

Synthesis and Structural Studies of a New Polydentate Ligand and its Ni (II) Complex

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Abstract

A new polydentate ligand *N*-(2-hydroxyphenyl)-2-[(2-aminophenylamino)] acetamide, (HPAPAA) has been synthesized in the reaction between *N*-(2-hydroxyphenyl)-2-chloroacetamide and *o*-phenylenediamine. Ni (II) complex of the ligand was synthesized and characterized on the basis of their spectral (IR, NMR, UV-Vis, and AAS), elemental analyses, conductivity and magnetic susceptibility measurements. Ni (II) metal complex was synthesized in methanolic media. Metal-to-ligand ratios were found to be 1:1 for complex. Conductivity measurements suggested that complex was non-electrolytes. Binuclear Ni (II) complex exhibited subnormal magnetic moments indicating the possibility of antiferromagnetic interaction through a possible super exchange mechanism. The ligand behaves as dibasic tridentate, employing ONO donor sequence in chelation including phenoxide bridging. Based on the analytical, infrared, conductivity, magnetic susceptibility and electronic spectral data it may be concluded that octahedral geometry for Ni (II) complex was suggested.

Keywords: Polydentate ligand, Ni (II) complex, HPAPAA

Introduction

A metal complex consists of a central metal atom or ion surrounded by a set of ligands that have one or more atom(s) bearing lone pairs of electron(s). These 'donor' atoms are bound electrostatically and covalently to the metal ion. In non-transition metal complexes, the binding is largely electrostatic, while in transition metal complexes there is significant covalency. Generally ligands are Lewis bases that have lone pairs on nitrogen, oxygen, sulphur, etc and that bind transition metals that are Lewis acids. These Lewis bases (ligands) can be divided into unidentate, bidentate and multidentate types, according to whether one, two or more atom(s) is (are) involved in such bonding [1-7].

Ligands are also grouped traditionally as O- donors and N-donors in which the division is based on selection of metal ions for complexation. The N-donor ligands complex well with the smaller transition metal ions

derived from Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Cu. The O-donor ligands tend to complex with metal ions such as the larger alkali, alkaline earth metal ions and large post transition metal ions [1, 2, 5].

Some ligands are bonded to the metal through two or more different ligand atoms and thus form parts of heterocyclic ring (usually five and six member) in which the metal is one of the members. Such metal complex is termed as metal chelate. But sometimes, the stereochemistry of some ligands does not allow all the binding sites to be simultaneously bonded to the same metal, i.e. a ligand potentially tridentate ligand, may function only as a bidentate ligand [8].

Large numbers of suitably substituted aliphatic heterocyclic and aromatic metal binding sites have provided an integrated approach towards a branch that can be classified as coordination chemistry. Multidentate ligands, which possess 'NO', 'ON', 'ONNO' and 'NS' donor systems, are of considerable structural interest as some of them may be involved in bridging two or more metal ions and generate unpaired spin-spin interactions on centers [9,10].

Nickel (II) complexes

The electronic configuration of the Ni(II) is d^8 . Octahedral Ni(II) complexes having $^3A_{2g}$ ground state are expected to have three spin allowed transitions $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{1g}(P)$ and $^3A_{2g} \rightarrow ^3T_{1g}(F)$ in the range of 7000-13000, 11000-20000 and 19000-27000 cm^{-1} , respectively. In addition to these three transitions, two spin-forbidden transitions $^3A_{2g} \rightarrow ^1E_g$ and $^3A_{2g} \rightarrow ^1T_{2g}$ are also observed one at near the second spin-allowed transition and another band between second and third spin-allowed transitions. Five coordinate Ni(II) complexes have structures, which are generally near to one of the two limiting geometries, namely the square pyramid and the trigonalbipyramid. The electronic ground state of Ni(II) in the five coordinate complexes can be either a spin singlet (low-spin) or a spin triplet (high-spin). Low-spin trigonalbipyramidal Ni (II) species, which exhibit three transitions, namely $^1A_1 \rightarrow ^1B_1$, $^1A_1 \rightarrow ^1E$ and $^1A_1 \rightarrow A_2$ lie in the region 15000-18000, 21000-24000 and 27000-29000 cm^{-1} , respectively.

The majority of four coordinate Ni(II) complexes are square-planar and diamagnetic, while other are pseudo tetrahedral Ni(II) complexes have spectral transitions in the visible region with a much greater intensity than the octahedral ones. Tetrahedral Ni(II) complexes with 3T_1 ground state generally exhibit four transitions. They are ${}^3T_1 \rightarrow {}^3A_2$, ${}^3T_1 \rightarrow {}^1E$, ${}^3T_1 \rightarrow {}^3T_1$ (P) and ${}^3T_2 \rightarrow {}^1T_1$. The band ${}^3T_1 \rightarrow {}^3T_1$ (P) is a strong band of high intensity when compared with others. In square planar Ni(II) complexes, three spin allowed d-d bands corresponding to ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$ transitions are expected. Majority of the square planar Ni(II) complexes exhibit strong absorptions in 15000-25000 and 23000-30000 cm^{-1} region. The square planar Ni(II) complexes don't have any absorption band below 10000 cm^{-1} , due to large crystal field splitting. Hence they can be clearly distinguished from octahedral and tetrahedral complexes [2].

