Synthesis and Characterization of a New N'' -[(1Z,2E)-2- (Hydroxyimino)-1-phenylpropylidene]- N''' -[(1E)-phenylmethylene]thiocarbonohydrazide and its Complexes with Co(II), Ni(II) and Cu(II)

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Abstract: Synthesis and characterization of a new N'' -[(1Z,2E)-2-(hydroxyimino)-1-phenylpropylidene]- N''' -[(1E)-phenylmethylene]-thiocarbonohydrazide and its metal complexes with Co(II), Ni(II) and Cu(II) metal ions. The ligand synthesis and characterization is reported for first time. The complexes of divalent metal ions were synthesized in 1:2 molar proportion using ethanol as solvent. The ligands as well as its metal complexes were characterized using various physicochemical techniques such as elemental analysis, spectral and magnetic measurements and electrical conductivity measurements in case of the metal complexes only. The data for the metal complexes reveals that they may be represented by ML_2 . The metal complexes show interesting features of coordination structure.

Keywords: Isonitrosopropiophenone, Thiocarbonohydrazide, Benzaldehyde, Low spin octahedral geometry, Copper-copper interaction.

Introduction

The reaction between thiocarbonohydrazide and isonitrosopropiophenone is premised to yield the compound N'' -[(1E,2Z-(hydroxyimino)-1-phenylpropylidene]thiocarbonohydrazide¹. This ligand having nitrogen, oxygen, sulfur donor atoms promises interesting coordination chemistry. The free NH_2 group of this ligand is reactive and may be condensed with aldehydes and ketones yielding new and interesting set of ligands¹⁻². Varieties of metal complexes of symmetrical dihydrazones of thiocarbonohydrazones derived have been prepared and their stereochemistry reported in literature²⁻⁵. In the present work we propose to study the synthesis and characterization of N'' -[(1Z,2E)-2-(hydroxyimino)-1-phenylpropylidene]-

N'''-[(1*E*)-phenylmethylene]thiocarbonohydrazide and its derivatives. Literature survey shows that the compounds mentioned in this work are scantily reported with respect to their synthesis, characterization as well as complex formation.

Experimental

All chemicals and solvents used were of Analytical grade. Metal(II) chlorides were used. The elemental analyses were carried by standard methods⁵. The molar conductance measurements of the complexes in dimethylformamide (DMF) were obtained using an Equiptronic EQ-660 conductivity meter. IR spectra were recorded on a FTIR -1615 of Perkin-Elmer spectrometer in KBr pellets. A PMR spectrum of the ligand was recorded on Bruker AMX-500 spectrometer in (D₆) DMSO. Chemical shifts relative to tetra methyl silane (TMS) used as internal standard were obtained in δ unit. 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 using Pascal's constants⁶. The UV-Visible spectra were recorded on a Shimadzu UV-190 spectrophotometer brand.

Synthesis

Isonitrosopropiophenone was prepared by following the procedure of Hartung and Munch⁷ Thiocarbonohydrazide was prepared by following procedure of L.F.Audieth, Earle S., Scott and Pery S. Kippur⁸. *N''*-[(1*E*,2*Z*)-2-(hydroxyimino)-1-phenylpropylidene]thiocarbonohydrazide (HPTCHOPD) was prepared by reported procedure¹.

*Synthesis of Schiff base N''-[(1*Z*,2*E*)-2-(hydroxyimino)-1-phenyl propylidene]-N'''-[(1*E*)-phenylmethylene]thiocarbonohydrazide (HL)*

Benzaldehyde (6.1 g, 0.058 M) in ethanol (65 cm³) was added to an ethanol solution (260 cm³) of 2-*N''*-[(1*E*,2*Z*)-2-(hydroxyimino)-1-phenyl propylidene]thiocarbonohydrazide (13.0 g, 0.052 M) and 10 g conc. HCl at 50 °C. The mixture refluxed for 3 h and kept overnight, whence, a yellow solid product was obtained which was filtered, washed with ethanol and dried. Crystallization from hot ethanol gave product that melted at 247-248 °C. The purity of product was monitored by TLC using silica gel. Analyzed for C, H N, S by elemental analysis. The yield of a product was 10.20 g, 58% of the theoretical. The ligand so obtained is insoluble in water, hydrochloric acid, chloroform, acetonitrile, benzene and glacial acetic acid, soluble in DMF, DMSO, 0.5 M NaOH and partly soluble in methanol, ethanol.

