EDUCATUM JSMT Volume 11 Number 2 (2024)
ISSN 2289-7070 / e-ISSN 2462-2451(1-7)
https://ejournal.upsi.edu.my/index.php/EJSMT/index

Synthesis and Characterization of Mixed Schiff Base- Salicylic Acid Metal Complexes

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Received: 11 January 2024; **Accepted:** 22 July 2024; **Published:** 13 August 2024

To cite this article (APA): Bamigboye, M., Wahab, O., Deborah, S., Ikechukwu, E., & Mustapha, A. Synthesis and Characterization of Mixed Schiff Base- Salicylic Acid Metal Complexes. *EDUCATUM Journal of Science, Mathematics and Technology, 11*(2), 1–7. https://doi.org/10.37134/ejsmt.vol11.2.1.2024

To link to this article: https://doi.org/10.37134/ejsmt.vol11.2.1.2024

Abstract

New Schiff base [M(NaNp)(Sal)Cl_2] metal complexes, where M = Mn(II), Ni(II), Cu(II), or Fe(III), were synthesized. The Schiff base, previously prepared from the reaction of 2-hydroxynaphthaldehyde and naphthalene-1-amine, was mixed with salicylic acid to synthesize the complexes. The characterization of these complexes was performed using powder X-ray diffraction (PXRD), ultraviolet-visible spectroscopy (UV-Vis), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The functional groups involved in the bonding were identified by comparing the FTIR spectra of the Schiff base and its metal complexes. Except for the Fe(III) complex, which was found to be octahedral, the Schiff base complexes were determined to be tetrahedral in geometry based on the FTIR spectra. It was discovered that these compounds coordinate via the carbonyl-O atom, the hydroxyl group's oxygen, and the azomethine group's nitrogen. The UV-Vis spectroscopy data revealed a hypsochromic shift in the complexes. The crystalline nature of the compounds was validated by PXRD analysis, which showed distinct crystalline peaks. SEM analysis demonstrated the complexes' controlled morphological structure and agglomeration. Given the structural and chemical properties have a variety of applications. The analytical and spectroscopic findings suggest potential applicability of the complexes in various fields such as medicinal chemistry, environmental science, catalysis, and materials science, warranting further exploration of their properties and applications. Specific applications may include as a potential antioxidant, antimicrobial agent, anticancer agents and in drug delivery systems.

Keywords Spectroscopy, Tetrahedral, Hypsochromic shift, Crystalline, Schiff-base

INTRODUCTION

Schiff base complexes are of tremendous interest to inorganic chemists due to their structural, spectral and chemical characteristics [1-6]. These complexes offer biological models for comprehending the structure of biomolecules and biological processes, making their study crucial in the field of bioinorganic chemistry [7]. Research has highlighted the production of these coordination compounds as a means of mitigating the damage that reactive oxygen species (ROS) inflict on the body's cells [8].

The most widely used technique for creating a Schiff base was found by Hugo Schiff, an Italian scientist with German nationality who obtained naturalization. This process entails the condensation of an amine with an aldehyde or ketone in a variety of organic solvents, including methanol, tetrahydrofuran, and

1,2-dichloroethane, under various reaction conditions [9]. These Schiff base ligands can form complexes with several metal ions and are readily produced [10]. Schiff base ligands, typically bidentate or multidentate, facilitate the construction of stable compounds with transition metals [11]. Additionally, schiff base ligands adjust the metal-centered electronic environment and induce substrate chirality, enhancing the stability and solubility of homogeneous or heterogeneous catalysts [13]. They also play a role in monitoring the reactivity of metal ions for catalytic applications and stabilizing them [14]. The presence of azomethine linkage increases the basicity of each nitrogen atom, contributing to the chemical stability of Schiff base complexes [8].

