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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF SOME DIVALENT METAL(II) COMPLEXES DERIVED FROM 1-[(4-IODO-PHENYLIMINO)-METHYL]-NAPHTHALEN-2-OL SCHIFF BASE

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ABSTRACT

Schiff base derived from condensation of 2-hydroxy-1-naphthaldehyde and 4-iodoaniline was synthesized and used for the preparation of Co(II) and Ni(II) complexes. The complexes were characterized by IR, Powder-XRD, Solubility test, thermal analysis, conductivity measurement, magnetic susceptibility and elemental micro analysis. IR study indicated a strong band in the spectra of the Schiff base at 1603 cm^{-1} assigned to azomethine v(C=N) stretching vibration. It shifted to new frequency regions (1618 - 1622 cm^{-1}) in the spectra of the complexes indicating the formation of the desired complexes. The decomposition temperatures of the complexes are in the range of (260-265) ^oC , molar conductance values are in the range of (4.51 -11.31) $Ohm^{-1}cm^2\ mol^{-1}$, indicating non electrolytic nature of the synthesized complexes in DMF. Magnetic susceptibility measurement indicated that Co(II) and Ni(II) complexes are paramagnetic and exhibit magnetic moment in the range of 2.92-3.24 BM, the values correspond to the square planar geometry. The Powder x-ray diffraction analysis showed the patterns of the metal(II) complexes were different from the reactants, signifying that reactants were changed to product. The CHN analysis results show the formation of 1:2 metal to ligand ratio. The synthesized compounds have been studied for antimicrobial activity using pathogenic bacteria and fungal pathogens by disc diffusion method. The results indicated that metal complexes (10 – 15 mm inhibition zone) are more active compared to Schiff base (8 – 12 mm inhibition zone) against the test organisms.

Keywords: Schiff base, Complexes, azomethine, 4-Iodoaniline, 2-hydroxy-1-naphthaldehyde,

INTRODUCTION

Schiff bases are imines prepared by condensation of primary amines with carbonyl compounds. Schiff-bases are common ligands in coordination chemistry. The imine nitrogen is basic and exhibits pi-acceptor properties. The ligands are typically derived from diamines and aromatic aldehydes (Hernández, 2003). Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerized while those of aromatic aldehydes are more effective, stable due to conjugation (Mittal *et. al*, 1986). 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. (Sakıyan *et al.*, 2004). Schiff base intermediates are involved in the enzyme catalyzed reactions such as transamination, racemization and decarboxylation. The metal complexes are vitally important in enzyme actions, metabolism and transport phenomena (Said and Tuck, 1989).

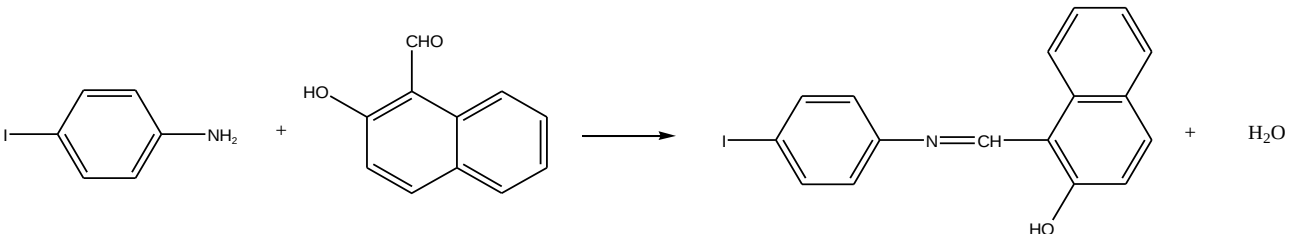
Mechanochemical synthesis or mechanochemistry refers to the use of mechanical energy (generally in the form of grinding or shaking) to drive reactions. Mechanochemical synthesis is generally thought of as a solid-state synthetic method, although liquid reagents and small amounts of solvent can be used during synthesis, as has been reviewed. (Braga *et al*. 2013). Mechanochemistry offers several benefits over traditional methods such as calcinations, hydrothermal reactions and solution-based chemistry. The benefits include the ability to perform reactions without the use of solvents or inputs of heat, decrease of technological stages to simplify processes, and the ability to synthesize metastable phase (Balaz, 2008). This paper reports the mechanochemical synthesis and characterization of cobalt(II) and nickel(II) Schiff base complexes derived from 2-hydroxy-1-napthaldehyde and 4-Iodoaniline.

