

Schiff Base [(Z)-2-((2-Aminoethyl)Imino)-1,2-Diphenylethanol] and Their Metal Complexes: Synthesis and Characterization

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Abstract

The condensation of aliphatic diamine [ethylene diamine] with benzoin under specified conditions yielded a new Schiff base ligand. The complexes of Cu(II), Ni(II), Co(II), Zn(II) and Fe(II) with 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. The free ligands and their metal complexes have been isolated in the solid state. The spectroscopic data of the complexes suggest their 1:2 complexes structures which are investigated by elemental analysis, FT-IR, ¹H NMR spectroscopy. The spectroscopic studies suggested the octahedral structure for the all complexes and the results are reported and discussed below.

Keywords: Complexes; Schiff base; metal complexes; ethylenediamine.

1. Introduction

Schiff's bases, that first reported by Hugo Schiff in 1864, are an important class of organic compounds[1,2]. These bases are condensation products of primary amines with carbonyl compounds. The main structural character of these compounds is the azomethinegroup with a general formula of RHC = N-R1, where R and R1= alkyl, aryl, cycloalkyl, or heterocyclic groups [1]. Chemically, a Schiff's base (or azomethine) is a nitrogenousanalogue of an aldehyde or ketone in which the carbonyl group (>C = O) is replaced by an imine or azomethine group.

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Schiff's bases have been found to exhibit a wide range of biological activities, including antibiotic, anti-proliferative, anti-inflammatory, and antipyretic properties [3,4]. The imine groups are present in various natural, derived, and synthetic compounds. This imine group present in Schiff's base compounds has been found to be essential to their biological activities of [5-7]. These compounds are also important owing to their wide range of industrial applications [8], such as in the photostabilization of polyvinyl chloride polymers against photodegradation by ultraviolet radiation [9-11], used to improve polymethyl methacrylate from degradation [12], and to prevent polystyrene from photodegradation by their addition to polymer films [13,14].

2. Experimental

2.1 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 was recorded on Bruker 300 MHz spectrometers with TMS as an internal reference using DMSO-d₆ 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.

2.2 Synthesis of Schiff base [(Z)-2-((2-aminoethyl)imino)-1,2-diphenylethanol]

To a hot ethanolic solution of benzoin (0.02 mol, 4.24g) and ethylenediamine (0.02 mol, 1.2g) was added some drops of glacial acetic acid and the mixture refluxed for 3 hours. The hot solution was cooled into room temperature upon orange precipitate of the Schiff's base separated: it was filtered. Washed with water, dried and recrystallized from glacial acetic acid[15]

2.3 Synthesis of Cu(II), Ni(II), Co(II), Zn(II) and Fe(II) complexes

All the new complexes were prepared by the same procedure: A hot ethanolic solution of the ligand of (Z)-2-((2-aminoethyl)imino)-1,2-diphenylethanol (*AIDOH*) (0.001 mol) in absolute ethanol (10 ml) was prepared and then CuBr₂, NiCl₂·6H₂O, CoCl₂·6H₂O, ZnCl₂ and FeBr₂ (0.0005 mol) in absolute ethanol (10 ml) was added to the hot solution of *AIDOH* 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: glacial acetic acid (1:1) then dried. The analytical and physical data of the complexes are listed in Table 1.

3. Results and discussion

The Schiff base **AIDOH** is formed in good yield by the condensation of 2-hydroxy-1,2-diphenylethanone (benzoin) **structure 1** with 1,2-diaminoethane. Elemental analytical data (Table 1) of the compounds suggest that the condensation of 2-hydroxy-1,2-diphenylethanone (benzoin) with 1,2-diamino ethane occurred in the 1:1

ratio as in structure 2 (Figure 1).

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

Comp.	color	Melting point (°C)	Analysis (%) ^a			Yield %
			C	H	N	
AIDOH	Yellow	85 - 87	75.56 (75.31)	7.13 (7.00)	11.01 (11.99)	91
Cu(AIDOH)₂ [1]	Yellowish - White	110 -112	67.65 (67.33)	5.68 (5.47)	9.86 (9.75)	63
Fe(AIDOH)₂ [2]	Yellow	73 -75	68.58 (68.10)	5.75 (5.33)	10.00 (10.33)	74
Zn(AIDOH)₂ [3]	yellow	99 - 100	67.43 (67.22)	5.66 (5.34)	9.83 (9.61)	67
Ni(AIDOH)₂ [4]	Dark yellow	105 -107	68.23 (68.35)	5.73 (5.32)	9.95 (9.54)	77
Co(AIDOH)₂ [5]	Yellowish - white	130-132	68.20 (68.45)	5.72 (5.63)	9.94 (9.43)	82