Transition metals are crucial to many biological processes essential to life. In various models, these metals can interact with the O- or N-terminals of proteins. Tetradentate and tridentate Schiff bases, along with their corresponding metal complexes that include N- and O-donors, have demonstrated the ability to scavenge DPPH and ABTS radicals [16]. These Schiff bases have been shown to have remarkable antibacterial, antiradical, anticancer, antifungal, and antiviral properties [8]. Their potential to combat specific microorganisms has been assessed using the p-iodonitrotetrazolium chloride (INT) colorimetric assay [12]. Schiff base complexes are among the most thoroughly investigated systems and have applications in both therapeutic and analytical domains. They might also be applied to the immobilization of enzymes. Almost all reported complexes are shown to be stable in the following order: Mn < Fe < Co < Ni < Cu > Zn, regardless of the type of coordinated ligands [17].

In this research study, we will report on the synthesis and characterization of mixed Schiff base-salicylic acid metal complexes.

MATERIALS AND METHODS

For this investigation, analytical grade chemicals and reagents were all utilized without additional purification. Guangdong Guanghua Sci-Tech Co., Ltd., located in Shantou City, China, produced the following compounds: nickel chloride hexahydrate ($NiCl_2.6H_2O$), copper chloride dihydrate ($CuCl_2.2H_2O$), manganese chloride tetrahydrate ($MnCl_2.4H_2O$), and iron (III) chloride hexahydrate ($FeCl_3.6H_2O$). The solvents used in the study were purchased from BDH Chemicals Ltd. in Poole, England. Elmer, USA's FT-IR spectrum-100 was used for the infrared spectroscopy. The Jenway 6405 UV/Vis spectrophotometer at the University of Ilorin's Department of Chemistry was used to measure the complexes' UV at a wavelength range of 200 to 1000 nm. The TESCAN VEGA SEM from the Czech Republic was used to perform the SEM analysis. The PXRD investigation was performed with an X-ray diffractometer, a Rigaku Ultima IV.

PREPARATION OF SCHIFF BASE LIGAND (1-{(*E*)-[(naphthalen-1-yl) imino] methyl} naphthalen-2-ol (NaNp))

A prewarmed ethanolic solution of 2-hydroxynaphthaldehyde (0.01 M) was carefully mixed with a 25 ml ethanolic solution of naphthalene-1-amine (0.01 M). After refluxing for 4 hours and stirring for an additional 8 hours at room temperature, the solution was filtered, washed with ethanol, and allowed to air dry until the desired orange-yellow solid was obtained.

PREPARATION OF THE COMPLEXES

Salicylic acid (0.14 g) and Schiff base ligand (0.3 g) were separately dissolved in 20 ml of ethanol. The two solutions were combined and added to the ethanolic solution of metal chlorides ($NiCl_2$ [0.24 g, 1 mmol], $CuCl_2$ [0.17 g, 1 mmol], $MnCl_2$ [0.20 g, 1 mmol], and metal(III) chlorides ($FeCl_3$ [0.27 g, 1 mmol]), respectively. The combined solution was refluxed at 78 °C for three hours while being continuously stirred. The resultant-colored precipitates were observed for each metal and were filtered, cleaned, and dried in a desiccator for two days [11]. The precipitates were retained for additional analysis.

RESULTS AND DISCUSSION

Infrared Interpretation

Figure 1 shows the FT-IR spectra data for NaNp and its mixed complexes. By comparing the FT-IR data of the ligands with their metal complexes, the sites of coordination were inferred. The medium-sized, crisp bands in the 3696–3619 cm^{-1} region that were seen in the ligands and complexes' spectra can be linked to the free O–H stretching. The usage of the functional group in cooperation with the metals is highlighted by the hydroxyl group's removal in the produced compounds. The FT-IR spectra of the free Schiff base revealed a distinct and robust band at 1626 cm^{-1}, which was identified as the azomethine's ν(C=N) vibration. Higher frequencies (1632 - 1641 cm^{-1}) were observed in the band, suggesting the azomethine nitrogen atom in the coordination sphere, which also shows the nitrogen of azomethine's connection with the core metal ions. New bands resulting from the production of ν(M–Cl) vibrations were seen in the low-frequency range at 670–684 cm^{-1}. A band attributed to ν(C=O) vibrations was visible in the FT-IR spectrum of salicylic acid at 1650 cm^{-1}. This band migrated to 1738 cm^{-1} in the spectra of Mn (II) complexes and vanished for the other complex. Coordination in Mn (II) is mediated by the oxygen of the hydroxyl and carbonyl groups [8, 16, 18].

