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Spectral Properties and Biological Activities of Binuclear Mixed-Metal Bridged Thiocyanate Complexes Containing Schiff Bases Derived from Isatin †

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Abstract: This study introduces two novel Schiff base ligands synthesized through the condensation of isatin with primary amines. These ligands were characterized using infrared (IR), ultraviolet-visible (UV-Vis) spectroscopy, mass spectrometry, and elemental analysis. The ligands were further treated with tetrathiocyanate in a 1:1 molar ratio to yield binuclear mixed-metal monomeric bridged complexes of the form $LMCd(SCN)_4$, where M represents Co(II) or Ni(II). Various spectral techniques and magnetic susceptibility measurements were employed for the identification of these complexes. The findings revealed that all the complexes possessed a coordination number of four and exhibited non-electrolytic behavior. Additionally, the cobalt complexes demonstrated paramagnetic properties, whereas the nickel complexes were diamagnetic. The antimicrobial efficacy of the Schiff base ligands and their complexes was also evaluated against selected microorganisms, revealing significant antimicrobial activities.

Keywords: isatin; thiocyanate; spectral analysis; Schiff base; binuclear complexes; biological activity

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1. Introduction

Schiff bases are condensation products formed between primary amines and ketones or aldehydes under specific conditions [1]. These compounds are known for their ability to stabilize metal ions in various oxidation states and are involved in a wide range of catalytic and industrial applications. Furthermore, they exhibit extensive biological activities [1,2]. Despite being discovered nearly a century ago, Schiff bases continue to be essential ligands in the realm of metal coordination chemistry. They are especially noteworthy as macrocyclic ligands due to their multifaceted applications [3–5]. Isatin-derived Schiff bases are integral in the synthesis of various pharmaceutically active components. These bases are renowned for their antimicrobial, antiviral, and antitumor properties [6–8]. Bimetallic thiocyanates that incorporate Schiff bases have also garnered attention, particularly in biological applications, owing to their coordinated systems that feature thiocyanate (SCN) bridges [9,10]. The primary objective of the current research encompasses the preparation, spectroscopic characterization, and biological evaluation of selected Schiff base ligands and their tetrathiocyanate complexes. These complexes have the general formula $[LMCd(SCN)_4]$, where M is either Co(II) or Ni(II) ions, and L represents the Schiff base ligand.

2. Materials and Methods

2.1. Materials

All utilized chemicals, analytical reagents, and metal salts were procured without further purification. Isatin, 2-aminopyridine, and phenyl hydrazine were obtained from Fluka

(Buchs, Switzerland), whereas cobalt(II) nitrate, nickel(II) nitrate, potassium thiocyanate, dimethyl sulfoxide (DMSO), methanol, and ethanol were sourced from Sigma-Aldrich (Taufkirchen, Germany).

2.2. Instruments

The melting points of both Schiff base ligands and their complexes were determined using an Electro-Thermal Fisher (Goteborg, Sweden). The elemental composition was ascertained using an ECS-4010 CHNSO NC Technologies (Milano, Italy). The metal content in the complexes was quantified through atomic absorption on phoenix-986 AAS, Sedico Ltd (Nicosia, Cyprus). Infrared spectra, ranging from 400 to 4000 cm^{-1}, were obtained using KBr pellets using FT-IR 84005 Shimadzu (Basrah, Iraq) at room temperature. Ultraviolet-visible (UV-Vis) spectra were measured in ethanol using a UV-1800 Shimadzu (Basrah, Iraq). The ^{1}HNMR and ^{13}CNMR spectra were recorded in DMSO-d6 on a Varian-500 MHZ NMR spectrophotometer (Tehran, Iran). The magnetic susceptibility of the prepared complexes was gauged at room temperature using an MSB-MKI instrument (Baghdad, Iraq) through the Faraday method. Molar conductance values were recorded in dimethylformamide (DMF) at room temperature using a Jenway pcmb conductivity meter (Basrah, Iraq).Mass spectra for the prepared ligands were captured using an MS model 5975C VL MSD (Tehran, Iran) with an electron ionization energy of 70 eV.

2.3. Preparation of Schiff Base Ligands

Ligand L_1 was synthesized following a procedure analogous to a previous study [11]. Specifically, 0.55 g (0.002 mol) of isatin was dissolved in 30 mL of ethanol. Separately, 0.18 g (0.002 mol) of 2-aminopyridine was also dissolved in 30 mL of ethanol. Both solutions were combined, and a few drops of glacial acetic acid were added to initiate the reaction. The resulting mixture was subjected to reflux conditions for a duration of 9 h. The product was subsequently filtered and washed with hot ethanol, yielding a compound with a melting point of 235 °C and a yield of 78%. The second ligand, L_2, was synthesized following a similar methodology, but employing isatin and phenyl hydrazine as the reactants (Figure 1). The synthesized compound exhibited a melting point of 155 °C and a yield of 82%.

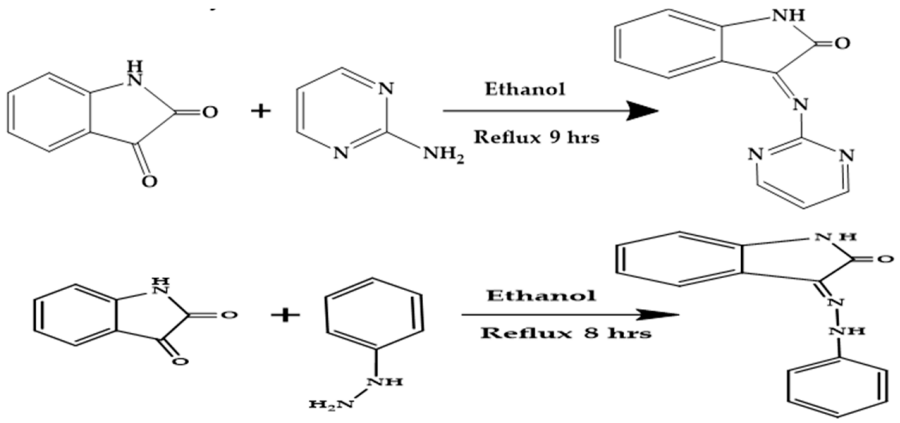

Figure 1. Synthesis of ligands L_1 and L_2.

