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Synthesis and Characterisation of Transition Metal Coordination Compounds of Oximno Hydrazone

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Abstract: A novel ligend (1-(2-hydroxyphenyl) ethylidene) hydrazono)-1-phenylpropan-2-one oxime, (HHPEHPPO) have synthesised, characterised for the first time. Interest in this ligand was its ambidenticity, chelation ability, large number of metal chelates have been synthesised and have been studied for their analytical applications[1-3]. Ligands of this type are also known for their antibacterial activity[4].

Metal coordination compounds of Co (II), Ni (II), Cu (II) and Pd (II), of synthesised ligand was prepared and characterised of their structures by various methods.

Keywords: Co (II), Ni (II), Cu (II) and Pd (II), coordination compound, oximino hydrazones, ligand.

I. INTRODUCTION

Oximino hydrazone metal coordination compounds are extensively studied for its synthetic flexibility, better complexing ability, structural resemblance with natural biological substances and their potency to act as biologically active compounds[5-7]. These ligands are known to report metal coordination compounds of varied geometries, stabilities and applications. A survey of the literature shows that, no study on synthesis and characterisation of the present ligand and its metal coordination compounds has not been done so far.

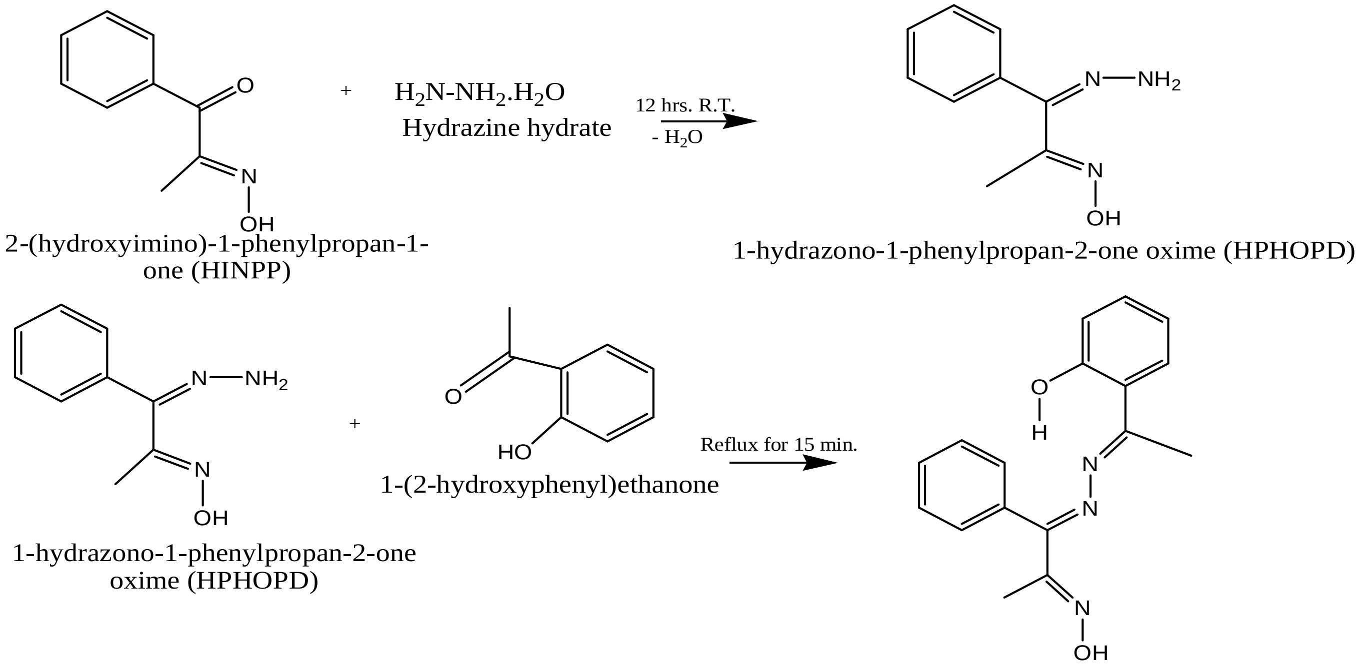
II. EXPERIMENTAL

A. Materials and Methods

All chemicals used were of AR grade. Other chemicals if used were purified by standard methods before use. The organic solvents used were purified by standard methods. All metal salts, M(II), were used as their chlorides salts. IR spectra were recorded on Shimadzu iTR, UV Visible spectra were obtained on PMR spectra were obtained from SAIF. IIT Bombay, Magnetic measurements were made on Gouy Balance at Institute of Science. Mumbai.

