
SCHIFF BASE COMPOUND PREPARATION FROM BENZOIN AND GLYCINE REACTION: A CHARACTERIZATION TECHNIQUE.

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ABSTRACT

A new series of complexes containing benzoin and glycine compounds were prepared as ligands, ligand was prepared by the reacting between benzoin and glycine to give the corresponding Schiff base compound ((E)-2-((2-hydroxy-1,2-diphenylethylidene) amino) propanoic acid). The complexes $M(\text{HDPENP})_2$ - of Cu(II), Ni(II), Co(II), Zn(II) and Fe(II) containing Schiff base compound has been synthesized by the reacting between copper bromide, hydrate nickel chloride, hydrate cobalt chloride, zinc chloride, and iron bromide and Schiff base in 1:2 mole ratio. It has been isolated in the solid state and characterized by (C.H.N) data, IR and ^1H NMR spectroscopy. Six coordinate and octahedral complexes were produced and the results are reported and discussed below.

KEYWORDS: Benzoin, Complexes, Schiff Base, Glycine, Metal Complexes

INTRODUCTION

When an aldehyde or a ketone is condensed with a primary amine, a Schiff base is synthesized, a compound containing imine or azomethine group ($R - C = N -$)[1]. The common structural feature of these compounds is the azomethine group with a general formula $\text{RHC}=\text{N-R}_1$, where R and R_1 are alkyl, aryl, cycloalkyl or heterocyclic groups which may be differently substituted. Schiff bases were known since 1864 when Hugo Schiff discovered the condensation of primary amines with carbonyl compounds [2].

Structurally, a Schiff's base is considered as a nitrogen analogue of an aldehyde or ketone in which the carbonyl group ($>\text{C} = \text{O}$) is substituted by an imine or azomethine group.

Schiff's bases have also been shown to exhibit a wide range of biological activities, including antifungal, antibacterial, anti-malarial, anti-proliferative, anti-inflammatory, antiviral, and antipyretic properties [3,4]. Imine or azomethine groups found in various natural, naturally derived, and non-natural compounds. The imine group present in such compounds has been shown to be crucial to their biological activities [5-7]. Therefore, complexes of Schiff base were recognized for many fields including; bioinorganic chemistry, biomedical applications, supramolecular chemistry, catalysis and material science, separation and encapsulation processes, and synthesis of compounds with unusual properties and structures.

Benzoin is an α -hydroxy ketone, which is prepared by benzoin condensation reaction. The benzoin condensation is a reaction between two aromatic aldehydes to form a new carbon-carbon bond, known as the benzoin condensation. Since the beginning of organic chemistry, α -amino acids have been an attractive target for synthetic chemists. In a recent study, they described the preparation of Ni(II) complexes of glycine Schiff base with α -phenyl ethylamine-derived ligands [8]. This paper reports the preparation and characterization of five new compounds formed by ligand produced from benzoin and glycine amino acid as Schiff base.

EXPERIMENTAL

Chemicals and Apparatus

Chemicals obtained from Sigma-Aldrich, Fluka and BDH used without purification. Melting point was determined by using open capillary tube melting point apparatus. ^1H NMR spectra were recorded on Bruker 300 MHz spectrometers with TMS as an internal reference using DMSO- d_6 solvent. Infra-red spectra were recorded with KBr disks using a FTIR spectrophotometer Shimadzu model 8400 S in range 4000-400 cm^{-1} . Elemental analysis for Carbon, Hydrogen and Nitrogen were performed by using a Euro vector EA 3000A Elemental Analysis (Italy). Melting points of all solid compounds were determined using a MPS10 electrically heated melting point apparatus.