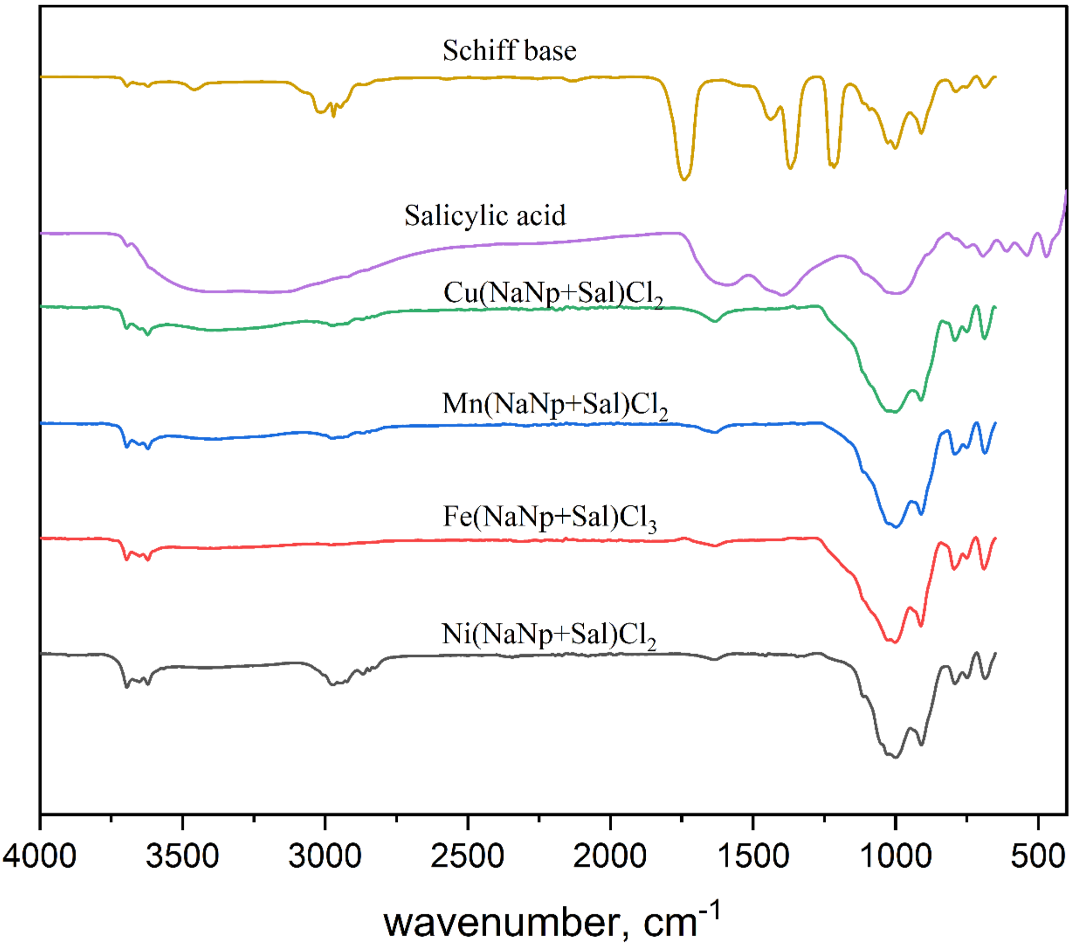

Figure 1: FTIR spectra of the Ligands and their metal complexes

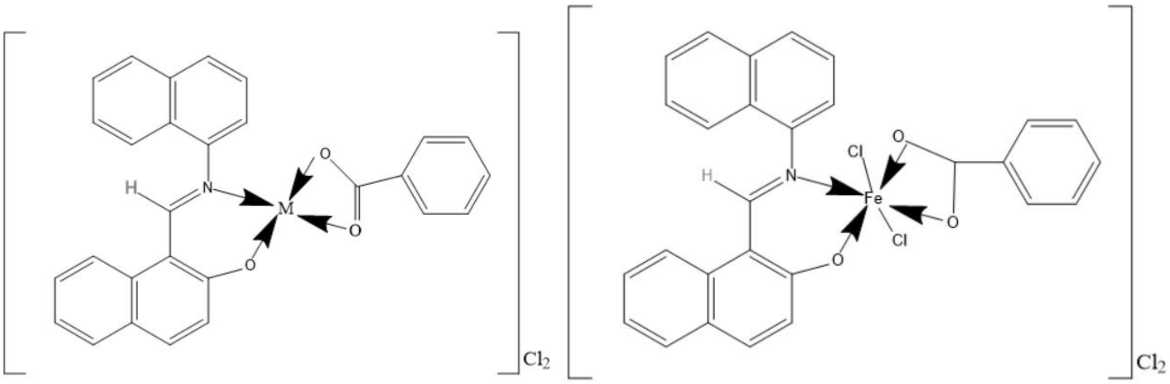

Figure 2: Proposed structure of Schiff base metal complexes

Where M= Transition metals [Ni (II), Cu (II), Mn (II)]

UV-VISIBLE INTERPRETATION

Salicylic acid's mixed ligand complexes and the Schiff base ligand's absorption spectra were all obtained in DMF. The free Schiff base ligand's absorption spectra revealed absorption bands at 230 nm, which were caused by the aromatic ring's π–π^* electronic transition and the azomethine group's presence, respectively. The table below also includes absorption bands in the spectra of Mn(II), Ni(II), Cu(II), and Fe(III) complexes, which could potentially be related to the visible spectrum transition. Chelation with metal ions caused the bands in the spectra of mixed complexes to shift significantly, suggesting a hypsochromic shift as a result of substitution [11 ,20].

Table 1: UV Spectra of the metal complexes

S/no	Complex ion	Wavelength (nm)	
1	Copper complex ion	490 - 520	512
2	Nickel complex ion	545 - 565	550
3	Manganese complex ion	420 - 435	427
4	Iron complex ion	575 - 595	591

PXRD SPECTRA DISCUSSION

Figure 3 displays the range in which the ligand and metal complex PXRD patterns were recorded (2θ = 0-90°). The compounds' PXRD pattern reveals distinct crystalline peaks, proving that the materials are crystalline. Scherrer's formula $D = k\lambda/\beta\cos\Theta$, where D is the particle size, k is the Scherrer's constant (0.94), λ is the x-ray wavelength, β is the full width at half maximum (FWHM) of the diffraction peak, and Θ is the diffraction angle, was used to determine the crystallite size of the sample. The complexes may be nanocrystalline because the average crystallite sizes for Ni (II), Fe (III), and Cu (II) are 30.7 nm, 10.6 nm, and 21.7 nm, respectively [19].

