

UDC 547.3+615.3.

SYNTHESIS AND CHARACTERIZATION OF NEW Mn(II), Co(II), Ni(II), Cu(II), Zn(II) And Cd(II) COMPLEXES WITH [(z)-3((6-AMINOPYRIDINE-2-yl) IMINO) INDOLIN-2-ONE] LIGAND

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Received 12.10.2023

Accepted 23.12.2023

Abstract: A Schiff base ligand, 3-((6-amino-1,6-dihydropyridin-2-yl)imino)indolin-2-one, was synthesized by condensing isatin with 2,6-diaminopyridine in this study. Elemental analysis, NMR spectroscopy, and infrared spectroscopy enabled confirmation of the structure of the pyridine-incorporated ligand. Additional coordination compounds of this ligand with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) metals were synthesized with metal-to-ligand proportions verified through trace elemental examinations using CHN. Various spectroscopic techniques including UV-visible absorption spectrophotometry, IR spectrophotometry, electrical conductivity quantifications, melting point determinations, and magnetic susceptibility analyses facilitated characterization of the produced complexes. The antimicrobial potential of the organic ligand and inorganic complexes was screened against *Bacillus subtilis* and *Staphylococcus aureus* bacterial strains through the agar disc diffusion technique. Both the uncoordinated ligand and metal-ligand coordination compounds displayed appreciable antibacterial effects on the tested microorganisms. Tetrahedral configurations were proposed for all prepared complexes based on combined analytical and spectroscopic evidence.

Keywords: Schiff base ligand, Isatin, NMR spectrum, Infrared.

DOI: 10.32737/2221-8688-2024-1-103-114

Introduction

Schiff base ligands and their metal coordination complexes with transition metal ions have become an extensively explored research area in coordination chemistry. This can be ascribed to the versatile structural motifs, tunable characteristics, and diverse coordination geometries accessible when transition metals are complexed with Schiff base ligands [1]. Among organic compounds, Schiff bases synthesized from isatin have been one of the most thoroughly explored systems, with comprehensive theoretical and experimental studies [2]. The strong donor atoms like

carbonyl O₂ and imine nitrogen found in Schiff bases are essential for structural diversity, catalysis, and several biological applications [3]. The distinctive properties of Schiff bases containing the isatin molecular motif enable their demonstrated antimicrobial, antifungal, antiviral, anti-HIV, antileprotic, anti-leukemia, analgesic and anticancer effects. Isatin-derived Schiff base metal complexes have garnered significant research attention within bioinorganic chemistry applications [4-15].

Since isatin nucleus contains carbonyl groups at position 2 and 3 in the lactam and keto

forms respectively, it can undergo either addition reaction at CO-O bond or condensation reactions eliminating water [16]. Transition metal complexes with polydentate ligands have attracted interest in chemistry owing to the ability of transition metals to exhibit multiple oxidation states [17-19]. Transition metal ions and Schiff base ligands are two pivotal components required to form stable complexes and are essential to the progression of coordination chemistry [20,21].

Novel ligands featuring the isatin scaffold, synthesized recently, were utilized to construct hitherto unknown coordination complexes with copper(II), nickel(II) and cobalt(II). Several spectroscopic methods including Fourier-transform infrared spectroscopy, ultraviolet-visible absorption spectroscopy, and proton nuclear magnetic resonance spectroscopy enabled comprehensive characterization of the synthesized metal-ligand complexes. Spectroscopic investigations intimated octahedral arrangements around cobalt and copper centers whereas a tetrahedral geometry was proposed for nickel based on the recorded spectra [22].

Pyridine and its derivatives have been extensively used to construct macrocyclic Schiff base ligands. Various transition metal complexes containing chromium(III), manganese(II), iron(III), cobalt(II), nickel(II)

and copper(II) have been synthesized by sequential reactions of the metal ions with 2,6-dicetylpyridine and 1,2-di(o-aminophenyl)thioethane. Additionally, lead(II) complexes containing non-transition metals and pyridine-based Schiff bases have been synthesized, with the formula $[Pb=(BT)(BI)_2(SCN)_2]$ where BT and BI represent benzotriazole and benzoimidazole units respectively [23, 24].