MATERIALS AND METHODS

All chemicals and solvents used were of analytical grade. 4-nitroaniline and 2-hydroxy-1-naphthaldehyde were obtained from Sigma-Aldrich and were used without further purification.

Synthesis of 1-[(4-Iodo-phenylimino)-methyl]-naphthalen-2-ol Schiff-Base (SB)

In the reaction, 2-hydroxy-1-naphthaldehyde (1 mmol, 0.17218 g) and 4-iodoaniline (1 mmol, 0.21902 g) were weighed carefully into a mortar. The mixture of the reactants was grinded for fourty five (45) minutes to obtain a yellow brown powder and dry in air. The product was removed from the mortar and stored in a sample bottle (Vladimir *et al.*, 2012).



Scheme 1: Synthetic reaction of SB Schiff base

Synthesis of [M(SB)$_2$] complexes

The metal complexes were synthesized using modified procedure reported by Vladimir *et al.,* 2012 by grinding the reaction mixture of the metal(II) acetate (1mmol) and Schiff base (2 mmol) in a mole ratio 1:2 in a mortar and pestle for 1hour and obtained coloured powder complexes. The products were dried in air at room temperature.

Antibacterial activity

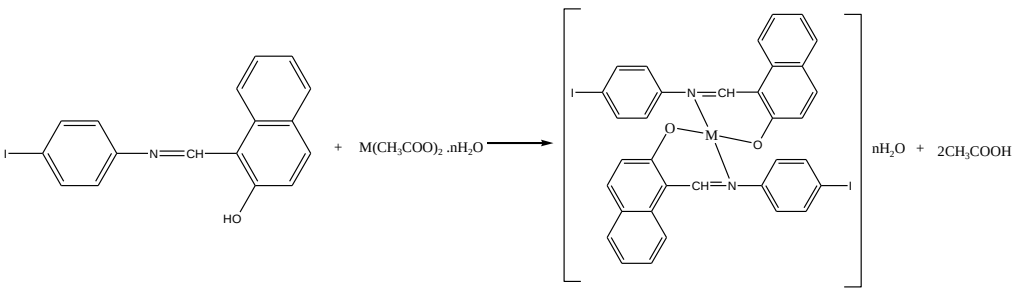
The standard inoculum of the isolate (*S. aureus*, *E. coli* and *S.* typhi) obtained from Aminu Kano Teaching Hospital was swabbed on to the surface area of the prepared and solidified nutrient agar plates. The prepared solution of the test compounds and the standard antibiotic concentration made (ciprofloxacin) were placed inside the agar well of the inoculated plates. The plates were incubated at 37 ^{o}C for 24 hours and the inhibition zone was measured (Yusha'u and Sadisu, 2011).

Antifungal activity

The standard Inoculant of the isolate (*C. albican, A. flavus* and *A. fumigatus*) obtained from Aminu Kano Teaching Hospital was swabbed on to the surface of the prepared and solidified potato agar in separate petri-dishes. The prepared solution of the compounds and the standard antibiotic (Ketoconazole) were placed inside the well of the inoculated media at intervals of 15 mm. The plates were incubated at 37 ^{o}C for 72 hours before observation for the measurement of zone of inhibition (Yusha'u and Sadisu, 2011)

RESULTS AND DISCUSSION

The Co(II) and Ni(II) complexes were synthesized by reaction of metal salts with Schiff base (SB) derived from 4-Iodoaniline and 2-hydroxy-1-naphthaldehyde (Scheme 2). The synthesized compounds were characterized by infrared spectroscopy, thermal analysis, powder x-ray diffraction, conductivity measurement, magnetic susceptibility and elemental analysis.



Scheme 2: Synthetic reaction of Complexes
M = Co(II) or Ni(II) and n = number of water of hydration

The synthesized compounds were coloured. The Schiff base has a melting point of 180 ^{o}C while decomposition temperature of 260 and 265 ^{o}C for Co(II) and Ni(II) complexes respectively, indicating good stability. The complexes have decomposition temperature higher than the Schiff base melting point due to complexation (Table 1).

Table 1: Physical Properties of Schiff base (SB) and its Complexes

Compound	Molecular Formula	Colour	Melting point (^{o}C)	Decomposition Temp. (^{o}C)
SB	($C_{17}H_{12}NOI$)	Yellow	180	-
[Co(SB)$_2$]	[Co($C_{17}H_{12}NOI)_2$]	Green Yellow	-	265
[Ni(SB)$_2$]	[Ni($C_{17}H_{12}NOI)_2$]	Yellow	-	260

The Schiff base and metal complexes are generally 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 (Table 2).

