

Schiff Base Complexes of Di(2-Pyridyl) Ketone Derivatives with Transition Metals, Synthesis and Characterization

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Abstract

This study focuses on the synthesis of novel Schiff bases derived from aminopyridine and ketone, followed by their complexation with transition metals to form coordination compounds. The structure of these complexes was evaluated. The classical method of Schiff base synthesis which involves refluxing at 70°C for 5 hours, followed by solvent removal using a rotary evaporator was employed in this study. In the synthesis process, di(2-pyridyl) ketone is dissolved in absolute methanol, then combined with a solution of 2-aminopyridine, followed by refluxing. Transition metal salts in methanol were added, and further refluxing occurs. After crystallization and filtration, the products were formed and subjected to characterization using solubility test, melting point, molar conductivity, elemental analysis, and FTIR spectroscopy. The compounds show varied properties, with melting points from 123°C to 298°C, and conductivity ranging from 12.4 μScm^{-1} to 21.2 μScm^{-1} , indicating non-electrolytic behaviour. Elemental analysis validates experimental accuracy. FTIR spectra reveal imine bond formation in synthesized compounds. Coordination with metals is evident in complex spectra. Notably, M-N and M-Cl absorptions suggest metal-ligand bonding. The ligands exhibit both bidentate and monodentate coordination with transition metals, leading to diverse geometries, including octahedral.

Keywords: Schiff bases, Transition metals, Complexes, FTIR spectroscopy

INTRODUCTION

Historical background

Schiff bases, first described by Hugo Schiff in 1864, are a pivotal class of organic compounds formed by the condensation of primary amines with carbonyl compounds, resulting in the characteristic imine or azomethine ($\text{C}=\text{N}-$) functional group. This structural mode not only defines their inherent chemical reactivity but also underpins their ability to form coordination compounds with transition metals, particularly in complexes derived from di(2-pyridyl) ketone derivatives (Kajal et al., 2013).

Coordination compounds are composed of a metal atom or ion and one or more **ligands** (atoms, ions, or molecules) that donate electrons to the metal. This definition includes compounds with metal-carbon bonds, or organometallic compounds. *coordination compound* comes from the coordinate covalent bond, which historically was considered to form by donation of a pair of electrons from one atom to another. In coordination compounds

the donors are usually the ligands, and the acceptors are the metals. Coordination compounds are examples of acid–base adducts frequently called **complexes** or, if charged, **complex ion**.

Although the formal study of coordination compounds really begins with Alfred Werner (1866–1919), coordination compounds have been used as pigments and dyes since antiquity. Examples include Prussian blue ($\text{KFe}[\text{Fe}(\text{CN})_6]$), aureolin yellow, ($\text{K}_3[\text{Co}(\text{NO}_2)_6] \cdot 6\text{H}_2\text{O}$), and alizarin red dye (the calcium aluminum salt of 1,2-dihydroxy-9,10-anthraquinone). The tetraamminecopper (II) ion, actually $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ in solution, which has a striking royal blue color—was known in prehistoric times. The formulas of these compounds were deduced in the late nineteenth century, providing background for the development of bonding theories (Lever A.B.P, 1987).

Synthesis of Schiff Bases and Metal Complexes

The synthesis of Schiff bases typically involves a two-step process. Initially, the ligand is prepared by condensing a primary amine with an aldehyde or ketone, forming the imine group ($>\text{C}=\text{N}-$). Subsequently, the prepared Schiff base ligand is reacted with metal salts to yield transition metal complexes, which often adopt distinct geometries such as octahedral or square planar (Mumtaz et al., 2020; “Synthesis, Characterization and Biological Activities of Schiff Bases and Their Transition Metal Complexes”, 2023).

Characterization Techniques

A range of analytical techniques is employed to verify the formation of the imine group and to elucidate the coordination environment and geometry of these complexes. Fourier-transform infrared spectroscopy (FTIR) and UV-visible spectroscopy are frequently used to identify characteristic bonds and electronic transitions, while magnetic moment analysis and single crystal X-ray diffraction provide insights into the molecular geometry and structural details of the complexes (Guèye et al., 2024; Akramullazi et al., 2024).

Biological and Industrial Applications

Schiff base metal complexes have attracted significant interest owing to their enhanced biological activities compared to their free ligands. They exhibit a spectrum of pharmacological properties, including antimicrobial, anticancer, anti-inflammatory, analgesic, and antitubercular effects (Kajal et al., 2013; Mumtaz et al., 2020). In addition to their biomedical potential, these complexes serve important roles in catalysis and materials science. They are utilized in the development of dyes, pigments, polymer stabilizers, and corrosion inhibitors, thereby finding applications in diverse industrial processes (“Schiff Bases and Their Metal Complexes: Synthesis, Structural Characteristics and Applications”, 2023).

Green Chemistry Approaches

Recent advancements have emphasized the importance of developing environmentally friendly and cost-effective methods for synthesizing Schiff base complexes. Green chemistry approaches are being integrated into the synthesis protocols to reduce waste and energy consumption, further broadening the applicability of these compounds in both scientific research and industrial settings (Kajal et al., 2013; Mumtaz et al., 2020; “Synthesis, Characterization and Biological Activities of Schiff Bases and Their Transition Metal Complexes”, 2023).

MATERIALS AND METHODS

Safety Precautions

General laboratory rules and regulations were strictly followed. No accidents occurred, ensuring the reliability of the procedures.

Reagents, Solvents, and Apparatus

Reagents

Reagents included 2-aminopyridine, di-2-pyridyl ketone, various metal salts (Zinc Chloride, Cobalt Chloride, Copper Chloride, Nickel Chloride), tetraoxosulphate (VI) acid, glacial acetic acid, silica gel, furaldehyde, glycine, and aniline.