^a calculated values are in parentheses

Schiff base is crystalline in nature and is soluble in common organic solvents. It's formed well defined and crystalline complexes with of Cu(II), Ni(II), Co(II), Zn(II) and Fe(II) ions. The results of elemental analysis (C, H, N) with molecular formula and the melting points are presented in Table 1. The results obtained are in good agreement with those calculated for the suggested formula and the melting points are sharp, indicating the purity

of the prepared Schiff base and their complexes. The structures of the Schiff base and their complexes under study are given below (Figure 2). The structure of these Schiff bases is also confirmed by IR and ^1H NMR spectra, which will be discussed in a detailed manner.

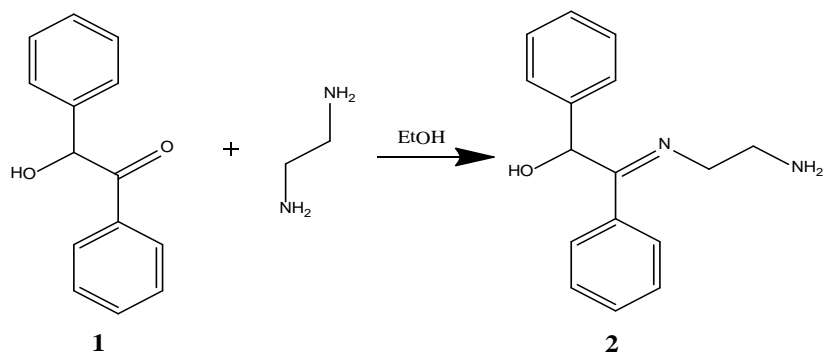
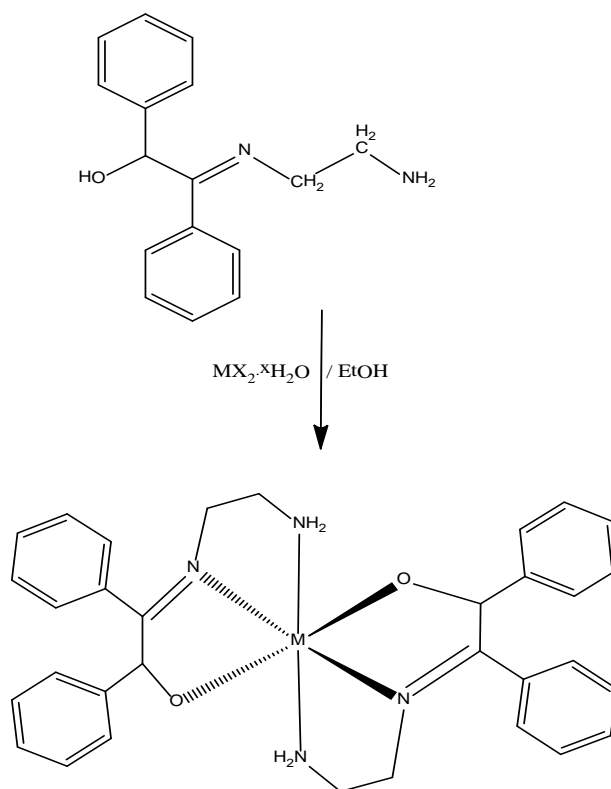


Figure 1: Preparative method for base [(Z)-2-((2-aminoethyl)imino)-1,2-diphenylethan-1-ol]



Where $\text{MX}_2 \cdot x\text{H}_2\text{O} = \text{CuBr}_2; \text{NiCl}_2 \cdot 6\text{H}_2\text{O}; \text{ZnCl}_2; \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or FeCl_2

Figure 2: Preparative methods for complexes (1:2) molar ratio

3.1 Infrared spectra

The IR spectra of Schiff base ligand (AIDOH) and their complexes are presented in Table 2. The IR spectra of the ligands and complexes synthesized are shows two strong bands appeared at range $(3015\text{-}3122) \text{ cm}^{-1}$ and

(2855-2944) cm^{-1} due to stretching aromatic (C-H) and aliphatic (C-H) respectively. [16,17] The IR spectra of the complexes were compared with of the free ligand (AIDOH) in order to determine the coordination sites that may be involved in chelating. There were some guide peaks in the spectra of the ligands, which were helpful in achieving this goal. The position and/or the intensities of these peaks are expected to change upon chelating. New peak is also guide peak, as M-N-C in chelating. This guide peak are shown in Table 2. Upon comparison This band was shifted to higher or lower wave numbers in the complexes, indicating the participation of the azomethine nitrogen in coordination (M—N)[18] New bands are found in the spectra of the complexes in the regions (543-586) cm^{-1} which are assigned to $\nu(\text{M-O})$ stretching vibrations for (AIDOH) metal complexes[16,17] Several medium intensity bands appeared in the (1490-1585) cm^{-1} region of the spectra are due to the stretching of various (C=C) vibrations. The IR spectra of the ligand and complexes synthesized are shows two strong bands appeared at range (1233 - 1245) cm^{-1} and (1671 - 1693) cm^{-1} due to stretching aliphatic (C-N) and (C=N) respectively[16,17]

