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Solvents Influence Upon Complex Formation of 7-Chloro-4-hydrazinoquinoline Schiff Base Ligand and Transition Metal(II) by Using Conductometric Method

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7-Chloro-4-hydrazinoquinoline Schiff base was synthesized and characterized by elemental analyses, IR, ^{1}H NMR, electronic spectra and mass spectrometry. The complex formation of Schiff base hydrazone ligand with Co(II), Ni(II), Cd(II), Zn(II), Cu(II) and Fe(III) in 75 % (v/v) ethanol -water, acetone-water and isopropanol-water mixtures at 30, 40 and 50 °C, assigned that the ligand behaves as a monoprotic. The stability constants of the formed complexes decreased with increasing temperature, reflecting that the complexation process is an exothermic process. Thermodynamics parameters are computed and analyzed in order to investigate the bond character between metal and ligand. The calculated values for ΔG, ΔH and ΔS suggested that the complexation process is spontaneous. The calculated dissociation constant of ligand (HL) depends on the relation between the basicity of the ligand and dielectric constant of different solvents.

Keywords: 7-Chloro-4-hydrazinoquinoline, Hydrazone, Schiff base ligand, Metal complexes, Stability constant.

INTRODUCTION

Hydrazone considers one of the important reagents in inorganic and analytical chemistry, where it uses its ability to form stable complexes with ions and other transition elements and in the separation of lanthanides elements [1-6]. The electronic spectrum which determines the extraction constant at different concentrations and pHs in the analysis of Co, Ni in iron and steel [7]. The complexes of transition elements are of particular importance and is used in many areas as catalysts and in electroluminescent devices [8,9]. They are also found in many of the enzymes associated with mineral particles large ring molecules such as heme ring or linked to donor centers in peptide chains [10-14]. Hydrazones and their derivatives are among the most common treatments for tuberculosis disease and also used as antibacterial [15,16]. Some of them work as antituberculosis that caused by *Mycobacterium tuberculosis*. In the present investigation, we reported the synthesis and characterization of transition metal complexes of hydrazone having quinoline moiety Schiff base and spectral studies of solutions and titration of molar conductance.

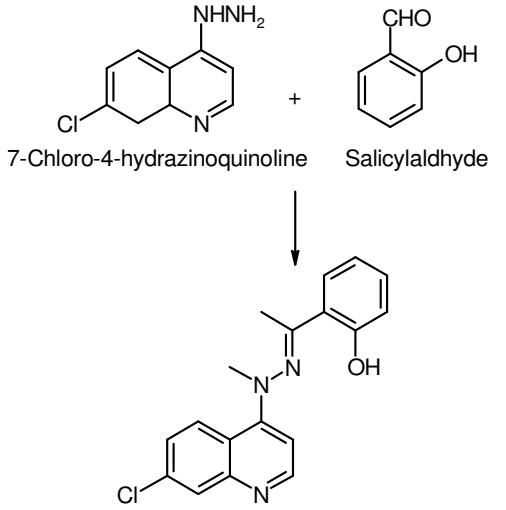
EXPERIMENTAL

Nitrate salts of Co(II), Ni(II), Cd(II), Zn(II), Cu(II), Fe(III), sodium hydroxide, potassium, ammonium, potassium sodium tartrate, hexamine, potassium hydrogen phthalate, ethylenediaminetetraacetic acid disodium salt (EDTA) and murexide, Eirochrom black-T, xylenol orange, ammonium thiocyanate evidence and ethyl alcohol, acetone, isopropanol alcohol and salicylaldehyde (100 %) hydrazine hydrate are from BDH or Merck grades.

Preparation of EDTA solution: The EDTA solution was prepared by dissolving known weight of disodium salt EDTA in a given volume of double distilled water and then make sure from concentration by titration with standard solution of zinc sulfate [11].

Synthesis of ligand [17]: 7-Chloro-4-(*o*-hydroxy benzilidene-hydrazo)quinoline (HL) was synthesized as reported method. 7-Chloro-4-hydrazinoquinoline (2 g, 1 mmol) was dissolved in 10 mL of absolute ethanol. To this solution, salicylaldehyde (13 mL, 1.1 mmol) was added. The reaction mixture was refluxed for 2 h. After cooling, the yellow precipitate was filtered and finally washed with 5-10 mL absolute ethanol and purified by recrystallization from ethanol (80 %, m.p. 235 °C) (**Scheme-I**).

The pH was measured by using Hanna Model 302 digital pH-meter with a double pole. The BDH buffer solvents were used to calibrate the device. Measurements were conducted using water bath at 30, 40, 50 °C on a circulator water bath in a double glass cell under nitrogen gas purified the glass towers



Scheme-I: Synthesis of Schiff base ligang

containing pyrogallol and copper sulfate. All the measurements were conducted on 60 mL ligand solution in 75 % (v/v) ethanol-water, acetone-water and isopropanol-water media. Electrical conductance measurements were performed using a WTW. D 8120 Weilheim LF. 42. Spectral measurements were conducted on Shimadzu Model UV-probe.

