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Imidazolium Salt-Derived N-Heterocyclic Carbene Ligands for Silver(I) Complex Formation: Synthesis, Spectroscopic Investigation

Alaa Fadhil Razzaq[1],Duaa Abdulzahraa Al-Rammahi[2],Hasan M. Marhoon[3]

[1]Department of Pharmacy, Technical Institute /Kufa, Al Furat AL Awsat Technical University

[2]Department of Community Health Techniques, College of Health and Medical Techniques /Kufa, Al Furat AL Awsat Technical University, Najaf, Iraq

[3]Department of Chemistry, College of Science, University of Kufa, Najaf-54001, Iraq.

ABSTRACT: New imidazolium salts have been prepared from methyl imidazole via nucleophilic substitution reactions using diverse alkyl and functional halides. These salts were subsequently used as precursor compounds for the preparation of nitrogen-cyclic heterogeneous carbene complexes with silver (Ag–NHC) by reaction with silver oxide in methanol. The synthesized ligands and their corresponding metal complexes were characterized using several spectroscopic techniques, including Fourier transform infrared spectroscopy, UV–visible spectroscopy, proton nuclear magnetic resonance (1H NMR), and nuclear magnetic resonance-13 (^{13}C NMR), high-resolution mass spectrometry, and elemental analysis (CHN). The spectral data confirmed the successful formation of bonds and the coordination of silver ions across the carbene carbon atom, as evidenced by the characteristic spectral changes and the disappearance of the C2–H proton signal of imidazolium upon complex formation. The antibacterial activity of the synthesized compounds was evaluated and compared. The results showed that silver(I) compounds with heterocyclic carbene (NHC) possessed remarkably enhanced antibacterial activity compared to their initial imidazolium salts counterparts. This remarkable improvement is attributed to the synergistic effect of silver coherence and stability provided by the heterocyclic carbeny bond framework. These results indicate that Ag–NHC compounds derived from imidazolium salts are a promising candidate for the development of novel antimicrobial agents.

KEYWORD: Antibacterial; Carbene ; Heterocyclic; Organometallic

INTRODUCTION

Imidazole is a completely water-soluble compound that is colorless and estimated to have a large dipole moment [1]. Depending on where the hydrogen atoms are located It appears in two separate stoichiometric forms on each side of the nitrogen atoms in the heterocyclic. Imidazole is classified as an aromatic molecule because it has sextet electrons, which are two electrons from the proton nitrogen atom and one from each of the four other atoms in the ring[2]. as shown in Figure (1).

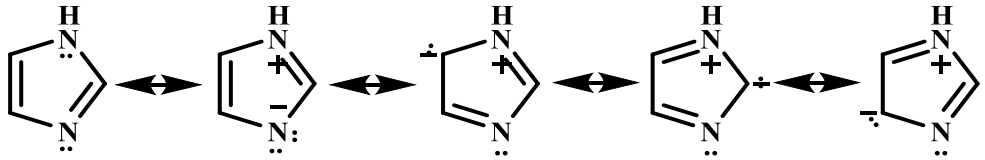
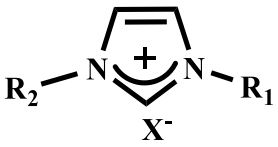


Figure 1. Resonance structures of imidazole.

Imidazole is present in several significant natural substances, including nucleic acids, histidine, and histamine. Both a basic and a weak acid can be created by imidazole. Due to their potent therapeutic properties, imidazole derivatives have been used to create a large number of innovative chemotherapeutic medicines, and they play a key role in medicinal chemistry[3]. Imidazole compounds have a number of pharmacological qualities, including analgesic, anti-inflammatory, antiviral, anti-cancer, and anti-neoplastic activities [4,5]. Notice the difference in imidazolium salts between the organic base hydrochloride and the quaternary ammonium salts as shown in Figure (2). The proton or a number of functional groups at positions 1 and 3 of the imidazole ring can readily form these salts. In engineering science, imidazolium salts have been used as ionic fluids and as the building blocks for the creation of NHCs Scheme (1.1), which are frequently used as ligands or natural catalysts.[6,7]

Imidazolium Salt-Derived N-Heterocyclic Carbene Ligands for Silver(I) Complex Formation: Synthesis, Spectroscopic Investigation



R_1, R_2 = H, alkyl, aryl, alkyl-aryl.

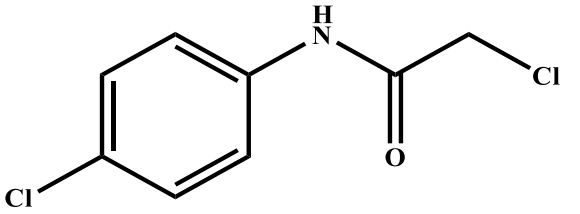
Figure 2. General representation of imidazolium salts.

N-Heterocyclic carbenes, also known as NHCs, are cyclic carbenes with at least one -amino substituent. They are commonly abbreviated as NHCs.[8] N-heterocyclic carbenes act as ligands with metal complexes in organocatalyzed reactions.[9]

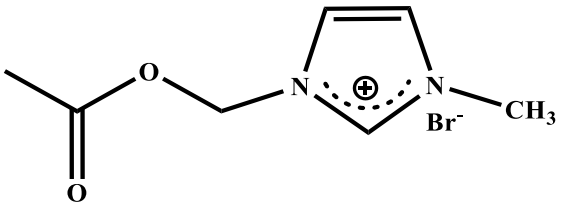
MATERIALS AND MEASUREMENTS

Synthesis of 2-Chloro-N-(4-Chlorophenyl) acetamide(R)

4-Chloroaniline (3.0 g, 0.021 mol) and toluene (10 mL) as a solvent, followed by the addition of trimethylamine (1.5 mL). After stirring for 20 minutes, $C_2H_2Cl_2O$ (1.6 mL, 0.014 mol) was added dropwise at 250 °C. These reductions were counteracted by 30 atoms, through continuous filtration and reduction of distilled water, and then the ethanol was recrystallized, resulting in the removal of the R substance in the falling blackheads (83%, suitable temperature 130-133°C) [10,11].

