

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

FATMA SAMY^{1,2,*}, A.A.T. RAMADAN¹, H.S. SELEEM¹ and A. TAHA¹

¹Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt ²Department of Chemistry, Faculty of Science, Tabuk University, Saudi Arabia

*Corresponding author: E-mail: f_ibrahim@ut.edu.sa; fatma_chem2000@yahoo.com

|--|

Binary and ternary complexes have been synthesized by reaction of the hydrazone ligand, (HL) with cobalt(II) nitrate and nickel(II) nitrate in absence and presence of second ligands. The new complexes have been characterized by elemental and thermal analyses, conductivity and magnetic susceptibility measurements as well as IR, UV-visible, ESR and mass spectra. The binary complexes have tetrahedral geometry, but ternary complexes have square planar, square pyramidal and octahedral geometries. The ligand acts as a monobasic tridentate and bidentate donor, for binary and ternary complexes, respectively. The pH metric studies at different temperature are used to calculate stepwise stability constants and thermodynamic parameters of Co(II) and Ni(II) complexes in 75 % (v/v) dioxane-water. The hyperchem 7.52 program utilized to determine the optimized structures of the ligand and its complexes. The correlation between theoretical and the experimental data of (IR and UV-visible) spectra of the complexes are good. The metal complexes exhibited remarkable antimicrobial activity.

Keywords: Cobalt, Nickel, Pyrrole, Triazine, PM3 studies, pH metric studies, ESR, Binary and Ternary complexes.

INTRODUCTION

Hydrazones and their derivatives act as antibacterial, antifungal and antitumor agents [1-3]. Triazines and their metal complexes have a wide range of biological activity such as anticancer [4], antiviral [5], antimicrobial [6,7], anthelmintic, antimalarial, anti-inflammatory agents [8]. The complexation may enhance the biological activity of the organic compounds. The present study, is an extension to our work, including 3hydrazino-5,6-diphenyl-1,2,4-triazine [9a]. Binary and ternary Cu(II)-complexes of the HL ligand; {(1E)-1-aza-2-pyrrol-2ylvinyl}{5,6-diphenyl(1,2,4-triazin-3-yl)}amine have been synthesized and characterized [9b]. The first aim of the current work is studying the effect of ligand towards Co(II) and Ni(II) ions in presence and in absence of secondary ligand. The structures of the metal complexes were characterized by elemental analyses, IR, ESR, UV-visible and mass spectra, conductivity and magnetic susceptibility measurements as well as thermal analyses. The second aim of the current work is pH metric and PM3 studies for Co(II) and Ni(II) complexes in solution and in solid state respectively.

EXPERIMENTAL

 $Co(NO_3)_2$ ·6H₂O, Ni(NO₃)₂·6H₂O, LiOH·H₂O, hydrazine hydrate (100 %), thiosemicarbazide, benzil, glacial acetic acid,

pyrrole, POCl₃, 8-hydroxyquinoline (8-HQ), 1,10-phenanthroline (Phen), N,N,N',N'-tetramethylethylenediamine (tmen), EDTA disodium salt, mureoxide, xylenol orange and nitric acid were either Aldrich, BDH or Merck products. Organic solvents were reagent grade chemicals and were used without further purification.

Synthesis of hydrazone ligand and its complexes: The hydrazone ligand; {(1E)-1-aza-2-pyrrol-2-ylvinyl}{5,6-diphenyl-(1,2,4-triazin-3-yl)}amine was prepared as described in previous publication [9b].

The complexes were prepared by addition of aqueous LiOH solution to the methanolic ligand solution and then add methanolic solution of metal salt in the molar ratio 1:1:1 (LiOH:L:M), with stirring. In case of the synthesis of ternary complexes, methanolic solution of the secondary ligand (phen), (tmen) or (8-HQ) was added to the above mixture in molar ratio 1:1:1:1 (LiOH:L:M:second ligand), then refluxed the above mixture for 6-8 h. The solid complexes were filtered off. 50 % (v/v) methanol-water solution is utilized to washing the complexes, then washed with diethyl ether. The desiccator over anhydrous CaCl₂ is employed in drying the complexes.

Measurements were carried out as described in our previous publication [9b]. The pH metric measurements were carried out as described, with change the Cu(II) solution by Co(II) or Ni(II) solution [9b].

Molecular modeling: The optimized structures of the ligand and its metal complexes were theoretically computed by using the PM3 level as implemented in hyperchem 7.52 program [10].

Antimicrobial activity: The standardized disc-agar diffusion method [11] was followed to determine the activity of the synthesized compounds against Gram-positive bacteria: *Staphylococcus aureus* (ATCC 25923) and *Bacillus subtilis* (ATCC 6635), Gram-negative bacteria: *Escherichia coli* (ATCC 25922) and *Salmonella typhimurium* (ATCC 14028), Yeast: *Candida albicans* (ATCC 10231) and Fungus: *Aspergillus fumigatus*.

Preparation of tested compound: The tested compounds were dissolved in dimethyl formamide (DMF) solvent and prepared in two concentrations; 100 and 50 mg/mL and then 10 μ L of each preparation was dropped on disk of 6 mm in diameter and the concentrations became 1 and 0.5 mg/disk respectively. In case of insoluble compounds, the compounds were suspended in DMF and vortexes then processed.

Testing for antibacterial and yeasts activity: Bacterial cultures were grown in nutrient broth medium at 30 °C. After 16 h of growth, each microorganism, at a concentration of 10^8 cells/mL, was inoculated on the surface of Mueller-Hinton agar plates using sterile cotton swab. Subsequently, uniform size filter paper disks (6 mm in diameter) were impregnated by equal volume (10 µL) from the specific concentration of dissolved compounds and carefully placed on surface of each inoculated plate. The plates were incubated in the upright

position at 36 °C for 24 h. Three replicates were carried out for each extract against each of the test organism. Simultaneously, addition of the respective solvent instead of dissolved compound was carried out as negative controls. After incubation, the diameters of the growth inhibition zones formed around the disc were measured with transparent ruler in millimeter, averaged and the mean values were tabulated.

