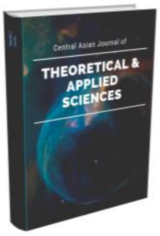


CENTRAL ASIAN JOURNAL OF
THEORETICAL AND APPLIED
SCIENCE

CENTRAL ASIAN
STUDIES

https://cajotas.centralasianstudies.org/index.php/CAJOTAS
Volume: 05 Issue: 08 | December 2024 ISSN: 2660-5317

Article

Synthesis and Spectroscopic Study of Azo-Schiff Base Compound and Its Complexes with Cobalt and Nickel

Dhelal Ayad Shaker[1*], **Haider A. Mahdi**[2]

1,2. Department of Chemistry, Collage of Science, University of Thi-Qar, Iraq
* Correspondence: dhelal.shaker@utq.edu.iq

Abstract: Azo compounds are known for their diverse applications in coordination chemistry, yet their potential with specific ligands remains underexplored. This study aimed to synthesize and characterize a new azo compound through a two-step reaction involving 4-nitroaniline and 2-hydroxynaphthaldehyde, followed by condensation with 4,4-diaminodiphenylmethane. The resulting ligand was then complexed with cobalt and nickel. The ligand and its metal complexes were characterized using elemental analysis, FT-IR, mass spectrometry, and ^{1}H NMR. The findings provide insights into the structural properties of the ligand and its complexes, contributing to the understanding of their potential in catalysis, materials science, or pharmaceutical applications.

Keywords: Azo compounds, Coordination chemistry, Ligand synthesis, Cobalt complexes, Nickel complexes

1. Introduction

In 1858 Peter Geriss made the discovery of this kind of organic chemical. Azo-Schiff. bases are. substances that include both azo and azomethine groups [1]. It has good donor qualities and is capable of forming stable compounds with transition metal ions [2]. The azomethine molecules are more recent than the azo. and Schiff base [3]. The locations of the two functional groups. The nitrogen atom's electron pair that is not in a bond [(-N=C-) & (-N=N-)] that had special physical and chemical characteristics qualities. Azo-Schiff blends can synchronize in a variety of its ability to coordinate with azomethine is the most important of them.

Secondly by employing both types of nitrogen [4], compounds (azomethine and azo) [5] and, finally by the use of only of azo nitrogen [6]. The dye and pigment industries depend on azo chemicals (-N=N-) in both their homocyclic and heterocyclic forms [7, 8]. It had a major effect on the manufacturing of pharmaceuticals and other medications [11], LCD color filters [12], and analytical chemistry [9, 10].

Depending on the chemical's characteristics and reaction conditions, there are two ways to create azo-Schiff base compounds. The Schiff base reaction is performed once the azo-moiety has been produced [13]. In the second technique, Schiff base is synthesized and coupled to produce azo compounds [14]. Numerous biological [15] and commercial applications, such as textile dye and photoelectric [16], have been made possible by these compounds and their combinations. Numerous compounds use azole groups, which are -N=N-linked to two carbon atoms. Aliphatic azo compounds like azobisisobutyronitrile (AIBN.) can function as radical initiators when alkenes are polymerized to form polymers.

Citation: Dhelal Ayad Shaker, Haider A. Mahdi. Synthesis and Spectroscopic Study of Azo-Schiff Base Compound and Its Complexes with Cobalt and Nickel. Central Asian Journal of Theoretical and Applied Science 2024, 5(8), 685-692.

Received: 3th Sept 2024
Revised: 14th Oct 2024
Accepted: 20th Nov 2024
Published: 28th Dec 2024

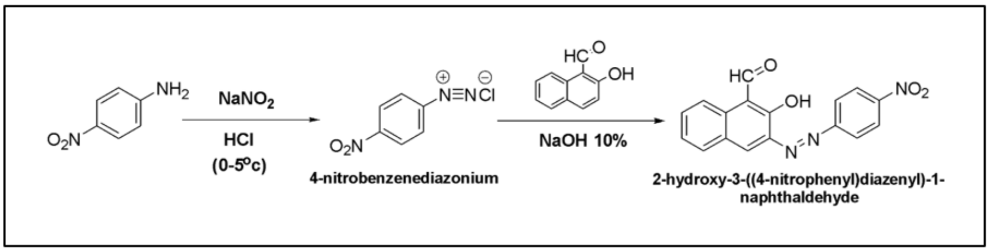
Aromatic azo compounds are used. as commercial colorants for clothing, plastics, cosmetics, and food and drink items, as well as biological stains and acid-base indicators. Many azo-dyes can be used as acid-base indicators since they can function as weak acids or bases. Methyl red, methyl orange and congo red are a few examples of these hues [17].