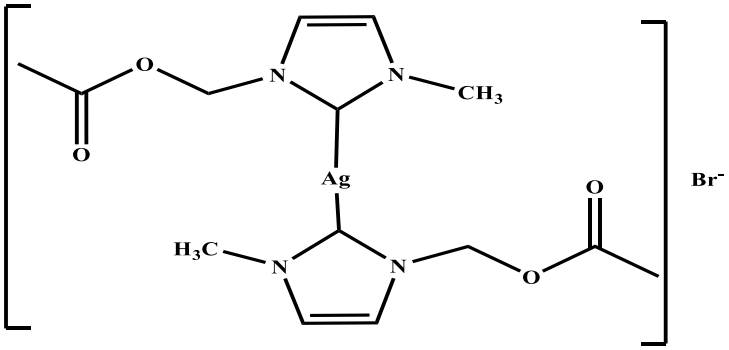


(3-methyl-2,3-dihydro-1H-imidazol-1-yl) methyl acetate (Z)



One gram of methylimidazole (0.0121 mol) was dissolved in 5 mL of acetonitrile in a 50 mL round-bottom flask. Then, 5 mL of acetonitrile was mixed with 1.86 g of bromomethyl acetate (0.0121 mol), and this mixture was added to the solution. The mixture was heated under reflux for 24 hours at 90 °C. After the reaction was complete, the solvent was evaporated and then recrystallized from methanol. Two grams (70%) were obtained as a pale red ionic liquid (melting point 128–132 °C).

2 bis(1-(acetoxymethyl)-3-methyl-2,3-dihydro-1Himidazol-2-yl) silver (B)



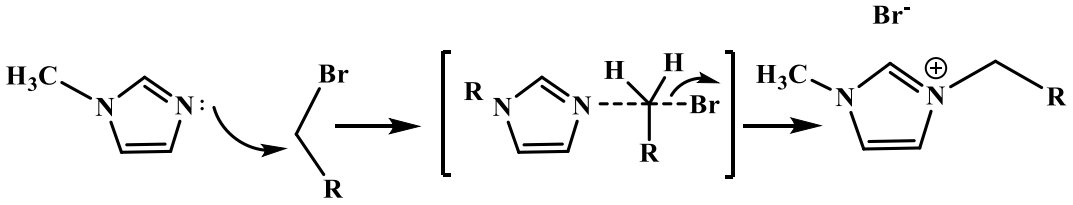
Silver oxide (0.75 g, 0.0032 mol) was added to a solution of compound (Z) (1 g, 0.0064 mol) in 20 mL of methanol. The mixture was stirred in a glass container for 10 hours under an aluminum foil cover. The solvent was removed under vacuum after filtering the dark suspension through slate to remove excess Ag_2O, yielding a pale red solid weighing 1.3 g (74%) (melting point = 178–182 °C).

RESULTS AND DISCUSSION

Synthesis and Identification of ligand.

Mathylimidazole has been chosen as a starting material since it is readily available and a comparatively inexpensive compound. The synthetic route was outlined in such away to be simple, reproducible, and relatively accessible. The R group is associated with the

nitrogen of methylimidazole. The first step was the preparation of ((3-methyl-2,3-dihydro-1H-imidazol-1-yl) methyl acetate) compound (Z) this compounds prepared from the reaction of the methylimidazole(one mol) with (one mol) bromobutane /bromoacetonitril/ bromomethylacetate /2-chloro-N-(4-chlorophenyl) acetamide in acetonitrile solvent was obtained as a white powder in 70-83% yield after purification. The reaction was allowed to complete 24 hours. Moreover, the purity of this compound is reasonable, which was proved by the sharp melting point at the beginning and by the FTIR spectrum later on. The reaction followed the S_N2 mechanism when the pair of electrons on the nitrogen group in the compounds attaches to the carbon of the alkyl halide, at the same time, the bromo-group was left to be counter ion of the new positively charged cation. Scheme (1).



Scheme 1. General S_N2 mechanism of synthesis of ligand (Z).

ELECTRONIC SPECTRA OF LIGANDS

Electronic transitions in transition metal compounds can be divided into three types: charge transitions, rotationally allowed d-d transitions, and rotationally forbidden d-d transitions. Charge transition bands occur when an excited electron moves from a metal-center orbital to a bond-center orbital (MLCT), or when an excited electron moves from a bond-center orbital to a metal-center orbital (LMCT). MLCT bands are more common than LMCT bands. Rotationally allowed and forbidden d-d transitions refer to the movement of an excited electron from one d orbital to another. In a rotationally allowed transition, the spin quantum number (or, more precisely, spin angular momentum) is the same in the ground and excited states, while in a rotationally forbidden transition, the spin state changes during excitation. Bond spectra were recorded in methanol. Calibrated UV-Vis spectra of the Z-link showed two absorption bands in the low UV range (230-290 nm). As shown in table (1), the bands observed below 250 nm are related to π–π* transitions for aromatic rings, and above 250 nm to typical n–π* transitions between (C=N) (C=O) bonds.

