

SYNTHESIS AND CHARACTERIZATION OF BENZIL CROWN CYCLIC SCHIFF BASE LIGAND AND ITS METAL COMPLEXES

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ABSTRACT. The reaction between benzil and hexamethylenediamine formed a new ligand [L], [(1Z,3Z)-2,3-diphenyl-5,6,7,8,9,10-hexahydro-1,4-diazecine], of the type [N₂], was synthesized by the condensation reaction through Schiff base reaction between benzil and hexamethylenediamine. The new Schiff base ligand reacts with Mnⁿ, Ni^m and Coⁿ metal ions to give the complexes with the general formula: [M(L)Cl₂]. The elemental investigations have been used to analyze the ligand and its complexes by CHN, FT-IR, UV-Vis, TLC, mass spectrum, melting point with the study of biological activity to the formed compounds. From the data obtained, the proposed molecular structure adopts square planar structure about the metal ions. The study reveals the formation of a new ligand type [N₂] and its metal ion complexes with square planar structures metal:ligand ratio of 1:1, which can be employed in a variety of fields such as medicine and industry.

KEY WORDS: Benzil, Hexamethylenediamine, Metal complexes, Square planar structure

INTRODUCTION

Due to their many characteristics and applications, Schiff bases are an important class of chemicals. They are used as biological system models [1] and as catalysts [2] in a variety of chemical and photochemical reactions [3], these compounds have gotten a lot of attention. Antibacterial [4], antifungal [5], and anticancer [6] properties have been observed for this sort of substance. The structural elucidation of Schiff base spectra was investigated [7]. H₂N(CH₂)₆NH₂ is the formula for hexamethylenediamine, an organic molecule that made up of a hexamethylene hydrocarbon chain with amine functional groups, the amine odor is strong in the colorless solid (yellowish in certain commercial samples). Annually, over 1 billion kg are manufactured [8]. It is nearly entirely employed to make polymers, an application that takes advantage of its structure. The chemical molecule benzil also known as (1,2-diphenylethane-1,2-dione) has the formula (C₆H₅CO)₂, which is commonly written as (PhCO)₂. One of the most frequent diketone is a yellow solid. Most benzil is used in the free-radical curing of polymer networks. Ultraviolet radiation decomposes benzil, generating free-radical species within the material, promoting the formation of cross-links. Benzil is a potent inhibitor of human carboxylesterases, enzymes involved in the hydrolysis of carboxylesters and many clinically used drugs [9]. The majority of benzil is primarily used in the curing of polymer networks by free radicals, It decomposes in the presence of ultraviolet radiation, generating free radical species that encourage the formation of cross-links within the material. Human carboxylesterases, which are enzymes involved in the hydrolysis of carboxyl esters, are inhibited by benzyl and they are found in many therapeutically utilized medications [10]. The manuscript includes the description of the synthesis and physical

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characterization of [(1Z,3Z)-2,3-diphenyl-5,6,7,8,9,10-hexahydro-1,4-diazecine] ligand [N₂] type in the ratio of 1:1 (benzil and hexamethylenediamine), and its new square planar metal ion complexes. This proposal was supported by results obtained from analytical techniques such as FT-IR, UV-Vis, CHN elemental analysis, TLC, and mass spectrometry, with (1:1) metal:ligand ratio forming a new bands of (M-N) of a new compounds by the condensation reaction which has been characterized by FT-IR, UV-Vis, elemental analysis, thin layer chromatography (TLC), mass spectrum and study the biological activity for the ligand and its complexes.

EXPERIMENTAL

Synthesis of the [N₂] Schiff base ligand

Equimolar quantities (2.7 g, 12.84 mmol) of benzil and (1.5 g, 12.90 mmol) hexamethylenediamine with the addition of 5-6 drops of HBr, primary amine was dissolved in ethanol (40 mL). The mixture was cooked at (110 °C) in a reflux cooker for (4 h). Filtration was used to isolate the precipitate, which was recrystallized from ethanol dried under vacuum. Yield (2.2 g, 82 %), (m.p. 155 °C).