Solvents

The solvents used were methanol, ethanol, dichloromethane, acetone, diethyl ether, ethyl acetate, distilled water, DMSO, DMF, N-hexane, petroleum ether, and chloroform.

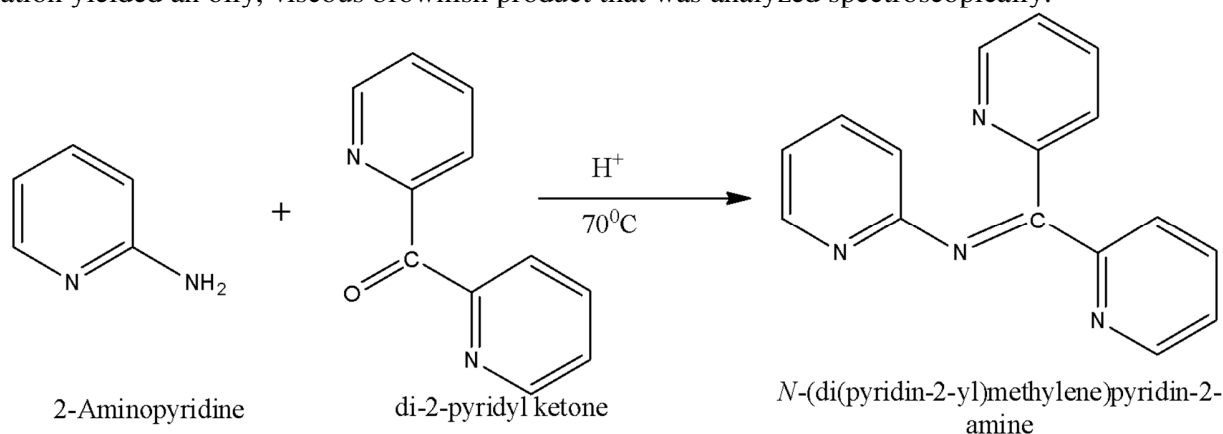
Apparatus

Equipment included a retort stand, weighing balance, rotary evaporator, hot plate, magnetic stirrer, pH meter, conductivity meter, capillary tubes, TLC plate, beakers, reflux condenser, desiccator, funnel, test tubes, micropipette, and general laboratory glassware.

Experimental Procedures

Synthesis of Schiff's Base Ligand

Equimolar amounts of di(2-pyridyl)-ketone and 2-aminopyridine were dissolved separately in ethanol. The ketone solution was added drop-wise to the pyridine solution with gentle stirring, along with two drops of acetic acid. The mixture was then refluxed at 70°C for 5 hours. After cooling, the solvent was removed using a rotary evaporator, followed by liquid-liquid partitioning between distilled water and dichloromethane. Extended evaporation yielded an oily, viscous brownish product that was analyzed spectroscopically.



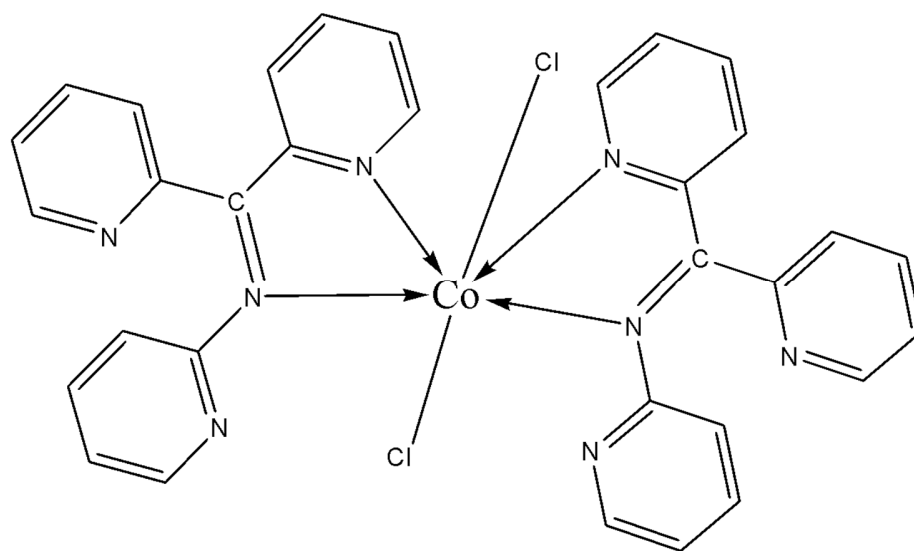
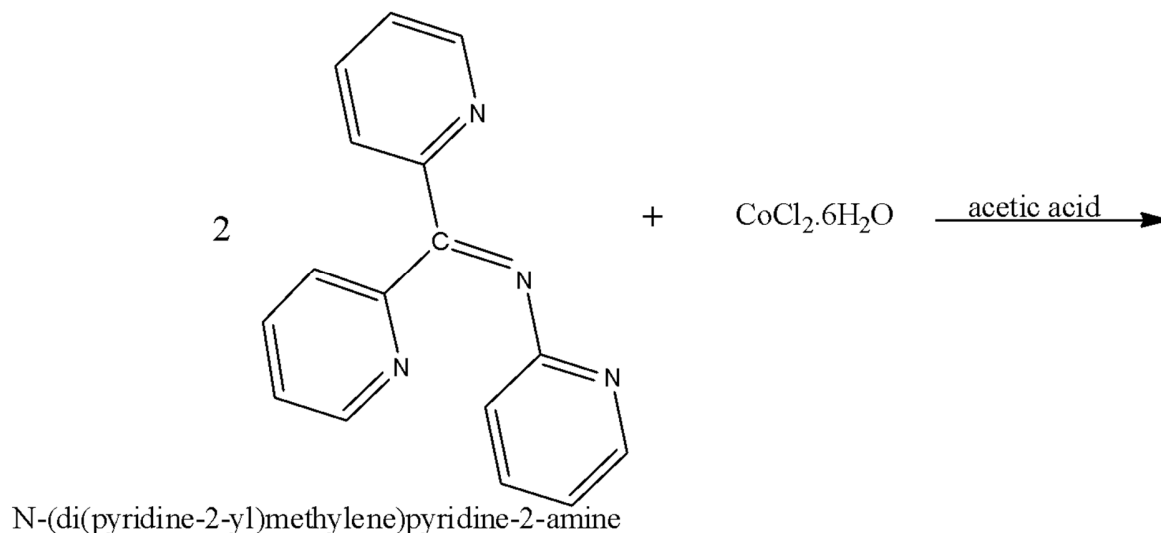
Equation 10: Synthesis of N-(di(pyridine-2-yl)methylene)pyridine-2-amine Schiff's base