RESULTS AND DISCUSSION

The physico-chemical data of the ligand is given in Table-1. The electronic absorption of ligand in 75 % (v/v) ethanol-water media displayed absorption bands at 48076.92 and 44642 cm^{-1} assigned for π-π^* transitions within the aromatic and quinoline rings, respectively. The band observed at 36231.88 cm^{-1} assigned to n-π^* transition of C=N group. The absorption bands at 26178.01 and 24752.48 cm^{-1} assigned for CT transitions. The band at 24752.48 cm^{-1} lies in the visible region [18]. The IR spectrum of the ligand shows a strong band at 3530 cm^{-1} which assigned to ν(OH) of the phenolic group. The stretching vibration of NH group appears as weak bands at 3300 cm^{-1}. The spectrum also shows the vibrational bands at 1605, 1600 and 1140, 1130 cm^{-1} which are assigned for C=N and N-N groups, respectively. The deformation vibration of phenolic OH group appears at 1278 cm^{-1}. The vibrational band observed at 2570 cm^{-1} is assigned to the intra molecular hydrogen bonding [17].

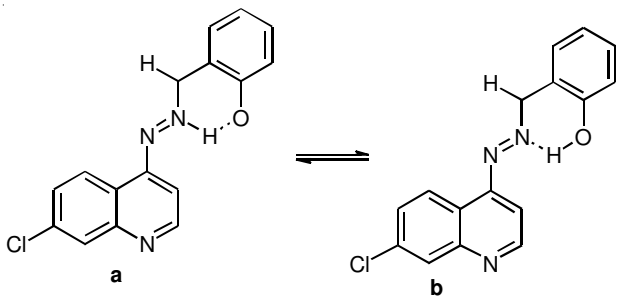
The electronic spectra of ligand in 3×10^{-5} M in 75 % (v/v) ethanol-water showed three absorption bands primarily at 247.5, 368 and 361.5 nm, which is firstly due to π^*-π transition for gasoline and quinoline rings and secondly attributed to n-π^* transition of C=N group. This transition assigned broad summit which could be taken as evidence to the presence of these compounds in the form of frequency shifting proton from one form to another tautomeric form [19]. The charge transfer encroaches on the visible region and impacts the yellow colour of ligand (Table-2).

pH-metric titrations: Calibration pH measurement is necessary to identify the number of protons, which can be ionized through the calculation of the ligand dissociation constant (pK_a). All the measurements were conducted on 60 mL solution of ligand (0.1 and 0.05 M) in 75 % (v/v) ethanol-water, acetone-water and isopropanol-water. Measurements were conducted at 30, 40 and 50 °C.

It is found that ligand behaves as monoprotic and the dissociation constant (basicity of ligand) affected by the presence of dielectric constants of the solvent used, thus the following series was:

Acetone-water > Isopropanol-water > Ethanol-water

The results showed that ligand exhibits a monoprotic weak acid due to the disintegration of a single proton probably from phenolic -OH group (**a**), there is a probability to remove a proton from the hydrazone group (-NH-N=), despite in the existence of -OH phenolic group (**b**), is due to the composition of intra molecular H-bonding and in all cases formation of hexa ring involving a group hydrazone (-NH-N=). The structure can be represented as follow:



Tables 3-5 represent dissociation constant (pK_a) values of proton -OH phenolic group. Similar results [20] were obtained from the dissociation of *o*-hydroxybenzoylacetone

TABLE-1
PHYSICO-CHEMICAL ANALYSIS DATA OF LIGAND HL

Compound m.f. (m.w.)	Elemental analysis (%): Found (calcd.)				Colour	Yield (%)	m.p. (°C)	IR frequencies (ν, cm^{-1})			
	C	H	N	Cl				ν(C=N)	ν(N-H)	ν(N-N)	Other IR bands
HL, $C_{16}H_{12}N_3OCl$ (297.5)	64.80 (64.73)	3.50 (3.70)	14.45 (14.14)	12.22 (11.94)	Yellow	94	225	1605s	3222w	1140s	3530 ν(OH-phenol), 3060 ν(C-H)

TABLE-2
ELECTRONIC SPECTRAL DATA OF THE LIGAND

Band	λ_{max} (nm)	Absorbance	log ε	Assignment
Band A	361.5	0.631	4.320	Charge transfer, CT
Band B	368.0	0.162	3.732	n-π^* and π-π^* of the azomethine group
Band C	247.5	0.313	4.080	π-π^* of the quinoline and benzene rings

TABLE-3
DISSOCIATION CONSTANT VALUES OF LIGAND (HL) IN 75 % (v/v) ETHANOL-WATER; V_o = 60 mL; μ = 0.05 M KNO_3; $[L_o] = 3 \times 10^{-3}$; [KOH] = 0.04017 M

