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Synthesis, Spectroscopic and Antimicrobial Studies of Co(II), Ni(II), Cu(II) and Zn(II) Complexes Derived from Benzoic acid Bidentate Schiff Base Ligand

***[1]ADO, I., [1]NA'ALIYA, J., [2]SANI, S; [3]HALEELU, MM**

*[*1]Department of Pure and Industrial Chemistry, Bayero University Kano, P.M.B 3011, Kano, Nigeria.*
[2]Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, P.M.B. 2346, Sokoto, Nigeria
[3]Department of Chemistry, Federal university Dutsanma Katsina, Nigeria
**Correspondence author Email: adobichiibrahim@gmail.com*

ABSTRACT: The Schiff base was synthesized by condensation of 2-hydroxy-1-naphthaldehyde with 3-aminobenzoic acid in 1:1 molar ratio. The Schiff base ligand formed complexes with Co (II), Ni (II), Cu (II) and Zn (II) acetate via mechanochemical synthesis. The synthesized compounds were characterized by solubility test, thermal analysis, FT-IR, powder x-ray diffraction, molar conductance measurement, magnetic susceptibility and elemental analysis. The Schiff base has a melting point of 190 ºC. The decomposition temperature of complexes was found to be in the range 289 – 302 ºC. The Schiff base and its metal (II) complexes were soluble in DMF, DMSO and sparingly soluble in acetonitrile, chloroform, diethyl ether and insoluble in n-hexane which indicate the polar nature of the synthesized compounds. The IR spectral analysis of the free Schiff base shows a band at 1622 cm^{-1}, assigned to *v*(C=N) stretching vibrations. This band was shifted in the spectra of complexes (1607 – 1633 cm^{-1}), indicating coordination of the Schiff base to the metal ion through the azomethine group. The molar conductance of complexes determined are in the range 9.51 – 14.87 $Ohm^{-1}cm^2mol^{-1}$ which indicate the non-electrolytic nature in DMF. Magnetic susceptibility measurements of Co (II), Ni (II) and Cu (II) complexes exhibit a magnetic moment in the range 1.25 – 3.08 BM. The values correspond to square-planar geometry. The magnetic moment value of Zn (II) complex indicates a diamagnetic behaviour. The elemental analysis of the complexes for C, H and N determined showed that the observed and the calculated percentages of the elements are in good agreement.

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Mechanochemical synthesis or mechanochemistry refers to the use of mechanical energy (generally in the form of grinding or shaking) to drive reactions. Mechanochemical synthesis is generally thought of as a solid-state synthetic method, although liquid reagents and small amounts of solvent can be used during synthesis, as has been reviewed. (Braga et al., 2013). Mechanochemistry is the coupling of mechanical and chemical phenomena on a molecular scale and includes mechanical breakage, chemical behaviour of mechanically stressed solids (e.g., stress-corrosion cracking or enhanced oxidation). Mechanochemical synthesis could become the most efficient synthetic technique because of the environmentally friendly nature of the technique and less release of hazardous by-products during synthesis or purification (Walsh et al., 2007; Cinčić and Kaitner, 2011).

Schiff bases are imines prepared by condensation of primary amines with carbonyl compounds. They can be considered a sub-class of imines, being either secondary ketimines or secondary aldimines depending on their structure. The term is often synonymous with azomethine which refers specifically to secondary aldimines. The imine nitrogen is basic and exhibits pi-acceptor properties. The ligands are typically derived from alkyl diamines and aromatic aldehydes (Hernández, 2003).

The chemistry of Schiff base complexes is fast developing, especially those involving aldehydes and amines. This is because of the wide variety of possible structure of ligands (Sani and Siraj, 2021).

Schiff bases play an important role because of their many uses in organic synthesis, biological activity, etc. (Thankamony and Mohanan, 2007; Raman et al., 2007; Halli and Patil, 2011). Aliyu and Sani (2012) reported the synthesis of Schiff base prepared from the interaction of ethanolic solutions of 2-hydroxy-1–naphthaldehyde and butylenediamine. This paper reports the mechanochemical synthesis and characterization of Cobalt (II), Nickel (II) Copper (II) and Zinc (II) Schiff base complexes.

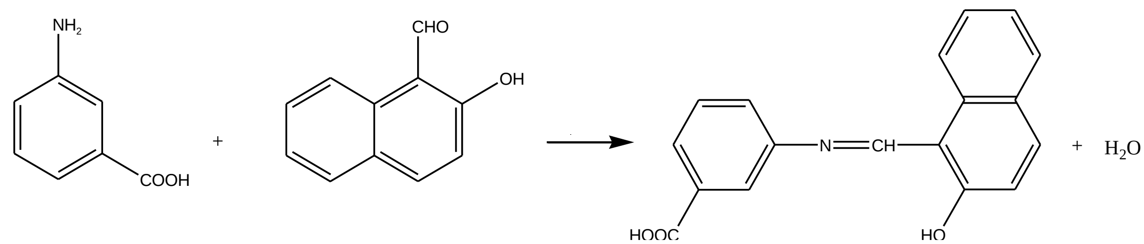
**Correspondence Author Email: adobichiibrahim@gmail.com*

MATERIALS AND METHODS

All the reagents used are of analytical grade obtained from Sigma-Aldrich and were used without further purification.

