

Study of stability constant of N-[(E 2Z)-2- (hydroxyimines)-1-phenylpropylidene] N'-[(1E)-{[2-(E)-(2-hydroxyphenylmethylene) thiocarbonohydrazide (HINPHTSAL) with cobalt, nickel, copper and zinc in aqueous solution

Ganga. S. Gore^{1*}, R.G. Deshmukh²

¹D.U.B. Senior Science College, Dapoli, Dist: Ratnagiri, India

²Konkan Gyanpeth Karjat College, Karjat, Dist. Raigad, Maharashtra 410201, India

*Corresponding author: E-Mail: ggore3@gmail.com, Phone no. 9764544360

ABSTRACT

The ligand N'-[(E 2Z)-2- (hydroxyimines)-1— phenylpropylidene] N''-[(1E)-{[2-(E)-(2-hydroxyphenyl methylene) thiocarbonohydrazide. (HINPHTSAL) has been synthesized by freshly condensation of isonitro propiophenone thiocarbonohydrazide and salicylaldehyde in 1:1 molar proportion in presence of ethanol. The study of metal -ligand complexes has been performed by potentiometrically in the mixed solvent system i.e. dioxane and water at various ionic strengths to obtain the acidity constant of the ligand and metal – ligand formation constants .The amount of distribution of the complexes in solution was evaluated as a function of pH. Stoichiometry and stability Constants for the complexes formed with the ligand are discussed and reported.

KEY WORDS: Ionic strength, stability constant, metal ion complexes, potentiometric titration.

1. INTRODUCTION

Over the past decades Coordination complexes of oximino ketones and their derivatives have attracted great attention due not only to their facile syntheses and the accessibility of diverse structural modifications, but also to their wide application in analytical¹, bioinorganic system², catalyst^{3,4}, medicine^{5,6} etc. This is primarily due to the various positions of probable donor atoms, presence of >C=N-group biologically important group as it shows microbial activity and inherent ambidentate character of the ligand. As such, these ligands are known to report metal complexes of varied geometries, stabilities and applications. A survey of the literature reveals that there is no any study has done on the proton dissociation constant of the above mentioned ligand and stability constants of its metal complexes. In the present study we are therefore reporting the effect of change in ionic strength on the dissociation constant and stability constants of Cu⁺², Co⁺²Ni⁺², Zn⁺²complexes of the said ligand(HINPHTSAL). The chemistry of thiosemicarbazone in the ligand has received considerable attention because of their variable bonding modes, structural diversity. Due to the inherent, ambident character of the ligand, it is having various positions of probable donor atoms, hence ligands forms the metal complexes with varied geometries, stabilities and applications. With this interest we are reporting a new ligand N'-[(E 2Z)-2- (hydroxyimines)-1— phenylpropylidene] N''-[(1E)-{[2-(E)-(2-hydroxyphenyl methylene) thiocarbonohydrazide. (HINPHTSAL) synthesized from a reaction between N'-[(1E, 2Z)-2-(hydroxyimino)-1-phenylpropylidene]-thiocarbonohydrazide and salicylaldehyde.

The ligand N'-[(E 2Z)-2- (hydroxyimines)-1— phenylpropylidene]N''-[(1E)-{[2-(E)-(2-hydroxyphenyl methylene) thiocarbonohydrazide (HINPHTSAL) is monobasic in nature, owing to bifunctionality and retained ambient nature of isonitropropiophenone, this ligand assures interesting coordination chemistry with a variety of metal complexes. The active group –CO-C=NOH is capable of coordinating to the metal ion through carbonyl oxygen and oximino nitrogen. The NH₂ group from thiocarbonohydrazide react to salicylaldehyde to form an interesting ligand due to presence of imine group (-N=CH-) which impart biological activity.

2. EXPERIMENTAL SECTION

Materials and Methods: The stock solution of the ligand (0.05M) was prepared by 17.75g of the ligand in a minimum volume of dioxane subsequently diluted to 1litre with dioxane. All chemicals used in this experiment were Analytical Grade. KCL, HCL, and KOH. Chlorides of metal ions were used for the preparation of metal ion solution of 0.01M. Standardized metal ion solutions by using standard EDTA solution, volumetrically. The ionic strength of 0.05, 0.075, 0.10 mol / dm³ was maintained by using 1M KCL solution. The carbonate free KOH solution (0.1M) was prepared by using double distilled water and standardized against standard succinic acid solution.