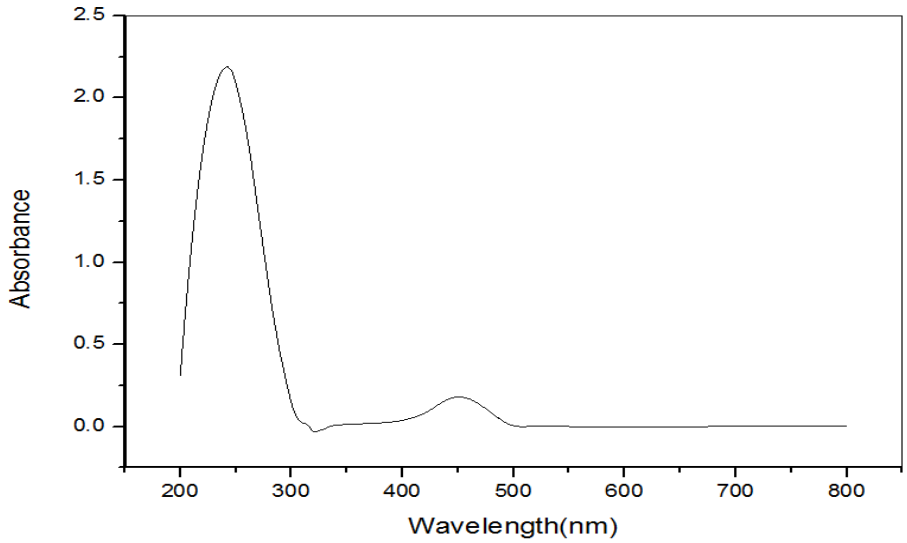


Figure 3. UV.VIS. of ligand Z.

Table (1) UV-Vis spectroscopy of the (Z-ligand) (B Ag(I) complexes)

Ligand	Absorption band(nm)	Assigned transition	Com Ag(I)	Absorption band(nm)	Assigned transition	Com Pd(II)	Absorption band(nm)	Assigned transition
Z	250 450	π---π* n—π*			π---π* M.L.C.T			

Infrared Spectra Of The Ligands

The ligand (Z) was synthesized using the reactions shown in the diagram. The ligands were characterized using Fourier transform infrared spectroscopy. First, the Fourier transform infrared spectrum showed characteristic peaks, including but not limited to the following: The absorption at (2936.12, 2866.43-2963.56, 2896.67-2993.56, and 2851.69-2953.69) cm^{-1} is attributed to the aliphatic (C-H) bond stretching vibrations, while the beam at (1539.67, 1565.82, 1567.1, and 1570.39) cm^{-1} corresponds to the (C=N) bond

stretching vibrations, whereas the beam at (1295.3, 1245.13, 1290.26, and 1225.58) cm^{-1} may be related to the (C-N) bond stretching vibrations. Table (2) shows the values of the infrared spectrum with the Fourier transform of the bond.

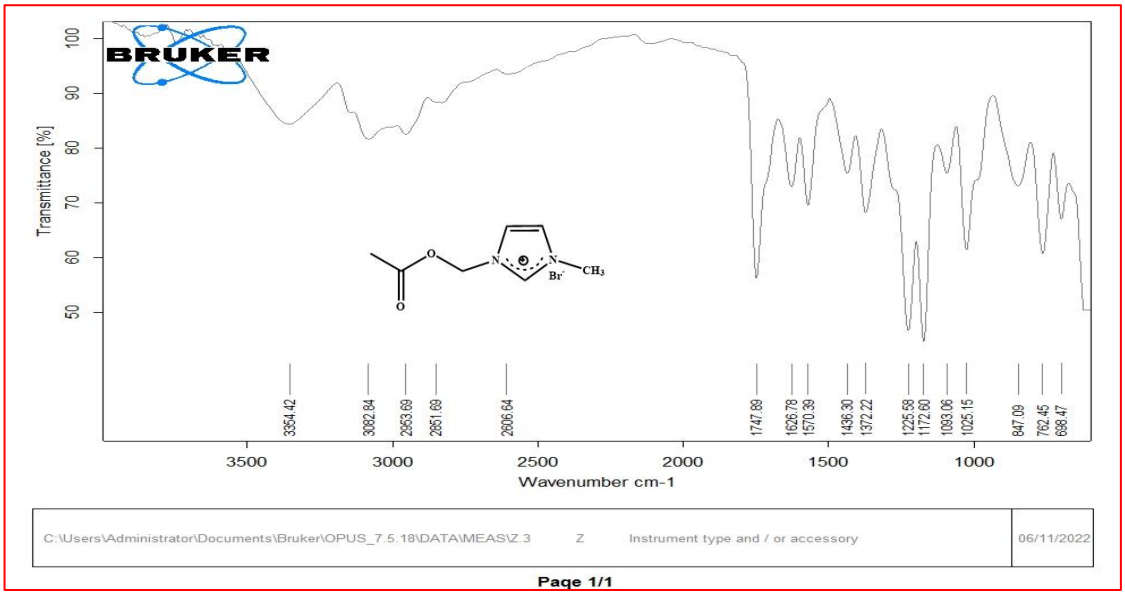


Figure 4. FTIR spectrum of ligand Z.

Table (2) FTIR peaks of ligands

Com.No.	Molecular Formula	C-N	N-H	C-H ar.	C-H al.	C=O	C=N	C=C	CΞN
Z	$C_7H_{11}BrN_2O_2$	1226	-------	3083	2953 2851	1748	1570	1436	------

3.1.3 Identifications Via ^{1}hnmr Spectra Of Ligands

In the proton (5) and (6) NMR spectra of the Z-link, distinct peaks were observed, confirming the structure of the target product. The single signal at 1.87 ppm is attributed to the methyl group directly bonded to the carbonyl group. Additionally, the single signal at 5.41 ppm can be attributed to the methylene group bonded between the nitrogen atom in the imidazole ring and the oxygen atom in methyl acetate.