The molecule 2,6-diaminopyridine (dap) functions as an N-donor ligand possessing characteristics of both a heterocyclic N-terminal group and an aromatic amine. Specific dap complexes, notably $[PdCl_2(dap)] \cdot H_2O$, $[Pt(dap)_2]Cl_2 \cdot 2HCl$, and $RhCl_3(dap) \cdot 2H_2O$ have been explored for the antimutagenic and antiviral properties of 2,6-diaminopyridine. Earlier studies reliant solely on infrared spectroscopy data showed that dap exhibits dimeric ligand tendency with Pd(II), Pt(II) and Rh(III) ions, binding through both pyridine-nitrogen and NH_2 nitrogen centers. However with Pt(II) complexes, coordination of HCl molecules to free NH_2 groups was noted [25,26]. The current work involves the synthesis and characterization of an isatin-incorporated ligand using 2,6-diaminopyridine and its respective complexes with chosen transition metals including Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Materials and Methods

All chemicals utilized were of analytical grade and obtained from either FLUKA or B.D.H. suppliers. Melting point or decomposition temperature was quantified using a digitally-controlled thermoelectric melting point equipment. A Jenway conventional conductivity device (model 4070) facilitated molar conductivity assessments on $10^{-3}M$ complex DMSO solutions at $25^\circ C$. Shimadzu UV 160 instruments for ultraviolet visible and infrared spectroscopy enabled spectral recordings, on KBr pellets (400 to 4000 cm^{-1} range) and on $10^{-3}M$ DMSO solutions respectively, employing 1 cm quartz cuvettes at room temperature. The magnetic susceptibility profiles of powdered metal coordination complexes were examined at $25^\circ C$ employing

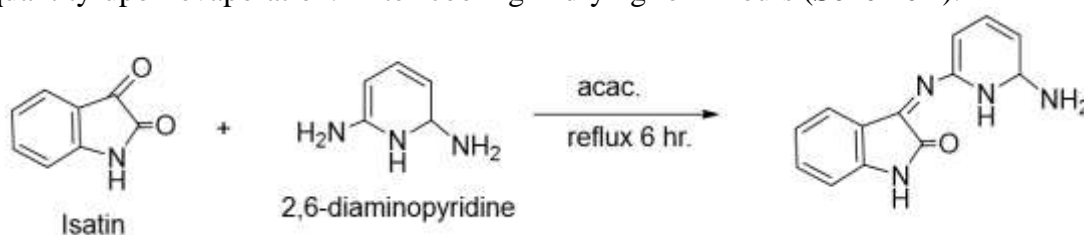
the Faraday methodology with a Bruker BM6 superconducting quantum interference device (SQUID) magnetometer.

Elemental composition analyses (CHN) were executed in duplicate at ORDU University deploying conventional microanalytical methods on a Perkin Elmer 2400 (IEES) machine. Metal content quantifications were achieved using a PYEUNI-CAM SPg atomic absorption spectrophotometer. Proton nuclear magnetic resonance (1H NMR) spectral data of synthesized ligands are documented as chemical shifts (ppm) taking tetramethylsilane (TMS) as an internal reference standard.

Ligand Preparation: In a round bottom flask, isatin (0.01 mol, 1.47 g) and 2,6-diaminopyridine (0.01 mol, 1.09 g) were

combined with a few drops of glacial acetic acid. The resultant mixture was refluxed for 6 hours, allowing the volume to reach half of the initial quantity upon evaporation. After cooling

the flask, the brown precipitate obtained was isolated via filtration and washed sequentially with ethanol and diethyl ether prior to vacuum drying for 4 hours (**Scheme 1**).



Scheme 1: Synthesis of Schiff base ligand.

Preparation of Metal Complexes: The ligand L (0.01 mol, 2.3 g) was dissolved in 30 mL of hot ethanol. The corresponding metal chloride salts (0.01 mol), namely $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$, were separately dissolved in 30 mL of hot ethanol and added to the refluxing ligand solution following 3 hours

of heating at room temperature. The products formed were filtered, washed sequentially with ethanol and diethyl ether and then vacuum dried for 4 hours to obtain the anticipated metal-ligand (1:1) chelates. Physical and analytical data for the ligands and their complexes are compiled in **Table 1**.

