Nigerian Research Journal of Chemical Sciences **(ISSN: 2682-6054)**
Volume 8, Issue 1, 2020

MECHANOCHEMICAL SYNTHESIS, CHARACTERIZATION, THERMAL ANALYSIS AND ANTIMICROBIAL STUDIES OF CO(II) SCHIFF BASE COMPLEX

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ABSTRACT

The Schiff base ligand was synthesized by condensation of 2-hydroxy-3-methoxybenzaldehyde with *m*-phenylenediamine via liquid-assisted mechanochemical synthesis using dimethylformamide (DMF) as liquid-assisted solvent. The Co(II) complex was synthesized and characterized by Infra-red spectroscopy (IR), Solubility test, melting point, Thermogrametric/Differential thermal analysis (TG/DTA), Energy dispersive X-ray analysis (EDX), Powder-XRD, Conductivity measurement, magnetic susceptibility measurement and CHNS/O, macro-analysis. Infrared spectral study indicated a band in the spectra of ligand at 1617 cm^{-1} assigned to azomethine $\nu(C{=}N)$ stretching vibration. It shifted to lower frequency regions in complexation indicating the formation of complex compound. The absence of hydrated water in the complex was confirmed by TGA thermogram with decomposition temperature of 218 ^{o}C. The Powder-XRD analysis revealed the change in phase of the synthesized compounds with respect to the starting constituents. The relative percentage of the constituent elements obtained from EDX and CHN analysis were similar, which suggested the uniform distribution of the elements in the synthesized compounds. The antimicrobial activity results showed that the complex have higher antimicrobial activity than the free Schiff base.

Keywords: Antimicrobial activity, Complex, Mechanochemical, Schiff Base, Thermal study.

INTRODUCTION

The one-step mechanochemical synthesis is a class of spontaneous self-assembly synthesis of metal complexes that has made rapid progress over the last twenty-five years, not only in Inorganic Chemistry, but also in Organic synthesis and Organometallic Chemistry. Researchers identified this method after so many years of studies, as a powerful approach that has significantly expanded the scope of spontaneous self-assembly synthesis. The first recorded example of an entirely solvent-free mechanochemical reaction can be accredited to Faraday, who in 1820 reduced AgCl to Ag using either Zn, Cu, Sn or Fe by grinding in a pestle and mortar [1]. Though, it was worked by Carey Lea in the 1890s which showed that mechanochemical reactions could give different products to thermal ones favouring decomposition of mercury and silver halides to their elements rather than melting or sublimation. This work might therefore be seen as the point at which mechanochemistry became a truly distinct sub-topic in chemistry [2].

Mechanochemistry is typically promoted by either manual grinding or mechanical milling. This process may engage in interaction between carbon-hetero atom covalent interactions, hydrogen bond deformation, and formation of metal-ligand coordination bonds or even rearrangement of bonds [3-4]. Mechanochemical synthesis is becoming a more mainstream technique because, it can promote reactions between solids quickly and quantitatively, with either no added liquid/solvent or only a minimal amount. Very small amounts of added liquid also called liquid assisted grinding (LAG) can considerably accelerate and even enable mechanochemical reactions between solids. Often the molar equivalents added are similar to those of the reactants themselves and are orders of magnitude smaller than the quantities used in typical solution-based reactions. Such reactions are therefore more properly described as ‘‘minimal solvent’’ rather than strictly ‘‘solvent-free’’ [5].

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 for purification and recycling [6, 7]. The aim of the research work was to synthesize Schiff base and Co(II) complex mechanochemically and then screen both the Schiff base and the complex for their antimicrobial activity.

MATERIALS AND METHODS

Reagents used were obtained from Sigma Aldrich UK and were used without further purification. Solid state IR spectra were recorded on a Perkin-Elmer FTIR Spectrum-400. PXRD measurements were carried out on a PAN analytical Empyrean X’Pert Pro X-ray diffractometer in the range 0-40 ^{o}C. Copper was used as the X-ray source with a wavelength of 1.5405 Å. Energy dispersive X-ray (EDX) were determined using FESEM/EDX Hitachi brand model SU8220. Thermal analysis studies of complexes (TGA) were performed using Perkin-Elmer

Pyris Diamond TG/ DTA Heated in flowing Nitrogen (200 mlmin^{-1}). Magnetic susceptibility measurements were carried out using Sherwood scientific MSB1 magnetic susceptibility balance. Melting point were determined using digital melting point MPA100. Conductivity measurements were carried out using LMCM-20 conductivity meter. Elemental microanalysis for C, H and N were determined using Perkin-Elmer CHNS/O 2400 series II microanalyse, in the Department of Chemistry University of Malaya, Malaysia.

