

Synthesis and Characterization of Zn(II), Cd(II), Hg(II) and Pd(II) Complexes of N''-[(1E,2Z)-2-(hydroxyimino)-1-phenylpropylidene]thiocarbohydrazide

R.G. DESHMUKH*, DILIP C. SAWANT and SATISH G. PINGALE

Department of Chemistry, K.T.S.P. Mandal's, K.M.C. College

Khopoli, Raigad-410 203, India

E-mail: ravideshmukh@vsnl.net

The ligand, N''-[(1E,2Z)-2-(hydroxyimino)-1-phenylpropylidene]thiocarbohydrazide (HPTCHOPD) has been synthesized by condensation of isonitrosopropiophenone with thiocarbohydrazide in 1:1 molar proportion in presence of ethanol. The complexes of Zn(II), Cd(II), Hg(II) and Pd(II) with ligand HPTCHOPD have been synthesized and characterized. The diamagnetic nature of Zn(II), Cd(II), Hg(II), suggested tetrahedral geometry and square planar geometry for Pd(II) complexes.

Key Words: Isonitrosopropiophenone, Diamagnetic tetrahedral, Thiocarbohydrazide, Square planar.

INTRODUCTION

The ligand, N²-[(1E,2Z)-2-(hydroxyimino)-1-phenylpropylidene]-thiocarbohydrazide (HPTCHOPD) is mono basic in nature. Owing to bifunctionality and retained ambidentate nature of isonitrosopropiophenone, this ligand promises interesting coordination chemistry with a variety of metal ions¹⁻³. 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 atom⁴. Further, the coordination compounds formed with this ligand have potential application in analytical chemistry as well as in antimicrobial studies⁵. The carbonyl function in this ligand is susceptible to condensation with compounds containing free NH₂ group to yield an interesting set of ligand called imino-oximes. In the present paper we report the synthesis and characterization of metal complexes of Zn(II), Cd(II), Hg(II) and Pd(II) of N''-[(1E,2Z)-2-(hydroxy-imino)-1-phenylpropylidene]-thiocarbohydrazide (HPTCHOPD).

EXPERIMENTAL

All chemicals used were of analytical grade. The elemental analyses were carried by standard methods⁶. The molar conductance measurement of the complexes in dimethyl formamide were obtained using an equiptronic

EQ-660 conductivity meter. IR spectra were recorded on a FTIR-1615 of Perkin-Elmer spectrometer in KBr pellets. PMR spectrum of the ligand was recorded on Bruker AMX-500 spectrometer in (*d*₆)DMSO. Chemical shifts relative to tetramethyl 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 constants⁷. The UV-Visible spectrum was recorded on Shimadzu UV-190 spectrophotometer brand. Molecular weights were determined by Rast's method.

Synthesis of N''-[(1E,2Z)-2-(hydroxyimino)-1-phenylpropylidene]-thiocarbohydrazide: Isonitrosopropiophenone was prepared by following the procedure of Hartung and Munch⁸. Thiocarbohydrazide was prepared by reported method⁹.

HPTCHOPD was prepared by mixing hot aqueous solution of thiocarbohydrazide 10.000 g (0.094 mol) with ethanolic solution of isonitrosopropiophenone 10.002 g (0.061 mol) in presence of sodium acetate (20.012 g), in a 100 mL three necked round the bottom flask fitted with a condenser, thermometer and separatory funnel, the mixture was refluxed for 5 h on a water bath and kept overnight, a yellow solid was obtained. This was filtered through buckner funnel at the suction pump and washed by large amount of water and dried at 80 °C for 1 h. 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 9.1802 g, 59.61 % of the theoretical. Melting point is 150 °C]. The ligand is insoluble in water, chloroform, acetonitrile and benzene. Partly soluble in methanol, ethanol 0.5 M HCl. Soluble in DMF, DMSO, 0.5 NaOH, conc. HCl and glacial acetic acid.

