

Synthesis and Characterization of 2-(Hydroxyimino)-1-(phenylpropylidene)thiocarbonohydrazide and its Metal Complexes with Co(II), Ni(II) and Cu(II) Ions

A.VENKATCHALLAM*, R.G.DESHMUKH and DILIP C. SAWANT.

Department of P.G. Studies & Research in Chemistry,
Bhavan's College, Andheri (w), Mumbai- 58, India.
avenkatchalam@yahoo.co.in; dilip@hindustanmonomers.com

Received 18 December 2008; Accepted 5 February 2009

Abstract: Synthesis and characterization of 2-(hydroxyimino)-1-(phenyl propylidene) thiocarbonohydrazide (called 'HPTCHOPD') was studied. The synthesized compound having the molecular formula $C_{10}H_{13}N_5OS$, where in isonitrosopropiophenone is reacted with thiocarbonohydrazide in presence of sodium acetate in ethanol-water mixture. The yield which is comprises effecting the reaction in the presence of sodium acetate. Also the present work report a process for producing metal complexes having the formula ML_2 and $(ML)_2Cl$, wherein M is the divalent metal cation, like cobalt (Co^{+2}), nickel (Ni^{+2}) and copper (Cu^{+2}). The compound HPTCHOPD is admixed with a basic divalent compound that is halide, mainly chloride of Co^{+2} , Ni^{+2} and Cu^{+2} in presence of methanol-water mixture. The metal complexes so produced are characterized on the basis of spectral, elemental and magnetic analysis; reveal interesting geometries and bonding features. The data suggested square planar geometry for Co^{+2} complex, a distorted tetrahedral/square planar-octahedral geometry for Ni^{+2} complex and a bridged structure for Cu^{+2} complex.

Keywords: Isonitrosopropiophenone, Thiocarbonohydrazide, Anomalous magnetic moments.

Introduction

Isonitrosopropiophenone belongs to a rather widely studied class of oximino^{1,2} ligands. The significance of this class of ligands lies in their bifunctionality and ambidentacy as well as a variety of analytical applications³. The reactive group $-CO-C=NOH$ is capable of coordinating to the metal ion through carbonyl oxygen and oximino nitrogen and/or oxygen as donor atoms⁴. The carbonyl function in these ligands is susceptible to condensation with

compounds containing free NH_2 group to yield an interesting set of ligand called imino-oximes. The derivatives of isonitrosopropiophenone with the various types of amines like hydroxylamine, thiosemicarbazide are known. Scanning of literature shows that this premised derivative of isonitrosopropiophenone with thiocarbonylhydrazide belongs to similar family, is scantily reported with respect to its synthesis, characterization as well as its coordination chemistry with metal ions of transition as well as non-transition metals is reported for the first time. Thiocarbonylhydrazide $[\text{NH}_2\text{NHC}(\text{S})\text{NHNH}_2]$ is useful in analytical chemistry for the identification and estimation of both organic and inorganic compounds⁵. It is expected to yield mono and/or dihydrazono derivatives containing N, O, and S donor atoms⁶. In this paper we report the synthesis and characterization of N'' -[(1*E*,2*Z*)-2-(hydroxyimino)-1-phenylpropylidene]thiocarbonylhydrazide and its metal complexes with Co(II), Ni(II) and Cu(II).

Experimental

All chemicals used were of analytical grade. The elemental analyses were carried by standard methods⁷. 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 (D_6) DMSO. Chemical shifts relative to tetramethylsilane (TMS) used as internal standard were obtained in δ unit. Magnetic susceptibility measurements were carried out by employing Gouy's balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The effective magnetic moments were calculated after diamagnetic correction for ligand component using Pascal's constants⁸. The UV-visible spectrum was recorded on Shimadzu UV-190 spectrophotometer brand. Molecular weights were determined by Rast's method.