Apparatus and procedure: The digital pH meter EQ-610; inbuilt temperature compensation and 0.0 to 14 pH range with an accuracy of ± 0.01 pH Unit with combined glass electrode were used for the measurements of pH. The experiments were carried out at 29°C temperature and in inert atmosphere and by maintaining ionic strength of 0.05, 0.075, 0.10 mol/dm³ in aqueous medium. The pH meter was calibrated by using 4.0, 7.0 and 9.2 pH standard buffer solutions before every set of titrations. For smooth working of electrode, the necessary precautions were taken. The following three set of solutions were titrated separately against standard carbonate free 0.102M KOH solution.

- Free acid titration (A): HCL (1x10⁻² M) - 5 cm³ of 0.10 mol /dm³ HCL +30 ml Dioxane + 13ml distilled water

- Free acid + ligand titration (A +L): A (1×10^{-2} M) + L (1×10^{-3} M)- 5 cm³ of 0.10 mol /dm³ HCL +5 cm³ of 0.05mol /dm³ ligand+ 25 ml Dioxane + 13 ml distilled water
- Free acid + ligand + metal titration (A +L+M): A (1×10^{-2} M) + L (1×10^{-3} M) + M (1×10^{-4} M). -5 cm³ of 0.10 mol /dm³ HCL +5 cm³ of 0.05mol /dm³ ligand+ 5 cm³ of 0.01mol /dm³ metal salt + 25 ml Dioxane + 8.05 ml distilled water.

To maintain the ionic strength 0.05, 0.075, 0.1 mol/dm³ constant, the appropriate quantity of 1M KCL was added. Total volume of the solution is maintained about 50 ml, with ratio of 60:40 (V/V) to dioxane and water media. This solution was titrated against 0.102M standard KOH solution. The titration was discontinued when solution shows the colour change and turbidity, also shows sudden change in readings of pH meter. The readings was taken after fixed interval until stable readings obtained. The titration for each set was carried out at least four to five times in order to check the reproducibility of the data. Then the graph is plotted pH against volume of alkali (0.102MKOH) added. (Fig.c) and calculated proton ligand dissociation constants at different ionic strengths using Irving –Rosotti method.

Synthesis of ligand: Ligand *N''*-[(1E 2Z)-2-(hydroxyimino)-1-phenylpropylidene]*N'''*-[(1E)-{2-[(E)-(2-hydroxyphenyl)methylene]thiocarbonohydrazide.(HINPPSALTH))- prepared by mixing hot alcoholic solution of 5% *N''*-[(1E,2 Z)-2-(hydroxyimino)-1-phenylpropylidene]-thiocarbonohydrazide compound with alcoholic solution of 10% salicylaldehyde in presence of HCL. The HCL is added drop wise with constant stirring and refluxed the solution about 3 hrs. The yellowish brown coloured compound is formed, filtered and washed with large amount of water and air dried at 80°C for 1 hr. recrystallized this compound with ethanol to obtain fine crystals. The purity of product was checked by TLC using silica gel, Melting point of the compound is 250°C.

