SYNTHESIS AND CHARACTERIZATION OF CO(II), NI(II), CU(II) AND PD(II) COMPLEXES OF 1-[2-(2-HYDROXYBENZILIDENE)HYDRAZONO]-1-PHENYLPROPAN-2-ONE OXIME

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Abstract: A new ligand 1-[2-hydroxybenzilidene)hydrazono]-1-phenylpropan-2-one oxime (HHBHPPO) have been synthesized. Interest in this ligand was due to the ambidenticity as well as probable multidenticity in coordination with metal ions of the transition element series. The ligand has two probable dissociable protons, yet our studies reveal that it is monobasic in nature. The synthesis and characterization of the ligand and its complexes of the type ML_2 where M is Co(II), Ni(II), Cu(II) and Pd(II) is described. Ligand and its complexes with transition metals were characterized on the basis of elemental analysis, conductivity measurement, IR, PMR, UV-VISIBLE spectroscopy and magnetic susceptibility. Based on the results, probable structures of these complexes have been proposed. Co(II) and Ni(II) complexes have octahedral geometry while Cu(II) and Pd(II) complexes have square planar structure.

Keywords: Oximino compound, Salicylaldehyde, metal complexes, structural analysis.

1. INTRODUCTION:

Coordination compounds 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[1], bioinorganic system[2], catalyst[3,4], medicine[5,6] etc. 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. As such, these ligands are known to report metal complexes of varied geometries, stabilities and applications. A survey of the literature shows that no study on synthesis and characterization of the present ligand and its metal complexes has been done so far.

2. EXPERIMENTAL:

2.1. Material and methods

All chemicals used were of A.R. grade. Other chemicals if used were purified by standard methods before use. The organic solvents used were purified by standard methods. Volumetric glass wares were calibrated before use. Carbonate free double distilled water was prepared by standard method prescribed by Vogel [7]. An Equiptronics Conductivity-meter (EQ-660A) was used for conductivity measurements of the complexes. It was calibrated using 0.1M KCl solution.

2.2. Synthesis of ligand (HHBHPPO) and its complexes:

1-[2-(2-hydroxybenzilidene)hydrazono]-1-phenylpropan-2-oneoxime(HHBHPPO) was prepared by the method as reported earlier by the condensation of salicylaldehyde with hydrazonyl derivative of isonitrosopropiophenone(HPHOPD) [8]. The metal complexes of Co(II), Ni(II), Cu(II) and Pd(II) of the ligand have been synthesized by a general procedure which was as follows: The aqueous solution of the appropriate metal ion salt was treated with an alcoholic solution of the ligand in stoichiometric ratio. The pH

of the reaction mixture were adjusted at an appropriate value. The reaction mixture was required to be refluxed on a hot water bath, except for the Pd(II) complex which was obtained without being required to be refluxed. The precipitated complexes were filtered through Whatman filter paper using Buchner funnel on a suction pump and washed thoroughly with water. The complexes so obtained were dried in an oven at 110^0C, recrystallized from ethanol and analyzed for C, H, and N. The yields were 72-85%. The melting points of ligand and all the 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 [7]. The solubility of the complexes were examined in different polar and nonpolar solvents. The magnetic susceptibility measurement of the complexes were done on Guoy balance using Hg[Co(SCN)$_4$] as the standard. Molar conductivity of the ligand and its complexes were measured using 1 x 10^{-3} M solution in nitrobenzene on Equiptronic Conductivity-meter (EQ-660A). The electronic absorption spectrum of complexes were recorded using DMF as solvent on Shimadzu UV-VIS spectrophotometer. FTIR spectrum of ligand and its complexes were recorded in the range of 4000-400cm^{-1} in KBr disk on Perkin Elmer instrument. PMR spectrum were recorded in deuteriated DMSO solution using Bruker 300MHz spectrometer.