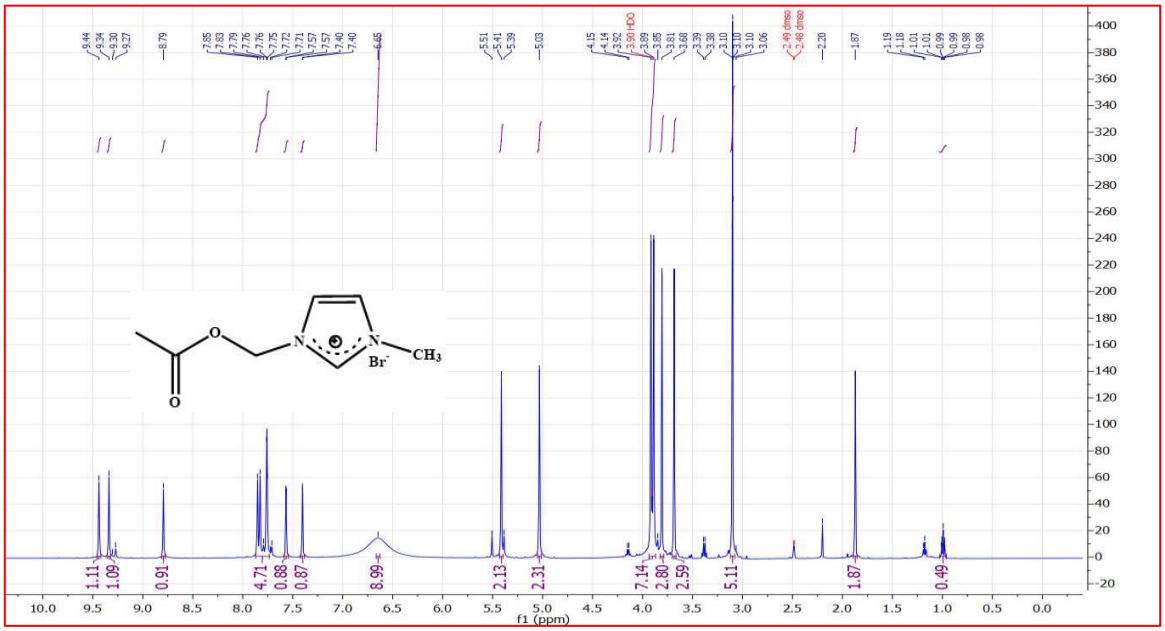


Figure 5. ^{1}HNMR full spectrum of ligand Z.

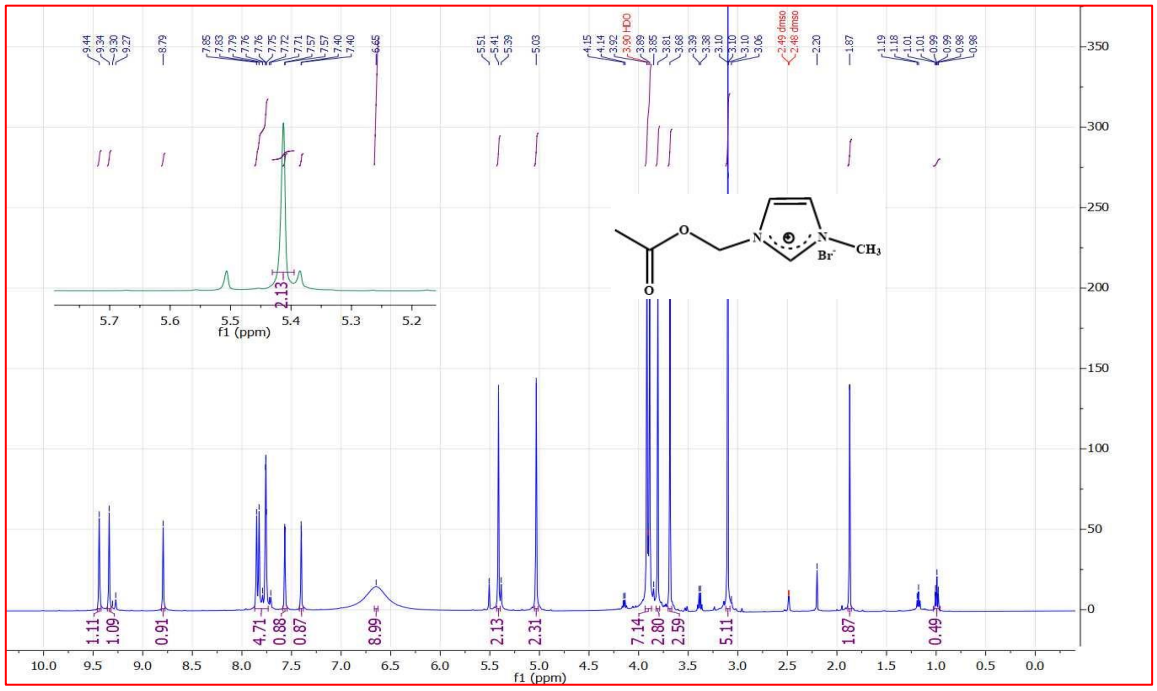


Figure 6. ^{1}HNMR EX spectrum of ligand Z.

Table (3) ^{1}HNMR (500 MHz) data of ligands.

Functional group	**^{1}HNMR Chemical shift range (ppm)Ligand Z**
NH-amide	----------
N**CH**N	9.44
Ar-H	----------
CH=CH-imidazole ring	7.72,7.40
CO-**CH_2**-N	----------
CH_3 –terminal	3.89
N-**CH_2**-CN	----------
CH_2-imidazole	5.41
CH_3-CH_2-CH_2-	----------
Carbonyl-CH_3	1.87

3.1.4 Identifications Via ^{13}cnmr Spectra Of Ligands

The signal at 21.64 ppm was attributed to the carbon atom in the methyl group bonded to the carbonyl group in the Z-link. The signal at 62.28 ppm was attributed to the carbon atom in the methylene group bonding the nitrogen atom in the imidazole ring to the oxygen atom. The signals at 168.61 ppm were attributed to the carbonyl group (C=O), as shown in Figures 7 and 8. Table 4 summarizes the NMR spectra of carbon-13 in the Z-links.