2. Materials and Methods

Every chemical and, reagent utilized in this investigation was of analytical grade and was acquired from Sigma-Aldrich. Using KBr pellets the)Cole-Parmer MP 200 (melting point equipment and the FT-.IR affinity (Shimadzu) spectrophotometer were used to evaluate the melting points of produced compounds. Although the Bruker 500MHZ instrument captured their 1HNMR in DMSO-d6, the internal standard is TMS.

Step1:

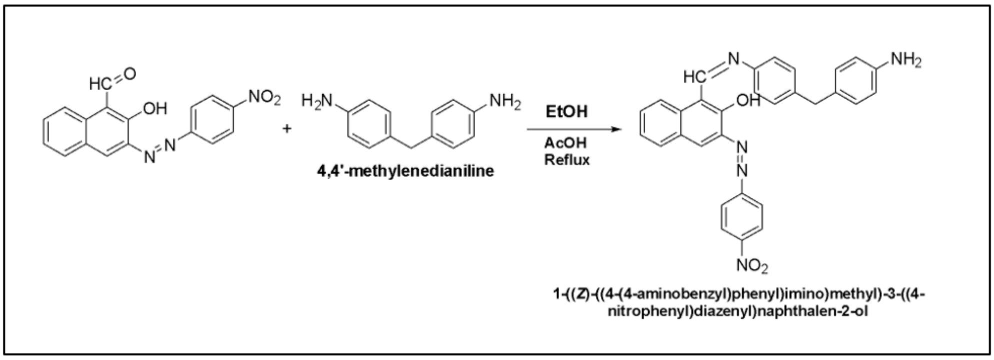
The Azo compound was made by dissolving 4-nitroaniline (0.01 moles, 0.94g.) in 6 ml of strong HCl and 14. ml of distilled water. To create diazonium salt, a stirring solution of sodium nitrite (0.01 moles, 0.80 g in 5 ml distilled water) was then added drop by drop at (0–5) co. a 0.01 mole (1.72 g) solution. To make 2-hydroxy-1-naphthaldehyde alkaline, the diazonium salt indicated above was added to 10 milliliters of (10%) NaOH Next, add diluted HCl to the created dye to convert it from sodium to hydrogen (to maintain a pH value of 6.5–7.5) to eliminate any substances that haven't reacted yet. After cleaning with distilled water and drying in a dryer, the product was recrystallized using ethanol as a solvent. suction for a few hours at 50°C [18]. According to scheme (1).



Scheme [1]

Step2:

The ligand was created through the reaction of 4,4'-methylenedianiline (0.198 g, 0.01 mol) with either compound (0.27 gm, 0.01 mol) and the mixture were then refluxed in 20 milliliters of ethanol with a little amount of glacial acetic acid acting as a catalyst. The precipitate mixture was acquired through filtering, ethanol washing, and drying. As seen in scheme (2).



Scheme [2]

Synthesis of complexes

The ligand was dissolved in 15 milliliters of ethanol to create the complexes. Next, the metal salts CoCl2.2H2O (0.001 mol) or NiCl2.6H2O (0.001 mol) were added dropwise to the ligand mixture. The mixture was then refluxed for three hours at a constant temperature of 70 to 80 °C while stirring continuously. The mixture was filtered, and the resultant participant was repeatedly rinsed with cold ethanol. Scheme (3) illustrates the Metal Complex Synthesis pathway. Complexes' melting point, hues, and yields are all included in Table (1).

