



Spectral studies of N'' -[(1Z,2Z)-2-(hydroxyimino)-1-phenylpropylidene]- N''' -[(Z)-(2-hydroxyphenyl)methylidene]thiocarbonohydrazide(HINSALTH) metal complexes.

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ABSTRACT

The complexes of new ligand with the transition metal Co (II), Ni (II), Cu (II), and Zn (II) have been synthesized and reported for the first time. Ligand act as the ambidentate nature. The geometry of the complexes investigated on the basis of magnetic susceptibility and spectral data. IR studies shows that the ligand behaves as bidentate in metal like Co(II), Ni(II), Cu(II), Zn(II) and coordinate through oximino and azomethanine nitrogen. Based on these results probable structure of these complexes have been proposed, for Ni(II), Zn(II) tetrahedral, Ni(II) octahedral and Cu(II) have square planar structure.

KEY WORDS: Thiocarbonohydrazide, magnetic moment, spectral properties, ESR spectra.

INTRODUCTION:

Chelating ligands containing oxime group have been the subject of many investigations during the last three decades [1,2]. A major aim to study such compounds originates from the fact that these types of ligands gives coloured chelates showing different interesting properties regarding their geometries [3], and biological importance [4,5]. Transition metal complexes with potential biological activity are the focus of extensive investigations [6]. Oximes and dioximes have often been used as chelating ligands in the field of coordination chemistry and their metal complexes have been of great interest for many years. The biological importance of oximes and their complexes is very well known [6,10]. Coordination complexes of oximino ketones and their derivatives have attracted great attention over the past decades due not only to their facile syntheses and the accessibility of diverse structural modifications, but also to their wide application in analytical [11], bioinorganic system [12], catalyst [13, 14], medicine etc [15,16]. This is primarily because of 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.

This paper reports a synthesis and characterization of the complexes of Co(II), Ni(II), Cu(II), and Zn(II) of N'' -[(1E,2Z)-2-(hydroxyimino)-1-phenylpropylidene] N''' -[(Z)-(2-hydroxyphenyl)methylidene]thiocarbonohydrazide(HINSALTH). The ligand is a condensation product of N'' -[(1E,2Z)-(hydroxyimino)-1-phenylpropylidene]thiocarbonohydrazide [11] and salicylaldehyde having nitrogen, oxygen, sulfur donor atoms promises interesting coordination chemistry [12].

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2. EXPERIMENTAL SECTION

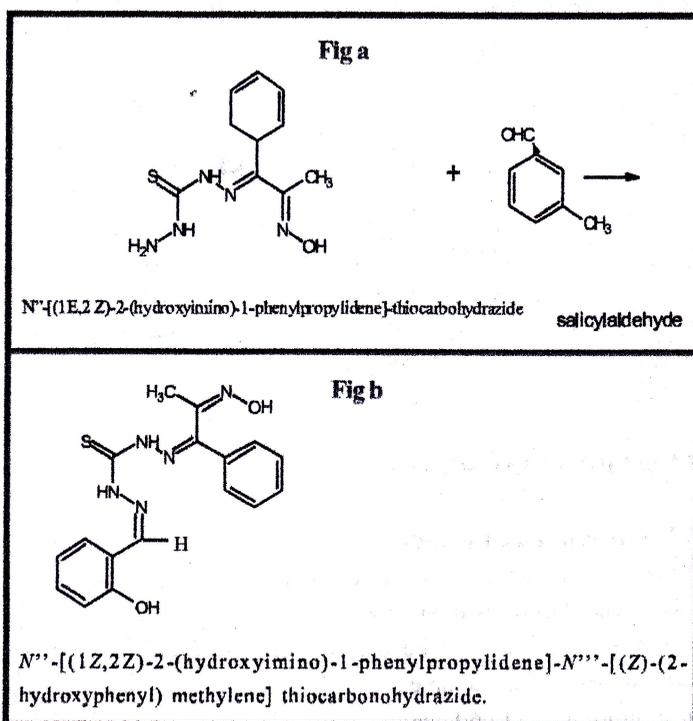
2.1. Materials and Methods

All chemicals and solvents used were of Analytical grade. The organic solvents used were purified by standard methods. Volumetric glass wares were calibrated before use. The molar conductance measurements of the complexes in nitrobenzene were obtained using an Equiptronic EQ-660 conductivity meter. It was calibrated with 0.1 M KCl solution. IR spectra were recorded on a FTIR -1615 of Perkin-Elmer spectrometer in KBr pellets.