Table 2: Solubility Test of Schiff base (SB) and its Complexes

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

Key:
S-Soluble, SS- Slightly soluble, IS- Insoluble

The important infrared bands of the Schiff base and their complexes are presented in Table 3. Generally, the absorption peaks for the stretching vibration of O–H bonds in the Schiff base is at 3082 cm^{-1}. The Schiff base formation was confirmed by the presence of strong imine (C=N) bands occurring at of 1603 cm^{-1}. The azomethine stretching frequency of Schiff base was shifted to 1618 and 1622 cm^{-1} in the spectra of Co(II) and Ni(II) complexes respectively. This indicates the coordination of metal center with azomethine nitrogen group (Cindrić *et al.,* 2012; Kubaisi and Ismail, 1994: Joseyphus *et al.,* 2006). In the low-frequency region, the band of the complexes show medium intense bands in the range 434–437 cm^{-1} corresponding to the stretching vibration of the M–O group, and a band in the region of 575–556 cm^{-1} can be assigned to the stretching vibration of the M–N bonds (Nakamoto, 2006; Zhong et al., 2012). The values obtained for M-O and M-N were similar to the values reported by Selwin *et al.* 2010.

Table 3: Infrared Spectra of Schiff base (SB) and its Complexes

Compound	v(OH) cm^{-1}	v(C=N) cm^{-1}	v(M-O) cm^{-1}	v(M-N) cm^{-1}
SB	3082	1603	-	-
$[Co(SB)_2]$	-	1618	434	575
$[Ni(SB)_2]$	-	1622	437	556

The molar conductance values measured in DMF solution (10^{-3} M) for the complexes are shown in Table 4. It was concluded from the results that Co(II) and Ni(II) complexes were found to have molar conductance values of 11.32 and 4.51 $\Omega^{-1}cm^2mol^{-1}$ respectively, indicating the non-electrolytic nature because of the lower conductivity values and the values been found to be very low to account for any dissociation of the complexes in DMF (Geary, 1971).

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

Compound	Conc ($Moldm^{-3}$)	Specific conductance ($Ohm^{-1}cm^{-1}$)	Molar conductance ($Ohm^{-1}cm^2mol^{-1}$)
$[Co(SB)_2]$	1×10^{-3}	11.32×10^{-6}	11.32
$[Ni(SB)_2]$	1×10^{-3}	4.51×10^{-6}	4.51

The powder x-ray diffraction pattern of the synthesized Schiff base (Fig. 1) was different from the starting materials. Moreover, no intense peak derived from the starting materials were observed in the powder x-ray pattern of the Schiff base, indicating that, the starting materials were converted to product. The sharp reflections in the patterns testified to the crystallinity of the synthesized compound, a similar validation was reported by (Cinčić and Kaitner, 2011).

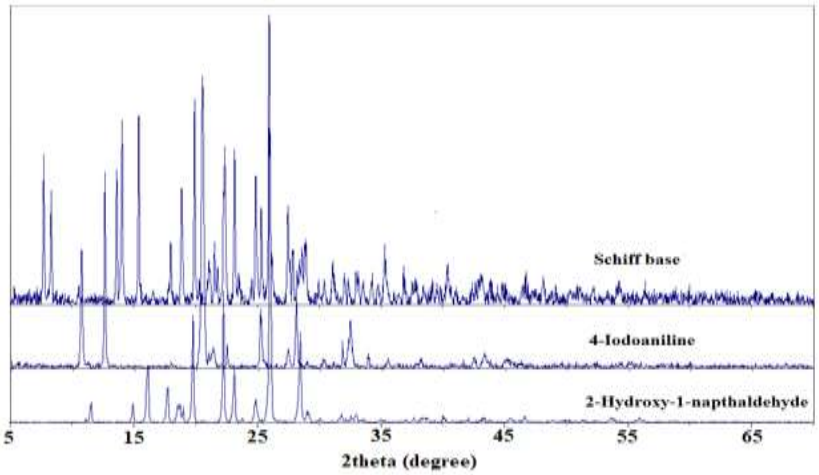


Figure 1: Comparison of Powder x-ray diffraction Patterns of 2-Hydroxy-1-napthaldehyde, 4-Iodoaniline and Schiff base.