3. Results and Discussion

Table 1. Tcontained all of the ligand and its complexes' physical characteristics, elemental microanalysis and atomic information.

No.	Chemical Formula	M.Wt	Color	M.p°c	Yield %
1	L($C_{30}H_{23}N_5O_3$)	502	Yellowish brown	257-259	80
2	[Ni(L)Cl_2]	631	orange	255 d*	77
3	[Co(L)Cl_2]	631	Light brown	253 d*	75

d* = decomposition degree

FT-IR spectral

The synthesized ligand FT-IR data was compiled into the table (2). As illustrated in figures (1), the FT-IR spectrum of the ligand revealed stretching characteristic vibration bands that appeared at (3256), (3026), (2936), (1644), (1542), and (1493) cm−1. These bands were caused by the υ (O-H) group, υ (C-H) aromatic group, υ (C-H) alaphtic group υ (C=N) azomethine group, υ (C=C) and υ (N=N) [19] group respectively.

Table 2. Infrared spectra of. Ligand and its metal complexes (υ cm^{-1})

compound	υ (OH)	υ (C-H) aromatic	υ (C-H) aliphatic	υ (C=N) azomethine	υ (C=C)	υ (N=N)
L	3256	3026	2936	1644	1542	1493
[Ni(L)Cl_2]	3441	3041	2924	1624	1544	1500
[Co(L)Cl_2]	3433	3028	2922	1624	1543	1500

