Original Research Article

Synthesis and Characterization of Bioactive Schiff base ligand derived from 2-hydroxy-1-napthaldehyde and 4-aminobenzonitrile and its Co(II), Ni(II) and Cu(II) Complexes

ABSTRACT

The Schiff base derived from 2-hydroxy-1-napthaldehyde and 4-aminobenzonitride (L) and its corresponding Co(II), Ni(II) and Cu(II) complexes were synthesized and characterized by means of FT-IR spectroscopy, thermal analysis, powder x-ray analysis (PXRD), conductivity measurement, magnetic susceptibility and elemental analysis. The mononuclear complexes have been obtained by liquid-assisted mechanochemical method. The Schiff base was synthesized in high yield > 90% with negligible waste. FT-IR study indicates a strong band in the spectra of the Schiff base at 1577 cm^{-1} assigned to azomethine *v*(C=N) stretching vibration which shifted to new frequency regions in the spectra of complexes indicating the formation of the anticipated complexes. The Schiff base melted at 197 ^{o}C while decomposition temperatures of the complexes were in the range of 265 - 300 ^{o}C, signifying good thermal stability. Molar conductance values were in the range of 4.39 - 1349 $\Omega^{-1}cm^{2}mol^{-1}$, indicating non electrolytic nature of the synthesized complexes. Magnetic susceptibility measurement showed that Co(II), Ni(II) and Cu(II) complexes are paramagnetic and exhibit magnetic moment in the range of 1.50 - 3.19 BM, the values correspond to the tetrahedral geometry. The relative percentage of the constituent elements (C, H, N) obtained from CHN analysis and calculated values using the proposed structures are similar and are in good agreement. The Schiff base and metal complexes were evaluated as agent for inhibiting growth of pathogenic bacteria using disc diffusion method. The results indicated that metal complexes are more active compared to Schiff base ligand against the test organisms.

Keywords: Schiff base; complexes; mechanochemical synthesis; antimicrobial activity.

1. INTRODUCTION

Schiff base are compounds with an azomethine group (-HC=N-). Hugo Schiff described them for the first time in 1864. They are condensation products of aldehydes or ketones with primary amine [1]. The Schiff base formation is really a sequence of two types of reactions, i.e. addition followed by elimination. A large number of aldehydes and ketones have been condensed with various amines to give Schiff bases. The most common catalysts for the formation of Schiff bases are heat, acids or bases. The formation is generally driven to the completion by separation of the product or removal of water, or both. Many Schiff bases can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base. Schiff bases are generally bidentate, tridentate, tetradentate or polydentate ligands capable of forming very stable complexes with transition metals via chelation [2].

Schiff bases are among the most common organic compounds. They are utilized as pigments and dyes, catalysts, organic synthesis intermediates, and polymer stabilizers. Schiff bases have also been demonstrated to have antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic effects [3]. The presence of an imine group in such compounds has been proven to be critical to their biological actions [4–6].

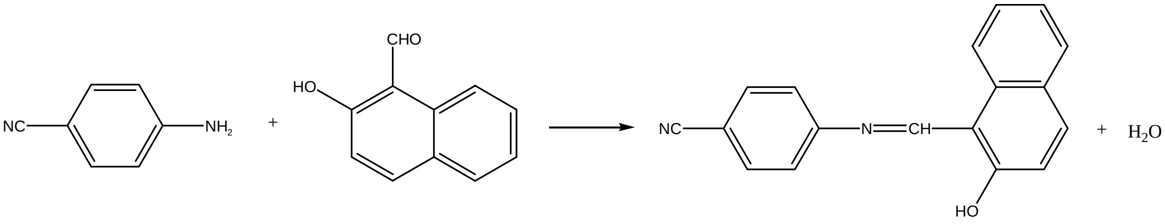
Mechanochemistry can be as easy as grinding two reactants together in a pestle and mortar. Using mechanochemical synthesis can reduce environmental pollution and be more convenient than solvent-based synthesis [7]. Several groups have used this method to demonstrate mechanochemical synthesis of metal complexes [8,9]. Surprisingly, mechanochemical synthesis is often faster and more convenient than solvent-based techniques. As a society, we are becoming more conscious of the environmental effects of human activities and, as a result, of the need to produce cleaner, more energy-efficient technologies [10]. In this paper, we will look at recent studies on the use of mechanochemistry (grinding) to generate Schiff base and metal complexes.