Synthesis of Schiff base (SB): 2-hydroxy-1-naphthaldehyde (0.1722 g, 1 mmol) and 3-aminobenzoic acid (0.1371 g, 1 mmol) were weighed carefully into a mortar. The mixture of the reactants was crushed (ground) for forty five (45) minutes to obtain a yellow powder product. The powdered product was removed from the mortar and dried in air (Vladimir et al., 2012).

Synthesis of [M(SB)] complex: The metal complexes were synthesized by grinding the reaction mixture of the metal (II) acetate (1mmol) and Schiff base (0.5846 g, 2 mmol) 1:2 mole ratio in a mortar with pestle for 1hour and obtained coloured powder complexes. (M = Co, Ni, Cu or Zn) (Vladimir et al., 2012).



Scheme 1: Synthesis of Schiff base (SB)

RESULTS AND DISCUSSION

The complexes were synthesized by reaction of metal acetate with Schiff base derived from 2-hydroxy-1-naphthaldehyde and 3-aminobenzoic acid. The complexes were characterized by infrared spectroscopy (IR), Solubility test, conductivity measurement magnetic susceptibility, elemental analysis. All the synthesized compounds were coloured. The colour of complexes are due to *d-d* transitions of electrons. The Schiff base have melting point of 190 ^oC while decomposition temperature of complexes ranges from 289 to 302 ^oC, indicating good thermal stability. All complexes have decomposition temperature higher than the Schiff base melting point as a result of complexation (Table 1). The metal complexes and Schiff base are generally soluble in DMF, DMSO and sparingly soluble in acetonitrile, chloroform, and diethyl ether and insoluble in n-hexane which indicate the polar nature of the synthesized compounds (Table 2).

Table 1: Physical properties of Schiff base and its metal complexes

Compound	Molecular Formula	Colour	Melting point	Decomp. Temp.
(SB)	$(C_{18}H_{12}NO_3)$	Yellow	190	-
[Co $(SB)_2$]	$[Co(C_{18}H_{12}NO_3)_2]$	Yellow Brown	-	302
$[Ni(SB)_2]$	$[Ni(C_{18}H_{12}NO_3)_2]$	Yellow Orange	-	295
$[Cu(SB)_2]$	$[Cu(C_{17}H_{12}N_2O_3)_2]$	Yellow Orange	-	289
$[Zn(SB)_2]$	$[Zn(C_{18}H_{12}NO_3)_2]$	Mustard	-	290

Table 2: Solubility Test of Schiff base and its metal complexes

Compound	DMF	DMSO	Acetonitrile	Diethyl ether	Chloroform	Acetone	N-hexane
(SB)	S	S	SS	SS	SS	SS	IS
$[Co(SB)_2]$	S	S	SS	SS	SS	SS	IS
$[Ni(SB)_2]$	S	S	SS	SS	SS	SS	SS
$[Zn(SB)_2]$	S	S	SS	SS	SS	SS	IS

SB = Schiff base; S = Soluble; IS = Insoluble; SS.= Slightly soluble

Table 3: Infrared spectra result for Schiff base and complexes.

Compound	v(OH) cm^{-1}	v(C=N) cm^{-1}	v(M-O) cm^{-1}	v(M-N) cm^{-1}
(SB)	3633	1622	-	-
$[Co(SB)_2]$	-	1633	460	549
$[Ni(SB)_2]$	-	1625	478	586
$[Cu(SB)_2]$	-	1610	448	530
$[Zn(SB)_2]$	-	1607	475	571

The important infrared bands of the Schiff base and their complexes are presented in Table 3. The absorption peaks for the stretching vibration of O–H bonds in the Schiff base was observed at 3357 cm^{-1}. The Schiff base formation was confirmed by the presence of strong imine (C=N) bands occurring at