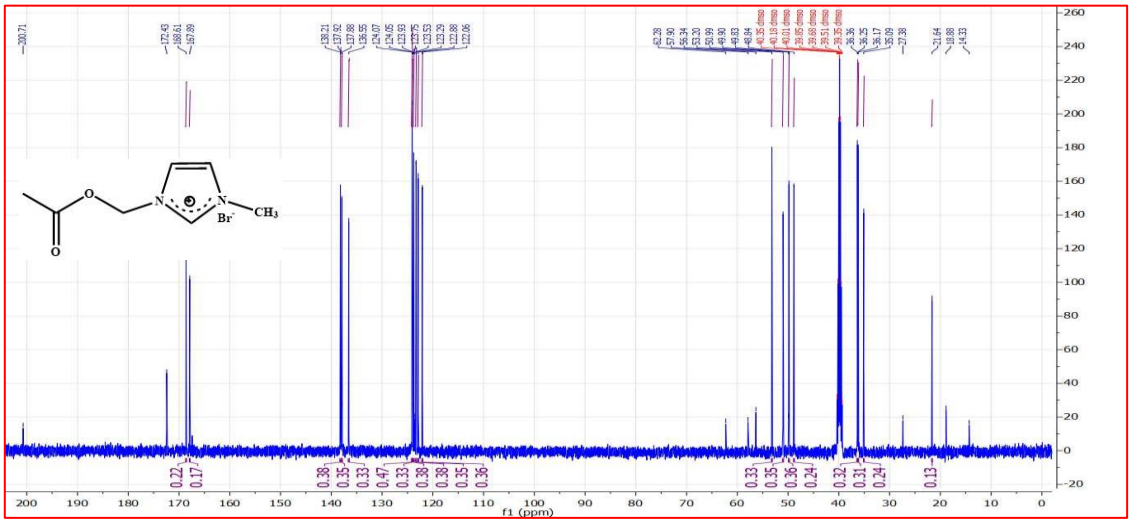


Figure 7. ^{13}CNMR full spectrum of ligand Z.

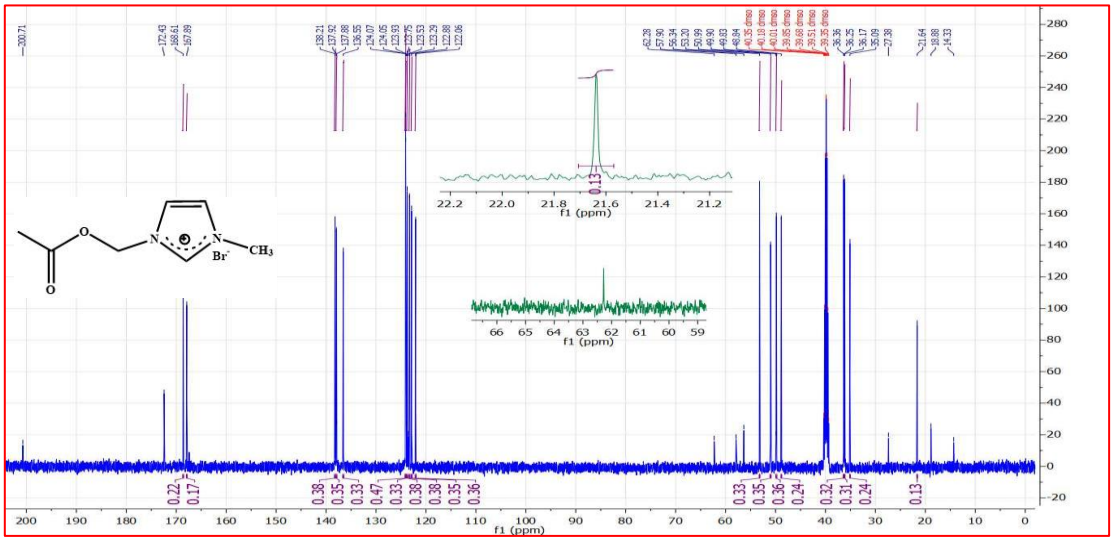


Figure 8. ^{13}CNMR EX spectrum of ligand Z.

Table (4) ^{13}C NMR (500 MHz) data of ligands**.**

Functional group	**^{13}CNMR Chemical shift range (ppm) Ligand Z**
C=O	172.43
N**C**HN	138.21
Ar-C aromatic ring	---------
C=C-imidazole ring	124.05,122.88
carbony-**CH_2**-imidazole ring	---------
N-**CH_2**-CN	---------
CH_3 –terminal	36.36
CN	---------
Butyl chain	
-**CH_2**-imidazole ring	62.28
carbony-**CH_3**	21.64

Identifications Via C.H.N Technique Of Ligand

Furthermore, the C.H. N analysis confirmed the purity as well as the acceptable carbon, hydrogen, and nitrogen ratios in the Z ligand, as show in the Table (5).

Table (5) C.H.N ratio and some physical properties of ligands

Com. No.	Molecular Formula	M.wt	Color	m.p. ^{0}C	Yield%	C% Calc. Found	H% Calc. Found	N% Calc. Found
Z	$C_7H_{11}BrN_2O_2$	234	Pale red	128-132	70	35.89 35.76	4.7 4.2	11.96 11.32

High Resolution Mass Spectrum Of Ligand

Figure (9) show the mass and fragmentation (MS/MS) spectra of (Z) ligands, respectively. The richness of the segmentation spectra allows confirming the initial formation of the ligands as well as providing useful hints for their structure.