Materials and Methods

Chemicals:All the chemicals used in the investigation were of AnalaR grade. These include orthoaminophenol, chloroacetylchloride and 1,2-phenylenediamine. The metal salts used to synthesize the complexes are : $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. Solvents used during the investigation include; MeOH, EtOH, C_6H_6 , THF, DMSO, DMF, CHCl_3 , H_2O , CH_3CN , petroleum ether, diethyl ether, ethylacetate, dimethylglyoxime and 1,4-dioxane. Other chemicals used also include: HCl, HNO_3 , AgNO_3 , NaOH and NH_4OH . **Instrumentation:**UV-Vis spectrophotometric measurements were made in the range 200-750 nm using Spectronic Genesys 2PC spectrophotometer. Determinations of melting points or decomposition temperatures of the products were done with Stuart SMP3 Digital Melting Point apparatus. Nuclear magnetic resonance data were collected using BRUKER ARX 400 NMR spectrometer. Infrared (IR) spectra were recorded using a Perkin-Elmer Spectrum 65 spectrophotometer in the range 4000-400 cm^{-1} with samples prepared using KBr pellets. Magnetic susceptibility measurements were performed using MSB Auto, Sherwood. The molar conductivity measurements were carried out using EC 214 Bench type conductivity meter (Hanna Instrument). The metal complexes were analyzed for their metal contents using Analytik Jena Model Zeenit 700P atomic absorption spectrometer. The purity of the complex was checked by thin layer chromatography (TLC). Elemental analyses of the complexes were carried out on Elemental analyzer EA 1112 (CE instruments).

Synthesis of the precursor, ligand and metal complexes

Synthesis of the precursor: To 5.5 g (0.05mol) of o-aminophenol in benzene, 4.5 ml of chloroacetylchloride

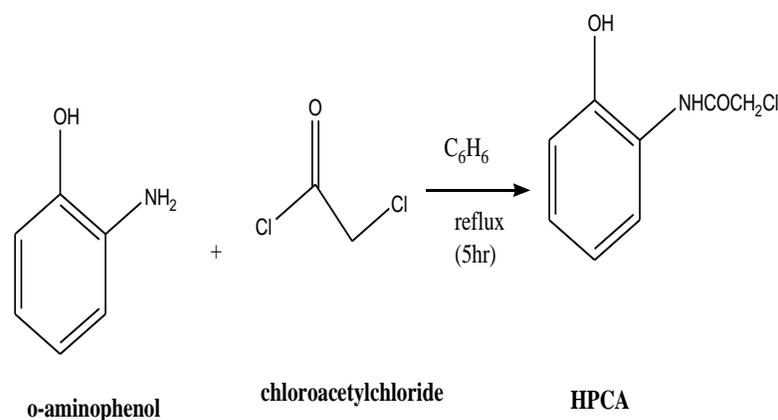
was slowly added drop wise with continuous stirring. It was then refluxed for about 5 hours with stirring on water bath. The precipitate of the product was filtered, washed with benzene and diethyl ether and then dried in air.

Yield: 7.95g (85%),

Color: bright white

Appearance: crystalline product,

Melting point: 141-142 $^{\circ}$ C.



Scheme 1: Synthesis of HPCA

Synthesis of the ligand

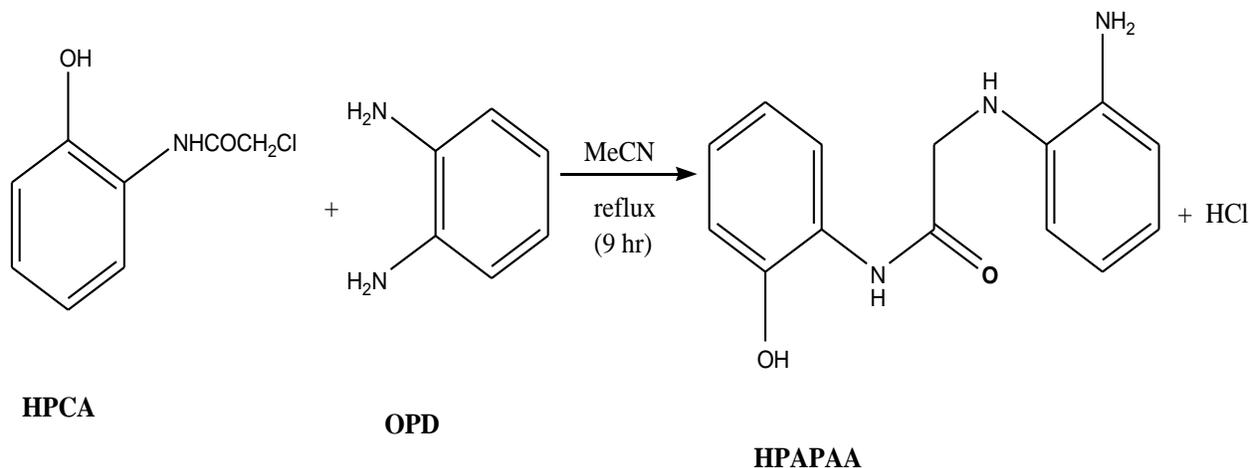
N-(2-hydroxyphenyl)-2-chloroacetamide (0.004 mol, 0.7 g) in 20 ml MeCN was mixed with o-phenylenediamine (0.004 mol, 0.42 g) in 20 ml MeCN. The solution was refluxed for about 9 hours with stirring on water bath and then concentrated. The resulting deep red product was filtered and repeatedly washed with MeCN and ether. The product was then dried in open air and stored in a desiccator.

Yield: 62 %

Color: deep red

Appearance: solid product,

Decomposes partially: 194-195 $^{\circ}$ C.



Scheme 2: Synthesis of HPAPAA

Synthesis of Ni (II) complex: A solution of metal chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g, 0.001 mol) was prepared in MeOH (20 mL) in a round bottom flask. To this, a solution of ligand (0.257 g, 0.001 mol) in 20 mL of MeOH was added. The pH of the resultant solution was 3. As a result, the following color changes were observed: (dark greenish for Ni (II)). The pH of the mixture was raised to 5 by drop-wise addition of 1% NH_4OH solution in methanol. The mixture was stirred while heating on hot water bath for 7 hours at $55\text{--}60^\circ\text{C}$. The metal complexes thus synthesized were concentrated. Then they were washed with methanol and diethyl ether and dried. Yield: Ni (II) complex, 0.33 g (85.5%).