2.4. Preparation of Thiocyanate Complexes

The preparation of thiocyanate complexes was carried out according to established methods [12]. Initially, metal dithiocyanates, specifically [$Co(SCN)_2$, $Ni(SCN)_2$, $Cd(SCN)_2$], were synthesized by reacting metal nitrates with potassium thiocyanate in methanol. The by-product, potassium nitrate, was subsequently removed via filtration. The resultant dithiocyanate solutions were reserved for further reactions. Tetrathiocyanate complexes, denoted as $MM'(SCN)_4$, where M = Co, Ni, and M′ = Cd, were prepared by mixing solutions of $M(SCN)_2$ and $M'(SCN)_2$ in a 1:1 molar ratio, followed by stirring for 36 h. The

tetrathiocyanate solutions in methanol were combined with synthesized ligands L_1 or L_2 in the same solvent in a 1:1 molar ratio. Solid products were obtained, filtered, and washed with ether.

The resultant complexes showed the following properties: L_1Co with a melting point of 270 °C and a yield of 75%, L_2Co with a melting point of 213 °C and a yield of 79%, L_1Ni with a melting point of 280 °C and a yield of 85%, and L_2Ni with a melting point of 204 °C and a yield of 83%. The general reaction can be represented as shown in Figure 2.

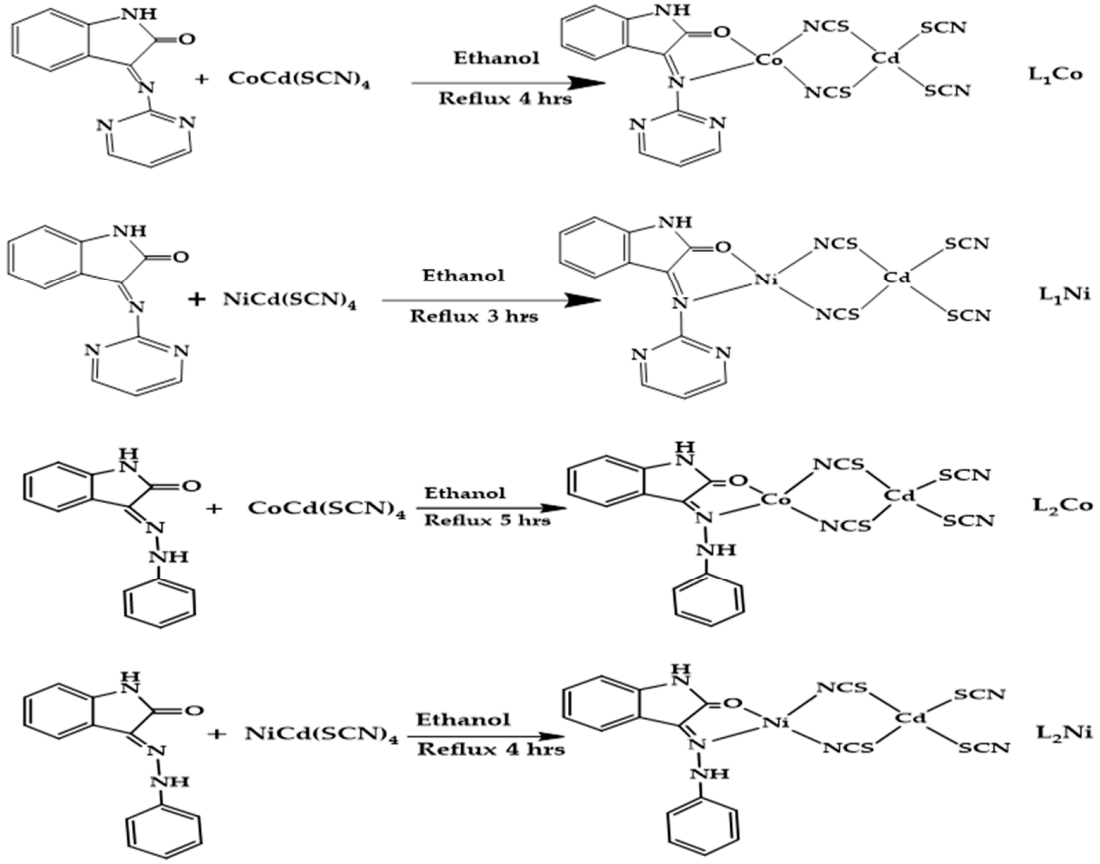

Figure 2. Synthesis of thiocyanate complexes.

3. Results and Discussion

3.1. Elemental Analysis

Elemental analysis revealed that the percentages of carbon, hydrogen, nitrogen, cobalt, and nickel in the Schiff base ligands and their complexes closely align with their theoretical values, thereby confirming the proposed chemical formulas for these compounds [11]. The empirical data are summarized in Tables 1 and 2.

Table 1. The percentage of elements in the Schiff base ligands and their complexes (Part 1).

Compound.	M.wt (g/mol)	%C (cal./found)	%H (cal./found)	%N (cal./found)	%Co (cal./found)	%Ni (cal./found)
L_1	224.22	64.28/64.32	3.60/3.52	24.99/24.92	-/-	-/-
L_2	237.26	70.87/70.81	4.67/4.63	17.71/17.25	-/-	-/-
L_1Co	627.88	30.61/30.57	1.28/1.19	17.85/17.81	9.39/9.17	-/-
L_1Ni	627.64	30.62/30.59	1.28/1.24	17.85/17.34	-/-	9.35/9.52
L_2Co	772.02	33.73/33.70	1.73/1.82	15.30/15.51	9.20/9.43	-/-
L_2Ni	771.78	33.75/33.54	1.73/1.69	15.30/15.45	-/-	9.16/9.82

Table 2. Chemical formulas of the Schiff base ligands and their complexes.

Compound.	Formula
L_1	C12H8N4O
L_2	C12H8N4O
L_1Co	CoCd(SCN)4C12H8N4O
L_1Ni	NiCd(SCN)4C12H8N4O
L_2Co	CoCd(SCN)4C14H11N3O
L_2Ni	NiCd(SCN)4C14H11N3O

3.2. Spectral Properties

3.2.1. Infrared Spectra

The data are summarized in Tables 3 and 4. The infrared spectra of the Schiff base ligands and their complexes are illustrated in Figures 3–8. For ligands L_1 and L_2, absorption bands corresponding to the azomethine group appeared at 1620 cm^{-1} and 1618 cm^{-1}, respectively. These bands shifted to lower wavenumbers in their cobalt and nickel complexes, implicating the azomethine nitrogen in metal ion coordination [11].

Table 3. Important infrared bonds of the ligands and their complexes (Part 1).