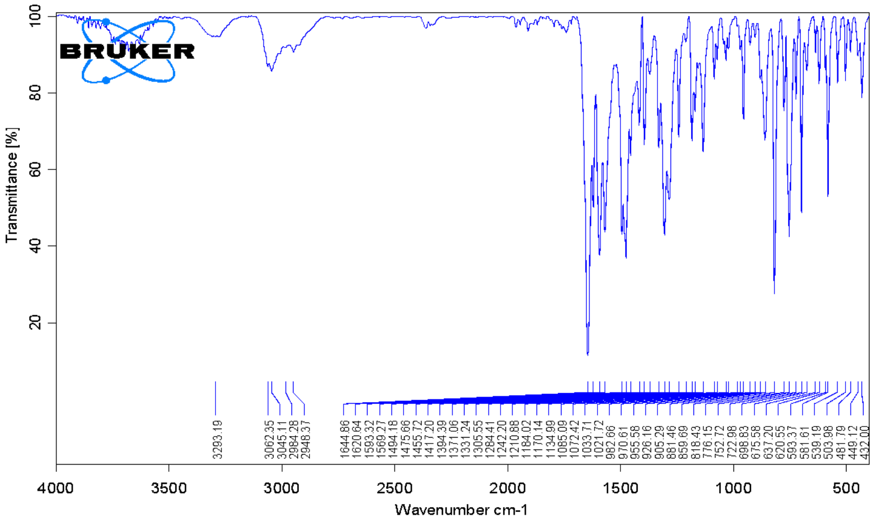


Figure 1. FT-.IR of L

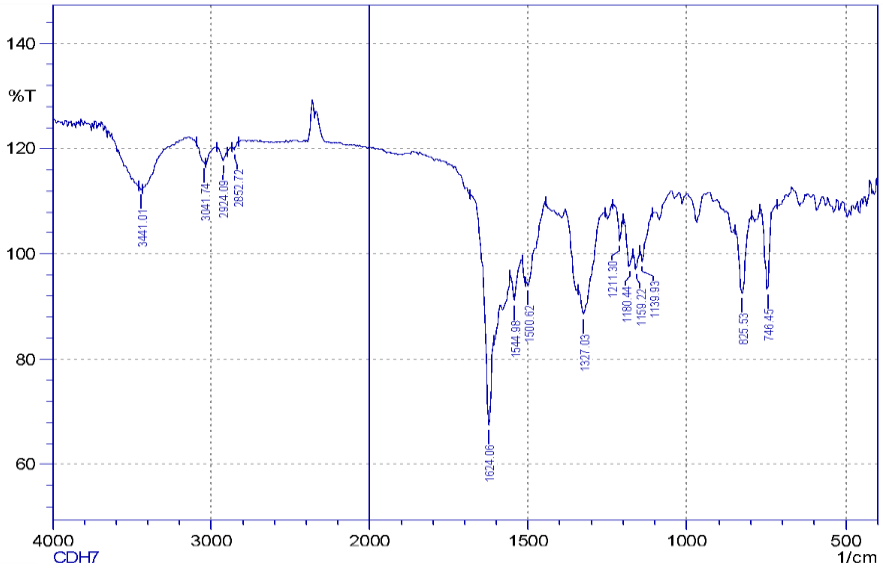


Figure 2. FT-.IR of [Ni(L)Cl_2]

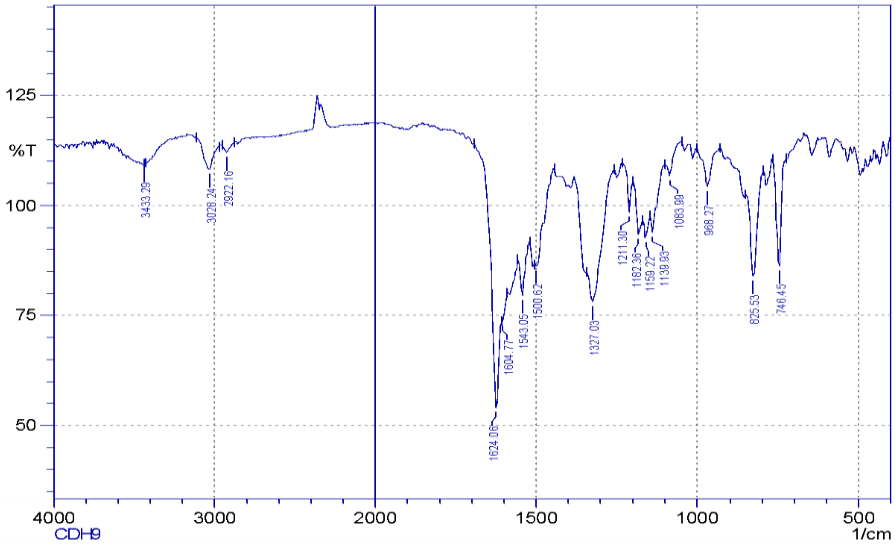
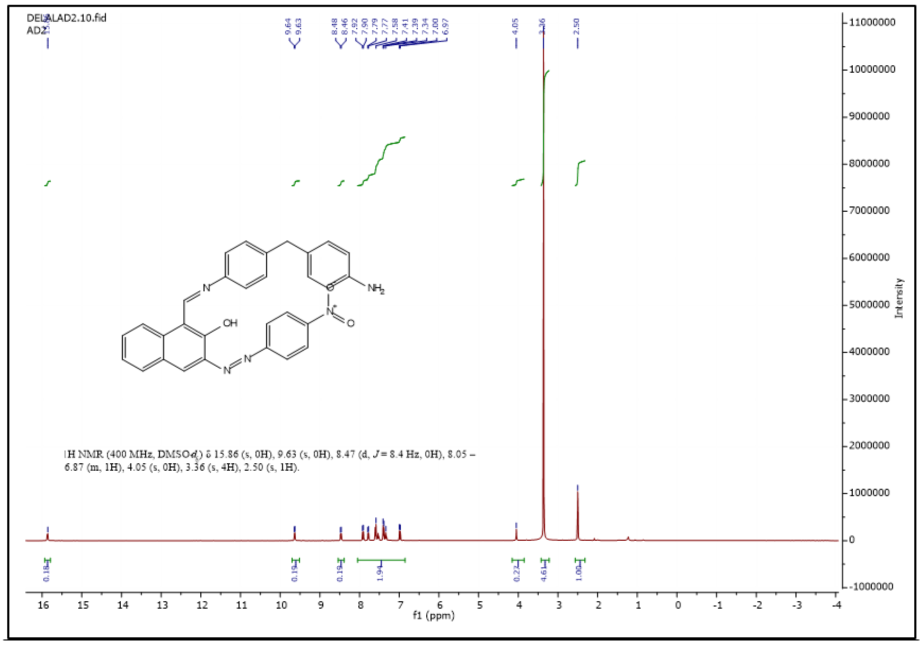


Figure 3. FT-IR of [Co(L)Cl_2]

$_1$H-NMR

The solvent (DMSO and H2O) caused two signals to appear in the ligands' 1H-NMR spectra at (2.5 and 3.36 ppm).