Results and Discussion: In this part, physical properties and the results related to, spectral studies such as IR, NMR, UV-Vis, AAS, melting or decomposition

temperature, conductivity and magnetic moment measurements of the precursor, the ligand as well as the metal complexes will be discussed.

Characterization of N-(2-hydroxyphenyl)-2-chloroacetamide
General Properties of HPCA: O-hydroxyphenylchloroacetanilide (HPCA, $\text{C}_8\text{H}_8\text{NO}_2\text{Cl}$, molar mass 185.7 g/mol) is a bright white crystalline powder. It does not melt at $141\text{--}142^\circ\text{C}$. It is soluble in solvents, such as DMSO and CH_3CN and also sparingly soluble in H_2O , MeOH, EtOH and CHCl_3 .

Elemental Analysis:

The experimentally obtained C, H and N percent elemental analysis shows a good agreement with the theoretically calculated value. Accordingly the structure of the precursor can be presented as in figure below.

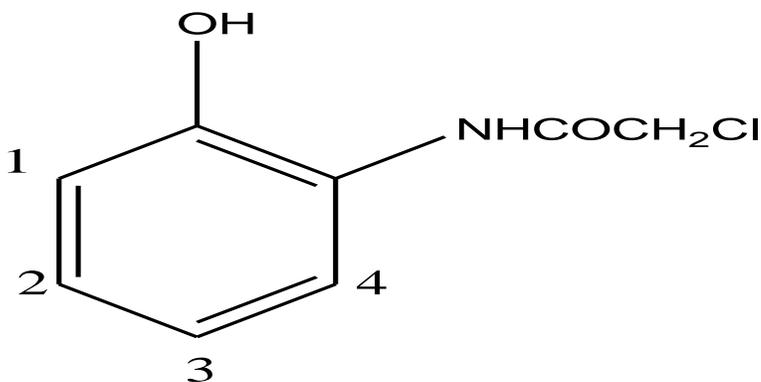


Figure 1: Structure of HPCA

Table 1:Elemental analysis results of the precursor (HPCA)

Precursor	calculated (found) %		
C ₈ H ₈ NO ₂ Cl	C	H	N
	51.4 (51.5)	4.4 (4.3)	7.5 (7.5)

IR Spectrum of HPCA: The IR spectrum (appendix 2) of the precursor HPCA shows a sharp band at 3368 cm⁻¹ due to ν-NH stretching. The broad band at 3180 shows the presence of hydrogen bonded OH (phenolic OH) in the compound. The bands at 1657, 1551, 1442, 1270 and 752 cm⁻¹ are because of C=O (amide), C=C, CH₂ (bending), C-OH (phenolic group) and C-Cl (halide group) or 1, 2 disubstituted (-Ar) respectively [18-26]. Structural differences between orthoaminophenol and HPCA are listed out in table 4.

Table 2: Comparison of AP and HPCAIR absorption frequencies (in cm⁻¹)

Compounds	ν _{NH,NH2}	ν _{OH}	ν _{C=O}	ν _{C=C}	ν _{CH2}	ν _{C-OH}	ν _{C-Cl/-Ar}
AP	3376,3269	3053	---	1513	---	1268	742
HPCA	3368(m,s)	3180(b)	1657(s,s)	1551(s)	1442	1270	750

NMR Spectra:The NMR data were obtained in CD₃CN solution for HPCA. The chemical shifts, integral values, and DEPT patterns of HPCA confirm the expected structures shown in figure 6.

¹H NMR Spectrum of HPCA: The ¹H NMR spectrum (appendix 6) of the precursor HPCA was measured in CD₃CN. The spectrum could be resolved in to seven different region of proton broad singlet at δ 4.3(S,2H,CH₂), at δ 4.85 (S,1H,OH), at δ 8.3(S,1H,NH) , δ 6.90 (D,1H,CH),at δ 7.84(D,1H,CH) , at δ 6.95 (t,1H,CH) and at δ 7.1 (t,1H,CH) which is in agreement with the proposed structure

Table 3: ¹H NMR spectrum of HPCA

HPCA	Types of proton(s)	Number of Proton(s)	δ in ppm (appearance)	Solvent CD ₃ CN
	CH ₂	2(s)	4.3	
	OH	1(s)	4.85	
	NH	1(s)	8.3	
	CH ¹	1(d)	6.9	
	CH ²	1(t)	7.1	
	CH ³	1(t)	6.95	
	CH ⁴	1(d)	7.84	

where s=singlet,d=doublet,t=triplet

¹³C NMR Spectrum of HPCA: The ¹³C NMR spectrum (appendix 7) of the precursor HPCA was also recorded in CD₃CN.At δ 44.12 (CH₂), atδ 117.02-126.63 (arom.C), at δ 126.54(C-NH), at δ 148.21 (C-OH)and at δ 166.13(C=O, amide).

The DEPT spectrum :The DEPT spectrum(appendix 8) show that there are 1CH₂ group downfield at (44.07), 4 CH group up fieldbetween (116.97-126.58).

Table 4: ¹³C NMR and DEPT spectrum of HPCA

	Types of carbon(s)	δ in ppm (appearance)	DEPT Data (δ in ppm)	Remarks	Solvent
	CH ₂	44.12	44.07	C-H ₂	
	C-NH	126.54	-----	Quaternary	
	C-OH	148.21	-----	Quaternary	

HPCA	C=O(amide)	166.13	_____	Quaternary	CD ₃ CN
	¹ CH	117.02	116.97	C-H	
	² CH	122.35	126.58	C-H	
	³ CH	118.36	121.00	C-H	
	⁴ CH	121.05	122.30	C-H	

Characterization of the ligand

General Properties of HPAPAA

N-(2-hydroxyphenyl)-2-[(2-aminophenylamino)]acetamide (HPAPAA, C₁₄H₁₅N₃O₂·HCl, molar mass 293.5 g/mol) is a deep red solid. It is soluble in solvent such as MeOH, EtOH, CD₃CN and DMSO. It is insoluble in diethylether, C₆H₆ and CHCl₃.