Synthesis of Metal Complexes

Cobalt Complex (Method I)

A methanolic solution of di(2-pyridyl) ketone was combined with a 2-aminopyridine methanolic solution. The mixture was refluxed for 24 hours, after which a cobalt salt solution was added drop-wise and refluxed for an

additional 3 hours. The resulting bluish-green precipitate was filtered, washed with distilled water, and stored in a desiccator.

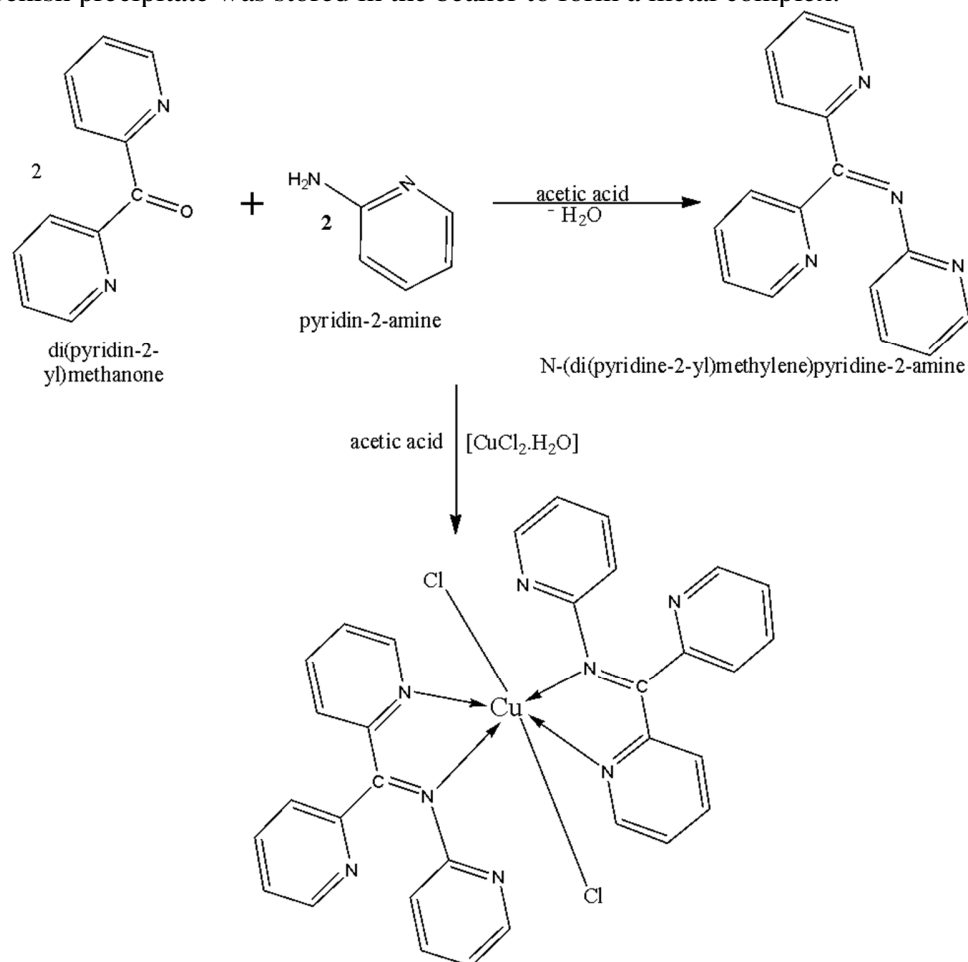


Equation 11: The Proposed Structure of N-(Di(Pyridine-2-yl)Methylene)Pyridine-2-Amine Schiff Base of Cobalt Complex.

Synthesis of Copper Complex of N-(di(Pyridine-2-yl)methylene)pyridine-2-Amine Schiff Base

A one-pot synthesis technique was employed for this cobalt complex. Di(2-pyridyl) ketone (0.092 g) was dissolved in 5 mL of 100% methanol together with 0.499 mmol of a 2-aminopyridine methanolic solution. The ketone solution was added drop-by-drop to the 2-aminopyridine solution and refluxed for 24 hours. Then, the salt solution (notably, the original text states “copper salt solution” though the title indicates a cobalt complex) was

added drop-by-drop and refluxed for an additional 3 hours, making a total reaction time of 1 day and 3 hours. The resulting greenish precipitate was stored in the beaker to form a metal complex.