Two signals arising from the proton of the (CH2) and (NH2) groups respectively were detected in the 1H-NMR spectrum of the ligand (L1) at (4.05) and (6.9) ppm. Melti signals were detected at (7.00-8.48) ppm, owing to the aromatic group [20]. The azomethine groups showed a signal at (9.63) ppm and the phenolic, groups at (15.83) ppm. As depicted in Figure (2)



1H NMR (400 MHz, DMSO-d_6) δ 15.86 (s, 0H), 9.63 (s, 0H), 8.47 (d, J = 8.4 Hz, 0H), 8.05 – 6.87 (m, 1H), 4.05 (s, 0H), 3.36 (s, 4H), 2.50 (s, 1H).

Figure 4. $_1$H-NMR of the ligand

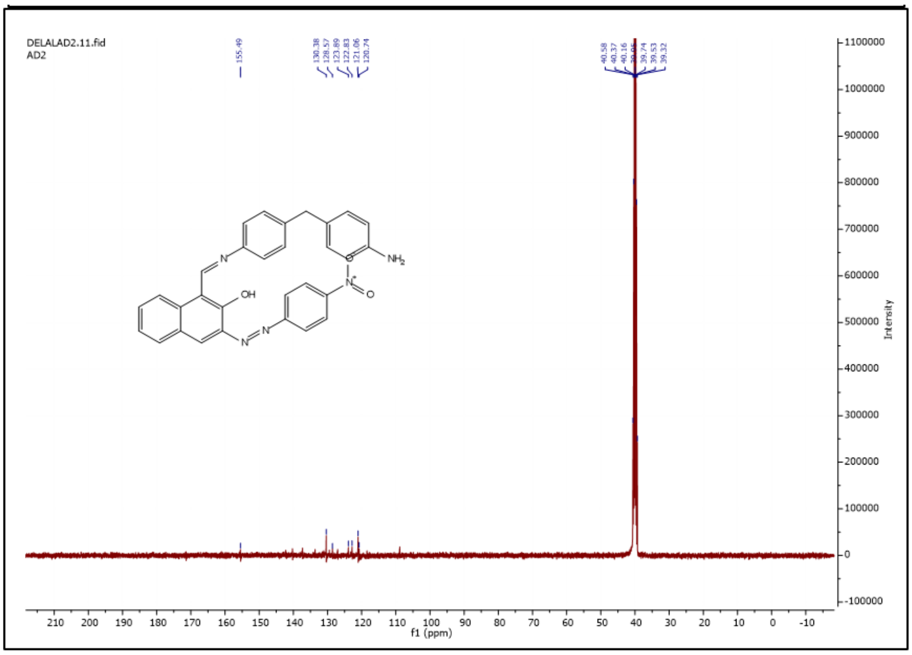


Figure 5. $_{13}$C-NMR of the ligand

The mass spectra

Molecular species have been successfully investigated using mass spectrometry; the pattern of the mass spectrum indicates the target compound's gradual decay, with a succession of peaks representing the different fragments. Their intensity provides a sense of how stable [20] Using, mass spectra recorded at room temperature (21 °C) in Table (3) and pictures (5–7) the stoichiometry of compounds was compared. Both the suggested structure and the synthetic chemicals matched the molecular ion fragment.