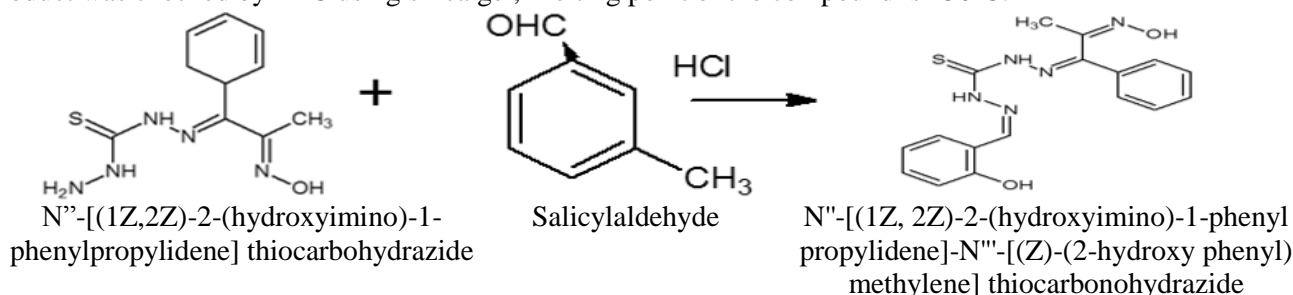


Figure.a. Synthesis of Ligand

3. RESULT AND DISCUSSION

Characterization of the ligand is done by using analytical data obtained from FTIR, PMR, UV-VISIBLE spectroscopy, GC-MS and elemental analysis etc. The molecular weight of ligand is 355gmol⁻¹ determined by GC-MS, it melts at 250°C. It is yellowish brown crystalline solid, soluble in chloroform, acetone, DMF, DMSO, dioxane, dilute alkali etc. and is partially soluble in methanol and ethanol. Several structures are possible depending on the hydrogen bonding but from the studies of FTIR, PMR, UV-VISIBLE spectroscopy, GC-MS and elemental analysis etc. reveals that the following structure (Fig.b) has most stable, which is also supported by ligand-KOH titration curve (monobasic acid).

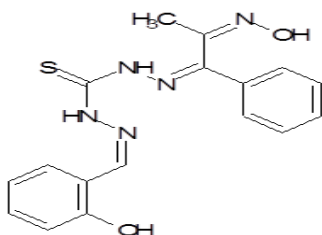


Fig.b. *N''*-[(1Z, 2Z)-2-(hydroxyimino)-1-phenylpropylidene]-*N'''*-[(Z)-(2-hydroxyphenyl)methylene] thiocarbonohydrazide

Table.1. Elemental analysis for title ligand

Compound	Color	Molecular wt. by GC-MS	Melting point °C
HINPHTSAL	Yellowish brown	355	250

Compound	Elemental Analysis				
	%C Found (calculated)	%H Found (calculated)	%N Found (calculated)	%O Found (calculated)	%S Found (calculated)
HINPHTSAL	58.10 (57.46)	4.87 (4.78)	20.01 (19.71)	9.09 (9.01)	9.10 (9.01)

UV-Visible: The electronic absorption spectra of the ligand (HINPHTHSAL) in the ultra-violet region shows high intensity band at 27.32kk ($\epsilon = 20638\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$), 33.56kk ($\epsilon = 12765\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and at 44.44kk ($\epsilon = 11914\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$). This is due to the intra ligand ($\pi \rightarrow \pi^*$) (allowed) transitions of azomethine environment in the molecule. In many isonitrosoketones¹⁻⁶ including Isonitrosopropiophenone, a band occurs at similar positions and intensity, is reported as the ($\pi \rightarrow \pi^*$) transitions in the ligand⁵. The methanol spectra of the hydrazone derivative of Isonitrosopropiophenone⁵ shows three bands at 48.54 kk ($\epsilon = 10610\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$), 39.22kk ($\epsilon = 11820\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and 29.20 kk ($\epsilon = 6930\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) which have been assigned to presence of the two azomethine groups and one oximino group^{9,10}. The electronic absorption spectra of the methanolic solution of the ligand HINPHTHSAL in the ultra-violet region also shows one less intense band at low energy at 29.20 kk ($\epsilon = 6930\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) due to ($\pi \rightarrow \pi^*$) transition. The ultra-violet spectrum of the titled ligand (HINPHTHSAL) in dilute alkali solution (0.1N NaOH) solution reveals that the band observed at 26.74kk ($\epsilon = 10909\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) in the methanol solution spectra somewhat suppressed and shifted to the higher wavelength i.e. bathochromic shift in the band at 26.74kk. The lowering of intensity suggests formation of anion HINPHTHSAL in the alkaline solution due to the deprotonation of the oximino group¹⁻⁵.