Chloride Test

HPAPAA decomposed/dissolved in nitric acid were subjected to chloride identification. Presence of white

precipitate formation after addition of 0.1 M AgNO₃ solution indicated the presence of chloride in the sample. This might be because of presence of HCl along with the expected product. It may be recalled that HPAPAA is formed by the reaction between HPCA and OPD, in which HCl is also a product.

Elemental Analysis

The experimental and calculated values of the elemental composition of H and N analysis data are in good match with the molecular formula of HPAPAA C₁₄H₁₅O₂N₃·HCl. Elemental analysis results of the ligand are presented in table 7.

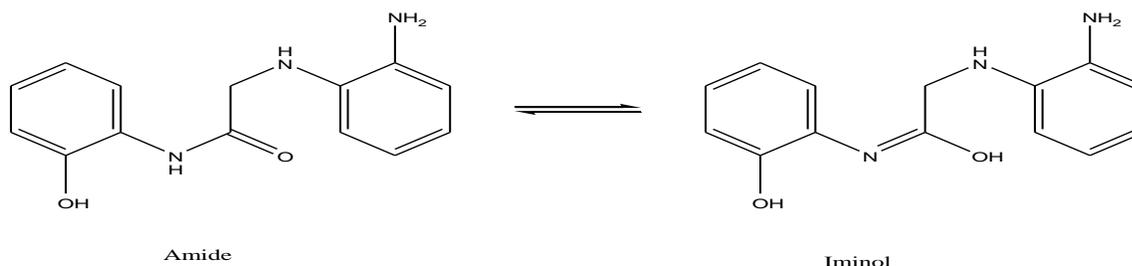
Table 5: Elemental analysis results of the ligand (HPAPAA)

Ligand	calculated (found) %		
C ₁₄ H ₁₅ O ₂ N ₃ ·HCl.	C	H	N
	—	5.45 (5.45)	14.28 (14.3)

From the above table, the experimentally obtained Hand N percentages are in good agreement with the theoretically calculated value. However, inconsistent deviations were observed between the theoretical and experimental values of carbon. This might be because of incomplete decomposition of the ligand with respect to its carbon content during the estimation. However in view of satisfactory IR, ¹H NMR and ¹³C NMR results, the formation of HPAPAA as HCl adduct was concluded.

IR Spectrum of the ligand: The IR spectrum (appendix 3) of the ligand HPAPAA shows broad band at 3401 cm⁻¹ indicating the presence of OH group while at 3200 -3000 cm⁻¹ confirm the presence of secondary

amine. The presence of OH band is indicative of the possible tautomerization (Scheme 8) in the ligand. Strong band at 1661 cm⁻¹ indicated the presence of amide moiety also and thus further supports the existence of the two possible tautomers (either keto-enol or amide-iminol) with the amide tautomer as the dominant one. A weak band at 2925 cm⁻¹, which is due to ν C-H aromatic. The bands at 1401 and 1305 cm⁻¹ are due to CH₂ (bending) and (C-OH) respectively. The medium sharp band at 1506 cm⁻¹ indicated the presence of conjugated (C=C) as a characteristic band of aromatic system, while a strong absorption peak at 750 cm⁻¹ was assigned to 1,2 disubstituted (C-Ar) bond absorption frequency. The IR data of the spectra of the ligand is presented in table 8.



Scheme 3: Amide-iminol tautomerism in the ligand.

Table 6: Important IR absorption frequencies (in cm^{-1}) of the ligand

Ligand	ν_{OH}	$\nu_{\text{NH, NH}_2}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$	ν_{CH_2}	$\nu_{\text{C-OH}}$	$\nu_{\text{C-Ar}}$	$\nu_{\text{C-N}}$
HPAPAA	3401(b)	3200-3000	1661(s)	1506(m)	1401	1305	750(s)	1121

NMR Spectra:The NMR data were obtained in CD_3CN solution for HPAPAA. The chemical shifts, integral values, and DEPT patterns of HPAPAA confirm the expected structures shown in scheme 7

^1H NMR Spectrum of HPAPAA:

In the ^1H -NMR spectrum (appendix 9), the signals between 7.9 and 6.6 ppm with their characteristic proton couplings indicate the presence of aromatic protons. The

singlet at 8.9 ppm indicates the presence of an amide-imino tautomerism in the target molecule, while a singlet at 3.9 ppm represented the presence of CH_2 . The broad singlet (2H) at 4.3 ppm is assigned to NH_2 protons. From the spectral data, it is concluded that the ligand involves tautomerism in solution phase (in CD_3CN) with the amide form being a dominant tautomer.

Table 7: ^1H NMR spectrum of HPAPAA

HPAPAA	Types of proton(s)	Number of Proton(s)	δ in ppm (appearance)	Solvent
	CH_2	2(s)	3.9	
NH_2	1(s)	4.3		
OH/NH	1(s)	8.9		
CH^1	1(d)	6.6		
CH^2	1(t)	6.65		
CH^3	1(t)	6.75		
CH^4	1(d)	6.7		
CH^5	1(d)	7.9		
CH^6	1(t)	6.95		
CH^7	1(t)	7.1		
CH^8	1(d)	6.9		

^{13}C NMR Spectrum of HPAPAA:The ^{13}C NMR spectrum (appendix 10) of the ligand HPAPAA was also measured in CD_3CN . At δ 43.12 (CH_2), at δ 120.02-125.63 (arom.C), at δ 126.54 (C-NH), at δ 134.0 may be (C=N, tautomeric), at δ 147.21 (C-OH), and at δ 165.2 (C=O, amide).

The DEPT spectrum:The DEPT spectrum (appendix 11) of the ligand HPAPAA was measured in the same solvent from the above. The DEPT spectra show that there are 1 CH_2 group downfield at (43.20), 8 CH group up field between (116.75-126.68).