*Synthesis of N'' -[(1*E*,2*Z*)-2-(hydroxyimino)-1-phenylpropylidene] thiocarbonylhydrazide*

Isonitrosopropiophenone was prepared by following the procedure of Hartung and Munch⁹. Thiocarbonylhydrazide was prepared by following procedure of L.F.Audieth, Earle S., Scott and Pery S. Kippur¹⁰. As such for brevity, the ligand N'' -[(1*E*,2*Z*)-2-(hydroxyimino)-1-phenylpropylidene]thiocarbonylhydrazide is named 1-phenyl, 1-thiocarbonylhydrazido, 2-oximino, 1,2-propane dione so that it may be easily abbreviated as HPTCHOPD, where the first H signifies the removable proton in the molecule.

The HPTCHOPD was prepared by mixing hot aqueous solution of thiocarbonylhydrazide (10.0008 g, 0.0943 mole) with ethanolic solution of isonitrosopropiophenone (10.0022 g, 0.0613 mole) in presence of sodium acetate (20.0128 g), in a 100 mL three necked round the bottom flask fitted with a condenser, thermometer and separatory funnel. The mixture was refluxed for five hours on a water bath and kept overnight; hence a yellow solid was obtained. This was filtered through a buckner funnel at the suction pump and washed by large amount of water and dried in oven at 80 °C for one hour. The purity of product was monitored by TLC using silica gel. Analyzed for C, H, N and S by elemental analysis. [The yield of a product was 9.1802 g, 59.6164% of the theoretical. Melting point is 150 °C]. The ligand is insoluble in water, chloroform, acetonitrile and benzene. Partly soluble in methanol, ethanol and 0.5 M HCl. Soluble in DMF, DMSO, 0.5 M NaOH, conc. HCl and glacial acetic acid.

Synthesis of metal complexes

Co(PTCHOPD)₂

A solution of 0.9501 g (0.0040 mole) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 20 cm^3 water was added slowly and with stirring to hot solution of (2.0015 g, 0.0080 mole) HPTCHOPD in 30 cm^3 methanol(AR). pH of the reaction mixture was maintained at 4.5 and refluxed for 1 hours on water bath. Kept for overnight

in stoppered flask and the coffee colored solid thus obtained was filtered through suction and washed thoroughly with water. The complex was dried at 110 °C, crystallised from chloroform and analysed for Co, C, H, N and S. (Yield 1.3438 g, 60.3000% on theoretical basis).

Ni(PTCHOPD)₂

Ni(PTCHOPD)₂ was prepared similarly using of (0.9470 g, 0.0040 mole) NiCl₂.6H₂O in 20 cm³ water and 2.0007 g (0.008mole) of HPTCHOPD in 30cm³ methanol(AR).

Ni(PTCHOPD)₂.py

0.9126 g Ni(PTCHOPD)₂ was dissolved in 6.0 cm³ pyridine. The reaction mixture was then refluxed for half an hour and cooled to room temperature. It was slowly allowed to evaporate to dryness on petri dish. Then reddish colour solid thus appeared was recrystallised from diethyl ether and analysed for Ni, C, H, N and S. (Yield 0.9475 g, 90.9624% on theoretical basis).

Cu(PTCHOPD)Cl

A solution of 1.7051 g (0.0100mole) of CuCl₂.2H₂O in 25 cm³ water was added slowly with stirring to hot solution of 2.5022 g (0.0100 mole) of HPTCHOPD in 35cm³ methanol(AR). Refluxed for one hour on water bath and kept for overnight in stoppered flask and the greenish brown colored solid thus obtained was filtered through suction and washed thoroughly with water. The complex was dried at 110 °C and analysed for Cu, C, H, N and S. (Yield 1.7403 g, 50.0207% on theoretical basis).

Results and Discussion

Characterization of the ligand HPTCHOPD

The analytical data of the ligand and its complexes are given in Table 1. The molecular weight of the ligand HPTCHOPD was found to be 249 (Expected 251) by using Rast's method corresponds to the empirical formula C₁₀H₁₃ON₅S hence it is suggested that the ligand is monomeric in nature. It was obtained in a crystalline form, which melts at 150 °C. Solubility of product in dilute alkali and dilute acid solutions indicating the acidic nature of the oximino proton and the protonable free NH₂ group which may form a salt with the acid solution.