Synthesis Mnⁿ complex

Equimolar quantities (1.3 g, 4.48 mmol) of the ligand and (0.9 g, 4.55 mmol) MnCl₂·4H₂O dissolved in methanol (40 mL). The mixture was cooked with a low temperature in a reflux cooker (110 °C for 2 h). Filtration was used to isolate the precipitate that was re-crystallized from methanol and dried. Yield (0.8 g, 62%), (m.p. 190 °C) (Table 1).

Table 1. Showed the characteristics of the ligand and its metal complexes.

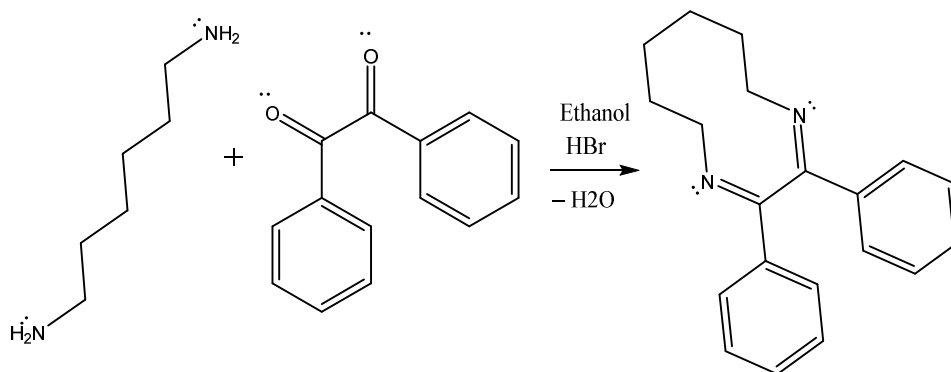
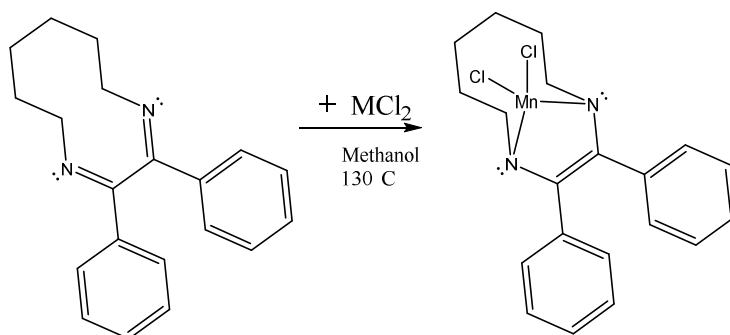
No.	Compounds	M.wt. (g/mol)	Yield %	Colour	m.p. °C	Found (calc. %)			
						M	C	H	N
1	C ₁₉ H ₂₀ N ₂	290.41	82	Yellow	155	-	(82.72)	(7.64)	(9.65)
						-	80.05	6.61	9.86
3	C ₁₉ H ₂₀ Cl ₂ MnN ₂	416.25	62	Mustered	190	(13.20)	(57.71)	(5.33)	(6.73)
						11.22	55.03	4.44	5.00
3	C ₁₉ H ₂₀ Cl ₂ NiN ₂	420.00	71	Green	230	(13.97)	(57.19)	(5.28)	(6.67)
						13.82	55.12	4.00	5.11
4	C ₁₉ H ₂₀ Cl ₂ CoN ₂	420.24	66	Pale Green	177	(14.02)	(57.16)	(5.28)	(6.67)
						13.01	53.83	3.81	5.10

The same way has been used to prepare the Ni, Co metal ion complexes and their data shown in Table 1.

RESULTS AND DISCUSSION

The [N₂] type ligand was produced by reacting benzil with hexamethylenediamine in a 1:1 ratio in acidic conditions (Scheme 1).

The reaction of metal chlorides occurs according to Scheme 2 which shows the synthetic route of the ligand type [N₂]. The yield of the ligand and its complexes ranges from (62% to 71%). CHN, FT-IR, UV-Vis, melting point, mass spectrum, and thin-layer chromatography TLC were used to describe the compounds.


 Scheme 1. Synthetic route for [N₂] type ligand.

