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Energy-Efficient Synthetic Method, X-Ray Diffraction Analysis and Thermal Decomposition of Cobalt (II) and Nickel (II) Schiff Base Complexes Derived from 2-Aminobenzothiazole

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ABSTRACT

A Schiff base was synthesized from the condensation reaction of 2-hydroxybenzaldehyde and 2-aminobenzothiazole via energy-efficient liquid-assisted mechanochemical synthesis (LAG). The Co (II) and Ni (II) complexes were also synthesized and characterized using IR, Solubility, TGA, PXRD, UV-Visible analysis, magnetic susceptibility measurement, conductivity measurement, and CHNS/O micro-analysis. In the IR analysis, the Schiff base spectrum revealed a prominent band at 1603 cm-1 (assigned to the azomethine v(C=N) stretching vibration), and the azomethine band shifted to 1621 and 1599 cm-1 in the Co (II) and Ni (II) complexes, respectively (indicating the formation of the expected complexes). In the TGA thermogram, Ni (II) and Cu (II) Schiff base complexes had decomposition temperatures of 184 and 181°C, respectively. The PXRD analysis revealed that the patterns of the ground mixture were different from the starting constituents, implying that the raw components were converted into the final product. The theoretical and experimental analytical data of C, H, and N for the Schiff base and complexes are in good agreement. The Schiff base ligand and its complexes were evaluated as agents for inhibiting the growth of pathogenic bacteria using the agar well diffusion method. According to antimicrobial activity studies, complexes exhibit stronger antibacterial activity than the Schiff base.

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1. INTRODUCTION

Solid-solid mechanochemical reactions are characterized as solid-state reactions caused by mechanical energy, including grinding with a mortar and pestle or in ball mills (James *et al.*, 2012). It is getting a lot of attention since it can speed up and quantitatively promote solid-solid reactions with no or very little additional solvent.

Schiff bases are a common class of ligands in the coordination chemistry of transition and main group elements. In coordination chemistry, they are commonly utilized as ligands. The Schiff base complex has attracted the interest of many researchers due to its intriguing structural features and wide-ranging applications (Collinson & Fenton, 1996; Sani & Kurawa, 2016).

Schiff bases are a class of organic compounds. They are used as pigments and dyes, as well as catalysts, organic synthesis intermediates, and polymer stabilizers. In addition to antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties (Priya *et al.*, 2009). The presence of an imine group in such compounds is essential for their biological effects (Ashraf *et al.*, 2011; Bringmann *et al.*, 2004; Guo *et al.*, 2007).

Metal complexes containing N and S chelating ligands have attracted a lot of attention because of their unique physicochemical characteristics and significant biological and pharmacological activities. The N and S atoms help metals coordinate at the active sites of many metallobiomolecules (Sakıyan *et al.*, 2004).

The benzothiazole ring can be found in a variety of marine and terrestrial natural substances with biologically beneficial properties (Bénéteau *et al.*, 1999). The clinical applications of 2-aminobenzothiazole and its derivatives are well-known (Krishnankutty *et al.*, 2010). Due to its unusual structure and importance as a pharmacophore in a variety of diagnostic and therapeutic drugs explored in the 1950s, 2-aryl benzothiazole has attracted a lot of attention among benzothiazoles. It has been shown to have cytotoxic action on cancer cells and is employed as a radioactive amyloid imaging agent and anticancer medicine (Heo *et al.*, 2006; Piscitelli *et al.*, 2010). Thiazole derivatives are commonly utilized in the manufacture of pharmaceuticals such as sulphathiazole (Borisenko *et al.*, 2006).

The research work aims to provide an alternative synthetic route to the synthesis of Schiff base and complexes via energy-efficient solid-solid mechanochemical reaction. The existing reliance on solvents seems to be increasingly unsustainable because it wastes fossil-derived materials in terms of solvent production, purification, and recycling, environmentally problematic, dangerous, and energy-intensive (Sani *et al.*, 2018).

2. METHODS

Solid-state IR spectra were recorded using a Perkin-Elmer FTIR Spectrum-400. A PANanalytical Empyrean X'Pert Pro X-ray diffractometer was used to perform the PXRD measurements. The x-ray source was made of copper. Diffractograms were commonly performed with a step size of 0.0167° and a range of 5–40°. The digital melting point MPA100 was used to obtain the melting point. Perkin-Elmer Pyris Diamond TG/ DTA was used to determine thermal analysis (TGA), heated at 10° min^{-1} in flowing nitrogen (200 mL/min). Using a Shimadzu UV-Vis 240 spectrophotometer, electronic absorption spectra were obtained. Sherwood scientific MSB1 magnetic susceptibility balance was used to test magnetic susceptibility. The LMCM-20 conductivity meter was used to test the conductivity. An elemental microanalyzer (Perkin-Elmer CHNS/O 2400 series II) was used to do elemental microanalyses (C, H, N, and S) at the University of Malaya in Malaysia.