Magnetic susceptibility measurements were carried out by employing Gouy's balance using $Hg[Co(SCN)_4]$ as calibrant. The effective magnetic moments were calculated after diamagnetic correction for ligand component by using Pascal's constants [17]. The UV-visible spectra was recorded on Shimadzu UV-190 spectrophotometer. ESR spectra of copper complexes were recorded on a Varian E-line century series spectrometer equipped with a dual cavity and operating at the x-band (~9.1GHz) with 100 KHz modulation frequency. TCNE was used as field marker.

2.2. Synthesis of ligand:

Isonitrosopropiophenone was prepared by following the procedure of Hartung and Munch [18]. Thiocarbonylhydrazide was prepared by procedure of L.F.Audieth, Earle S., Scott and Perry S. Kippur [19]. Ligand N'' -[(1E,2Z)-2-(hydroxyimino)-1-phenylpropylidene] N''' -[(1E)-{2-[(E)-(2-hydroxyphenyl)methylene]thiocarbonylhydrazide. (HINPPSALTH) was prepared by mixing hot alcoholic solution of 5% N'' -[(1E,2Z)-2-(hydroxyimino)-1-phenylpropylidene]-thiocarbonylhydrazide compound with alcoholic solution of 10% salicylaldehyde (Fig a) in presence of HCl which is added drop wise with constant stirring and refluxed about 3 hrs. The yellowish coloured compound is formed (Figb), filtered and washed with large amount of water and air dried at 80°C for 1 hr and recrystallized with ethanol to obtain fine crystals. The purity of product was monitored by TLC using silica gel. Melting point is 250°C, and analyzed for C, H and N.



2.3. Synthesis of metal complexes:

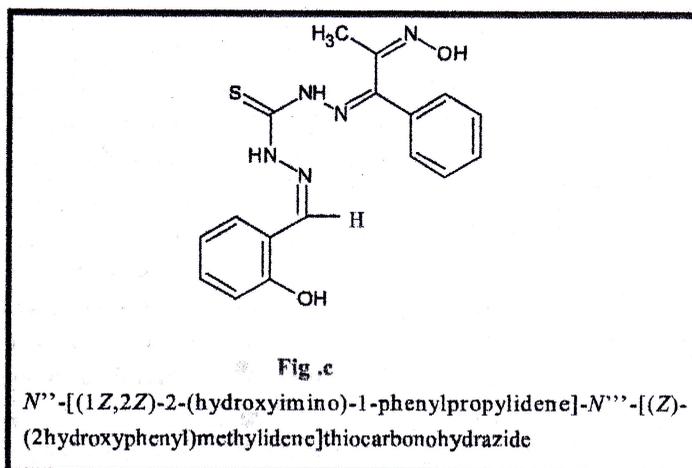
The metal complexes were synthesized by refluxation-precipitation method. The hot ethanolic solution of ligand (0.004 mol) was mixed with ethanolic solution of metal chloride (0.002 mol) and alcoholic ammonia solution were added drop wise till complex formation and resulting mixtures were refluxed for 30 minutes for completion of reaction. The precipitated complexes were through whatmann filter paper no. 1 and washed with water and dried at 110°C. The melting points of all ligand and metal complexes were determined by open capillary method. The metal content of the metal complexes were determined by the methods given in Vogel's quantitative analysis [25].

The solubility of the complexes were examined in different polar and non-polar solvents. Molar conductivity of the ligand and its complexes were measured using 1×10^{-3} M solution in nitrobenzene on Equiptronic Conductivity-meter (EQ-660A). The electronic absorption spectrums of complexes were recorded using DMF as solvent on Shimadzu UV-VIS spectrophotometer.