Testing for antifungal activity: Active inoculum for experiments were prepared by transferring many loopfuls of spores from the stock cultures to test tubes of sterile distilled water (SDW) that were agitated and diluted with sterile distilled water to achieve optical density corresponding to 2.0×10^5 spore/mL. Inoculum of 0.1 % suspension was swabbed uniformly and the inoculum was allowed to dry for 5 min then the same procedure was followed as described above.

The antibiotic chloramphenicol, cephalothin and cycloheximide ware used as standard reference in the case of Gramnegative bacteria, Gram-positive bacteria, yeasts and fungi, respectively.

RESULTS AND DISCUSSION

All the metal complexes have been characterized by elemental (Table-1), thermal analyses, conductivity and magnetic susceptibility measurements as well as IR, UV-visible, ESR and mass spectra. All the isolated complexes are soluble in DMSO and DMF. The complexes have high thermal stability, confirmed by their melting point, which is above 300 °C (Scheme-I).



M = Co(2), Ni(6)

Scheme-I: Proposed structures of the binary and ternary-complexes of HL, ligand

AN	ANALYTICAL AND PHYSICAL DATA OF THE FREE LIGAND (HL) AND ITS BINARY AND TERNARY METAL COMPLEXES											
Comp.	Reactants	Complay	f	Colour	Yield	Element	Elemental analysis (%): Found (calcd.)					
No.	(HL + LiOH + Metal salt)	Complex	1.w.	Coloui	(%)	С	Н	Ν	М			
	HL	-	340.39	Orange	65	70.52	4.94	24.50	-			
						(70.57)	(4.74)	(24.69)				
1	$Co(NO_3)_2 \cdot 6H_2O$	$[Co(L)(NO_3)] \cdot 1.5H_2O$	487.34	Brown	80	49.18	3.89	20.41	12.00			
						(49.29)	(3.72)	(20.12)	(12.09)			
2	$Co(NO_3)_2 \cdot 6H_2O + temn$	[Co(L)(temn)(OH)]	531.53	Black	81	60.85	5.51	21.53	11.31			
						(58.75)	(6.07)	(21.08)	(11.09)			
3	$Co(NO_3)_2 \cdot 6H_2O + phen$	$[Co(L)(phen)(NO_3)]$	640.53	Black	76	60.14	3.79	19.50	9.30			
						(60.01)	(3.62)	(19.68)	(9.20)			
4	$Co(NO_3)_2 \cdot 6H_2O + 8-HQ$	$[Co(L)(8-HQ)] \cdot 1.5H_2O$	569.49	Black	65	61.30	4.27	17.30	10.17			
						(61.16)	(4.25)	(17.22)	(10.35)			
5	$Ni(NO_3)_2 \cdot 6H_2O$	[Ni(L)(NO ₃)]MeOH	492.13	Reddish	85	51.59	3.77	20.12	11.81			
				brown		(51.25)	(3.89)	(19.92)	(11.93)			
6	$Ni(NO_3)_2 \cdot 6H_2O + temn$	[Ni(L)(temn)(OH)]	531.30	Green	51	59.59	5.62	21.40	11.02			
						(58.78)	(6.07)	(21.09)	(11.05)			
7	$Ni(NO_3)_2 \cdot 6H_2O + phen$	$[Ni(L)(phen)(NO_3)]$	640.30	Brown	61	60.76	4.16	19.55	9.25			
						(60.03)	(3.62)	(19.69)	(9.17)			
8	$Ni(NO_3)_2 \cdot 6H_2O + 8-HQ$	$[Ni(L)(8-HQ)(H_2O)_2]$	578.27	Green	41	59.74	4.38	15.03	10.00			
						(60.24)	(4.36)	(16.96)	(10.15)			
temn = 1	N N N' N'-tetramethylethylene	diamine: phen = 1 10-phena	nthroline 8	-HO = 8-hyd	Iroxyanino	line						

TABLE-1

IR spectra: Table-2 showed that, v(NH) and/or v(OH)of the coordinated or non-coordinated water or methanol molecules appear in the range 3595-3058 cm⁻¹, which are confirmed by elemental and thermal analyses [12]. The bands of $v(C=N)_{azomethine}$, $v(C=N)_{triazine}$ and $v(N=N)_{triazine}$ of the free ligand shifted to higher frequencies for most complexes, indicates that the ligand coordinate to the central metal ions via the (azomethine and triazine) nitrogen atoms [13-15]. The monodentate coordinated NO₃⁻ group in nitrato complexes (1 and 5) showed band at 1383 and 1378 cm^{-1} , respectively, [14,15]. The conductance data of the complexes confirmed that NO₃⁻ group monodentate coordinated (Table-3). The IR spectra of ternary complexes showed new bands for (C=N)_{phen}, {(C=N)_{8-HQ} and $(C-O)_{8-HO}$ or $(CH_2)_{temn}$ bond, at (1567-1565 and 846), (1571-1570 and 1242-1225) or 856-855 cm⁻¹, respectively, supporting the coordination of the secondary ligand to the metal ion [16-18]. The appearance of new medium or weak bands in the ranges 549-522 cm⁻¹ and 445-404 cm⁻¹, may be assigned to v(M-O) and v(M-N) modes; respectively [6].

Molar conductance measurements: The molar conductance in DMF solution $(1 \times 10^{-3} \text{ M})$ of the most complexes

(Table-3) are in the range 4.96-15.64 ohm⁻¹ cm² mol⁻¹, indicate a non-electrolytic nature for all complexes [15], but the molar conductance of the complex (1) is 23.00 ohm⁻¹ cm² mol⁻¹, indicates that partial solvolysis of (NO₃⁻) group by DMF [6]. This indicates that the deprotonation of the ligand and coordination of anion, which agree with IR data.