Synthesis of Schiff Base (H_2L)

The ligand was prepared by condensation reaction between 2-hydroxy-3-methoxybenzaldehyde (1.5215 g, 10 mmol) and *m*-phenylenediamine (0.5405 g, 5 mmol). The two reactants were carefully weighed into agate mortar. The mixture was ground using mortar and pestle. A small amount of dimethylformamide (typically, 1.0 drop) was added to allow the formation of paste. After 30 minutes of continuous grinding, light orange coloured product was obtained. The obtained product was allowed to dry in air [7].

Synthesis of Complex [Co(L)]

The Schiff base $H_2(L)$(0.3764 g, 1 mmol) and Cobalt tetrahydrate (0.2491 g, 1 mmol) were weighed in to agate mortar, a small amount of DMF (1.0 drop) was added and the mixture was ground for 30min to obtain purple solid product. The compound was dried in air at room temperature [7].

Antimicrobial Activity Test

The microbial isolates were obtained from the Department of Chemical Pathology, Aminu Kano Teaching Hospital Kano, Nigeria and were identified using Gram staining and biochemical test. The antimicrobial activities of the Schiff base and complex in dimethylsulfoxide were carried out *in vitro* by agar well diffusion method [8].

RESULTS AND DISCUSSION

The liquid-assisted mechanochemical method adopted produced Schiff base and metal complex with percentage yield of 89.5 and 81.6% respectively within a shorter reaction time of 30 minutes. The Schiff base and complex synthesized were coloured (Table 1). The colour of the complex was as a result of d-d transitions of electrons between energy levels. In addition, the metal complex exhibits higher decomposition temperature than that of the Schiff base which suggests that the metal complex is more stable as compared to the Schiff base. The higher stability of the metal complex is attributed to complexation [9]. The elemental analysis of the Schiff base and complex for C, H, N (Table 1) are consistent with the calculated results from the empirical formula of the proposed structure of each compound.

Table 1: Physical properties and Elemental Analysis of the Schiff Base and its Co(II) Complex

Compound	Molecular formula	Colour	Yield (%)	Melting point (^{O}C)	Found (Calculated) (%) C	H	N
(H_2L)	($C_{22}H_{20}N_2O_4$)	Light orange	89.5	133	70.43(70.20)	5.18(5.36)	7.28(7.44)
[Co(L)]	[Co($C_{22}H_{18}N_2O_4$)]	Purple	81.6	218	61.24(60.98)	4.37(4.19)	6.18(6.46)

The Schiff base was found to be sparingly soluble in polar solvents such as methanol, ethanol, DMSO, DMF and THF but insoluble in non-polar solvent (toluene and hexane). The metal complex showed solubility in polar solvent such as methanol, ethanol, DMF, DMSO and THF while the solubility in nonpolar solvent goes from slightly soluble to insoluble in both hexane and toluene. These suggested the polar nature of the synthesized compounds (Table 2).

Table 2: Solubility Test of Schiff Base and its Co(II) Complex

Compound	Methanol	Ethanol	DMSO	DMF	THF	Toluene	Hexane
(H_2L)	S	S	S	S	S	IS	IS
[Co(L)]	S	SS	S	SS	S	SS	IS

Where: S – Soluble, SS – Slightly Soluble, IS – Insoluble

The infrared spectroscopy of the Schiff base and its metal complex were presented in Table 3. Strong band at 1617 cm^{-1} is characteristics of the azomethine present in the Schiff base (H_2L) [10]. This shifted to 1594 cm^{-1} in the complex, which indicated the coordination of the metal to the azomethine nitrogen. The spectra of the Schiff base exhibited strong peak at 3371 cm^{-1} assigned to O-H stretching vibration. The phenolic C-O stretching frequency of Schiff base was observed at 1203 cm^{-1} [11]. The O-H broad band in the Schiff base was no longer found in the spectra of investigated complex and also phenolic C-O stretching frequency shifted in the complex indicating deprotonation and coordination of the hydroxyl oxygen to the metal ion as