Sym. of Comp.	C-H Arom	HC=N	C=C	C=O	NH
L_1	3061/3113	1620	1566	1732	3412
L_1Co	3062/3113	1616	1589	1730	3404
L_1Ni	3061	1617	1590	1737	3427
L_2	4057/3132	1618	1597	1728	3438
L_2Co	3057/3134	1616	1597	1732	3425
L_2Ni	3059	1610	1597	1734	3436

Table 4. Important infrared bonds of the ligands and their complexes (Part 2).

Sym. of Comp.	C-N in M-SCN	S-C in M-SCN	C-N in M-SCN-M	M←N	M-NSC	M-SCN
L_1	-	-	-	-	-	-
L_1Co	2063	748	2148	572	507	449
L_1Ni	2073	748	2148	573	508	453
L_2	-	-	-	-	-	-
L_2Co	2075	746	2137	510	470	447
L_2Ni	2088	748	2148	515	468	451

The spectra of the prepared complexes also featured new bands in the ranges of 2063–2088 cm^{-1} and 2137–2148 cm^{-1}, attributed to nitrogen-bonded and sulfur-bonded thiocyanate, respectively [12]. Additionally, bands in the range of 510–573 cm^{-1} were ascribed to the formation of M–N bonds [13].

3.2.2. Ultraviolet-Visible Spectra

The UV-Vis spectra of the Schiff base ligands and their complexes are presented in Figure 9. The ultraviolet-visible spectra of the Schiff base ligands exhibited absorption bands at 280 nm and 295 nm, respectively, ascribed to π–π* transitions of the azomethine group. Bands appearing at 460 nm for L_1 and 404 nm for L_2 were suggestive of π–π* transitions in aromatic rings, internal charge transfer, or carbonyl groups [14].

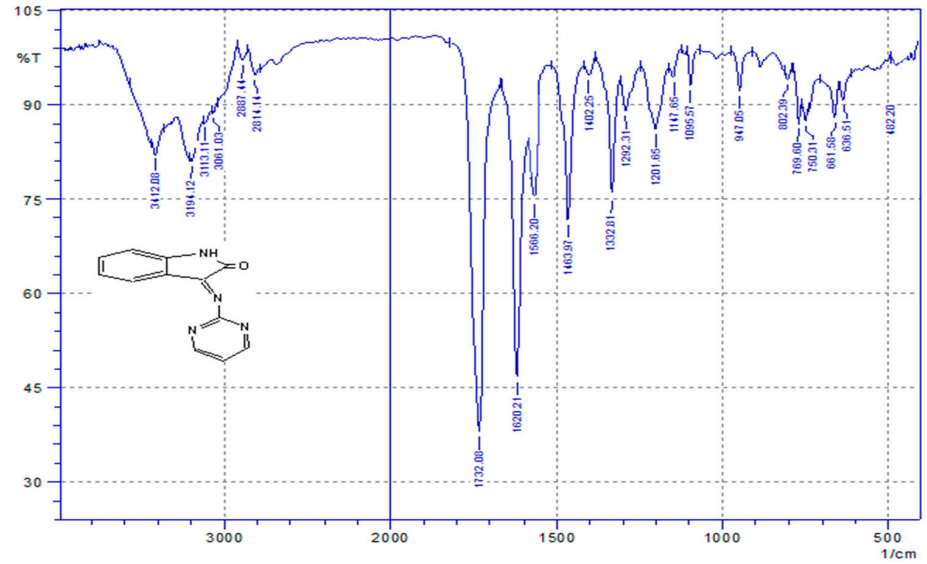

Figure 3. Infrared Spectrum of ligand L_1.

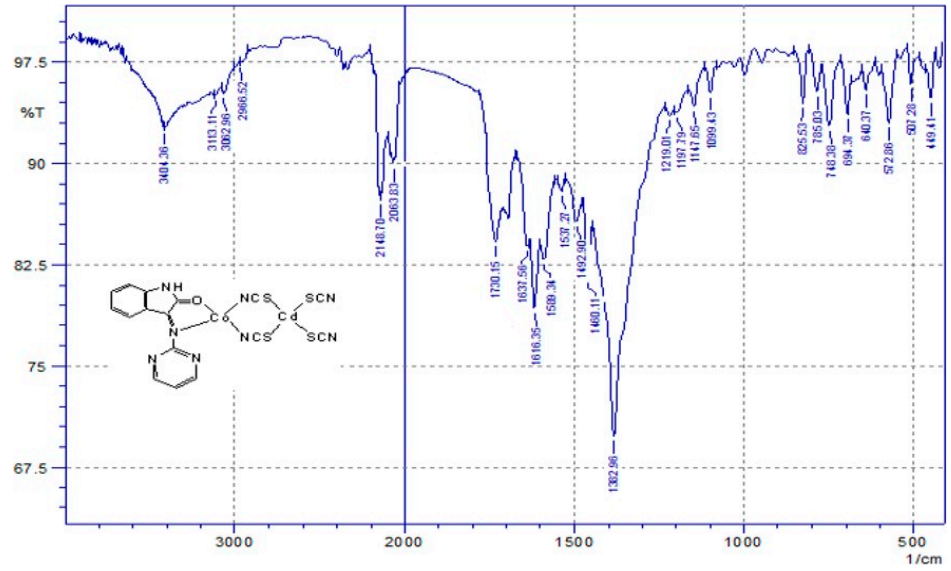

Figure 4. Infrared Spectrum of complex L_1Co.

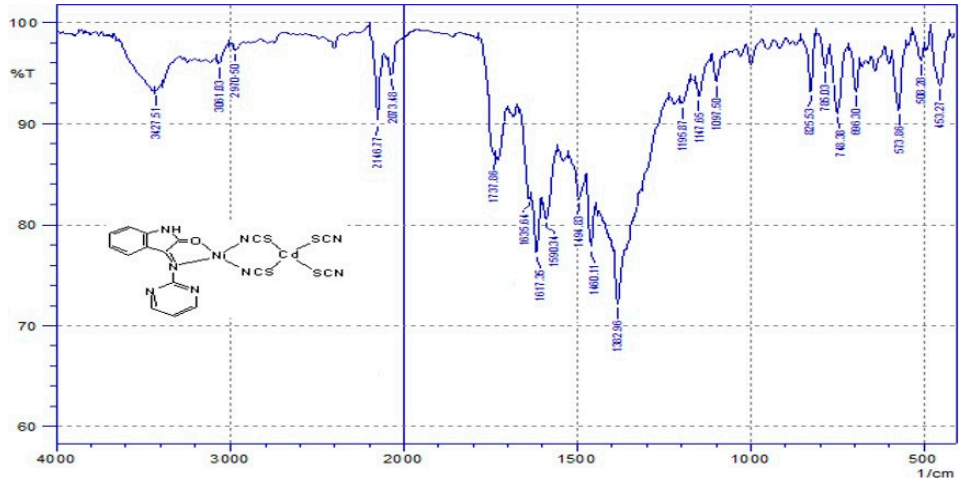

Figure 5. Infrared Spectrum of complex L_1Ni.