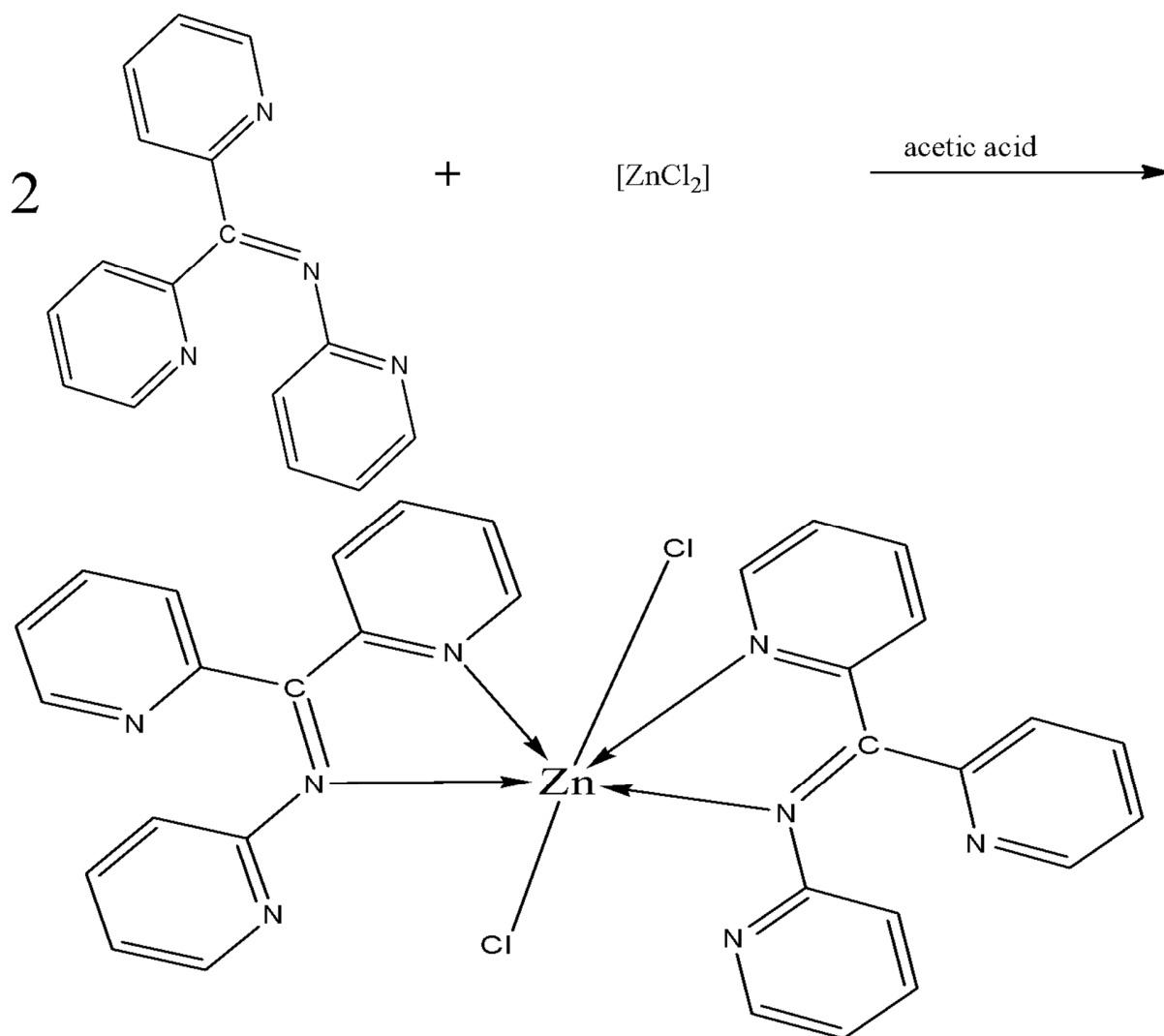


Proposed structure of Copper Complex of N-(di(pyridine-2-yl)methylene)pyridine-2-amine

Scheme 3: Proposed Structure of N-(Di(Pyridine-2-yl)Methylene)Pyridine-2-Amine Schiff Base of Copper Complex

Zinc Complex

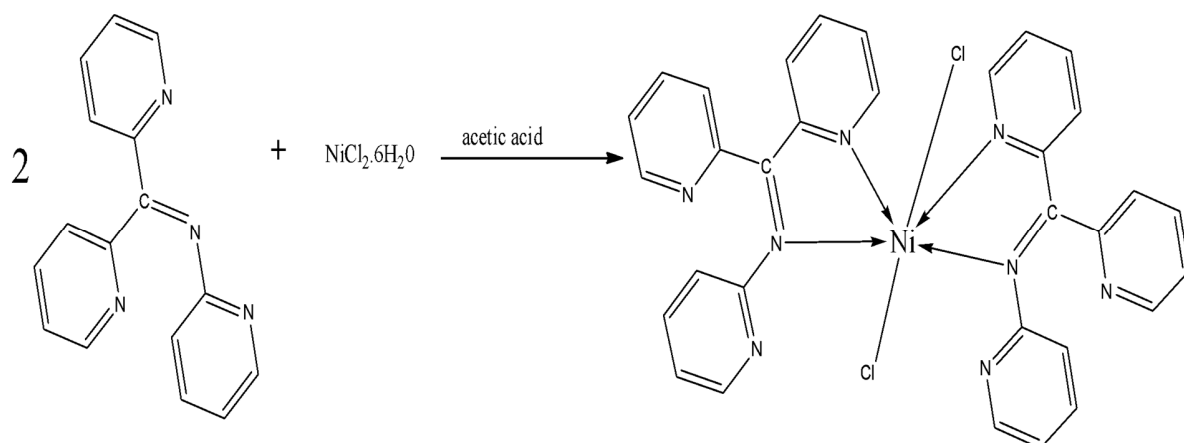
The one-pot synthesis involved mixing di(2-pyridyl) ketone and 2-aminopyridine in methanol, followed by the drop-wise addition of the zinc salt solution. The reaction mixture was refluxed for 24 hours, and the resulting milky substance was left undisturbed for crystallization.