Table 8: ^{13}C NMR and DEPT spectrum of HPAPAA

HPAPAA	Types of carbon(s)	δ in ppm (appearance)	DEPT Data (δ in ppm)	Remarks	Solvent
	CH_2	43.12	43.20	C- H_2	
C-NH	126.54	_____	Quaternary		
C=N	134.0	_____	Quaternary		
C-OH	147.21	_____	Quaternary		
C=O (amide)	165.23	_____	Quaternary		
^1CH	119.02	116.97	C-H		
^2CH	120.08	126.58	C-H		
^3CH	121.44	121.00	C-H		
^4CH	117.02	116.71	C-H		
^5CH	125.68	124.28	C-H		
^6CH	121.02	121.00	C-H		
^7CH	124.54	125	C-H		
^8CH	119.05	122.30	C-H		

Characterization of Ni (II) complex

General Properties of the metal complex

The metal complexes form colored compounds. They are soluble in hot (MeOH, EtOH, CD₃CN) and DMSO. It is insoluble in diethylether, C₆H₆ and CHCl₃. Some of the important physical properties of the metal complex are summarized in the following table 11.

Table 9: Some physical characteristics of the metal complexes

Complexes	NiL·4H ₂ O
Mol. Formula	NiC ₁₄ H ₁₅ O ₂ N ₃ ·4H ₂ O
Mol Weight (g/mol)	385.69
Color	Dark greenish
Appearance	Solid
Yield (%)	85.5
M.P/Decom.temp (°C)	101-102 (melt)

Elemental Analysis of the metal complex

The experimental and the calculated values of the elemental composition of C, H, and N of the metal complexes are presented in table 12.

Table 10: Elemental analysis results of Ni (II) complex

Metal Complexes	calculated (found) %		
	C	H	N
NiC ₁₄ H ₁₅ O ₂ N ₃ ·4H ₂ O	—	5.4 (5.4)	10.48 (10.89)

Results obtained from the elemental analyses of Ni(II) complex, given as experimental (calculated) was % H 5.4 (5.4) and % H 4.0 (4.4) N 10.48 (10.89). However, deviations were observed between the theoretical and experimental values of carbon. This may be due to incomplete decomposition of the complex during the analysis. As such, the formulae were matched with N, H and metal percentages.

Quantitative Determinations of the metal complexes Chloride ion estimation

Samples of the complexes were well digested in concentrated nitric acid. When 0.1M solution of silver nitrate was added to the cooled acid solutions and left overnight, there was no formation of any precipitate. This observation leads to the conclusion that the complexes do not contain any chloride ion in their structures.

Metal Estimation using AAS

The molar ratios of the metal to ligand of both the complexes were obtained from absorbance measurements using atomic absorption spectroscopy. The results obtained are tabulated as follows.

Table 11: Estimation of metals in HPAPAA-metal complexes by AAS

Element	λ absorbance (nm)	(%) of Metal cal(exp)	Metal to ligand ratio
Nickel	232	15.69 (15.21)	1:1

The results show that, theoretical and experimental (AAS) values are in good agreement, suggesting a metal to ligand ratio of 1:1 in complex according to the proposed structures.

Molar Conductance Measurement of the metal Complexes

The molar conductance (Λ_m) values were calculated from conductivity measurements in MeOH and DMF. Specific conductance (Sc) is a measure of how well solution conducts electricity. Conductibility increases with increasing concentration and mobility of ions. These ions come from the breakdown of a compound and conduct electric current because they are positively and negatively charged when dissolved in the solvent. The specific conductance of 0.001M solution of Ni (II) complex was measured in MeOH and DMF at 21°C and found to be 25.49 μScm^{-1} . The molar

conductance of each complex was calculated from the following equation.

$$\Lambda_M = \frac{1000K}{C}; \text{ Where } \Lambda_M = \text{Molar conductance}$$

C= concentration of the sample (10^{-3})

κ = specific conductivity of the complex

non-electrolytes. In view of the non-electrolytic nature, absence of chloride in both the complexes, it is concluded that the ligand undergoes enolization and subsequent deprotonation of enolic and phenolic hydrogen to form a dinegative anion (ONO^{2-}) during complexation. As such the enol form of the ligand is proposed for chelation. This derives further support from spectral and magnetic data.

The molar conductance values which summarized in table-14 indicate that both Ni (II) Zn (II) complexes are

Table 12: Conductivity data for the metal complexes

Complexes	Solvent	Molar conductance, $\text{Scm}^2\text{mol}^{-1}$	Ions ratio	Type
NiL·4H ₂ O	DMF	25.49	—	Non-electrolyte

Magnetic susceptibility of the metal Complexes

Magnetic susceptibility measurements were recorded at room temperature (23 °C). The gram magnetic susceptibility measurements for Ni (II) complex is 4.416×10^{-6} . The result indicates Ni (II) complex is

paramagnetic with magnetic moment values 2.0 (BM). This value is significantly sub-normal and can be explained on the basis of substantial anti-ferromagnetic interaction at room temperature [28, 29]. Octahedral geometry for the Ni (II) complex have been proposed.

The experimentally obtained gram magnetic susceptibility (χ_g), calculated magnetic moment and nature of complexes are summarized in table 15.

