Potentiometric study of metal complexes of some imidazole contained ligands.

Part I: The determination of dissociation constant of 2-(2-hydroxyphenyl)-4,5-diphenylimidazole and the stability of its complexes with some transition metal ions.

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Abstract

The study aims to determine the dissociation constant of 2-(2-hydroxyphenyl)-4,5-diphenylimidazole (HPI) ligand, and also to study the complexes formation, in mixed (30 % H_2O / 70 % dioxane), between the ligand and Cu (II), Ni (II), Co (II) and Zn (II). Complex formation was traced and followed through measuring the stability constants of the formed complexes.

Potentiometric technique was used, to follow the change in concentration of one constituent in the reaction (titration) vessel during the coordination in solution. The titration vessel contains: ligand, diluted strong acid and electrolyte salt to maintain constant ionic strength of 0.1 mol.dm^{-3} KCl; a solution of divalent metal added in case of the determination of complex stability constants. In this investigation a hydrogen concentration was followed through measuring the pH of the solution at various stages where basicity of the solution alters via adding alkali.

Coordination and measurements were taken place at 35 °C, and the dissociation constant of the ligand with the stability constant of all the species formed in the solution were calculated by means of the HYPERAUADE 2008 computer program.

الخلاصة

يرمي البحث الى حساب ثابت التأين لليكاند 2-(2-hydroxyphenyl)-4,5-diphenylimidazole ، بالاضافة الى دراسة تكوين المعقدات في مذيب مكون من مزيج من (30 % ماء + 70 % دايوكسان) بين هذه الليكاند وأيونات كل من النحاس(II) والنيكل(II) والكوبالت(II) اضافة الى الخارصين(II). إن دراسة تكوين هذه المعقدات يكون عن طريق قياس ثوابت الاستقرار لهذه المعقدات.

لقد تم إستخدام تقنية التسحيح المجهادي لقياس التغير في احد مكونات المحلول في وعاء التفاعل خلال عملية تكوين المعقد. يحتوي المحلول في وعاء التفاعل على الليكاند وحامض قوي مخفف ومحلول الكتروليتي قوي لضمان الحصول على قوة أيونية ثابتة في المحلول (كلوريد البوتاسيوم 0.1 مول.دسم$^{3-}$). ويضاف الى مكونات وعاء التفاعل هذا محلول الايون الفلزي في حالة حساب ثوابت الاستقرار للمعقدات. تم في هذا البحث قياس ومتابعة حامضية المحلول (pH) في المراحل المتعددة لتكوين المعقد عند إضافة المحلول القاعدي الى وعاء التفاعل.

إن التناسق وكذلك القياسات قد تم اخذها في درجة حرارة 35 °م ، و تم حساب ثابت التفكك لليكاند وكذلك ثوابت الاستقرار لجميع اشكال المعقدات المتكونة في المحلول بواسطة برنامج الكومبيوتر HYPERQUADE 2008

Introduction

The importance of 2-Hydroxy phenyl imidazole derivatives considered in this investigation is owing to its imidazole contained. The imidazole is regarded as an essential molecule in bioinorganic chemistry, there are several imidazole derivatives (imidazoles) exist in biological systems, and also exist in other natural compounds such as enzymes, nucleic acids, alkaloids and others, which they are of vital biological importance (1,2). Imidazole and its derivatives have a considerable importance in the field of organic synthesis (3), super molecular chemistry (4,5) and other fields.

The biological activity of these types of ligands becomes more profound when their transition metal complexes used instead of ligand alone (6). In other words the biochemical and biological activities of these ligands are associated with the contribution of metal ion (7). Metal complexes with N-heterocycles include imidazole can be used to develop metallo-enzymes and metallo-proteins (8) .The presence of imidazole nucleus in histamine and histidine would certainly make imidazole and imidazole derivatives very important in biochemistry; as the imidazole group of histidine is indeed and in generally responsible for most of the buffering power of proteins in the physiological pH range (9) and a metal coordinating site (10). In other words the imidazole moiety of the biologically essential molecules behaves as ligands with regard to metal ions.

The coordination between the 2-(2-hydroxyphenyl)-4,5-diphenylimidazole (HPI) ligand and metal ion would be through N3 of heterocyclic molecule and hydroxy group. The other nitrogen in the imidazole, the pyrrole nitrogen doesn't involve in the coordination process (11). The coordination yields five-membered chelat ring; which leads to dissociation of the hydroxy group to end up with hydrolyzed (de-protonated) complexes. Bearing in mind that hydrolyzed complexes might occur as a result of dissociate of water molecules attached to the metal ion (12).

The present investigation includes, the determination of the dissociation constant of the (HPI) ligand and the stability constants of the metal complexes using potentiometric titration technique to study of the basicity of the ligand, structure of ligands and complexes formed, the influence of hydrogen bonding and steric hindrance, dissociation of the complexed ligands and the distribution of the complexes formed in solution as a function of pH.

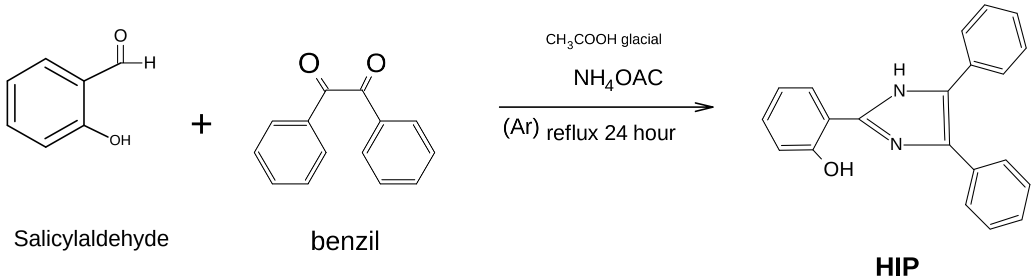
Experimental Details

Chemicals: BDH analytical grade KOH and HCl supplied in 0.1 M ampoules were used after dilution to the appropriate concentrations. The other reagents used were of analytical quality and were used without further purification. Distilled de-ionized water was used to prepare the solution. The cell of reaction kept under inert atmosphere by using pure Argon gas.