Table 3. Mass spectra of synthesized compound

Compound .	Calculated. mass	Obtain.mass (m/z)	Peak .assigned
L	502	503	M+1H
[Ni(L)Cl$_2$]	63	631	M$^+$
[Co(L)Cl$_2$]	631	631	M$^+$

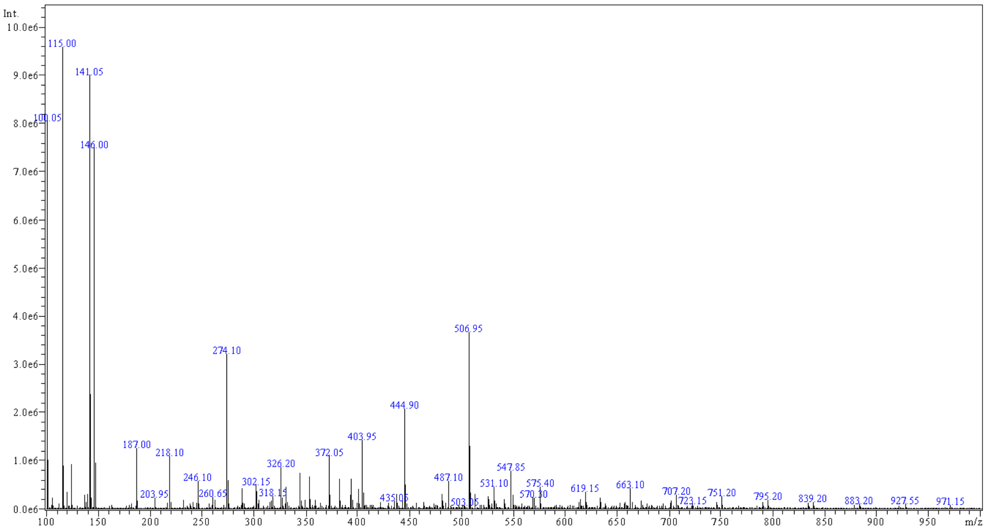


Figure 6. Mass spectra of L

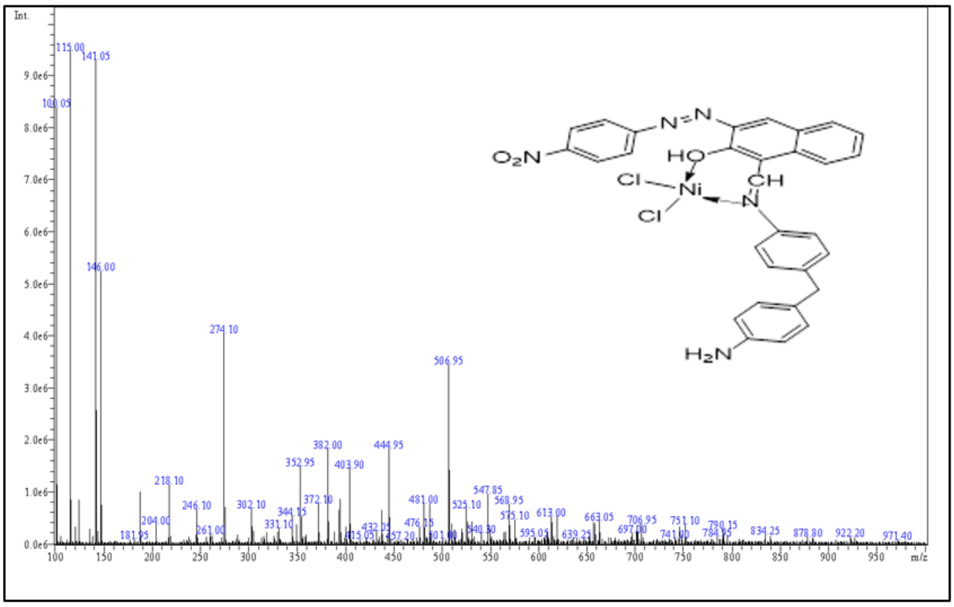


Figure 7. Mass spectra of [Ni(L)Cl2]