Table.2. Uv-Visible Spectral data for HINPHTHSAL

No.	Compound	solvent	Band position in kk	Intensity ($\epsilon\text{indm}^3\text{mol}^{-1}\text{cm}^{-1}$)	Assignment
1	HINPHTHSAL	Methanol	44.44	11914	$\pi \rightarrow \pi^*$ transition
			33.56	12765	$\pi \rightarrow \pi^*$ transition
			29.20	6930	$\pi \rightarrow \pi^*$ transition
		0.1N NaOH	29.85	14737	$\pi \rightarrow \pi^*$ transition
			26.74	10909	$\pi \rightarrow \pi^*$ transition

¹HNMR: HINPHTHSAL was recorded in deuteriated DMSO. Two (singlet) at $\delta 12.25$.ppm (*d, 1H*) and at $\delta 12.00$ ppm (*d, 1H*) were observed. The oximino group is not expected to release the proton much easily than the phenolic proton, since the deshielding effect is more on the proton of the phenolic group than that on the oximino group, therefore the singlet at $\delta 12.25$ ppm may be ascribed to phenolic proton in the ligand and the singlet at $\delta 12.00$ ppm (*d, 1H*) is for oximino group. The singlet at $\delta 10.10$ and 10.85 ppm may be ascribed to proton of the secondary amine. This is also confirmed by D₂O exchange pmr spectrum in which above four peaks disappeared.

A singlet at $\delta 8.30$ ppm (*s, 1H*) attributed to azomethine ($>C=N-NH-$) proton. A singlet at $\delta 2.50$ ppm ascribed to the methyl group in the ligand (HINPHTHSAL). The multiplets in the region $\delta 6.8$ ppm to $\delta 7.8$ ppm were ascribed to the aromatic ring protons in the ligand (HINPHTHSAL).

FTIR Spectra: -The spectrum shows a band at 3229.73cm^{-1} with shoulder at 3272.49cm^{-1} is due to the presence of two -OH groups i.e. oximino and phenolic. Assignment of this band was based on the basis of comparison with other isonitrosoketones and hydrazone derivatives.^{2,6} This is also supported by the IR spectra of isonitro propiophenone and its hydrazone derivative which shows the bands due to oximino-OH at 3224cm^{-1} and at 3250cm^{-1} respectively. The IR spectra of isonitrosopropiophenone thiocarbohydrazide as the intermediate product indicating two bands at 3635cm^{-1} and 3656cm^{-1} which are absent in the titled ligand indicating a successful replacement of the amino group by the aldehyde group during the formation of ligand. Also another band observed at 3032cm^{-1} in the FTIR spectra of the ligand is ascribed to aromatic C-H stretching vibrations and the aliphatic C-H group band is merged into aromatic C-H stretching which are observed in the isonitrosopropiophenone thiocarbohydrazide intermediate compound. Rest of the bands observed in title ligand is almost at the same frequencies in comparisons with bands of isonitrosopropiophenone thiocarbohydrazide (Table-III).

A strong broad band is observed at 1615.15cm^{-1} for $>C=N$ it may be chiefly due to perturbed stretching vibrations of the azomethine group in HINSALTH and at 1526cm^{-1} is due to aromatic $>C=C<$ vibrations in a HINSALTH. The band at 1616cm^{-1} is assigned to $\nu(N=CH)$ of the oximino group. The band at 951cm^{-1} may be assigned to $=N-N=$ stretching vibrations. The peak observed at 1029cm^{-1} is ascribed to N-O vibrations this is supported by Bhargava (1986). The band at 1195cm^{-1} is due to C-O stretching.

Table.3. FT(IR) spectral data for Ligand

Compound	$\nu(\text{O-H})_{\text{Ali}}$	$\nu(\text{C-H})_{\text{Aliphatic}}$	$\nu(\text{N-H})$	C-O	N=CH	-CS	N-O	N-N	Mono Sub-Benzene	m-Di Sub-Benzene
Ligand	3032	2985	3272	1195	1616	1280	1001	1093	755	630

CALCULATIONS: The average number of the protons associated with ligand at different pH values, n_A was calculated from the titration curves of the acid in the absence and presence of ligand from equation (1)

$$n_A = \frac{(V_2 - V_1)(N^0 + E^0)}{(V^0 + V_1) T C^0_L} \quad \text{-----} 1$$

Where Y = the number of ionizable proton(s) in ligand ($Y = 1$), V_1 = Volume of 0.1M KOH required, V_2 = volume of ligand required to reach the same pH on the titration curve of 0.1M KOH, V^0 = the initial volume (50.0 cm³) of the mixture, T^0C_L = the total concentration of the ligand, N^0 = the normality of potassium hydroxide solution, E^0 = the initial concentration of the free acid.