Synthesis of the (HPI) ligand:

This ligand was synthesized by the reaction between salicylaldehyde and benzil [(13)]. The reaction was arranged to reflux for a whole day, and as follows: (6.105 g, 0.05 mol) of salicylaldehyde was mixed with (10.5 g, 0.05 mol) of benzil, together with (26.54 g, 0.07 mol) of ammonium acetate and 150 ml. of glacial acetic acid. A yield was a whit solid, which was filtered and washed with hot distilled water several times to remove the glacial acetic acid. Litmus paper was used to check the full removal of the acid from the precipitate. The precipitate then re-crystallized by a mixture of 20 % of water and 80 % ethanol, and the yield left over night in the room temperature, then dried in oven at (60 °C for several hours. The product weight is 13.71 gm, so the yield is 87 %. The product melting point is (217- 219 °C).

Analysis: IR (KBr): [3408 (O – H), 3205 (N – H), 1595 (C = N)] ; H NMR: δ= 13.01 (NH), 8.03 (OH), 6.92 – 7.57 (ArH) ppm.



HIP

Titration procedure:

The stock solution 0.1 mol.dm^{-3} of the metal ions were prepared for $ZnCl_2$, $CuCl_2.2H_2O$, $NiCl_2.6H_2O$ and $CoCl_2.6H_2O$ and standardized with ethylene diaminetetraacetic acid (EDTA) [(10)]. Diluted solutions for any individual metal ion can be simply obtained by volumetric dilution. Calibration of the pH electrode was achieved by using a buffer solution of (0.05 M) potassium hydrogen phthalate (KHP).

Measurement of all potentiometric titrations were carried out under control temperature, using mixed water and dioxane. A temperature of 35 °C was selected as it can be maintained to the limit of ± 0.05 °C by thermostated water bath, as the water circulating through large water bath via water circulator (type Combenstat). The water bath was design in away to hold the titration vessel, where the water in the bath cover most of the vessel to assure stable temperature of the vessel contents. The titration vessel contents have to be under inert atmosphere, Argon gas with high purity was used to maintain such atmosphere. Three necks, 100-ml round bottom flask was adapted as titration vessel, where burette was fitted inside the vessel through one neck while Argon gas was passing through the second neck with inlet and outlet ports. The Argon gas has been passed through two washing bottles, one partially filled with potassium hydroxide to trap any traces of carbon dioxide, if exists and the second washing bottle contains amount of potassium chloride (background electrolyte).

The acid which has been used in this research is hydrochloric acid, this is acid was acquired from BDH ampoules. The acid solution was prepared by the dilution, with double distilled de-ionized water, to the required concentration. The acid then standardized by the titration versus sodium tetra-borate, and a mixed methyl/methylen blue indicator (14) was used in the standardization.

The alkali used was potassium hydroxide, which was obtained from BDH ampoules. The alkali solution was prepared by the dilution, with double distilled de-ionized water, to the required concentration, and then it was stored in polyethylene container. The alkali was standardized by the titration versus potassium hydrogen phthalate using phenolphthalein as an indicator (14).

In case of determination of the dissociation constants for the ligand, an acidified ligand solution was added in the titration vessel together with certain amount of electrolyte background (potassium chloride) to keep constant ionic strength. On the other hand and with the determination of stability constants of metal complexes, the same substances were added in addition to calculated amount metal ion (as a chloride salt). Ligand metal ratio was arranged to be approximately as 2:1 where mono and bis, binary complexes together with their hydrolyzed species might be expected. Preliminary acid base where achieved in order to check the linearity of the glass electrode (WTW- type). The titration curve (Fig. 1), was obtained by using BATE-Chem-Buddy software, other titration curves for the ligand was also produced (Fig.2); the glass electrode used was of.

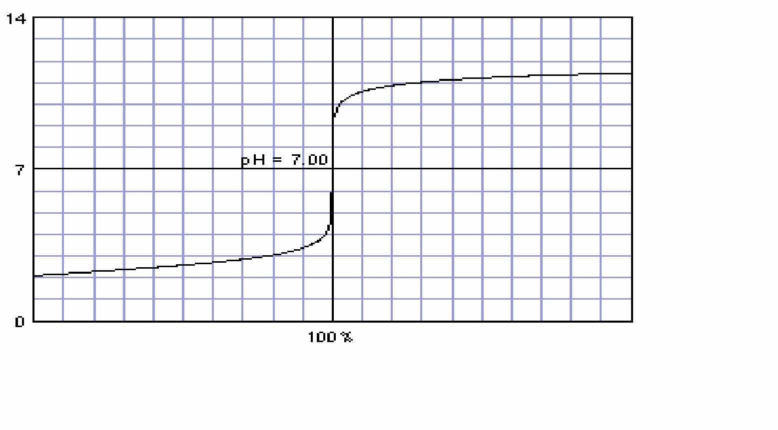


Fig. (1) Acid base (HCl vs KOH)

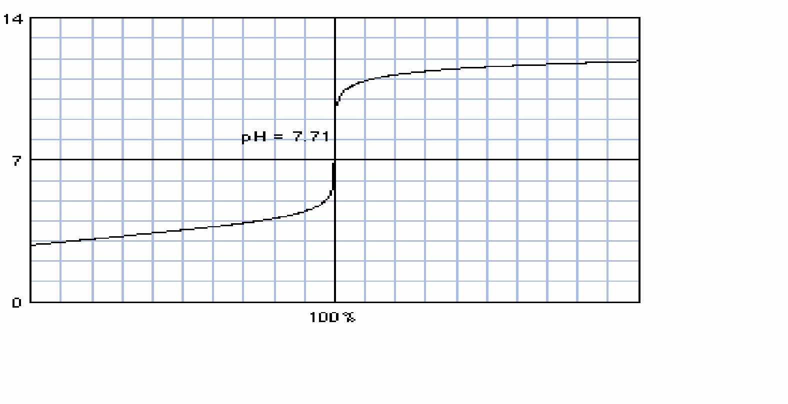


Fig. (2) HPI ligand titration curve

The dissociation constant for the ligand (HPI) (Fig. 3) was calculated by using HYPERQUAD 2008 (15) computer program, which design to process data from potentiometic titration.