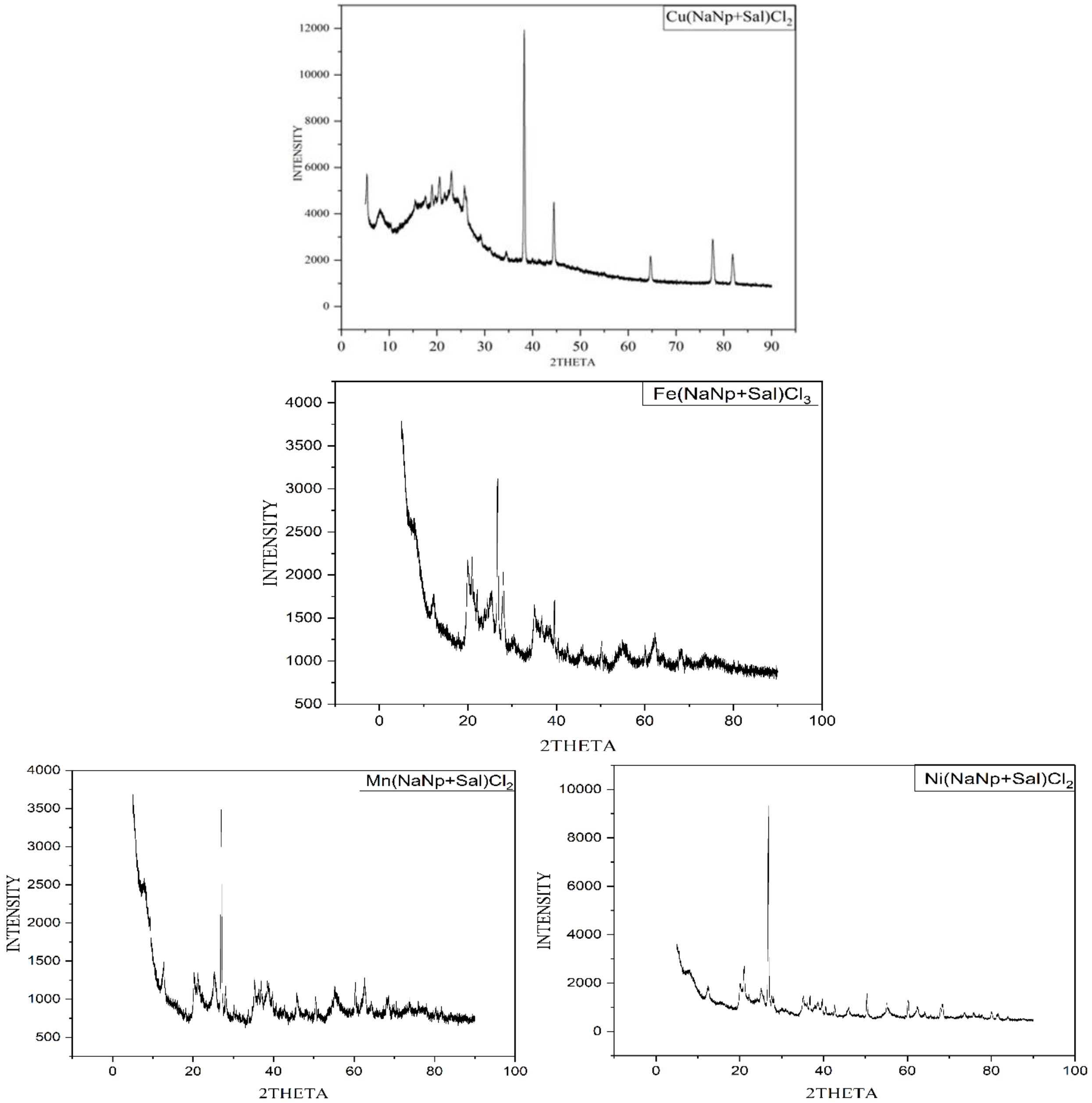

Fig 3: PXRD spectra of metal complexes

SEM STUDIES

Figure 4 illustrates how SEM was used to examine the surface appearance and purity of the ligands and metal complexes that were produced. The coordination of metal ions to the donor sites in the ligand causes a substantial difference in the SEM micrographs of the ligands and metal complexes. SEM micrographs of the metal complexes demonstrated that altering the metal ions modifies the surface appearance of the metal complexes. The well-formed amorphous shape of the complexes is evident from the acquired SEM micrographs. The metal complexes' SEM micrographs reveal that the particles are agglomerated with a regulated morphological structure and that there are small grains of varying sizes present [21, 22].