2.1. Synthesis of Schiff base ($H_2(L')$)

A modified procedure was used to synthesize the Schiff base (**Figure 1**), as described by (Cinčić & Kaitner, 2011). In the reaction, 2-hydroxy-1-naphthaldehyde (1.722 g; 10 mmol) and 2-aminobenzothiazole (1.502 g; 10 mmol) were weighed into an agate motor, and a small quantity of DMF (0.1 ml) was introduced, and the mixture was ground for 30 minutes to get a brown solid product that was dried in air (**Figure 2**).

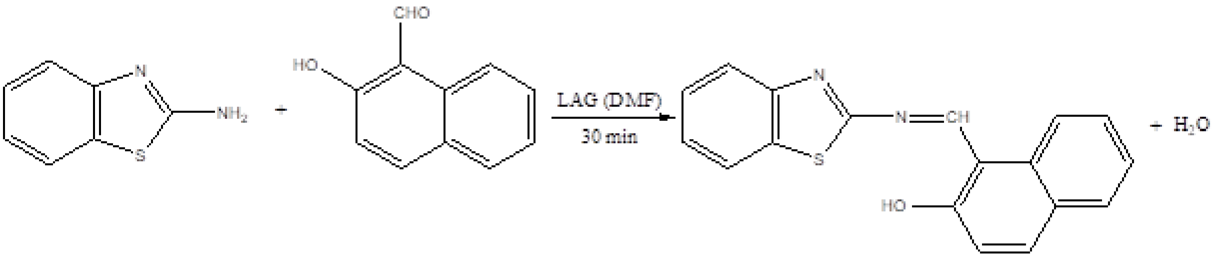

Figure 1. Synthetic reaction of $H_2(L')$ Schiff base.

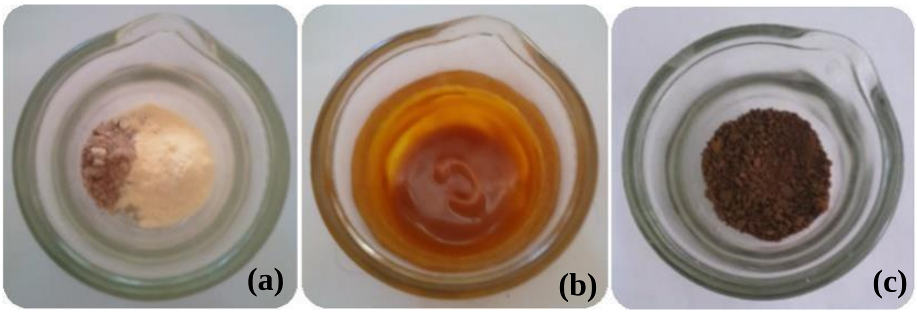

Figure 2. Digital photograph of (a) reactants, (b) intermediate, and (c) $H_2(L')$ Schiff base, showing the steady change in color of the reactants and the formation of Schiff base.

2.2. Synthesis of Complexes

Complexes were synthesized using a modified procedure reported by (Cinčić & Kaitner, 2011). The Schiff base (0.30438 g; 1 mmol) and metal acetate, $M(CH_3COO)_2{\cdot}nH_2O$ (1 mmol) (M can be Co or Ni) were placed into an agate motor, and a little quantity of DMF (0.1 ml) was added, and the mixture was ground for 30 minutes to produce colored compounds. The resulting compounds were dried in the open air at room temperature.

2.3. Antimicrobial activity

The microbial isolates were collected from the Aminu Kano Teaching Hospital's Department of Chemical Pathology and identified using Gram staining and biochemical tests. Agar well diffusion method was used to test antibacterial activity. Bacteria strains (*Staphylococcus aureus* and *Escherichia coli*) and fungi (*Candida albicans* and *Aspergillus fumigatus*) were investigated. Separate amounts of Schiff base and complexes were dissolved in dimethylsulfoxide to obtain three distinct concentrations (15, 30, and 60 mg/mL).

2.3.1. Antibacterial Bioassay

The isolate's standard inoculum was swabbed onto the prepared and solidified nutrient agar plates' surface area. The test chemical solution and the standard antibiotic concentration (ciprofloxacin) were mixed and deposited in the agar wells of the inoculation plates. The inhibitory zone was measured after 24 hours of incubation at 37°C (Yusha'u & Sadisu, 2011).

2.3.2. Antifungal Bioassay

In separate Petri-dishes, the isolate's standard inoculant was swabbed on the surface of the prepared and solidified potato agar. At intervals, the prepared solution of the compound and the standard antibiotic (Ketoconazole) were placed within the wells of the inoculation media. The plates were incubated for 72 hours at 37°C before being observed for the zone of inhibition assessment (Yusha'u & Sadisu, 2011).