Magnetic measurements and electronic spectra: The complex **1** showed 4.03 BM, indicated a tetrahedral geometry, which is related to three unpaired electrons, which could be considered as a further evidence to the assignment of *d-d* transition (Table-3). Furthermore, square pyramid geometry for complexes **2** and **3** showed 3.96 and 3.89 BM, respectively, which is related to three unpaired electron [19]. On the other hand, square planar complex **4** have one unpaired electron, where $\mu_{\text{eff}} = 2.63$ BM [19]. Furthermore, the μ_{eff} value of Nicomplexes (**6**, **7** and **8**) are 2.86, 3.01 and 3.07 BM, respectively, indicated a square pyramid and octahedral geometries, respectively, which is related to two unpaired electrons [19].

The complex **5** has subnormal magnetic value (2.25 BM), which is lower than the experimental range 3.4-3.8 BM for tetrahedral Ni(II) complexes. This may be attributed to the

TABLE-2
SELECTED IR ABSORPTION BANDS (cm ⁻¹) OF THE FREE LIGAND (HL) AND ITS BINARY AND TERNARY METAL COMPLEXES

Commed					IR s	spectra (cm ⁻	¹)	
No.	Complex	$\nu(NH)$ and/ or $\nu(OH)$	v(C=N) azomethine	v(C=N) triazine	v(N=N) triazine	ν(М–О)	v(M–N)	Other bands
	HL	3049	1618	1522	1445	-	-	-
1	$[Co(L)(NO_3)] \cdot 1.5H_2O$	3595, 3321	1648	1526	1449	523	421	1383 v(NO ₃ ⁻)
2	[Co(L)(temn)(OH)]	3337	1629	1524	1461	541	404	856 ν(CH ₂) rocking
3	$[Co(L)(phen)(NO_3)]$	3399	1627	1515	1461	549	417	1567, 846 v(C=N)(1,10-phen)
4	[Co(L)(8-HQ)]·1.5H ₂ O	3363	1621	1524	1463	535	411	1571 v(C=N)(8-HQ),
								1225 v(C-O) phenolic
5	[Ni(L)(NO ₃)]MeOH	3425, 3058	1630	1525	1477	535	418	1378 ν(NO ₃ ⁻)
6	[Ni(L)(temn)(OH)]	3365	1629	1536	1460	522	421	855 v(CH ₂) rocking
7	[Ni(L)(phen)(NO ₃)]	3392	1625	1516	1448	543	436	1565, 846 v(C=N)(1,10-phen)
8	$[Ni(L)(8-HQ)(H_2O)_2]$	3407	1606	1536	1465	540	445	1570 v(C=N)(8-HQ),
								1242 v(C–O)phenolic

Synthesis, Spectral, pH Metric, Antimicrobial and PM3 Studies of Co(II) and N(II) Complexes of Hydrazone 2653 Vol. 28, No. 12 (2016)

	MAGNETIC MOMENTS, MOLAR CONDUCTIVITY DATA AND ELECTRONIC SPECTRA OF THE LIGAND (HL) AND ITS BINARY AND TERNARY METAL COMPLEXES										
Compd.	Complex	$\mu_{\rm eff}$	Λ (ohm ⁻¹	Electronic spect	ral bands (nm)	Assignment	Coomatry				
No.	Complex	(BM)	$cm^2 mol^{-1}$)	Nujol mulls	DMF	Assignment	Geometry				
	HL	-	-	240, 365		Intra-ligand, CT	-				
1	[Co(L)(NO ₃)]·1.5H ₂ O	4.03	23.00	255, 320, 435sh	268, 438sh, 550sh	Intra-ligand, CT, ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$	Tetrahedral				
2	[Co(L)(temn)(OH)]	3.96	8.43	276, 363, 441sh	268, 385sh	Intra-ligand, CT	Square pyramid				
3	$[Co(L)(phen)(NO_3)]$	3.89	7.53	270, 361, 515	270, 400sh	Intra-ligand, CT, ${}^{2}A_{1} \rightarrow {}^{2}B_{2}$	Square pyramid				
4	[Co(L)(8-HQ)]·1.5H ₂ O	2.63	4.97	278, 500, 580sh	275, 393sh	Intra-ligand, CT, ${}^{2}A_{1g} \rightarrow {}^{2}A_{2g}$	Square–planar				
5	[Ni(L)(NO ₃)]MeOH	2.25	15.64	280, 389, 484	269, 280sh, 404	Intra-ligand, CT, ${}^{3}T_{1} \rightarrow {}^{3}T_{1}(P)$	Tetrahedral				
6	[Ni(L)(temn)(OH)]	2.86	5.75	256sh, 322, 494, 614sh	287, 405, 581sh	Intra-ligand, CT, ${}^{1}A_{1} \rightarrow {}^{1}E''$	Square pyramid				
7	[Ni(L)(phen)(NO ₃)]	3.01	5.98	267, 464, 618sh	269, 398	Intra-ligand CT, ${}^{1}A_{1} \rightarrow {}^{1}E''$	Square pyramid				
8	[Ni(L)(8-HQ)(H ₂ O) ₂]	3.07	4.96	346, 444, 619sh	272, 337sh, 401	Intra-ligand, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P),$ ${}^{3}A_{2e}(F) \rightarrow {}^{3}T_{1e}(F)$	Octahedral				

TABLE-3
MAGNETIC MOMENTS, MOLAR CONDUCTIVITY DATA AND ELECTRONIC SPECTRA OF
THE LIGAND (HL) AND ITS BINARY AND TERNARY METAL COMPLEXES

mixed stereochemistry of square-planar and tetrahedral structure. The percentage of square-planar is (33.8 %), which is calculated by relating the measured values to 3.4 B.M [19,20].

Electronic spectra of the complexes (Table-3) showed new bands [12,15-17]. The electronic spectra of the cobalt(II) complexes (1, 3 and 4) (Table-3) exhibit one absorption band at 550sh, 515 and 500 nm, respectively which could be assigned to ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$, ${}^{2}A_{1} \rightarrow {}^{2}B_{2}$ and ${}^{2}A_{1g} \rightarrow {}^{2}A_{2g}$, respectively. These d-d transitions suggest tetrahedral, square pyramid and squareplanar structures, respectively [21-23]. On the other hand, the spectrum of the cobalt(II) complex (2) exhibits strong CT band, at 441 nm, which obscured the weak d-d transitions occurring in the same region.