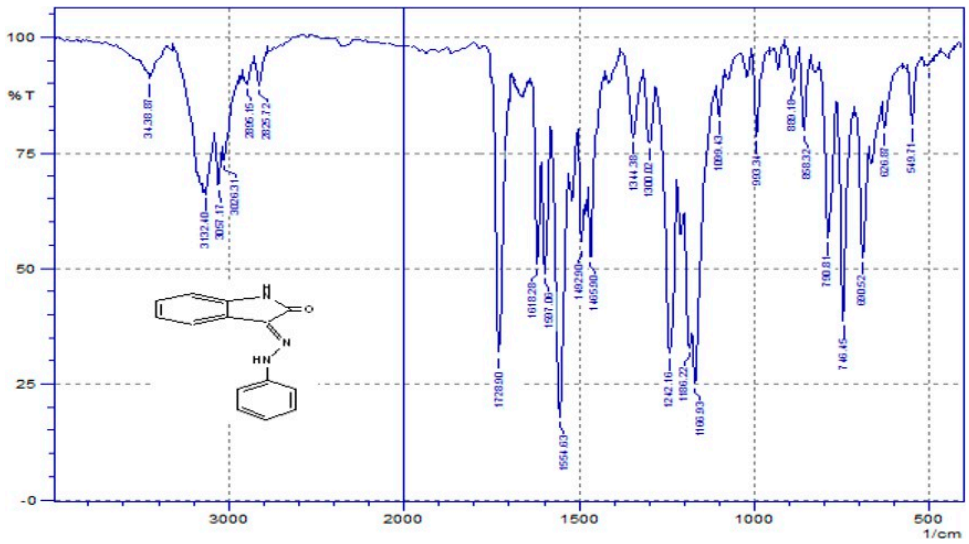

Figure 6. Infrared Spectrum of ligand L_2.

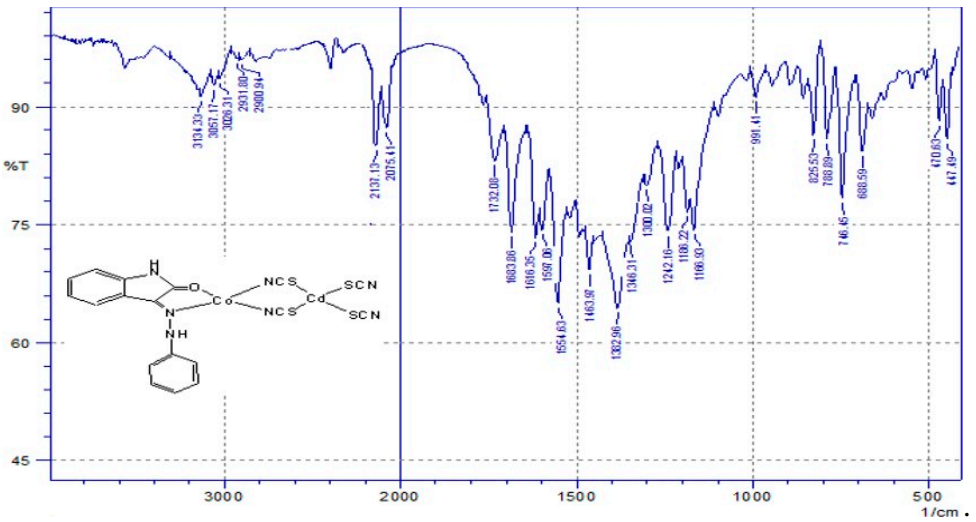

Figure 7. Infrared Spectrum of complex L_2Co.

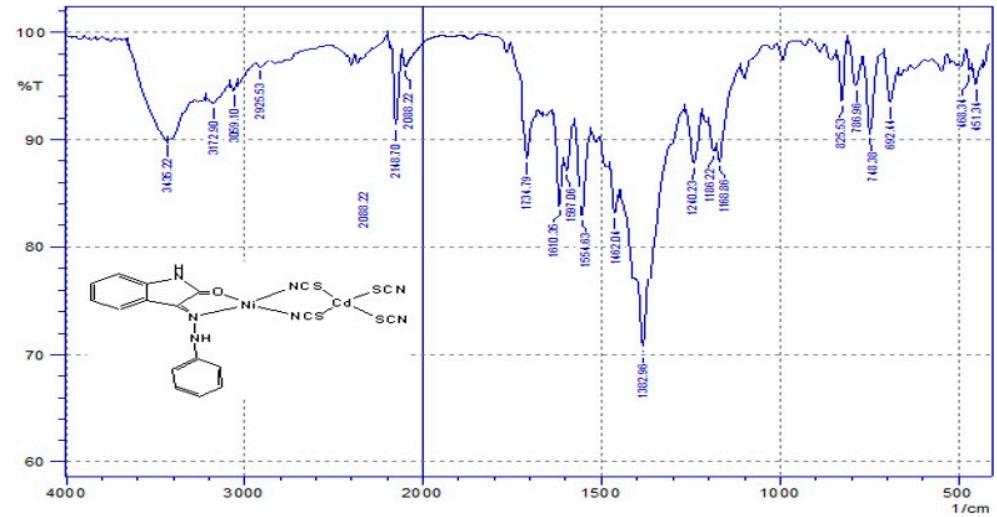

Figure 8. Infrared Spectrum of ligand L_2Ni.