 Scheme 2. Synthetic route for the complexes, where the [M = Mn^{II}, Ni^{II} and Co^{II}].

Ligand's FT-IR spectrum

In the FT-IR spectrum of hexamethylenediamine (Figure 1A) the two bands at the range of (3400-3420 cm⁻¹) are due to the $\nu(\text{NH}_2)$ [11], while at the same time there is a strong peak at (1700 cm⁻¹) which assign to the $\nu(\text{C}=\text{O})$ [12] is belong to benzil (Figure 1B), these peaks are vanish in the spectrum of the free ligand (Figure 1A).

As a result of the coordination between hexamethylenediamine and benzil, a new peak at (1500 cm⁻¹) that belongs to the $\nu(\text{C}=\text{N})$ [13] has appeared. and replaced by a new peak at (1500 cm⁻¹) which is belongs to the $\nu(\text{C}=\text{N})$ as a result of the coordination between hexamethylenediamine and benzil [14]. In contrast to the spectra of the unbound ligand, which shows Schiff base reaction, a new peak at (1500 cm⁻¹) belongs to the $\nu(\text{C}=\text{N})$ as a result of coordination between hexamethylenediamine and benzil. As a result of the coordination action and the delocalization of electron pi density of the ring at (3077 cm⁻¹), the bands owing to the phenyl group [15] of the benzil are transferred to a higher frequency as shown in Table 2.

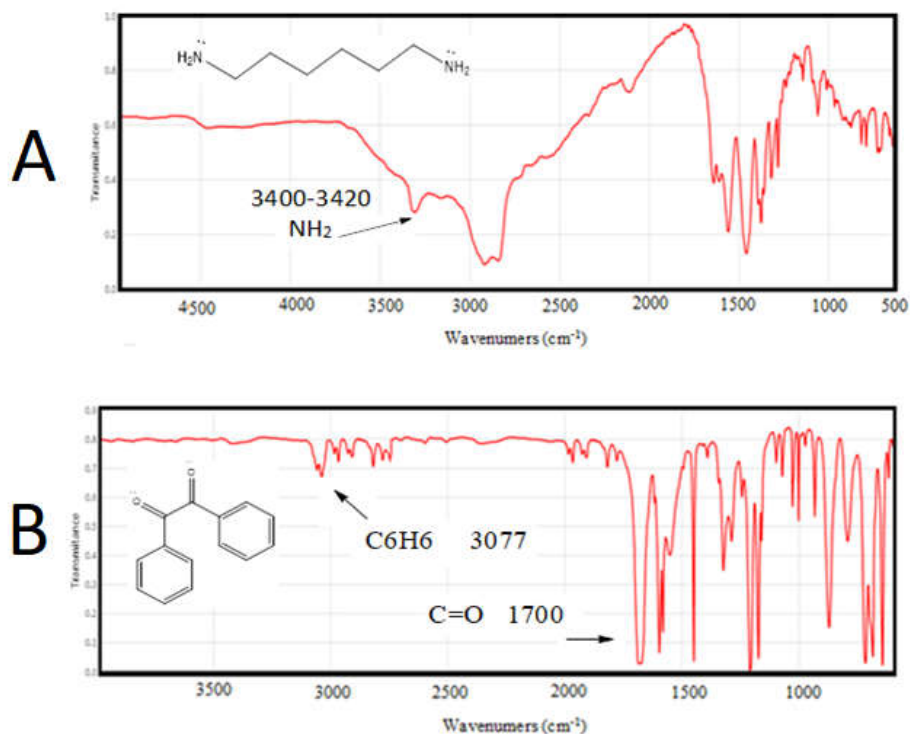


Figure 1. (A) Hexamethylenediamine's FT-IR spectrum and (B) FT-IR spectrum of benzil.

Mn complex's FT-IR

There is a significant band at (1500 cm^{-1}) assign to $\nu(\text{C}=\text{N})$ of the (ligand-metal) ion interface as a result of the coordination between both of them as shown in Figure 2A. This band has been pushed to a higher frequency in comparison to the spectrum of the Mn complex (Figure 2B). The characteristic new created band at (500 cm^{-1}) was ascribed to the $\nu(\text{Mn}-\text{N})$ [16] for the produced complexes in Table 2.