Equation 12: Proposed Structure of Zinc Complex N-(di(Pyridine-2-Yl)Methylene)Pyridine-2-Amine Schiff's Base

Nickel Complex

Di(2-pyridyl) ketone and 2-aminopyridine in methanol were refluxed for 24 hours. After adding the nickel salt solution drop-wise, the reaction continued for another 3 hours. A greenish product was obtained and left to crystallize.

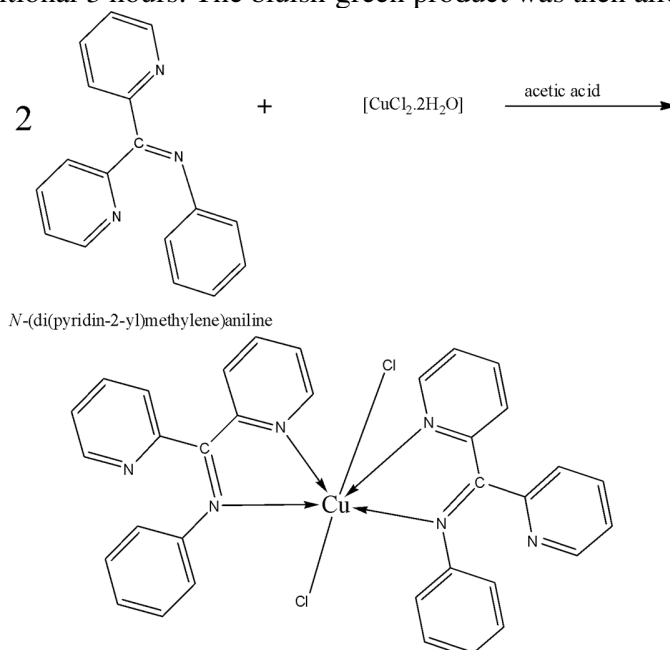


Synthesis of *N*-(Di(Pyridine-2-Yl)Methylene) Aniline Schiff Base and Its Metal Complexes

A similar procedure was followed for synthesizing the aniline derivative and its metal complexes.

Copper Complex with Aniline Schiff Base

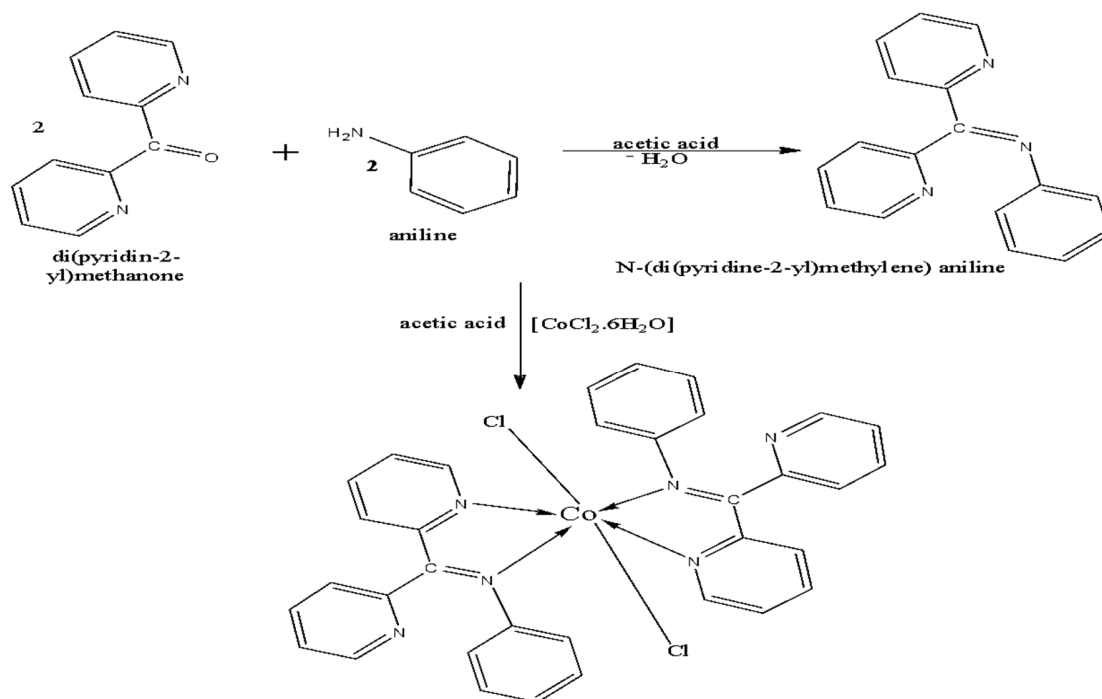
Di(2-pyridyl) ketone was reacted with aniline in methanol. After a 24-hour reflux, copper salt was added drop-wise and refluxed for an additional 3 hours. The bluish-green product was then allowed to crystallize.



Equation 14: Structure of *N*-(di(pyridine-2-yl)methylene) Aniline Schiff's base of Copper Complex.