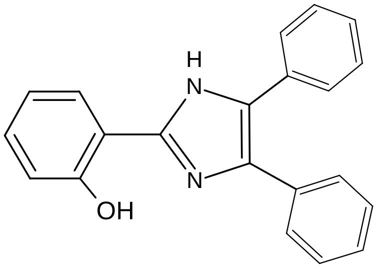


Figure (3) 2-(2-hydroxyphenyl)-4,5-diphenylimidazole

Accurate stability constants were obtained for the Zn(II), Cu(II), Ni(II) and Co(II) metal ions complexes with(HPI) ligand in this investigation in all cases, as in each case several titration process were achieved and only the reliable constants which show consistent values were considered. The results obtained by the HYPERQUAD-2008 showed that more than one type of complexes was formed under the experimental conditions adapted. The first ones are the neutral (with no dissociation of the ionizable) binary, mono and bis metal complexes. The other types of complexes are the hydrolyzed species, which occur as a result of the dissociation of the hydroxy group.

Results and Discussion

Dissociation Constant of HPI:

The ligand investigated in this work can be symbolized as L which represents the neutral form of the ligand, which exists in the neutral and slightly acidic or basic solution; while the LH represents the protonated ligand. LH carries singly positive charge (charge is removed for the sake of simplicity). In acidic medium the proton attach to pyridine nitrogen in imidazole moiety of the ligands, as this donor atom is more basic the other donor atoms available in this ligand. The dissociation (de-protonation) equilibrium can be represented as in the following equations:

$$LH \leftrightarrow L + H$$

The dissociation (de-protonation) constant K_a is given as:

$$K_a= [L][H]/[LH]$$

(K_a may be represented as K_{N-H} in this research)

The dissociation constant, also called acidity constant, of a ligand is quite important factor for the assessment of the basicity of that ligand. This property assist to set up the experimental conditions required for the coordination of the ligand with the metal ion. It is usually expressed in pKa rather than Ka.

As it was mentioned in the experimental section, all the measurements were taken in mixed water and dioxane. It has been found that the dissociation constant changes with the change of the mixed solvents component, which in fact depends on electrostatic and non-electrostatic factors, and generally less value than the aqueous solution (16-18). The dissociation constant is determined, through data taken in the acidic part of the potentiometric-titration and compared with some imidazole derivatives (Table 1). There is no pK_{N-H} values, in the literature, for the ligands under consideration up to our knowledge, at any experimental conditions, which has been confirmed by searching through "Stability Constants Database" (SCD) issued by Protonic software.

The $pK_{(N-H)}$ for ligands under investigation is less in value than that of imidazole molecule, this is expected on the light, that the introduction of three withdrawing aromatic groups around the imidazole molecule would certainly affect the pair of electrons on the pyridine nitrogen which leads to reduce the basicity of this donor atom. In other words the basicity of the pyridine nitrogen donor atoms was influenced significantly through electronic interactions between the four aromatic rings. It is difficult to assess, precisely, the impact of withdraw properties of the aromatic rings in ligand molecule on the value of its pK_{N-H} but still we have noticed that the decrease in pK_{N-H} is more than expected on the basis of existing these withdrawing aromatic groups around the imidazole moiety. The decrease of the basicity of the pyridine nitrogen may, probably, be justified by the fact that a repulsion will build up between the proton attached to the pyridine nitrogen atom and the hydrogen of the hydroxyl group, which cause destabilize the protonated molecule whereby decreasing the pK_{N-H} value. So, to decrease the repulsion between the two parts of molecule, a possible twisting or orientation around the C – C between both hydroxy and imidazole moieties is expected (19-20), but not to extent to allow the formation of trans configuration. The orientation of 180° will bring up similar situation where the other -protonated nitrogen (imino hydrogen) will be in the same position instead. So it is quite safe to assume that possible orientation with 90° or more or less, might occur in the protonated ligand molecule (LH), which keeps both hydrogen atoms in imidazole with equal distance from the hydroxy group. In other words it is assumed that in the protonated ligand, both imidazole moiety and hydroxy phenol moiety to be in two different planes as a result of the repulsion between them.

The pKa value of these ligands is roundabout (3), now this value is low in comparison with the pKa of imidazole and other imidazole derivatives. pKa of free imidazole molecule and other related molecules are embodied in Table (1). It is well documented that pK_a of a certain protonated donor atom, or a certain group, reliant on the nearby attachments (23). So it is an expected that the pKa associated with the pyridine nitrogen will have different (less) value than that of the pyridine nitrogen in free and the other imidazoles. The decreased value of the pK_a due to the withdrawing properties of the hydroxyl phenyl and other aromatic groups attached in position 2, 4 and 5 positions respectively.

Table 1: pK_{N-H} values for HPI together with pK_{N-H} values for other imidazole contained ligands

No.	Ligand	pKa (pK_{N-H})	Reference
1	Imidazole	7.1	21
2	4- methylimidazole	7.56	22
3	2-phenylimidazole	6.39	22
4	1-methylimidazole	7.02	22
5	2-methyl imidazole	7.88	22
6	2-(2-hydroxyphenyl)-4,5-diphenylimidazole	3.39	Present work

Table (2) concentrations of different species ($mole.dm^{-3}$) available at any pH considered during the titration of (HPI) solution against KOH, where pK_{N-H} is extracted. (As given by computer output data)