3. RESULTS AND DISCUSSION

3.1. Powder x-ray diffraction

The crystalline or amorphous nature is revealed by the x-ray diffraction patterns of produced compounds. Although the newly synthesized Schiff base and complexes were soluble in polar organic solvents like DMSO and DMF, single crystals appropriate for single-crystal x-ray examinations were not found. All of the compounds produced have different powder x-ray diffraction (PXRD) patterns than the starting constituents. Furthermore, there was no sharp peak formed from the initial constituents, indicating that they were transformed into the product. The crystallinity of the LAG products was demonstrated by clear reflections in the patterns. A similar rationale was provided by (Cinčić & Kaitner, 2011). The powder x-ray diffraction spectra of 2-hydroxy-1-napthaldehyde and 2-aminobenzothiazole, respectively, show a prominent and intense peak at 18.932° and 17.712°, which is absent in the powder x-ray diffraction of the Schiff base (Fig 1). Instead, additional sharp and strong peaks were observed at 13.189°, 21.051°, and 27.352°, implying that the target Schiff base has formed (Zhong *et al*., 2012). The sharp reflections in the Schiff base powder x-ray diffraction patterns indicate that the products are crystalline (Cinčić & Kaitner, 2011; Cindrić *et al*., 2012). Different reflection peaks are also visible in the diffractogram of the complexes concerning the reactants (**Figure 3 - 5**).

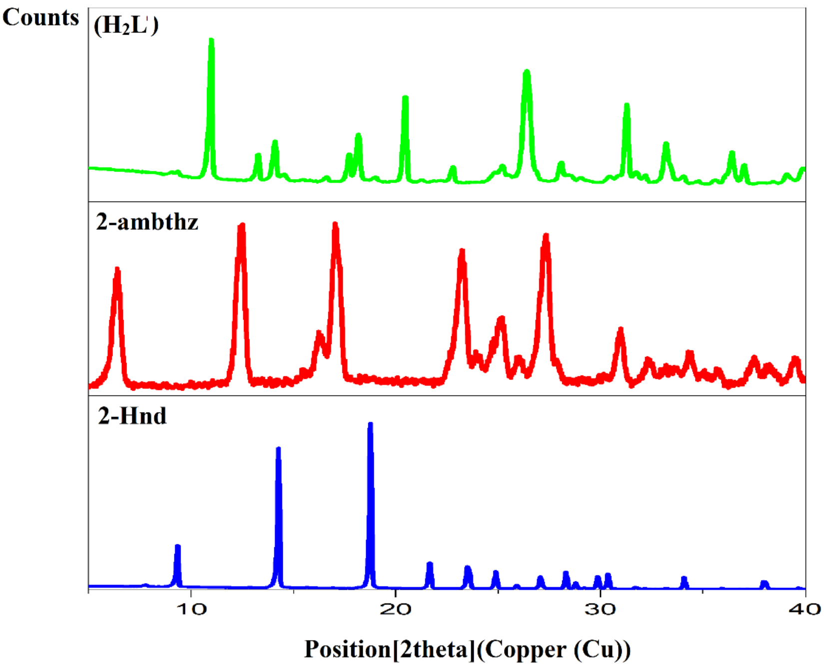

Figure 3. Comparison of PXRD Patterns of 2-Hydroxy-1-napthaldehyde (2-Hnd), 2-aminobenzothiazole (2-ambthz), and (H_2L') Schiff base.

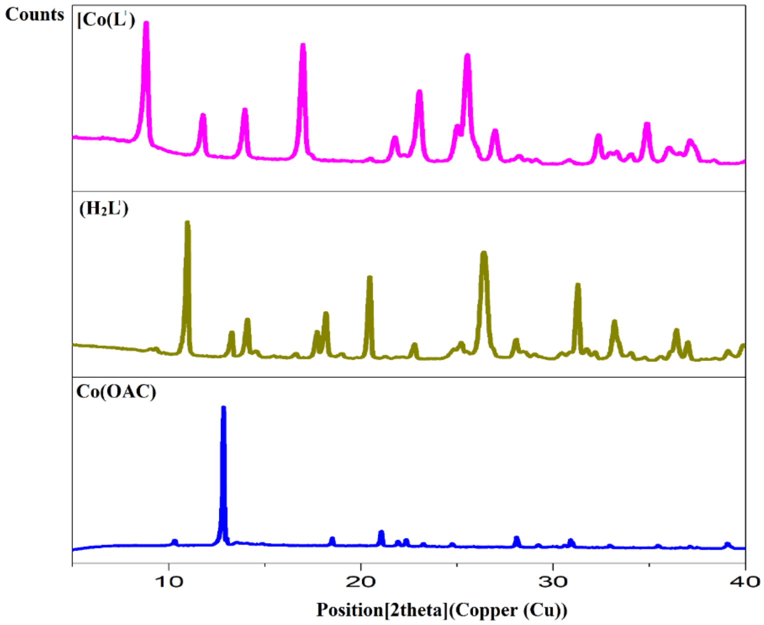

Figure 4. Comparison of PXRD Patterns of Co(II) acetate tetrahydrate (Co(OAC)), (H_2L') Schiff base and $[Co(L')_2]$ Complex.