3. RESULTS AND DISCUSSION:
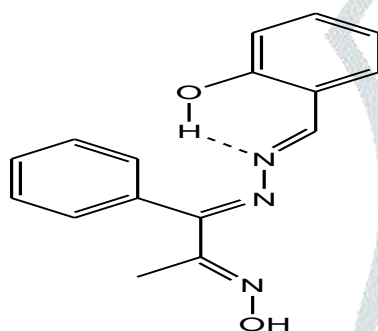### 3.1. Characterization of Ligand and its Metal Complexes:

Fig.1

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 281gmol^{-1} determined by GC-MS. It is yellow crystalline solid, soluble in chloroform, acetone, DMF, DMSO, dioxane, dilute alkali etc. and is partially soluble in methanol and ethanol. Several structures are possible depending on the hydrogen bonding but computational studies reveals that the structure shown in Fig.1 has least energy i.e. most stable, which is also supported by ligand-KOH titration curve (monobasic acid) [8].

The ligand and its complexes decompose above 200^0C indicates ligand as well as its metal complexes are air stable. The complexes are insoluble in water but are soluble in methanol, chloroform, carbon tetrachloride, acetone, DMF, DMSO. 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. The low molar conductivities of all the complexes (11–26 Scm^2 mol^{-1}) indicates their nonelectrolyte nature [9].

Table 1: Physical and analytical data of ligand and metal complexes:

Compound (Colour)	M.W.	Yield (%)	Λ_m Scm^2 mol^{-1}	Elemental analysis in % found (calculated)				μ_{eff} (B.M.)
				C	H	N	Metal	
HHBHPPO (Yellow)	281	93.29	---	68.28 (68.32)	5.29 (5.34)	14.91 (14.95)	---	---
[Co(HBHPPO)$_2$(H$_2$O)$_2$] (brown)	654.93	72.00	11.31	58.60 (58.63)	4.87 (4.89)	12.79 (12.83)	8.817 (8.998)	4.93
Ni(HBHPPO)$_2$ (brown)	618.69	84.56	12.88	62.03 (62.07)	4.51 (4.53)	13.54 (13.57)	9.54 (9.49)	3.14
Cu(HBHPPO)$_2$ (greenish Brown)	623.54	85.60	17.62	61.53 (61.58)	4.43 (4.49)	13.42 (13.47)	10.15 (10.19)	2.07
Pd(HBHPPO)$_2$ (Green)	666.40	84.76	26.12	57.61 (57.62)	4.18 (4.20)	12.58 (12.60)	15.91 (15.97)	Diamagnetic

3.2. IR Spectral Studies:

The prominent infrared spectral data with the tentative assignments of the ligand (HHBHPPO) and its Co(II), Ni(II), Cu(II), and Pd(II) complexes are presented in Table 2.

Table 2: IR spectral bands of the ligand (HHBHPPO) and its metal complexes (cm^{-1}):

Tentative assignments	Ligand	Co(II) complex	Ni(II) complex	Cu(II) complex	Pd(II) complex
Hydrogen bonded OH group	3222 (Oximino and phenolic)	3188 (Phenolic)	3200 (Phenolic)	3200 (Phenolic)	3200 (Phenolic)
>C=NOH	1621	---	---	---	---
N=CH	1610	1600	1600	1600	1600
C-O	1204	1211	1188	1198	1199
N-O	1021	1014	1010	1014	994
N→O	---	1359, 1531	1315, 1530	1327, 1556	1360, 1541
M-N	---	520	531	520-550	557
M-O	---	489	490	---	---
>C=C< Aromatic	3054	3057	3055	3055	3059

The spectrum shows a broad band at $3222 cm^{-1}$ due the presence of two –OH groups (oximino and phenolic) in the ligand. Assignment of this band was based on comparisons with other Isonitrosoketones and their hydrozonyl derivatives [1-5]. The IR spectrum of isonitrosopropiophenone (HINPP) and its hydrozonyl derivative (HPHOPD) shows band due to oximino-OH at $3244 cm^{-1}$ and $3250 cm^{-1}$ respectively. For the phenolic –OH group in the salicylaldehyde, a very weak band at $3200 cm^{-1}$ is observed due to the intramolecular hydrogen bonding. Since in the ligand also, the phenolic –OH group is strongly hydrogen bonded with nitrogen of the same molecule (intramolecular hydrogen bonding), the band for phenolic –OH group may be merged in the broad band of oximino –OH group. The band observed at $3054 cm^{-1}$ in the FTIR spectrum of the ligand is ascribed to the aromatic C-H stretching vibrations. The band at $1621 cm^{-1}$ and $1610 cm^{-1}$ may be chiefly due to the perturbed >C=N-OH and –CH=N stretching vibrations of the azomethine (-HC=N-N=) group respectively and $1600 cm^{-1}$ is due to the aromatic>C=C< vibrations. The band observed at $973 cm^{-1}$ may be assigned to =N-N= stretching vibrations. The same band is observed at $997 cm^{-1}$ in HPHOPD [5]. A shift by $24 cm^{-1}$ towards lower frequency may be due to the condensation of HPHOPD and salicylaldehyde. In isonitrosopropiophenone a peak at $1000 cm^{-1}$ is attributed to N-O. The Bhargava et al [10] have assigned two bands in the region $1100 cm^{-1}$ and $1000 cm^{-1}$ to two N-O vibrational modes, therefore a band at $1021 cm^{-1}$ and a shoulder at $1012 cm^{-1}$ may be assigned to the N-O vibrations. The band at $1204 cm^{-1}$ is due to phenolic C-O stretching.