Table 2. FT-IR spectral data for the ligand and its complexes.

No.	Compounds	$\nu(\text{NH}_2)$ cm^{-1}	$\nu(\text{C}_6\text{H}_6)$ ring cm^{-1}	$\nu(\text{C}=\text{O})$ cm^{-1}	$\nu(\text{C}=\text{N})$ cm^{-1}	$\nu(\text{M}-\text{N})$ cm^{-1}
A	Hexamethylenediamine	3400-3420	-	-	-	-
B	Benzil	-	3077	1700	-	-
1	$\text{C}_{19}\text{H}_{20}\text{N}_2$	-	3100	-	1500	-
2	$\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{MnN}_2$	-	3095	-	1540	500
3	$\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{NiN}_2$	-	3087	-	1570	490
4	$\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{CoN}_2$	-	3070	-	1520	480

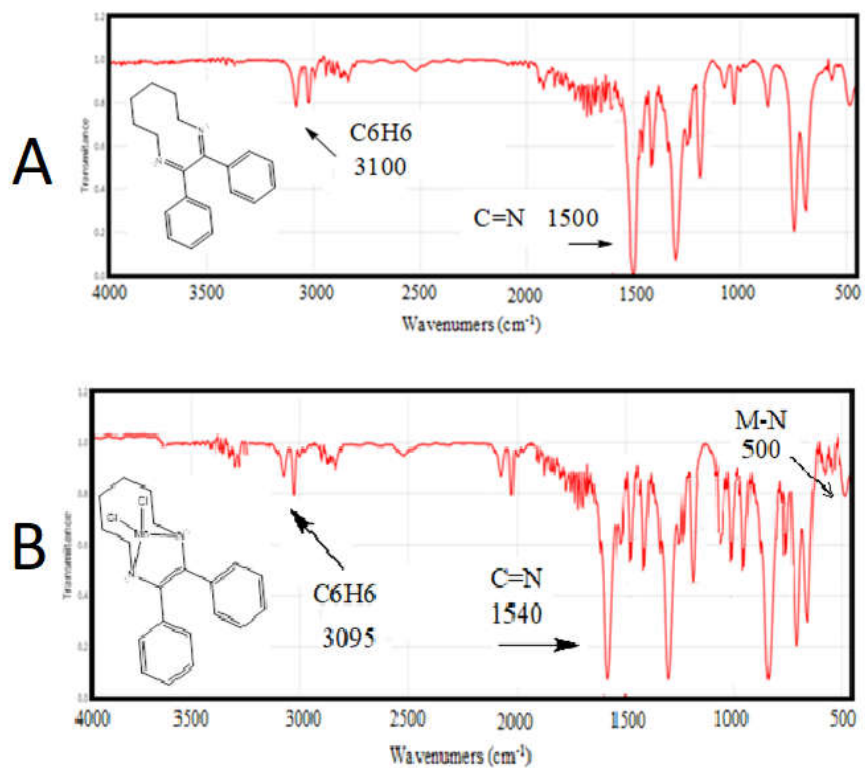


Figure 2. (A) FT-IR spectrum of the free ligand. (B) Mn^{II} complex's FT-IR spectrum.

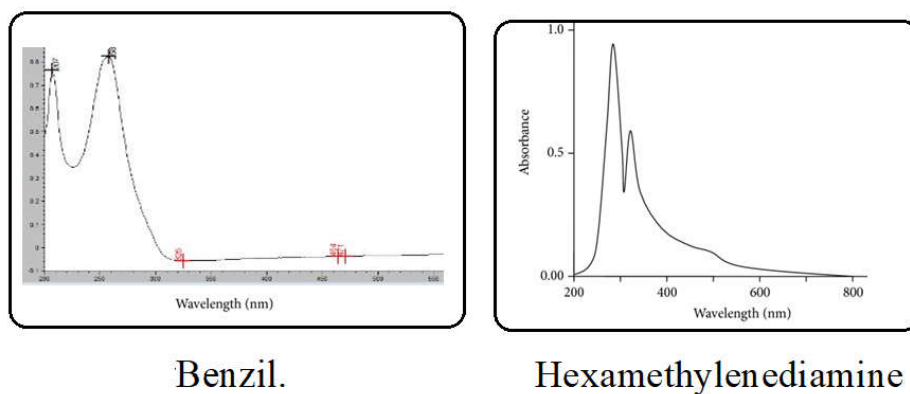


Figure 3. The starting materials's (benzil and hexamethylenediamine) UV-Vis spectrum.