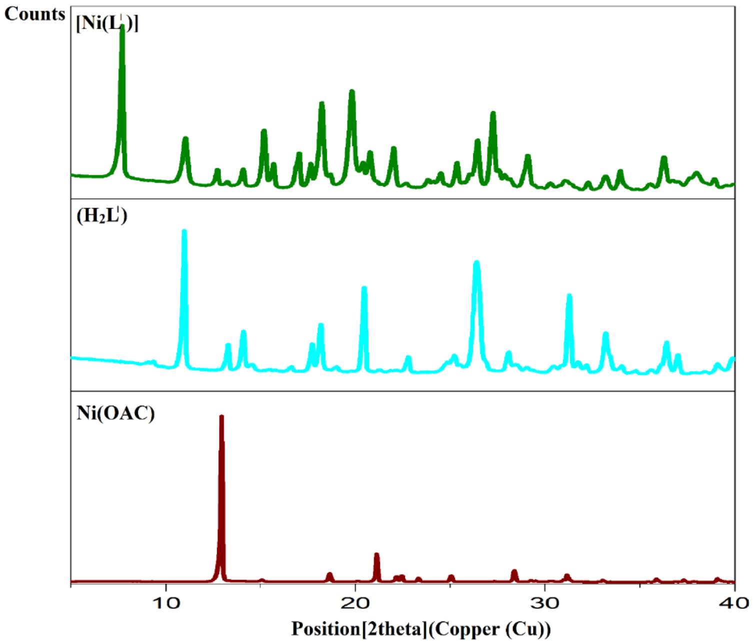

Figure 5. Comparison of PXRD Patterns of Ni(II) acetate tetrahydrate (Ni(OAC)), (H_2L') Schiff base, and $[Ni(L')_2]$ Complex.

3.2. Properties

Schiff base and its metal complexes were synthesized using a mechanochemical process with a percentage yield ranging from 79.1 to 89.6%. The Schiff base and complexes produced were colored. The color of complexes is caused by electronic d-d transitions between energy levels. Schiff base was discovered to be crystalline solids with a melting point of 124 °C. Complexes have a greater decomposition temperature than Schiff's base melting point, indicating that they are more stable (Nejo *et al*., 2010) (**Table 1**).

Table 1. Molecular formula, Colour, Melting point, Decomposition Temperature, and Percentage yield of $H_2(L')$ Schiff base and its Complexes.

Compound	Molecular Formula	Colour	Melting Point (°C)	Decomposition Tempt. (°C)	Yield (%)
$H_2(L')$	$(C_{18}H_{12}N_2OS)$	Brown	124	-	89.6
$[Co(L')_2]$	$[Co(C_{18}H_{11}N_2OS)_2]$	Maroon	-	184	81.6
$[Ni(L')_2]$	$[Ni(C_{18}H_{11}N_2OS)_2]$	Brown	-	181	79.1

3.3. Solubility test

The Schiff base is soluble in polar solvents like DMSO, DMF, methanol, ethanol, and acetonitrile, but not in non-polar solvents like hexane. The metal complexes were shown to be soluble in polar solvents such as DMF, DMSO, methanol, and ethanol, but nonpolar solvents such as hexane were just slightly soluble. This indicated that the produced compounds were polar due to the existence of some polar groups (**Table 2**).

Table 2. Solubility Test of $H_2(L')$ and its Complexes in Some Common Solvents.

Compound	DMSO	Methanol	Ethanol	Acetonitrile	DMF	Acetone	Hexane
$H_2(L')$	S	S	S	S	S	IS	IS
$[Co(L')_2]$	S	S	S	S	S	IS	IS
$[Ni(L')_2]$	SS	S	S	SS	SS	IS	SS

Key:
$H_2(L')$ = Schiff base derived from 2-hydroxy-1-napthaldehyde and 2-aminobenzothiazole.
S – Soluble, SS – Slightly Soluble, IS – Insoluble.

3.4. Infrared spectroscopy

The type of the functional group linked to the metal atom can be determined using the FT-IR spectra (**Table 3**). The absence of IR bands indicative of amino and carbonyl groups was used to make a preliminary identification of the ligand, which was verified by the presence of a new band due to azomethine's -C=N-. The azomethine (-C=N-) stretching vibration is responsible for the strong band seen in the spectra of Schiff base at 1603 cm^{-1} (Jayanthi *et al.*, 2017). In the spectra of Co(II) and Ni(II) complexes, the azomethine stretching frequency of the Schiff base was displaced to 1621 and 1599 cm^{-1} respectively. This shows that the metal center is coordinated with the azomethine group. The coordination of nitrogen of the azomethine group to the metal ion is expected to lower the electron density in the azomethine link, resulting in a shift in azomethine absorption (Cindrić *et al.*, 2012; Joseyphus *et al.*, 2006; Kubaisi & Ismail, 1994).