The magnetic susceptibility of the complexes was measured using Gouy method-PICO at room temperature and the magnetic moments were calculated as shown in Table 5. The synthesized metal(II) complexes were found to be paramagnetic. Co(II) effective magnetic moment value (μ_{eff} = 3.24 BM) is typical of low spin d^7 systems with one unpaired electron (Kalia *et al.,* 2007). 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 with Ni(II) complex due to its effective magnetic moment value (μ_{eff} = 2.92 BM) (Parameswari, *et al*., 2013).

Table 5: Magnetic Susceptibility Measurement of the Complexes

Compound	$X_g(ergG^{-2}g^{-1})$	$X_m(ergG^{-2}mol^{-1})$	μ_{eff}(BM)
$[Co(SB)_2]$	$+5468.57\times10^{-9}$	4.392×10^{-3}	3.24
$[Ni(SB)_2]$	$+3970.78\times10^{-9}$	3.565×10^{-3}	2.92

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. Insignificant difference in some of the values obtained are within the acceptable range (Tigineh and Liu, 2014) (Table 6).

Table 6: Elemental Analysis Results of the Complexes

Compound	C (%) Found(Calculated)	H (%) Found(Calculated)	N (%) Found(Calculated)
$[Co(SB)_2]$	48.82(49.54)	3.47 (3.06)	2.53 (3.04)
$[Ni(SB)_2]$	45.51 (45.48)	3.81 (3.59)	2.59 (3.12)

The result of Schiff base (Table 7) shows least activity against *S. aureus* with inhibition zone of 10 mm at 60 $mgml^{-1}$ concentrations. The results of the complexes indicated that, $[Co(B)_2]$ and $[Ni(B)_2]$ complexes are much more antibacterial active than Schiff base against *S. aureus, E. coli* and *S. typhi* with inhibition zone of 12, 14 and 12 mm respectively at 60 $mgml^{-1}$ concentrations.

Table 7: Antibacterial Sensitivity test of Schiff base (SB) and its Complexes Showing the Inhibition zone in (mm) Diameter

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	10	07	--	12	09	--	12	09	--
$[Co(SB)_2]$	12	10	--	14	--	--	12	09	--
$[Ni(SB)_2]$	14	12	09	15	11	12	14	13	--

Antifungal strains, against *C. albican, A. flavus* and *A. fumigatus* showed good activity with inhibition zone ranging between 11 - 15 mm with the metal complexes having higher zone of inhibition more than the Schiff base at 60 $mgml^{-1}$ concentrations (Table 8).

The increase activity of complexes over the Schiff base was due to coordination which reduced the polarity of the metal and increased its lipophilic nature to the lipid layer of bacterial cell membrane (Nishat *et al.,* 2011). By binding to various cellular target areas, the metals are said to impair normal cellular processes in living organisms.

Table 8: Antifungal Sensitivity test of Schiff base (SB) and its Complexes Showing the Inhibition zone in (mm) Diameter

Compound	*C. albicum*			*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	11	09	08	10	--	--	08	--	--
$[Co(SB)_2]$	11	09	08	14	07	--	13	15	--
$[Ni(SB)_2]$	10	11	--	15	14	10	12	10	08

CONCLUSION

The Schiff base were synthesized by the one step mechanochemical reaction of 4-Iodoaniline with 2-hydroxy-1-naphthaldehyde and their corresponding Co(II) and Ni(II) complexes. The Schiff base and complexes were characterized by FT-IR, powder x-ray diffraction, thermal analysis, conductivity measurement, magnetic susceptibility and elemental analysis. The solvent assistant mechanochemical synthesis is faster than the solvent-based synthesis. This method is simple, convenient, high yield, save energy and environmentally friendly, is in accordance with the requirement of green chemistry.

The general molecular structure is proposed as shown in Fig 2 based on the analyses of the Schiff base and complexes carried out.

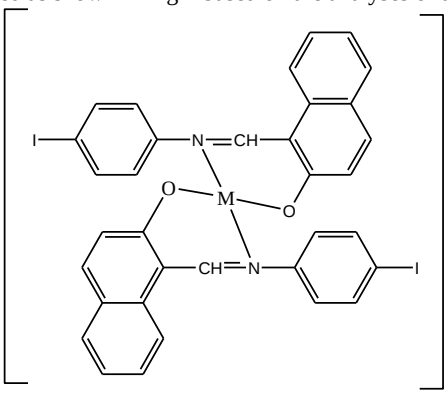


Figure 2: Proposed structure of complexes
Where M = Co^{2+} or Ni^{2+}

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