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion (n) versus the free ligands exponent P_L , according to Irving and Rossotti⁷. The average number of the reagent molecules attached per metal ion (n), and free ligands exponent, P_L , can be calculated using (2) and (3) respectively,

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 + V_2) n_A T^0 C_M} \quad \text{-----2}$$

$$P_L = \text{Log}_{10} \left(\frac{\sum_{n=0}^{n=j} \beta_n (1/\text{Antilog pH})^n (V^0 + V_3)}{T^0 C_L^{-n} T^0 C_M} * \frac{V^0}{V^0} \right) \quad \text{-----3}$$

Where, $T^0 C_M$ = total concentration of the metal ion present in the solution, $T^0 C_L$ = total concentration of the Ligand present in the solution, β^H = overall proton-reagent stability constant, V_1 = volumes of hydrochloric acid I, n terms of 0.102M KOH, V_2 = volumes of ligand required to reach the same pH on the titration curves of 0.102M KOH, V_3 = volumes of metal ion required to reach the same pH on the titration curves of 0.102M KOH.

From the analysis of these curves the metal-ligand stability constants were determined. The values of the stability constants ($\log K_1$ and $\log K_2$) are given in Table below.

Table.4. Stepwise stability constants for ML and ML₂ complexes in 60:40 (by volume) dioxane water mixture at room temperature (301K)

Ionic strength	Proton –ligand constant (LogK)		pK
	By half integral method	By graphical method	
0.05	10.20	10.20	10.20
0.075	10.18	10.18	10.18
0.10	10.16	10.16	10.16

[A] $\mu = 0.05$ pK=10.20 $\sqrt{0.05} = 0.22$

Compound	Log K ₁		Log K ₂		Log $\beta = \text{Log}(K_1 + K_2)$
	By half integral method	By graphical method	By half integral method	By graphical method	
Co(II)	9.18	9.16	7.16	7.19	16.34
Ni(II)	9.26	9.25	7.56	7.61	16.83
Cu (II)	9.54	9.55	8.14	8.14	17.68
Zn (II)	9.47	9.48	7.79	7.80	17.27

[B] $\mu = 0.075$ pK=10.22 $\sqrt{0.075} = 0.2738$

Compound	Log K ₁		Log K ₂		Log $\beta = \text{Log}(K_1 + K_2)$
	By half integral method	By graphical method	By half integral method	By graphical method	
Co (II)	8.94	8.94	7.19	7.17	16.12
Ni (II)	9.16	9.14	7.40	7.40	16.55
Cu (II)	9.43	9.38	8.03	8.04	17.43
Zn (II)	9.30	9.30	7.80	7.80	17.10

[C] $\mu = 0.10$ pK=10.23 $\sqrt{0.10} = 0.3162$

Compound	Log K ₁		Log K ₂		Log $\beta = \text{Log}(K_1 + K_2)$
	By half integral method	By graphical method	By half integral method	By graphical method	
Co (II)	8.68	8.76	6.65	6.66	15.38
Ni (II)	9.00	9.04	6.88	7.02	15.93
Cu (II)	9.44	9.47	7.44	7.46	16.91
Zn (II)	9.24	9.24	7.16	7.18	16.40

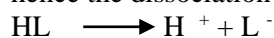
Table.5. Ionic strength and metal stability constant

Ionic strength μ	$\sqrt{\mu}$	Co (II)	Ni (II)	Cu (II)	Zn (II)
0.05	0.2267	16.34	16.83	17.68	17.27
0.075	0.2738	16.12	16.55	17.43	17.10
0.10	0.3162	15.38	15.93	16.91	16.40

Formation of Complexes in Solution: The ligand is yellowish brown in colour in 60: 40 % (V/v) dioxane water mixture. During the course of titration of ligand against 0.102M KOH, light yellow coloured appeared at low pH. As the titration goes on, the yellow colour become deepens at high pH ~ 5.80. This is because of the dissociation of proton from the oxime –OH group.