UV-Visible spectral properties

A methanolic solution spectrum of HPTCHOPD in the UV region (Table 1) shows a prominent peak at 41.67 kk ($\epsilon=12600$). This may be ascribed to the π electron system arising from significant conjugation in the ligand (Table 2). It seems that owing perhaps, to a higher degree of conjugation in HPTCHOPD the two types of $\pi \rightarrow \pi^*$ transitions expected¹¹, are overlapping with each other. The UV spectrum of HPTCHOPD in dilute NaOH solution reveals a band at 44.84 kk ($\epsilon=12343$) and a suppressed, bathochromically shifted broad band around 33.90 kk ($\epsilon=9853$). It is suggested therefore that the band at 33.90 kk in the UV spectrum of HPTCHOPD may be due to the oximino function while the band at 44.84 kk may be due to the thiocarbonohydrazido function.

The PMR spectra

The PMR spectrum of HPTCHOPD in (D₆)DMSO solvent reveals the oximino proton at 12.4 δ since it is expected to be rather acidic and therefore the weakest shielded proton in the molecule. A broad peak corresponding to ~two protons, is observed at 4.5 δ . The intensity of the peak suggests that it appears to be due to the presence of terminal-NH₂ group in the ligand. A singlet at 2.10 δ assigned to the methyl group, occurs at the usual position for methyl proton in the ligand. The one proton signal of the NH group may be merged in broad band of the NH₂ proton. A broad multiplet Between 7.4 to 7.8 δ has its origin in the phenyl ring protons of the ligand. The signal at 8.6 δ , then be ascribed to either the NH or SH moiety, such an assignment is favored by the thione=thiol tautomerism possible in the ligand.

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

Compound	Colour	Yield %	Melting point / Dec.point °C	Elemental Analysis					Magnetic Moments μ B.M.	Electrical Conductance 10^{-3} M(in DMF) mhos
				% M Found (Calcd)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% S Found (Calcd)		
HPTCHOPD	Yellow	59.6	150	-----	47.70 (47.81)	5.22 (5.18)	28.02 (27.89)	13.05 (12.75)	----	0.018
Co(PTCHOPD) ₂	Coffee	60.3	262	10.20 (10.54)	43.40 (42.94)	4.30 (4.29)	24.80 (25.05)	11.42 (11.45)	2.28	0.3437
Ni(PTCHOPD) ₂	Coffee	72.3	>290	11.03 (10.51)	42.62 (42.96)	4.20 (4.30)	25.50 (25.06)	11.64 (11.46)	1.73	0.0701
Ni(PTCHOPD) ₂ .py	Coffee	90.9	211-215	8.6 (9.21)	46.90 (47.04)	4.20 (4.55)	24.61 (24.15)	10.60 (10.04)	1.86	0.0843
Cu(PTCHOPD)Cl	Greenish brown	50.0	>280	17.70 (18.21)	34.50 (34.38)	3.20 (3.44)	19.70 (20.05)	10.05 (9.17)	1.60	0.5063

Table 2. Electronic spectral data for HPTCHOPD and its metal complexes.