1622 cm^{-1} (Quaresma et al., 2017; Sani et al., 2018). Azomethine band of the Schiff base are shifted in the spectra of synthesized complexes (1607 – 1633 cm^{-1}) which indicated the coordination of the metal to the azomethine nitrogen. In the low-frequency region, the band of the complexes show medium intense bands in the range 448 - 475 cm^{-1} corresponding to the stretching vibration of the M - O group, and a band in the region of 530 - 586 cm^{-1} can be assigned to the stretching vibration of the M - N bonds. The values obtained for M - O and M - N were similar to the values reported by Saleem et al., 2003. Powder X-ray diffraction patterns of the mechanochemical products indicate the crystalline nature of the synthesized compound. The powder x-ray diffraction pattern of Schiff base was different from that of the reactants (2-hydroxy-1-napthaldehyde and 3-aminobenzoic acid). New peaks corresponding to the mechanochemical product were observed indicating the formation of new phase (Figure 1). The molar conductance values measured in DMF solution (10^{-3} M) for the complexes are in the range of 8.37 – 14.87 $Ohm^{-1}cm^{2}mol^{-1}$ (Table 4) and the values been found to be very low to account for any dissociation of the complexes in DMF indicating its non-electrolytic nature. (Shaker et al., 2009). The magnetic susceptibility of the complexes was measured at room temperature and the magnetic moments were shown in Table 5. Co(II) effective magnetic moment value (μ_{eff} = 5.6 BM.) is typical of low spin d^7 systems with one unpaired electron. The obtained magnetic parameter is in accordance with a square-planar system. Therefore, dz^2 orbital of Co(II) forms electronic ground state containing the unpaired electron in such a system. Similar situation may occur for Ni (II) and Cu (II) complexes due to their effective magnetic moment value (μ_{eff} = 3.08 and 1.25 BM respectively) indicative for a predominantly dx^2-y^2 ground state occupied with one unpaired electron. (Parameswari, et al., 2013). The magnetic moment value of Zn (II) complex indicates a diamagnetic behaviour. The elemental analysis of the complexes for C, H and N determined showed that the observed and the calculated percentages of the elements are in good agreement (Table 6).

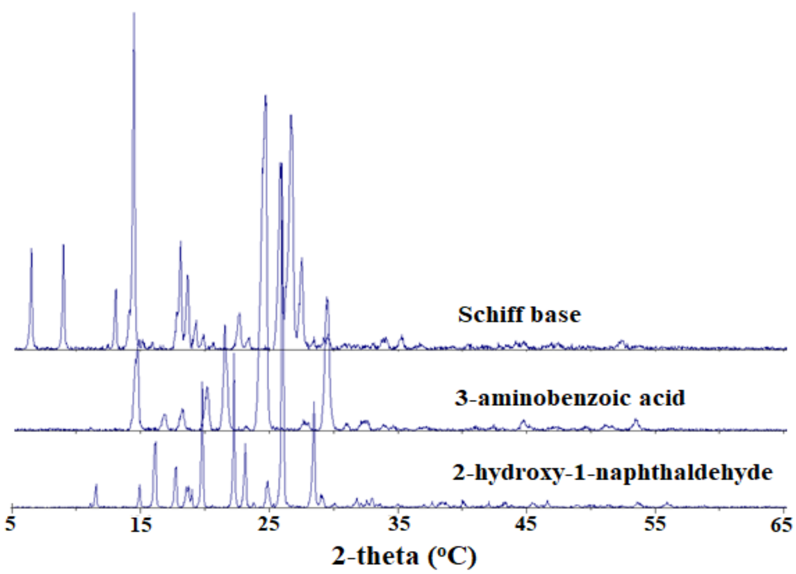


Fig. 1: Powder x-ray diffraction pattern of Schiff base, 3-aminobenzoic acid and 2-hydroxy-1-napthaldehyde showing different reflection peaks

Table 4: Molar Conductance of the Complexes in 10^{-3}M DMF Solution

Compound	Conc ($Moldm^{-3}$)	Specific conductance ($Ohm^{-1}cm^{-1}$)	Molar conductance ($Ohm^{-1}cm^{2}mol^{-1}$)
$[Co(SB)_2]$	1×10^{-3}	9.51×10^{-6}	9.51
$[Ni(SB)_2]$	1×10^{-3}	8.57×10^{-6}	8.57
$[Cu(SB)_2]$	1×10^{-3}	8.37×10^{-6}	8.37
$[Zn(SB)_2]$	1×10^{-3}	14.87×10^{-6}	14.87

Table 5: Magnetic Susceptibility Measurement of the Complexes

Compound	$X_g(ergG^{-2}g^{-1})$	$X_m(ergG^{-2}mol^{-1})$	μ_{eff}(BM)
$[Co(SB)_2]$	$+20264.15\times10^{-9}$	1.326×10^{-2}	5.62
$[Ni(SB)_2]$	5579.36×10^{-9}	3.968×10^{-3}	3.08
$[Cu(SB)_2]$	$+1010.63\times10^{-9}$	6.509×10^{-4}	1.25
$[Zn(SB)_2]$	-203.64×10^{-9}	-1.388×10^{-4}	--