3. RESULT AND DISCUSSION:

3.1. Ligand characterization:

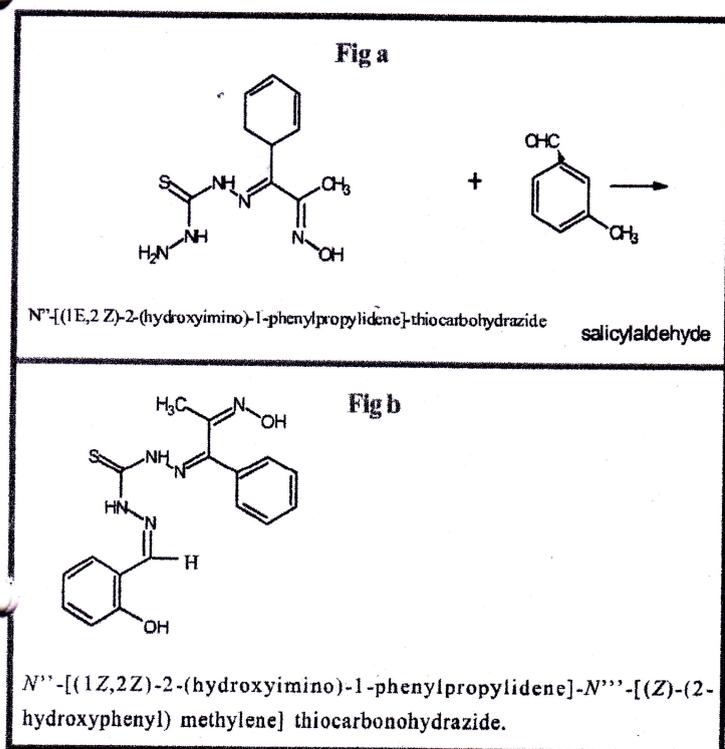
Characterization of the ligand is done by using analytical data obtained from FTIR, PMR, UV-VISIBLE spectroscopy, GC-MS, elemental analysis etc. The molecular weight of ligand is 355 gmol^{-1} determined by GC-MS. It is yellow crystalline solid, soluble in chloroform, acetone, ethanol DMF, DMSO, dioxane, dilute alkali etc. and is partially soluble in methanol. Several structures are possible depending on the hydrogen bonding but computational studies reveals that the structure shown in Fig.c below has least energy i.e. most stable, which is also supported by ligand- KOH titration curve (monobasic acid). In order to check the purity of the complex, prepared the ligand and its soluble metal complexes were subjected to TLC studies.



The ligand and complexes are stable in air and stable at 200 °C indicating high thermal stability and hence strong metal to ligand bond. All complexes are insoluble in water, dilute hydrochloric acid: partly soluble in methanol, ethanol, and Chloroform and highly soluble in DMF, DMSO, carbon tetrachloride, acetone etc. The molar conductance values of the complexes in nitrobenzene (0.50 to $16.285 \text{ Scm}^2 \text{ mol}^{-1}$) are too low to account for the dissociation, therefore the complexes are considered to be non-electrolytes [26]. The elemental analysis shows 1:2 (metal: ligand) stoichiometry for all the complexes. The analytical data and physical properties of ligand and metal complexes are given in table 1.

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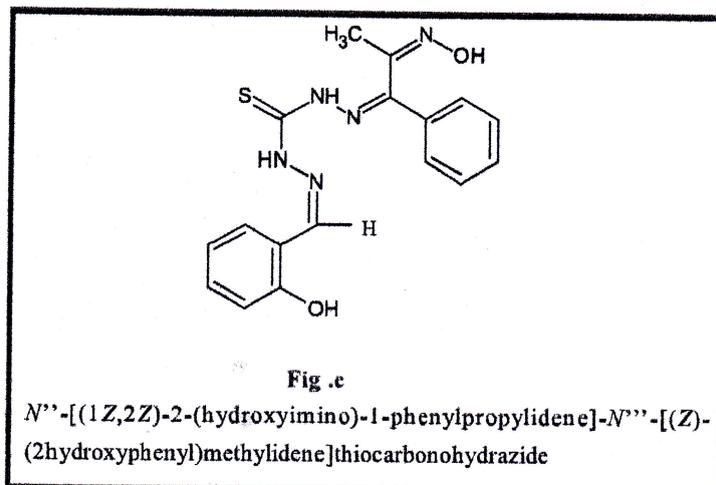
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Table 1: Analytical and physical data of the ligand and its metal complexes