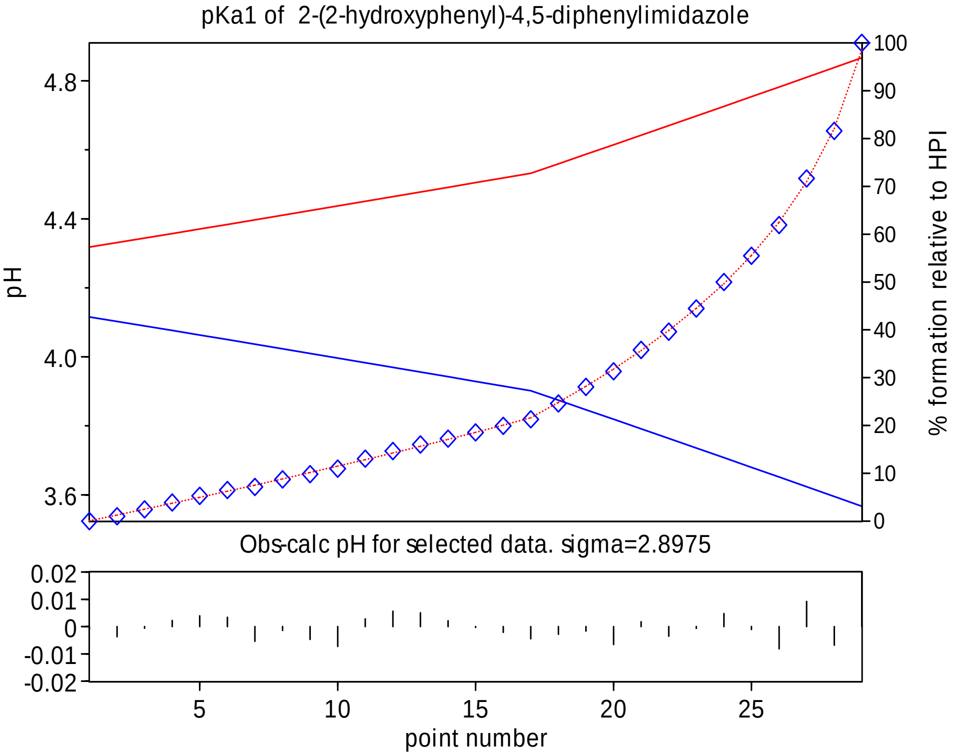
Experimental details:
Temperature 35.0 ± 0.05 °C ; ionic background 0.1 M KCl; pK_w =13.69
the followings were put in the titration vessel:
1) 0.4729 millimoles of HPI ligand
2) 0.4736 millimoles of Acid (HCl)
3) 50.00 ml. of KCl
total volume = 55.00 ml.

Titrant was 0.1018 $mole.dm^{-3}$ potassium hydroxide

Point	Titre	Total(HPI)	Total(H)	Free(HPI)	p[H]	HPIH
1	2.5	8.2243E-03	3.8104E-03	4.7125E-03	3.525	3.5118E-03
2	2.55	8.2172E-03	3.7187E-03	4.7858E-03	3.542	3.4314E-03
3	2.6	8.2101E-03	3.6271E-03	4.8593E-03	3.559	3.3508E-03
4	2.65	8.2029E-03	3.5356E-03	4.9329E-03	3.576	3.2700E-03
5	2.7	8.1958E-03	3.4444E-03	5.0067E-03	3.593	3.1891E-03
6	2.75	8.1887E-03	3.3532E-03	5.0806E-03	3.611	3.1081E-03
7	2.8	8.1817E-03	3.2623E-03	5.1547E-03	3.628	3.0270E-03
8	2.85	8.1746E-03	3.1715E-03	5.2289E-03	3.646	2.9457E-03
9	2.9	8.1675E-03	3.0808E-03	5.3031E-03	3.665	2.8644E-03
10	2.95	8.1605E-03	2.9903E-03	5.3775E-03	3.683	2.7830E-03
11	3.0	8.1534E-03	2.9000E-03	5.4520E-03	3.702	2.7015E-03
12	3.05	8.1464E-03	2.8098E-03	5.5266E-03	3.721	2.6199E-03
13	3.1	8.1394E-03	2.7198E-03	5.6012E-03	3.741	2.5382E-03
14	3.15	8.1324E-03	2.6299E-03	5.6759E-03	3.761	2.4565E-03
15	3.2	8.1254E-03	2.5402E-03	5.7507E-03	3.781	2.3747E-03
16	3.25	8.1185E-03	2.4506E-03	5.8255E-03	3.802	2.2929E-03
17	3.3	8.1115E-03	2.3612E-03	5.9004E-03	3.823	2.2111E-03
18	3.4	8.0976E-03	2.1829E-03	6.0503E-03	3.868	2.0473E-03
19	3.5	8.0838E-03	2.0051E-03	6.2004E-03	3.915	1.8834E-03
20	3.6	8.0700E-03	1.8280E-03	6.3505E-03	3.965	1.7195E-03
21	3.7	8.0562E-03	1.6514E-03	6.5007E-03	4.018	1.5556E-03
22	3.8	8.0425E-03	1.4755E-03	6.6509E-03	4.077	1.3917E-03
23	3.9	8.0289E-03	1.3002E-03	6.8010E-03	4.141	1.2278E-03
24	4.0	8.0153E-03	1.1254E-03	6.9512E-03	4.212	1.0641E-03
25	4.1	8.0017E-03	9.5127E-04	7.1012E-03	4.294	9.0046E-04
26	4.2	7.9882E-03	7.7770E-04	7.2512E-03	4.390	7.3698E-04
27	4.3	7.9747E-03	6.0472E-04	7.4010E-03	4.508	5.7366E-04
28	4.4	7.9613E-03	4.3232E-04	7.5507E-03	4.662	4.1054E-04
29	4.5	7.9479E-03	2.6050E-04	7.7003E-03	4.890	2.4762E-04

Refinement converged successfully after 1 iteration

pK_{N-H} = 3.397 standard deviation 0.0012 s**igma = 2.897**



(Fig. 3). Titration curve of HPI produced by HYPERQUAD 2008, together with distribution curves for species available in solution.

Stability Constants of Complexes

HPI tends to coordinate through the N3 atom of imidazole ring and oxygen of the hydroxyl group in phenol moieties, there are adequate verifications to signify that ligand (HPI) coordinates in this manner, and imino nitrogen (pyrrole nitrogen) will not contribute in coordination (24- 25). Solubility was the main difficulty in this study; and this of course due to the large part of the hydrocarbon skeleton, accordingly mixed water to dioxane was used as a solvent. Despite the relative high dioxane ratio used but this would not expect to affect, seriously, the physical measurements applied. The mixture water/dioxane solvent is commonly used in potentiometric investigation.