Synthesis

Preparation of (E)-2-((2-hydroxy-1,2-diphenylethylidene)amino)propanoic acid ligand

To a hot ethanolic solution of benzoin (0.01 mol, 2.12g) and glycine (0.01 mol, 0.89g) was added some drops of glacial acetic acid and the mixture refluxed for 3 hours. The hot solution was cooled into room temperature upon pall- yellow precipitate of the Schiff's base separated: it was filtered. Washed with water, dried and recrystallized from ethanol.⁽⁹⁾

Empirical formula: $\text{C}_{17}\text{H}_{17}\text{NO}_3$; formula weight: 283.32 g mol^{-1} ; yield: 93% ; appearance: pall- yellow crystals; m.p. = 72-74 $^\circ\text{C}$; Elem. analysis: calc. C, 72.07 %; H, 6.05 %; N, 4.94 %; found: C, 72.30 %; H, 6.10 %; N, 4.72 %; FTIR: 3110 cm^{-1} $\nu(\text{C-H})$ aromatic, 2900 cm^{-1} $\nu(\text{CH})$ aliphatic, 3000 cm^{-1} $\nu(\text{O-H})$ aliphatic, 1753 cm^{-1} $\nu(\text{C=O})$, 1665 cm^{-1} $\nu(\text{C-N})$ aromatic, 1210 cm^{-1} $\nu(\text{C-N})$ aliphatic. ^1H NMR (ppm): 7.21-7.74 (m, 10H, aromatic), 1.34 (d, 3H, CH_3), 4.20 (q, 1H, N-CH), 4.55 (s, 1H, CH-OH), 10.55 (s, 1H, OH- Carboxylic), 3.73 (s, 1H, OH-CH).

Preparation of the complexes from 1-5

A hot ethanolic solution of the ligand of (E)-2-((2-hydroxy-1,2-diphenylethylidene) amino) propanoic acid (**HDPENP**) (0.001 mol) in absolute ethanol (10 ml) was prepared and then CuBr_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 and FeBr_2 (0.0005 mol) in absolute ethanol (10 mL) was added to the hot solution of **HDPENP** ligand. The mixture of ligand and metal halide were

refluxed for 2 hrs. The product colored solution was left standing at room temperature to crystallize. The product was filtered to obtain precipitate washed with cooled absolute ethanol. Recrystallized from methanol then dried. The analytical and physical data of the complexes are:

Cu(HDPENP)₂ [1]

Empirical formula: C₃₄H₃₂CuN₂O₆; formula weight: 628.17 gmol⁻¹; yield: 73% ; appearance: pall- yellow crystals; m.p. = 102-104 °C; Elem. analysis: calc. C, 65.01 %; H, 5.13 %; N, 4.46 %; found: C, 65.33 %; H, 5.42 %; N, 4.75 %; FTIR: 3115cm⁻¹ v(C-H) aromatic, 2910 cm⁻¹ v(CH) aliphatic, 3050 cm⁻¹ v(O-H) aliphatic, 1750 cm⁻¹ v(C=O), 1605 cm⁻¹ v(C-N) aromatic, 1215 cm⁻¹ v(C-N) aliphatic. 1H NMR (ppm): 7.33- 7.80 (m, 20H, aromatic), 1.43 (d, 6H, CH₃), 4.25 (q, 2H, N-CH), 4.50 (s, 2H, CH-OH), 10.85 (s, 2H, OH-Carboxylic).

Fe(HDPENP)₂ [2]

Empirical formula: C₃₄H₃₂FeN₂O₆; formula weight: 620.47 gmol⁻¹; yield: 64% ; appearance: yellow crystals; m.p. = 93-95 °C; Elem. analysis: calc. C, 65.81 %; H, 5.20 %; N, 4.51 %; found: C, 65.40 %; H, 5.13 %; N, 4.70 %; FTIR: 3012cm⁻¹ v(C-H) aromatic, 2877 cm⁻¹ v(CH) aliphatic, 2900 cm⁻¹ v(O-H) aliphatic, 1705 cm⁻¹ v(C=O), 1653 cm⁻¹ v(C-N) aromatic, 1235 cm⁻¹ v(C-N) aliphatic. 1H NMR (ppm): 7.38-7.85 (m, 20H, aromatic), 1.39 (d, 6H, CH₃), 4.22 (q, 2H, N-CH), 4.50 (s, 2H, CH-OH), 10.99 (s, 2H, OH- Carboxylic).