The broad peak observed at $3222 cm^{-1}$ in the IR spectrum of the ligand assigned to oximino (OH), which is found to have disappeared in all the complexes, and a broad peak with less intensity at $3200 cm^{-1}$ is now visible thereby indicating deprotonation of oximino group while the phenolic -OH group remains intact, this may be because of strong intramolecular hydrogen bonding of phenolic hydrogen with azomethine nitrogen. This reveals the involment of oximino group in coordination. Appearance of two new bands in all complexes at $\sim 1350 cm^{-1}$ and $\sim 1522 cm^{-1}$ corresponds to presence of $N \rightarrow O$ group which indicate oximino group coordinate through nitrogen and not through oxygen[5]. The band assigned to phenolic C-O in ligand is shifted to the lower wave number in Ni complex indicates involvement of phenolic oxygen in coordination whereas the same band remains intact in Co, Cu and Pd complexes [11], this is further supported by appearance of new band at $490 cm^{-1}$ in Co and Ni complexes corresponding to M-O bond whereas no such band is observed in Cu and Pd complexes. Appearance of band at in the region 520-550 cm^{-1} in all complexes corresponds to M-N bonding. The coordination of oximino and azomethine nitrogen is confirmed by the disappearance of a band $1621 cm^{-1}$ (>C=NOH) and shifting of the band $1610 cm^{-1}$ (-

CH=N-) towards lower frequencies in all the complexes [11], which is assigned to azomethine nitrogen in the ligand. In Cobalt complex of HHBHPPO additional broad band in the region of 3300-3400cm^{-1} indicates presence of two water molecules (moisture content by Karl-Fischer method) [11]. Since no change in the position of v_{C-O} band due to phenolic group is observed, phenolic OH is not involved in coordination, but a band at 490cm^{-1} is observed in this complex which is assigned to M-O bonding, it is suggested therefor that the water molecules are present in coordination sphere and coordinated to Co(II) through oxygen.

3.3. ^{1}HNMR:

The ^{1}Hnmr spectrum of HHBHPPO were recorded in deuterated DMSO. Two (singlets) at δ12.16ppm and at δ10.82ppm were observed. The oximino group is expected to release the proton much more easily than the phenolic proton of the salicylaldehyde moiety of the ligand, since the deshielding effect is more on the proton of the oximino group than that on the phenolic group. The singlet at δ12.16ppm therefore may be ascribed to oximino proton of the ligand. The pmr spectrum of hydrazonyl derivative of isonitrosopropiophenone (HPHOPD), reveal the oximino proton at δ 8.10ppm [5], while in the related nitro salicylaldehyde derivative of HPHOPD, the same is reported at δ12.27ppm [12]. This is expected since the replacement of the two hydrogen by the nitrosalicylaldehyde, the oximino proton is easily releasable. Hence it is suggested that the singlet observed in HHBHPPO at δ12.16ppm is due to the oximino group. The singlet at δ10.82ppm in the pmr spectrum of the ligand HHBHPPO may be assigned to the phenolic proton. This is also confirmed by D$_2$O exchange pmr spectrum in which these two peaks δ12.16ppm and δ10.82ppm disappears. A singlet at δ2.20ppm assigned to the methyl group of the ligand. A singlet at δ8.84ppm is attributed to azomethine proton. The multiplets in the region between δ6.74ppm to δ7.52ppm were assigned to the aromatic ring protons.