The spectrum of Ni(II) complex (8) offers two bands at (Table-3) (444; 619sh), which could be assigned as ${}^{3}A_{2g}(F) \rightarrow$ ${}^{3}T_{1g}(P)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ transitions, referring to octahedral structure. The third transition band that assigned to ${}^{3}A_{2g}(F) \rightarrow$ ${}^{3}T_{2g}(F)$ transition was not observed, as it appears in the near infrared and thus out of the range of the instrument [19]. However, Ni(II) complex (5) showed one band at 484, which might attributed to tetrahedral or square planner. Since the complex is paramagnetic, so the geometry proposed is tetrahedral geometry with ${}^{3}T_{1} \rightarrow {}^{3}T_{1}(P)$ transition [20]. While the spectra of Ni(II) complexes (6 and 7) exhibit one band at 614sh and 618sh, respectively, which is accordingly assigned as ${}^{1}A_{1} \rightarrow {}^{1}E''$ transition referring to square pyramid structure [23]. The UV-visible spectra of the complexes are agree with magnetic values.

ESR spectra: X-band ESR spectrum of [Co(L)(NO₃)]·1.5H₂O (1) (Fig. 1) exhibits two bands, one of them is sharp with g =2.00 and the other is weak with g = 2.03. The ESR shape, UVvisible assignments and magnetic value of the complex confirmed its tetrahedral geometry.

The spin Hamiltonian parameters were calculated from the ESR spectrum (Fig. 1) of the complex (1). Molecular orbital coefficients, α^2 (covalent in-plane σ -bonding) and β^2 (covalent in-plane π -bonding) were calculated [24]:

$$\alpha^{2} = (A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7 (g_{\perp} - 2.0023) + 0.04$$
$$\beta^{2} = (g_{\parallel} - 2.0023) E/(-8\lambda\alpha^{2})$$



 $\lambda = -170 \text{ cm}^{-1}$ for the free Co(II) ion and E is the electronic transition energy. Complete ionic character for $\alpha^2 = 1$ and 100 % covalent for $\alpha^2 = 0.5$. α^2 values indicate slight covalent nature of the metal-ligand δ -bonding and β^2 indicate plane π -bonding contribution in metal-ligand π -bonding [24].

Complex = [Co(L)]	$(NO_3)] \cdot 1.5H_2O$	$g_{\parallel} = 2.01$
$g_{\perp} = 2.001$		$g_{iso} = 2.0$
$A_{II} \times 10^{-4} = 28$	$\alpha^2 = 0.126$	$\beta^2 = 0.82$

Thermal gravimetric analyses (TGA): Complexes 1 and 5 were taken as representative examples for thermal analysis. The thermogram of $[Co(L)(NO_3)]$ · 1.5H₂O (1) (Fig. 2) presents a weight loss up to 114 °C which corresponds to the loss of 1.5 lattice water molecules [25].

$$[Co(L)(NO_3)] \cdot 1.5H_2O \xrightarrow{-1.5H_2O} [Co(L)(NO_3)]$$

In case of [Ni(L)(NO₃)].MeOH (5), the weight loss in the range 24-119 °C corresponds to the loss of one solvated methanol molecule.

$$[Ni(L)(NO_3)] \cdot MeOH \xrightarrow{-MeOH} [Ni(L)(NO_3)]$$

The E and A parameters have been calculated using Coats-Redfern relation [26]:



 $\ln \left[-\ln(1-\alpha)^{1-n}/(1-n)T^2 = \ln(AR/E\beta) - E/RT \text{ for } n \neq 1 \right]$

 $\ln \left[-\ln(1-\alpha)/T^2\right] = \ln(AR/E\beta) - E/RT \text{ for } n = 1 \quad (II)$

where α refers to the fraction of sample decomposed at time t, $\alpha = (w_0 - w_t)/(w_0 - w_\infty)$, w_0 , w_t and w_∞ are the weight of the sample before the degradation at temperature t and after total conversion, respectively. T is the derivative peak temperature. β is the heating rate = dT/dt. E and A are the activation energy and the Arrhenius pre-exponential factor, respectively. A straight line is obtained from plotting $\ln[-(\ln(1-\alpha))/T^2]$ against 1/T, whose slope E/R and whose intercept is used to decide the pre-exponential factor (A). The relationships; $\Delta H = E - RT$, $\Delta S = R[\ln (Ah/kT)^{-1}]$ and $\Delta G = \Delta H - T \Delta S$, are employed to limit other thermodynamic parameters (Δ H, Δ S and Δ G), where k is the Boltzmann's constant and h is the Plank's constant. The kinetic parameters (Table-4) show that (i) the values of ΔH mean that the decomposition processes are endothermic for first steps and exothermic for third steps. (ii) The energy of activation values E for the first step of decomposition of complexes is highest, this means that the rate of decomposition for this stage is the slowest one than the other stages. The relatively low and positive values of ΔG^* indicate that thermal decomposition of the complexes are non-spontaAsian J. Chem.

neous processes. The activation energy values of complex 1 have higher than that for complex 5, indicating that the rate of decomposition for complex 1 is slower than that for complex 5 (Table-4).

Mass spectra: Scheme-II offered mass fragmentation patterns of the complexes 1 and 5. The molecular ion peaks (Fig. 3) appear at m/e (488 and 492), confirming their formula weight (f.w. = 487.34 and 492.13), respectively. The peaks at m/e (460 and 462), (Fig. 3) agree non-hydrated complex [Co(L)(NO₃)] (f.w. = 460.31) and desolvated complex [Ni(L)(NO₃)] (f.w. = 460.09), respectively.



pH metric studies: The pH-titration curves (Fig. 4) indicates that the ligand behaves as mono-protic species with the dissociation of hydrazo group proton, where a = 1 (a = moles of base added per moles of ligand present). Fig. 4 displays a sharp inflection at m = 2.0 indicating to the formation of ML₂⁺ⁿ⁻² as higher formed species.