The UV-Vis spectrum for the ligand

The electronic spectra of the complexes were obtained using (UV-Visible) spectrophotometer type Shimadzu in the range (900-200 nm) by using quartz cells of (1.0 cm) length and concentration of (10^{-3} M) in DMSO solvent. The UV-Vis spectrum for the ligand (Figure 3A) shows two peaks at the ligand field which are due to the ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions, these two peaks are differ from the ligand field transitions of the starting materials (benzyl and hexamethylenediamine) as shown in Figure 3. all the data are in Table 1.

In the UV-Vis spectrum (Figure 3A) two significant absorption peaks may be seen at (225 nm), (44444 cm^{-1}), ($\epsilon_{\text{max}} = 1640 \text{ molar}^{-1} \cdot \text{cm}^{-1}$) and (265 nm), (37735 cm^{-1}), ($\epsilon_{\text{max}} = 1100 \text{ molar}^{-1} \cdot \text{cm}^{-1}$) which are due to the ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions respectively [17] (Table 3).

Table 3. The ligand and its complexes' electronic spectrum data are listed in.

No.	Compounds	Band Position λ_{nm}	Electronic transition(cm^{-1})	$\epsilon_{\text{max}} (\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$	Assignme nt	Suggested configuration
A	hexamethylene diamine)	290	34482	900	$\pi \rightarrow \pi^*$	
		350	28571	700	$n \rightarrow \pi^*$	
B	Benzil	215	46511	780	$\pi \rightarrow \pi^*$	
		260	38461	8100	$n \rightarrow \pi^*$	
1	$\text{C}_{19}\text{H}_{20}\text{N}_2$	225	44444	1640	$\pi \rightarrow \pi^*$	
		265	37735	1100	$n \rightarrow \pi^*$	
2	$\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{MnN}_2$	235	42553	1590	$\pi \rightarrow \pi^*$	
		270	37037	900	$n \rightarrow \pi^*$	
3	$\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{NiN}_2$	565	17699	100	$d-d$	S.P
		240	41666	1400	$\pi \rightarrow \pi^*$	
		290	34482	720	$n \rightarrow \pi^*$	
4	$\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{CoN}_2$	510	19607	110	$d-d$	S.P
		260	38461	1450	$\pi \rightarrow \pi^*$	
		295	3898	820	$n \rightarrow \pi^*$	
		620	16129	100	$d-d$	S.P

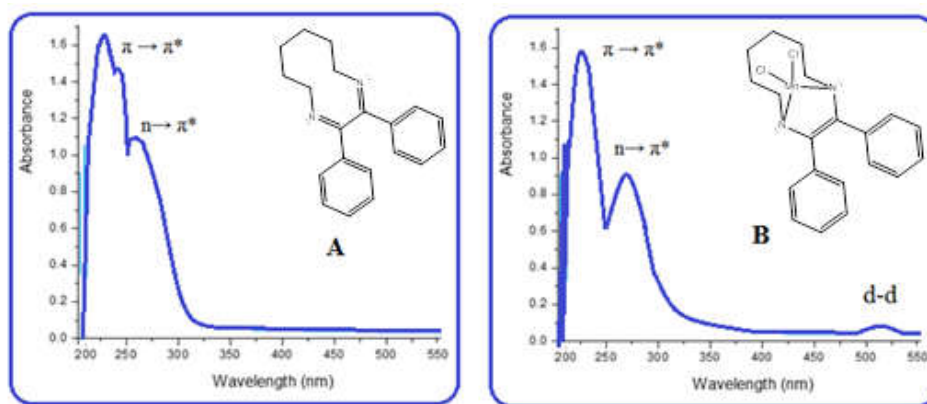


Figure 4. The ligand's UV-Vis spectrum (A) and the Mn ion complex's UV-Vis spectrum (B).