KOH (mL)	30 °C				40 °C				50 °C			
	pH	pHc	$\log\frac{[L_o]-[KOH]}{[KOH]}$	pKa	pH	pHc	$\log\frac{[L_o]-[KOH]}{[KOH]}$	pKa	pH	pHc	$\log\frac{[L_o]-[KOH]}{[KOH]}$	pKa
0.35	9.85	9.59	1.071983	10.66198252	9.83	9.57	1.07198252	10.64198	9.67	9.41	1.071983	10.48198
0.40	9.99	9.73	1.008702	10.73870191	9.94	9.68	1.00870191	10.6887	9.73	9.47	1.008702	10.4787
0.45	10.03	9.77	0.952196	10.72219554	10.02	9.76	0.95219554	10.7122	9.79	9.53	0.952196	10.4822
0.50	10.10	9.84	0.901017	10.74101737	10.06	9.8	0.90101737	10.70102	9.84	9.58	0.901017	10.48102
0.55	10.15	9.89	0.854135	10.74413549	10.12	9.86	0.85413549	10.71414	9.92	9.66	0.854135	10.51414
0.60	10.23	9.97	0.810787	10.78078746	10.18	9.92	0.81078746	10.73079	9.97	9.71	0.810787	10.52079
0.65	10.26	10	0.770394	10.7703938	10.22	9.96	0.7703938	10.73039	10.03	9.77	0.770394	10.54039
0.70	10.29	10.03	0.732504	10.76250358	10.30	10.04	0.73250358	10.7725	10.06	9.8	0.732504	10.5325
0.75	10.35	10.09	0.696759	10.78675886	10.32	10.06	0.69675886	10.75676	10.12	9.86	0.696759	10.55676
0.80	10.39	10.13	0.662871	10.79287063	10.33	10.074	0.66287063	10.73687	10.15	9.89	0.662871	10.55287
0.85	10.44	10.18	0.630602	10.81060205	10.39	10.13	0.63060205	10.7606	10.18	9.92	0.630602	10.5506
0.90	10.47	10.21	0.599756	10.80975647	10.42	10.16	0.59975647	10.75976	10.22	9.96	0.599756	10.55976
0.95	10.51	10.25	0.570169	10.82016869	10.44	10.18	0.57016869	10.75017	10.24	9.98	0.570169	10.55017
1.00	10.53	10.27	0.541699	10.81169853	10.46	10.2	0.54169853	10.7417	10.28	10.02	0.541699	10.5617
1.05	10.56	10.3	0.514226	10.81422584	10.49	10.23	0.51422584	10.74423	10.32	10.06	0.514226	10.57423
1.10	10.59	10.33	0.487647	10.81764683	10.52	10.26	0.48764683	10.74765	10.34	10.08	0.487647	10.56765
1.15	10.63	10.37	0.461871	10.83187105	10.55	10.29	0.46187105	10.75187	10.37	10.11	0.461871	10.57187
1.20	10.65	10.39	0.436819	10.82681915	10.57	10.31	0.43681915	10.74682	10.39	10.13	0.436819	10.56682
3.35	11.37	11.11	-0.4716	10.6384	11.25	10.99	-0.4716	10.5184	11.09	10.83	-0.4716	10.3584
3.40	11.38	11.12	-0.49767	10.62233	11.27	11.01	-0.49767	10.51233	11.10	10.84	-0.49767	10.34233
3.45	11.39	11.13	-0.52458	10.60542	11.28	11.02	-0.52458	10.49542	11.11	10.85	-0.52458	10.32542
3.50	11.40	11.14	-0.55242	10.58758	11.29	11.03	-0.55242	10.47758	11.12	10.86	-0.55242	10.30758
3.55	11.41	11.15	-0.5813	10.5687	11.30	11.04	-0.5813	10.4587	11.13	10.87	-0.5813	10.2887
3.60	11.42	11.16	-0.61135	10.54865	11.31	11.05	-0.61135	10.43865	11.14	10.88	-0.61135	10.26865
3.65	11.44	11.18	-0.64271	10.53729	11.32	11.06	-0.64271	10.41729	11.15	10.89	-0.64271	10.24729
3.70	11.45	11.19	-0.67558	10.51442	11.34	11.08	-0.67558	10.40442	11.16	10.90	-0.67558	10.22442
3.75	11.46	11.2	-0.71014	10.48986	11.35	11.09	-0.71014	10.37986	11.18	10.92	-0.71014	10.20986
3.80	11.47	11.21	-0.74666	10.46334	11.37	11.11	-0.74666	10.36334	11.19	10.93	-0.74666	10.18334
3.85	11.48	11.22	-0.78546	10.43454	11.38	11.12	-0.78546	10.33454	11.20	10.94	-0.78546	10.15454
3.90	11.50	11.24	-0.82692	10.41308	11.39	11.13	-0.82692	10.30308	11.21	10.95	-0.82692	10.12308
3.95	11.51	11.25	-0.87154	10.37846	11.40	11.14	-0.87154	10.26846	11.22	10.96	-0.87154	10.08846
4.00	11.52	11.26	-0.91995	10.34005	11.41	11.15	-0.91995	10.23005	11.23	10.97	-0.91995	10.05005
4.05	11.53	11.27	-0.97302	10.29698	11.42	11.16	-0.97302	10.18698	11.24	10.98	-0.97302	10.00698
4.10	11.55	11.29	-1.03191	10.25809	11.43	11.17	-1.03191	10.13809	11.25	10.99	-1.03191	9.958091
4.15	11.56	11.3	-1.09828	10.20172	11.44	11.18	-1.09828	10.08172	11.27	11.01	-1.09828	9.911722
4.20	11.57	11.31	-1.17461	10.13539	11.46	11.2	-1.17461	10.02539	11.29	11.03	-1.17461	9.855389
4.25	11.58	11.32	-1.26486	10.05514	11.47	11.21	-1.26486	9.94514	11.30	11.04	-1.26486	9.77514
4.30	11.59	11.33	-1.3759	9.954104	11.48	11.22	-1.3759	9.844104	11.31	11.05	-1.3759	9.674104
4.35	11.61	11.35	-1.52136	9.828636	11.49	11.23	-1.52136	9.708636	11.32	11.06	-1.52136	9.538636
4.40	11.62	11.36	-1.7352	9.624796	11.50	11.24	-1.7352	9.504796	11.33	11.07	-1.7352	9.334796
pK_a			10.751				10.544				10.371	