Cobalt Complex with Aniline Schiff Base

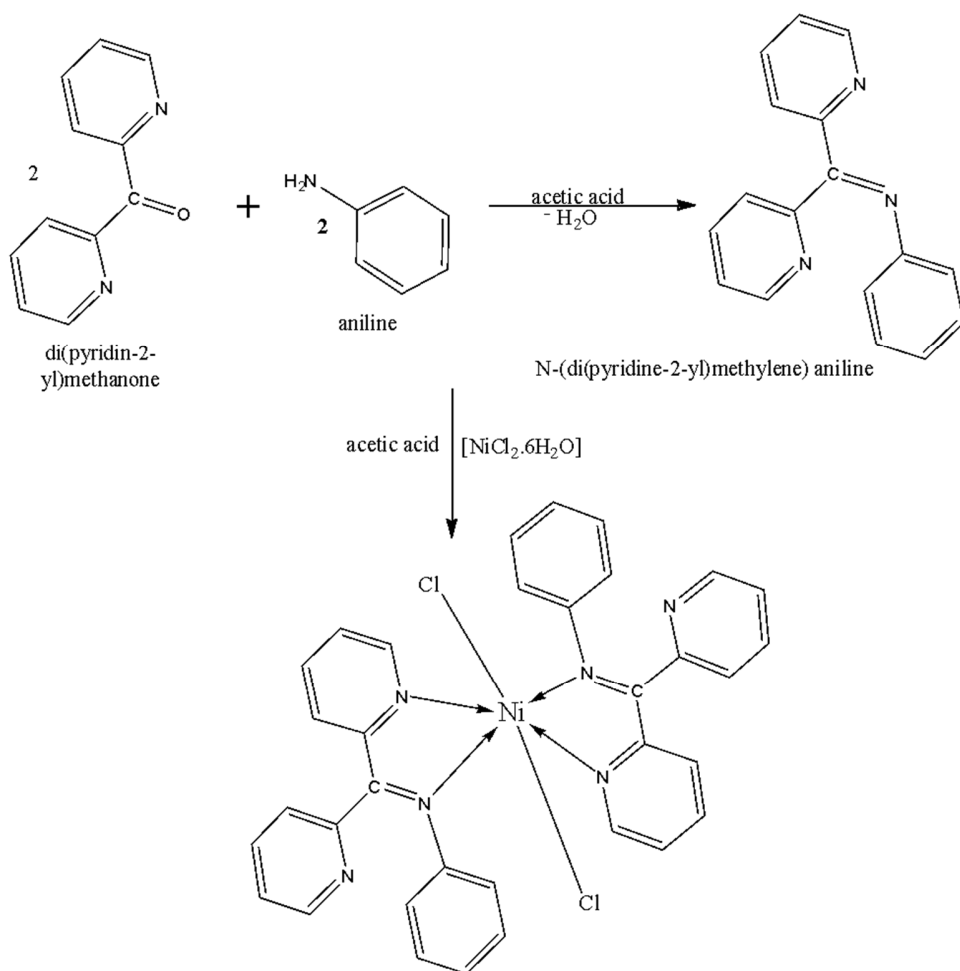
The reaction with cobalt salt was carried out following the same initial steps, resulting in a green precipitate that was left for crystallization.



Scheme 4: Proposed synthesis of N-(di(pyridine-2-yl)methylene) aniline Schiff's base of Cobalt Complex

Nickel Complex with Aniline Schiff Base

After reacting di(2-pyridyl) ketone with aniline in methanol and refluxing for 24 hours, the nickel salt was added. The mixture was further refluxed for 3 hours to yield a green precipitate, which was collected for analysis.

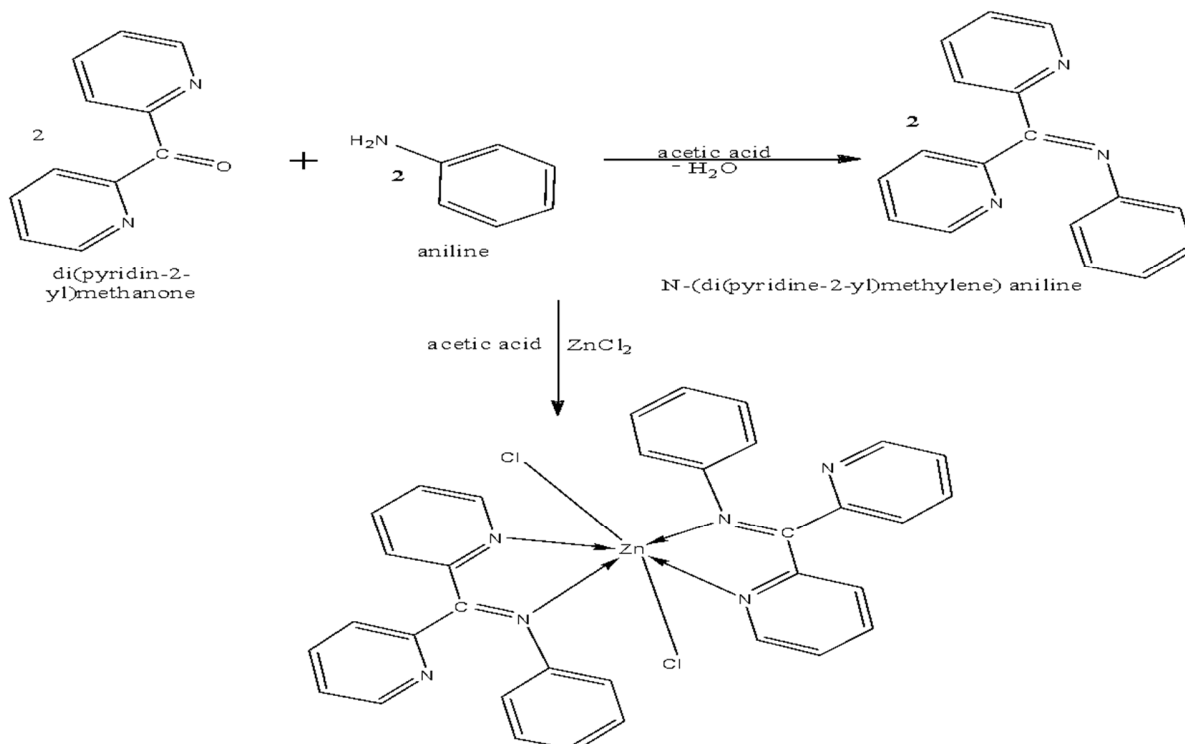


Proposed structure of Cobalt Complex of N-(di(pyridine-2-yl)methylene) aniline

Scheme 5: Proposed synthesis of N-(di(pyridine-2-yl)methylene) aniline Schiff's base of Nickel Complex.