Table 1: Ligand and its complexes Physical and analytical data

No.	Structure	Colour	Yield %	M.P. (C°)	The analysis discovered (calc.)%		
					C.	H.	N.
L	$\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}$	Light Brown	96	170-173	98.20 (97.0)	6.91 (5.80)	3.22 (9.28)
1	$[\text{Mn}(\text{L})]\text{Cl}_2$	Brown	94	380	85.32 (84.22)	5.46 (4.32)	6.06 (5.72)
2	$[\text{Co}(\text{L})]\text{Cl}_2$	Dark red	95	300	84.40 (83.30)	5.40 (4.77)	6.02 (5.86)
3	$[\text{Ni}(\text{L})]\text{Cl}_2$	White	92	290	71.36 (68.87)	5.37 (4.17)	6.01 (5.63)
4	$[\text{Cu}(\text{L})]\text{Cl}_2$	Dark green	94	310	83.49 (82.76)	5.34 (4.64)	5.92 (4.68)
5	$[\text{Zn}(\text{L})]\text{Cl}_2$	Dark brown	91	306	83.05 (82.41)	5.31 (4.84)	5.38 (4.82)
6	$[\text{Cd}(\text{L})]\text{Cl}_2$	Brown	94	295	75.79 (74.32)	4.85 (3.21)	6.98 (5.85)

Results and discussion

Infrared Spectral Analyses of Ligand and Complexes: Infrared spectroscopy was utilized in this work to probe the vibrational fingerprints of the synthesized free ligands and metal coordination assemblies in KBr disc form across the $400\text{-}4000\text{ cm}^{-1}$ region. To verify and validate coordination centers, infrared signals from the metal complexes were compared and contrasted with the unbound ligand spectrum

using the following diagnostic characteristics:

The intense infrared stretch at 1699 cm^{-1} in the spectrum of the free ligand attributed to the carbonyl stretch ($\nu(\text{C}=\text{O})$) of the isatin moiety displays shifts to higher or lower wavenumbers in the spectra of complexes, indicating binding of the metal center with the carbonyl oxygen atom.[27]

Two intense infrared bands detected at 1558 cm^{-1} and 1614 cm^{-1} , representing the azomethine stretching frequencies $\nu(\text{C}=\text{N})$, demonstrate wavenumber shifts in the infrared profiles of the synthesized manganese(II), cobalt(II), nickel(II), copper(II), cadmium(II), and zinc(II) coordination compounds. Such displacements confirm coordination of the ligand framework to the metal ions through the nitrogen atoms of the two imine groups [28,29].

The ligand serves as a neutral tetradentate chelator bonded to the metals via the isatin ring nitrogen, oxygen atoms and two azomethine nitrogen atoms within its structure.

The carbonyl forms a four-membered chelate ring. Distinctive infrared signals for the complexes are compiled in **Table 2**, further supported by novel bands observed between $480\text{--}491\text{ cm}^{-1}$ attributable to the $\nu(\text{M-N})$ stretch (**Figure 1**) [30].