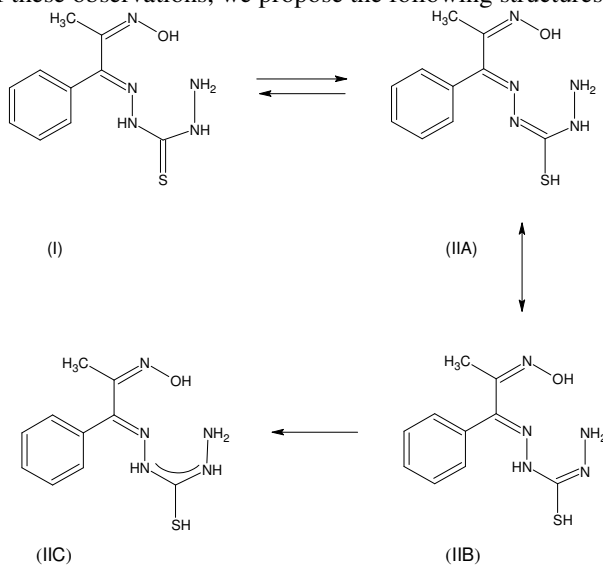
No.	Compound	Solvent	Band position in kk	Intensity ϵ	Assignment
1	HPTCHOPD	Methanol	41.67	12600.0	$\pi - \pi^*$ transition
			44.84	12343.1	$\pi - \pi^*$ transition
		0.1N NaOH	33.90	9853.6	$\pi - \pi^*$ transition
2	$\text{Co}(\text{PTCHOPD})_2$	Methanol	42.55	18683.5	Intra ligand transition
			32.26	14733.9	Charge transfer M→L transition
		CHCl_3	24.39 – 23.81	~ 1052.9	Charge transfer M→L transition
			22.73 – 20.83	~ 1088.2	Charge transfer M→L transition
			35.71	6826.35	Intra ligand transition
			28.17	3512.97	Charge transfer M→L transition
3	$\text{Ni}(\text{PTCHOPD})_2$	Methanol	27.78 – 17.54	~ 880	Charge transfer M→L transition
			13.70 – 12.99	~ 780	d – d transition are masked by the Charge transfer transition
		CHCl_3	39.22	6819.9	Intra ligand transition
			35.71	6257.0	Intra ligand transition
			28.17	3395.8	Charge transfer M→L transition
			25.00 – 24.39	~ 1971	Charge transfer M→L transition
			20.83 – 20.00	~ 2152	Charge transfer M→L transition
			13.51 – 13.16	~ 285.4	d – d transition are masked by the Charge transfer transition
4	$\text{Ni}(\text{PTCHOPD})_2 \cdot \text{py}$	Methanol	39.22	6819.9	Intra ligand transition
			35.71	6257.0	Intra ligand transition
		CHCl_3	28.17	3395.8	Charge transfer M→L transition
			25.00 – 24.39	~ 1971	Charge transfer M→L transition
			20.83 – 20.00	~ 2152	Charge transfer M→L transition
			13.51 – 13.16	~ 285.4	d – d transition are masked by the Charge transfer transition

The infrared spectrum

The FT infrared spectrum of HPTCHOPD in KBr disc in the region $4500\text{--}400\text{ cm}^{-1}$. A significant feature of the IR spectrum of HPTCHOPD is the absence of a strong band due to $\nu\text{C=O}$ seen at 1661 cm^{-1} in isonitrosopropiophenone, indicating a successful replacement of the carbonyl oxygen by the thiocarbohydrazone group, during schiff base formation. The spectrum of HPTCHOPD shows sharp peaks at 3306 cm^{-1} , which are ascribed to the asymmetrical and symmetrical vibrations of the $-\text{NH}_2$ group present in the ligand (Table 3). The appearance of the symmetrical and asymmetrical N-H vibrations in HPTCHOPD at frequencies lower than the expected may be due to strong inter and/or intra molecular hydrogen bonding in the ligand. This is further supported by the observed absorption due to

the ν O-H of the oximino group at $\sim 3270\text{ cm}^{-1}$, since the O-H vibrations are also expected to lower down from their usual range of $\sim 3500\text{ cm}^{-1}$ on account of H-bonding. The broad moderate intensity band at 1646 cm^{-1} may be chiefly due to the perturbed C=N stretching vibrations of the azomethine ($>\text{C}=\text{N}-\text{NH}_2$) groups in HPTCHOPD with perhaps a small contribution from the C-C vibration not being ruled out. The intense band at 1618 cm^{-1} shows $\nu\text{C}=\text{N}$ stretching vibration of the oximino ($>\text{C}=\text{NOH}$) groups in HPTCHOPD. The band observed at 1000 cm^{-1} may be assigned to $\nu\text{N}-\text{O}$ stretching vibrations. In isonitrosopropiophenone a peak at 997 cm^{-1} is attributed to $\nu\text{N}-\text{O}$. The characteristic absorption of the ligand in the range of 1287 cm^{-1} is proposed to $\nu\text{C}=\text{S}$ combination band with C=C, it is affected by various factors including adjacent group. A medium intense band at 1533 cm^{-1} shows C-S-H linkage, which is shown at 1531 cm^{-1} in parent compound thiocarbohydrazide. Also the weak band at 1262 cm^{-1} ascribed -C(S)-N< linkage, which is shown at similar frequency in parent compound thiocarbohydrazide. A weak band at 2345 cm^{-1} may be ascribed to the single bond C-S vibration due to its thione-thiol tautomerism, which is shown at around 2346 cm^{-1} in thiocarbohydrazide.