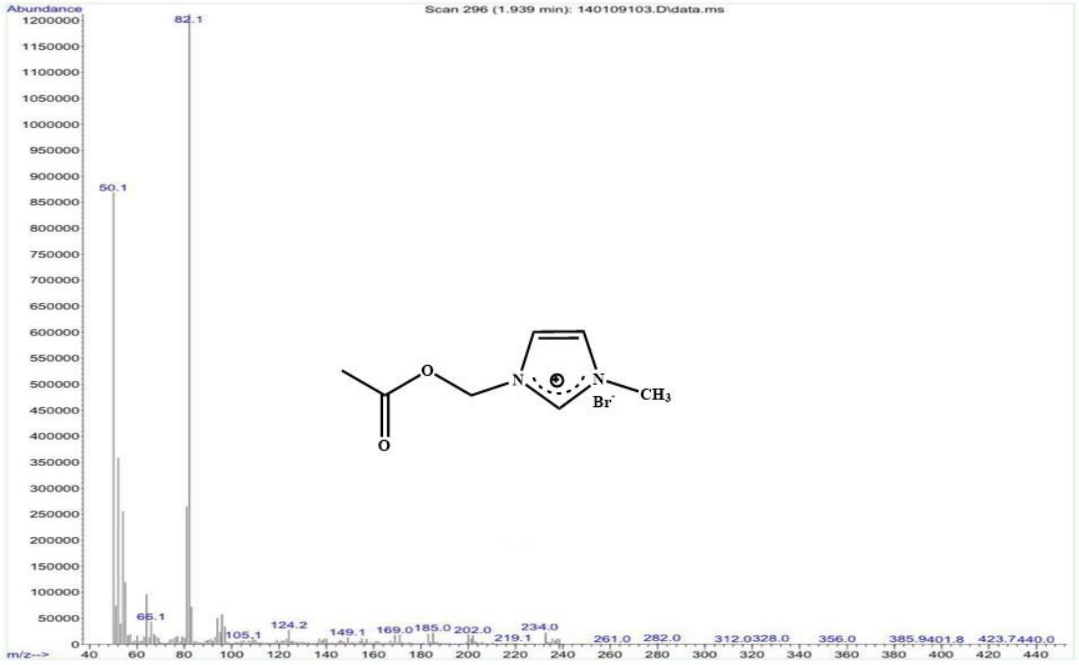
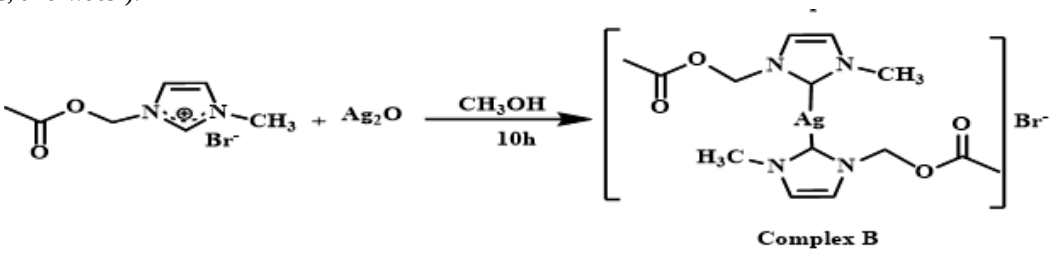


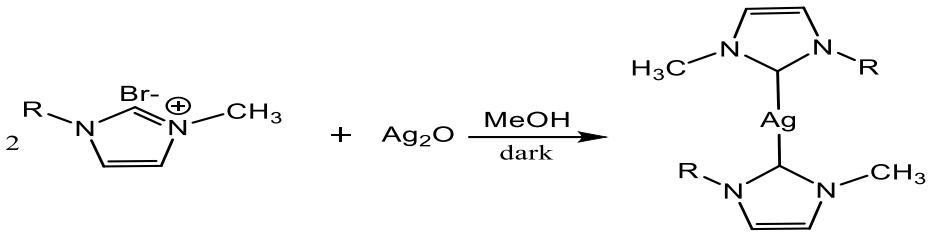
Figure 9. HRMS spectrum of ligand Z.

SYNTHESIS OF SILVER (I) NHC

The Ag-NHC complexes were synthesized in analogous to the reported procedure by Wang and Lin. The imidazolium salts (Z) reacted with the Ag_2O (2:1mol) in alcohol at reflux for 10h to form the desired Ag-NHC complex **B as** shown in Scheme (2) and the Scheme (3) shows the general equation of complexes synthesis. All silver complexes are characterized by FT.IR, ^{1}H-NMR, ^{13}CNMR described the complexes. Ag-NH complexes are soluble in solvents such (CH_2Cl_2, DMSO and dioxane) but insoluble in (hexane, toluene, and water).



Scheme 2. preparation of complexes (B)



Scheme 3. General synthesis of complexes

ELECTRONIC SPECTRA OF SILVER(I) COMPLEXES

The electron spectra of the synthesized silver compounds show strong absorption in the UV-Vis region, from about 250 to 380 nm, characteristic of charge transfer from the 4d to 4s orbital of the metal at relatively high energies. The Ag(I)(B) compound did not exhibit any d-d transition due to its d10 electronic configuration, as d-d transitions are prohibited by Laporte's selective rule. This confirms the absence of any d-d transitions and the lack of absorption in the visible region of its electron spectra. Furthermore, the electron spectrum showed a band at 330 nm, 300 nm, and 320 nm resulting from a charge transfer from the metal to the bond (LMCT), and a band at 250, 253, and 255 nm resulting from a π-π* transition associated with the aromatic imidazole ring. The redshift of these bands and the variation in absorption values confirm a complex synthesis process.