Synthesis of metal complexes

Zn(PTCHOPD)₂: A solution of 1.145 g (0.004 mol) ZnCl₂·7H₂O in 20 cm³ water was added slowly and with stirring to hot solution of 2.001 g (0.008 mol) HPTCHOPD in 30 mL methanol AR. pH of the reaction mixture is maintained *ca.* 4.5 and refluxed for 1 h on water bath. It was kept for overnight in stoppered flask and the red coloured solid thus obtained was filtered through suction and washed thoroughly with water. The complex was dried at 110 °C, crystallized from chloroform and analyzed for Zn, C, H, N, and S (Yield 1.297 g, 57.52 % on theoretical basis).

Cd(PTCHOPD)₂: Cd(PTCHOPD)₂ was prepared similarly using of 0.733 g (0.004 mol) CdCl₂ in 20 mL water and 2.001 g (0.008 mol) HPTCHOPD in 30 mL methanol AR. The red colour solids obtained. The complex was dried at 110 °C, crystallized from chloroform and analyzed for Cd, C, H, N and S (Yield 0.579 g, 23.75 % on theoretical basis).

Hg(PTCHOPD)₂: Hg(PTCHOPD)₂ was prepared similarly using of 1.080 g (0.004 mol) HgCl₂ in 20 mL water and 2.002 g (0.008 mol) HPTCHOPD in 30 mL methanol AR. The red colour solids obtained. The complex was dried at 110 °C, crystallized from chloroform and analyzed for Hg, C, H, N and S (Yield 1.641 g, 58.74 % on theoretical basis).

Pd(PTCHOPD)₂ Red: A solution of 20 mL 1 % PdCl₂ (0.0005 mol) was added to a hot solution of 0.566 g (0.002 mol) HPTCHOPD in 20 mL methanol. The pH of the reaction mixture was maintained *ca.* 3 and reflux for 0.5 h. Kept for overnight in stoppered flask and the red coloured solid thus obtained was filtered through suction and washed thoroughly with water. The complex was dried at 110 °C, crystallized from chloroform and analyzed for Pd, C, H, N and S (Yield 0.190 g, 27.80 % on theoretical basis).

Pd(PTCHOPD)₂ Green: A solution of 20 mL 1 % PdCl₂ added in a slight warm solution of 0.565 g (0.002 mol) HPTCHOPD in 10 mL methanol. The pH of the reaction mixture is maintained *ca.* 3. Shake and stirred well, digest for 0.5 h in warm water bath. Kept for overnight in stoppered flask and the green coloured solid thus obtained was filtered through suction and washed thoroughly with water. The complex was dried at 110 °C, crystallized from chloroform and analyzed for Pd, C, H, N and S (Yield 0.448 g, 65.74 % on theoretical basis).

RESULTS AND DISCUSSION

The analytical data of the ligand and its complexes are given in Table-1. The molecular weight of the ligand HPTCHOPD is found to be 249 (expected 251) by using Rast's method suggests its monomeric nature.

UV-Visible spectral properties: A methanolic solution spectrum of HPTCHOPD in the UV region 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. It seems that owing perhaps, to a higher degree of conjugation in HPTCHOPD the two types of $\pi \rightarrow \pi^*$ transitions expected¹⁰, 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, bathchromically 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.

PMR spectra: PMR spectrum of HPTCHOPD in (*d*₆)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

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE LIGAND AND
ITS METAL COMPLEXES