Synthesis of metal complexes

A common method of synthesis was used to obtain the corresponding metal complexes. The method of synthesis as used for Co(L)₂ is given as under: A warm ethanol solution (60 cm³) of the ligand (3.0 g, 0.009 M) was added to a stirred solution of cobalt chloride hydrate (1.04 g, 0.004 M) in ethanol (10 cm³). The mixture was refluxed for 3 h and cooled to room temperature. On cooling, brown precipitates were formed which were filtered, washed with ethanol and water and dried by suction. Crystallization from ethanol gave the desired metal complex.

Results and Discussion

Characterization of the ligand HL

The analytical data of the ligand and its complexes are given in Table 1. The molecular weight of the ligand is found to be 339 by using Rast's method suggests its monomeric nature.

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

Compound	Colour	Yield %	Melting, °C	Elemental Analysis					Magnetic Moments μ B.M.	Molar Conductance $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
				% M Found (Calcd)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% S Found (Calcd)		
HL	Yellow	58.00	245-246	-	61.36 (60.10)	4.30 (4.15)	21.00 (20.62)	10.26 (9.43)	diamagnetic	0.586
Co(L) ₂	Dark red	68.36	238-240	7.38 (8.01)	53.24 (55.45)	3.61 (4.35)	17.34 (19.03)	9.40 (8.70)	1.80	1.095
Ni(L) ₂	Brown	20.12	>250	8.00 (8.00)	53.21 (55.47)	3.92 (4.35)	17.55 (19.03)	9.36 (8.70)	0.552	29.54
[Cu(L) ₂] ₂	Brown	50.46	238-240	7.95 (8.58)	53.41 (55.11)	3.84 (4.32)	17.83 (18.91)	9.44 (8.64)	diamagnetic	25.93

Solubility

Solubility of ligand in dilute alkali indicates the acidic nature which may be due to the replaceable proton of oximino group yielding the ligand anion.

Ligand is insoluble in dilute HCl indicating absence of protonable free NH_2 group. The ligand is sparingly soluble in organic solvents like methanol and ethanol and somewhat soluble in solvents like dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF).

UV-Visible spectral properties

The aromatic band of the ligand at 40.82kk ($\epsilon=9095$) is attributed to benzene $\pi \rightarrow \pi^*$ transition. The band around 29.85kk ($\epsilon=14737$) and 25.64kk ($\epsilon=14042$) is due to $n \rightarrow \pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine and oxime group in the Schiff base.

The PMR spectra

The PMR spectrum (Table 2) of HL in (D_6) DMSO solvent reveals the oximino proton at 12.4 δ , which is shown at same position in PMR spectra of parent molecule¹ since it is expected to be rather acidic and therefore the weakest shielded proton in the molecule support by disappearance of the signal in D_2O PMR spectra of a ligand. A singlet shown at 12.0 assigned to N-H proton and at 10.7 δ assigned to imino $\text{CH}=\text{N}$ proton⁹ may suggest successful condensation of parent molecule and benzaldehyde molecule. A singlet at 1.50 δ assigned to the methyl group, occurs at the usual position for methyl proton in the ligand. A broad multiplet at 7.0 to 8.0 δ has its origin in the phenyl ring protons of the ligand.