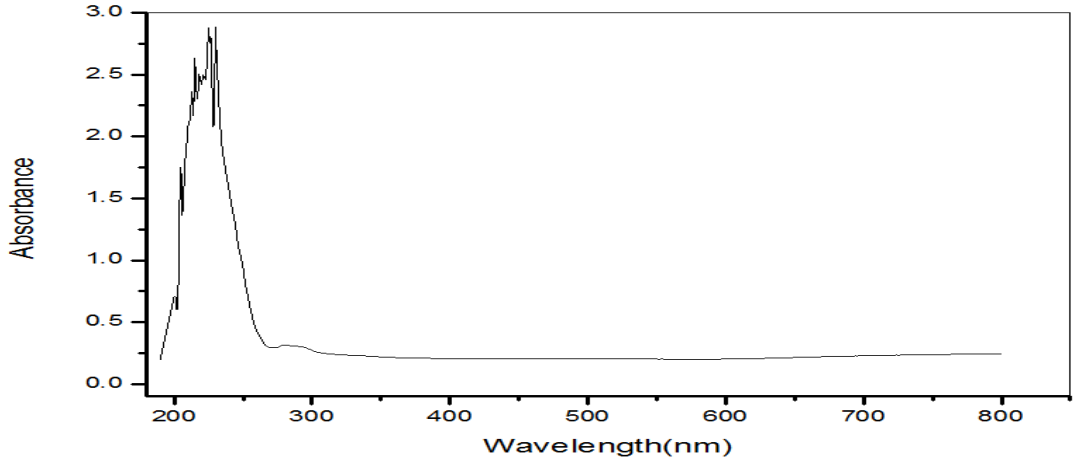


Figure 10. UV.VIS. of complex B

IDENTIFICATION VIA F.T.I.R SPECTRA OF SILVER(I) COMPLEXES

In the infrared spectrum of the compound, key band peaks were found, which were interpreted as the main functional groups. The band at (2868.69–3151.98, 3119.34–3151.91, 3116.7–3230.46, 3117.53–3261.16) cm^{-1} is associated with the starch vibrations (C–H aliphatic) of the alkane, while the band at (1606.51, 1613.2, 1689.8, 1618.58) cm^{-1} is attributed to the (C=C) group. Additionally, the bands at (1168, 1589.13, 1554.59, 1565.66) cm^{-1} are attributed to (C–N), as shown in Figure 11. Table (6) shows the Fourier transform infrared spectral values for Ag(I) compounds.

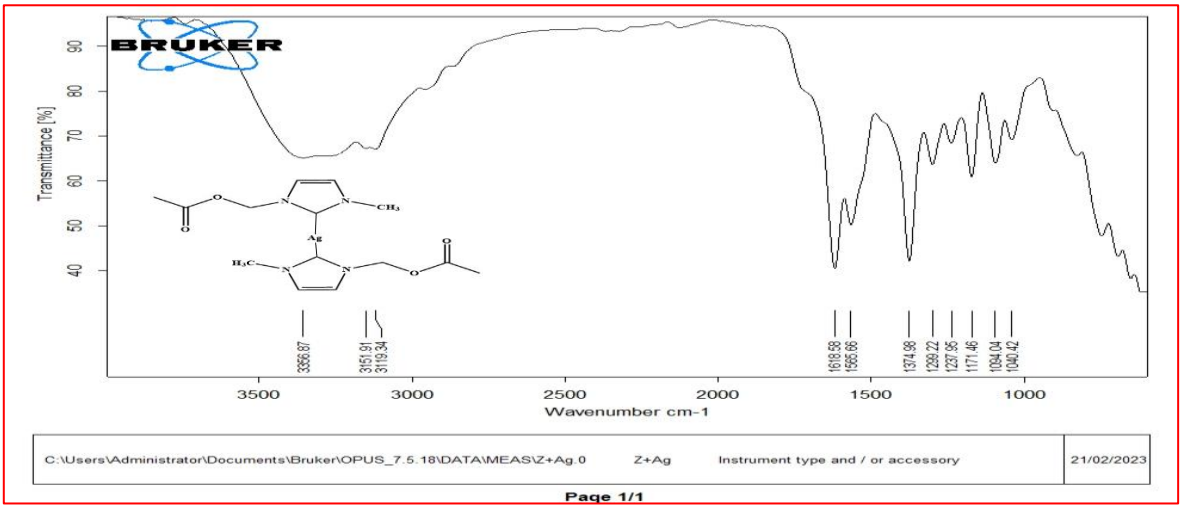


Figure 10. FTIR spectrum of complex B.

Table (6) FTIR peaks of Ag(I) complexes

Com. No.	Molecular Formula	N-H	C-H ar.	C-H al.	C=O	C=N	CΞN	C=C
B	$C_{14}H_{20}AgBrN_4O_4$	-----	3152	3119	1748	1566	-----	1619

Identifications Via ^{1}hnmr Spectra Of Silver (I) Complexes

The proton nuclear magnetic resonance spectrum (Figure 12) shows characteristic peaks that confirm the desired product structure. In compound B, we observe that the single signal at 1.08 ppm is attributed to the methyl group directly attached to the carbonyl group. Furthermore, the single signal at 4.5 ppm can be attributed to the methylene group connected between the nitrogen atom in the imidazole ring and the oxygen atom in the methyl acetate.

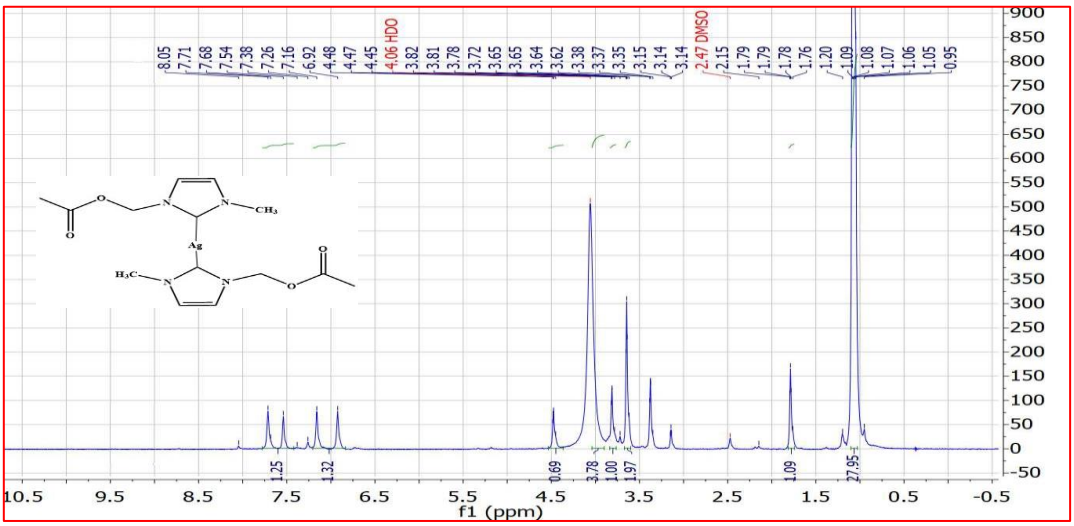


Figure 12. ^{1}HNMR full spectrum of complex B.