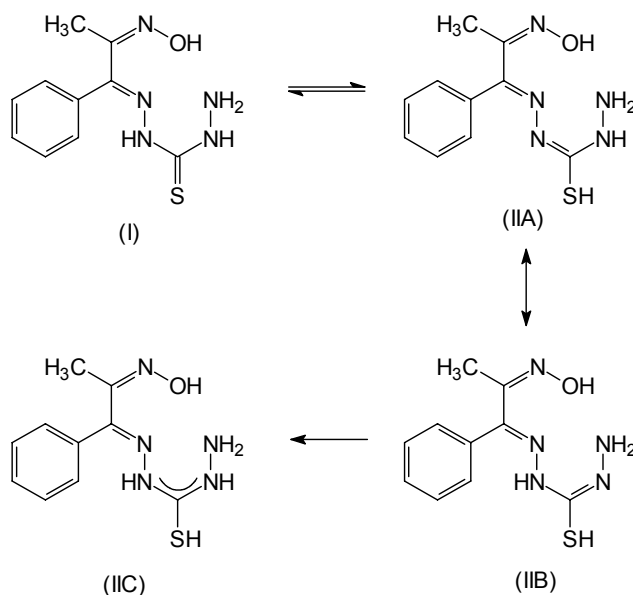
Compound (Colour)	Yield (%)/ m.p. (°C)	Elemental analysis: Found (Calcd.) %					Electrical conductance 10 ⁻³ M (in DMF) mhos
		M	C	H	N	S	
HPTCHOPD (Yellow)	59.6 (150)	–	47.70 (47.81)	5.22 (5.18)	28.02 (27.89)	13.05 (12.75)	0.0180
Zn(HPTCHOPD) ₂ (Red)	57.52 (>280)	11.63 (11.56)	42.10 (42.45)	4.20 (4.24)	24.90 (24.76)	11.92 (11.32)	0.0352
Hg(HPTCHOPD) ₂ (Red)	58.74 (>260)	28.12 (28.63)	33.92 (34.26)	3.52 (3.43)	20.11 (19.98)	9.29 (9.14)	0.0724
Cd(HPTCHOPD) ₂ (Red)	23.75 (176)	17.50 (18.36)	38.81 (39.19)	4.07 (3.92)	22.22 (22.86)	10.17 (10.45)	0.1096
Pd(HPTCHOPD) ₂ (Green)	65.74 (225)	17.23 (17.55)	39.71 (39.58)	3.82 (3.96)	22.82 (23.09)	10.62 (10.55)	0.1516
Pd(HPTCHOPD) ₂ (Red)	27.8 (225)	17.20 (17.55)	39.72 (39.58)	3.79 (3.96)	23.18 (23.09)	10.77 (10.55)	0.1379

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 have been merged to broad band. 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 favoured by the thione \rightleftharpoons thiol tautomerism possible in the ligand.

Infrared spectrum: The FT infrared spectrum of HPTCHOPD in KBr disc are performed in the region 4000-400 cm⁻¹. A significant feature of the IR spectrum of HPTCHOPD is the absence of a strong band due to $\nu(\text{C}=\text{O})$ seen at 1661 cm⁻¹ in isonitrosopropiophenone, indicating a successful replacement of the carbonyl oxygen by the thiocarbonyl group, during Schiff base formation. The spectrum of HPTCHOPD shows two sharp peaks at 3306 cm⁻¹, which may be ascribed to the asymmetrical and symmetrical vibrations of the -NH₂ group present in the ligand. 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 $\nu(\text{O}-\text{H})$ of the oximino group at *ca.* 3270 cm⁻¹, since the O-H vibrations are also expected to lower down from their usual range of *ca.* 3500 cm⁻¹ on account of H-bonding.

The broad moderate intensity band at 1646 cm^{-1} may be mainly 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 vibrations 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, the following structure of the ligand has been proposed:



Characterization of metal ion complexes of HTCHOPD

Elemental analysis data of the complexes of HPTCHOPD with Zn(II), Cd(II), Hg(II) and Pd(II) can be represented by the general formula ML_2 (Table-1). 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 the complexes are insoluble in water while partly soluble in methanol, ethanol and chloroform and highly soluble in DMF and 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 dimethyl formamide show that they are non-electrolytic in nature.

Magnetic susceptibility measurements: The observed diamagnetism, as shown by the room temperature magnetic moments of the red as well as green palladium(II) complexes reveals square planar geometry for these complexes, with a dsp^2 type hybridization¹¹. The $Zn(PTCHOPD)_2$, $Cd(PTCHOPD)_2$ and $Hg(PTCHOPD)_2$ also show diamagnetic nature, suggesting a tetrahedral geometry for these complexes.