Despite that the imino nitrogen in imidazole does not participate in coordination, as mentioned above, but it engaged in hydrogen bonding with the oxygen atom of the hydroxy group (26 – 27). Other intra hydrogen bonding would be established also between the hydrogen of hydroxy group and the N3 atom. The possible rotation through C – C bonding between the phenol moiety and imidazole moiety will certainly enhance the coordination of the ligand with the proton or metal ions, by adapting suitable position where the pyridine nitrogen atom will be in cis location, so both moieties will be also in one plan.

The metal : ligand ratio was found to metal was arranged to be approximately 1:2 in all the experiments, so several possible species can be searched in solution such as neutral complexes (neutral mono-complexes) ML (110), ML_2 (120), and hydrolyzed species ML_{-1} (11-1), ML_{2-1} (12-1) and ML_{2-2} (12-2) [the last three species represent the dissociated species exist in the solution as a result of dissociation of the hydroxy group in the ligand) and other species might also exist. Only, the species which formed in appreciable amount have been considered and accurate determinations for their stability constants have been obtained. The computer program is quite powerful to detect any appreciable amount of hydroxy, de-protonated or polynuclear species might occurred in the solution, within any given pH. No trace of polynuclear species were detected in solution according to the output data of the computer program. This is an expected due to the low concentration of the metal ion in solution. Table (3) show the over-all stability constants of the HPI with Zn(II), Cu(II), Ni(II) and Co(II).

Table (3) log stability constants of HPI-metal complexes

HPI	**log β_{110}**	**log β_{11-1}**	**log β_{120}**	**log β_{12-1}**	**log β_{12-2}**
Zn (II)			**7.984**	**3.258**	
Cu(II)		**1.329**		**2.381**	**-1.089**
Ni(II)		**-2.932**	**6.464**		**-5.781**
Co(II)			**7.340**	**1.140**	

Calculation of stability constants of each single ion requires processing experimental data via HYPERQUAD 2008 to obtain the constants. Table (4) shows the computer output data for the Zn(II)-HPI complexes (for illustration); the other metal ions also show similar output data (they are available on request).

Table (4) detailed of concentrations of he species (mole.dm-3) available in solution at any pH value considered during the formation of Zn-HPI complex, where stability constants are calculated.

Zn-HPI Complexes

Temperature 35.0 ± 0.05 °C ; ionic background 0.1 M KCl; pK_w =13.69
the followings were put in the titration vessel:
1) 0.1987 millimoles of HPI ligand
2) 0.0937 millimoles of Zn ion.
2) 0.4666 millimoles of Acid (HCl)
3) 50.00 ml. of KCl
total volume = 65.00 ml.

Titrant was 0.0989 mole.dm^{-3} potassium hydroxide

Point	Titre	Total(Zn)	Total(L)	Total(H)	Free(Zn)	Free(L)	p[H]	LH	ZnL2	ZnL2H-1
1	3.0	1.3779E-03	2.9221E-03	2.4985E-03	3.3548E-04	1.7843E-04	2.733	6.5871E-04	1.0320E-03	1.0432E-05
2	3.05	1.3769E-03	2.9199E-03	2.4240E-03	3.2948E-04	1.8044E-04	2.747	6.4457E-04	1.0366E-03	1.0829E-05
3	3.1	1.3759E-03	2.9178E-03	2.3496E-03	3.2343E-04	1.8253E-04	2.762	6.3027E-04	1.0412E-03	1.1252E-05
4	3.15	1.3749E-03	2.9156E-03	2.2753E-03	3.1734E-04	1.8468E-04	2.777	6.1582E-04	1.0459E-03	1.1704E-05
5	3.2	1.3739E-03	2.9135E-03	2.2012E-03	3.1121E-04	1.8690E-04	2.793	6.0121E-04	1.0505E-03	1.2187E-05
6	3.25	1.3729E-03	2.9114E-03	2.1271E-03	3.0503E-04	1.8921E-04	2.809	5.8642E-04	1.0552E-03	1.2704E-05
7	3.3	1.3719E-03	2.9092E-03	2.0531E-03	2.9881E-04	1.9159E-04	2.825	5.7147E-04	1.0598E-03	1.3259E-05
8	3.35	1.3709E-03	2.9071E-03	1.9793E-03	2.9253E-04	1.9406E-04	2.843	5.5633E-04	1.0645E-03	1.3856E-05
9	3.4	1.3699E-03	2.9050E-03	1.9056E-03	2.8621E-04	1.9662E-04	2.860	5.4101E-04	1.0692E-03	1.4500E-05
10	3.45	1.3689E-03	2.9028E-03	1.8319E-03	2.7984E-04	1.9928E-04	2.879	5.2549E-04	1.0738E-03	1.5196E-05
11	3.5	1.3679E-03	2.9007E-03	1.7584E-03	2.7343E-04	2.0204E-04	2.898	5.0978E-04	1.0785E-03	1.5951E-05
12	3.55	1.3669E-03	2.8986E-03	1.6850E-03	2.6696E-04	2.0491E-04	2.918	4.9385E-04	1.0832E-03	1.6771E-05
13	3.6	1.3659E-03	2.8965E-03	1.6117E-03	2.6045E-04	2.0790E-04	2.939	4.7771E-04	1.0878E-03	1.7666E-05
14	3.65	1.3649E-03	2.8944E-03	1.5385E-03	2.5388E-04	2.1102E-04	2.960	4.6135E-04	1.0924E-03	1.8645E-05