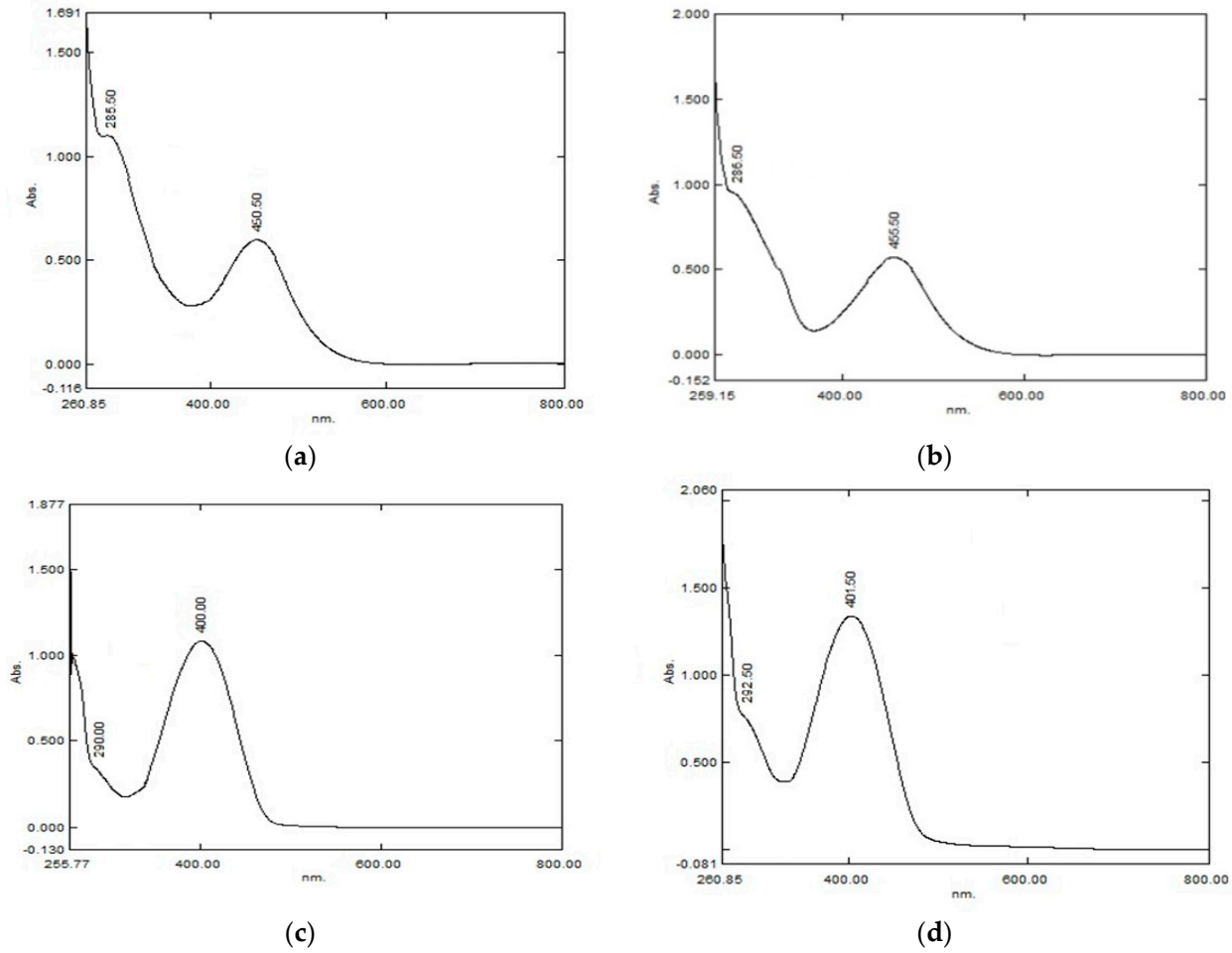

Figure 9. Ultraviolet visible spectra of the Schiff base ligands and their complexes: (**a**) L_1Co; (**b**) L_1Ni; (**c**) L_2Co; (**d**) L_2Ni.

3.3. NMR and Mass Spectra

Both the ^{1}HNMR and ^{13}CNMR spectra of the ligands showed all the expected signals as shown in Figures 10–13. The chemical shifts for ^{1}HNMR, ^{13}CNMR are detailed in Tables 5 and 6, respectively. The mass spectra indicate the presence of molecular ions and other characteristic peaks, further validating the chemical structure of the ligands [13]. The mass spectrum of ligand L_2 is shown in Figures 14 and 15.

Table 5. Chemical shifts of ^{1}HNMR for the Schiff base ligands.

Ligand	^{1}HNMR Chemical Shifts (ppm)
L_1	7.13–7.53 (5H, Ar-H), 8.73 (2H, HC=N-), 13.23 (1H, NH)
L_2	7.10–7.46 (9H, Ar-H), 10.16 (1H, NH-N), 10.20 (1H, NH-CO)

Table 6. Chemical shifts of ^{13}CNMR for the Schiff base ligands.

Ligand	^{13}CNMR Chemical Shifts (ppm)
L_1	C1(123.08), C2(132.77), C3(113.92), C4(143.95), C5(117.97), C6(125.82), C7(167.66), C8(142.75), C9(161.13), C10(158.14), C11(121.57)
L_2	C1(122.46), C2(128.49), C3(112.74), C4(138.91), C5(120.09), C6(120.75), C7(167.21), C8(130.05), C9(143.98), C10(115.63), C11(129.22), C12(123.43)