Zn(HDPENP)₂ [3]

Empirical formula: C₃₄H₃₂ZnN₂O₆; formula weight: 630.01 gmol⁻¹; yield: 70% ; appearance: white - yellow

crystals; m.p. = 89-91 °C; Elem. analysis: calc. C, 64.82 %; H, 5.12 %; N, 4.45 %; found: C, 65.10 %; H, 5.22 %; N, 4.63 %; FTIR: 3010cm⁻¹ v(C-H) aromatic, 2950 cm⁻¹ v(CH) aliphatic, 3150 cm⁻¹ v(O-H) aliphatic, 1707 cm⁻¹ v(C=O), 1660 cm⁻¹ v(C-N) aromatic, 1215 cm⁻¹ v(C-N) aliphatic. 1H NMR (ppm): 7.33- 7.94 (m, 20H, aromatic), 1.44 (d, 6H, CH₃), 4.17 (q, 2H, N-CH), 4.33 (s, 2H, CH-OH), 11.21 (s, 2H, OH-Carboxylic).

Ni(HDPENP)₂ [4]

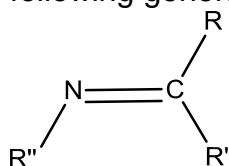
Empirical formula: C₃₄H₃₂NiN₂O₆; formula weight: 623.32 gmol⁻¹; yield: 81% ; appearance: green- yellow crystals; m.p. = 110-112 °C; Elem. analysis: calc. C, 65.51 %; H, 5.17 %; N, 4.49 %; found: C, 65.36 %; H, 5.12 %; N, 4.55 %; FTIR: 3100cm⁻¹ v(C-H) aromatic, 2950 cm⁻¹ v(C-H) aliphatic, 3000 cm⁻¹ v(O-H) aliphatic, 1735 cm⁻¹ v(C=O), 1676 cm⁻¹ v(C-N) aromatic, 1215 cm⁻¹ v(C-N) aliphatic. 1H NMR (ppm): 7.35- 7.75 (m, 20H, aromatic), 1.54 (d, 6H, CH₃), 4.15 (q, 2H, N-CH), 4.45 (s, 2H, CH-OH), 10.95 (s, 2H, OH-Carboxylic).

Co(HDPENP)₂ [5]

Empirical formula: C₃₄H₃₂CoN₂O₆; formula weight: 623.56 gmol⁻¹; yield: 75% ; appearance: yellow crystals; m.p. = 125-127 °C; Elem. analysis: calc. C, 65.49 %; H, 5.17 %; N, 4.49 %; found: C, 65.40 %; H, 5.33 %; N, 4.13 %; FTIR: 3105cm⁻¹ v(C-H) aromatic, 2920 cm⁻¹ v(CH) aliphatic, 3300 cm⁻¹ v(O-H) aliphatic, 1745 cm⁻¹ v(C=O), 1643 cm⁻¹ v(C-N) aromatic, 1217 cm⁻¹ v(C-N) aliphatic. 1H NMR (ppm): 7.25-7.81 (m, 20H, aromatic), 1.44 (d, 6H, CH₃), 4.28 (q, 2H, N-CH), 4.39 (s, 2H, CH-OH), 10.93 (s, 1H, OH- Carboxylic).

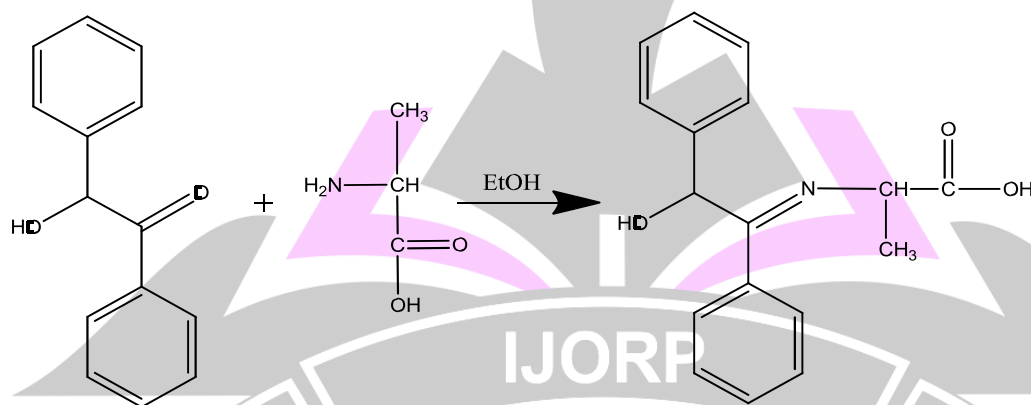
RESULTS AND DISCUSSION

A Schiff base or Schiff's base is a type of chemical compounds containing a carbon-nitrogen double bond as functional group, where the nitrogen atom connected to aryl group or alkyl group (R) but not hydrogen. The Schiff base is synonymous with an azomethine. These compounds were named after Hugo Schiff and has the following general structure:



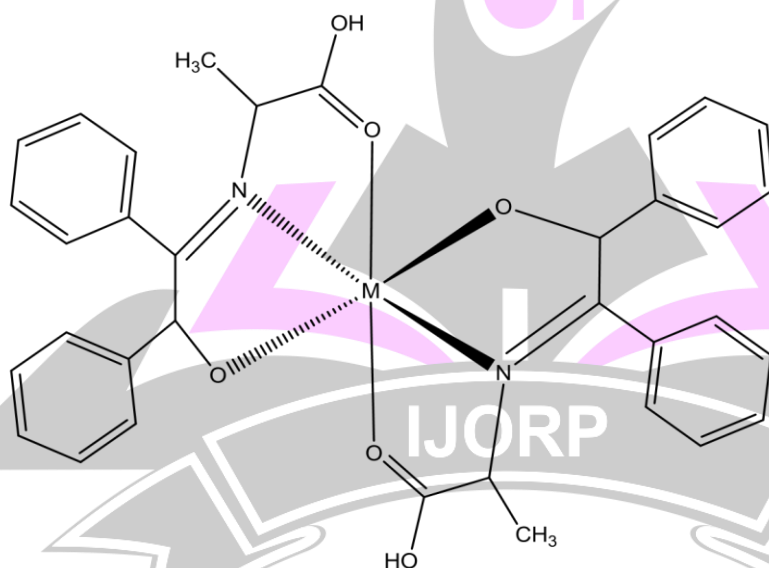
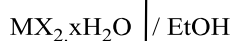
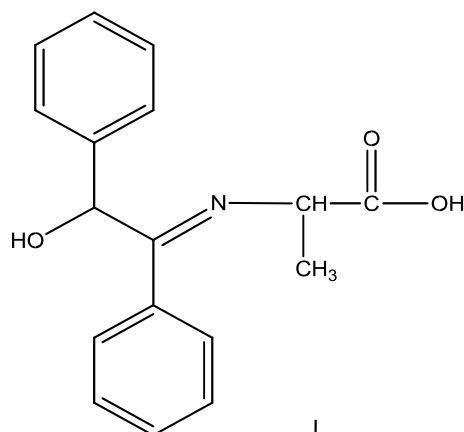
1,2diphenylethylidene)amino)propanoic acid (**HDPENP**), [Scheme 1.].

Where R stands for a phenyl or alkyl group which makes the Schiff base a stable imine. This kind of ligands is able to coordinate metal ions through the imine nitrogen and another group, usually linked to the aldehyde. The synthesis of Schiff base compound was completed by the reaction between benzoin and glycine amino acid depend on literature with minor modification⁽⁹⁾, to give the corresponding Schiff base (E)-2-((2-hydroxy-



SCHEME 1. Preparative methods for (E)-2-((2-hydroxy-1,2-diphenylethylidene)amino)propanoic acid (HDPENP**)**

The complexes were prepared at 2:1 molar ratio and occurred in pure form. Reactions of (Cu, Ni-, Zn-, Co- and Fe- halides) with (E)-2-((2-hydroxy-1,2-diphenylethylidene)amino) propanoic acid (**HDPENP**) in 2:1 molar ratio in ethanol are represented in Scheme 2.



Where $MX_2 \cdot xH_2O$ = $CuBr_2$; $NiCl_2 \cdot 6H_2O$; $ZnCl_2$; $CoCl_2 \cdot 6H_2O$ or $FeCl_2$

SCHEME 2. Preparative methods for complexes (2:1) molar ratio

The elemental analysis data (CHN) of ligands and all their complexes are in a good agreement with the calculated values as shown in Table 1.