TABLE-4
CALCULATION OF DISSOCIATION CONSTANT OF HL LIGAND IN 75 % (v/v) ACETONE-WATER; V_o = 60 mL; μ = 0.05 M KNO_3; $[L_o] = 3 \times 10^{-3}$; [KOH] = 0.04335 M

mL KOH	30 °C				40 °C				50 °C			
	pH	pHc	$\log\frac{[L_o]-[KOH]}{[KOH]}$	pKa	pH	pHc	$\log\frac{[L_o]-[KOH]}{[KOH]}$	pKa	pH	pHc	$\log\frac{[L_o]-[KOH]}{[KOH]}$	pKa
0.35	10.45	10.17	1.035973	11.20597	10.26	9.98	1.035973	11.01597	10.18	9.9	1.035973	10.93597
0.40	10.54	10.26	0.972232	11.23223	10.36	10.08	0.972232	11.05223	10.22	9.94	0.972232	10.91223
0.45	10.59	10.31	0.915253	11.22525	10.44	10.16	0.915253	11.07525	10.36	10.08	0.915253	10.99525
0.50	10.65	10.37	0.86359	11.23359	10.5	10.22	0.86359	11.08359	10.48	10.2	0.86359	11.06359
0.55	10.69	10.41	0.816211	11.22621	10.55	10.27	0.816211	11.08621	10.52	10.24	0.816211	11.05621
0.60	10.76	10.48	0.772352	11.25235	10.61	10.33	0.772352	11.10235	10.57	10.29	0.772352	11.06235
0.65	10.8	10.52	0.731434	11.25143	10.66	10.38	0.731434	11.11143	10.62	10.34	0.731434	11.07143
0.70	10.85	10.57	0.693004	11.263	10.71	10.43	0.693004	11.123	10.67	10.39	0.693004	11.083
0.75	10.9	10.62	0.656705	11.2767	10.75	10.47	0.656705	11.1267	10.70	10.42	0.656705	11.0767
0.80	10.93	10.65	0.622246	11.27225	10.79	10.51	0.622246	11.13225	10.73	10.45	0.622246	11.07225
0.85	10.97	10.69	0.589391	11.27939	10.83	10.55	0.589391	11.13939	10.79	10.51	0.589391	11.09939
0.90	10.99	10.71	0.557941	11.26794	10.86	10.58	0.557941	11.13794	10.82	10.54	0.557941	11.09794
0.95	11.04	10.76	0.527732	11.28773	10.9	10.62	0.527732	11.14773	10.88	10.6	0.527732	11.12773
1.00	11.07	10.79	0.498621	11.28862	10.92	10.64	0.498621	11.13862	10.90	10.62	0.498621	11.11862
1.05	11.1	10.82	0.470487	11.29049	10.96	10.68	0.470487	11.15049	10.92	10.64	0.470487	11.11049
3.35	12.08	11.8	-0.62074	11.17926	11.90	11.62	-0.62074	10.99926	11.88	11.6	-0.62074	10.97926
3.40	12.1	11.82	-0.65512	11.16488	11.92	11.64	-0.65512	10.98488	11.90	11.62	-0.65512	10.96488
3.45	12.12	11.84	-0.69133	11.14867	11.94	11.66	-0.69133	10.96867	11.92	11.64	-0.69133	10.94867
3.50	12.14	11.86	-0.72965	11.13035	11.96	11.68	-0.72965	10.95035	11.93	11.65	-0.72965	10.92035
3.55	12.16	11.88	-0.77045	11.10955	11.97	11.69	-0.77045	10.91955	11.94	11.66	-0.77045	10.88955
3.60	12.18	11.9	-0.81417	11.08583	11.99	11.71	-0.81417	10.89583	11.96	11.68	-0.81417	10.86583
3.65	12.2	11.92	-0.86137	11.05863	12.02	11.74	-0.86137	10.87863	11.98	11.7	-0.86137	10.83863
3.70	12.23	11.95	-0.91282	11.03718	12.03	11.75	-0.91282	10.83718	12.00	11.72	-0.91282	10.80718
3.75	12.25	11.97	-0.96954	11.00046	12.05	11.77	-0.96954	10.80046	12.02	11.74	-0.96954	10.77046
3.80	12.27	11.99	-1.03293	10.95707	12.07	11.79	-1.03293	10.75707	12.03	11.75	-1.03293	10.71707
3.85	12.29	12.01	-1.1051	10.9049	12.09	11.81	-1.1051	10.7049	12.05	11.77	-1.1051	10.6649
3.90	12.32	12.04	-1.18923	10.85077	12.11	11.83	-1.18923	10.64077	12.07	11.79	-1.18923	10.60077
3.95	12.35	12.07	-1.29071	10.77929	12.13	11.85	-1.29071	10.55929	12.09	11.81	-1.29071	10.51929
40	12.37	12.09	-1.41951	10.67049	12.16	11.88	-1.41951	10.46049	12.11	11.83	-1.41951	10.41049
4.05	12.39	12.11	-1.5978	10.5122	12.18	11.90	-1.5978	10.3022	12.13	11.85	-1.5978	10.2522
4.10	12.42	12.14	-1.8947	10.2453	12.19	11.91	-1.8947	10.0153	12.15	11.87	-1.8947	9.975295
4.15	12.45	12.17	-3.26603	8.903967	12.22	11.94	-3.26603	8.673967	12.17	11.89	-3.26603	8.623967
pKa			11.1676				10.9989				10.9011	