B. Synthesis of Ligand

HPHOPD was synthesised by reported method[8] and the ligand of interest, (1-(2-hydroxyphenyl)ethylidene)hydrazono)-1-phenylpropan-2-one oxime, (HHPEHPPO) have been synthesised by refluxing an ethanolic mixture of 0.05 mol (9.650 g) of HPHOPD and 0.05 mol (6.800 g) of 1-(2-hydroxyphenyl)ethanone, 50 mL, for 1.5 hour, completion of reaction was monitored by TCL. A bright yellow solid product formed, was filtered, washed thoroughly with water followed with cold ethanol and dried in oven at 110 ˚C. it was recrystallized from ethanol and characterised.



2-(hydroxyimino)-1-phenylpropan-1-one (HINPP)

1-hydrazono-1-phenylpropan-2-one oxime (HPHOPD)

1-hydrazono-1-phenylpropan-2-one oxime (HPHOPD)

1-(2-hydroxyphenyl)ethanone

1-(2-(1-(2-hydroxyphenyl)ethylidene)hydrazono)-1-phenylpropan-2-one oxime

C. *Synthesis of Metal Coordination compounds of Ligand*

1) *Synthesis of Co(II) coordination compound of Ligand:*Hot ethanolic solution of ligand (0.004 mol) was added drop-wise to a hot ethanolic solution of Co(II) chloride salt (0.002 mol), with constant stirring, after complete addition of ligand, to the resultant solution, ethanolic ammonia solution was added drop-wise till coordination compound precipitated (precipitation occurred at nearly neutral pH), this was refluxed for 30 min for reaction completion. The precipitated coordination compound was filtered at suction pump, through whatman paper no. 1, washed with water followed by cold ethanol and then dried in oven at 110˚C.
2) *Synthesis of Ni(II) coordination compound of Ligand:*Hot ethanolic solution of ligand (0.004 mol) was added drop-wise to a hot ethanolic solution of Ni(II) chloride salt (0.002 mol), with constant stirring, after complete addition of ligand, to the resultant solution, ethanolic ammonia solution was added drop-wise till coordination compound precipitated (precipitation occurred at pH = 7.5), this was refluxed for 30 min for reaction completion. The precipitated coordination compound was filtered at suction pump, through whatman paper no. 1, washed with water followed by cold ethanol and then dried in oven at 110˚C.
3) *Synthesis of Cu(II) coordination compound of Ligand:* Hot ethanolic solution of ligand (0.004 mol) was added drop-wise to a hot ethanolic solution of Cu(II) chloride salt (0.002 mol), with constant stirring, after complete addition of ligand, to the resultant solution, ethanolic ammonia solution was added drop-wise till coordination compound precipitated (precipitation occurred at nearly neutral pH), this was refluxed for 30 min for reaction completion. The precipitated coordination compound was filtered at suction pump, through whatman paper no. 1, washed with water followed by cold ethanol and then dried in oven at 110˚C.
4) *Synthesis of Pd(II) coordination compound of Ligand:* Hot ethanolic solution of ligand (0.004 mol) was added drop-wise to a hot aqueous, acidic (HCl) solution of Pd(II) chloride salt (0.002 mol) with constant stirring, the coordination compound precipitated out without adding ethanolic ammonia. The precipitated product was refluxed for 30 min for reaction completion, then filtered in G3 crucible, washed thoroughly with water followed by cold ethanol and then dried in oven at 110˚C.The metal content of the metal complexes were done by the methods given in Vogel's Quantitative Analysis[9]. The solubility of complexes were examined in different polar and non-polar solvents. The magnetic susceptibility measurements were made on Guoy balance using $Hg[Co(SCN)_4]$ as the standard. Molar conductivity measurements were done on Conductivity meter (Equiptronics) and were suggesting non-electrolytic nature.