The infrared spectrum

A significant feature of the IR spectrum of HL in KBr disc in the range of 4500-400 cm^{-1} , is the absence of any band between 3200 to 3300 cm^{-1} due to the symmetrical and asymmetrical vibrations of the primary amines NH_2 , reported at 3208 and 3306 cm^{-1} in parent molecule^{3,10} indicating a successful replacement of the NH_2 hydrogen by the aldehyde during Schiff base formation. This is further supported by the observed¹¹ absorption due to $\text{HC}=\text{N}$ of the imino group at 1520 cm^{-1} and absence of a characteristic band of aldehyde at 2827 cm^{-1} due to aldehyde C-H stretching. A single medium band at 3260 cm^{-1} may be assigned to secondary amine N-H stretching¹²⁻¹³. The broad moderate intensity band at 1602 cm^{-1} may be chiefly due to the perturbed $\text{C}=\text{N}$ stretching vibrations of the azomethine ($>\text{C}=\text{N}-\text{NH}_2$) groups¹⁴ in HL with perhaps a small contribution from the C-C vibration not being ruled out. The intense band at 1442 cm^{-1} shows $\nu\text{C}=\text{N}$ stretching vibration of the oximino ($>\text{C}=\text{NOH}$) groups in HL¹⁴⁻¹⁶. The shifting values of $\text{C}=\text{N}$ may be explained on the basis of drift of the lone pair density of the nitrogen molecule. The presence of oximino group supported by a significant weak band shown at 3225.8 cm^{-1} . Since the O-H vibration are also expected to lower down from these usual ranges of Ca.3500 cm^{-1} an account of strong inter and/or intra molecular hydrogen bonding in the molecule²⁻³. The out of plane O-H vibration observed 897 cm^{-1} and oximino N-O stretching vibration observed at 1006 cm^{-1} , which is shown at 1009 cm^{-1} in parent molecule¹. The characteristic absorption of the ligand in the range of 1286 cm^{-1} is proposed to $\nu\text{C}=\text{S}$ combination band with $\text{C}=\text{C}$, it is affected by various factors including adjacent group, supported by a band observed¹⁷⁻¹⁸ at 762 cm^{-1} due to free $\delta\text{C}=\text{S}$. These two bands observed at 1287 and 756 cm^{-1} in thiocarbohydrazide. Also the band at 1491 cm^{-1}

ascribed N-C=S linkage¹⁹, which is shown at similar frequency in parent molecule and thiocarbohydrazide. This may be suggested the ligand is in thione form, supported by absence of band in region 2800 cm^{-1} due to C-S stretching vibration hence rules out the possibility of thione-thiol tautomerism². A medium intensity band at 3054.8 cm^{-1} and another weak band at 3000 cm^{-1} may be due to C-H stretching vibration of methyl group. On the basis of these observations the following structure is proposed for the ligand:

N''-[(1*Z*,2*E*)-2-(Hydroxyimino)-1-phenylpropylidene]-*N'''*-[(1*E*)-phenylmethylene]thiocarbonyl hydrazide.

Characterization of metal ion complexes of HL

Physical data

Elemental analysis data of the complex (Table 1) represented by the general formula ML_2 . Molecular weight determined by Rast's method with camphor as a solvent confirms empirical formula $\text{C}_{34}\text{H}_{34}\text{MN}_{10}\text{O}_2\text{S}_2$, where M is Co(II), Ni(II) and Cu(II).

The complex prepared, have been found to be insoluble in dilute NaOH solution suggesting the absence of oximino proton ($>\text{C}=\text{NOH}$) or deprotonation of the O-H located at the oxime group. Insoluble in water, dilute hydrochloric acid, partly soluble in methanol, ethanol and chloroform and highly soluble in DMF, DMSO. The complex is stable in air and stable at 200°C indicating high thermal stability and hence strong metal to ligand bond. The molar conductance values of the complexes in dimethyl formamide (0.091 to $29.5\Omega^{-1}\text{ cm}^3\text{ mol}^{-1}$) are too low to account for the dissociation, therefore the complexes are considered to be non-electrolytes²⁰. In order to check the purity of the complex prepared the ligand HL and its soluble metal complexes were subjected to TLC studies.