Table 6: Elemental Analysis Results of the metal (II) Schiff base complexes

Compound	C (%) Found(Calculated)	H (%) Found(Calculated)	N (%) Found(Calculated)
$[Co(SB)_2]$	68.51(69.22)	3.81 (4.10)	3.59 (4.75)
$[Ni(SB)_2]$	59.66 (60.78)	4.96 (4.53)	3.09 (3.94)
$[Cu(SB)_2]$	68.73 (69.44)	4.39 (4.11)	4.42 (4.76)
$[Zn(SB)_2]$	62.50(63.40)	4.50(4.14)	3.53(4.11)

The antibacterial sensitivity test results revealed that metal (II) complexes show more toxic to the tested bacterial strains than the Schiff base ligand. The highest antibacterial activity of the complexes was observed at 60 $mgml^{-1}$ concentrations against *S. typhi* (Table 7). Schiff base shows moderate antibacterial activity against *S. aureus* especially at higher concentration. On the other hand, the Schiff base showed weak antifungal activity towards *C. albican*. The highest activity was observed against *A. fumigatus* with inhibition of 16 mm at 60 $mgml^{-1}$ concentration (Table 8). The Azomethine group in the Schiff base compound has been shown to be responsible for their antimicrobial activities (Bringmann et al., 2004; Guo et al., 2007; Souza et al., 2007). the improvement of the antimicrobial activity of complex was achieved by the overlapping of ligand orbital with metal orbital in the complex which courses partial sharing of the positive charge of metals with the donor group on the ligand. This coordination decreases the polarity of metal and thus increasing the lipophilic nature of the metal to the lipid layer of bacterial cell membrane (Nishat et al., 2011). Based on the results obtained, the proposed tentative structure of complexes is as shown in Figure 2.

Table 7: Antibacterial sensitivity test of Schiff base and its metal (II) complexes

Compound	*S. aureus*			*E. coli*			*S typhi*		
Conc.(mg/ml)	60	30	15	60	30	15	60	30	15
Gentamycin (standard)	--	32	--	--	30	--	--	35	--
DMSO(Control)	6	6	6	6	6	6	6	6	6
(SB)	12	10	08	09	08	--	12	11	--
$[Co(SB)_2]$	14	13	11	13	08	--	13	08	--
$[Ni(SB)_2]$	15	13	11	12	09	10	12	--	13
$[Cu(SB)_2]$	10	07	--	13	08	--	12	09	10
$[Zn(SB)_2]$	15	14	--	09	07	--	16	13	--

Table 8: Antifungal sensitivity test of Schiff base and its metal (II) complexes

Compound	*C. albican*			*A. flavus*			*A. fumigatus*		
Conc(mg/ml)	60	30	15	60	30	15	60	30	15
Nystatin (standard)	--	32	--	--	30	--	--	35	--
DMSO(Control)	6	6	6	6	6	6	6	6	6
(SB)	10	--	--	10	09	09	10	10	08
$[Co(SB)_2]$	11	09	08	14	12	10	12	--	--
$[Ni(SB)_2]$	15	15	11	10	12	--	15	14	09
$[Cu(SB)_2]$	08	--	--	10	13	08	09	07	--
$[Zn(SB)_2]$	14	13	10	15	11	08	16	14	13

Key: mm = millimeter (diameter of zone of inhibition); (SB) = Schiff base derived from 2-hydroxy-1-naphthaldehyde and 3-aminobenzoic acid

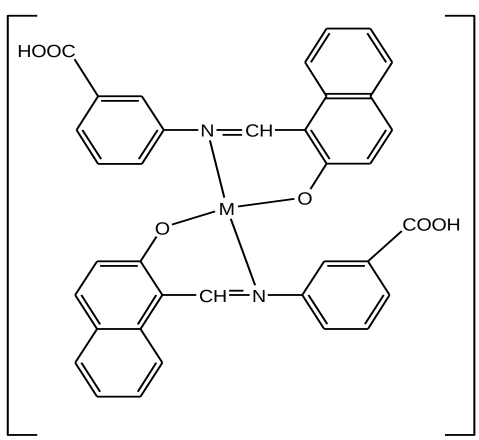


Fig. 2. Proposed structure of Complexes. Where M = Co^{2+} Ni^{2+} Cu^{2+} or Zn^{2+}

*Conclusion***:** The Schiff base was synthesized by mechanochemical reaction of 2-hydroxy-1-naphthaldehyde with 3-aminobenzoic acid and their corresponding complexes. The Schiff base and complexes were characterized. The study highlights the fact that mechanochemical synthesis provide a way to reduce the need for solvents both as reaction media and for purification. This method is convenient, result in high yield, save energy and environmentally friendly.

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