III. RESULTS AND DISCUSSION

A. Ligand Characterisation

Characterisation of ligand is done by using analytical data obtained from FTIR, PMR, UV Visible spectroscopy, GC-MS, elemental analysis, etc. The Molecular mass of the ligand is 265 as determined by GC-MS, its melting point is 203° C. It is bright yellow crystalline solid, soluble in chloroform, acetone, DMF, DMSO, dioxane, dilute alkali, etc. and partially soluble in methanol and ethanol.

B. UV Visible spectral studies

The electronic absorption spectrum of the methanolic solution of the ligand HHPEHPPO in the ultra-violet region (Table-5.2 and Figure.5.4) shows three high intensity band at 48.78kK (Ɛ = 11480dm^{3}mol^{-1}cm^{-1}), 42.37 kK (Ɛ= 9350dm^{3}mol^{-1}cm^{-1}) and at 34.13kK (Ɛ= 13680dm^{3}mol^{-1}cm^{-1}). This may be due to intra ligand, $\pi^*\leftarrow\pi$ (allowed) transitions of azomethine environment in the molecule.The electronic absorption spectrum of the methanolic solution of the ligand HHPEHPPO in the ultra-violet region also shows one less intense band at low energy at 29.20 kK (Ɛ= 6930dm^{3}mol^{-1}cm^{-1}) due to $\pi^*\leftarrow\pi$ (allowed) transitions . The ultra-violet spectrum of the ligand HHBHPPO in dilute alkali solution (0.1N NaOH) solution reveals that the band observed at 29.20kK (Ɛ=6930dm^{3}mol^{-1}cm^{-1}) in the methanol solution spectrum somewhat suppressed and shifted to the higher wavelength i.e. at 24.94kK (Ɛ=6100dm^{3}mol^{-1}cm^{-1}). The bathochromic shift in the band at 24.94kK and the lowering of intensity suggests formation of anion HBHPPO$^-$ in the alkaline solution due to the deprotonation of the oximino group.

C. IR spectral studies

FTIR spectrum of HHPEHPPO in the range of 4000-400cm^{-1} were recorded on Shimadzu iTR instrument. The spectrum is quit complex due the presence of a large number of bands with varying intensities. It is therefore impossible to assign all the bands. An attempt however has been made to assign some of the important bands. The spectrum shows a broad band at 3222cm^{-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. The IR spectrum of isonitrosopropiophenone (HINPP) and its hydrozonyl derivative (HPHOPD) shows band due to oximino-OH at 3244cm^{-1} and 3250cm^{-1} respectively. This indicates that strong inter molecular hydrogen bonding result in the lowering of band position as well as the increase narrowness of the band.

D. ^{1}H NMR spectral studies

The ^{1}H NMR spectrum of ligand was recorded in deuteriated DMSO. Two (singlets) at δ11.775 and δ11.39 were observed. The oximino group is expected to release the hydron relatively more easily than the phenolic hydron, since the deshielding effect is more on the hydron of oximino group than that on the phenolic group, therefore the singlet at δ11.775 may be ascribed to oximino proton of the ligand, whereas, the singlet at δ11.39 may be ascribed to phenolic hydron. This is also confirmed by D_2O exchange PMR spectrum in which these two peaks disappear.

E. Characterisation of Metal coordination compounds:

FT-IR bands for Metal Coordination Compounds, [M(HHPEHPPO)$_2$], and their assignments

Coordination Compounds	C=N frequency	Phenolic C—O frequency	M—N frequemcy	M—O frequency
[Co(HPEHPPO)$_2$]	1621	1399	554	448
[Ni(HPEHPPO)$_2$]	1623	1341	558	453
[Cu(HPEHPPO)$_2$]	1620	1344	553	462
[Pd(HPEHPPO)$_2$]	1618	1355	552	-----