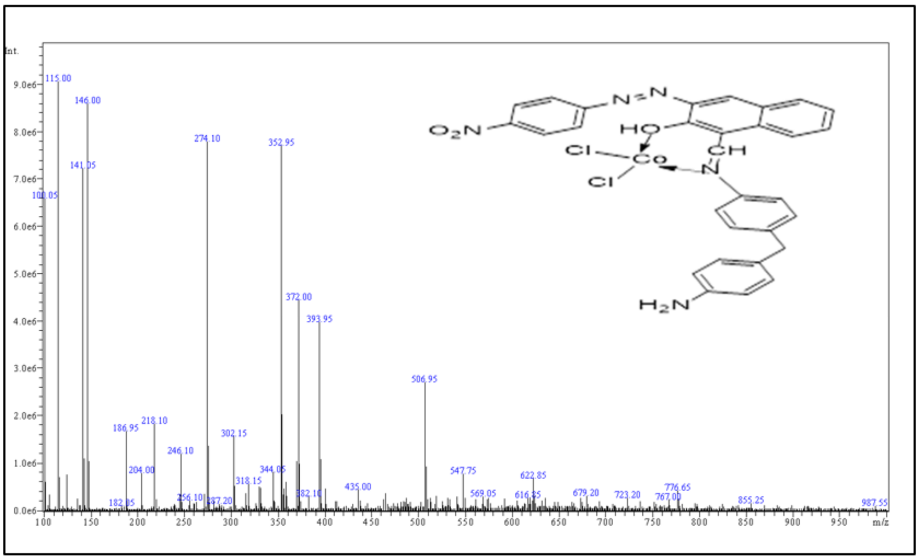


Figure 8. Mass spectra [Co(L)Cl₂]

4. Conclusion

The synthesized azo-Schiff base ligand and its cobalt and nickel complexes were successfully characterized using various spectroscopic and analytical techniques, including FT-IR, 1H-NMR, mass spectrometry, and elemental analysis. The ligand demonstrated the presence of key functional groups such as azomethine (-C=N-) and azo (-N=N-) groups, which contribute to its strong coordinating ability with transition metal ions. The metal complexes exhibited distinct physical and chemical properties, including thermal stability and unique spectral shifts indicative of coordination. These findings underline the ligand's potential in catalysis, materials science, and pharmaceutical applications due to its structural versatility and stability. Future research should focus on exploring the catalytic efficiency, biological activity, and electronic properties of these complexes in various industrial and medicinal contexts.

REFERENCES

[1] E. Yates and A. Yates, "Johann Peter Griess FRS (1829–88): Victorian Brewer and Synthetic Dye Chemist," Notes and Records of the Royal Society: Journal of the History of Science, vol. 70, no. 1, pp. 65–81, 2016.

[2] N. E. Borisova, M. D. Reshetova, and Y. A. Ustynyuk, "Metal-Free Methods in the Synthesis of Macrocyclic Schiff Bases," Chemical Reviews, vol. 107, no. 1, pp. 46–79, 2007.

[3] S. M. Mahdi and A. M. Ali, "Preparation and Identification of New Azo-Schiff Ligand with Its Complexes," Iraqi National Journal of Chemistry, vol. 15, no. 2, pp. 214–236, 2015.

[4] M. Sarigul, S. E. Kariper, P. Deveci, H. Atabey, D. Karakas, and M. Kurtoglu, "Multi-Properties of a New Azo-Schiff Base and Its Binuclear Copper (II) Chelate: Preparation, Spectral Characterization, Electrochemical, Potentiometric, and Modeling Studies," Journal of Molecular Structure, vol. 1149, pp. 520–529, 2017.

[5] M. Al-Noaimi, M. Sunjuk, M. El-Khateeb, S. F. Haddad, A. Haniyeh, and M. AlDamen, "Cis-Trans Isomerism in Mixed-Ligand Ruthenium (II) Complexes Containing Bis(Phosphine) and Azoimine Ligands," Polyhedron, vol. 42, no. 1, pp. 66–73, 2012.

[6] E. H. S. Lomax and J. F. Lomax, "The Synthesis and Characterization of Historical Novel Azo Pigments: Implications for Conservation Science," Heritage Science, vol. 7, no. 1, p. 101, 2019.

[7] Z. A. Sallal and H. T. Ghanem, "Synthesis and Identification of New Oxazepine Derivatives Bearing Azo Groups in Their Structures," Iraqi Journal of Science, vol. 59, no. 1, pp. 1–10, 2018.