dcs/	Compound	Colour	Yield %	Melting/Dec. point °C	Elemental Analysis					
					% M Found (Calcd)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% O Found (Calcd)	% S Found (Calcd)
L	HINSALTH	Yellow	77.02	250	-	58.1	4.87	20.01	9.09	9.1
A	CO(HINSALTH) ₂	Brown	78.82	<250	8.12	-57.46	-4.78	-19.71	-9.01	-9.01
B	Ni (HINSALTH) ₂	Greenish Brown	75.75	<250	-7.68	-53.19	-4.17	-18.26	-8.23	-8.23
C	Zn (HINSALTH) ₂	Yellow	85.65	<250	8.32	55.55	4.63	19.06	9.28	9.14
D	Cu (HINSALTH) ₂	Brown	81	246	-7.66	-53.21	-4.17	-18.26	-8.34	-8.34
					9.23	53.45	5.19	19.78	9.42	9.15
					-8.472	-52.74	-4.13	-18.02	-8.27	-8.27
					9.76	54.66	4.98	20.1	8.89	9.56
					-8.23	-52.8	-4.14	-18.26	-8.29	-8.29

3.2. IR Spectral Studies:

The IR data with tentative assignments of the ligand (HINSALTH) and its metal Co (II), Ni (II), Cu (II), and Zn (II) complexes are presented in table 2. The spectrum are quite complex due to presence of large number of bands with varying intensities. It is therefore impossible to assign all bands an attempt however have been made to assign some bands on the of several FTIR spectrum reported for isonitroketones and diacetylmonoxime. The spectrum shows a broad 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 in the ligand. Assignment of this band was based on the basis of comparison with other isonitroketones and hydrazone derivatives.^[11-15] This is also supported by the IR spectrum of isonitropropiophenone and its hydrozonyl derivative shows the bands due to oximino-OH at 3224cm⁻¹ and 3250cm⁻¹ respectively. The IR spectrum of isonitropropiophenone-thiocarbohydrazide 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 Schiff base formation. Also another band observed at 3032cm⁻¹ in the FTIR spectrum 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 iso-nitropropiophenone thiocarbohydrazide intermediate compound. Rest of the bands observed in title ligand is almost at the same frequencies in comparisons with bands of iso-nitro-propiophenone-thiocarbohydrazide (Table-2).

A strong and 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 1526 cm⁻¹ is due to aromatic >C=C< vibrations in a HINSALTH. The band at 1616cm⁻¹ due to $\nu(C=N)$ of the oximino group in ligand was shifted to lower frequencies at in the region 1602-1612cm⁻¹ in its complexes suggests that the coordination of oximino group with the metal ion^[21,22].

The band at 951 cm⁻¹ may be assigned to =N-N= stretching vibrations. The peak observed at 1029 cm⁻¹ is attributed to N-O vibrations this is supported by Bhargava et al.^[23] have assigned two bands at 1000 cm⁻¹ and 1100 cm⁻¹ to two N-O vibrations. The band at 1195 cm⁻¹ is due to C-O stretching.

The broad peak is observed at 3229.73 cm⁻¹ in the IR spectrum of the ligand assigned to oximino (OH), which is found have disappeared and a new peak is observed at 2916 cm⁻¹ is now visible in all the complexes thereby indicating deprotonation of oximino group. This reveals the involvement of oximino group in coordination. The appearance of two new bands ~ 1338cm⁻¹ to ~ 1506cm⁻¹ corresponds to presence of N-O group which indicates oximino group coordinate through nitrogen not oxygen.^[15] The band at 1195 cm⁻¹ to phenolic C-O in the ligand remains same intact in all metal complexes. This is further supported by appearance of new band at ~ 427cm⁻¹ to ~ 457cm⁻¹ in all metal complexes. Appearance of new band at ~ 516 cm⁻¹ to ~ 551cm⁻¹ in all complexes corresponds to M-N bonding.

Table 2 - FT(IR) spectral data for Ligand and its metal complexes

Compound	$\nu(O-H)$ Ali	$\nu(C-H)$ Aliphatic	$\nu(N-H)$	C-O	N=CH	-CS	N	$\rightarrow O$	N-O	N-N	Mono Sub-Benzene	m-Di Sub-Benzene	M-N
Ligand	3032	2985	3272	1195	1616	1280	-	1001	1093	755	630	-	-
Co(L) ₂	-	2916	3320	1195	1602	1288	15,061,338	1006	1063	754	692	516, 551	
Ni(L) ₂	-	2916	3351	1199	1602	1284	15,061,338	1006	1049	752	694	516, 555	
Zn (L) ₂	-	2916	3358	1199	1612	1288	15,061,338	1008	1056	752	694	516, 549	
Cu(L) ₂	-	2916	3358	1195	1597	1284	15,061,338	1001	1056	785	692	516, 549	

3.3. ¹HNMR:

The ¹Hnmr spectrum of HINSALTH was recorded in deuteriated DMSO. Two (singlet) at δ12.25 ppm and at δ12.00ppm were observed. The oximino group is expected to release the proton much less 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 δ12.25 ppm may be ascribed to phenolic proton of the ligand. The singlet at δ10.10 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 δ8.30ppm attributed to azomethine proton. A singlet at δ2.50ppm assigned to the methyl group of the ligand. The multiplets in the region between δ 6.8 ppm to δ7.8 ppm were assigned to the aromatic ring protons.