Magnetic susceptibility measurements

The red coloured, $\text{Co}(\text{L})_2$, shows room temperature magnetic moments of 1.80BM corresponding to the presence of one unpaired electron. The magnetic moments of the square planar Co(II) complexes are expected to show higher magnetic moments than the spin only value of 1.73BM and observed moment is in range of 2.1 – 2.8BM for these complexes⁶ hence ruled out the possibility. The observed magnetic moment is closer to magnetic moment than the spin only value of 1.73BM which may be suggested low spin octahedral geometry since the ground state $(t_{2g})^6(e_g)^1$ allows no orbital contribution and observed value slight excess than spin only value arise from orbital contribution of the first excited state due to spin-orbit coupling²¹⁻²². The square planar Ni(II) complexes are diamagnetic²³. The present red coloured, $\text{Ni}(\text{L})_2$ are found to be only feebly paramagnetic ($\mu = 0.55\text{BM}$ at 298K) suggestive a planar environment of ligands around nickel(II) ion²³. The $\text{Cu}(\text{L})_2$ complex found to be diamagnetic. Simple oxidation-reduction experiments showed that in the complex copper is present +2 oxidation state. This is one of the few Cu(II) complexes in which the spin paramagnetism is completely quenched ($\mu_{\text{eff}}=0$) at room temperature. The diamagnetism indicates that there is strong

spin-spin interaction between two cupric ions or due to the covalent nature of the metal-sulfur bond^{14,24}. This may take place either by the formation of a σ or δ bond by the overlap of the two d -orbital whereby spins of the electrons are paired up or by the formation of extended molecular orbital by the extended overlap of copper and one of the two ligand donor orbital. However, in quite a large number of diamagnetic Cu(II) complexes, partial or complete quenching is explained by the super exchange mechanism²⁴. It is very difficult to decide without complete X-ray work, whether spin-spin interaction takes place because of σ or δ bond formation or by super exchange phenomenon.

UV-Visible spectral properties

The electronic spectra of all the complexes were recorded in chloroform. A clear analogy is evident among the results for all compounds. In the spectra of free ligand $\pi \rightarrow \pi^*$ transitions in the range, 31.25 to 42.55kk are not significantly altered on complex formation. In the complexes, the $n \rightarrow \pi^*$ 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 Co(L)₂ complex exhibits two bands in chloroform at 18.86kk ($\epsilon \sim 13706$) and 17.79kk ($\epsilon \sim 14793$) which attribute to charge transfer transitions and assigned to $^2A_{1g} \rightarrow ^2B_{1g}$ and $^2A_{1g} \rightarrow ^2E_g$ transition respectively. The electronic spectra of planar nickel(II) Schiff base complexes have been the subject of several studies²⁵. Depending on the symmetry of the complexes three or four transitions are expected within the d -orbital manifold of the metal ion. The present nickel(II) complex shows two bands at 27.48kk ($\epsilon \sim 8266$) and 19.79kk ($\epsilon \sim 4152$) assigned to $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$ transition respectively²⁶⁻²⁷. The fact that no band is observed below 10.00kk indicates square planer structure for this complex²⁸ that may be also be deduced from their brown colour. The other $d-d$ bands possibly remain hidden by the intense $\pi \rightarrow \pi^*$ transitions. The spectra of diamagnetic Cu(L)₂ complex show an intense band at 33.33kk ($\epsilon \sim 12222$) and 26.67kk ($\epsilon \sim 14400$). Harries *et al*²⁹ have proposed structure for the diamagnetic Cu(II) complex of diazoaminobenzene in which there is metal-metal interaction and Cu(II) ion has square planner geometry. Tsuchida and co-workers³⁰⁻³¹ indicated that all the copper complexes in which the paramagnetism is partially or completely quenched absorb around 26.66KK region. In our complex, a band at 26.66kk appeared which may be similar band as detected by Tsuchida and co-workers³⁰⁻³¹. This complex is completely insoluble in all noncoordinating solvents. Thus, the insolubility in the inorganic and organic noncoordinating solvents, stoichiometry diamagnetism, visible and IR spectral data indicate square-planar polymeric structure for the copper complex.