Table 13: Magnetic moments of the metal complexes

Complexes	$\chi_g \times 10^{-6}$	$\chi_m = \chi_g \text{MW}$	$\mu = 2.824[\chi_m]^{1/2}$	Nature of the complex
NiL·4H ₂ O	4.416	0.00225	2.0 (BM)	Paramagnetic

Infrared spectra of the metal complexes

The IR spectra of the complexes were compared with those of the free ligand in order to determine the coordination sites that may be involved in coordination (appendix 3-5). The spectrum of HPAPAA (ligand), show some characteristic bands. The main bands are in the regions corresponding to ν_{OH} and $\nu_{C=O}$ functions besides, $\nu_{C=C}$, ν_{C-H} and other related bands. An intense broad band centered at 3401 cm^{-1} observed due to ν_{OH} in the spectrum of the free ligand was absent in the spectra of metal complexes. However, more intense and broad bands were observed at $3468\text{-}3500\text{ cm}^{-1}$ in the metal complexes spectra. They are assignable to ν_{OH} , due to H_2O molecules which are present in both the complexes.

Comparison of the free ligand and metal complexes spectra indicates that the ligand undergoes tautomerization to iminol form (scheme 7) during complexation. Strong bands at 1661 and 1506 cm^{-1} in free ligand assignable to $\nu_{C=O}$ and $\nu_{C=C}$ are replaced by intense, sharp and multiple bands in the regions $1656\text{-}1487\text{ cm}^{-1}$ in Ni (II) complex. These bands are assignable to $\nu_{C=N}$, $\nu_{C=C}$, ν_{NH_2} , ν_{H_2O} of the enol tautomer and of H_2O present in the complexes. The absorptions around 1500 cm^{-1} in the complex can be attributed to $\nu_{C=C}$ stretching vibration of aromatic carbon, which is in agreement with previous observations. The bands at 1402 and 750 cm^{-1} are due to CH_2 (bending) and 1, 2 disubstituted (-Ar) respectively.

The phenolic ν_{C-O} stretching vibrations appeared at 1305 cm^{-1} in the free ligand, undergo a shift towards lower frequencies (1251 and 1261 cm^{-1}) in the complexes. This shift confirms the participation of oxygen in the formation of C-O-M bond. Significant lowering of ν_{C-O} may be attributed to the involvement of deprotonated phenolic oxygen in bonding and bridging interaction. This is proposed as the reason for sub-normal magnetic moment of Ni (II) complex, leading to metal-metal interaction via phenoxide bridging.

The band at 1121 cm^{-1} assigned for C-N stretching side chain in the free ligand is shifted to lower wave number (1107 and 1117 cm^{-1}) in the complexes. This suggests that the nitrogen atom of the ligand is involved in coordination with the metal ions.

Further evidence for bonding by nitrogen and oxygen atoms is provided by far IR spectra of complexes. Due to interference of skeletal vibrations of ligands with M-N and M-O vibrations, definite assignments of bands are difficult. Therefore only tentative assignments are made on the basis of information available in literature.

Spectra of both complexes showed weak bands at $600\text{-}550\text{ cm}^{-1}$ and $480\text{-}450\text{ cm}^{-1}$ vibrations, which may be assigned to the ν_{M-N} and ν_{M-O} stretching [16, 17]

The presence of coordinated water in Ni (II) complex was suggested by very broad absorption centered around 3468 cm^{-1} in the infrared spectrum. Some of the weak bands between $640\text{-}400\text{ cm}^{-1}$ are due to the wagging mode of water and those between $1038\text{-}750\text{ cm}^{-1}$ are assigned for rocking mode of coordinated water. Based on geometrical consideration four water molecules are assumed to be in coordination sphere while the remaining is in lattice sites.

Based on IR data, it is proposed that the ligand behaves as dibasic tridentate, employing ONO donor sequence in chelation. Deprotonated phenolic oxygen, imine nitrogen and deprotonated iminolic oxygen are proposed for the chelation. The donor sequence will form complexes with bicyclic structural components, in which a five membered ring and a four membered ring combine to stabilize the chelate, while gaining further support from phenoxide bridging. This appears to be a unique feature of this metal-ligand interaction. The IR data of the spectra of the ligand and their metal complexes are presented in Table 14.

Table 14: IR absorption frequencies (in cm^{-1}) of HPAPAA and its metal complexes

Band assignments	HPAPAA/ cm^{-1}	Ni (II) complex/ cm^{-1}
$\nu_{(OH)}$	3401	3500
$\nu_{(NH, NH_2)}$	3200-3000	3100
$\nu_{(C=O)}$	1661 (s)	—
$\nu_{(C=N)}$	—	1656
$\nu_{(C=C)}$	1506	1487
$\nu_{(CH_2)}$	1401	1403
$\nu_{(C-OH)}$	1305	1251
$\nu_{(C-N)}$	1121	1107
$\nu_{(C-Ar/C-Cl)}$	750	752
ν_{M-N}, ν_{M-O}	—	600-550, 480-450

UV-VIS Spectrum of HPAPAA and its metal complex

Electronic spectra measurements are very useful for assigning the stereochemistry of the complex based on the position and number of d-d transitions. The electronic absorption spectra of the complexes were recorded at room temperature using the solvent methanol.

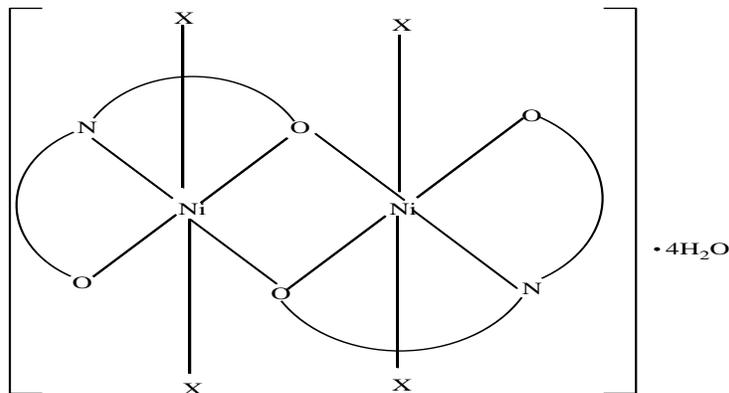
The UV-Vis spectrum of the ligand is characterized mainly by two absorption bands at 396 nm (25253 cm^{-1}), and 286 nm (34965 cm^{-1}). The first band in the spectrum of the ligand was assigned to transition due to extended conjugation of the ligand (HPAPAA). The second band was attributed to transition due to aminophenol chromophore moiety (Appendix 12-14).