				TABLE	-4					
	THERMAL ANALYSES DATA (TG-DSC) of COBALT(II) AND NICKEL(II) COMPLEXES									
Compd.	Complex	Temperature	Loss in	wt (%)	DSC peak (°C)		Assignment			
No.	Complex	range (°C)	Found	Calc.	Endo	Exo	- ΔH (Jg)	Assignment		
	[Co(L)(NO ₃)]·1.5H ₂ O	25-114	5.68	5.55	-	-	-	1.5H ₂ O (lattice)		
1		114-319	16.95	16.21	-	177	-4.35	HCN; $2C_2H_2$		
		319-504	25.58	25.85	-	261	-6.32	NO_2 ; (CN) ₂ ; N ₂		
		24-119	4.00	4.33	50	-	40.95	2/3 MeOH (solv.)		
5	[Ni(L)(NO)].MeOH	119-473	34.44	34.68	325, 357	-	54.89, 5	1/3 MeOH; NO; phCN; HCN		
		473-800	22.02	20.93	-	-	-	phCN		
		Above 800	39.46	39.97	_	-	_	Residue, [NiC ₆ H ₄ N ₂ O ₂]		

TABLE-4a

TEMPERATURE OF DECOMPOSITION AND ACTIVATION PARAMETERS (E*, Δ H*, Δ S* AND Δ G*) DETERMINED											
FROM DTG RESULTS FOR THE DECOMPOSITION OF COBALT(II) AND NICKEL(II) COMPLEXES											
Compd. No.ComplexStageDTG peak (°C)E*A ΔH^* ΔS^* ΔG^*											
-		1 st	68.7	40.1456	341907	39.5747	36.1031	37.0944			
	$[Co(L)(NO_3)] \cdot 1.5H_2O$	2^{nd}	249.6	-7.4117	-3929	-9.4859	-	-			
1		3 rd	411.2	11.0764	0.17901	7.65933	-98.95	48.3477			
		4^{th}	624.1	-7.8282	-0.0034	-13.014	_	_			
5		1^{st}	74.4	38.5002	145735	37.882	28.3544	35.7724			
	[INI(L)(INO ₃)]·MEOH	3 rd	609	-6.1103	-0.0033	-11.171	-	-			
E* and A are t	he activation energy and the	Arrhenius n	re-exponential factor	r respectively							



Scheme-IIa: Mass fragmentation patterns of [Co(L)(NO₃)]·1.5 H₂O (1)



ñ (average number of ligand ions attached/one metal ion) and pL (the free ligand exponent) are calculated from Irving-Rossotti equations [27]. The stepwise formation constants of the complexes at different tempreature are listed in Table-5. The higher species in solution is ML_2 , where the value of \tilde{n} is between 0.1-1.9. The metal-ligand stability constants (Table-5) decrease as temperature increases [28,29]. indicates that The steric hindrance for the second coordination, lead to the Coulombic attractions between ML^+ and L are lower than those between M^{2+} and L (Table-5), this lead to log $K_1 > \log K_2$.

Electrostatic and non-electrostatic thermodynamic functions: The linear least square method is applied to calculate the thermodynamic parameters (ΔH° and ΔS°). This method gives a straight line whose slope = $-\Delta H^{\circ}/4.57$ and its intercept = $\Delta S^{\circ}/4.57$. The known relationship: $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ gave the free energy (ΔG°) change. The coordination process is the spontaneously and exothermic, where ΔG° and ΔH° have negative values [28]. The greater release of water of hydration accompanied to complexation, so that ΔS° become positive value.

Table-6 represents electrostatic and non-electro-static thermodynamic functions of the chelates. Table-8 revealed that (i) The temperature and environment affected on chelation process, where ΔG°_{1el} and ΔG°_{2el} have negative values. (ii) The degree of covalency of ML₂ complexes is higher than that of ML complexes, where $-\Delta G^{\circ}_{2non}$ is higher than $-\Delta G^{\circ}_{1non}$. (iii) The M-L bond strength is higher in the 2nd coordination than the 1st coordination, where ΔH°_{2non} has higher negative value than ΔH°_{1non} .

Distribution curves: The known expressions [30] are employed to calculate the distribution diagrams of the complexes as a function of pH (Table-7). The concentration of ML^+ increases to reaches maximum its concentration at pH = 6.01 for Co ion and at pH = 6.46 for Ni ions at 303 K. On the other hand, free M(II) and ML₂ change monotonically with pH.

Molecular modeling: The optimized structure of the ligand and its metal-complexes has been performed using PM3 semiempirical method in hyperchem 7.52 program [10]. Structures (I) presents the molecular structure with atom numbering of $[Co(L)(8-HQ)] \cdot 1.5H_2O$ (4) complex.

STABILITY CONSTANTS AND log (K ₁ /K ₂) FOR THE COBALT(II) AND NICKEL(II) COMPLEXES IN 75 % (v/v) DIOXANE-WATER AT VARIOUS TEMPERATURES												
	283 K				293 K			303 K 313 K				
Cation	log K ₁	log K ₂	$log (K_1/K_2)$	log K ₁	log K ₂	$log (K_1/K_2)$	log K ₁	log K ₂	$log (K_1/K_2)$	log K ₁	log K ₂	$log (K_1/K_2)$
Co(II)	10.78	10.46	0.32	10.74	10.35	0.39	10.66	10.16	0.50	10.60	10.02	0.58
Ni(II)	10.19	9.91	0.28	10.17	9.89	0.28	10.10	9.80	0.30	10.05	9.73	0.32