Zinc Complex with Aniline Schiff Base

Di(2-pyridyl) ketone and aniline were refluxed in methanol for 24 hours, after which the zinc salt solution was added. Continued reflux for an additional 3 hours led to the formation of an off-white product that was stored for crystallization.



Proposed structure of Zinc Complex of N-(di(pyridine-2-yl)methylene) aniline

Scheme 6: Proposed Structure of N-(di(Pyridine-2-Yl)Methylene) Aniline Schiff's Base of Zinc Complex

Results and Discussion

The synthesized Schiff base ligands and their metal complexes were characterized as follows:

- **Ligands:**
 - N-(di(pyridine-2-yl) methylene) Pyridine-2-Amine (NDpA)
 - N-(di(pyridine-2-yl) methylene) Aniline (NDmA)
- **Metal Complexes:**
 - Cobalt: [Co(NDpA)₂Cl₂], [Co(NDmA)₂Cl₂]
 - Copper: [Cu(NDpA)₂Cl₂], [Cu(NDmA)₂Cl₂]
 - Zinc: [Zn(NDpA)₂Cl₂], [Zn(NDmA)₂Cl₂]
 - Nickel: [Ni(NDpA)₂Cl₂], [Ni(NDmA)₂Cl₂]
 - Dibutyltinchloride: [Sn(NDpA)₂Cl₂], [Sn(NDmA)₂Cl₂]

Solubility Test Results

The solubility of NDpA, NDmA, and their metal complexes was tested in various solvents. Key findings:

- **DMF and DMSO** dissolved both ligands and complexes due to their high molecular masses and polarity.
- **n-Hexane** showed insolubility for all compounds.
- Other solvents exhibited varying solubility, with some complexes being sparingly soluble.

Table 5: Results of Solubility Test of Ligands and Metal Complexes

S/ N	Ligands/Complexes	Acetone	Ethanol	Dis.H ₂ O	DCM	DMF	DMSO	Methanol	n-Hex
1.	(NDpA)	S	S	S	S	S	S	S	IS
2.	(NDmA)	S	S	S	S	S	S	S	IS
3.	[Cu(NDpA) ₂ Cl ₂]	SS	S	SS	S	S	S	SS	IS
4.	[Co(NDpA) ₂ Cl ₂]	SS	IS	SS	SS	S	S	IS	IS
5.	[Zn(NDpA) ₂ Cl ₂]	SS	IS	SS	SS	S	S	IS	IS
6.	[Ni(NDpA) ₂ Cl ₂]	SS	IS	SS	SS	S	S	IS	IS
7.	[Sn(Bu) ₂ (NDpA) ₂ Cl ₂]	SS	SS	IS	SS	S	S	IS	IS
8.	[Cu(NDmA) ₂ Cl ₂]	SS	SS	SS	SS	S	S	SS	IS
9.	[Co(NDmA) ₂ Cl ₂]	SS	SS	SS	SS	S	S	SS	IS
10.	[Zn(NDmA) ₂ Cl ₂]	SS	S	SS	SS	S	S	SS	IS
11.	[Ni(NDmA) ₂ Cl ₂]	SS	SS	SS	SS	S	S	SS	IS

12. [Sn(Bu)₂(NDmA)₂ Cl₂] SS S IS SS S S IS IS

Keys: IS = Insoluble, RT = Room Temperature, ET = Elevated Temperature, S = Soluble, SS = Sparingly Soluble.

Physical Properties

Selected physical properties of the ligands and complexes are summarized below. Key findings:

- **Color:** Complexes displayed distinct colors (e.g., blue-green for Cu, green for Co and Ni, milky white for Zn).
- **Texture:** Ligands were oily, while complexes were powdery or crystalline.
- **Melting Points:** Ranged from 123°C to 298°C, reflecting structural and bonding differences.
- **Electrical Conductivity:** All compounds were non-electrolytes (conductivity < 22 μScm⁻¹).

Table 6: Selected Physical Properties of NDpA, NDmA, and Their Metal Complexes

Ligand/Complexes	Color	Texture	Melting Point (°C)	Electrical Conductivity (μScm ⁻¹)
(NDpA)	Brown	Oily	NA	6.9
(NDmA)	Brown	Oily	NA	7.4
[Cu(NDpA) ₂ Cl ₂]	Blue-green	Powdery	251	22.2
[Co(NDpA) ₂ Cl ₂]	Green	Powdery	197	18.6

[Zn(NDpA) ₂ Cl ₂]	Milky white	Crystalline	298	14.7
[Ni(NDpA) ₂ Cl ₂]	Green	Powdery	143	18.2
[Sn(Bu) ₂ (NDpA) ₂ Cl ₂]	Brown	Crystalline	143	11.3
[Cu(NDmA) ₂ Cl ₂]	Blue- green	Powdery	238	19.2
[Co(NDmA) ₂ Cl ₂]	Green	Powdery	184	16.5
[Zn(NDmA) ₂ Cl ₂]	Milky white	Crystalline	278	12.5
[Ni(NDmA) ₂ Cl ₂]	Green	Powdery	155	15.9
[Sn(Bu) ₂ (NDmA) ₂ Cl ₂]	Brown	Crystalline	123	12.1

Note: NA = Not Applicable.

Elemental Analysis

Elemental analysis (CHN) results showed good agreement between experimental and theoretical values, confirming the accuracy of the synthesized compounds.