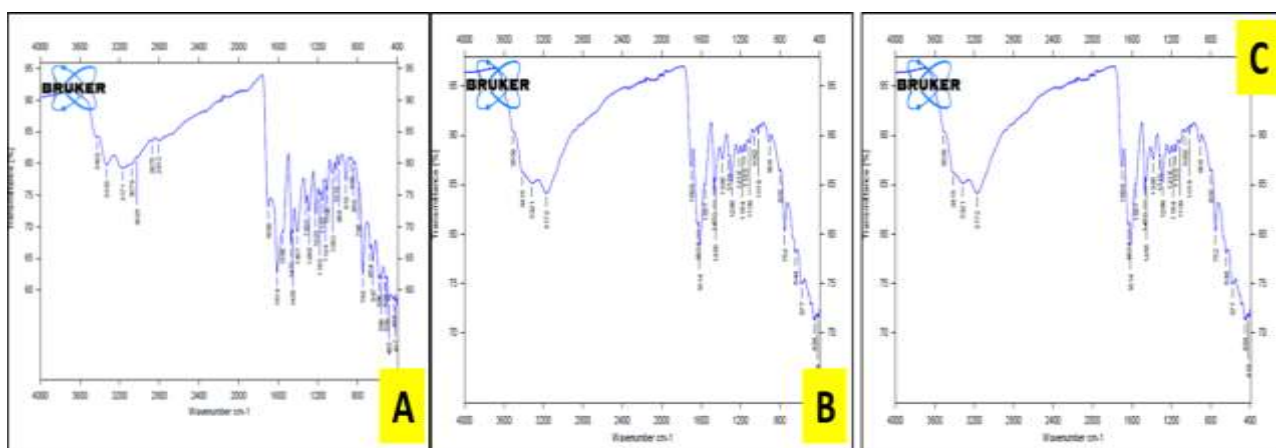


Fig. 1. Infrared spectrum of (A) ligand (B) complexes $[\text{Co}(\text{L})]\text{Cl}_2$ (C) complexes $[\text{Ni}(\text{L})]\text{Cl}_2$

Table 2: Infrared and electronic spectral data for compounds and ligand

No.	NH_2	$\text{N}(\text{C}=\text{O})$	$\text{N}(\text{C}=\text{N})$ Isatin	$\nu(\text{C}=\text{N})$	M-N.	M-O.
L	3429_s	1699_s	1614_s	1558_s	---	---
1	3315_m	1695_s	1613_m	1556_m	482_m	440_w
2	3544_s	1704_s	1614_m	1553_m	488_m	506_m
3	3509_m	1699_s	1614_w	1557_w	488_w	454_w
4	3434_m	1707_s	1616_s	1553_w	483_m	455_m
5	3321_m	1698_m	1615_m	1575_m	486_m	432_m
6	3449_m	1699_s	1615_m	1557_w	491_m	459_w

Electronic Spectral Analyses: The electronic absorption profiles of the synthesized uncoordinated ligand and metal coordination complexes were acquired and the accrued spectroscopic data documented in **Table 3**.

According to Laporta's rule, high spin Mn(II) complexes are not expected to display d-d type transitions in the discernible region owing to parity-forbidden and spin-forbidden nature [31]. As outlined in **Table 3**, the electronic profile of the manganese(II) complex

shows signature charge transfer bands emanating from metal-ligand interactions along with $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions [32].

The electronic spectrum of the cobalt complex displays signature charge transfer bands comprising of an UV peak at 32043 cm^{-1} and a visible absorption at 15635 cm^{-1} , attributable to the $4A^2(F) \rightarrow 4T^1(P)$ (ν_3) transition, corroborating a tetrahedral geometry around the cobalt(II) metal center [33-36].

Characteristic absorptions detected at

14850 cm^{-1} and 28843 cm^{-1} in the electronic spectrum of the nickel analog, attributable to $3T^1(F) \rightarrow 3T^1(P)$ (v_3) transitions and charge transfer bands respectively, are indicative of a tetrahedral arrangement [37,38].

Copper complexes exhibited an intense band at 10430 cm^{-1} in their electronic

spectra, denoting a tetrahedral configuration [39].

Absence of electronic transitions in d orbitals resulted in no observable absorption bands in the electronic spectra of saturated Cd and Zn complexes [40,41].

Table 3: Ligand and its complex's electronic spectra

Complex	Transition		C.T.
L	3325	$\pi \longrightarrow \pi^*$	---
	23061	$n \longrightarrow \pi^*$	
[Mn(L)]Cl ₂	34181	$\pi \longrightarrow \pi^*$	27370
	30431	$n \longrightarrow \pi^*$	25638
[Co(L)]Cl ₂	15635	${}^4A_2(F) \longrightarrow$ ${}^4T_1(p)(v_3)$	32043
[Ni(L)]Cl ₂	14850	${}^3T_1(F) \longrightarrow$ (v_3) ${}^3T_1(p)$	---
[Cu(L)]Cl ₂	10430	${}^2T_2 \longrightarrow$ 2E	

Magnetic Analyses: The magnetic moment value of 5.9 B.M. for the manganese(II) complex signifies a tetrahedral environment around the manganese(II) center [42]. A magnetic moment of 4.3 B.M. for the Co(II) complex agrees with three unpaired electrons, indicating a tetrahedral geometry for the Co(II) ion [43]. The Ni(II) complex exhibited a magnetic moment of 3.9 B.M., consistent with a tetrahedral arrangement at room temperature [44]. The copper (II) complex

displayed a magnetic moment of 2.1 B.M., potentially indicating a tetrahedral structure [45].