TABLE-5
CALCULATION OF DISSOCIATION CONSTANT OF HL LIGAND IN 75 % (v/v) ISOPROPANOL-WATER; V_o = 60 mL; μ = 0.05 M KNO_3; $[L_o] = 3 \times 10^{-3}$; [KOH] = 0.0402 M

mL KOH	30 °C				40 °C				50 °C			
	pH	pHc	$\log\frac{[L_o]-[KOH]}{[KOH]}$	pKa	pH	pHc	$\log\frac{[L_o]-[KOH]}{[KOH]}$	pKa	pH	pHc	$\log\frac{[L_o]-[KOH]}{[KOH]}$	pKa
0.35	9.79	9.42	1.0716308	10.491631	9.63	9.26	1.0716308	10.331631	9.52	9.15	1.0716308	10.221631
0.40	9.93	9.56	1.0083459	10.568346	9.78	9.41	1.0083459	10.418346	9.68	9.31	1.0083459	10.318346
0.45	10.06	9.69	0.9518351	10.641835	9.86	9.49	0.9518351	10.441835	9.80	9.43	0.9518351	10.381835
0.50	10.17	9.8	0.9006524	10.700652	10.00	9.63	0.9006524	10.530652	9.99	9.62	0.9006524	10.520652
0.55	10.28	9.91	0.8537659	10.763766	10.13	9.76	0.8537659	10.613766	10.07	9.7	0.8537659	10.553766
0.60	10.39	10.02	0.8104131	10.830413	10.22	9.85	0.8104131	10.660413	10.19	9.82	0.8104131	10.630413
0.65	10.47	10.1	0.7700145	10.870015	10.29	9.92	0.7700145	10.690015	10.25	9.88	0.7700145	10.650015
0.70	10.54	10.17	0.7321193	10.902119	10.38	10.01	0.7321193	10.742119	10.30	9.93	0.7321193	10.662119
0.75	10.59	10.22	0.6963694	10.916369	10.43	10.06	0.6963694	10.756369	10.35	9.98	0.6963694	10.676369
0.80	10.65	10.28	0.6624759	10.942476	10.49	10.12	0.6624759	10.782476	10.42	10.05	0.6624759	10.712476
0.85	10.71	10.34	0.6302019	10.970202	10.57	10.2	0.6302019	10.830202	10.47	10.1	0.6302019	10.730202
0.90	10.76	10.39	0.5993507	10.989351	10.62	10.25	0.5993507	10.849351	10.52	10.15	0.5993507	10.749351
0.95	10.81	10.44	0.5697572	11.009757	10.67	10.3	0.5697572	10.869757	10.57	10.2	0.5697572	10.769757
1.00	10.84	10.47	0.5412811	11.011281	10.71	10.34	0.5412811	10.881281	10.60	10.23	0.5412811	10.771281
1.05	10.9	10.53	0.5138023	11.043802	10.75	10.38	0.5138023	10.893802	10.63	10.26	0.5138023	10.773802
3.40	11.99	11.62	-0.4990165	11.120983	11.81	11.44	-0.4990165	10.940983	11.68	11.31	-0.4990165	10.810983
3.45	12	11.63	-0.52599	11.10401	11.83	11.46	-0.52599	10.93401	11.70	11.33	-0.52599	10.80401
3.50	12.01	11.64	-0.5539015	11.086098	11.85	11.48	-0.5539015	10.926098	11.72	11.35	-0.5539015	10.796098
3.55	12.03	11.66	-0.582862	11.077138	11.87	11.5	-0.582862	10.917138	11.74	11.37	-0.582862	10.787138
3.60	12	11.63	-0.613	11.017	11.88	11.51	-0.613	10.897	11.76	11.39	-0.613	10.777
3.65	12.05	11.68	-0.6444661	11.035534	11.90	11.53	-0.6444661	10.885534	11.77	11.4	-0.6444661	10.755534
3.70	12.06	11.69	-0.6774388	11.012561	11.91	11.54	-0.6774388	10.862561	11.79	11.42	-0.6774388	10.742561
3.75	12.09	11.72	-0.7121315	11.007869	11.93	11.56	-0.7121315	10.847869	11.80	11.43	-0.7121315	10.717869
3.80	12.11	11.74	-0.7488025	10.991197	11.95	11.58	-0.7488025	10.831197	11.81	11.44	-0.7488025	10.691197
3.85	12.13	11.76	-0.7877695	10.97223	11.97	11.6	-0.7877695	10.81223	11.83	11.46	-0.7877695	10.67223
3.90	12.14	11.77	-0.8294284	10.940572	11.99	11.62	-0.8294284	10.790572	11.85	11.48	-0.8294284	10.650572
3.95	12.17	11.8	-0.8742825	10.925718	12.01	11.64	-0.8742825	10.765718	11.87	11.5	-0.8742825	10.625718
4.00	12.18	11.81	-0.9229848	10.887015	12.02	11.65	-0.9229848	10.727015	11.89	11.52	-0.9229848	10.597015
4.05	12.2	11.83	-0.9764052	10.853595	12.04	11.67	-0.9764052	10.693595	11.91	11.54	-0.9764052	10.563595
4.10	12.22	11.85	-1.0357381	10.814262	12.06	11.69	-1.0357381	10.654262	11.92	11.55	-1.0357381	10.514262
4.15	12.24	11.87	-1.1026884	10.767312	12.08	11.71	-1.1026884	10.607312	11.95	11.58	-1.1026884	10.477312
4.20	12.26	11.89	-1.1798111	10.710189	12.09	11.72	-1.1798111	10.540189	11.96	11.59	-1.1798111	10.410189
4.25	12.28	11.91	-1.2711939	10.638806	12.11	11.74	-1.2711939	10.468806	11.98	11.61	-1.2711939	10.338806
4.30	12.3	11.93	-1.3839963	10.546004	12.13	11.76	-1.3839963	10.376004	11.99	11.62	-1.3839963	10.236004
4.35	12.32	11.95	-1.5325979	10.417402	12.15	11.78	-1.5325979	10.247402	12.01	11.64	-1.5325979	10.107402
4.40	12.35	11.98	-1.7535241	10.226476	12.16	11.79	-1.7535241	10.036476	12.02	11.65	-1.7535241	9.8964759
4.45	12.36	11.99	-2.2072631	9.7827369	12.17	11.8	-2.2072631	9.5927369	12.04	11.67	-2.2072631	9.4627369
pKa			10.9473				10.792				10.674	