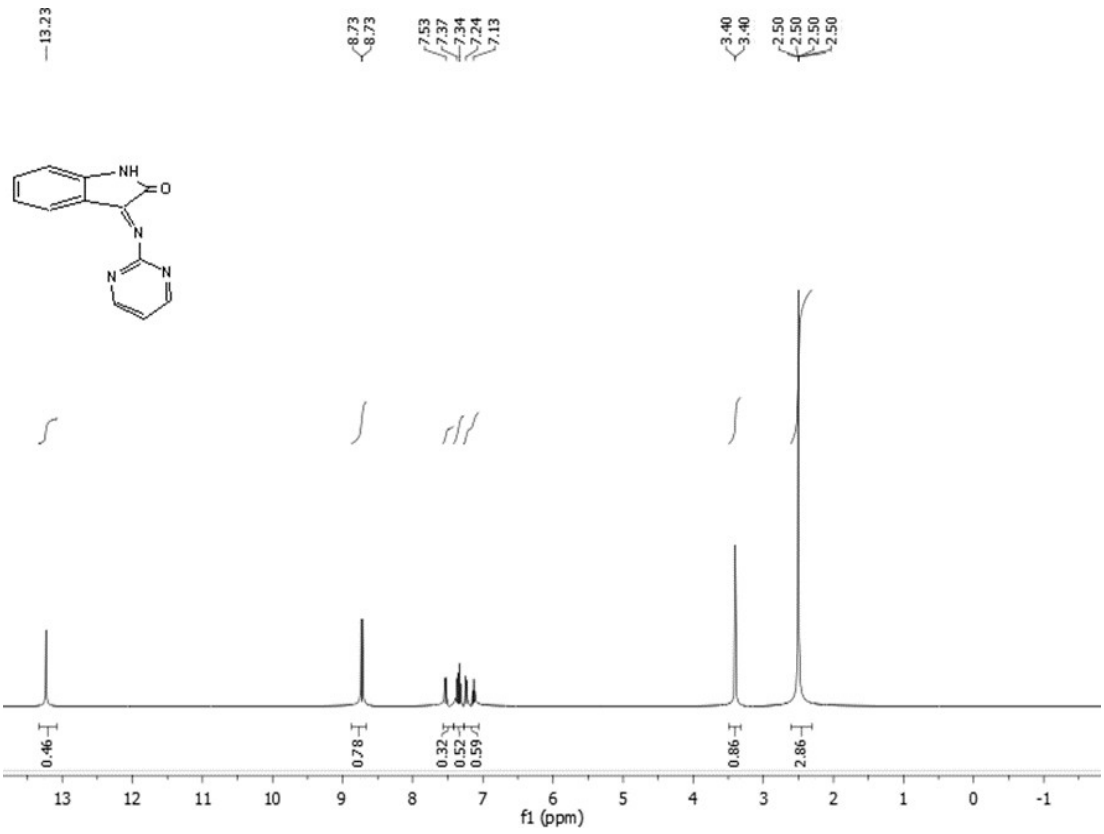

Figure 10. ^{1}HNMR spectrum of the ligand L_1.

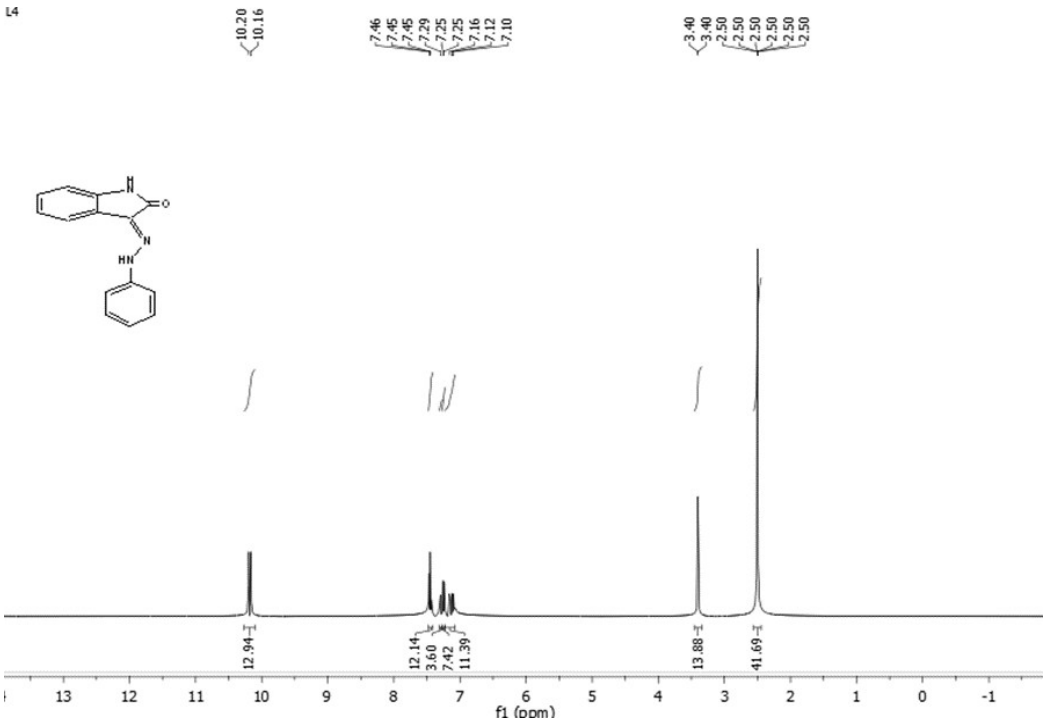

Figure 11. ^{1}HNMR spectrum of ligand L_2.