The signal at δ 8.842 (s, 1H) due to the azomethine group in the ligand is shifted to downfield in the region δ 9.01 (s, 1H) in the spectrum of Pd(II) complex confirms the coordination of "N" of (–HC=N–) group in bonding with Pd [13]. The singlet at δ10.82ppm 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 Spectrum and Magnetic Susceptibility:

The electronic absorption spectrum of the methanolic solution of the ligand HHBHPPO in the ultra-violet region shows three high intensity bands at 48780cm^{-1} (Ɛ = 11480dm^{3}mol^{-1}cm^{-1}), 42373 cm^{-1} (Ɛ= 9350dm^{3}mol^{-1}cm^{-1}) and at 34130 cm^{-1} (Ɛ= 13680dm^{3}mol^{-1}cm^{-1}). This may be due to intra ligand $(\pi \to \pi^*)$ transitions of azomethine environment in the molecule. In many isonitrosoketones [1-6] including isonitrosopropiophenone, a band occurring at similar positions and intensity, is reported to be the $(\pi \to \pi^*)$ transitions in the ligand [5]. The methanol spectrum of the hydrazonyl derivative of isonitrosopropiophenone [5] shows three bands at 48540 cm^{-1} (Ɛ=10610dm^{3}mol^{-1}cm^{-1}), 39220 cm^{-1} (Ɛ=11820dm^{3}mol^{-1}cm^{-1}) and 29200 cm^{-1} (Ɛ = 6930dm^{3}mol^{-1}cm^{-1}) which have been assigned to the presence of the two azomethine groups and one oximino group. The electronic absorption spectrum of the methanolic solution of the ligand HHBHPPO in the ultra-violet region also shows one less intense band at low energy at 29200 cm^{-1} (Ɛ= 6930dm^{3}mol^{-1}cm^{-1}) due to$(\pi \to \pi^*)$ transition. The ultra-violet spectrum of the ligand HHBHPPO in dilute alkali solution (0.1N NaOH) solution reveals that the band observed at 29240 cm^{-1} (Ɛ=6930dm^{3}mol^{-1}cm^{-1}) in the methanol solution spectrum somewhat suppressed and shifted to the higher wavelength i.e. at 26596 cm^{-1} (Ɛ=5558dm^{3}mol^{-1}cm^{-1}). The bathochromic shift in the band at 29240 cm^{-1} and the lowering of intensity suggests formation of anion HBHPPO $^-$ in the alkaline solution due to the deprotonation of the oximino group [1-5]. The spectrum also shows that the high intensity band at 34130 cm^{-1} (Ɛ= 13680dm^{3}mol^{-1}cm^{-1}) in methanol solution spectrum is disappear in the spectrum of dilute alkali solution, this may be because of disappearance of >C=N- bonding of >C=N-OH group due to resonance of HBHPPO$^-$ moiety.

Table 3: Electronic spectral bands and ligand field parameters of Co(II), Ni(II) and Cu(II) complexes in DMF:

Complexes	Transitions in cm^{-1}			Dq (cm^{-1})	B' (cm^{-1})			
	(v_1)	(v_2)	(v_3)			β	β%	v_2/v_1

Co(II)complex	8051	17241	20202	919	886	0.91	9	2.141
Ni(II) complex	9569	17241	24096	957	842	0.81	19	1.80
Cu(II) complex		15106 Broad		1510	----	------	---	---