and benzoyl acetone ligand, which behaves as a single proton [16]. The ligand give single proton and can take HL symbol, hence dissociation equation is as follow:

$$m = 0 \rightarrow 1$$

m is the number of KOH moles added per mole of ligand.

$$HL + OH^- \overset{K^H}{\rightleftharpoons} L^- + H_2O$$

As a result ligand HL, coordinates in all complexes as monoprotic bidentate ON ligand *via* oxygen atom of phenolic OH and nitrogen atom of azomethine -C=N groups [21].

Dissociation constants: pH measurements at 30, 40, 50 °C were conducted in presence and absence of Cu(II), Ni(II), Cd(II), Co(II), Zn(II), Mn(II), Fe(III) cations. However, in the beginning calibration of ligand with Cu(II) deposition occurred, this may be due to the formation of metal hydroxide.

Effect of dielectric constant of solvents on dissociation constant: As ligand is insoluble in water, so it is recommended to determine the relationship between dissociation constant (pK_a) of water and organic solvents medium (ethanol-water, acetone-water, isopropanol-water) and the dielectric constant (D) for each solvent. The dissociation constant of ligand is ranged from 10.4 to 10.6.

From Table-6, the order of dissociation constant of the ligand in organic solvents-water medium at 30 °C followed as:

Acetone-water > Isopropanol-water > Ethanol-water

While this arrangement does not change with the increase of temperature to 40 or 50 °C ,which indicates that this change is due to the dielectric constant D of the solvents. This arrangement is compatible with the results derived from spectral measurements which is also consistent with the results previously recorded [22].

According to Braude [23], the equilibrium proton-ligand in different aqueous solutions depends on: (1) dielectric constant (D) of the medium *i.e*. an increase in D of the solvent reduces the dissociation constant pKa and *vice-versa*. (2) Effect of organic solvent on hydrogen bond in water *i.e*. when the hydrogen bonding in water decrease by organic solvent the affinity water increases to acquire proton. (3) Protonated organic solvent *i.e.* receive organic solvent to the proton,the more hydration of the proton by organic solvent the higher values of pKa.

The pKa values of ligand in 75 % (v/v) ethanol-water at 50, 40, 30 °C are 10.371, 10.544, 10.751, respectively, which means that the ligand base increased by increasing temperature.

The increase in acid dissolution constant can be attributed to the decrease of the dielectric constant of organic solvent due to the electrostatic forces between ions, which facilitates the formation of molecular parts. However, in case of ethanol and isopropanol, increasing the dielectric constant of the solvent leads to increase in the values of dissociation constant of ligand *i.e*. the solvent which has a dissociation constant increase further, hydration of anions and cations in equilibrium, which leads to an increase in size and redueces the spaces between the ions in ion-pair. It means that the role of decrease the polar solvent leads to decrease dissociation constant and subsequently weaken the hydration of each cations and anions. We concluded that solvents with low dielectric constant prove non-polar alkane [22-25], while solvents with high dielectric constant reduces the energies of excited state orbitals of the ionic structures, leaving the non-polar unchanged.

The application of dissociation-ligand constant, the order according to the increase in dielectric constant as:

Acetone-water > Ethanol-water > Isopropanol-water

But we obtained as:

Acetone-water > Isopropanol-water > Ethanol-water

where there is change in location of ethanol-water and isopropanol-water, inspite that ethanol has a dielectric constant greater than isopropanol. This difference may due to other factors such as temperature.

Stability constants of complexes at 30, 40, 50 °C and in 75 % (v/v) binary mixed solvents of water with organic solvents: The calibration titration curves of ligand [3×10^{-3} M] in the presence of Cd(II), Mn(II), Ni(II), Zn(II), Co(II), Fe(III) [1×10^{-3} M] extracted from the results of calibration titration at 30, 40, 50 °C (Table-7). It is noted that in the case of Cu(II), the calibration could not be completed due to the immediate deposition.