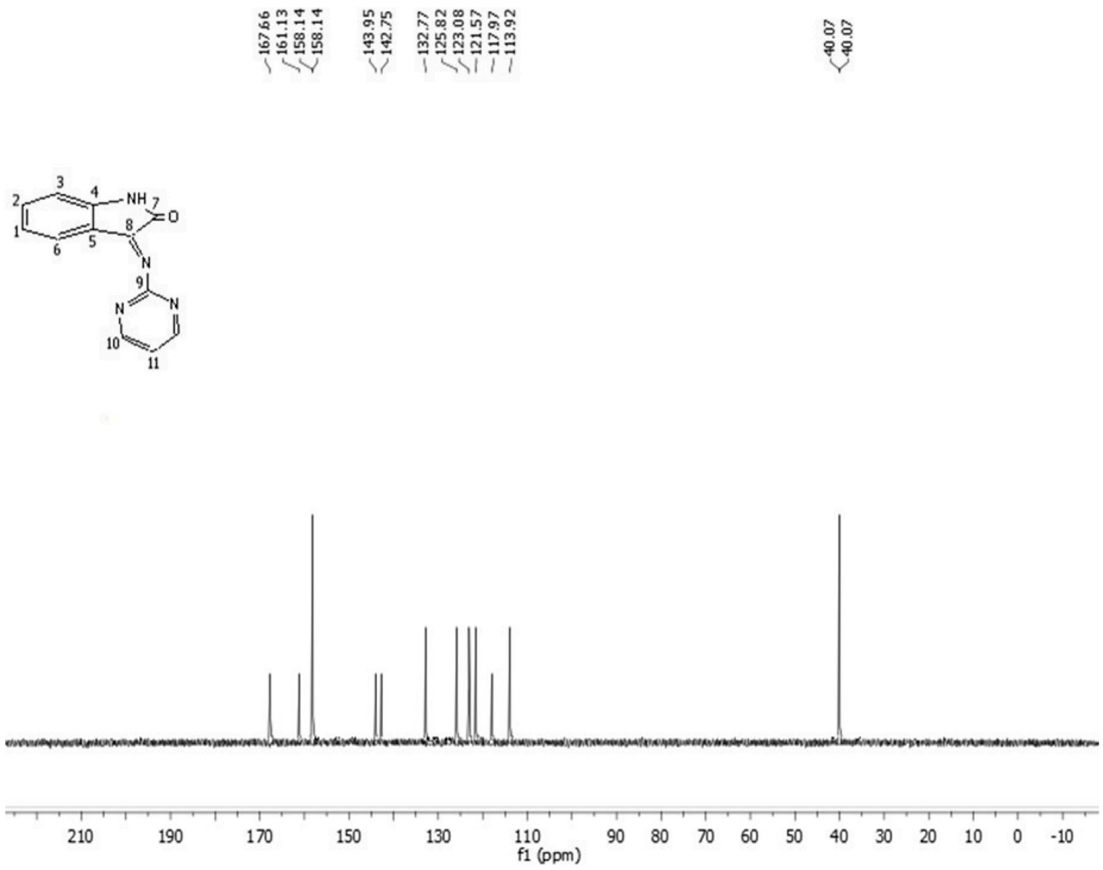

Figure 12. ^{13}CNMR spectrum of ligand L1.

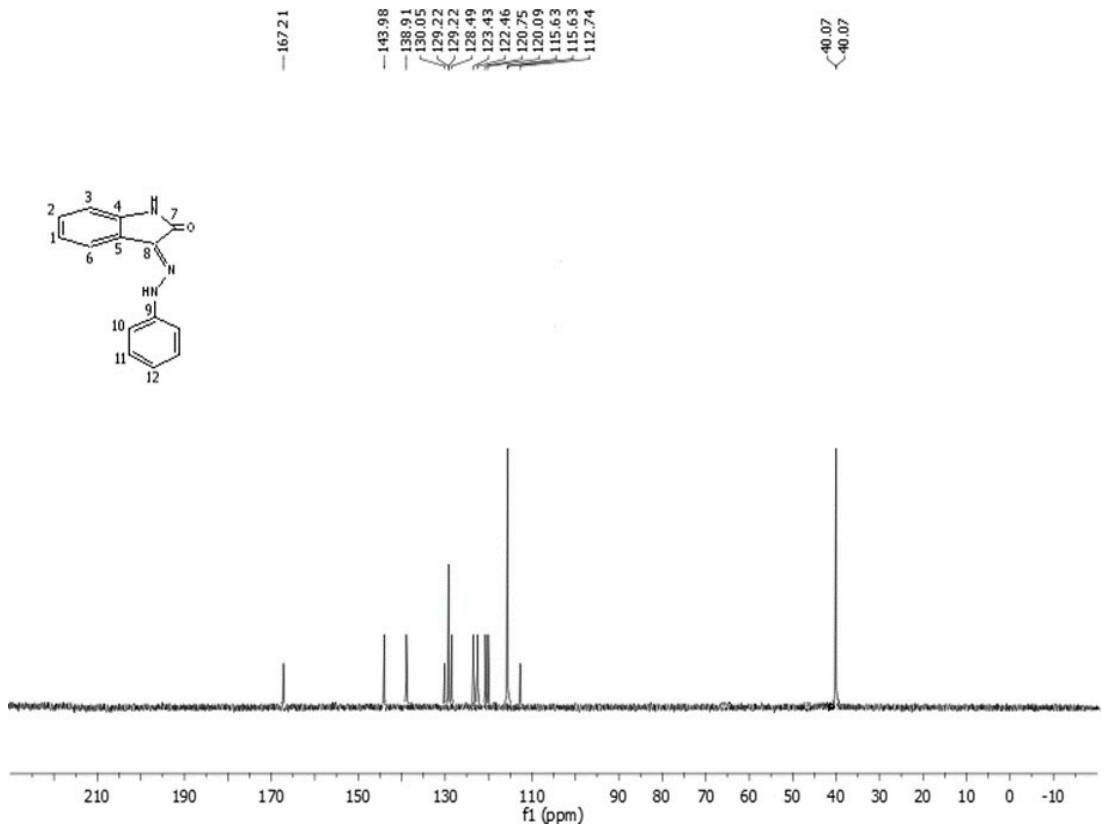

Figure 13. ^{13}CNMR spectrum of ligand L_2.

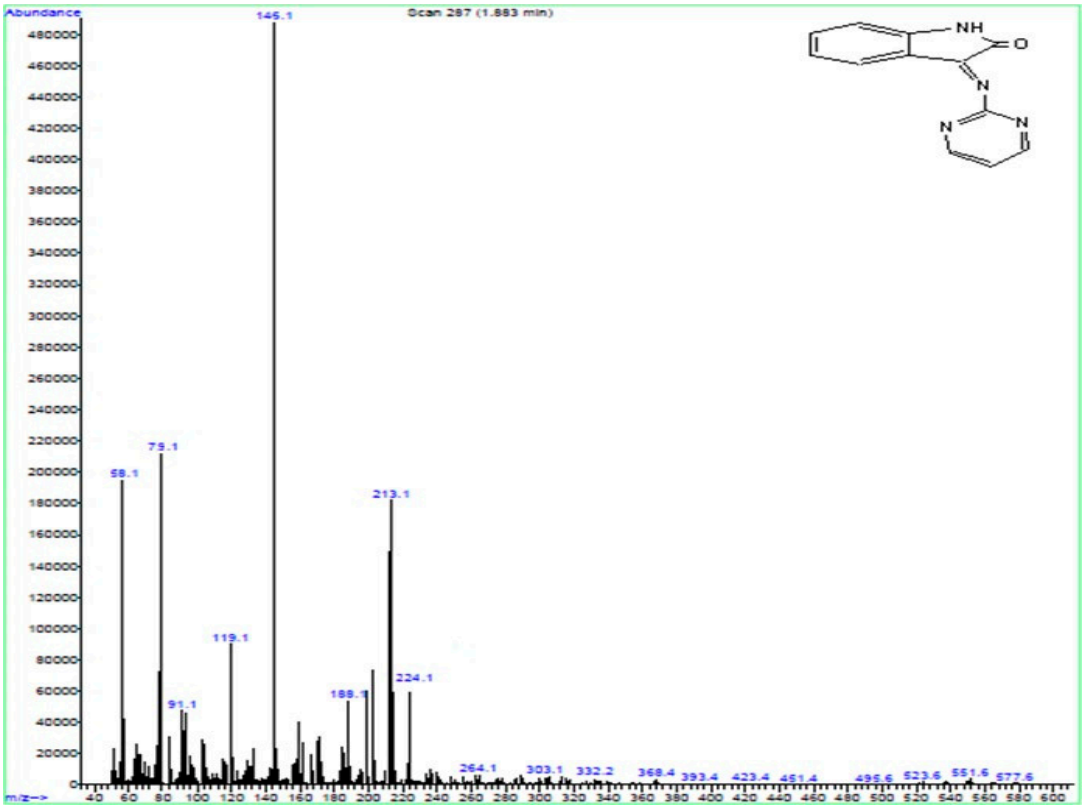

Figure 14. Mass spectrum of ligand L_1.