Conductivity Measurements: All the soluble complexes recorded molar conductivities between 31.9 and 37.4 $\text{cm}^2\text{mol}^{-1}$ in DMSO solutions 10 to 3 M at room temperature signifying their high ionic nature (1:1 type) with high conductivity [46]. The conductivity values are given in **Table 4**.

Table 4: Magnetic moment μ_{eff} & molar conductivity of the complexes

No.	Structure	Molar-conductivity ($\text{S.c.m}^2\text{mol}^{-1}$)	μ_{eff} (B.M.)
1	[Mn(L)]Cl ₂	34.6	5.9
2	[Co(L)]Cl ₂	35.8	4.3
3	[Ni(L)]Cl ₂	37.4	3.9
4	[Cu(L)]Cl ₂	31.9	2.1

¹H-NMR Data: The ¹H-NMR chemical shifts (ppm) of synthesized compounds matched well with other reported isatin derivatives providing considerable support for the proposed structures [47]. ¹HNMR spectra of ligand L in DMSO showed signals at (7.26) ppm due to aromatic ring proton [48] and a chemical shift at (10.71) ppm attributed to N-H proton of isatin ring [49-

54] (**Figure 2**).

The carboxyl proton in the ¹H NMR spectra of the prepared M(II) complexes appeared as a sole signal between 2.2-2.3 ppm, signifying the absence of the N-H peak of the isatin ring thus corroborating direct metal-nitrogen bonding as shown in **Scheme 2** [55-57].

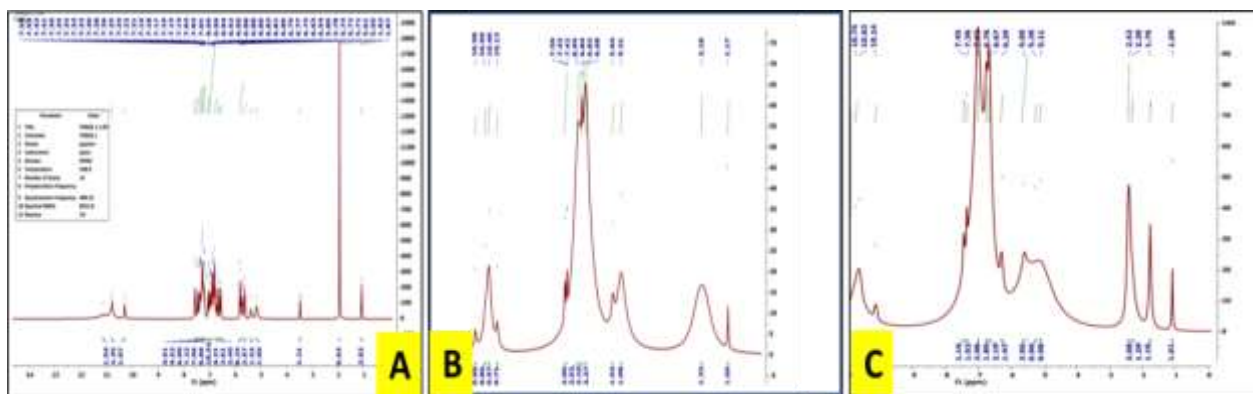


Fig. 2: $^1\text{H-NMR}$ spectra of (A) ligand (B) Co(II) compound (C) Ni(II) compound.

Biological activities: The bacterial activity of a synthetic ligand(1) and its metal complexes was studied. Application of biological activity to various species of bacteria detected in the laboratory using biochemical and microscopic tests was included in this study. These isolated bacteria are thought to be the source of many human ailments. The study comprised two types of bacteria that cause human disease, the first of which was negative bacteria (**Table 5**). Gram-positive bacteria are

represented by *Bacillus subtilis*, and Gram-negative bacteria are represented by *Staphylococcus aureus* [58,59].

The ligand (L) inhibited growth of both bacteria after 24 hours with increase in zone of inhibition after 48 hours (**Figure 3**). Additionally, experimental data revealed immobilized complexes were less active than free ligands against the same bacterial species under comparable conditions.