 TABLE-6

 ELECTROSTATIC AND NON-ELECTROSTATIC THERMODYNAMIC FUNCTIONS^{a,b}

 OF COBALTII) AND NICKEL(II) CHELATES IN 75 % (v/v) DIOXANE-WATER

Commissi	1 st Coordination									
Complex	$-\Delta G^{\circ}{}_{1}$	$-\Delta G^{\circ}_{el}$	$-\Delta G^{\circ}_{non}$	$-\Delta H^{\circ}{}_{1}$	$-\Delta H^{\circ}_{el}$	$-\Delta H^{\circ}_{non}$	$-\Delta S^{\circ}_{1}$	$-\Delta S^{\circ}_{el}$		
Co(II)	14.76	10.61	4.15	2.50	4.07	6.57	40.45	48.45		
Ni(II)	13.99	10.43	3.55	1.97	4.00	5.98	39.64	47.64		
Commlan	2 nd Coordination									
Complex	$-\Delta G_2^{\circ}$	$-\Delta G^{\circ}_{el}$	$-\Delta G^{\circ}_{non}$	$-\Delta H^{\circ}{}_{2}$	$-\Delta H^{\circ}_{el}$	$-\Delta H^{\circ}_{non}$	$-\Delta S^{\circ}_{2}$	$-\Delta S^{\circ}_{el}$		
Co(II)	14.07	9.28	4.79	3.66	3.56	7.21	34.37	42.37		
Ni(II)	13.57	10.47	3.10	1.51	4.02	5.53	39.79	47.79		

 ${}^{a}\Delta G^{\circ}_{x}$, ΔH°_{x} are in k cal mol⁻¹, while ΔS°_{el} is in cal mol⁻¹ K⁻¹ (x = el or non).

 ${}^{b}\Delta S^{\circ}_{non} = \text{constant} = -8 \text{ cal mol}^{-1} \text{ K}^{-1} \text{ (not included in the table).}$

OPTI C	OPTIMUM pH VALUES OF THE COMPLEX FORMATION OF ML ⁺ OBTAINED FROM THE DISTRIBUTION CURVES OF COBALT(II) AND NICKEL(II) COMPLEXES IN 75 % DIOXANE-WATER AT DIFFERENT TEMPERATURE										
Complay	283 K		293	3 K	303	3 K	313 K				
Complex	pH _c	α_1	pH_c	α_1	pH_c	α_1	pH_c	α_1			
Co(II)	6.16	0.419	6.06	0.439	6.01	0.467	5.95	0.493			
Ni(II)	6.72	0.404	6.55	0.402	6.46	0.414	6.32	0.419			

Structure-I: Optimized structures of [Co(L)(8-HQ)]·1.5H₂O (4)

Tables 8 and 9 offer the bond lengths and angles, the energies of the frontier molecular orbitals (E_{HOMO} and E_{LUMO}),

electronegativity (χ), chemical potential (μ), energy band gap (Δ E), global hardness (η), global softness (S), global electrophilicity index (ω) and softness (σ) [28].

The importance of η and σ is in measuring the molecular stability and reactivity. A hard molecule has a large energy gap and a soft molecule has a small energy gap. Soft molecules are more reactive than hard ones because they can easily offer electrons to an acceptor [28]. The prepared molecules are stable, where E_{HOMO} and E_{LUMO} have negative values [28]. ΔE_{gap} of the complexes are smaller than that of its ligand, elucidates that the reactivity of complexes is higher than that of its ligand. The electrophilicity index (χ) is a positive. The tautomeric form (I) is favourable, where its heat of formation is lower than that of the tautomeric form (II). Generally, bond lengths of (N-N and C=N)triazine and (C=N)azomethine are longer in complexes than in the free ligand. When the M-N bond is formed, it weakens the C=N bond [7]. This finding agrees well with Guttmann bonds rule which states "When a Lewis base (ligand) reacted with a Lewis acid (metal ion), the bonds attached directly with the reacting centers will be elongated" [31].

TABLE-8 STRUCTURAL PARAMETERS OF THE LIGAND (HL) AND ITS METAL COMPLEXES												
Compd. No.	Property	Heat of formation (kcal/mol)	Dipole moment	HOMO energy (EV)	LUMO energy (EV)	ΔE_{gap}	ω	χ	S	σ	η	
	HL^{a}	185.03	4.721	-8.741	-0.995	7.746	3.059	4.868	0.129	0.258	3.873	
	HL^{b}	189.09	3.568	-8.349	-1.232	7.117	3.225	4.791	0.141	0.281	3.559	
1	[Co(L)(NO ₃)]-1.5H ₂ O	-82.75	7.172	-6.297	-2.008	4.289	4.02	4.153	0.233	0.466	2.145	
2	[Co(L)(temn)(OH)]	-169.92	7.892	-3.434	-0.707	2.727	1.572	2.071	0.367	0.733	1.364	
3	$[Co(L)(phen)(NO_3)]$	86.11	14.88	-5.475	-2.229	3.246	4.571	3.852	0.308	0.616	1.623	
4	[Co(L)(8-HQ)]·1.5H ₂ O	-39.32	4.79	-4.702	-1.485	3.217	2.975	3.094	0.311	0.622	1.609	
5	[Ni(L)(NO ₃)]MeOH	-36.35	9.601	-8.725	-1.925	6.800	4.17	5.325	0.147	0.294	3.4	
6	[Ni(L)(temn)(OH)]	-56.14	10.49	-7.371	-0.287	7.084	2.07	3.829	0.141	0.282	3.542	
7	[Ni(L)(phen)(NO ₃)]	167.25	6.46	-7.914	-1.549	6.365	3.517	4.732	0.157	0.314	3.183	
8	[Ni(L)(8-HQ)(H ₂ O) ₂]	-160.40	7.931	-7.688	-0.906	6.782	2.723	4.297	0.147	0.295	3.391	
- 0	and h											

 L^{a} tautomer (**I**^a), L^{b} tautomer (**II**^b)

TABLE-9 SELECTED BOND LENGTHS OF OPTIMIZED STRUCTURES OF THE LIGAND (HL) AND ITS METAL COMPLEXES													
Dand	Ligand		Complexes										
Dolla	HL ^a	HL^{b}	1	2	3	4	5	6	7	8			
N10-C11(azo)	1.297	1.301	1.496	1.326	1.333	1.378	1.369	1.325	1.364	1.319			
N4-C5(T)	1.391	1.440	1.396	1.423	1.397	1.423	1.395	1.398	1.366	1.407			
N3-N4(T)	1.272	1.362	1.303	1.342	1.259	1.364	1.289	1.315	1.379	1.307			
C-NX1	-	-	-	1.509	1.358	1.404	-	1.517	1.324	1.396			
C-NX2				1.524	1.362			1.509	1.336				
N10-M	_	_	1.918	1.913	1.894	1.865	1.859	1.856	1.962	1.864			
N4-M	-	-	1.877	1.915	3.596	1.861	1.838	2.209	1.922	1.875			
NX1-M	-	-	-	1.983	1.951	1.878	-	1.925	3.900	1.874			
NX2-M				2.064	2.133			1.903	1.988				
Npyr-M	_	-	1.932	-	-	-	1.851	-	-	-			
HI ^a tautomer (I ^a) HI ^b tautomer (II ^b): M = Co (1.4) Ni (5.8): NX1 and NX2 = N-term, phen or 8-HO													