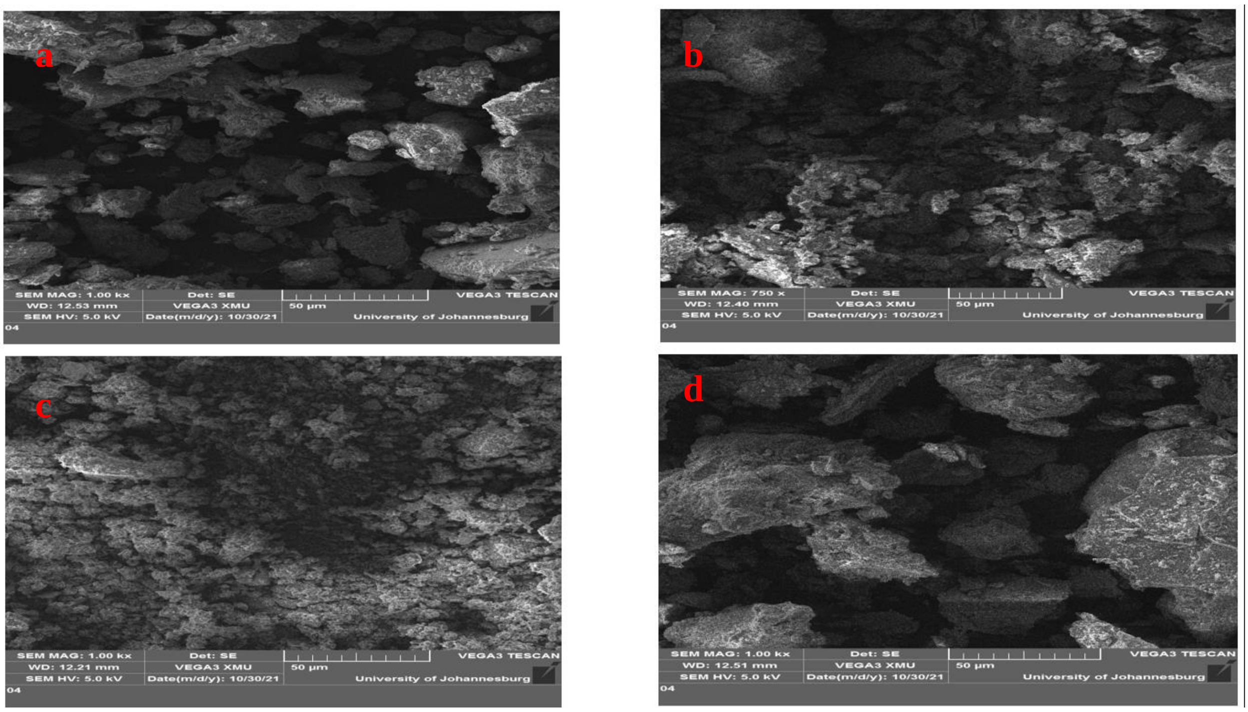

Fig 4: SEM micrograph of the metal complexes. (a=Cu, b=Mn, c=Ni, and d=Fe)

CONCLUSION

The mixed Schiff base-salicylic acid transition metal complexes of Cu^{2+}, Mn^{2+}, Ni^{2+}, and Fe^{3+} were synthesized in a 1:1:1 ratio. These complexes were characterized using various techniques, including X-ray diffraction, scanning electron microscopy, ultraviolet-visible spectroscopy, and infrared spectroscopy. The infrared spectroscopy results revealed shifts in functional groups and the emergence of new functional groups, indicating successful coordination. This study demonstrates that, with the exception of the Fe(III) complex, which exhibits octahedral geometry, the ligands function as bidentate, and the resulting complexes have tetrahedral geometry.

These synthesized complexes have potential applications in several fields. In medicinal chemistry, they could be explored for their antimicrobial, anticancer, and antioxidant properties, given their ability to scavenge radicals. In catalysis, these complexes might serve as effective catalysts in organic synthesis reactions due to their stable geometric configurations. Additionally, in environmental science, they could be used for the detection and removal of pollutants. Their stability and structural properties also make them suitable for use in materials science for the development of new materials with unique electronic and magnetic properties.

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