On the basis of these observations, we propose the following structures to the ligand:



Scheme 1.

Characterization of metal ion complexes of HPTCHOPD

Elemental analysis data of the complexes of HPTCHOPD with Ni(II), Co(II), can be represented by the general formula ML_2 and analysis data of the Cu(II) complex suggested the formula $[\text{Cu}(\text{L})\text{Cl}]_2$ for it (Table 1). The pyridine adducts of the Ni(II) complex may be described by the formula $\text{ML}_2\cdot\text{py}$. All the complexes prepared, have been found to be insoluble in dilute NaOH solution suggesting the absence of oximino proton ($>\text{C}=\text{NOH}$), in these complexes. All complexes are insoluble in water: partly soluble in methanol, ethanol, and chloroform and highly soluble in DMF, DMSO. The complexes are all stable up to 200°C indicating high thermal stability and hence strong metal to ligand bond. In order to check the purity of the complexes prepared the ligand HPTCHOPD and its soluble metal complexes were subjected to TLC studies. The results of the electrical conductance measurements of the soluble complexes in dimethylformamide (DMF) show that they are non-electrolytic in nature.

Table 3. Infrared spectral data for HPTCHOPD and its metal complexes.

Compound	$\nu\text{O-H}$ cm^{-1}	$\nu\text{N-H}$ cm^{-1}	$\nu\text{C-S-H}$ cm^{-1}	$\nu\text{C=N}$ cm^{-1} azo methine	$\nu\text{C=N}$ cm^{-1} oximino	$\nu\text{C=S}$ with $\nu\text{C=C}$ cm^{-1}	$\nu\text{N}\rightarrow\text{O}$ cm^{-1}	$\nu\text{N-O}$ cm^{-1}	$\delta\text{N-H}$ cm^{-1}	$\nu\text{M-N}$ cm^{-1}	$\nu\text{M-O}$ cm^{-1}
HPTCHOPD	3273 oximino	3306 3209	2345	1647	1618	1287	1185 $\nu\text{N=O}$	1000	1560 936	-----	-----
Co(PTCHOPD) ₂	-----	3308 3056	2344	1636	1617	-----	1205	-	1559 922	616	-----
Ni(PTCHOPD) ₂	-----	3308	2345	1636	1617	-----	1203	-	1560 903	616	-----
Ni(PTCHOPD) ₂ Py	-----	3146	2344	1636	1617	-----	1203	-	1559 922	617	-----
Cu(PTCHOPD)Cl	-----	3342 3198	2344	1636	1617	-----	1240	-	1560 850	618	-----

Magnetic susceptibility measurements

The coffee coloured, Co(PTCHOPD)₂, complex shows magnetic moments of 2.80 B.M. (Table 1) at room temperature. Octahedral cobalt(II) complexes normally exhibit magnetic moments in the range of 4.7–5.2 B.M.⁸ whereas tetrahedral Co(II) complexes are known to have moments of 4.2–4.8B.M. The magnetic moments of the square planar Co(II) complexes are expected to show higher magnetic moments than the spin only value of 1.73B.M. This is perhaps due to the ineffective quenching of the orbital moments, in a square planar ligand field. As such, the observed room temperature magnetic moments is 2.80B.M. are within the range expected for square planar Co(II) complexes. The coffee coloured Ni(PTCHOPD)₂ reveals weak paramagnetism at room temperature, with the magnetic moment of 1.73B.M. The phenomenon of intraligand where in the same complex exists in different geometrical configurations, could be a possible explanation for such intermediate magnetic moments for the Ni(II) complex. Examples of square planar-octahedral or square planar-tetrahedral complexes are known^{12,13}, where the magnetic moments are found to vary zero to 3.20B.M. It is possible that such an intermediate magnetic moment as observed in the present case of Ni(PTCHOPD)₂ may arise due to the coexistence in the solid state of two species in equilibrium which contain bivalent nickel in the triplet (paramagnetic) and singlet (diamagnetic) ground terms. However further studies like low temperature magnetic measurements are required to arrive at any precise idea about the structure of this complex. The magnetic moment of Ni(PTCHOPD)₂.Py are 1.86B.M. shows that the nature of pyridine adduct is similar to Ni(PTCHOPD)₂. [Cu(PTCHOPD)Cl] shows a room temperature magnetic moment of 1.60B.M., which is lower than the spin only expected value of 1.73B.M. for Cu(II) complexes. Octahedral Cu(II) complexes are known to exhibit higher moments ranging from 1.75–2.2B.M. low magnetic moments for Cu(II) complexes may occur due to antiferromagnetic coupling which may arise due to possible copper-copper interactions¹⁴. In many bridging complexes, wherein two Cu(II) centers are bridged through O, OH⁻ or X⁻ ligands, lower magnetic moments are reported. Consistent elemental analysis and TLC studies conforms with the composition [Cu(PTCHOPD)Cl] for this complex. As such it is tentatively suggested that the complex may be polymeric, atleast dimeric such that two copper(II) species are bridged by Cl⁻ ligand. Such a structure conforms to a square planar geometry and the observed low magnetic moments for the complex, at room temperature.