Table 3. Infrared Spectral data of $H_2(L')$ Schiff base and its Complexes (cm^{-1}).

Compound	v(C=N)	v(C=N) (Ring)	v(O–H)	v(C–O)	M-N	M-O
$H_2(L')$	1603	1529	3331	1246	-	-
$[Co(L')_2]$	1621	1551	-	1212	679	475
$[Ni(L')_2]$	1599	1555	-	1249	668	553

New bands appeared in the spectra of Co(II) and Ni(II) complexes at 679 and 688 cm^{-1}, respectively conforming to the v(M-N) band, which were not present in the Schiff base spectra. Moreover, for Co(II) and Ni(II) complexes, the respective peaks at 475 and 553 cm^{-1} have been assigned to (M-O) vibrations (Zhong *et al*., 2012). The presence of M-N and M-O vibrations indicates that N and O atoms are involved in the complexation with the metal ions being studied.

3.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) curves determine and provide information regarding the temperature at which complexes lose moisture or ignited to the required chemical form. Thermal data can also be incorporated with the other experimental methods to improve the results obtained. Understanding the coordination structure of the complexes can be aided by studying the thermal disintegration process of distinct Schiff base complexes (Zhong *et al*., 2012). Figures 4–5 summarize the likely thermal decomposition process as well as the experimental results for the thermal examination of the complexes. The weight loss for the complexes based on TGA was obtained for each stage and compared to the theoretically calculated weight loss for the proposed formula based on elemental analysis results (Etaiw *et al*., 2011).

Within a temperature range of 40 – 800 °C, three separate thermal breakdown stages for $[Co(L')_2]$ were found (**Figure 6**). Up to 185 °C, there was no apparent mass loss, indicating the lack of hydration or coordinated water, but between 185 and 230 °C, there was a 19.3% weight loss, indicating the disintegration of the first component ($C_7H_5N_5$). The weight loss of 19.3% is in line with the theoretical value of 20.3%. The second stage of disintegration follows the first and stops around 480 °C. The measured weight loss of 28.5% matches the theoretical weight loss of 25.80%, indicating that the second fragment is being decomposed ($C_{11}H_7NO$). At temperatures ranging from 480 to 800 °C, the third breakdown phase was seen. The 41.9% weight loss observed matches the expected weight loss of 43.30% due to the breakdown of the third fragment ($C_{18}H_{12}N_2S$). The residue's weight of 10.30% corresponds to the CoO (Stilinović *et al*., 2012).

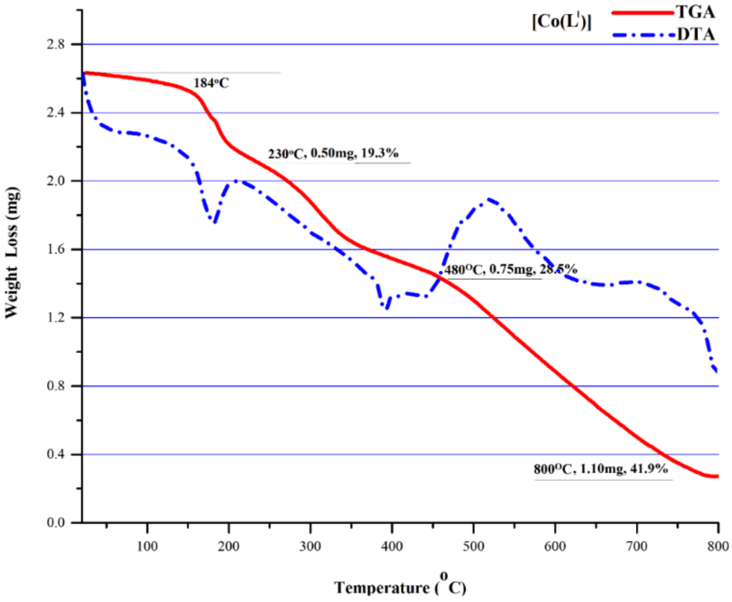

Figure 6. TG/DTA Analysis of $[Co(L')]$ Complex.

The thermal decomposition process of $[Ni(L')_2]$ was studied in the temperature range of 40 - 800°C. The complex is thermally decomposed in three decomposition steps as depicted in **Figure 7**. The complex decomposed gradually and broke at 216 °C, with a weight loss of

18.69%, which corresponds to complex breakdown to release (C_7H_5NS). This observed weight loss of 18.69% corresponds to a potential weight loss of 18.80%. At 436 °C, the complex decomposed further, releasing ($C_{18}H_{12}N_2S$). This 44.92% weight loss is in line with the theoretical weight decrease of 40.10%. The compound degraded gradually up to 800 °C and beyond. The final residue's weight corresponds to the formation of nickel(II) oxide.