Proposed structure of Co(II), Ni(II) and Cu(II) coordination compounds

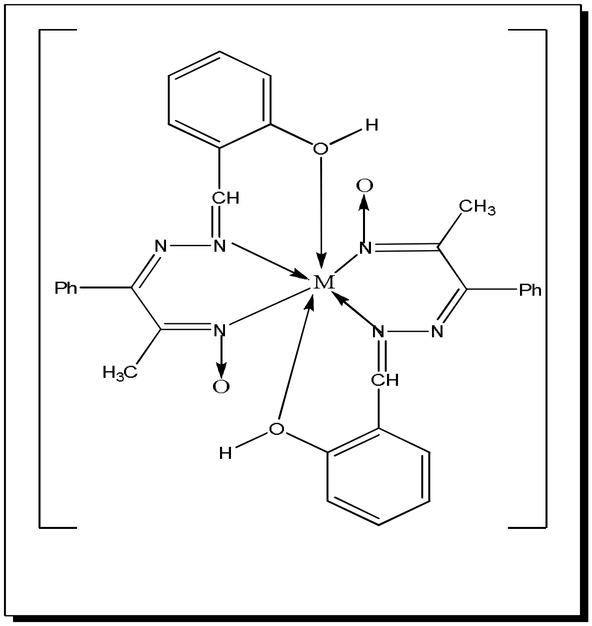


Fig. 1

1H NMR spectrum of Pd(II) coordination compound, [Pd(HPEHPPO)$_2$] The pmr spectrums of [Pd(HPEHPPO)$_2$] reveals that the peak for oximino proton of the ligand δ11.74 is disappeared in the pmr spectrums of this complex confirms the deprotonation of oximino proton and involvement of oximino group in coordination with metal ion. The signal at *δ*8.945 (s, 1H) due to the azomethine group in HHPEHPPO is shifted to downfield in the region ~*δ*9.1 (s, 1H) in the spectrum of Pd(II) complex confirms the coordination of "N" of (-HC=N–) group in bonding with this metal ion. The singlet at δ11.139ppm in the pmr spectrum of the ligand assigned for phenilic –OH group remains unaltered in the pmr spectrum of Pd(II) complex confirms the non-coordination of phenolic OH with these metal ions.

Proposed structure of Pd(II) cordination compound

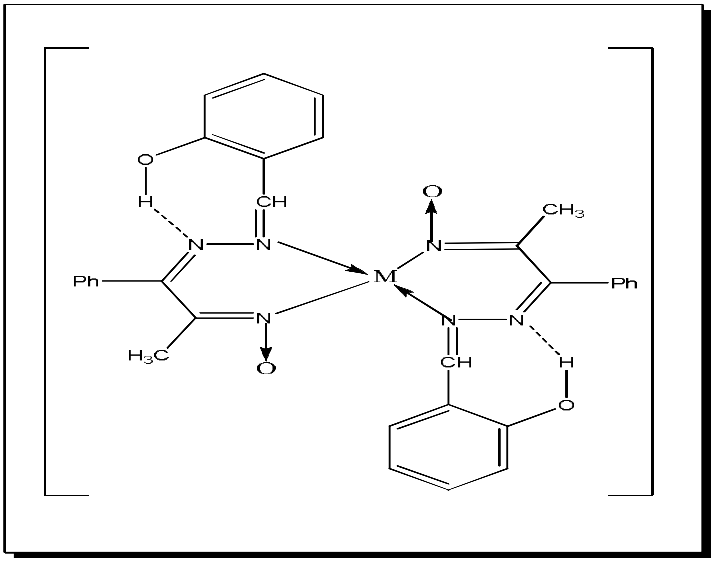


Fig. 2

Electronic absorption spectrum of complexes were in concordant with the IR spectral data, wherein, Co(II) and Ni(II) shows octahedral environment, Cu(II) spectrum suggests, distorted octahedral environment, that may be ascribed to Jahn-Teller distortion effect, and a very high intensity transitions were observed in [Pd(HPEHPPO)$_2$] suggests an fairly allowed charge transfer transitions.

IV. CONCLUSION

The present study shows that the synthesised ligand HHPEHPPO acts as a bidentate or tridentate ligand and have a good chelating ability to yield stable coordination compounds. The ligand coordinates through azomethine nitrogen, oximino nitrogen and phenolic oxygen (in Co(II), Ni(II) and Cu(II) complexes). All complexes are non-electrolytic. And Electronic absorption studies and FTIR studies of complexes suggests octahedral environment to Co(II) and Ni(II) complexes, distorted octahedral for Cu(II) and square planar environment for Pd(II) complex.

