hydrazide, *J. Mol. Liquids*, **220**, 939-953 (2016).

39. Albert, A. and Serjeant, E.P. "*Ionization Constants of Acids and Bases*", Champan and Hall, Edinburgh, (1971).

40. Seleem, H.S., Stability constants and thermodynamics of complexation of Schiff base hydrazones derived from 3-hydrazino-6-phenylpyridazine and acetophenone derivatives, *J. Ind. Chem. Soc.,* **80,** 622-625 (2003).

41. Abdel-Moez, M.S., Abu El-Wafa, S., Seleem, H.S. and El-Shetary, B.A., Thermodynamics, stability constants and spectrophotometric studies of complexes of trivalent lanthanides and some divalent metals with 3-[a-(o-hydroxyphenyl) ethylidenehydrazino]-6-phenylpyridazine, *Thermochim Acta*, **49**, 317-329 (1989).

42. Seleem, H.S., El-Shetary, B.A., Khalil S.M.E. and Shebl, M., Potentiometric and spectrophotometric studies of the complexation of Schiff-base hydrazones containing the pyrimidine moiety, *J. Serb. Chem. Soc.,* **68,** 729-750 (2003).

43. Irving, H.M. and Rossotti, H.S., The calculation of formation curves of metal complexes from pH titration curves in mixed solvents, *J. Chem. Soc.,* 2904-2910 (1954).

44. Seleem, H.S., Stability constants and thermodynamic parameters of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, UO_2^{2+}, Th^{4+}, Ce^{3+} and Pr^{3+}-complexes with some Schiff base hydrazones containing the pyrimidine moiety, *Annal. di Chim.,* **93,** 305-322 (2003).

45. Castellani, C.B. and Carugo, O., Studies on lanthanide complexes with pyrone ligands—V. Terbium(III) and europium(III) complexes with a new ligand derived from the condensation of 4-oxo-4H-benzopyran-3-carboxyaldehyde and 2-amino-4-chlorophenol, *Polyhedron,* **9**, 1639-1644 (1990).

46. Tei, L., Blake, A.J., Wilson, C. and Schrder, M., Lanthanide complexes of new nonadentate imino-phosphonate ligands derived from 1,4,7-triazacyclononane: synthesis, structural characterisation and NMR studies, *J. Chem. Soc., Dalton Transition*, 1945-1952 (2004).

47. Tei, L., Blake, A.J., George, M.W., Weinstein, J.A., Wilson, C. and Schrder, Lanthanide complexes of iminocarboxylate ligands derived from 1,4,7-triazacyclononane: structural characterisation and relaxivity of the Gd^{III} and luminescence of the Eu^{III} complexes, *J. Chem. Soc., Dalton Transition*, 1693-1700 (2003).

48. Taha, A., Metal complexes of triazine schiff bases: synthetic, thermodynamic, spectroscopic, and electrochemical studies on complexes of some divalent and trivalent metal ions of 3-(α-benzoylbenzylidenhydrazino)-5,6-diphenyl-1,2,4-triazine, *Synth. React. Inorg. Met.-Org. Chem.,* **31**(2), 205-218 (2001).

49. Taha**,** A., "*Ph. D. Thesis*" Faculty of Science, Ain Shams University, Cairo, Egypt (1991).

50. Gergely, A., and Kiss, T., Thermodynamic study of copper(II) and nickel(II) complexes of alanine in mixed solvents, *J. Inorg. Nucl. Chem.,* **29**, 109-144 (1977).

51. Butler, I.S., El-Sherbeny, H.A.M., Kenawy, I.M. and Mostafa, S.I., Synthesis and spectroscopic characterization of complexes of Cr(III), Cr(VI), Cu(III), Zn(II), Mo(VI), Pd(II), Ag(III), Au(III) and W(VI) with telluric acid, *J. Mol. Struct.*, **1036**, 510-520 (2013).

52. Marco, D., Thermodynamic relationships of complex formation: Part II. Enthalpy-entropy interdependence in hard-hard interactions in aqueous solution, *Thermochim. Acta*, **189**, 213-222 (1991).

دراسات جهديه و نظرية لمتراكبات ٢-]الفا-(ارثو هيدروكسي فنيل)ايثيليدين هيدرازينو[-4و6-ثنائي ميثيل كينولين و2-]الفا-(ارثو ميثوكسي فنيل)ميثليدين هيدرازينو[-4و6-ثنائي ميثيل كينولين

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تم تخليق عوامل التراكب (-2]الفا-(ارثو هيدروكسي فنيل)ايثيليدين هيدرازينو[4-و-6ثنائي ميثيل كينولين و-2]الفا-(ارثو ميثوكسي فنيل)ميثليدين هيدرازينو[4-و-6ثنائي ميثيل كينولين) و تم التعرف عليهم بالتحليل العنصري وأطياف الأشعة تحت الحمراء و المرئية و الكتلة. و لقد أجريت " المعايرات " الجهدية و تم تعيين ثوابت التفكك لهذه الهيدرازونات و كذلك ثوابت الإستقرار لمتراكباتها فى 75 % (ح / ح) مذيب-ماء لعامل التراكب الثاني و عند درجات حرارة مختلفة لعامل التراكب الاول. و لقد تم حساب ثابت التفكك لعامل التراكب الثاني و ثوابت الاستقرار لمتراكباته في الماء عن طريق العلاقة بين ثابت التفكك و ثوابت الاستقرار مع عوامل المذيب. كما تم تعيين درجة الحرارة الحركية باستخدام التحليل الانحدار الخطي بين التغير في الانثالبي و التغير في الانتروبي لمتراكبات عامل التراكب الاول. و تم تحليل دوال الديناميكا الحرارية الي مكوناتها الكهروستاتيكية وغير الكهروستاتيكية . و تم الحصول علي الشكل المستقر لعوامل التراكب باستخدام برنامج هيبركم.