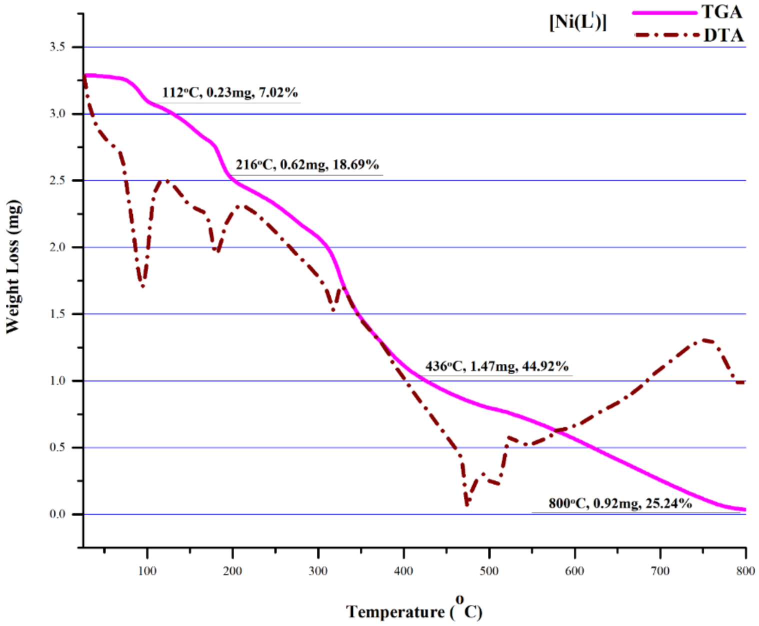

Figure 7. TG/DTA Analysis of [Ni(L')] Complex.

3.6. Electronic spectra, molar conductance, and magnetic susceptibility measurements

The UV-visible spectra of the Schiff base and complexes in methanol (10^{-4} M) were recorded at room temperature in the region of 185 to 700 nm, and the results are shown in **Table 4**. In UV-Vis spectroscopy, the azomethine (C=N), which is also a chromophore, is expected to absorb in a specific region ($n \rightarrow \pi^*$ transition). In coordination with the metal ion, the $n \rightarrow \pi^*$ transition of nonbonding electrons on the nitrogen of azomethine experiences a hypsochromic shift (Bhowon *et al.*, 1998). When compared to metal complexes, the azomethine functional group of a Schiff base absorbs at a lower energy (higher wavelength). The Schiff base has a strong band at 281 nm that is related to the $\pi \rightarrow \pi^*$ transition of the benzene ring (Etaiw *et al.*, 2011). Another prominent band in the lower energy range of the Schiff base's spectrum (385 nm) was associated with azomethine group $n \rightarrow \pi^*$ transitions. These transitions ($n \rightarrow \pi^*$) are also detected in the spectra of Co(II) and Ni(II) complexes, although at lower frequencies of 373 and 315 nm, confirming Schiff base ligand coordination to the metallic ions. The results for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ were identical (285–374 nm) to those published by (Joseyphus *et al.*, 2006).

At room temperature, the metal complexes' molar conductivity values in a 10^{-3} M solution in ethanol were measured. Table 4 displays the metal complexes' molar conductance (Λm) values. The results showed that Co(II) and Ni(II) complexes had molar conductance values of 4.55 and 5.90 $\Omega^{-1}.cm^2.mol^{-1}$, respectively, showing that they were non-electrolytic due to the lower conductivity values because a 1:1 electrolyte in methanol should have a value between 75 and 90 $\Omega^{-1}.cm^2.mol^{-1}$ (Shaker *et al.*, 2009).

Co(II) and Ni(II) complexes were found to be paramagnetic, with magnetic moments of 2.332 and 2.538 BM, respectively, as shown in **Table 4**. A comparable range of magnetic moment values (2.12 –2.31 BM) has been observed for Co(II) complexes of dithiocarbazate generated from isoniazid by other studies (Siraj & Kurawa, 2020). Correspond to one unpaired electron in square planar stereochemistry around Co(II) d^7 complexes. A review of the literature reveals that complexes of Co(II) and Ni(II) with magnetic moment values in the above-mentioned range suggest square planar stereochemistry around metal(II) complexes (Carabineiro *et al*., 2007; Fitzgerald & Brubaker, 1969; Tas *et al*., 2006; Zaky & Fekri, 2018). As a result, the square planar stereochemistry was proposed for Co(II) and Ni(II) complexes.

Table 4. Electronic spectra, Molar Conductance measurement (10^{-3}M Ethanol) and Magnetic susceptibility measurement.