15	3.7	1.3639E-03	2.8923E-03	1.4654E-03	2.4727E-04	2.1426E-04	2.983	4.4475E-04	1.0969E-03	1.9720E-05
16	3.75	1.3629E-03	2.8902E-03	1.3924E-03	2.4060E-04	2.1765E-04	3.006	4.2792E-04	1.1014E-03	2.0905E-05
17	3.8	1.3619E-03	2.8881E-03	1.3195E-03	2.3389E-04	2.2120E-04	3.031	4.1083E-04	1.1058E-03	2.2217E-05
18	3.85	1.3609E-03	2.8860E-03	1.2467E-03	2.2713E-04	2.2490E-04	3.057	3.9349E-04	1.1101E-03	2.3677E-05
19	3.9	1.3599E-03	2.8839E-03	1.1740E-03	2.2033E-04	2.2878E-04	3.084	3.7588E-04	1.1143E-03	2.5309E-05
20	3.95	1.3590E-03	2.8818E-03	1.1015E-03	2.1348E-04	2.3284E-04	3.113	3.5800E-04	1.1183E-03	2.7142E-05
21	4.0	1.3580E-03	2.8797E-03	1.0290E-03	2.0658E-04	2.3710E-04	3.144	3.3984E-04	1.1222E-03	2.9216E-05
22	4.05	1.3570E-03	2.8776E-03	9.5663E-04	1.9965E-04	2.4156E-04	3.176	3.2139E-04	1.1258E-03	3.1575E-05
23	4.1	1.3560E-03	2.8755E-03	8.8437E-04	1.9269E-04	2.4625E-04	3.210	3.0266E-04	1.1290E-03	3.4279E-05
24	4.15	1.3550E-03	2.8735E-03	8.1222E-04	1.8569E-04	2.5116E-04	3.247	2.8364E-04	1.1319E-03	3.7404E-05
25	4.2	1.3540E-03	2.8714E-03	7.4017E-04	1.7868E-04	2.5632E-04	3.287	2.6434E-04	1.1343E-03	4.1044E-05
26	4.25	1.3531E-03	2.8693E-03	6.6823E-04	1.7166E-04	2.6171E-04	3.329	2.4478E-04	1.1361E-03	4.5326E-05
27	4.3	1.3521E-03	2.8672E-03	5.9639E-04	1.6464E-04	2.6734E-04	3.375	2.2500E-04	1.1370E-03	5.0415E-05
28	4.35	1.3511E-03	2.8652E-03	5.2466E-04	1.5765E-04	2.7320E-04	3.425	2.0504E-04	1.1369E-03	5.6530E-05
29	4.4	1.3501E-03	2.8631E-03	4.5303E-04	1.5070E-04	2.7924E-04	3.479	1.8498E-04	1.1355E-03	6.3964E-05
30	4.45	1.3492E-03	2.8611E-03	3.8150E-04	1.4383E-04	2.8542E-04	3.538	1.6495E-04	1.1322E-03	7.3107E-05
31	4.5	1.3482E-03	2.8590E-03	3.1007E-04	1.3709E-04	2.9163E-04	3.603	1.4513E-04	1.1266E-03	8.4480E-05
32	4.55	1.3472E-03	2.8569E-03	2.3875E-04	1.3052E-04	2.9773E-04	3.674	1.2578E-04	1.1180E-03	9.8754E-05
33	4.6	1.3463E-03	2.8549E-03	1.6753E-04	1.2418E-04	3.0350E-04	3.752	1.0722E-04	1.1053E-03	1.1675E-04
34	4.65	1.3453E-03	2.8528E-03	9.6411E-05	1.1815E-04	3.0867E-04	3.836	8.9877E-05	1.0877E-03	1.3940E-04

Refinement converged successfully after1 iterations.

log β_{121} = 7.984 Standard deviation = 0.060 Sigma = 12.848

log β_{12-1} = 3.258 Standard deviation =0.052 Sigma = 12.848

Zn(II) Complex:

Only neutral and hydrolyzed bis complexes were formed in case of Zn(II) metal ion, similar to the case of Co(II). Value of stability constant of the neutral species 120 is (log β_{120} =7.984), which is higher than similar complexes in case of Co(II) complex and Ni(II) complex too. It is less common to be more stable than the Ni(II) complex (28); this is actually an indication of the existence of complex in form of tetrahedral. Where change in entropy operates in favor of increase the stability constants, as turning the aquated Zn(II)-complex from octahedral structure $[Zn(H_2O)_6]^{2+}$ into tetrahedral $[Zn(HPI)_2]^{2+}$ or $[Zn(HPI)_2]$ required displacement of six water molecules rather than four water molecules in case of both Ni(II) and Co(II). This of course necessitates more entropy which eventually leads to increase the stability constant of the bis complexes.

Maximum occurrence of 120 complex would be approximately 30 % from the total of Zn(II) ion in solution at pH just less than 3 (fig. 4). While the highest percentage which can be reached by the 12-1 is about 10 % from the total Zn(II) ion at pH less about 2.75.

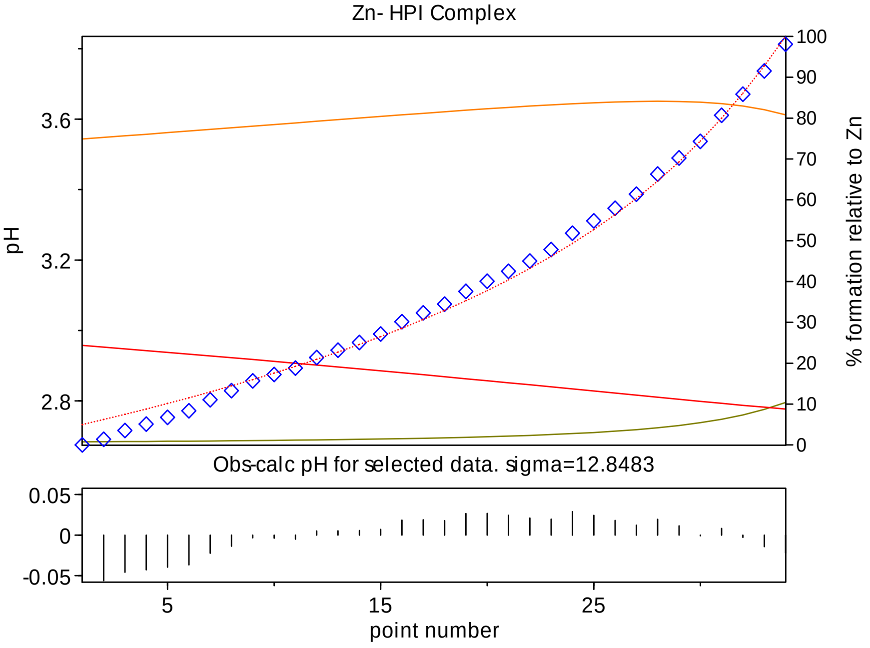


Fig. 4 Titration curve together with distribution curves for species available in solution within the pH used, in the process of Zn- HPI complex formation.