UV-Vis of the Mn complex

The Manganese complex spectrum (Figure 4B) discovered two notable peaks in the ranges of (235 nm), (42553 cm^{-1}), ($\epsilon_{\text{max}} = 1590 \text{ molar}^{-1} \cdot \text{cm}^{-1}$) and (270 nm), (37037 cm^{-1}), ($\epsilon_{\text{max}} = 900 \text{ molar}^{-1} \cdot \text{cm}^{-1}$), respectively [18]. The *d-d* electronic transition (${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$) is credited to the visible area's third peak, which was discovered at (565 nm), (17699 cm^{-1}) ($\epsilon_{\text{max}} = 100 \text{ molar}^{-1} \cdot \text{cm}^{-1}$). The electronic spectral data are listed in Table 3.

Thin layer chromatography (TLC) of the ligand and its complexes

After the sample has been applied on the plate, a solvent or solvent mixture (known as the mobile phase) is drawn up the plate via capillary action. Because different analytes ascend the TLC plate at different rates, separation is achieved.

The TLC for the complexes revealed the appearance of new spots with varied characteristics of R_f than the R_f of the ligand. Metal ion complexes of Mn, Ni, and Co revealed the development of the complexes. Because the positions of the spots in metal ion complexes varies from the position of the ligand's spot (Table 4).

Table 4. The [N₂] ligand T.L.C. complexes.

No.	Structural formula	Range of R_f (mm)
1	$\text{C}_{19}\text{H}_{20}\text{N}_2$	1.8
2	$\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{MnN}_2$	3.5
3	$\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{NiN}_2$	2.9
4	$\text{C}_{19}\text{H}_{20}\text{Cl}_2\text{CoN}_2$	4.9

Mass spectrum

The spectrum of the ligand has a peak that corresponds to the molecular ion (m/z 289), showing that the base peak represents relative abundance. The other peaks indicate pieces of ions. The molecular structure of the ligand is frequently revealed by the type of the fragments (Figure 5).

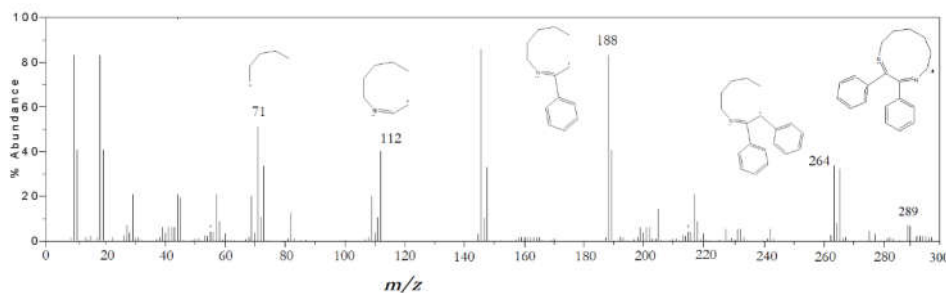


Figure 5. Mass spectrum of the ligand.

Biological processes

The antibacterial activity of substances was assessed in vitro using the agar ditch method against *S. aureus*, *S. facials*, and *E. coli* [19]. The stock solution was made by dissolving (40 mg) of each component in 1 mL of N,N-dimethylformamide (DMF), from which two-fold serial dilutions were obtained. The inhibition diameter of the ligand and its complexes with three different concentrations (25%, 50%, and 100%) for (24 h) has been shown in (25%, 50 h) has been shown in Table 5 [20].

Table 5. Zone of inhibition for antibacterial action.