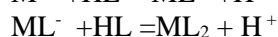
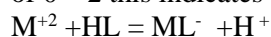
Similarly during metal ion titration, different colours are observed depending upon metal ions. For the titration of cobalt against 0.102M KOH reddish colour occur while for nickel- brown colour, for copper- green colour and for zinc- yellow colour appears at different pH. Thus the colour changes significantly indicate formation of complexes.

Proton –ligand dissociation constant: The ligand used in this study may be considered as monobasic in nature consisting of only one dissociable proton from oxime group which is supported by pmr, ir and electronic spectra hence the dissociation of HL represented as ---

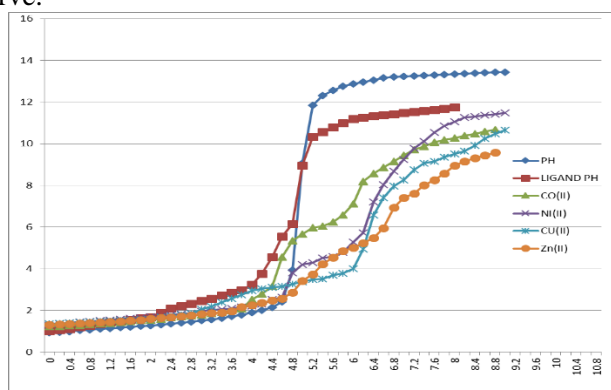
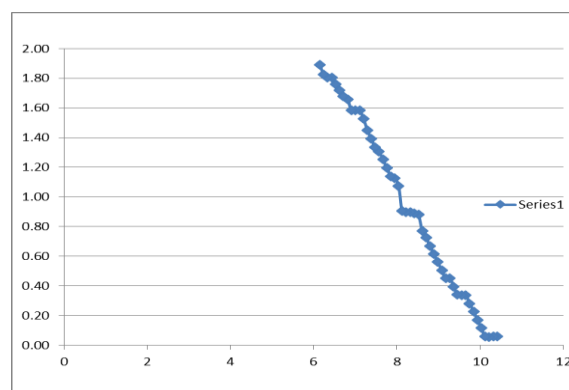


From the value of dissociation constants it is clear that pK values decreases with increase in ionic strength. This is according to Debye Huckel theory. The proton ligand formation number n_A value less than 1.5 indicates that ligand containing only one dissociable proton from oxime group.

Metal ligand stability constant: From the titration curves of metal ligand shows that the n values are in the range of 0 – 2 this indicates that the two formation constants of the metal –ligand complexes.



The first step gives the value of $\log k_1$ and second step gives the value of $\log K_2$, (Table.4) for metal –ligand bond stability. From the fig.c, it is found that the metal –ligand titration curves lie below the proton ligand titration curve.

**Fig.c. Proton and metal ligand titration curves****Fig.d. Formation of cobalt complex**

The formation curves for the metal complexes were obtained by plotting the average number of ligand attached per metal ion n Vs. P_L (the free ligand exponent) (Fig.d). According to the Irving and Rossotti, the values of $\log K_1$ and $\log K_2$ calculated at different ionic strength (Table.4, 5), shows that Higher the value of $\log K_1$ and $\log K_2$ then the ligand act as a strong chelating agent and vice versa.

From the data it is found that:

- The maximum value of n was ~ 2 indicating the formation of 1:2 (metal: ligand) complexes only (fig.d).
- The metal ion solution used in the present study was very dilute ($1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$); hence there was no possibility of formation of polynuclear complexes.
- The metal titration curves were displaced to the right hand side of the ligand titration curves along the volume axis, indicating release of proton upon formation of complex of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to the ligand titration curve indicates that the formation of strong metal complexes.
- For the same ligand at constant temperature, the stability of the metal complexes increases in the order Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} . This order largely reflects that the stability of Cu^{+2} complexes is considerably larger than those of other metals of the 3d series. The greater stability of Cu^{+2} complexes may be due to the Jahn-Teller effect which distorts the regular octahedron environment for the metal ion.