Table 1: Physical and analytical data for ligand and compounds 1-5

| | | | |
|--------|-------|------|------|
| Pall - | 72.07 | 6.05 | 4.94 |
| | 421 | | |

| Comp. | color | Melting point (C) | Analysis (%) | | | Yield % |
|-----------------------------|--------------|-------------------|------------------|----------------|----------------|----------|
| | | | C | H | N | |
| HDPENP 72- 74 93 | yellow | (72.30) 65.01 | | | | |
| Cu(HDPENP) ₂ [1] | Pall yellow | 102-104 | (6.10) (4.72) | 5.13 (5.42) | 4.46 (4.75) | 73 64 |
| Fe(HDPENP) ₂ [2] | Yellow | 93-95 | (65.33) 65.81 | | | |
| Zn(HDPENP) ₂ [3] | White yellow | 89-91 | (65.10) | 5.12 (5.22) | 4.45 (4.63) | 70 |
| Ni(HDPENP) ₂ [4] | Green yellow | 110-112 | 65.51 (65.36) | 5.17 (5.12) | 4.49 (4.55) | 81 |
| Co(HDPENP) ₂ [5] | Yellow | 125-127 | 65.49 (65.40) | 5.17 (5.33) | 4.49 (4.13) | 71 |
| | | | (65.40) 64.82 | | | |

^a calculated values are in parentheses

The IR spectra of the ligands and complexes synthesized are shows two strong bands appeared at range (3010-3110) cm⁻¹ and (2877-2950) cm⁻¹ due to stretching aromatic (C-H) and aliphatic (C-H) respectively.^(10, 11) The IR spectra of compounds 1-5 and ligand showed a strong band in range (1705-1753) cm⁻¹ can be attributed to (C=O) bond.^(10, 11) The IR spectra of the ligands and complexes synthesized are shows two strong bands appeared at range (1210-1235) cm⁻¹ and (1643-1676) cm⁻¹ due to stretching aliphatic (C-N) and aromatic (C-N) respectively.^(10, 11) A broad band in range (2900-3300) cm⁻¹ can be referred to (O-H) bond.^(10, 11) All the IR data suggest that the metal was bonded to the ligand through the oxygen in benzoin and nitrogen in glycine. As shown in Table 2.

Table 2: IR Spectroscopic data for Ligand and compounds 1-5

| Ligand/ complexes IR (cm ⁻¹) | λ _{max} in nm (ν in M ⁻¹ cm ⁻¹) |
|--|--|
| HDPENP | 3110cm ⁻¹ ν(C-H) aromatic, 2900 cm ⁻¹ ν(C-H) aliphatic, 3000 cm ⁻¹ ν(O-H) aliphatic, 1753 cm ⁻¹ ν(C=O), 1665 cm ⁻¹ ν(C-N) aromatic, 1210 cm ⁻¹ ν(C-N) aliphatic. |

| | |
|-----------------------------|--|
| Cu(HDPENP) ₂ [1] | 3115cm ⁻¹ v(C-H) aromatic, 2910 cm ⁻¹ v(C-H) aliphatic, 3050 cm ⁻¹ v(O-H) aliphatic, 1750 cm ⁻¹ v(C=O), 1605 cm ⁻¹ v(C-N) aromatic, 1215 cm ⁻¹ v(C-N) aliphatic. |
| Fe(HDPENP) ₂ [2] | 3012cm ⁻¹ v(C-H) aromatic, 2877 cm ⁻¹ v(C-H) aliphatic, 2900 cm ⁻¹ v(O-H) aliphatic, 1705 cm ⁻¹ v(C=O), 1653 cm ⁻¹ v(C-N) aromatic, 1235 cm ⁻¹ v(C-N) aliphatic. |
| Zn(HDPENP) ₂ [3] | : 3010cm ⁻¹ v(C-H) aromatic, 2950 cm ⁻¹ v(C-H) aliphatic, 3150 cm ⁻¹ v(O-H) aliphatic, 1707 cm ⁻¹ v(C=O), 1660 cm ⁻¹ v(C-N) aromatic, 1215 cm ⁻¹ v(C-N) aliphatic. |
| Ni(HDPENP) ₂ [4] | 3100cm ⁻¹ v(C-H) aromatic, 2950 cm ⁻¹ v(C-H) aliphatic, 3000 cm ⁻¹ v(O-H) aliphatic, 1735 cm ⁻¹ v(C=O), 1676 cm ⁻¹ v(C-N) aromatic, 1215 cm ⁻¹ v(C-N) aliphatic. |
| Co(HDPENP) ₂ [5] | 3105cm ⁻¹ v(C-H) aromatic, 2920 cm ⁻¹ v(C-H) aliphatic, 3300 cm ⁻¹ v(O-H) aliphatic, 1745 cm ⁻¹ v(C=O), 1643 cm ⁻¹ v(C-N) aromatic, 1217 cm ⁻¹ v(C-N) aliphatic. |