The PMR spectra

The PMR spectrum of metal complexes Co(L)₂ and Cu(L)₂ in (D₆) DMSO solvent reveals absence of oximino proton and N-H proton which is shown at 12.4 δ and 12.0 δ in free ligand respectively, may suggested coordination of oximino nitrogen and/or oxygen and azomethine nitrogen to central metal ion. A singlet shown at 13.8 δ assigned to imino CH=N proton⁹, may suggest non involvement of this group in complexation. A singlet at 1.2 to 1.50 δ assigned to the methyl group, occurs at the usual position for methyl proton in the ligand. A broad multiplet at 7.0 to 8.0 δ has its origin in the phenyl ring protons of the ligand.

Table 2. PMR data of the ligand and its metal complexes.

Compound	Assignment- δ in ppm							
	-CH ₃	DMSO	Water in DMSO	Phenyl ring	CH=N	N-H ₂	N-H	N=OH
HL	1.50	2.5	3.4	7.1-8.0	10.7	-	12.0	12.4
HL D ₂ O shaking	1.5	2.5	3.7	7.1-8.0	-	-	-	-
Co(L) ₂	1.2, 1.5	2.5	3.3	7.0-8.0	13.8	-	-	-
[Cu(L) ₂] ₂	1.2, 1.5	2.5	3.5	7.0-8.0	Not determined	-	-	-

Table 3. IR data of the ligand and its metal complexes.

Compound	ν O-H cm ⁻¹	oximino ν N-H cm ⁻¹	ν C-H Ar cm ⁻¹	ν C=N cm ⁻¹ new M-S-C=N	ν C=N cm ⁻¹ azomethine	ν C=N cm ⁻¹ imino	ν C=N cm ⁻¹ oximino	N-C=S	ν C=S with ν C=C cm ⁻¹	ν N $\rightarrow$ O cm ⁻¹ new	ν N-O cm ⁻¹	δ N-H ν N-N cm ⁻¹
HL	3226	3260	3000	-	1602	1521	1442	1491	1286	1180 ν N=O	1006	1562945
Co(L) ₂	-	3386	3066	1633	1595	1520	1439	1496	1254768	1312	1015	1570903
Ni(L) ₂	-	3419	3073	-	1589	-	1447	1488	1283766	1250	1016	1570905
[Cu(L) ₂] ₂	-	3406	3054	1632	1597	1519	1447	1489	1292767	-	1003	1567

The infrared spectrum in KBr

The characteristic IR bands 400-4500 cm⁻¹ for the free ligand from those of its complex provide significant indications regarding the bonding sites of the ligand. A common feature of the infrared spectra of metal complex in KBr discs is the absence of any absorption bands attributable to the various O-H vibrations like ν O-H, in plane and out of plane δ O-H seen at 3225, 1265 and 897 cm⁻¹ respectively in the spectrum of HL. This observation is amply supported by the fact that the complex is insoluble in the dilute alkali solutions indicating an absence of free oxime function in them. A medium intense band between 3385 to 3406 cm⁻¹, may be due to presence of secondary amines N-H vibrations¹²⁻¹³. Apart from these band, the complex show a weak intensity band around 1369 cm⁻¹ to 1393 cm⁻¹ which may be due to δ N-H vibrations. On the loss of -NH proton in phenyl methylene hydrazide moiety in the complex, an additional ν C=N absorption is found at higher energy than ν C=N of the uncomplexed hydrazide. This new absorption band observed at 1633-1632 cm⁻¹ for Co(II) and Cu(II) complex which is not shown in spectra of free ligand may be attributed to C=N vibration formed due to complexation of sulfur to the central metal ion, supported by shifting of absorption band observed due to ν C=S and free δ C=S to 1253-1292 and 768-766 cm⁻¹ respectively. These two bands observed at 1286 and 762 cm⁻¹ in free ligand respectively, the shifting of these bands to indicative of coordination of thiolate sulfur to central metal ion³². An absorption band observed due to ν C=S and free δ C=S to 1283 cm⁻¹ and 766 cm⁻¹ in spectra of Ni(II) complex, indicative of non coordination of thiolate sulfur to central metal ion. The absorption bands observed in between 1589 to 1597 cm⁻¹ are tentatively proposed to be due to azomethine and 1439 to 1447 cm⁻¹ tentatively proposed to be due to oximino C=N stretching vibration respectively. The downfield shift of these bands suggested azomethine