UV-Visible spectral properties

The electronic spectra of the metal complexes in methanol solution in the ultra-violet region show absorption bands due to the $\pi \rightarrow \pi^*$ transition in the region 31.25 to 42.55 kk. These bands are found to be shifted as compared to the position of the $\pi \rightarrow \pi^*$ transition band in methanol solution of HPTCHOPD. This indicates that the π electrons system of the ligand suffers considerable alteration on complex formation. The $\text{Co}(\text{PTCHOPD})_2$ complex exhibits two bands in chloroform at 20.83-22.73kk ($\epsilon \approx 1088$) and 23.81-24.39 kk ($\epsilon \approx 1052$) which attribute to charge transfer transitions and assigned to ${}^2A_{1g} \rightarrow {}^2B_{1g}$ and ${}^2A_{1g} \rightarrow {}^2E_g$ transition respectively, in view of the available report of square planar Cobalt(II) complexes¹⁵⁻¹⁶. The electronic spectrum of $\text{Ni}(\text{PTCHOPD})_2$ in chloroform solution does not conform to the spectrum of Ni(II) in an octahedral/tetrahedral environment. Neither does it agree to a square planar geometry for the nickel ion. The band at 12.99-13.70 kk ($\epsilon = 780$) has a high intensity not typical of octahedral or tetrahedral Ni(II) ion however, presence of this band is also a typical to the square planar environment. High intensities for Ni(II) complexes in tetragonally distorted complexes are possible⁴. However the strong bands at 20.0 kk ($\epsilon = 880$) and 27.78 kk ($\epsilon = 856$) are perhaps due to square planar geometry, which is expected to show absorption in this region due perhaps to the transition ${}^1B_{1g} \rightarrow {}^1A_{2g}$ and ${}^1B_{1g} \rightarrow {}^1B_{2g}$. However, the intensities observed, suggest that these transitions are masked by the charge transfer transitions. As such it is believed that the spectral data for this complex points towards an intrallogonous geometry for the complex, wherein square planar and octahedral geometries are in some form of equilibrium. However further work is required to arrive at some definite conclusion about the structure of the complex. On the basis of chemical analysis and magnetic data, the Coffee colour adduct of $\text{Ni}(\text{PTCHOPD})\text{Py}$ is suggested similar nature of complex than $\text{Ni}(\text{PTCHOPD})_2$. This complex exhibits bands in chloroform at 13.51-13.16kk ($\epsilon \approx 285$) which attributes d-d transition masked by charge transfer transition. Also two another bands observed at 20.00-21.28 kk ($\epsilon \approx 2152$) and 25.00-24.39 kk ($\epsilon = 1971.9$) attribute charge transfer transition. The electronic spectrum of $\text{Cu}(\text{PTCHOPD})\text{Cl}$ could not be recorded due to the poor solubility of this complex in most of the solvents tried.