[8] B. Abd El-Wahaab, K. Elgendy, and A. El-Didamony, "Synthesis and Characterization of a New Azo-Dye Reagent for Spectrophotometric Determination of Samarium(III) in Industrial and Blood Samples," Chemical Papers, vol. 74, no. 5, pp. 1439–1448, 2020.

[9] S. M. H. Al-Majidi and M. G. A. Al-Khuzaie, "Synthesis and Characterization of New Azo Compounds Linked to 1,8-Naphthalimide and Their Use as Acid-Base Indicators," Iraqi Journal of Science, vol. 60, no. 3, pp. 2341–2352, 2019.

[10] M. Roldo, E. Barbu, J. F. Brown, D. W. Laight, J. D. Smart, and J. Tsibouklis, "Azo Compounds in Colon-Specific Drug Delivery," Expert Opinion on Drug Delivery, vol. 4, no. 5, pp. 547–560, 2007.

[11] N. Hu, "Azo Dye Used for a Color Filter of an LCD," U.S. Patent, 2016.

[12] A. A. Jarrahpour and M. Zarei, "Synthesis of Novel Azo-Schiff Base Bis[5-(4-Methoxyphenylazo)-2-Hydroxy-3-Methoxybenzaldehyde]-1,2-Phenylenediamine," Molbank, vol. 2004, no. M377, pp. 1–5, 2004.

[13] W. Al Zoubi, A. A. S. Al-Hamdani, S. D. Ahmed, and Y. G. Ko, "A New Azo-Schiff Base: Synthesis, Characterization, Biological Activity, and Theoretical Studies of Its Complexes," Applied Organometallic Chemistry, vol. 32, no. 8, p. e3895, 2018.

[14] M. Gulcan, S. Özdemir, A. Dündar, E. Ispir, and M. Kurtoğlu, "Mononuclear Complexes Based on Pyrimidine Ring Azo Schiff-Base Ligand: Synthesis, Characterization, Antioxidant, Antibacterial, and Thermal Investigations," Zeitschrift für Anorganische und Allgemeine Chemie, vol. 640, no. 9, pp. 1754–1761, 2014.

[15] M. K. Sadigh, M. Hasani, and J. Rahimpour, "Studying Media Polarity Effects on the Photo-Physical Behaviors of Organometallic Complexes with Azo-Containing Schiff-Base Ligands," Zeitschrift für Physikalische Chemie, vol. 232, no. 11, pp. 1807–1820, 2018.

[16] A. A. El-Sherif, M. R. Shehata, M. M. Shoukry, and M. H. Barakat, "Synthesis, Characterization, Equilibrium Study, and Biological Activity of Cu(II), Ni(II), and Co(II) Complexes of Polydentate Schiff Base Ligand," Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, vol. 96, pp. 889–897, 2012.

[17] K. F. Mohammed and H. A. Hasan, "Synthesis, Chemical and Biological Activity Studies of Azo-Schiff Base Ligand and Its Metal Complexes," Chemical Methodologies, vol. 12, no. 9, pp. 905–913, 2022.

[18] N. O. Tapabashi, N. I. Taha, and M. N. El-Subeyhi, "Synthesis and Characterization of Some New Azo-Schiff Bases as Energy-Rich Candidate Compounds Derived from 1,5-Diaminoanthraquinone by Fusion Method," Kirkuk University Journal: Scientific Studies, vol. 16, no. 2, pp. 51–63, 2021.

[19] A. Prakash, B. K. Singh, H. K. Rajour, and N. Bhojak, "Synthesis, Characterization, and Bioactivities of New Schiff Bases with Main Group Metal Ions," Main Group Metal Chemistry, vol. 33, no. 4-5, pp. 183–200, 2010.

[20] E. Khalil, W. Mahmoud, and G. Mohamed, "Synthesis, Spectral, Thermal, and Biological Studies of Some Transition and Inner Transition Schiff Base Metal Complexes," Egyptian Journal of Chemistry, vol. 64, no. 7, pp. 3555–3571, 2021.