Reddy, et al. [12] reported similar range of value. The bands ν(M-N) and ν(M-O) were observed in the far infrared region of the complex. These bands were absent in the spectra of the Schiff base. The ν(M-N) was observed at 690 cm^{-1}which indicated coordination between the metal and the lone pair of electrons on the nitrogen atom of the ligand. Also, band observed at 466 cm^{-1}, indicated the formation of M-O bond for the complex [13]. The appearance of M-N and M-O vibration supported the involvement of N and O atoms in the complexation with metal ion under investigation.

Table 3: Infrared spectral data of Schiff Base and its Complex (cm^{-1})

Compound	ν(C=N)	ν(O–H)	ν(C–O–C)	ν(C–O)	ν(C–C)	M–N	M–O
(H_2L)	1617	3371	1119	1203	1451	-	-
[Co(L)]	1594	-	1166	1208	1446	690	466

Powder X-ray diffraction patterns (PXRD) of the liquid-assisted mechanochemical products revealed the crystalline nature of the synthesized compounds. The PXRD pattern of Schiff base and complex were different from that of their respective reactants. New peaks corresponding to the mechanochemical product were observed indicating the formation of new phase. The major peaks in PXRD pattern of (H_2L) Schiff base were observed at 2θ values10.31, 11.19, 15.89, 18.404, 20.372, 21.36^o while that of [Co(L)] complex were observed at 11.26, 18.92, 19.55, 22.28, 23.53 and 24.16^o (Figure 1),which were absent in the reactants indicating formation of new phase of the product.

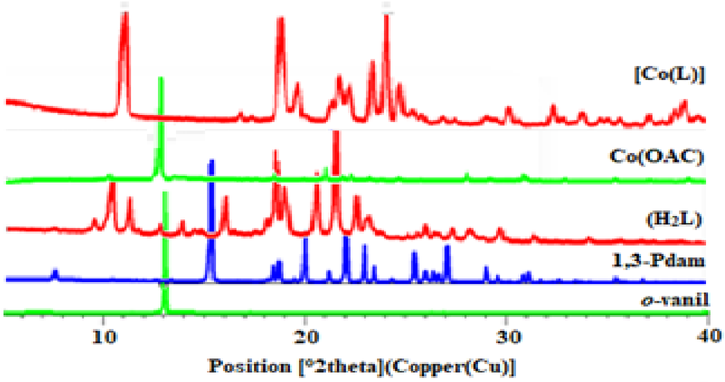

Figure 1: PXRD Patterns of *o*-vanillin (*o*-vanil), 1,3-phenylenediamine (1,3-Pdam), Schiff base (H_2L), Cobalt(II) acetate tetrahydrate (Co(OAC)), [Co(L)] complex product

The data generated by energy dispersive x-ray analysis included spectra showing peaks corresponding to the elements making up the true composition of the samples being analyzed. EDX results of $H_2(L)$ Schiff base showed that, carbon constitute the largest atomic percent (70.15%), followed by oxygen (18.38%) and nitrogen (11.47%). For Co(II) complex, the atomic percent of carbon, oxygen, nitrogen and cobalt were found to be 66.40, 0.81, 11.54 and 1.03% respectively (Table 4). The atomic percent of all the component elements were compared in all the points analyzed and the results (atomic percent of C, O, N and Co) were found to be in agreement with each other indicating the uniform distribution of all the constituent elements in the sample compound (Figure 2a and 2b). Furthermore, the relative percentage obtained from the EDX is compared with the results obtained from the CHN analysis. As expected, the relative percentage of carbon, oxygen and nitrogen obtained from EDX and CHN analysis are similar, which suggests the uniform distribution of the elements in the Schiff base [14].