TABLE-6
CORRELATION OF pKa's VALUES OF THE LIGAND IN DIFFERENT MIXED SOLVENTS AT 30, 40 AND 50 °C AND DIELECTRIC CONSTANTS, (D's) OF THE SOLVENTS

	Solvent-water at 30 °C			Solvent-water at 40 °C			Solvent-water at 50 °C		
	Ethanol	Acetone	Isopropanol	Ethanol	Acetone	Isopropanol	Ethanol	Acetone	Isopropanol
D	24.3	20.7	18.3	24.3	20.7	18.3	24.3	20.7	18.3
pKa	10.751	11.168	10.9473	10.544	10.999	10.792	10.365	10.9011	10.674
pKa in water		10.42			10.61			10.71	

TABLE-7
CORRELATION OF pKa's VALUES OF THE LIGAND IN DIFFERENT MIXED[a] SOLVENTS AT 30, 40 AND 50 °C AND DIELECTRIC CONSTANTS, (D's) OF THE SOLVENT

	Solvent-water at 30 °C			Solvent-water at 40 °C			Solvent-water at 50 °C		
	Ethanol	Acetone	Isopropanol	Ethanol	Acetone	Isopropanol	Ethanol	Acetone	Isopropanol
D	24.3	20.7	18.3	24.3	20.7	18.3	24.3	20.7	18.3
pKa	10.751	11.168	10.9473	10.544	10.999	10.792	10.365	10.9011	10.674
pKa in water		10.42			10.61			10.71	

[a]75 % (v/v) solvent-water and D = Dielectric constant

TABLE-8
THERMODYNAMICS FUNCTIONS AND STEPWISE FORMATION CONSTANTS OF 1:1 AND 1:2 METAL COMPLEXES AT 30, 40 AND 50 °C IN 75 % ETHANOL-WATER

Complex (HL)	30 °C		40 °C		50 °C		$\Delta G°_{30}$ (K cal mol^{-1})		$\Delta H°_{30}$ (K cal mol^{-1})		$\Delta S°_{30}$ (K^{-1} cal mol^{-1})	
	log k_1	log k_2	log k_1	log k_2	log k_1	log k_2	$\Delta G°_1$	$\Delta G°_2$	$\Delta G°_1$	$\Delta G°_2$	$\Delta G°_1$	$\Delta G°_2$
Co(II)	10.090	10.56	9.790	10.40	9.550	10.20	13.9903	14.6419	0.1208630	0.0803863	0.0457736	0.0480579
Cd(II)	9.880	10.99	9.690	10.60	9.520	10.10	13.6991	15.2381	0.0805280	0.1987040	0.0449457	0.0496351
Ni(II)	10.180	10.57	9.800	10.32	9.550	10.11	14.1150	14.6558	0.1411490	0.1029300	0.0461185	0.0480296
Zn(II)	9.210	9.69	8.930	9.31	8.610	9.00	12.7701	13.4356	0.1340380	0.1544200	0.0417032	0.0438324
Fe(III)	7.410	8.40	6.900	8.10	6.500	7.90	10.2743	11.6470	0.2036990	0.1120150	0.0332363	0.0380692
Mn(II)	9.910	10.61	7.960	10.47	6.700	10.30	13.7407	14.7113	0.7192720	0.0692309	0.0429749	0.0483235
pKa	10.751	–	10.544	–	10.371	–	14.9068	–	0.0850294	–	0.0489166	–

Curve of Mn(II) noted a significant broken when m = 1 (m = number of moles of KOH per mole of ligand) reflects the formation of complex to be 1:1 Mn L^+, which can be represented by the following equilibrium:

$$Mn^{2+} + HL \rightleftharpoons MnL^{+} + H^{+} \quad (m = 1)$$

This behaviour was not observed with the rest of metals cations, where we noted one overlapping buffer region between m = 0 to m = 2, which corresponds to *bis*-chelated complex 1:2 (M: L) and can be represented by the following equilibrium:

$$M^{n+} + 2HL \rightleftharpoons ML^{(n-2)+} + 2H^{+} \quad (m = 2)$$

A series of solutions containing 10 mL volume at constant concentration of 1×10^{-3} M HL, while Cu(II) concentration ranges between 1×10^{-4} to 1×10^{-3} M. The measured absorption spectrum at different wavelengths (625, 650, 680 nm) using a solution of HL concentration 1×10^{-4} M [HL] as a reference has been found that absorption increases with concentration of Cu(II) in a linear relationship. This means that absorption obey Beer-Lambert's law within the limits of concentration used.

Thermodynamic parameters: Thermodynamic parameters results and stability constants of the metal ions at 30 °C in 75 % (v/v) (Table-8) proved that the stability constants of complexes log K_1 ligand would be in the following order:

Ni(II) > Co(II) > Mn(II) > Cd(II) > Zn

We excluded Fe(III) ion because it must be compared with other trivalent iions. If we compare {Zn(II), Cd(II)} ions and {Co(II), Ni(II)} ions, we found that their positions are consistent with previous research publications [23-36]. Fig. 1 illustrates a linear relationship between dissociation constant of ligand and static stability of the complexes (log K_1). This linear relationship reflects the similarity of ionic nature of the reaction between metal and ligand [22,27].