Compound	π→π* (nm)	n→π* (nm)	Specific Conductance ($\Omega^{-1}cm^{-1}$)	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)	μ_{eff} (BM)
$H_2(L')$	281	385	-	-	-
$[Co(L')_2]$	255	373	4.55×10^{-6}	4.55	2.332
$[Ni(L')_2]$	276	315	5.90×10^{-6}	5.90	2.538

3.7. Elemental analysis

For the Schiff base and complexes, the theoretical and experimental analytical data of C, H, N, and S agree well (**Table 5**). A small difference in some of the values is acceptable (Tigineh & Liu, 2014).

Table 5. Elemental Microanalysis of (H_2L') Schiff base and its Complexes.

Compound	C	—	Found (Calculated) %	
		H	N	S
$H_2(L')$	71.69(71.03)	4.04(3.97)	8.96(9.20)	10.72(10.54)
$[Co(L')_2]$	63.83(64.96)	3.85(3.33)	7.28(8.42)	9.49(9.63)
$[Ni(L')_2]$	63.65(64.98)	3.39(3.33)	8.45(8.82)	9.20(9.64)

3.8. Antimicrobial activity

The antimicrobial activity of the newly synthesized Schiff base, complexes, and the parent drugs (as standard) was investigated using the agar well diffusion method. The objective was to determine the antimicrobial activity of Schiff base and their complexes and to compare the activity to that of the parent drugs used as standards.

The result of (H_2L') Schiff base shows the least activity against *E. coli* with an inhibition zone of 7 mm. The results of the complexes indicated that [Co(L')] and [Ni(L')] complexes are much more antibacterial active than Schiff base with an inhibition zone of 16 and 13 mm respectively at 60 mg/mL concentration (**Figure 8**). However, when compared to the reference drug (Ciprofloxacin), the activity against *S. aureus* was moderate to good in both Schiff base and complexes. At 60 mg/mL concentration, antifungal strains against *Candida albicans* and *Aspergillus fumigatus* demonstrated good activity with inhibition zones ranging from 14 to 18 mm, with metal complexes having a greater zone of inhibition than Schiff base (**Figure 9**). Similar findings have been reported by others (Aiyelabola *et al*., 2012).

Coordination was responsible for increased metal complex activity over the Schiff base, which reduces the polarity of the metal and increases its lipophilic nature to the lipid layer of the bacterial cell membrane (Nishat *et al*., 2011). Because of the organism's strongly negativecharged cell walls, metal ions will be adsorbed on the cell surfaces through passive biosorption (Chakravarty & Banerjee, 2012). The metals were reported as having the ability to disrupt normal cellular processes in living organisms by attaching to various cellular targeted cells (Wang *et al*., 2010).

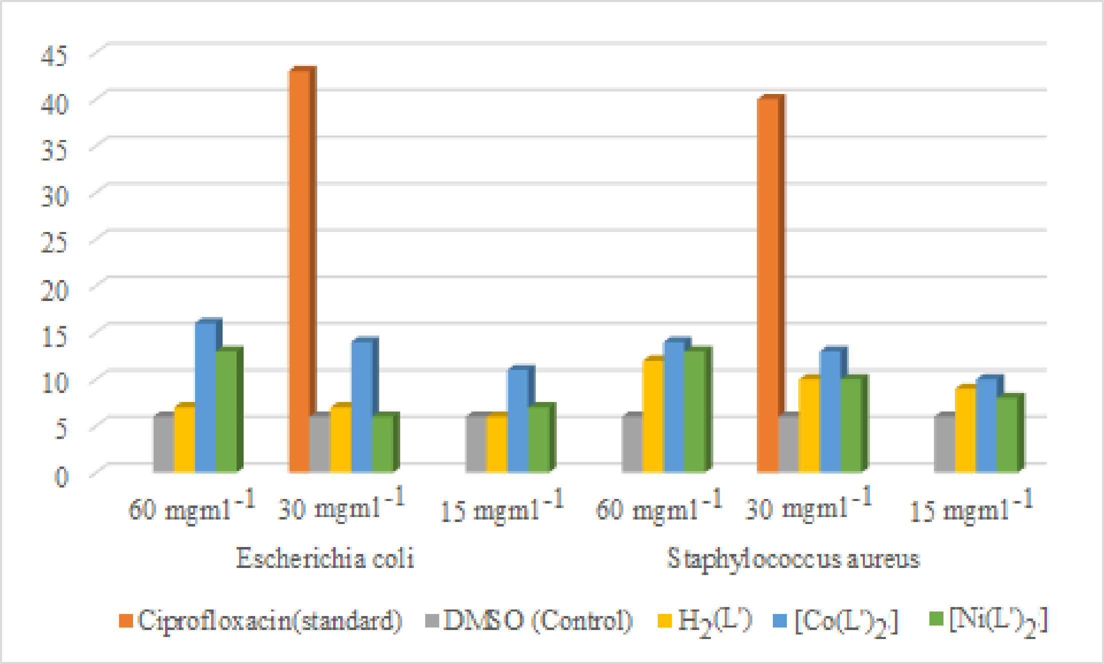

Figure 8. Antibacterial results of Schiff base and its complexes showing the inhibition zone against the concentration of the samples.