ESR spectra

Electron spin resonance (ESR) spectroscopy has also been proved quite valuable in the characterization of $\text{Cu}(\text{PTCHOPD})\text{Cl}$. The ESR spectrum of the Cu(II) complex of ligand HPTCHOPD at room temperature and liquid nitrogen temperature shown an isotropic signal at $g = 2.16246$ corresponding to the presence of two copper atoms in a square planar geometry¹⁷⁻¹⁸. The presence of g values (g_{\perp}), computed by Piesach and Blumberg's method¹⁹ suggested a planar geometry for the Cu(II) ion. It was also interesting to note that solid-state spectrum of Cu-Cu homodinuclear complex at RT and LNT both showed zero fields splitting at 3250G and it also gets resolved in perpendicular region only. The ESR spectrums of the $\text{Co}(\text{PTCHOPD})_2$ complex at the room temperature and at the liquid nitrogen temperature g values are 2.01019 and 2.00895. This value is suggested for a strong field complex.

The infrared spectrum

A common feature of the infrared spectra of all the metal complexes in KBr discs is the absence of any absorption bands attributable to the various O-H vibrations like $\nu\text{O-H}$, in plane and out of plane $\delta\text{O-H}$ seen at 3273, 1262 and 896 cm^{-1} respectively in the spectrum of HPTCHOPD. This observation is amply supported by the fact that all the complexes are insoluble in the dilute alkali solutions indicating an absence of free oxime function in them.

All metal complexes of HPTCHOPD exhibits medium intensity bands in the region 3300 to 3100 cm^{-1} that can be attributed to $\nu\text{N-H}$ vibrations. Apart from these bands, the complexes also show a weak intensity band around 1560 cm^{-1} , which may be due to $\delta\text{N-H}$ vibrations. This suggests the non-involvement of NH_2 groups in bonding in these complexes. The two absorption bands observed in between 1638 cm^{-1} and 1616 cm^{-1} these are tentatively proposed to be due to the azomethine and oximino C=N stretching vibration respectively. In ligand HPTCHOPD, a medium band at 1287 cm^{-1} may be attributed to C=S , which is absent in all the metal complexes of this ligand and a weak band observed in all metal complexes at around 2345 cm^{-1} may be attributed to C-SH vibrational frequency. This band is observed at 2345 cm^{-1} in HPTCHOPD. This may be suggests that in complex, ligand may be in thiol form and these unaffected C-SH band may be due to the noninvolvement of sulphur group to the metal ions of all the metal complexes of HPTCHOPD. The presence of two medium intensity bands at 1200-1300 cm^{-1} and 1100-1000 cm^{-1} ascribed respectively to the nitrogen bonded $\nu\text{N}\rightarrow\text{O}$ and oxygen bonded $\nu\text{N-O}$ vibrations. The last mentioned feature of the infrared spectra of these complexes inputs the possibility of:

1. M-N_4 type of chromophore with a symmetrical five membered ring structure for $\text{Co}(\text{PTCHOPD})_2$, $\text{Ni}(\text{PTCHOPD})_2$ and pyridine adduct of $\text{Ni}(\text{PTCHOPD})_2$. The analytical and spectral data of $\text{Co}(\text{PTCHOPD})_2$ tentatively suggested the square planar geometry. The anomalous magnetic behavior of $\text{Ni}(\text{PTCHOPD})_2$ may be due to slight interaction of metal ion with the sulphur of C-SH group of the neighboring molecule. Therefore it is suggested this complex may be distorted tetrahedron/square planar-octahedral geometry.
2. M-N_4 type of chromophore with a symmetrical five membered ring structure for $\text{Cu}(\text{PTCHOPD})\text{Cl}$. The analytical and spectral data of the complex tentatively suggested that the complex is polymeric, at least dimeric such that two copper(II) species are bridged by Cl^- ligand.

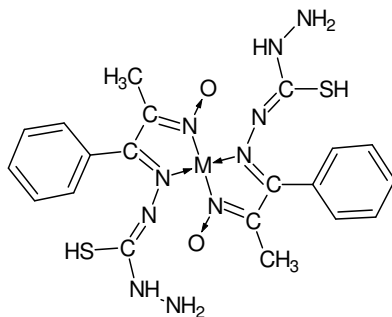


Figure 1. Proposed structure of $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ complex of HPTCHOPD.