In general, there is a wave length shift of both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands, which suggest modifications in electronic distribution of complexation. The electronic spectrum of Ni (II) complex shows characteristic bands in visible/near IR region which are assignable to d-d transition but in our case there is experimental limitation. However, Ni (II) complex have three spin allowed transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ in the range of 7000-13000, 11000-20000 and 19000-27000 cm^{-1} only two spin allowed transitions are observed in our case ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ at, 23923 and 27770 respectively. ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transition has not been resolved under the experimental condition. Based on the data presented in table 17 along with assignment of transitions, octahedral geometry has been assigned to Ni (II) complex [1].

Table 15: UV-VIS Spectrum of HPAPAA and its metal Ni (II) complex

Compounds	Abs. nm (cm^{-1})	Assignment of Transition
HPAPAA	396 (25253) 286 (34965)	Bands of extended conjugation Bands of aminophenol chromophore moiety
NiL·4H ₂ O	418 (23923) 360 (27770)	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$,

Based on the analytical, infrared, conductivity, magnetic susceptibility and electronic spectral data, octahedral geometry for Ni (II) complex was suggested and the proposed schematic structures are presented in figures 7 and 8.



Where X=H₂O

Figure 2: proposed schematic structure of Ni (II) complex

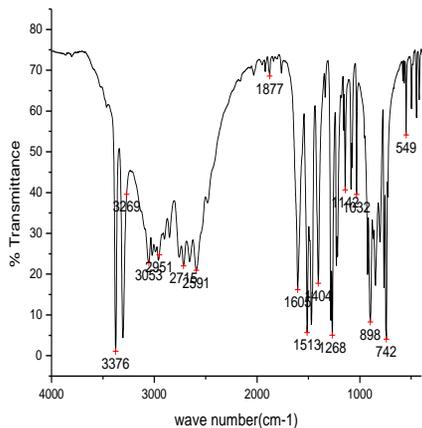
Conclusion

A new polydentate ligand N-(2-hydroxyphenyl)-2-[(2-aminophenylamino)] acetamide, (HPAPAA), has been synthesized in the reaction between N-(2-hydroxyphenyl)-2-chloroacetamide and o-phenylenediamine. The Ni(II) complex of the ligand was synthesized from methanolic media and subjected to structural elucidation based on spectral (IR, NMR, UV-VIS, AAS), conductivity and magnetic studies. The conductivity data revealed that the complex is non-electrolytes. In view of the non-electrolytic nature, absence of chloride in both the complexes, it is concluded that the ligand undergoes enolization and subsequent deprotonation to form a dinegative anion (ONO)²⁻ during complexation. The atomic absorption spectral data revealed metal to ligand ratio 1:1 for both Ni(II) complex. Binuclear Ni(II) complex exhibited subnormal magnetic moment indicating the possibility of antiferromagnetic interaction through a possible super exchange mechanism. Based on IR data, it is proposed that the ligand behaves as dibasic tridentate, employing ONO donor sequence in chelation including phenoxide bridging.

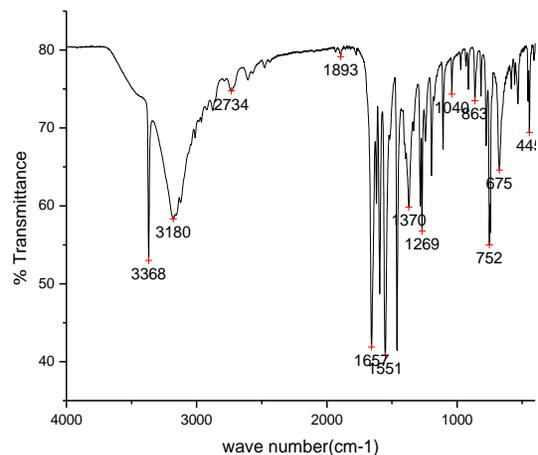
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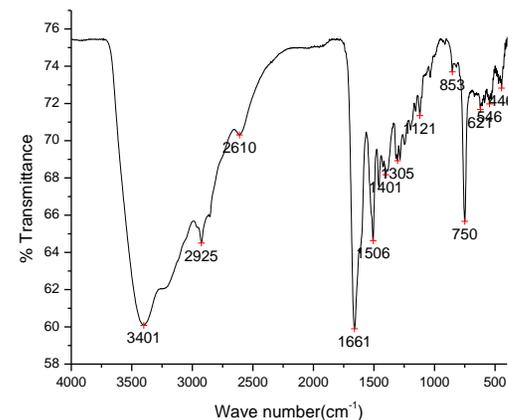
6. Appendices