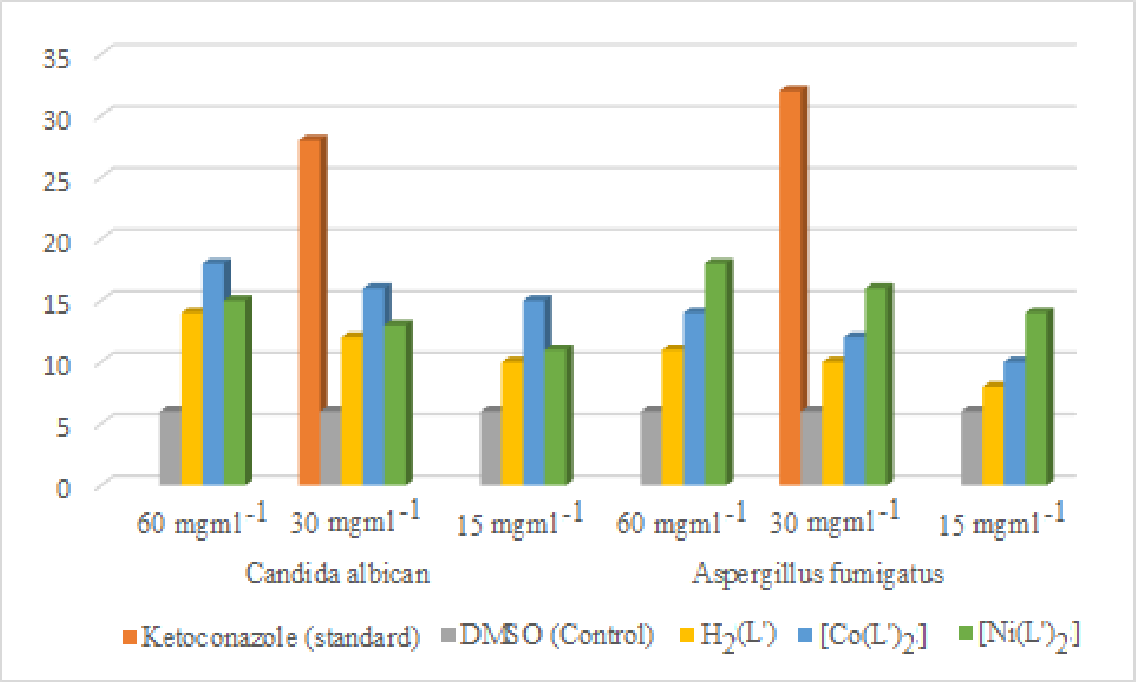

Figure 9. Antifungal results of Schiff base and its complexes showing the inhibition zone against the concentration of the samples.

4. CONCLUSION

The energy-efficient solvent-assisted solid-solid mechanochemical process was used to prepare Co(II) and Ni(II) Schiff base complexes obtained from 2-aminobenzothiazole and 2-hydroxy-1-naphthaldehyde. FTIR, PXRD, TG-DTA, conductivity measurement, magnetic susceptibility, UV-Visible analysis, and CHNS/O micro-analysis were used to evaluate the complexes' compositions and structures. The absence of coordinated water molecules can be seen in the complexes' infrared spectra and thermal decomposition process. The metal complexes were four-coordinated by the Schiff base ligand's two phenolic oxygen and two azomethine nitrogen atoms. The TG-DTA data reveal the potential decomposition processes in the complexes' thermal degradation process, as well as the observed and calculated percentage mass loss. Metal complexes have better antibacterial activity than Schiff base, according to antimicrobial investigations. Solid-solid mechanochemical synthesis is a faster and more energy-efficient synthetic route than synthesis under reflux in the presence of a bulk solvent.

The molecular structure is proposed in **Figure 10** based on the studies of the Schiff base and metal(II) complexes.

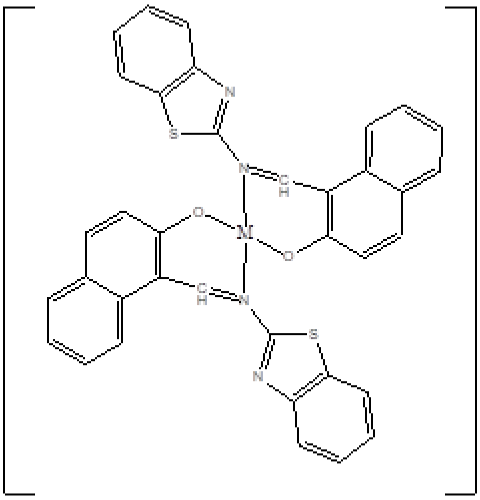

Figure 10. Proposed structure of [Co(L$'$)$_2$] and [Ni(L$'$)$_2$] Complexes, Where M = Co^{2+} or Ni^{2+}.

5. ACKNOWLEDGMENT

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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