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

Ligand/ complexes IR (cm^{-1})	λ_{max} in nm (ϵ in $\text{M}^{-1}\text{cm}^{-1}$)
AIDOH	3100 cm^{-1} $\nu(\text{C-H})$ Ar., 2935 cm^{-1} $\nu(\text{C-H})$ aliph., 1563 cm^{-1} $\nu(\text{C=C})$ Ar., 1173 cm^{-1} $\nu(\text{C-O})$ aliph., 3535 cm^{-1} $\nu(\text{O-H})$ aliph., 1636 cm^{-1} $\nu(\text{C=N})$, 1245 cm^{-1} $\nu(\text{C-N})$ aliph., 3405 cm^{-1} $\nu(\text{N-H})$
Cu(AIDOH)₂ [1]	3110 cm^{-1} $\nu(\text{C-H})$ Ar., 2855 cm^{-1} $\nu(\text{C-H})$ Aliph., 1563 cm^{-1} $\nu(\text{C=C})$ Ar., 1110 cm^{-1} $\nu(\text{C-O})$ Aliph., 1622 cm^{-1} $\nu(\text{C=N})$, 1233 cm^{-1} $\nu(\text{C-N})$ Aliph., 3410 cm^{-1} $\nu(\text{N-H})$, 433 cm^{-1} $\nu(\text{M-N})$, 575 cm^{-1} $\nu(\text{M-O})$.
Fe(AIDOH)₂ [2]	3099 cm^{-1} $\nu(\text{C-H})$ Ar., 2905 cm^{-1} $\nu(\text{C-H})$ Aliph., 1585 cm^{-1} $\nu(\text{C=C})$ Ar., 1152 cm^{-1} $\nu(\text{C-O})$ Aliph., 1631 cm^{-1} $\nu(\text{C=N})$, 1237 cm^{-1} $\nu(\text{C-N})$ Aliph., 3375 cm^{-1} $\nu(\text{N-H})$, 451 cm^{-1} $\nu(\text{M-N})$, 543 cm^{-1} $\nu(\text{M-O})$.
Zn(AIDOH)₂ [3]	3015 cm^{-1} $\nu(\text{C-H})$ Ar., 2933 cm^{-1} $\nu(\text{C-H})$ Aliph., 1490 cm^{-1} $\nu(\text{C=C})$ Ar., 1090 cm^{-1} $\nu(\text{C-O})$ Aliph., 1645 cm^{-1} $\nu(\text{C=N})$, 1238 cm^{-1} $\nu(\text{C-N})$ Aliph., 3392 cm^{-1} $\nu(\text{N-H})$, 476 cm^{-1} $\nu(\text{M-N})$, 582 cm^{-1} $\nu(\text{M-O})$.
Ni(AIDOH)₂ [4]	3103 cm^{-1} $\nu(\text{C-H})$ Ar., 2944 cm^{-1} $\nu(\text{C-H})$ Aliph., 1498 cm^{-1} $\nu(\text{C=C})$ Ar., 1098 cm^{-1} $\nu(\text{C-O})$ Aliph., 1635 cm^{-1} $\nu(\text{C=N})$, 1240 cm^{-1} $\nu(\text{C-N})$ Aliph., 3402 cm^{-1} $\nu(\text{N-H})$, 451 cm^{-1} $\nu(\text{M-N})$, 571 cm^{-1} $\nu(\text{M-O})$.
Co(AIDOH)₂ [5]	3122 cm^{-1} $\nu(\text{C-H})$ Ar., 2890 cm^{-1} $\nu(\text{C-H})$ Aliph., 1575 cm^{-1} $\nu(\text{C=C})$ Ar., 1115 cm^{-1} $\nu(\text{C-O})$ Aliph., 1640 cm^{-1} $\nu(\text{C=N})$, 1243 cm^{-1} $\nu(\text{C-N})$ Aliph., 3400 cm^{-1} $\nu(\text{N-H})$, 482 cm^{-1} $\nu(\text{M-N})$, 586 cm^{-1} $\nu(\text{M-O})$.