The signal at δ 8.30 (s, 1H) due to the azomethine group in the ligand is shifted in the region δ 8.99 (s, 1H) in the spectrum of Pd(II) complex confirms the oximinocoordination of "N" of (-C=N-) group in bonding with Pd(II). The singlet at δ12.00ppm in the pmr spectrum of the ligand remains unaltered in the pmr spectrum of palladium complex confirms the noncoordination of phenolic OH with Pd.

3.4. Electronic Spectra and Magnetic Susceptibility

The electronic spectra of all the complexes were recorded in chloroform. The wavelength of the absorption maxima are given in Table (III,IV). A clear analogy is evident among the results for all compounds. In the spectra of free ligand π-π* transitions in the range, 30.77 to 42.55kk are not significantly altered on complex formation. The n-π* transitions associated with nitrogen of the azomethine and oxime group in free ligand are found in the range 29.85kk (ε=14737) and 25.64kk (ε=14042). In the complexes, the n-π* transition are shifted to higher energy. These results indicate that the nitrogen and/or oxygen atom of the oxime groups are coordinated to the metal ions. The A complex shows magnetic moments 4.25BM, indicating that complex has tetrahedral configuration. The tetrahedral Co (II) complexes are reported to exhibit magnetic moments in the range 4.2 to 4.8BM. The electronic spectra of Co (II) exhibit two bands in DMF at 18.5kk and 15.62kk are assigned to ¹A_g → ²E_g and ²A_{1g} → ²B_{1g} transition respectively. In view of the available reports on square planar Co(II) complexes¹⁸⁻⁹¹. The greenish Ni(II) complex in chloroform solution exhibits a peak at 10.56kk which may be assigned to ³A_{2g} → ³T_{2g}(ν₁) transition, this value may be assigned to 10Dq of the Ni(II) complex. Another broad band is observed at 16.51kk which may be assigned to the ³A_{2g} → ³T_{2g}(F) (ν₂). The ratio ν₂/ν₁ is found to be 1.56, which falls in the range reported for the other octahedral complexes of Ni (II) supporting the assignment¹⁶¹. From the observed

position of these two transitions, the frequency of the third d-d transition ³A_{2g} → ³T_{1g}(P) (ν₃) and B values has been calculated employing the following equations¹²¹.

$$B = [(\nu_2 - 2\nu_1)(\nu_2 - \nu_1)] / (15\nu_2 - 27\nu_1)$$

$$\nu_3 = (225B^2 + 100Dq^2 + 180DqB)^{1/2}$$

The third band ν₃ is expected to occur at 19.27kk. However, this band is not observed in the solution spectrum of the complex probably because, it is masked by the tail-end of the strong charge transfer band around 25970cm⁻¹. The value of the Racah interelectronic repulsion parameter B is 7320cm⁻¹, calculated with the help of the appropriate equations¹²⁴

The ratio, β = B(Found) / B'(Free ion) the covalency factor is found to be 8216cm⁻¹ and is in close agreement octahedral Ni(II) complexes. The light Ni(II) complex shows room temperature magnetic moment of 3.17BM (Table.1). High spin Ni(II) complexes expected to be paramagnetic properties due to two unpaired electron. The observed magnetic moment for Ni (II) complex is in the range expected for octahedral Ni (II) complexes. The complexes C of Zn(II), are diamagnetic, therefore the tetrahedral arrangement of the ligand molecules around Zn(II) is assigned to these complex. The electronic spectra of complex Cu (II) show absorption band at 34.01kk due to the π-π* transition. This band is found to be shifted as compared to the position of the π-π* transition band in methanol solution of free ligand. This indicates that the π- electron system of the ligand suffers considerable alteration on complex formation. Another bands observed is 28.90kk, 27.55kk and 26.18kk may be due to charge transfer transition. The subnormal magnetic moments of the complex may suggest a binuclear structure even in the solid state. Generally, the low magnetic moment values of binuclear copper complexes are attributed to the anti-ferromagnetic moment interaction between two central metalions and/or it may be explained on the basis of the existence of a polymeric structure including copper-copper interaction or due to the covalent nature of metal-sulfur bond.