¹H NMR spectra of compounds **1-5** and ligand were recorded in DMSO-d₆ and shows in Table 3. The ¹H NMR spectrum of compounds shows a multiple broad signal at the range 7.21-7.94 ppm can be assigned to protons in aromatic ring of phenyl groups. The protons in N-(CH) can be obtained at range (4.15-4.28) ppm as quartet signal, also a doublet signal can be appeared at range (1.34-1.54) ppm due to methyl group in glycine. ^(10, 11) The protons in (OH) carboxylic can be appeared at the range (10.55 – 11.21) ppm as a singlet signal, ^(10, 11). The protons bonded with carbon atom in OH-(CH) can be happened at range (4.33-4.44) ppm as singlet signal^(10, 11).

A singlet signal at 3.73 ppm can be assigned to (OH) free in benzoic compound, ^(10, 11). but in complexes were disappeared in ¹H NMR spectra. This is refer to coordinate ligand **HDPENP** from OH group in benzoic.

Table 3: ¹H NMR Spectroscopic data for Ligand and compounds 1-5

| Ligand/ complexes | Chemical shift (ppm) |
|-----------------------------|--|
| HDPENP | 7.21- 7.74 (m, 10H, aromatic), 1.34 (d, 3H, CH ₃), 4.20 (q, 1H, N-CH), 4.55 (s, 1H, CH-OH), 10.55 (s, 1H, OH-Carboxylic), 3.73 (s, 1H, OH-CH). |
| Cu(HDPENP) ₂ [1] | 7.33- 7.80 (m, 20H, aromatic), 1.43 (d, 6H, CH ₃), 4.25 (q, 2H, N-CH), 4.50 (s, 2H, CH-OH), 10.85 (s, 2H, OH- Carboxylic). |
| Fe(HDPENP) ₂ [2] | 7.38- 7.85 (m, 20H, aromatic), 1.39 (d, 6H, CH ₃), 4.22 (q, 2H, N-CH), 4.50 (s, 2H, CH-OH), 10.99 (s, 2H, OH- Carboxylic). |
| Zn(HDPENP) ₂ [3] | 7.33- 7.94 (m, 20H, aromatic), 1.44 (d, 6H, CH ₃), 4.17 (q, 2H, N-CH), 4.33 (s, 2H, CH-OH), 11.21 (s, 2H, OH- Carboxylic). |
| Ni(HDPENP) ₂ [4] | 7.35- 7.75 (m, 20H, aromatic), 1.54 (d, 6H, CH ₃), 4.15 (q, 2H, N-CH), 4.45 (s, 2H, CH-OH), 10.95 (s, 2H, OH- Carboxylic). |

| | |
|-----------------------------|--|
| Co(HDPENP) ₂ [5] | 7.25- 7.81 (m, 20H, aromatic), 1.44 (d, 6H, CH ₃), 4.28 (q, 2H, N-CH), 4.39 (s, 2H, CH-OH), 10.93 (s, 1H, OH- Carboxylic). |
|-----------------------------|--|

All complexes were contained at the same ligand. Seem converged results for ¹H NMR and disappearance of the OH band from ¹H NMR spectra refer to coordinate ligand (**HDPENP**) from OH group in this complexes. In conclusion, several new coordination compounds containing benzoin and glycine were prepared in this study. These new compounds may be used as anticancer, we will study it in next research.

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