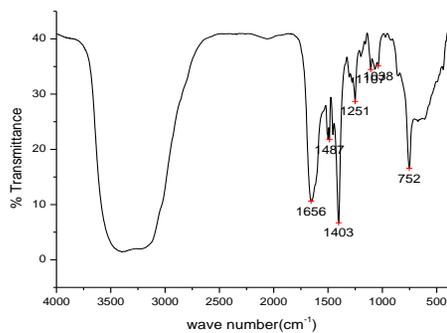
1: IR spectrum of 2-AP



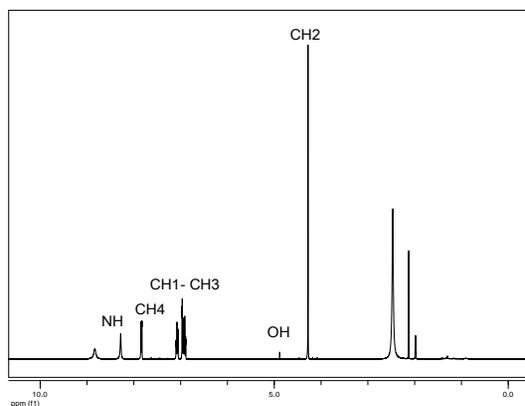
2: IR spectrum of HPCA



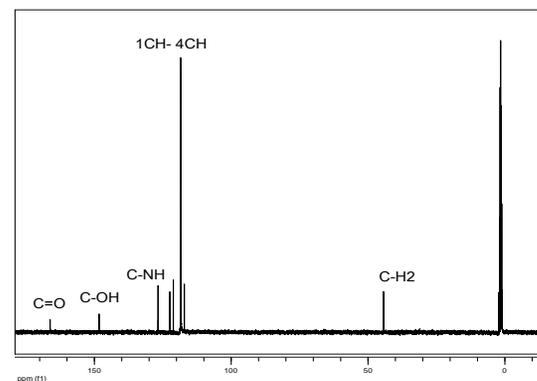
3: IR spectrum of HPAPAA



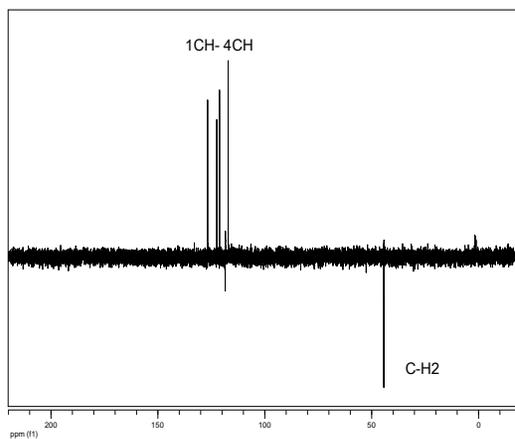
4: IR spectrum of Ni (II) complex



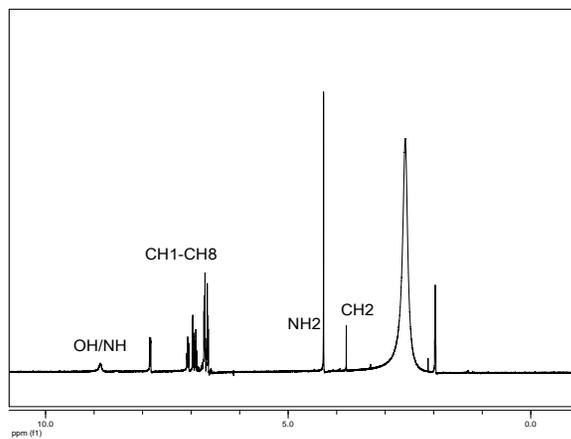
5: ¹H NMR spectrum of HPCA



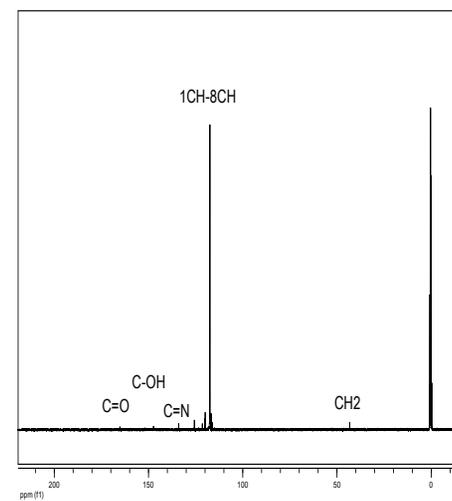
6: ¹³C NMR spectrum of HPCA



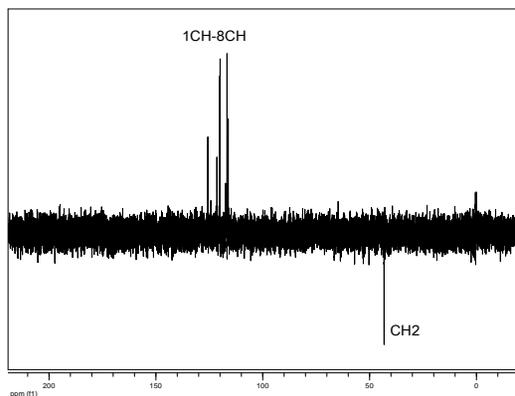
7 : DEPT-135 NMR spectrum of HPCA



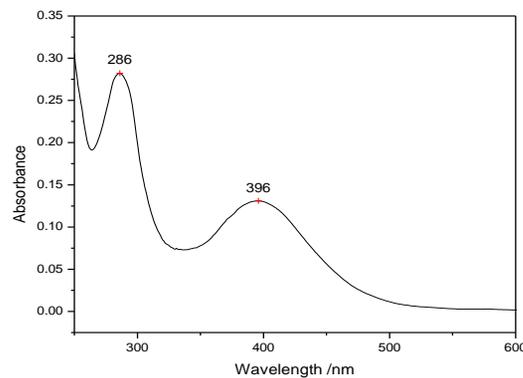
8 : ¹H NMR spectrum of HPAPAA



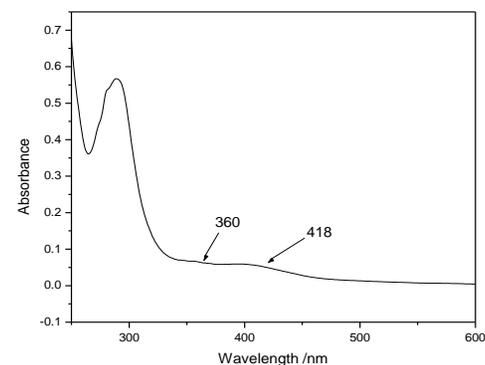
9: ¹³C NMR spectrum of HPAPAA



10: DEPT-135 NMR spectrum of HPAPAA



11: UV-VIS spectrum of HPAPAA



12: UV-VIS spectrum of Ni (II) complex