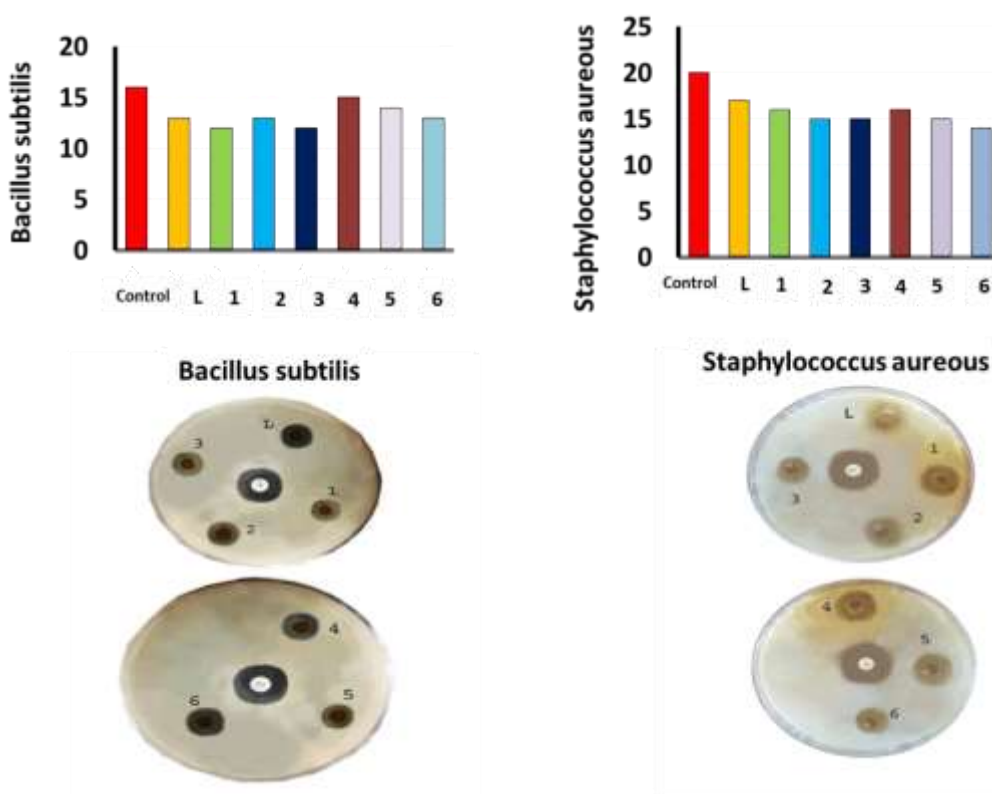
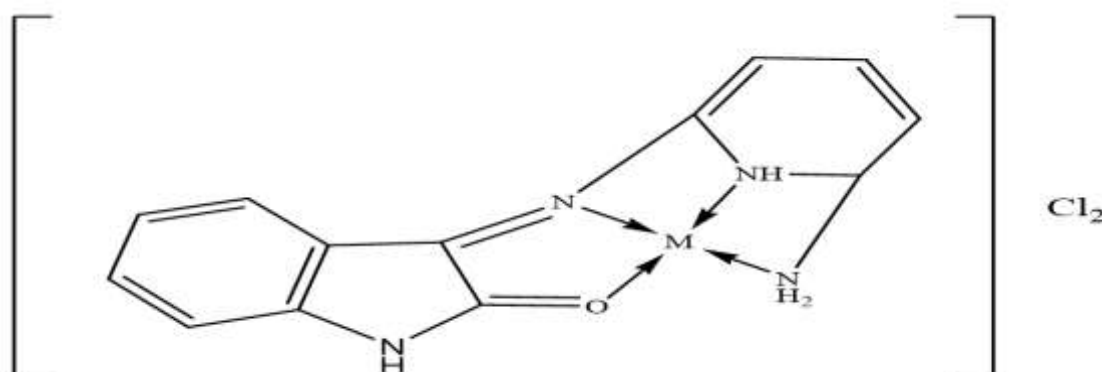


Fig. 3: The ligands' and complexes' biological functions using staphylococcus aureus and *Bacillus subtilis*

Proposed Structure: Considering the analytical, spectroscopic, magnetic susceptibility, and conductivity data collected, the suggested generalized structure for the synthesized coordination complexes is presented as follows (**Scheme 2**):



Scheme 2: Proposed structures of coordination complexes, where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II).