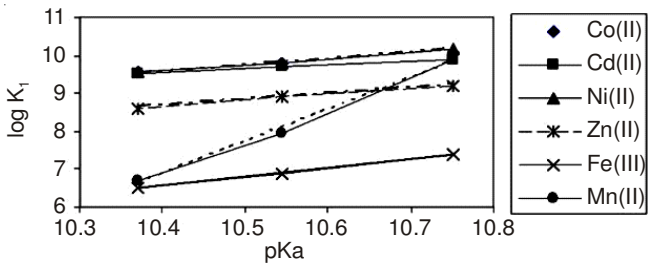


Fig. 1. Relationship between values of log K_1 and pK_a at 30 °C in 75 % (v/v) ethanol-water

Conclusion

This investigation support the ligand behaves as mono-basic (monoprotic) species (HL) towards the metal ions as evidenced from the titration curves. The dissociation process is non-spontaneous, endothermic and entropic ally unfavourable while the complexation (chelation) process is spontaneous, exothermic and entropic ally favourable. More stable complexes, will be formed with, hard-hard or soft-soft interactions of metal ions and ligand, higher charges and small sizes of the metal ions, high basicity of the ligand and lower temperatures.

REFERENCES

1. L.N. Suvarapu, Y.K. Seo, S.O. Baek and V.R. Ammireddy, *E-J. Chem.*, **9**, 1288 (2002).
2. T.S. Katiyar and S.N. Tandon, *Talanta*, **11**, 892 (1964).
3. G.S. Kouimtzis, Th.A. Kouimtzis and V.C. Vasiliades, *Microchem. J.*, **20**, 173 (1975).
4. M. Bonilla-Alvarez, M. Palmieri, D. Davis and J.S. Fritz, *Talanta*, **34**, 473 (1987).
5. A.A. El-Asmy, O.A. El-Gammal, H.A. Radwan and S.E. Ghazy, *Spectrochim. Acta*, **77**, 297 (2010).
6. M.M.E. Shakdofa, M.H. Shtaiwi, N. Morsy and T.M.A. Abdel-Rassel, *Main Group Chem.*, **13**, 187 (2014).
7. P.B. Martelli, B.F. Reis, E.A.M. Kronka, H.F. Bergamin, M. Korn, E.A.G. Zagtto, J.L.F.C. Lima and A.N. Araujo, *Anal. Chim. Acta*, **308**, 397 (1995).
8. A.M. Abu-Dief and I.M.A. Mohamed, *Beni-Suef Univ. J. Basic Appl. Sci.*, **4**, 119 (2015)
9. E. Holder, B.M.W. Langeveld and U.S. Schubert, *Adv. Mater.*, **17**, 1109 (2005).
10. Z.J. Wang, K.N. Clary, R.G. Bergman, K.N. Raymond and F.D. Toste, *Nature Chemistry*, **5**, 100 (2013).
11. M.J. Wiester, P.A. Ulmann and C.A. Mirkin, *Angew. Chem. Int. Ed.*, **50**, 114 (2010).
12. R. Breslow and L.E. Overman, *J. Am. Chem. Soc.*, **92**, 1075 (1970).
13. O. Pamies and J.E. Bäckvall, *Chem. Rev.*, **103**, 3247 (2003).
14. P. Krumlinde, K. Bogár and J.E. Bäckvall, *Chem. Eur. J.*, **16**, 4031 (2010).
15. S.G. Kücükgüzel, S. Rollas, I. Kücükgüzel and M. Kiraz, *Eur. J. Med. Chem.*, **34**, 1093 (1999).
16. S. Rollas and S. Güniz Kücükgüzel, *Molecules*, **12**, 1910 (2007).
17. M. El-Begery and H. El-Twigry, *Spectrochim. Acta A*, **66**, 28 (2007).
18. N.H. Al-Shaalan, *Molecules*, **16**, 8629 (2011).
19. R.M. Silverstein, G.C. Basster and T.C. Morrill, Spectrometric Identification of Organic Compounds, Wiley, New York, edn 5 (1991).
20. M. Mashaly, *Synth. React. Inorg. Met.-Org. Chem*, **26**, 211 (1996).
21. C. Dreti and G. Tosi, *Aust. J. Chem.*, **29**, 543 (1996).
22. S. Zhao, S. Chen, J.W.Y. Lam, Z. Wang, P. Lu, F. Mahtab, H.H.Y. Sung, I.D. Williams, Y. Ma, H.S. Kwok and B.Z. Tang, *J. Mater. Chem.*, **21**, 7210 (2011).
23. E.A. Braude, *J. Chem. Soc.*, 1971 (1948).
24. A. Gergely and T. Kiss, *J. Inorg. Nucl. Chem.*, **39**, 109 (1977).
25. W.M. Schubert, H. Steadly and J.M. Craven, *J. Am. Chem. Soc.*, **82**, 1353 (1960).
26. A.A.T. Ramadan, B.A. El Shetary, M.S. Abdel-Moez and H.S. Seleim, *Acta Chim. Hung.*, **130**, 25 (1993).
27. G.R. Choppin and W.F. Strazik, *Inorg. Chem.*, **4**, 1250 (1965).