No.	Structural formula	<i>E. Coli</i>			<i>S. Aureus</i>			<i>S. Facials</i>		
		25 %	50 %	100 %	25 %	50 %	100%	25 %	50 %	100%
1	C ₁₉ H ₂₀ N ₂	12	12	16	11	10	19	10	12	15
2	C ₁₉ H ₂₀ Cl ₂ MnN ₂	17	30	34	15	21	31	15	21	26
3	C ₁₉ H ₂₀ Cl ₂ NiN ₂	15	18	21	10	12	19	14	22	30
4	C ₁₉ H ₂₀ Cl ₂ CoN ₂	18	21	29	11	15	19	12	19	25
	DMF	-	-	-	-	-	-	-	-	-

CONCLUSION

The ligand [N₂] type was made by generating a novel complex with Mn, Ni, and Co metal ions through a Schiff base reaction between benzil and hexamethylenediamine, and it has a square planar structure around the metal ions. Spectroscopic tests have confirmed this. The type of the fragments in the mass spectrum can often reveal the ligand's molecular structure. In compared to the free ligand's spot, the TLC for the complexes displays different spots. The visible area's third peak for complexes in the UV-Vis reveals ligand-metal coordination, and the primary transitions assign to the square planar structure around the metal ions. While the FT-IR spectra the $\nu(\text{C}=\text{N})$ and $\nu(\text{NH}_2)$ of benzil and hexamethylenediamine respectively has been diapered and replaced by a new band $\nu(\text{C}=\text{N})$ in the range of (1500-1520) for the complexes. The antibacterial activity of the produced compounds [ligands and complexes] examined in DMF was shown to be reliant on both the Schiff base substituent and the solvent medium. Because it demonstrated more inhibitory effect at lower concentrations examined. Gram-positive bacteria were inhibited by all of the produced chemicals. As a result, these compounds can be utilized to make narrow-spectrum antibiotics for the treatment of gram-positive and gram-negative bacterial infections, particularly *S. aureus*, *S. facials*, and *E. coli*.

REFERENCES

1. Banik, I.; Becker, F.; Banik, K. Stereoselective synthesis of β -lactams with polyaromatic imines: Entry to new and novel anticancer agents. *J. Med. Chem.* **2003**, *46*, 12-15.
2. Al-Khafaji, Y.; Abd Alrazzak, N.; Saad, T.; Abbas, S.; Merdan, M. Aluminium complexes as catalysts for ring-opening polymerization of ϵ -caprolactone bearing Schiff base ligands derived from 4,4'-methylenebis (2,6-diisopropylaniline). *J. Phys. Conf. Ser.* **2019**, 1234, 012055.
3. Da Silva, M.; da Silva, L.; Modolo, V.; Alves, B.; de Resende, A.; Martins, V.; de Fátima, Â. Schiff bases: A short review of their antimicrobial activities. *J. Adv. Res.* **2011**, *2*, 1-8.
4. Shi, L.; Ge, M.; Tan, H.; Li, H.-Q.; Song, C.; Zhu, L.; Tan, X. Synthesis and antimicrobial activities of Schiff bases derived from 5-chloro-salicylaldehyde. *Eur. J. Med. Chem.* **2007**, *42*, 558-564.
5. Jarrahpour, A.; Khalili, D.; De Clercq, E.; Salmi, C.; Brunel, M. Synthesis, antibacterial, antifungal and antiviral activity evaluation of some new bis-Schiff bases of isatin and their derivatives. *Molecules* **2007**, *12*, 1720-1730.
6. T'ang, A.; Lien, J.; Lai, M. Optimization of the Schiff bases of N-hydroxy-N'-aminoguanidine as anticancer and antiviral agents. *J. Med. Chem.* **1985**, *28*, 1103-1106.
7. Schilf, W.; Szady-Chelminiecka, A.; Grech, E.; Przybylski, P.; Brzezinski, B. Spectroscopic studies of new Schiff and Schiff-Mannich bases of ortho-derivatives of 4-bromophenol. *J. Mol. Struct.* **2002**, *643*, 115-121.