Table 5: Shows the effectiveness (area of bacterial inhibition in mm for the prepared compound)

Compounds		Inhibition zone diameter (mm)	
		<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>
	Control	15	23
1	L	14	20
2	[Mn(L)]Cl ₂	12	18
3	[Co(L)]Cl ₂	10	14
4	[Ni(L)]Cl ₂	9	18
5	[Cu(L)]Cl ₂	8	23
6	[Zn(L)]Cl ₂	13	14

Conclusion

The present work successfully employed Schiff base ligand as a precursor for synthesizing a novel isatin derivative and extensively characterized its structural and molecular properties to ascertain efficacy. Antibacterial activity was thoroughly evaluated using bacterial isolate models, providing additional confirmation.

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[(z)-3((6-AMİNOPİRİDİN-2-İL) İMİNO) İNDOLİN-2-ON] LİQANDI İLƏ YENİ Mn(II), Co(II), Ni(II), Cu(II), Zn(II) VƏ Cd(II) KOMPLEKSLERİNİN SİNTEZİ VƏ XARAKTERİSTİKASI

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Xülasə: Bu işdə 3-((6-amino-1,6-dihidropiridin-2-il)imino)indolin-2-on Şiff əsaslı liqand izatinin 2,6-diaminopiridinlə kondensasiyası ilə sintez edilmişdir. Element analizi, NMR spektroskopiyası

və infraqırmızı spektroskopıya pıridinlə birləşdirilən liqandın strukturunu təsdiqləmişdir. Bu liqandın Mn(II), Co(II), Ni(II), Cu(II), Zn(II) və Cd(II) metalları ilə əlavə koordinasiya birləşmələri sintez edilmiş və metalların liqandlara nisbəti yoxlanılmışdır. Müxtəlif spektroskopik üsullar, o cümlədən, ultrabənövşəyi şüalarla görünən absorbsiya spektrofotometriyası, IR spektrofotometriyası, elektrik keçiriciliyinin kəmiyyətinin müəyyən edilməsi, ərimə nöqtəsinin təyini və maqnit həssaslığının təhlili əmələ gələn komplekslərin səciyyəvləndirilməsinə kömək etmişdir. Üzvi liqandın və qeyri-üzvi komplekslərin mikroblara qarşı potensialı diffuziya üsulu ilə Bacillus subtilis və Staphylococcus aureus bakteriya şammlarına qarşı tədqiq edilmişdir. Həm əlaqələndirilməmiş liqandlar, həm də metal-liqand koordinasiya birləşmələri sınaqdan keçirilmiş mikroorqanizmlərə qarşı əhəmiyyətli antibakterial təsir göstərmişdir.

Açar sözlər: Şiff əsaslı liqand, izatin, NMR spektri, İQ spektri.

СИНТЕЗ И ХАРАКТЕРИСТИКА НОВЫХ КОМПЛЕКСОВ Mn(II), Co(II), Ni(II), Cu(II), Zn(II) И Cd(II) С [(z)-3((6-АМИНОПИРИДИН-2-ИЛ) ИМИНО) ИНДОЛИН-2-ОН] ЛИГАНДОМ

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Аннотация: В данной работе методом конденсации изатина с 2,6-диаминопиридином синтезирован лиганд основания Шиффа - 3-((6-амино-1,6-дигидропиридин-2-ил)имино)индолин-2-он. Элементный анализ, ЯМР и инфракрасная спектроскопия позволили подтвердить структуру пиридин-инкорпорированного лиганда. Были синтезированы дополнительные координационные соединения этого лиганда с металлами Mn(II), Co(II), Ni(II), Cu(II), Zn(II) и Cd(II), соотношение металлов и лигандов было проверено с помощью микроэлементного анализа. Различные спектроскопические методы, включая УФ-видимую абсорбционную спектрофотометрию, ИК-спектрофотометрию, а также количественное определение электропроводности, определение температуры плавления и анализ магнитной восприимчивости, способствовали определению характеристик полученных комплексов. Антимикробный потенциал органического лиганда и неорганических комплексов был исследован против штаммов бактерий Bacillus subtilis и Staphylococcus aureus методом диффузии в агаре. Как некоординированные лиганды, так и координационные соединения металл-лиганд проявляли заметный антибактериальный эффект в отношении тестируемых микроорганизмов.

Ключевые слова: лиганд основания Шиффа, изатин, спектр ЯМР, ИК-спектр.