The IR spectra of compounds 1-5 and ligand showed a strong band in range (1090 - 1173) cm^{-1} can be attributed

to (C-O) bond. The replacement of the NH₂ proton in (AIDOH) ligand by metal ion is clearly indicated from the disappearance of the NH₂ deformation band of the free ligand in the spectra of all the complexes. The broad band in the region (3375 – 3410) cm⁻¹ cleared up in the spectra of all the complexes confirming the replacement of the hydrogen bonded NH₂ proton, Primary amine (in free ligand) produced two N-H stretch absorptions, while secondary amine (complexes) only one. A broad band in 3535 cm⁻¹ can be referred to (O-H) bond in free ligand but This peak will be disappeared in IR spectra of complexes was good and clear evidence to occurrence of reaction. Therefore; from the IR spectra it is concluded that the (AIDOH) behaves as a neutral tridentate ligand coordinated to the metal ion via azomethine N, hydroxy O and deprotonated Nitrogen group[16,17]

3.2 ¹H NMR spectra

¹H NMR spectral data in deturated DMSO solution of the synthesized compounds are given in Table 1, The ¹H NMR spectra of the Schiff base in DMSO exhibits multisignals within the 7.30 – 7.96 ppm range are assigned to the aromatic protons of both rings. The spectra of the complexes are examined in comparison with those of the parent Schiff base.

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

Ligand/ complexes	Chemical shift (ppm)
AIDOH	7.31 - 7.92 (m, 10H, aromatic), 4.30 (s, 1H, CH-OH), 3.55 (s, 1H, OH), 3.88 (t, 2H, CH ₂ -N), 3.09 (t, 2H, CH ₂ -NH ₂), 5.35 (s, 2H, Free NH ₂).
Cu(AIDOH)₂ [1]	7.35 - 7.85 (m, 10H, Ar.), 4.35 (s, 1H, CH-OH), 3.65 (t, 2H, CH ₂ -N), 3.06 (t, 2H, CH ₂ -NH ₂), 2.10 (s, 1H, NH).
Fe(AIDOH)₂ [2]	7.31 - 7.96 (m, 10H, Ar.), 4.22 (s, 1H, CH-OH), 3.43 (t, 2H, CH ₂ -N), 3.00 (t, 2H, CH ₂ -NH ₂), 2.03 (s, 1H, NH).
Zn(AIDOH)₂ [3]	7.38 - 7.92 (m, 10H, Ar.), 4.80 (s, 1H, CH-OH), 3.83 (t, 2H, CH ₂ -N), 3.06 (t, 2H, CH ₂ -NH ₂), 2.20 (s, 1H, NH).
Ni(AIDOH)₂ [4]	7.32 - 7.91 (m, 10H, Ar.), 4.21 (s, 1H, CH-OH), 3.65 (t, 2H, CH ₂ -N), 3.02 (t, 2H, CH ₂ -NH ₂), 2.00 (s, 1H, NH).
Co(AIDOH)₂ [5]	7.30 - 7.95 (m, 10H, Ar.), 4.35 (s, 1H, CH-OH), 3.85 (t, 2H, CH ₂ -N), 3.03 (t, 2H, CH ₂ -NH ₂), 2.05 (s, 1H, NH).

The ^1H NMR spectra of the Schiff base synthesized from benzoin and ethylene diamine revealed a signal at 3.55 ppm (singlet) due to the proton OH and The proton OH has disappeared in ^1H NMR spectra of complexes Schiff base, indicating that the OH proton is removed by chelation with the metal ion [19] The free NH_2 protons usually show a broad singlet peak in 5.35 ppm (singlet)[16,17], this signal is absent in the observed spectra of schiff base and observed other peak at the range 2.00 – 2.20 ppm as a broad singlet peak that referring to proton (NH group) which indicates the formation of the Schiff base and binding with central atom in complexes[16, 17].

The spectra of all the compounds show a singlet signal at the range 4.21 – 4. 80 ppm due to the proton CH of the benzoin compound in Schiff base and it's complexes. The triplet signals at 3.00 – 3.09 ppm 3.43 – 3.88 ppm suggested the attribution of the proton of the $\text{CH}_2\text{-NH}_2$ and $\text{CH}_2\text{-N}$ groups respectively[20]

4. Conclusion

A new Schiff base ligand has been prepared by the condensation of benzoin with 1,2-diaminoethane. Analytical IR, ^1H NMR and elemental analysis (CHN) revealed a 1:2 product in which one of azo – methine, OH and NH_2 groups is involved in Schiff base formation. In another study will be used this complexes in a wide range of biological activities, including antibiotic , anti-proliferative, anti-inflammatory, and antipyretic properties.

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