- The order of stability constant of metal complexes with respect to ligand was found to be $\text{Co (II)} < \text{Ni (II)} < \text{Cu(II)} > \text{Zn(II)}$ which is also agreement with Irving and Williams.
- The order of stability constant i. e. pK values decreases as increase in the ionic strength. This is according to Debye Huckel theory.
- The difference in between $\text{Log}K_1$ and $\text{Log}K_2$ is less than 2.5 indicating the simultaneous formation of 1:1 and 1:2 complexes.

4. CONCLUSION

The new ligand HINPTHSAL has been synthesized which is insoluble in water and in common organic solvent, but soluble in dilute alkali. It indicates it is in acidic nature.

The dissociation constant of ligand is $\text{p}K \sim 10.2$. The order of stability constant and dissociation constant pK decreases with increase in ionic strength. The order of stability constant with respect to metal ion is $\text{Co (II)} > \text{Ni (II)} > \text{Cu (II)} > \text{Zn (II)}$ which is in according with Irving –Williams natural order. From the data it is clear that the ligand forms the complexes with the metal ion in the ratio 1: 2.

5. ACKNOWLEDGEMENT

The Authors are grateful to the heads of the chemistry department, D.U.B.S.Sci. College, Dapoli and Konkan Gyanpeeth Karjat College (ASC), Karjat for providing the necessary facilities and their support.

REFERENCES

- Bates RG, Determination of PH Theory Practice, Wiley Inter science, New Publication, New York, 1973.
- Bhargava P.P, and Tyagi M, Studies on the complexes of some transition-metals with 2, 3-butanedione monoxime, 2, 4-pentanedione monoxime, Ind. J. Chem., 25A, 1986, 193.
- Chakrabarti A, Sahoo B, Transition-metal cluster complexes, Polynuclear metal-complexes of Copper (II), Nickel (II), Cobalt (II) and Cobalt (III), Ind. J. Chem., 20A, 1981, 431.
- Deshmukh R.G, and Thakkar N.V, Cobalt (III) and nickel (II) complexes of Isonitrosopropiophenone, Ind. J Chem., 24A, 1985, 1066.
- Irving H, and Rossotti H.S, Methods for computing successive stability constants from experimental formation curves, Journal of the Chemical Society, 1953, 3397–3405.
- Irving H, and Williams R, Order of Stability of Metal Complexes, Nature, 162, 1948, 746.
- Mellor D.P, and Maley L, Stability Constants of Internal Complexes, Nature, 159, 1947, 370.
- Patel N.J, and Haldar B.C, Synthesis and Characterization of Metal Complexes of Schiff Base Ligand Derived from Isonitrosoacetophenone and Hydrazine, J. Inorg. Nucl. Chem., 42, 1967, 843.
- Sawant Dilip, Pingle Satish G, and Deshmukh R.G, Synthesis and Characterization of a New $\text{N}''\text{-}[(1Z, 2E)\text{-}2\text{-}(\text{Hydroxyimino})\text{-}1\text{-phenylpropylidene}]\text{-N}'''\text{-}[(1E)\text{-phenylmethylene}]\text{thiocarbonohydrazide}$ and its metal complexes, A. J. of Chemistry, 20 (3), 2008, 2464.
- Shakru R, Satish Kumar K, Vijay Kumar Chityala, Shivraj, Potentiometric Studies of 3-Amino-5-Methyl Isoxazole Schiff Bases and Their Metal Complexes In Solution, Adv. Scient. Res., 2 (4), 2011, 58-62.
- Talwar U.B, and Haldar B.C, Isonitrosoacetylacetone and isonitrosoacetophenone as extractants and Spectrophotometric reagents for iron (II), J. Indi. Chem. Soc., 49, 1972, 785.
- Thakkar N.V, and Haldar B.C, Magnetic and spectral studies of complexes of isonitroso-acetophenone (HINAP) with Ni (II), Pd (II) and Pt (II), J Inorg. Nucl. Chem., 42, 1980, 843.