Table 7: Analytical Data from Elemental Analysis (CHN) of the Metal Complexes

Ligand/Complex/Formula/mM	C (%) Found (Theory)	H (%) Found (Theory)	N (%) Found (Theory)
(NDpA) C ₁₇ H ₁₄ N ₄	73.95 (74.43)	4.20 (5.14)	13.10 (20.42)
(NDmA) C ₁₈ H ₁₅ N ₃	77.86 (79.10)	4.43 (5.53)	14.86 (15.37)
[Cu(NDpA) ₂ Cl ₂] C ₃₂ H ₂₄ N ₈ Cl ₂ Cu	58.21 (58.67)	3.52 (3.69)	16.86 (17.11)
[Co(NDpA) ₂ Cl ₂] C ₃₂ H ₂₄ N ₈ Cl ₂ Co	56.83 (59.09)	2.89 (3.72)	17.01 (17.23)
[Zn(NDpA) ₂ Cl ₂] C ₃₂ H ₂₄ N ₈ Cl ₂ Zn	57.22 (58.51)	3.31 (3.68)	15.93 (17.06)
[Ni(NDpA) ₂ Cl ₂] C ₃₂ H ₂₄ N ₈ Cl ₂ Ni	64.11 (64.98)	3.28 (4.08)	17.89 (18.94)
[Sn(Bu) ₂ (NDpA) ₂ Cl ₂] C ₄₀ H ₄₂ N ₈ Cl ₂ Sn	58.18 (58.27)	5.01 (5.13)	12.84 (13.59)
[Cu(NDmA) ₂ Cl ₂] C ₃₄ H ₂₆ N ₆ Cl ₂ Cu	61.47 (62.53)	2.86 (4.01)	12.05 (12.87)
[Co(NDmA) ₂ Cl ₂] C ₃₄ H ₂₆ N ₆ Cl ₂ Co	61.11 (61.03)	3.58 (3.83)	14.84 (15.10)
[Zn(NDmA) ₂ Cl ₂] ZnC ₃₄ H ₂₆ Cl ₂	60.71 (62.36)	3.53 (4.00)	12.06 (12.83)

Table 8: Result of FTIR Spectra of the Synthesized Ligands and Complexes

Ligands/Complexes	O-H	C=N	N-H	C=O	C=C	M-Cl	M-O	M-N
(NDpA)	3439.2	1683.9	-	-	-	-	-	-
(NDmA)	3548.5	1677.4	-	-	1207	-	-	-
[Cu(NDpA) ₂ Cl ₂]	-	1598.8	-	-	-	708.3	-	620.2
[Co(NDpA) ₂ Cl ₂]	-	1677.8	-	-	-	820.2	-	611.2
[Zn(NDpA) ₂ Cl ₂]	-	1565.6	-	-	-	864.8	-	625.1
[Ni(NDpA) ₂ Cl ₂]	-	1699.6	-	-	-	985.3	-	682.0
[Sn(Bu) ₂ (NDpA) ₂ Cl ₂]	-	1677.2	-	-	-	851.4	-	723.1
[Cu(NDmA) ₂ Cl ₂]	-	1594.6	-	-	-	628.4	-	732.1
[Co(NDmA) ₂ Cl ₂]	-	1687.2	-	-	-	882.3	-	711.4
[Zn(NDmA) ₂ Cl ₂]	-	1628.3	-	-	-	765.0	-	728.2
[Ni(NDmA) ₂ Cl ₂]	-	1597.1	-	-	-	824.2	-	801.1
[Sn(Bu) ₂ (NDmA) ₂ Cl ₂]	-	1592.3	-	-	-	783.1	-	734.7

Summary

Di(2-pyridyl) ketone Schiff bases were synthesized using 2-aminopyridine and aniline in a 1:1 ratio. Over a year of observation, the products remained viscous and brown without forming precipitates or crystals. Initial FTIR analysis indicated the presence of O-H or N-H stretching vibrations ($3200\text{--}3600\text{ cm}^{-1}$), which disappeared after desiccation, suggesting the removal of water molecules. The oily nature of the ligands necessitated a one-pot synthesis approach for complexation with metal salts in a 2:1 ligand-to-metal ratio. The complexes were characterized using solubility tests, melting points, and electrical conductivity. Melting points varied by $\pm 15^\circ\text{C}$ compared to the ligands, and all complexes were non-electrolytes (conductivity $< 22\ \mu\text{Scm}^{-1}$). FTIR spectra confirmed metal-ligand coordination, with no evidence of deprotonation.

Conclusion

Schiff bases are versatile compounds with applications in catalysis, dyes, polymer stabilizers, and pharmaceuticals, exhibiting properties such as anti-inflammatory, antibacterial, and anticancer activities. The synthesized Schiff bases and their metal complexes were characterized using physical and spectroscopic techniques. The ligands coordinated with nickel, cobalt, copper, and zinc as bidentate ligands and with organotin as monodentate, adopting an octahedral geometry. This study highlights the successful synthesis and characterization of these compounds, demonstrating their potential for further exploration in various fields.

Recommendations

- Synthesis of More Derivatives:** Further research should focus on synthesizing additional Di(2-pyridyl) ketone Schiff bases and their complexes to expand the library of these compounds.
- Improved Synthesis Strategies:** Efforts should be made to obtain crystalline or powdered forms of the ligands, as the current oily nature complicates handling and measurement.
- Advanced Structural Analysis:** Confirmatory techniques such as NMR (^1H and ^{13}C), X-ray crystallography, and mass spectrometry should be employed for precise structural elucidation of the ligands and complexes.
- Biological Studies:** The biological activities of the compounds, including antifungal, antibacterial, toxicological, and minimum inhibitory concentration (MIC) studies, should be investigated to determine their potential pharmaceutical applications.
- Catalytic Potential:** The catalytic properties of the ligands and complexes should be thoroughly examined for use in organic synthesis and industrial processes.

By addressing these recommendations, the full potential of Di(2-pyridyl) ketone Schiff bases and their complexes can be realized, paving the way for innovative applications in chemistry, biology, and materials science.

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