Table 4**:** Energy Dispersive x-ray (EDX) of Schiff base and its metal complex

Compound	Element	Weight (%)	Atomic (%)	K Ratio	Line type
(H_2L)	C	63.65	70.15	0.01693	K Series
	N	14.16	11.47	0.00106	K Series
	O	22.19	18.38	0.00105	K Series
[Co(L)]	C	58.81	66.40	0.04981	K Series
	N	11.92	11.54	0.00185	K Series
	O	24.81	0.81	0.00269	K Series
	Co	4.96	1.03	0.00335	K Series

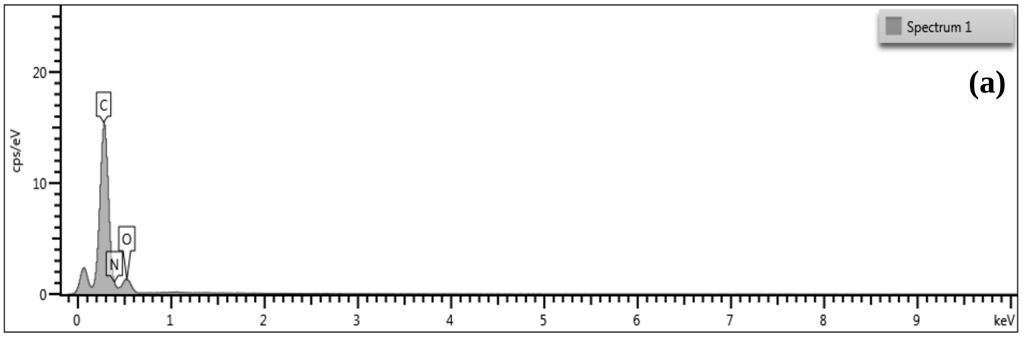

Figure 2a: EDX spectrum of Schiff base showing peak due to Carbon, Nitrogen, and Oxygen

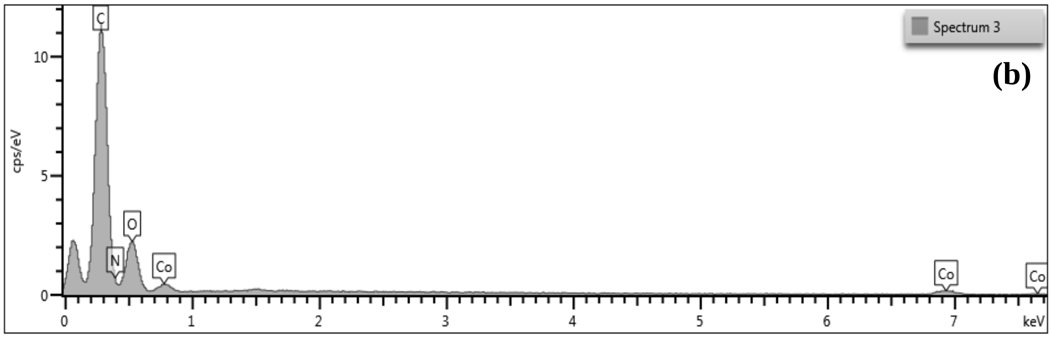

Figure 2b. EDX spectrum of Cobalt complex showing peak due to Carbon, Oxygen, Nitrogen and Cobalt.

Three successive thermal decomposition steps were observed for [Co(L)] complex within a temperature range of 40 – 450 °C (Figure 3). Initially, there was no reasonable mass loss up to 110 ° C which indicate the absence of water of hydration but shows weight loss at temperature range between 125 – 170 °C which indicated the loss of the residual acetic acid. The weight loss of 19.3% at 225 °C indicated the decomposition of the first fragment (C_7H_5NS). The 19.3% weight loss is in good agreement with theoretical value of 20.3%. The results obtained were similar to the values reported by Khalil et al., [15].

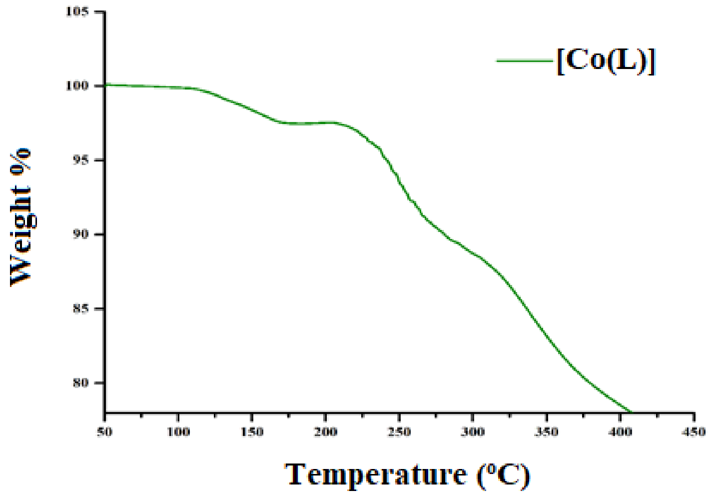

Figure 3: TGA Analysis of [Co(L)] Complex.

