

## SYNTHESIS AND STRUCTURAL STUDIES OF A NEW POLYDENTATE LIGAND AND ITS NI (II) AND ZN (II) COMPLEXES

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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. The Ni (II) and Zn (II) complexes of the ligand were synthesized and characterized on the basis of their spectral (IR, NMR, UV-Vis, and AAS), elemental analyses, conductivity and magnetic susceptibility measurements. The Ni (II) and Zn (II) metal complexes were synthesized in methanolic media. Metal-to-ligand ratios were found to be 1:1 for both complexes. Conductivity measurements suggested that both complexes were 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 and, square planar geometry for Zn (II) complex was suggested.

**KEYWORDS:** polydentate ligand, Ni (II) and Zn (II) complexes, HPAPAA.

## INTRODUCTION

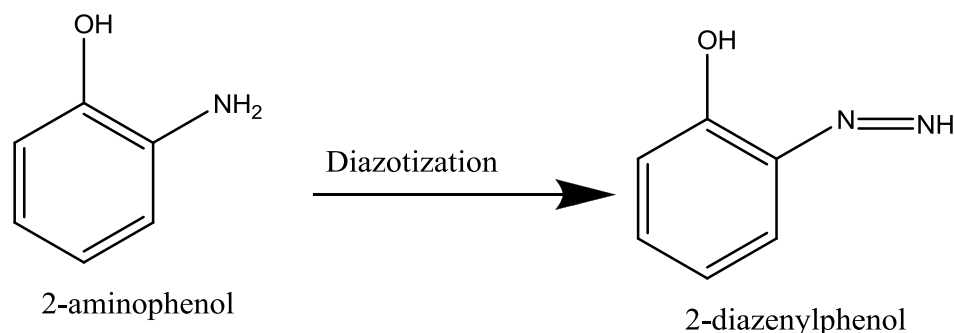
A metal complex consists of a central metal atom or ion surrounded by a set of ligands that have one or more atom(s) bearing lone pairs of electron(s). These 'donor' atoms are bound electrostatically and covalently to the metal ion. In non-transition metal complexes, the binding is largely electrostatic, while in transition metal complexes there is significant covalency.

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.

## MATERIALS AND METHODS

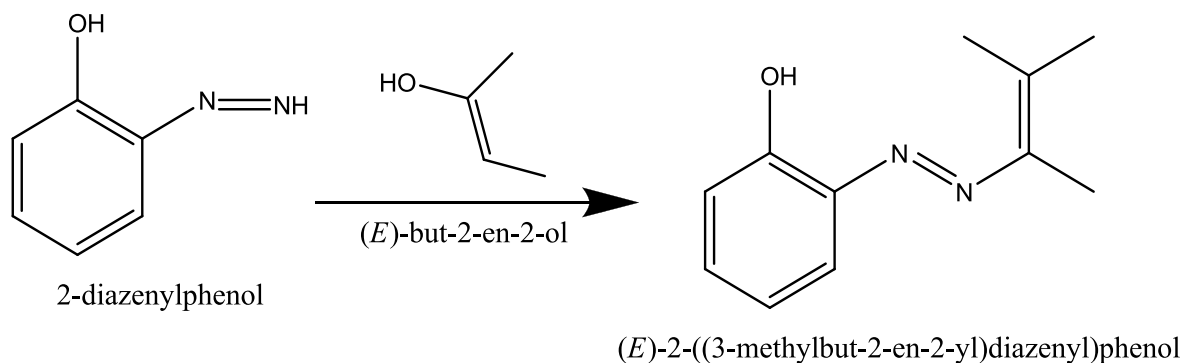
### Scheme of the work

#### STEP: 1. SYNTHESIS OF 2-DIAZENYLPHENOL.



Treatment of equimolar amounts of 2-amino phenol with phenyl hydrazine in ethanol at room temperature.

#### STEP:2. SYNTHESIS 2-((3-METHYLBUT-2-EN-2-YL) DIAZENYL) PHENOL

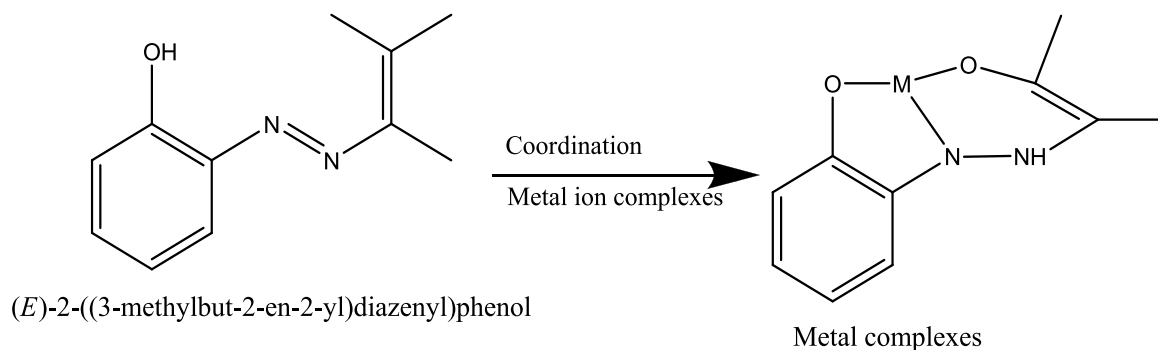


To a solution of compound 1 (0.2mole) in ethanol, but-2-en-2-ol (0.2mole) is added.