nitrogen and oximino nitrogen and/or oxygen coordination to the central metal ion³³⁻³⁵. One more band observed in this region at 1520 cm^{-1} due to $\text{HC}=\text{N}$ of imino nitrogen in free ligand observed in shape of shoulder and merged with an medium intense band at 1488 , and 1496 cm^{-1} may be due to $\text{N}-\text{C}=\text{S}$, may be suggested non involvement in complexation, as evident from PMR spectral data⁵. An oxime function is known to coordinate to the metal ion either through nitrogen or oxygen atom³⁶⁻³⁸. In the spectra an medium intensity band observed at 1003 to 1016 cm^{-1} attributed to the formation of $\text{N}-\text{O}$ linkage and a medium intensity band observed at 1132 to 1142 cm^{-1} is also assigned perhaps erroneously to the $\text{N}-\text{O}$ stretching vibrations^{3,39-40}. This may indicate the metal complexes with the ligand, in which an oxime group coordinate through oximino oxygen to the central metal ion^{3,36}. The newly formed medium intensity band at 1250 to 1312 cm^{-1} in Co(II) and Ni(II) complex respectively, due to $\text{N} \rightarrow \text{O}$ linkage may be suggested an oxime group coordinates through its nitrogen atom. The presence of the $\text{N}-\text{O}$ and $\text{N} \rightarrow \text{O}$ linkage in complex may indicate $\text{M}-\text{N}_3\text{O}$ type of chromophore with an unsymmetrical five and six member ring structure becomes probable when these two bands observed, may suggested the bonding through both the nitrogen as well as oxygen atoms of the oxime function³. In Cu(II) complex, no band observed in range of 1200 to 1300 cm^{-1} due to $\text{N} \rightarrow \text{O}$ linkage may be suggested an oxime group coordinates through its oxygen atom only. The presence of the $\text{N}-\text{O}$ linkage in complex may indicate $\text{M}-\text{N}_2\text{O}_2$ type of chromophore with a symmetrical six member ring structure.

Another set of medium intensity band at 694 cm^{-1} may be due to out of plane $\text{C}=\text{C}$ bending vibration of aromatic ring, supported a weak band 3054 to 3073 cm^{-1} due to $\text{C}-\text{H}$ stretching. Another weak absorption at 2922 to 2987 cm^{-1} may be due to $\text{C}-\text{H}$ stretching vibration of free methyl group. The proposed five and six member ring structure would require the appearance of $\text{M}-\text{N}$, $\text{M}-\text{O}$ and $\text{M}-\text{S}$ vibration, have been reported to occur over a wide range 200 to 650 cm^{-1} . The numbering scheme and tentative structure assigned to M(L)_2 is shown in the Scheme 1, 2 & 3, where M is Co(II) , Ni(II) and Cu(II) :

Scheme 1.

Scheme 2.

Scheme 3.

Conclusion

From the present investigation it has been observed that there is a possibility of formation of a new ligand *N*"-[(1*Z*,2*E*)-2-(hydroxyimino)-1-phenyl propylidene]-*N*"'-[(1*E*)-phenylmethylene] thiocarbonohydrazide and its complexation with metal ions like Co(II), Ni(II) and Cu(II). The data explain its geometrical symmetries *i.e.* low spin octahedral, square planar and square-planar polymeric structure respectively.

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