2. MATERIAL AND METHODS

All the reagents were purchased from Sigma-Aldrich UK and are of analytical grade. They were not further purified before use.

2.1 Synthesis of Schiff base

The solid reactants, 2-hydroxy-1-naphthaldehyde (1mmol, 0.17218 g) and 4-aminobenzonitrile (1mmol, 0.11814 g), were carefully weighed into a mortar. The reactant was ground for 45 minutes to yield a yellow orange powder. The powder was removed from the mortar and placed in a sample container [11].



Scheme 1: Synthetic reaction of Schiff base

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2.2 Synthesis of Complexes

The reaction mixture of the metal(II) acetate (1 mmol) and Schiff base ligand (2 mmol) in a 1:2 mole ratio was ground in a mortar and pestle for 60 minutes to produce the colored powder complexes. The products were air dried at room temperature (M = Ni or Cu) [11].

2.3 Antibacterial and Antifungal activities

Antibacterial and antifungal activities were tested using the paper disk diffusion method. *Staphylococcus aureus*, *Escherichia coli*, and *Salmonella typhi* strains of bacteria as well as *Aspergillus fumigatus* and *Aspergillus flavus* strains of fungi were examined. Gram staining and biochemical tests were used to identify the microbial isolates, which were obtained from the Aminu Kano Teaching Hospital's Department of Chemical Pathology [12].

3. RESULTS AND DISCUSSION

3.1 Physical properties, molar conductance and magnetic susceptibility

The Schiff base ligand and complexes that were synthesized were coloured. Electronic d-d transitions are what give complexes their colours. The percentage yield of the Schiff base and metal complexes synthesized by the mechanochemical method ranged from 84.5 to 92.2% (Table 1). A crystalline solid with a melting point of 197^{o}C was found to be the Schiff base. Complexation is the cause of all complexes having a decomposition temperature higher than the melting point of the Schiff base. The complexes decomposed in the 265 to 292^{o}C range, demonstrating good thermal stability [13].

The molar conductivity values of the complexes in a 10^{-3} M solution in DMF were measured. Within the bounds of their solubility, conductivity measurements have frequently been used to describe metal chelates. The higher molecular ions that a complex liberates in solution, the higher will be its molar conductivity, and vice versa. They offer a method of testing the degree of ionization of the complexes. The values of the molar conductance (Λm) of the metal complexes are shown in Table 1. The findings revealed that the molar conductance values of the Co(II), Ni(II), and Cu(II) complexes were 13.49, 9.54, and 4.39 $\Omega^{-1}cm^{2}mol^{-1}$, respectively. The conductivity data of the synthesized complexes make it abundantly clear that the complexes were discovered to be non-electrolytes and very low to account for any complex dissociation in DMF [14].

According to the effective magnetic moment values of the complexes (Table 1) derived from the Schiff base, Co(II), Ni(II), and Cu(II) complexes are paramagnetic in nature and have magnetic moments of 3.19, 2.67, and 1.50 BM, respectively, which are close to spin-only values and may be caused by orbital contribution and ligand effect. This value is less than the spin-only value reported by Kumari, 2017 (4.3–5.2 BM) for three unpaired electrons. Tetrahedral geometry matches the observed magnetic parameter [15].