The electronic spectral data of metal (II) complexes were recorded in DMF and is shown in Table 3. The electronic spectrum of the Co(II) complex displayed bands at 17241 cm^{-1} ($\mathcal{E}$=1362dm^{3}mol^{-1}cm^{-1}) and 20202 cm^{-1} ($\mathcal{E}$=3583dm^{3}mol^{-1}cm^{-1}). These two bands are assignable to $4_{A_{2g}} \leftarrow 4_{T_{1g}}(F)$ (v_2) and $4_{T_{1g}}(P) \leftarrow 4_{T_{1g}}(F)$ (v_3) transitions respectively. The lowest band $4_{T_{2g}} \leftarrow 4_{T_{1g}}(F)$ (v_1) could not be observed due to the limited range of the instrument used but could be calculated using the band fitting procedure $v_1 = v_2 - 10Dq$ suggested by Underhill and Billing [14] and is 8051 cm^{-1}. The value of v_2/v_1 (2.141) lies in the range 2.1–2.2, reported for most of the octahedral Co(II) compounds [15]. The spectral parameters for [Co(HBHPPO)$_2$(H$_2$O)$_2$] are Dq = 919cm^{-1}, B' = 886 cm^{-1}, B'/B= β=0.91 and β% = 9%. Reduction of Racah parameter from 971 cm^{-1} (free ion value) to 886 cm^{-1} and the β% value 9% indicate the covalent nature of the compound. The Co(II) complex shows a magnetic moment value of 4.93 B.M., which is within the range of 4.46–5.53 B.M. [Ni(HBHPPO)$_2$] shows three bands at 9569 cm^{-1} ($\mathcal{E}$=8.7dm^{3}mol^{-1}cm^{-1}), 17241 cm^{-1} ($\mathcal{E}$=980dm^{3}mol^{-1}cm^{-1}) and 24096 cm^{-1} ($\mathcal{E}$=3695dm^{3}mol^{-1}cm^{-1}) due to $3_{T_{2g}} \leftarrow 3_{A_{2g}}$ (v_1), $3_{T_{1g}} \leftarrow 3_{A_{2g}}$ (v_2) and $3_{T_{1g}}(P) \leftarrow 3_{A_{2g}}$ (v_3) transitions, respectively, in an octahedral symmetry [15]. The value of v_2/v_1 is 1.80 which lies in the usual range (1.60–1.82), reported for the majority of octahedral Ni(II) compounds [15,16]. The spectral parameters for [Ni(HBHPPO)$_2$] are Dq = 957cm^{-1}, B' = 842 cm^{-1}, B'/B=, β=0.81 and β% = 19%. Reduction of Racah parameter from 1030 cm^{-1} (free ion value) to 842 cm^{-1} and the β% value 19% indicate the covalent nature of the compound. The magnetic moment observed for Ni(II) complex lies in the range of 2.8–3.5B.M., showing a value of 3.14 which is consistent with the octahedral geometry of the complex. For square planar Cu(II) complexes, the expected transitions are $2_{A_{1g}} \leftarrow 2_{B_{1g}}$ and $2_{E_g} \leftarrow 2_{B_{1g}}$ with the respective absorption bands [15]. In general, due to Jahn–Teller distortion, square planar Cu(II) complexes give a broad absorption band between 600 nm(16666 cm^{-1}) and 700 nm (14286 cm^{-1}). The electronic spectrum of Cu(II) complex exhibit a broad band centered at 662 nm (15106 cm^{-1}, $\mathcal{E}$=6.72dm^{3}mol^{-1}cm^{-1}) indicating square planar geometry. The magnetic moment of Cu(II) complex is 2.07 B.M. A common feature of the electronic absorption spectrum in DMF solution for palladium complexes is the absence of any appreciable absorption beyond 14000 cm^{-1}. This is typical of square planar d^8 complexes. Gray and Ballhausen [17] have reported an analysis of the electronic absorption pattern of square planar d^8 complexes, such complexes are expected to show at least three closely spaced d-d transition weak bands. However, due to the proximity of this absorption to the high intensity charge transfer transitions, the former are masked. The high intensity transitions observed at 21277 cm^{-1} ($\mathcal{E}$=6476dm^{3}mol^{-1}cm^{-1}) and 17094 cm^{-1} ($\mathcal{E}$=258dm^{3}mol^{-1}cm^{-1}) in Pd(HBHPPO)$_2$ are suggested to be charge transfer transitions.

3.5. EPR Spectrum studies:

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 the magnetic field strength 3000 G. The analysis of spectra give $g\| = 2.13855$ and $g\perp = 2.0269$. The trend $g\| > g\perp > 2.0023$, observed for the complex, under study, indicates that the unpaired electron is localized in dx^2-y^2 orbital, characteristics of square planar geometry. Kivelson and Neiman [18] have reported that $g\|$ value is less than 2.3 for covalent character and is greater than 2.3 for ionic character of the metal ligand bond in the complex. For this complex the $g\|$ is less than 2.3 suggesting the covalent character of the metal-ligand bond.