The mixture is refluxed for 8 hours.

The solvent is evaporated and the solid obtained is recrystallized from petroleum ether.

### STEP: 3. SYNTHESIS OF P-OH-5-PHENYL-1H-PYRAZOLE-3-CARBOHYDRAZIDE



Compound 2 (0.1mole) in ethanol (10ml) 2ml of hydrazine hydrate in metal ion complexes is added.

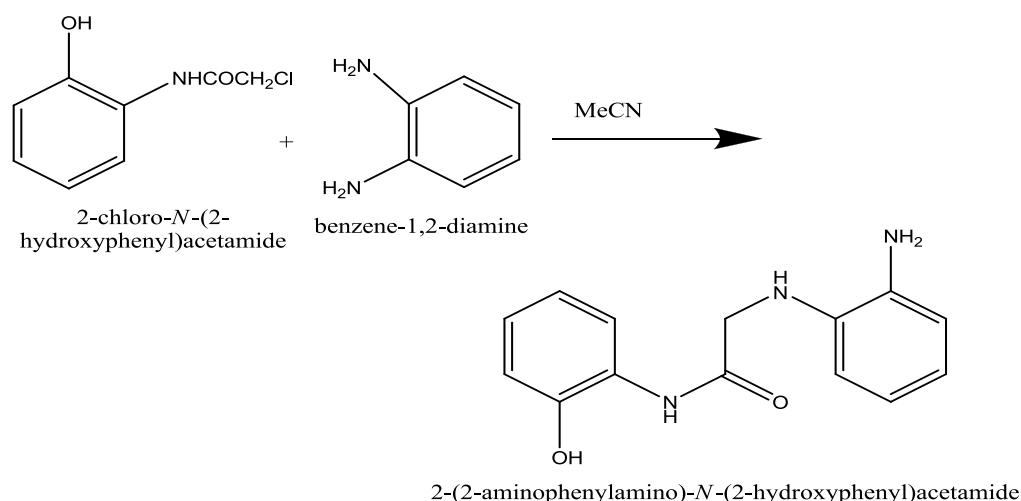
The mixture is maintained under reflux for 8 hours.

After cooling, the mixture is poured on ice and the solid formed is collected by filtration, washed with cold water and recrystallized from ethanol.

#### Physical Characterization

- ✓ Molecular formula :  $C_{10}H_{11}N_2O_2$
- ✓ Molecular weight (gm) : 191.21g/mol
- ✓ Soluble in Methanol, Ethanol, DMSO and DMF.
- ✓ Melting point : 135°C
- ✓ Melting points were determined using Veego Digital melting point apparatus.
- ✓ The purity of synthesis compound was monitored on TLC.
- ✓ Absorbent used : Precoated Silica gel- G plate
- ✓ Mobile Phase : Chloroform : Methnol (4:6)
- ✓  $R_f$  value: 0.80

### Synthesis of the ligand

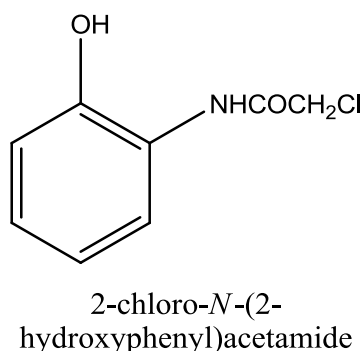


*N*-(2-hydroxyphenyl)-2-chloroacetamide (0.004 mol, 0.7 g) in 20 ml MeCN was mixed with *o*-phenylenediamine (0.004 mol, 0.42 g) in 20 ml MeCN. The solution was refluxed for about 9 hours with stirring on water bath and then concentrated. The resulting deep red product was filtered and repeatedly washed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

### Spectral analysis

#### Elemental Analysis of HPCA

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.



Precursor	calculated (found) %		
	C	H	N
<b>C<sub>8</sub>H<sub>8</sub>NO<sub>2</sub>Cl</b>	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<sup>-1</sup> due to  $\nu$ -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<sup>-1</sup> are because of C=O (amide), C=C, CH<sub>2</sub> (bending), C-OH (phenolic group) and C-Cl (halide group) or 1, 2 disubstituted (-Ar) respectively.

Compounds	$\nu$ NH,NH <sub>2</sub>	$\nu$ OH	$\nu$ C=O	$\nu$ C=C	$\nu$ CH <sub>2</sub>	$\nu$ C-OH	$\nu$ C-Cl/-Ar
AP	3376,3269	3053		1513		1268	742
HPCA	3368(m,s)	3180(b)	1657(s,s)	1551(s,s)	1442	1270	750

### NMR Spectra

The NMR data were obtained in CD<sub>3</sub>CN solution for HPCA. The chemical shifts, integral values, and DEPT patterns of HPCA confirm the expected structures shown in figure.