8. Lee, J.; Lee, Y.; Kim, S.; Kwon, E.; Lin, Y. A. Catalytic production of hexamethylenediamine from renewable feedstocks. *Korean J. Chem. Eng.* **2021**, *38*, 1079-1086.
9. Wadkins, M.; Hyatt, L.; Wei, X.; Yoon, K.P.; Wierdl, M.; Edwards, C.; Morton, L.; Obenauer, J.C.; Damodaran, K.; Beroza, P. Identification and characterization of novel benzil (diphenylethane-1,2-dione) analogues as inhibitors of mammalian carboxylesterases. *J. Med. Chem.* **2005**, *48*, 2906-2915.
10. Hatfield, J.; Umans, A.; Hyatt, L.; Edwards, C.; Wierdl, M.; Tsurkan, L.; Taylor, M. R.; Potter, P. M. Carboxylesterases: General detoxifying enzymes. *Chem. Biol. Interact* **2016**, *259*, 327-331.
11. Wang, X.; Zhao, Q.; Al-Khafaji, Y.; Mo, S.; Prior, J.; Elsegood, R.; Redshaw, C., Organoaluminium complexes derived from anilines or Schiff bases for the ring-opening polymerization of ϵ -caprolactone, δ -valerolactone and rac-lactide. *Eur. J. Inorg. Chem.* **2017**, *2017*, 1951-1965.
12. Varghese, T.; Panicker, Y.; Pillai, M.; Sheena, Y.; Raju, K.; Manojkumar, T.; Bielenica, A.; Van Alsenoy, C. Spectroscopic investigations and computational study of 4-(3-bromopropyl)-4-azatricyclo [5.2.2.0_{2,6}] undecane-3,5,8-trione. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2010**, *76*, 513-522.
13. Baran, J.; Viera, I.; Torre, H. Vibrational spectra of the Cu(II) complexes of L-asparagine and L-glutamine. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2007**, *66*, 114-117.
14. Sultan, S.; Alsalihi, E.; Al-Fahdawi S.; Jarad, J. New Schiff base crystal ligand type [NO 2] derived from the interacting of 2-aminophenol with glyoxylic acid, and its [N₂O₄] Mn^{II} complex, synthesizing and characterizing. *Egypt. J. Chem.* **2020**, *63*, 325-335.
15. Shaker A.; Khaledi, H.; Cheah, C.; Ali, M. New Mn(II), Ni(II), Cd(II), Pb(II) complexes with 2-methylbenzimidazole and other ligands. Synthesis, spectroscopic characterization, crystal structure, magnetic susceptibility and biological activity studies. *Arab. J. Chem.* **2016**, *9*, S1943-S1950.
16. Ali, A.; Mirza, H.; Butcher, J. Synthesis and characterization of copper(II) complexes of the methylpyruvate Schiff base of S-methyldithiocarbamate (Hmpsme) and the X-crystal structures of Hmpsme and [Cu(mpsme)Cl]. *Polyhedron* **2001**, *20*, 1037-1043.
17. Said, A.; Al-unizi, A.; Al-Mamary, M.; Alzahrani, S.; Lentz, D. Easy coordinate geometry indexes, τ_4 and τ_5 and HSA study for unsymmetrical Pd(II), Fe(II), Zn(II), Mn(II), Cu(II) and VO(IV) complexes of a tetradentate ligand: Synthesis, characterization, properties, and antioxidant activities. *Inorg. Chim. Acta* **2020**, *505*, 119434.
18. Griffith, M.; Szöcs, B.; Keogh, T.; Suponitsky Y.; Farkas, E.; Buglyó, P.; Marmion, J. Suberoylanilide hydroxamic acid, a potent histone deacetylase inhibitor; its X-ray crystal structure and solid state and solution studies of its Zn(II), Ni(II), Cu(II) and Fe(III) complexes. *J. Inorg. Biochem.* **2011**, *105*, 763-769.
19. Rehder, D. Biological and medicinal aspects of vanadium. *Inorg. Chem. Commun.* **2003**, *6*, 604-617.
20. Drevenšek, P.; Zupančič, T.; Pihlar, B.; Jerala, R.; Kolitsch, U.; Plaper, A.; Turel, I. Mixed-valence Cu(II)/Cu(I) complex of quinolone ciprofloxacin isolated by a hydrothermal reaction in the presence of L-histidine: Comparison of biological activities of various copper-ciprofloxacin compounds. *J. Inorg. Biochem.* **2005**, *99*, 432-442.