CORRELATIONS BETWEEN EXPERIMENTAL VALUES OF (UV-VISIBLE AND IR)

SPECTRA AND STRUCTURAL PARAMETERS OF THE METAL COMPLEXES									
Complexes	\mathbb{R}^2	Complexes							
$E_{LUMO} = -111 (\pm 0.361) + 0.203 (\pm 0.000670) v(M-O)$	100	2,5,8							
$E_{LUMO} = -30.2 (\pm 0.8073) - 0.0196 (\pm 0.0004949) \nu(C=N)(azo)$	99.9	1,4,7							
$E_{HOMO} = -1828 (\pm 93.47) + 1.12 (\pm 0.05745) v(C=N)(azo)$	99.7	2,3,7							
$E_{HOMO} = -304 (\pm 32.80) + +0.205 (\pm 0.02250) v(N=N)(T)$	98.8	2,4,7							
$E_{HOMO} = 36.2 (\pm 0.4398) - 0.0812 (\pm 0.0008214) \nu(M-O)$	100	1,7,8							
$E_{HOMO} = -28.7 (\pm 2.094) + 0.0411 (\pm 0.003881) \lambda_{max}$	99.1	1,4,5							
$\Delta E_{gap} = 241 (\pm 10.74) - 0.144 (\pm 0.006567) v(C=N)(azo)$	99.8	1,5,6							
$\Delta E_{gap} = 24.9 (\pm 2.094) - 0.0374 (\pm 0.0005479) \lambda_{max}$	100	1,4,5							
Heat of formation = 17728 (\pm 1169) - 11.6 (\pm 0.7665) v(C=N)(T)	99.1	3,6,7							
Heat of formation = 27902 (\pm 739.6) - 19.2 (\pm 0.5074) v(N=N)(T)	99.9	6-8							
Heat of formation = - 13753 (±172.9) + 25.6 (±0.3215) v(M-O)	100	4,5,7							
Length of C=N(azo) = 21346 (\pm 2044) - 14.0 (\pm 1.338) v(C=N)(T)	97.3	2,3,6,8							
Length of C=N(azo) = 2573 (± 233.8) - 6.13 (± 0.5507) v(M-N)	97.6	1,3,5,6,8							
^a v(C=N), v(M-N) and v(M-O) in cm ⁻¹ , λ in nm, Dipole Moment in D.									

 $^{b}E_{LUMO,} E_{HOMO}$ and ΔE_{gap} in ev, (C=N)_{azomethine}, (C=N)_{Triazine}, (M-N) and (M-O) in Å

TABLE-11 ANTIMICROBIAL ACTIVITY OF THE LIGAND (HL) AND ITS METAL COMPLEXES														
				Mean* of zone diameter, nearest whole (mm)										
	- -	Gram-positive bacterial				Gı	am-negat	ive bacteri	al	Yeast and Fungi**				
Complexes		Staphylococcus aureus (ATCC 25923)		Bacillus subtilis (ATCC 6635)		Salmonella typhimurium (ATCC 14028)		Escherichia coli (ATCC 25922)		Candida albicans (ATCC 10231)		Aspergillus fumigatus		
		Concentration (mg/mL)												
		1.0	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0	0.5	
1	HL	-	-	-	-	-	-	-	-	-	-	-	-	
2	$[Co(L)(NO_3)] \cdot 1.5H_2O$	10 L	7 L	-	-	-	-	10 L	8 L	18 I	15 I	-	-	
3	[Co(L)(temn)(OH)]	-	-	-	-	10 L	7 L	10 L	8 L	18 I	15 I	10 L	8 L	
4	[Co(L)(phen)(NO ₃)]	-	-	11 L	8 L	9 L	7 L	9 L	7 L	18 I	14 I	9 L	7 L	
5	$[Co(L)(8-HQ)] \cdot 1.5H_2O$	-	-	-	-	-	-	-	-	10 L	7 L	9 L	7 L	
6	[Ni(L)(NO ₃)]MeOH	-	-	-	-	-	-	-	-	9 L	7 L	-	-	
7	[Ni(L)(temn)(OH)]	-	-	9 L	7 L	-	-	-	-	18 I	13 I	9 L	7 L	
8	[Ni(L)(phen)(NO ₃)]	-	-	19 I	13 I	-	-	-	-	14 I	11 I	8 L	7 L	
9	$[Ni(L)(8-HQ)(H_2O)_2]$	_	_	8 L	7 L	_	_	_	_	12 I	8 L	10 L	7 L	

*Calculate from 3 values; **Identified on the basis of routine cultural, morphological and microscopical characteristics. - = No effect; L: Low activity = Mean of zone diameter $\leq 1/3$ of mean zone diameter of control; I: Intermediate activity = Mean of zone diameter $\leq 2/3$ of mean zone diameter of control; H: High activity = Mean of zone diameter > 2/3 of mean zone diameter of control; #: Chloramphencol in the case of Grampositive bacteria, cephalothin in the case of Gram-negative bacteria and cycloheximide in the case of fungi.