Cu(II)- Complexes:

No neutral species was formed in case of Cu(II) ion as only hydrolyzed species were formed in the coordination process. This actually reflects the strength bonding of metal – ligand bond which reflects in dissociation of the ionizable OH group leading to de-protonated complex.

The species formed are 11-1, 12-1 and 12-2 and it can be concluded that the third species formed in reasonable amount which reached to the amount just less than 20 % at pH 3.4 (see fig. 5). The second proton released into the solution is hard to decide whether it comes out from the dissociation of the second ionizable hydroxy group or the dissociation of the partially (complexed or aquated) metal ion. Releasing of one proton from one molecule would encourage the molecule to from intra-hydrogen bonding with the other hydrogen atom in the hydroxy group in the second ligand. Here, probably the intra-hydrogen bonding might be not of appreciable weight due to the possible steric hindrance produced by the bulky molecules.

It can be claimed that dissociation of water molecule attached to the metal ion in complex, may take place. As the association of two ligand molecules to the metal ion would facilitate the dissociation of water molecule attached to the metal ion. Two experiments were considered in the case of Cu (II)-HPI complex; one of them was used to assess the 11-1 and 12-1; while the other one was used to find out the possible formation of 12-2. Maximum occurrence of 12-1 in the solution is 27 % and minimum occurrence is 20 % at pH3.6 and pH 3.9. The other complex available at percentage of 60% at pH 3.9 and minimum occurrence 20 % at pH = 3.48 (see Fig. 5)

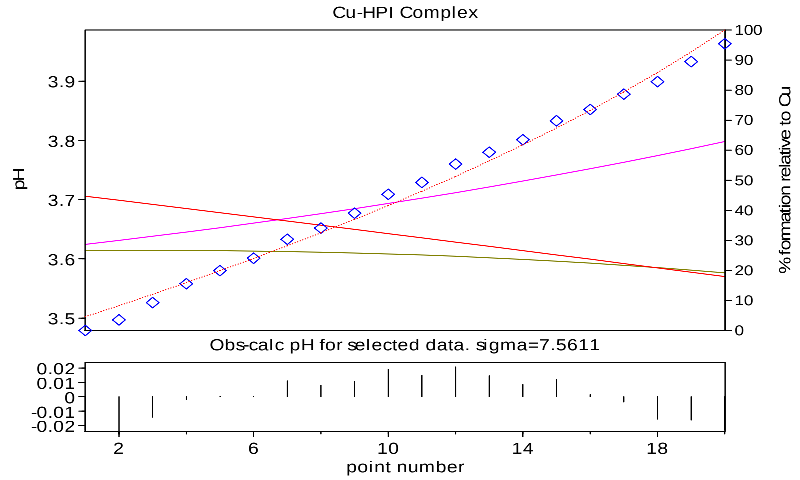


Fig. 5 Titration curve together with distribution curves for species available in solution within the pH used, in the process of Cu- HPI complex formation.

Ni(II)-Complexes:

Weak Ni (II)-complexes were formed at the experimental conditions employed in this work, 120 and 11-1. Results were obtained in two different experiments, the second complex (11-1) occurs at early stage of the coordination This is almost according to our expectation; on view of the existing of the ionizable OH group in the ligand molecules under investigation. But still, at the beginning it was assumed possible existence of 110, the hydrolysis (de-protonated) species 11-1 is expected to form from the dissociation of the ionizable OH. Of course other source of proton which is the dissociation of water molecules attached to the metal ion in solution (29); but this type of hydrolysis seems unlikely under the experimental condition used in this investigation The p*K_a of Ni(II) aquated ion is (54.77)(29). There is no way to judge what is the exactly source of the proton librated in the solution after the coordination. The computer program also cannot tell where the protons come from, but it can trace them in the solution. No trace of the existence of other type of hydrolyzed species such as 11-2. It seems that no such complexes could be existed at the pH range employed, so such assumption has been rejected by the program during the process of refinement of the constants. The de-protonated species formed under our experimental condition suggest that the coordination enhance the dissociation of the ionizable group, which has been noticed in the case of formation of other coordination compounds (30) as the de-protonation of the OH group in the ligand occurs at relatively low pH in comparison with the free ligand. This could simply be explained as a result of electron withdrawing toward the coordination center, which eventually leads to weaken the strength of the O – H bond, result in de-protonation. Bearing in mind that such de-protonation depends on the type of metal ion and its oxidation state.

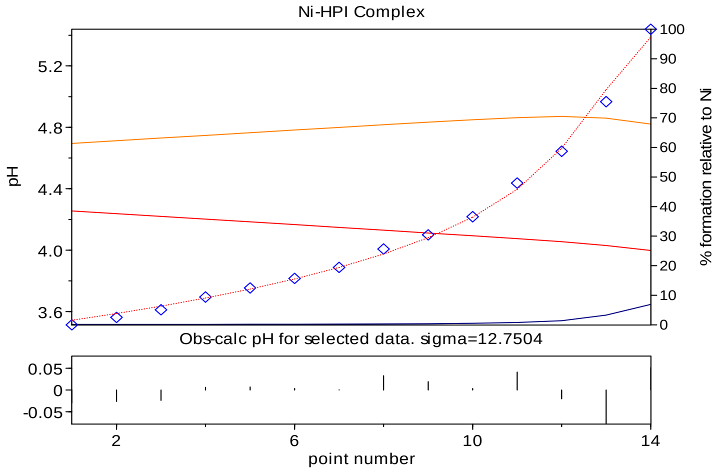


Fig. 6 (Experiment 1) Titration curve together with distribution curves for species available in solution within the pH used, in the process of Ni- HPI complex formation.

Maximum occurrence of 120 (see fig. 5) in the solution was at pH 4.4 with about 70 % of the total metal ion; and its minimum availability in solution is 61 % at the beginning of the coordination where pH is 3.5. The other species 11-1 is not really occurred in high quantity in solution as in it is less than 10 % at its maximum availability at the pH just above 5. This is due to the weakness of this complex as its stability constant is too low (see table 3). The other species 12-2 represented in (fig. 7); it is maximum availability in the solution is about 7 % at the final stage of coordination. Stability constant of this complex is not really quite reliable.