#### <sup>1</sup>H NMR Spectrum of HPCA

The <sup>1</sup>H NMR spectrum (appendix 6) of the precursor HPCA was measured in CD<sub>3</sub>CN. The spectrum could be resolved in to seven different region of proton broad singlet at  $\delta$  4.3 (S,2H,CH<sub>2</sub>), at  $\delta$  4.85 (S,1H,OH), at  $\delta$  8.3 (S,1H,NH),  $\delta$  6.90 (D,1H,CH), at  $\delta$  7.84 (D,1H,CH), at  $\delta$  6.95 (t,1H,CH) and at  $\delta$  7.1 (t,1H,CH) which is in agreement with the proposed structure.

<sup>1</sup>H NMR spectrum of HPCA.

HPCA	Types of proton (s)	Number of Proton(s)	$\delta$ in ppm (appearance)	Solvent  CD <sub>3</sub> CN
	CH <sub>2</sub>	2(s)	4.3	
	OH	1(s)	4.85	
	NH	1(s)	8.3	
	CH <sub>1</sub>	1(d)	6.9	
	CH <sub>2</sub>	1(t)	7.1	
	CH <sub>3</sub>	1(t)	6.95	
	CH <sub>4</sub>	1(d)	7.84	

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

## RESULTS AND DISCUSSION

### Synthesis

The present study report the Synthesis of ligands and metal ion complexes. Electrophilic substitution of 2-aminophenol was carried out stepwise at different temperature by hydrazine

hydrate. The first step involves the substitution 2-aminophenol and the next by 2-diazenyl phenol with ethanol. The final metal ion complex in the synthesized compound-3 was synthesized.

### Physical Characterization

Melting point of the synthesized compound was taken in open capillary tubes and was uncorrected and were found to be in the range of 120-140°C.

TLC was performed using precoated silica gel plates of 0.25mm thickness. Eluents used were Chloroform, Methanol (6:4). Spots were visualized in U.V. light.

At room temperature solubility of newly synthesized compound were determined by various organic solvents and it was found that compound were freely soluble in DMSO, DMF, Methanol and Ethanol.

### Elemental Analysis of HPCA

The Elemental analysis results of the precursor (HPCA) C 51.4(51.5), H 4.4 (4.3), N 7.5 (7.5).

### IR Spectrum of HPCA

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  $\text{cm}^{-1}$  are because of C=O (amide), C=C, CH<sub>2</sub> (bending), C-OH (phenolic group) and C-Cl (halide group) or 1, 2 disubstituted (-Ar) respectively.

### <sup>1</sup>H NMR Spectrum of HPCA

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### REFERENCES

1. Huheey, J.E.; Keiter, E.A.; Keiter, R.L. *Inorganic Chemistry*, 4th ed., Harper Collins college publishers: New York, 1993.
2. Murilla, C.A.; Cotton, F.A.; Wilkinson, G.; Bochmann M. *Advanced Inorganic Chemistry*, 6th ed., Wiley India Pvt. Ltd: India, 2007.
3. Atkins, P.W. *Shriver and Atkins inorganic chemistry*. 5th ed., Oxford University

- Press: UK, 2010.
- Lee, J.D. *A New Concise Inorganic Chemistry*, 3th ed., Oxford University Press: UK, 2013.
  - Miessler, G.L.; Fischer, P.J.; Tarr, D.A. *Inorganic Chemistry*, 5th ed., Prentice Hall Inc, 2013.
  - Canham, G.R. *Descriptive Inorganic Chemistry*, 2nd ed., W.H.Freeman and company: USA, 2000.
  - Gavrilova, A.L.; Bosnich, B. *Principles of mononucleating and binucleating ligand design*, Chem. Rev, 2004; 104: 349-383.
  - [http://en.wikipedia.org/wiki/Coordination\\_complex](http://en.wikipedia.org/wiki/Coordination_complex).
  - El-Sonbati, A.Z.; El-Bidarry, A.A. *Polish. J. Chem*, 2000; 74: 621-630.
  - Carneiro, T.M.G.; Beraldu, H. *J. Braz. Chem. Soc*, 1999; 10: 184-188.
  - Raman, N.; Muthuraj, V.; Ravichandrand, S.; Kulandasamy, A. *Proc.India, Acad.Sci*, 2003; 115: 3.
  - Raman, N.; Pitchaikani, Y.; Kulandasamy, A. *Proc. India, Acad. Sci*, 2001; 113.
  - Assayehegn, E. *Synthesis and Structural Studies on metal complex based on multidentate ligand derived from salicylaldehyde and resdiacetophenone- dihydrazone*, M.Sc. Thesis, Addis Ababa University, Addis Ababa, Ethiopia, 2007.
  - Gudasi, K.B.; Patil S.A.; Vadavi, R.S.; Shenoy, R.V.; Patil M.S. *J. Serb. Chem. Soc*, 2006; 71(5): 529–542.
  - Sisay, G. *Synthesis and Characterization of Some Transition Metal Complexes with O,N,O and O,O donor ligands*, M.Sc. Thesis, Addis Ababa University, Addis Ababa, Ethiopia, 2012.