The molar conductivity values in 10^{-3} M solution of Co(II) complex in ethanol were measured at room temperature. Table 5 shows the molar conductance (Λm) values of the Co(II) complex.

From the results the complex has molar conductance value of 5.53 $\Omega^{-1}cm^2mol^{-1}$, indicating the non-electrolytic nature because of the lower conductivity value.

Table 5: Molar Conductance Measurement of Co(II) Complexes

Compound	Concentration ($Moldm^{-3}$)	Specific Conductance ($\Omega^{-1}cm^{-1}$)	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)
$[Co(L^3)]$	1×10^{-3}	5.53×10^{-6}	5.53

Room temperature magnetic susceptibility measurements indicate that, Co(II) complex is paramagnetic in nature and exhibit a magnetic moment of 2.104 BM. as given in Table 6. The value lie in the range corresponding to one unpaired electron for square planar stereochemistry around Co(II), d^7 complexes.

Table 6: Magnetic Susceptibility Measurement of Co(II) Complex

Compound	X_g ($ergG^{-2}g^{-1}$)	X_m ($ergG^{-2}mol^{-1}$)	μ_{eff} (BM)
$[Co(L^3)]$	$+4.289 \text{ x}10^{-12}$	$1.857 \text{ x}10^{-3}$	2.104

The results of antimicrobial sensitivity test revealed that the Co(II) complex is more toxic to the tested bacterial strains than the Schiff base Ligand. The highest antibacterial activity of the complex was observed at 60 $mgml^{-1}$ concentration against *E. Coli* (gram negative), 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 *A. Niger*. The highest activity was observed against *A. Flavus* with inhibition of 23 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 [16-18].

The antimicrobial activity of complex was extensively studied by Mohamed, et al. [19] based on chelation theory, the enhancement to the increased lipophilic nature of the metal 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 reduces the polarity of metal and thus increasing the lipophilic nature of the metal to the lipid layer of bacterial cell membrane [20].

Table 7**:** Antibacterial Sensitivity Test of Schiff Base and Complex

Compound	Escherichia Coli Inhibition zone(mm)			Staphylococcus Aureus Inhibition zone(mm)		
	60 mgml^{-1}	30 mgml^{-1}	15 mgml^{-1}	60 mgml^{-1}	30 mgml^{-1}	15 mgml^{-1}
Ciprofloxacin(Standard)		43			40	
DMSO (Control)	-	-	-	-	-	-
(H_2L)	13	9	-	14	11	9
[Co(L)]	14	12	9	16	12	9

Table 8: Antifungal Sensitivity Test of Schiff Base and Complex

Compound	Aspergillus Flavus Inhibition zone(mm)			Aspergillus Niger Inhibition zone(mm)		
	60 mgml^{-1}	30 mgml^{-1}	15 mgml^{-1}	60 mgml^{-1}	30 mgml^{-1}	15 mgml^{-1}
Ketoconazole (Standard)		44			36	
DMSO (Control)	-	-	-	-	-	-
(H_2L)	12	10	7	-	-	-
[Co(L)]	23	19	12	17	13	10

CONCLUSION

The study highlights the fact that mechanochemical synthesis provide a way to reduce the need for solvents both as reaction media and for purification. On the basis of the analytical data obtained, the proposed tentative structure of Schiff base complex is as shown in Figure 4.

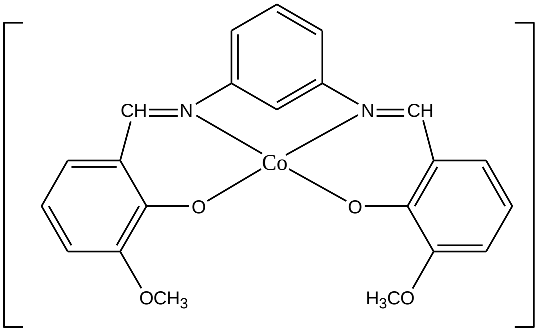

Figure 4: Proposed structure of [Co(L)]Complex

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