Table 1. Physical properties, molar conductance and magnetic susceptibility of Schiff base (H_2L) complexes

Compound	Molecular Formula	Colour	Melting Point/ Decomp.Temp (^{o}C)	Yield (%)	Molar conductance ($\Omega^{-1}cm^{2}mol^{-1}$)	μ_{eff} (BM)
(H_2L)	($C_{18}H_{12}N_2O$)	Orange	197	89.6	-	-
[Co(SB3)$_2$]	[Co($C_{18}H_{11}N_2O$)$_2$]	Red	292	90.2	13.49	3.19
[Ni(SB3)$_2$]	[Ni($C_{18}H_{11}N_2O$)$_2$]	Yellow	265	84.5	9.54	2.67
[Cu(SB3)$_2$]	[Cu($C_{18}H_{11}N_2O$)$_2$]	Tan	280	92.2	4.39	1.50

3.2 Powder x-ray diffraction

The powder x-ray diffraction analysis of 2-hydroxy-1-napthaldehyde and 4-aminobenzonitride revealed distinct and intense peaks that were missing from the Schiff base's powder x-ray diffraction (Fig 1). Instead, additional strong and sharp peaks were seen, indicating the formation of the target Schiff base [16]. Schiff base powder x-ray diffraction patterns show sharp reflections, indicating that the compound is crystalline [17,18]. The diffractogram of the complexes in relation to the reactants shows different reflection peaks as well.

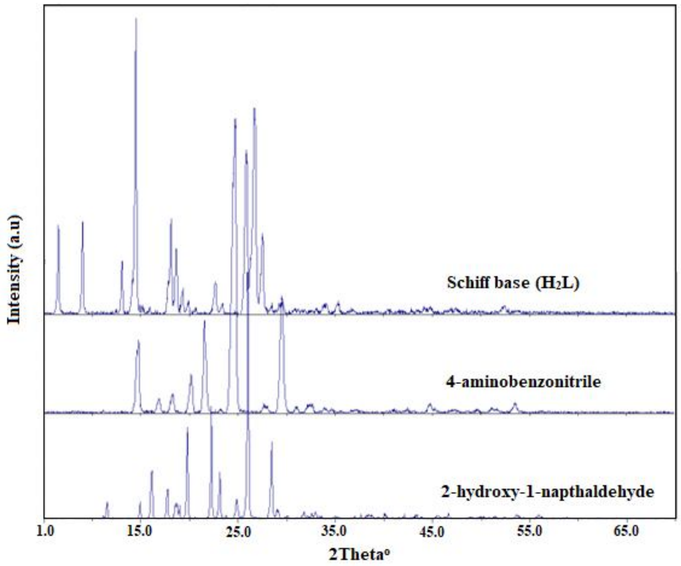

Figure 1: Comparison of PXRD patterns of 2-Hydroxy-1-napthaldehyde, 4-aminobenzonitrile and Schiff base

3.3 Solubility test

The Schiff base is insoluble in some nonpolar solvents, such as n-hexane, but is soluble in some polar solvents, such as DMSO, DMF, and acetonitrile. It was discovered that the metal complexes were soluble in polar solvents like DMF and DMSO, only slightly soluble in acetonitrile and acetone, and insoluble in some nonpolar solvents like n-hexane. Due to the presence of some polar groups, this suggested that the produced compounds were polar (Table 2).

Table 2. Solubility Test of Schiff base (H_2L) and its metal complexes

Compound	DMF	DMSO	Acetonitrile	Diethyl ether	Chloroform	Acetone	n-hexane
(H_2L)	S	S	SS	SS	S	SS	IS
[Co(SB3)$_2$]	S	S	SS	SS	SS	SS	IS
[Ni(SB3)$_2$]	S	S	SS	SS	S	SS	IS
[Cu(SB3)$_2$]	SS	SS	IS	SS	SS	SS	IS

3.4 Infrared spectroscopy

The Schiff base's IR spectra reveal the formation of a new peak (1577 cm^{-1}) caused by the azomethine group (Table 3). The O-H absorption bond in the Schiff base was also discovered to be present at 3692 cm^{-1}. The shift of the azomethine peak in the complex spectra from to 1599 cm^{-1} indicates that the coordination activity of the azomethine nitrogen. The emergence of the 434–475 cm^{-1} and 542–545 cm^{-1} bands in the low-frequency region for the respective M–O and M–N ions provided additional evidence in favor of the coordination of the Schiff base to the metal ion. In the spectra of the ligand, these bands were absent. These two novel bands (M-O and M-N) have metal ions that coordinate through phenolic oxygen and azomethine nitrogen [19,20].