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 (Table-2). 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 electronic spectrum of $Zn(PTCHOPD)_2$, $Hg(PTCHOPD)_2$ and $Cd(PTCHOPD)_2$ in chloroform solution reveals charge transfer transition in the region¹² 28-25 kk ($\epsilon = 598-951$). $Pd(PTCHOPD)_2$ occurs in two modification reactions, green and red. In the synthesis, the green form is first formed and is converted to the red form after refluxing. It is speculated without any substantial evidence that the two forms are *cis*- and *trans*-isomer¹³. A common feature of the electronic absorption in DMF solution for both red and green palladium complexes is the absence of any appreciable absorption beyond 14.00 kk. This is typical of square planar d^8 complexes. Gray and Ballhausen¹¹ have reported an analysis of the electronic absorption pattern of square planar d^8 complexes accordingly; such complexes are expected to show at least three $d-d$ transition bands. However, due to the proximity of this absorption the high intensity charge transfer transition, the former are marked. As such, the high intensity transition observed at 27.03-20.83 kk ($\epsilon = \sim 1379$) and 16.13-14.49 kk ($\epsilon = \sim 1272$) in green $Pd(PTCHOPD)_2$ and 22.22-18.52 kk ($\epsilon = \sim 1041$) and 14.49 kk ($\epsilon = 674.2$) in red $Pd(PTCHOPD)_2$, are suggested to be masked $d-d$ transition.

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 $\nu(O-H)$ in plane and out of plane $\delta(O-H)$ seen at 3273, 1262 and 896 cm^{-1} , respectively in the spectrum

TABLE-2
ELECTRONIC SPECTRAL DATA FOR HPTCHOPD AND ITS METAL COMPLEXES

Compound	Solvent	Band position (kk)	Intensity (ε)	Assignment
HPTCHOPD	Methanol	41.67	12600.0	π - π^* transition
	0.1 N NaOH	44.84	12343.1	π - π^* transition
		33.90	9853.6	π - π^* transition
Zn(PTCHOPD) ₂	Methanol	39.21	18686	Intra ligand transition
		34.48-33.33	~ 20040	Intra ligand transition
	21.50	3515	Charge transfer M→L transition	
	CHCl ₃	25.00-18.52	~ 598	Charge transfer M→L transition
Cd(PTCHOPD) ₂	Methanol	43.48-38.46	~ 13183	Intra ligand transition
		33.33-31.25	~ 13643	Intra ligand transition
	22.22-21.28	~ 2833	Charge transfer M→L transition	
	CHCl ₃	25.64-22.20	~ 951	Charge transfer M→L transition
Hg(PTCHOPD) ₂	Methanol	43.47-38.46	~ 6862	Intra ligand transition
		37.0-34.48	~ 6666	Intra ligand transition
	CHCl ₃	26.38-23.25	~ 618	Charge transfer M→L transition
Pd(PTCHOPD) ₂ Red	Methanol	45.45-30.30	~ 10442	Intra ligand transition
	CHCl ₃	22.22-18.52	~ 1041	Charge transfer M→L transition
		14.49	674.2	<i>d-d</i> transition are masked by the charge transfer transition
Pd(PTCHOPD) ₂ Green	Methanol	37.00-33.33	~ 23145	Charge transfer M→L transition
		23.80-22.22	~ 14620	Charge transfer M→L transition
	CHCl ₃	27.03-20.83	~ 1379	Charge transfer M→L transition
	CHCl ₃	16.13-14.49	~ 1272	<i>d-d</i> transition are masked by the charge transfer transition

of HPTCHOPD. This observation is 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 (Table-3). Apart from these bands, the complexes also show a weak intensity 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 and 1616 cm^{-1} these are tentatively proposed to be due to the azomethine and oximino $\text{C}=\text{N}$ stretching vibration, respectively.