Correlation's of experimental data with structural parameters: Table-10 showed the relationship between the experimental values of (UV-visible and IR) spectra and structural parameters of complexes, we can conclude the following remarks are concluded. The strength of C=N bond is decreased by increasing (E_{LUMO} and energy gap) and by decreasing E_{HOMO} *i.e.* increasing the interaction between the azomethine group with central metal ion. This emphasized by increasing of M-N bond strength [7]. The interpretation given above was further emphasized by increasing of λ_{max} with increasing E_{HOMO} and decreasing energy gap. iv) The positive slope of the linear relationship of the calculated bond length of (C=N)azo versus $v(M-N)/cm^{-1}$, indicates that as the $v(C=N)_{azo}$ frequency decreases as the (C=N)_{azo} bond length increases (elongated, weak bond strength) and this mean the interaction between the azomethine nitrogen and metal ion increases, which agree well with the Gutmann's bonds variation rule [31].

Antimicrobial studies: Table-11 exhibited the antimicrobial activity of the ligand and its metal complexes. Data revealed that the metal complexes showed an antimicrobial activities. Generally, coablt complexes have higher activity than nickel complexes towards the Gram-negative bacteria (E. coli and S. typhimurium) and yeasts and fungi, while nickel complexes displayed higher activity than coablt complexes towards Grampositive bacteria (B. subtilis).

Conclusion

The new complexes have been synthesized and characterized by elemental and thermal analyses, IR, electronic, ESR and mass spectra as well as conductivity and magnetic susceptibility measurements. The ligand acts as a monobasic NN bidentate donor for ternary complexes and as a monobasic NNN tridentate donor for binary complexes, via N-azomethine, N-triazine and N-pyrrole. The binary complexes exhibited tetrahedral geometry, while ternary complexes showed (square pyramid and octahedral) geometries. The best correlations were obtained between the calculated data (by using hyperchem 7.52 program) *versus* experimental data of complexes. The complexes showed antimicrobial activity, towards the Gramnegative bacteria (*E. coli* and *S. typhimurium*), Gram-positive bacteria (*B. subtilis*), yeasts and fungi.

REFERENCES

- N. Ozbek, S. Alyar, H. Alyar, E. Sahin and N. Karacan, *Spectrochim. Acta* A, 108, 123 (2013).
- E.N. Nfor, A. Husian, F. Majoumo-Mbe, I.N. Njah, O.E. Offiong and S.A. Bourne, *Polyhedron*, 63, 207 (2013).
- D.S. Raja, E. Ramachandran, N.S.P. Bhuvanesh and K. Natarajan, *Eur. J. Med. Chem.*, 64, 148 (2013).
- S.S. Machakanur, B.R. Patil, D.S. Badiger, R.P. Bakale, K.B. Gudasi and S.W. Annie Bligh, J. Mol. Struct., 1011, 121 (2012).
- M. Krecmerova, M. Masojidkova and A. Holy, *Bioorg. Med. Chem.*, 18, 387 (2010).
- M. Shebl, M.A. El-ghamry, S.M.E. Khalil and M.A.A. Kishk, Spectrochim. Acta A, 126, 232 (2014).
- 7. O.M.I. Adly and A.A.A. Emara, Spectrochim. Acta A, 132, 91 (2014).
- B. Machura, A. Switlicka, R. Kruszynski, J. Mrozinski, J. Klak and J. Kusz, Polyhedron, 27, 2959 (2008).
- (a) H.S. Seleem, A.A.T. Ramadan, A. Taha and F. Samy, *Res. J. Chem. Sci.*, 1, 109 (2011); (b) F. Samy, A. A.T. Ramadan, A. Taha, H.S. Seleem, *Wulfenia J.*, 22, 147 (2015).
- 10. Hyperchem version 7.5 Hypercube Inc. (2003).
- A.W. Bauer, W.W.M. Kirby, J.C. Sherris and M. Turck, *Am. J. Clin. Pathol.*, 45, 493 (1966).
- 12. H.S. Seleem, A.A.T. Ramadan, A. Taha, M.F. Eid and F. Samy, *Spectrochim. Acta A*, **78**, 1097 (2011).

13.

- H.S. Seleem, G.A. El-Inany, B.A. El-Shetary and M.A. Mousa, *Chem. Cent. J.*, 5, 2 (2011).
- M. Ghosh, M. Layek, M. Fleck, R. Saha and D. Bandyopadhyay, *Polyhedron*, 85, 312 (2015).
- M. Shebl, S.M.E. Khalil, A. Taha and M.A.N. Mahdi, *Spectrochim. Acta* A, **113**, 356 (2013).
- 17. J. Devi and N. Batra, Spectrochim. Acta A, 135, 710 (2015).
- K. Nakamoto, IR and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, edn 5 (1997).
- H.S. Seleem, A.A. Emara and M. Shebl, *J. Coord. Chem.*, **58**, 1003 (2005).
 A.A. El-Asmy and G.A.A. Al-Hazmi, *Spectrochim. Acta A*, **71**, 1885 (2009).
- 21. M. Shebl, S.M.E. Khalil and F.S. Al-Gohani, J. Mol. Struct., 980, 78 (2010).
- R. Atkins, G. Brewer, E. Kokot, G.M. Mockler and E. Sinn, *Inorg. Chem.*, 24, 127 (1985).
- A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, edn 2 (1984).
- 24. M.M. Hassanien, I.M. Gabr, M.H. Abdel-Rhman and A.A. El-Asmy, *Spectrochim. Acta A*, **71**, 73 (2008).
- 25. A.W. Coats and J.P. Redfern, Nature, 201, 68 (1964).
- 26. M. Shebl, Spectrochim. Acta A, 117, 127 (2014).
- H.M. Irving and H.S. Rossotti, J. Chem. Soc., 2904 (1954); H.M. Irving, H.S. Rossotti, K. Taugbøl, H. Theorell and B. Thorell, Acta Chem. Scand., 10, 72 (1956).
- T.A. Yousef, G.M. Abu El-Reash, O.A. El-Gammal and S.F. Ahmed, Polyhedron, 81, 749 (2014).
- 29. O.A. El-Gammal, G.M. Abu El-Reash and M.M. El-Gamil, *Spectrochim.* Acta A, **96**, 444 (2012).
- 30. M.T. Beck, Chemistry of Complex Equilibria, Van Nostrand (1970).
- V. Gutmanns, The Donor-Acceptor Approach to Molecular Interaction, Plenum Press, New York, London (1978).