Table 3: Electronic Spectrum (UV-visible spectra)

Compound	n-π*	π-π*	MLCT	d-d
Ligand in methanol(nm)	353,	314		
Ligand in NaOH (nm)	350,	303		
Co(L) ₂	368,	264	418	714
Ni(L) ₂	366,	276	447	705
Zn (L) ₂	364,	274	448	
Cu(L) ₂	348,	263	435	693

Table 4: Magnetic Moments and Electrical Conductance in mhos of the ligand and its metal complexes

dcs/	Compound	Magnetic Moments in B.M.	Electrical Conductance $10^{-3}M$ (in Nitrobenzene)mhos
L	(HINPPSALTH)	Diamagnetic	0.568
A	CO(HINPPSALTH) ₂	4.25	16.25
B	Ni(HINPPSALTH) ₂	3.17	0.192
C	Zn(HINPPSALTH) ₂	Diamagnetic	6.18
D	Cu(HINPPSALTH) ₂	2.13	0.656

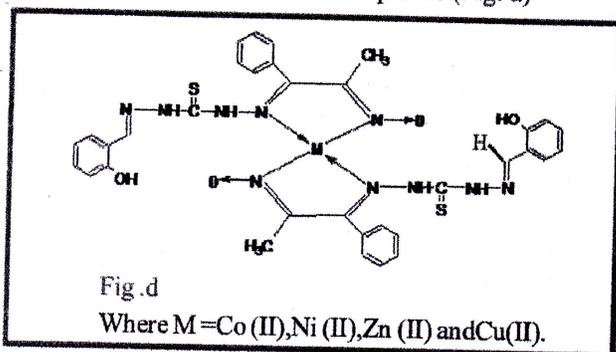
3.5. **The ESR Spectra:** EPR spectrum of Cu (II)-complex was recorded at LNT as polycrystalline sample and in chloroform solution, on the X-band at 9.1 GHz, under magnetic field strength 3000 G. From the observed 'g' values of these at room temperature are

Table 5: ESR Data

Parameters	Copper complex
g	2.00277
g _⊥	1.99
g _∥	2.22
H ₀	3214
G	9.85

The X-band ESR spectra of all Cu(II) complexes have been recorded in the polycrystalline state at room temperature. The ESR spectra of Cu(II) complexes exhibit a single broad signal due to dipolar broadening and enhanced spin lattice relaxation. The geometric parameter G, which is measure of exchange interaction between the copper centers in polycrystalline compound, is calculated using the equation $G = (g_{\parallel} - 2.0023) / (g_{\perp} - 1.97)$. If $G > 4$, the exchange interaction between Cu (II) centers is negligible and if $G < 4$, a considerable exchange interaction is indicated in the solid complex. In all the Cu (II) complexes $g_{\parallel} > g > 2.0023$ observed for the complexes under study indicates that the unpaired electron is localized in $d_{x^2-y^2}$ orbital, characteristics of the square planar geometry. Kivilson and Niwman [25] have reported that the g_{\parallel} is less than 2.3 for covalent character and is greater than 2.3 for ionic character of the metal ligand bond in the complexes. and G values within the range 9.85 are consistent with $d_{x^2-y^2}$ ground state. For these complexes g_{\parallel} is less than 2.3 indicate the covalent character of the metal-ligand bond.

The proposed structure of the complexes (Fig. d)



4. CONCLUSION

The present study reveals that complexes of new ligand with the transition metal Co (II), Ni (II), Cu (II), and Zn (II) have been synthesized. The geometry of the complexes investigated on the basis of magnetic susceptibility and spectral data. IR studies shows that the ligand behaves as bidentate in metal like Co(II), Ni(II), Cu(II), Zn(II) and coordinate through oximino and azomethanine nitrogen. Based on these results probable structure of these complexes have been proposed, for Co(II) and Zn(II) tetrahedral, Ni(II) octahedral and Cu(II) have square planar structure. An ESR spectrum shows the covalent character of the metal-ligand bond.

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