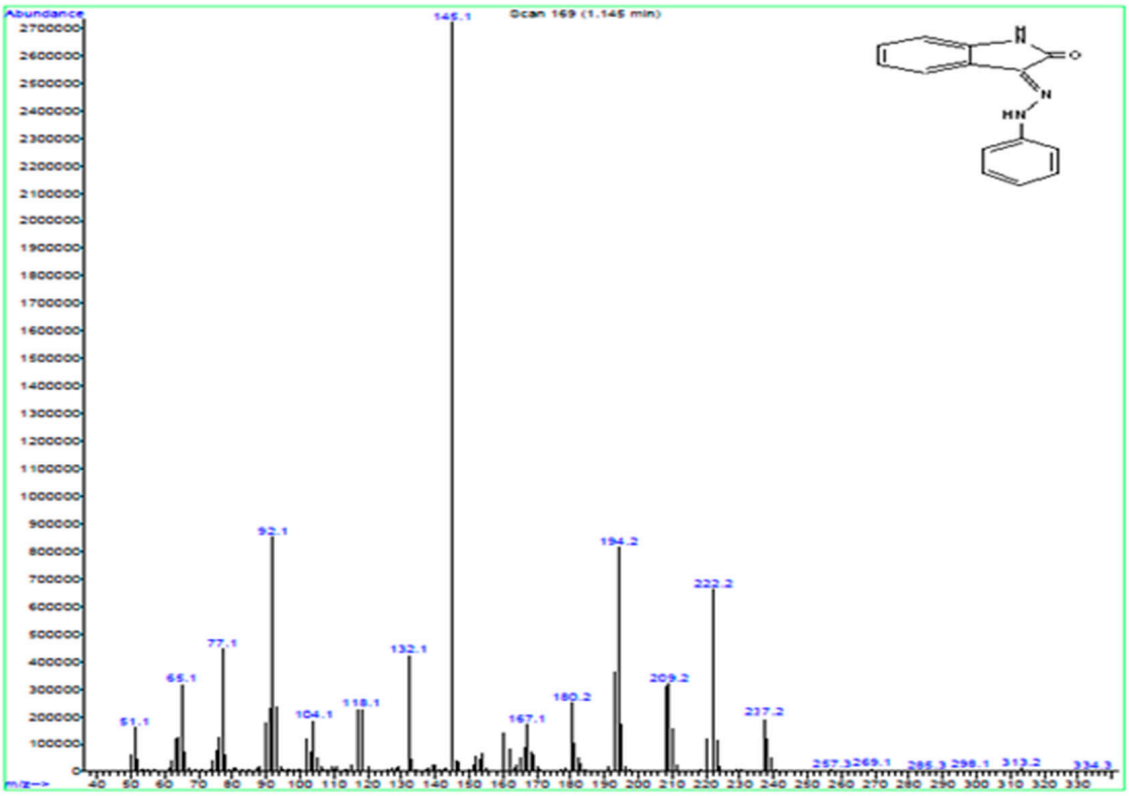

Figure 15. Mass spectrum of ligand L_2.

3.4. Magnetic and Conductivity Measurements

The magnetic susceptibility measurements indicated that the cobalt complexes possessed a tetrahedral geometry and paramagnetic properties, whereas the nickel complexes exhibited a square planar geometry and diamagnetic properties [15]. As shown in Table 7, the molar conductivity and magnetic moments of the complexes exhibit significant variations. Further details are provided in Table 8.

Table 7. Molar conductivity and magnetic moment of the complexes (Part 1).

Sym. of Complex	Formula of Complex	*μ*eff (B.M)	Molar Molar	Magnetic Properties	Hybridization
L_1Co	$CoCd(SCN)_4C_{15}H_{14}N_4O_5$ 748.99	4.031	18	Paramagnetic	sp3 (tetrahedral)

Table 8. Molar conductivity and magnetic moment of the complexes (Part 2).

Sym. of Complex	Formula of Complex	*μ*eff (B.M)	Molar Molar	Magnetic Properties	Hybridization
L_1Ni	$NiCd(SCN)_4C_{15}H_{14}N_4O_5$748.75	1.123	20	Diamagnetic	dsp2 (square planar)

3.5. Biological Activity

The Schiff base ligands and their complexes were tested for antibacterial and antifungal activities against Staphylococcus aureus, Basillus (bacteria) and Candida albicans (fungi). The results demonstrated that all compounds exhibited significant activity, attributed to the presence of the azomethine group and other functional groups [16]. The biological activity data for the ligands and their complexes are detailed in Tables 9 and 10.

Table 9. Biological activity data of the Schiff base ligands and their complexes (Part 1).

Compound	Concentration (mg/mL)	*Staphylococcus aureus*	*Basillus* sp.	*Candida albicans*
L_1	0.02	9	11	15
L_1	0.04	10	11	17

Table 10. Biological activity data of the Schiff base ligands and their complexes (Part 2).

Compound	Concentration (mg/mL)	*Staphylococcus aureus*	*Basillus* sp.	*Candida albicans*
L_1	0.06	10	12	20
L_1	0.08	11	12	25

4. Conclusions

This study successfully synthesized Schiff base ligands through the reaction of isatin with 2-aminopyridine or phenyl hydrazine. These ligands were further complexed with MCd(SCN)4, where M represents Co^{2+} or Ni^{2+}, in a 1:1 molar ratio. Comprehensive characterization was performed using various spectral techniques, confirming the bidentate nature of the ligands. The coordination complexes exhibited a coordination number of four, adopting a tetrahedral geometry for the cobalt complexes and a square planar geometry for the nickel complexes. Notably, both the ligands and their corresponding complexes demonstrated significant antibacterial and antifungal activities, making them potential candidates for further biological studies.

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Conflicts of Interest: The authors declare no conflicts of interest.

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