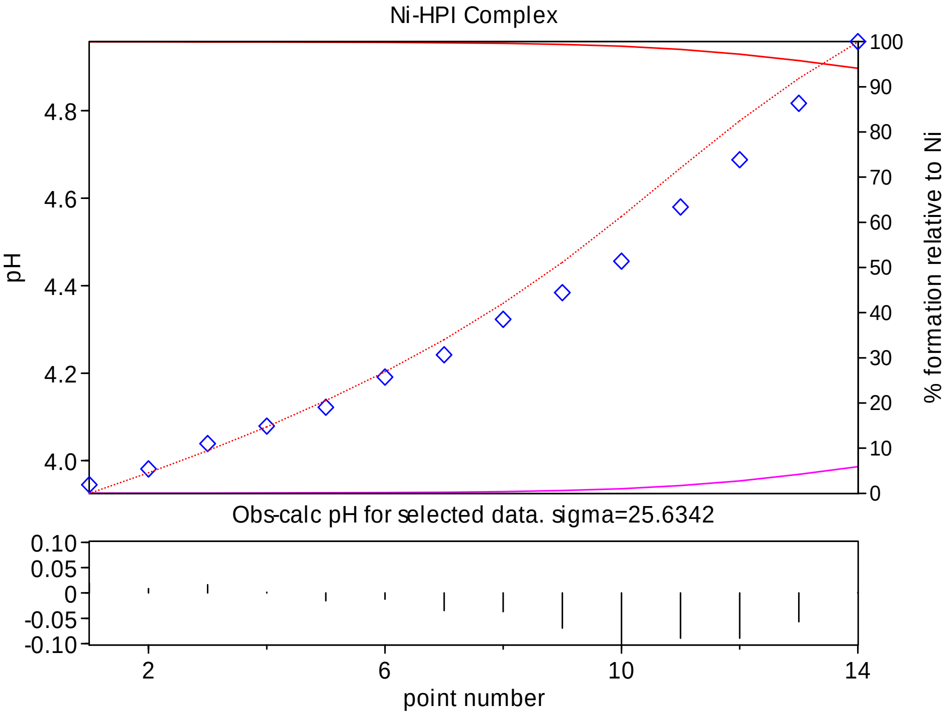


Fig. 7(Experiment 2) Titration curve together with distribution curves for species available in solution within the pH used, in the process of Ni- HPI complex formation.

Co (II) complexes:

Only bis complexes were formed in case of Co (II) metal ion, one of them is a neutral complex which is the 120 while the other one is a hydrolyzed complex 12-1. Value of stability constant of the neutral bis complex is 7.340 which is higher than that of Ni(II) for the same complex; this might be due to more enhancement for bonding been occurred in the Co(II) via back bonding. As imidazole molecule possess empty π^* orbital which can accommodate charge transfer from the d orbital in the metal ion. In other words partial oxidation may occur for Co(II) by means of the coordination. Change color was observed in one stage in the coordination of Co(II) which supports the above assumption. Experimental conditions were quite strict which left no chance for oxidation through the air, as all the reactions arranged to be achieved in inert atmosphere by using pumping Argon gas through the cell of reaction all the time.

Fig. 8 shows the distribution curves for both 120 and 12-1, it seems that the 120 complex dominant the solution right from the beginning of the coordination; while the species 12-1 exist in relatively small amount, and its maximum occurrence in the solution is less than 5 %. This is due in part to lower stability constant of the 12-1 species.

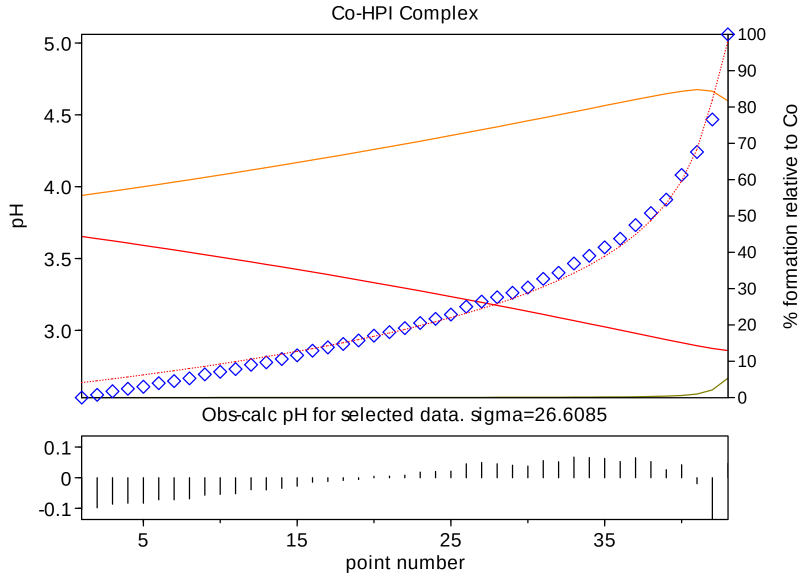
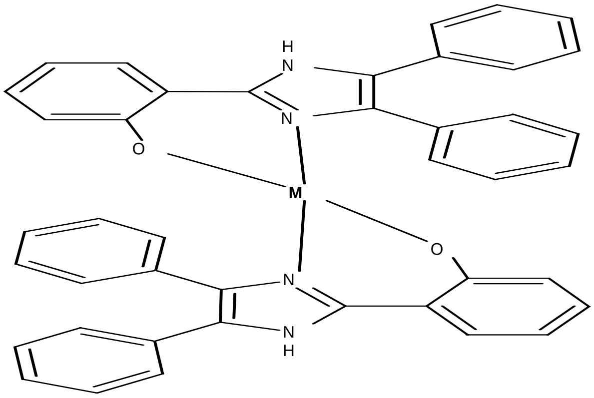


Fig. 7 Titration curve together with distribution curves for species available in solution within the pH used, in the process of Co- HPI complex formation.



M= Cu^{+2}, Co^{+2}, Ni^{+2} and Zn^{+2}

Fig. 8 The suggested structure of the metal complex in solution

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