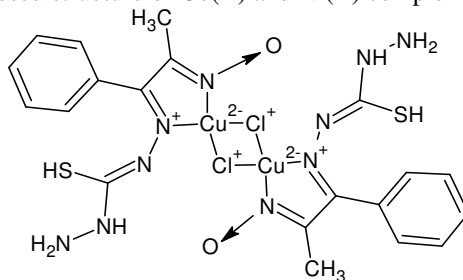


Figure 2. Proposed structure for $\text{Cu}(\text{II})$ complex of HPTCHOPD.

Conclusion

From the present investigation it has been observed that there is a possibility of formation of a new ligand of isonitrosopropiophenone with thiocarbohydrazide in 1:1 ratio and its complexation with metal ions like Co(II), Ni(II) and Cu(II). The data explain its geometrical symmetries *i.e.* square planar for Co(PTCHOPD)₂, Intrallogony for Ni(PTCHOPD)₂ and square planar bridged for Cu(PTCHOPD)Cl.

Acknowledgement

The authors wish to acknowledge the encouragement given by the H.R.Bandodkar Managing Director, Hindustan Monomers Pvt Ltd Dombivli. They are also thankful to the Head, Chemistry Department, IIT Mumbai, for the PMR and ESR spectral measurements, and The Director, The Institute of Science Fort Mumbai, for magnetic measurements. The help rendered throughout the present work by Mr.B.R.Aware, M/s ALTA Laboratories Limited Khopoli and M/s Hindustan Monomers Pvt. Ltd. Dombivli is gratefully acknowledged.

References

1. Chakravorty A, *Coord Chem Rev.*, 1974, **13**, 1.
2. Haldar B C, *J Indian Chem Soc.*, 1974, **51**, 224.
3. Singh R B, Garya B S and Singh R P, *Talanta*, 1979, **26**, 425.
4. R.G.Deshmukh, "Structural studies on some metal complexes of isonitrosopropiophenone", M.Sc Thesis. (by Research), University of Bombay, 1983.
5. Buu-Hoi N P and Loc T B, Xuong N D, *Bull Soc Chirn (France)*, 1955, 694; *Chem Abstr.*, 1956, **50**, 8375a
6. Ward D U, Shah C D, Kulkarni V H and Chandrasekhar S Bajgur, *Indian J Chem.*, 2000, **39A**, 415-420.
7. Jeffery G H and Bassett J, Longman Publication, Vogel's Textbook of Quantitative Chemical Analysis, 5th Ed., 1996,
8. Dutta R L and Syamal A, Elements of Magnetochemistry, S Chand & Company Ltd., Ramnagar, New Delhi, 1982.
9. Hartung W and Munch J C, *J Am Chem Soc.*, 1929, **51**, 2264.
10. Audrieth L F, Earle S Scott and Perry S Kippur, *Chem Abstr.*, 1955, 10857e.
11. Deshmukh R G, "Studies on transition metal complexes of some Imino-oximes", Ph.D Thesis, University of Bombay, 1992.
12. Rayner S H and Powell H M, *J Chem Soc.*, 1952, 319; *J Chem Soc.*, 1958, 3412.
13. Dave L D and Thampy S K, *Indian J Chem.*, 1981, **20A**, 405.
14. Furman N H, Standard Methods of Chemical Analysis, 6th Ed., Van Nostrand Reinhold Co., New York, 1962, **1**.
15. Patil R.B. *J Indian Chem Soc.*, 1983, **60**, 218.
16. Atre V, Reddy G V, Sharada L N and Ganorka M C, *Indian J Chem.*, 1982, **21A**, 935.
17. Daniel Kivelson and Robert Neiman, *J Chem Phys.*, 1961, 35,149.
18. El-Asmy A A, Al-Ansi T Y, Amine R R and Mounir M M, *Polyhedron*, 1990, **9**, 2029.
19. Peisach J and Blumberg W E, EPR of Metal Complexes Edited by Tech Fu Yen, Adam Higher Ltd. London, 1969, **71**.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