4. CONCLUSION:

The present study shows that the synthesized ligand (HHBHPPO) acts as tridentate/bidentate ligand coordinating through azomethine nitrogen, oximino nitrogen and phenolic oxygen to Ni(II) while through Azomethine nitrogen and oximino nitrogen to Co(II), Cu(II) and Pd(II). The synthesized new ligand and its

metal complexes have been characterised by the analytical data, IR, electronic, mass spectrometry, ^{1}H NMR, ESR spectral data, magnetic susceptibility, molar conductivity etc. From the analytical data and spectral studies, we propose octahedral geometry for the Co(II) and Ni(II) complexes and square planar geometry for Cu(II) and Pd(II) complexes.
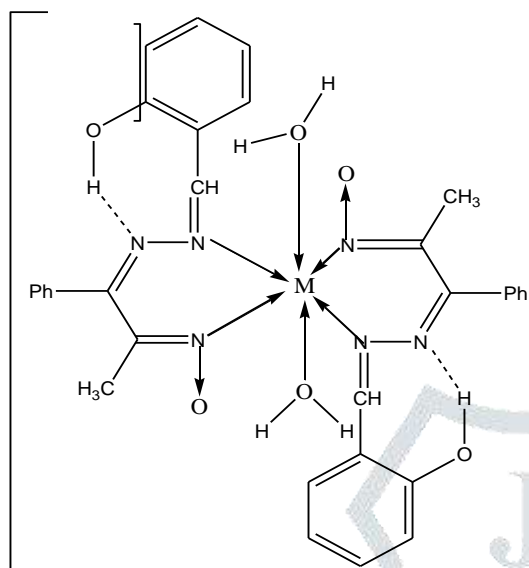

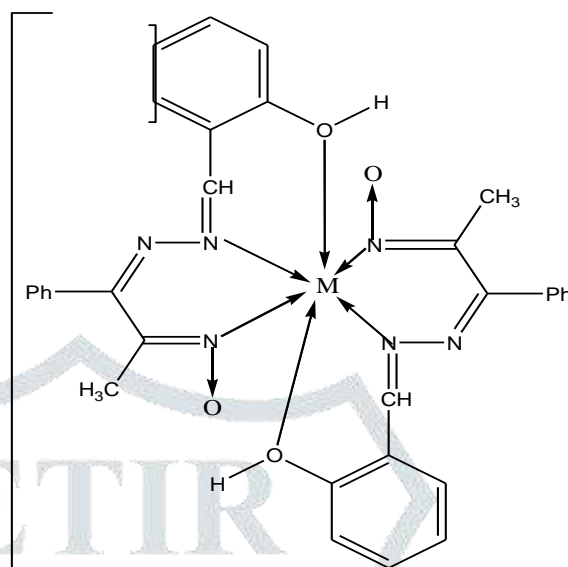Figure 2: Proposed structure of Co(II) complex (Octahedral, M=Co(II))

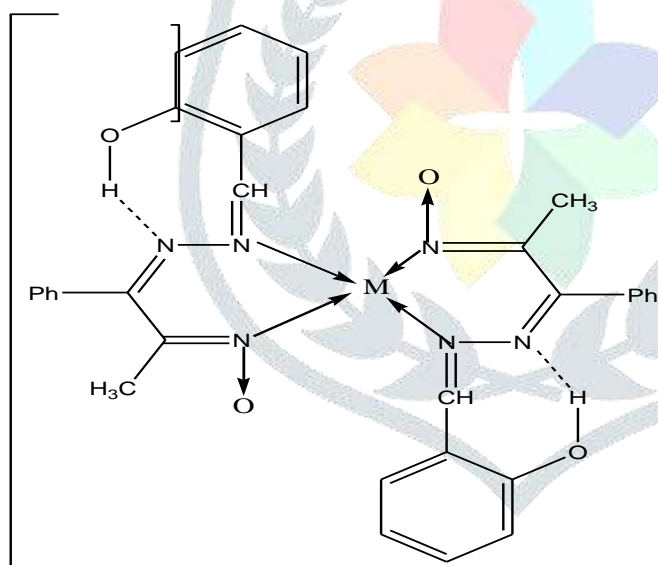Figure 3: Proposed structure of Ni(II) complex (Octahedral, M=Ni(II)).

Figure 4: Proposed structure of Cu(II) and Pd(II) complexes (Sqaure Planar, M=Cu(II) and Pd(II)).

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