TABLE-3
INFRARED SPECTRAL DATA (cm^{-1}) FOR HPTCHOPD AND
ITS METAL COMPLEXES

Compound	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\nu(\text{C-S-H})$	$\nu(\text{C=N})$ azomethine	$\nu(\text{C=N})$ oximino	$\nu(\text{C=S})$ with	$\nu(\text{C=C})$	$\nu(\text{N}\rightarrow\text{O})$	$\nu(\text{N-O})$	$\delta(\text{N-H})$	$\nu(\text{N-N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
HPTCHOPD	3273	3306	2345	1647	1618	1287	1185	1000	1560	-	-	-	-
		3209							936				
$\text{Zn}(\text{HPTCHOPD})_2$	-	3245	2344	1638	1617	-	1203	1007	1560	609	465		
		3184							904				
$\text{Cd}(\text{HPTCHOPD})_2$	-	3233	2344	1638	1616	-	1224	1009	1559	624	474		
		3202							904				
$\text{Hg}(\text{HPTCHOPD})_2$	-	3198	2344	1636	1617	-	1227	1009	1560	618	495		
									845				
$\text{Pd}(\text{HPTCHOPD})_2$	-	3309	2345	1624	1617	-	1268	1013	1522	615	473		
Red									912				
$\text{Pd}(\text{HPTCHOPD})_2$	-	3204	2344	1634	1617	-	1248	1008	1560	612	464		
Green									922				

In ligand HPTCHOPD, a medium band at 1287 cm^{-1} may be attributed to ($\text{C}=\text{S}$), which is absent in all the metal complexes of this ligand and a weak and 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 suggest that in complex, ligand may be in thiol form and these unaffected C-SH band may be due to the non-involvement of sulphur group to the metal ions of all the metal complexes of HPTCHOPD.

The infrared spectra of $\text{Zn}(\text{PTCHOPD})_2$, $\text{Cd}(\text{PTCHOPD})_2$ and $\text{Hg}(\text{PTCHOPD})_2$ shows two bands around 1100-1000 and 1300-1200 cm^{-1} would mean $\text{M-N}_3\text{O}$ type of chromophore with an unsymmetrical five and six membered ring structure, it is suggested that bonding through both the nitrogen as well as oxygen atoms of the oxime function. The medium band

at 1203 and 1007 cm^{-1} for $\text{Zn}(\text{PTCHOPD})_2$; at 1203 and 1009 cm^{-1} for $\text{Cd}(\text{PTCHOPD})_2$, at 1227 and 1009 cm^{-1} for $\text{Hg}(\text{PTCHOPD})_2$, which may be attributed to $\nu(\text{N}\rightarrow\text{O})$ and $\nu(\text{N}-\text{O})$ vibrations, respectively. The weak bands observed in the region 624-609 and 495-465 cm^{-1} may be attributed to M-N and M-O vibrations, respectively. The proposed tetrahedral structure of these complexes is as followed:

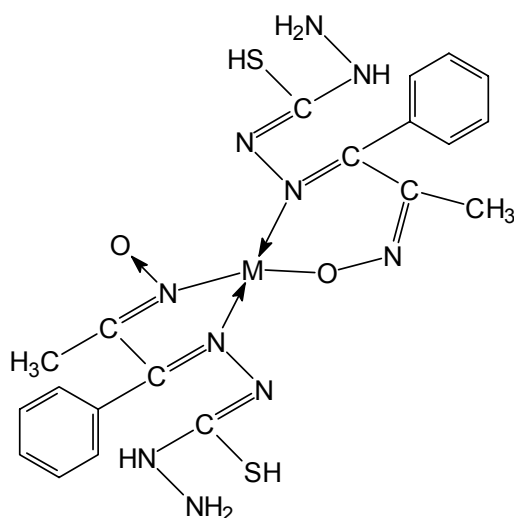


Fig. 1. Proposed structure for Zn(II), Cd(II) and Hg(II) complexes of HPTCHOPD

The IR spectra of green and red $\text{Pd}(\text{PTCHOPD})_2$ complexes are revealingly similar with marked splitting of the common bands in the green than their red counter parts. Consequently, owing to the multitude of bands in the green $\text{Pd}(\text{PTCHOPD})_2$, a *cis* and *trans* structure, shown more bands than the latter¹⁴. It should be interesting to study further the nature of these two Pd(II) complexes. The medium band at 1268 and 1013 cm^{-1} for red $\text{Pd}(\text{PTCHOPD})_2$ and at 1248 and 1008 cm^{-1} for green $\text{Pd}(\text{PTCHOPD})_2$; which may be attributed to $\nu(\text{N}\rightarrow\text{O})$ and $\nu(\text{N}-\text{O})$ vibrations, respectively. Would mean M-N₃O type of chromophore with an unsymmetrical five and six membered ring structure, it is suggested that bonding through both the nitrogen as well as oxygen atoms of the oxime function. The weak bands observed at 615 and 473 cm^{-1} in red $\text{Pd}(\text{PTCHOPD})_2$ and at 612 and 464 cm^{-1} in green $\text{Pd}(\text{PTCHOPD})_2$ may be attributed to M-N and M-O vibrations, respectively. The proposed square planar structure of these complexes is as followed:

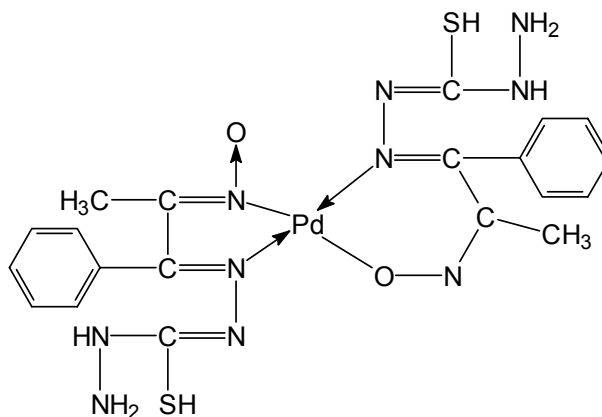


Fig. 2. Proposed structure for Pd(II) complexes of HPTCHOPD

Conclusion

From the present investigation it has been observed that a new ligand of isonitrosopropiophenone with thiocarbohydrazone in 1:1 ratio and its complexation with metal ions like Zn(II), Cd(II), Hg(II) and Pd(II). The data explain its geometrical symmetries *i.e.* tetrahedral for Zn(PTCHOPD)₂, Cd(PTCHOPD)₂ and Hg(PTCHOPD)₂. Pd(II) complexes reveals square planar geometry.

REFERENCES

1. A. Chakravorty, *Coord. Chem. Rev.*, **13**, 1 (1974).
2. B.C. Haldar, *J. Indian Chem. Soc.*, **51**, 224 (1974).
3. R.B. Singh, B.S. Garg and R.P. Singh, *Talanta*, **26**, 425 (1979).
4. R.G. Deshmukh, M.Sc. Thesis, University of Bombay, Bombay, India (1983).
5. N.P. Bui-Hoi, T.B. Loc and N.D. Xuong, *Bull. Soc. Chim. (France)*, 694 (1955).
6. A.I. Vogel's, in eds.: G.H. Jeffery and J. Bassett, *Textbook of Quantitative Chemical Analysis*, Longman Publication, edn. 5 (1996).
7. R.L. Dutta and A. Syamal, *Elements of Magnetochemistry*, S. Chand and Company Ltd., Ramnagar, New Delhi (1982).
8. W. Hartung and J.C. Munch, *J. Am. Chem. Soc.*, **51**, 2264 (1929).
9. L.F. Audrieth, E.S. Scott and P.S. Kippur, *Chem. Abstr.*, 10857e (1955).
10. R.G. Deshmukh, Ph.D. Thesis, University of Bombay, Bombay, India (1992).
11. H.B. Gray and C.J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).
12. N.S. Pai, Ph.D. Thesis, University of Bombay, Bombay, India (1981).
13. U.B. Talwar and B.C. Halder, *J. Inorg. Nucl. Chem.*, **32**, 213 (1970).
14. A.W. Herlinger, S.L. Wenhold and T.V. Long, *J. Am. Chem. Soc.*, **92**, 6474 (1970).