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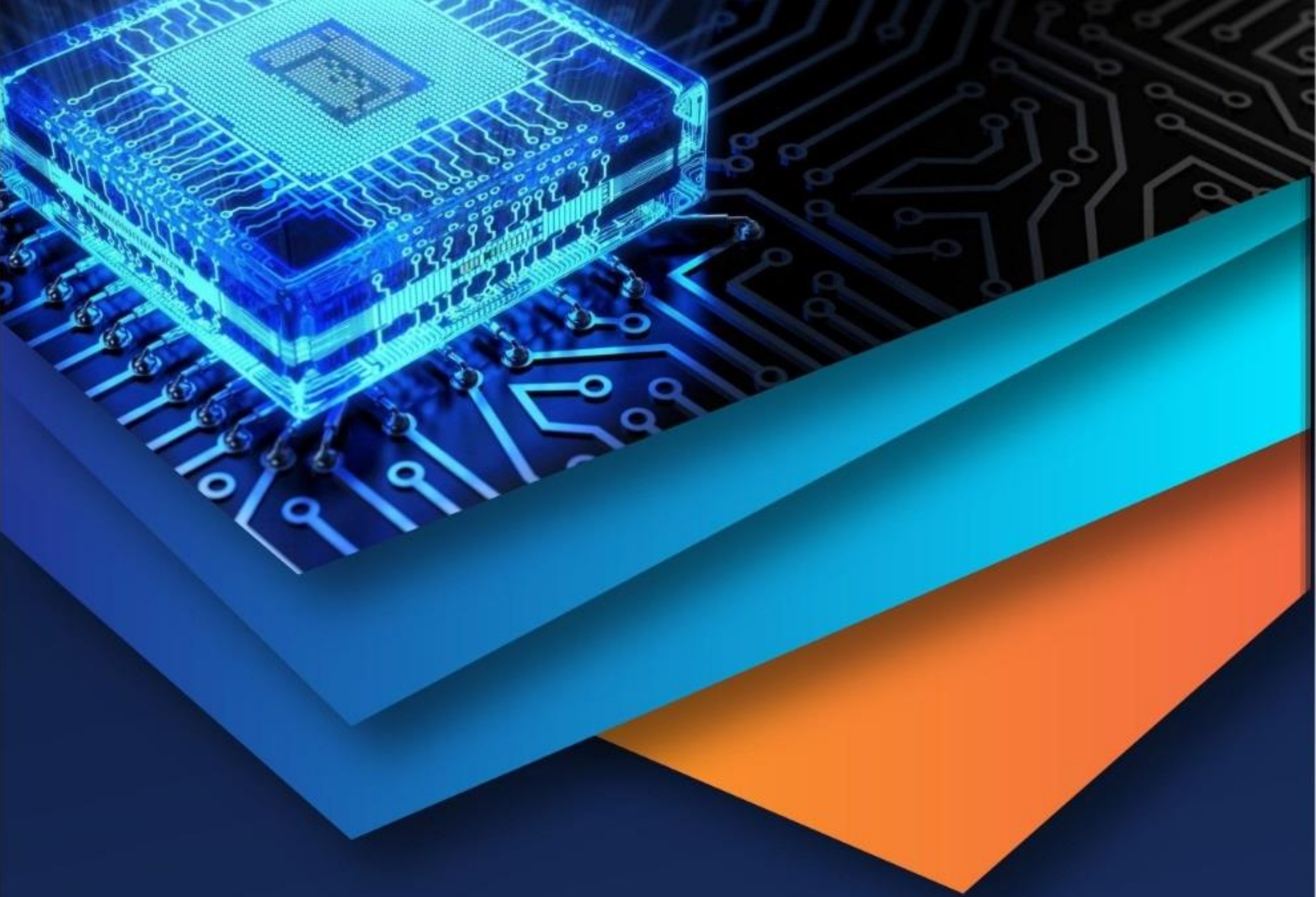

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