Table 3. Infrared spectra result of Schiff base (H_2L) and its complexes

Compound	v(OH) cm^{-1}	v(C=N) cm^{-1}	v(M-O) cm^{-1}	v(M-N) cm^{-1}
(H_2L)	3692	1577	-	-
[Co$(SB3)_2$]	-	1581	475	545
[Ni$(SB3)_2$]	-	1599	445	542
[Cu$(SB3)_2$]	-	1581	434	542

3.5 Elemental analysis

The calculated values using the suggested structures are similar to and in good agreement with the relative percentage of the constituent elements (C, H, and N) obtained from CHN analysis (Table 4). This is in support of the complexes' proposed structures. Small variations in some of the values that are within the allowable range are explained by [21].

Table 4. Elemental Analysis of Schiff base complexes

Compound	C (%) Found(Calculated)	H (%) Found(Calculated)	N (%) Found(Calculated)
[Co$(SB3)_2$]	70.60 (71.88)	3.22 (3.69)	8.72 (9.31)
[Ni$(SB3)_2$]	70.50 (71.91)	3.30 (3.69)	8.60 (9.32)
[Cu$(SB3)_2$]	70.02 (71.34)	3.20 (4.46)	8.60 (9.32)

3.6 Antimicrobial activity

The antibacterial activity of the Schiff base was reasonable against bacterial isolates, with a maximum zone of inhibition of 13 mm against *E. coli* (Table 5). The complexes derived from the Schiff base exhibit significant activity, particularly at higher concentrations against the organism tested with inhibition zone range of 08 - 16 mm. At varying concentrations of the tested fungal isolates, Schiff base and its complexes also exhibit moderate antifungal activity with inhibition zones ranging from 07 to 16 mm (Table 6).

It has been established that the synthesized compounds' antimicrobial properties are due to the azomethine group [2,4–6]. The chelation of the Schiff base with metal ions may be responsible for the increased activity of the metal(II) complexes compared to the free ligand. The polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbitals during the chelation process and the partial sharing of the metal ion's positive charge with donor groups, this will increase the permeability of the compounds through the lipid layer of cell membranes [22].

Table 5. Antibacterial activity of Schiff base and complexes showing the inhibition zone (mm)

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
(H_2L)	12	10	08	13	09	08	12	--	11

[Co(SB3)$_2$]	16	12	09	14	12	11	14	13	12
[Ni(SB3)$_2$]	15	13	11	15	13	09	12	11	--
[Cu(SB3)$_2$]	13	11	09	14	10	09	15	12	10

Table 6. Antifungal activity of Schiff base and complexes showing the inhibition zone (mm)

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
(H$_2$L)	10	08	07	12	11	09	11	09	--
[Co(SB3)$_2$]	15	11	--	15	13	10	16	10	09
[Ni(SB3)$_2$]	14	--	16	09	13	14	12	10	07
[Cu(SB3)$_2$]	14	10	--	14	12	10	10	16	09

4. CONCLUSION

This paper describes the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes containing N, O donor bidentate Schiff base ligand. A proposed structure is well supported by the complexes' spectroscopic data (Figure 1). The antimicrobial screening results of the test compounds show that they have mild to moderate antimicrobial activities when compared to standard drugs. The nonpolluting nature of the mechanochemical approach qualifies it as a green method for the synthesis of Schiff bases and complexes.

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