Table (7) ^{1}HNMR (500 MHz) data of Ag(I) complexes.

Functional group	**^{1}HNMR Chemical shift range (ppm) COMPLEX B**
NH-amide	-------
Ar-H	-------
CH=CH-imidazole ring	7.26, 7.71
CO-**CH_2**-N	4.5
CH_3 –terminal	3.15
N-**CH_2**-CN	-------
CH_2-imidazole	-------
CH_3-CH_2-CH_2-	-------
Carbonyl-CH_3	1.08

3.2.5 Identifications Via ^{13}cnmr Spectra Of Silver (I) Complexes

The carbon-13 (13) NMR spectrum showed distinct peaks that confirmed the structure of the target product. Similarly, the carbon-13 (3.40) NMR spectrum of compound B also showed distinct peaks that confirmed the structure of the target product. The signal at 31.15 ppm is attributed to the methyl carbon atom bonded to the carbonyl group; the signal at 66.99 ppm is attributed to the methylene carbon atom bonded between the nitrogen atom in the imidazole ring and the oxygen atom; and finally, the signal at 173.41 ppm is attributed to the carbonyl group (C=O).

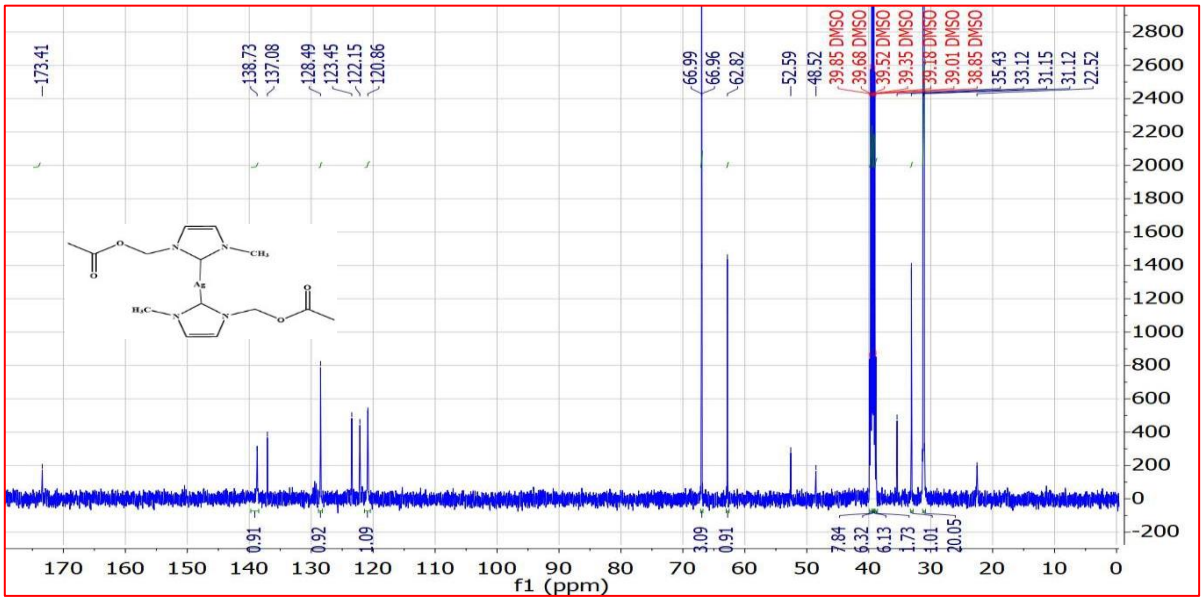


Figure 13. ^{13}CNMR spectrum of complex B.

The table (8) summarizes the ^{13}CNMR rustles for (B) complexes.

Functional group	**^{13}CNMR Chemical shift range (ppm) COMPLEX B**
C=O	173.41
N**C**HN	138.73
Ar-C aromatic ring	---------
C=C-imidazole ring	120.86,122.15, 123.45,128.49
carbony-**CH_2**-imidazole ring	66.99
N-**CH_2**-CN	---------
CH_3 –terminal	36.27
CN	----------
Butyl chain	----------
-**CH_2**-imidazole ring	----------
carbony-**CH_3**	----------

Identifications With C.H.N Technique Of Silver(I) Complexes

In comparison to the computed values, the C.H.N analysis of compounds A, B, C, and D (Table 9) was given approved values for carbon, nitrogen, and hydrogen.

Table (9) C.H.N ratio and some physical properties of Ag complexes

Com. No.	Molecular Formula	M.wt	Color	m.p.^{0}C	Yield%	C% Calc. Found	H% Calc. Found	N% Calc. Found
B	$C_{14}H_{20}AgBrN_4O_4$	494	Pale red	178-182	75	34.08 34.01	4.04 3.98	11.33 11.21

CONCLUSION

Imidazolium salts were successfully synthesized and used as starting materials for the synthesis of silver(I) complexes with nitrogen-containing heterocyclic carbenes. The synthesized methods were simple and reproducible, yielding the desired products in good proportions. Comprehensive analyses using Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, nuclear magnetic resonance spectroscopy, high-resolution mass spectrometry, and elemental analysis confirmed the structural integrity of both the ligands and their corresponding silver complexes. The disappearance of the C2–H proton signal of imidazolium in the nuclear magnetic resonance spectra provided clear evidence of carbene formation and efficient coordination with silver ions. Assessment of antibacterial activity showed that the silver complexes exhibited higher biological activity compared to the free ligands, highlighting the important role of metal coordination in enhancing antimicrobial properties. These results demonstrate the

potential of Ag–NHC complexes as valuable systems in coordination chemistry and medical applications. Further studies focusing on structural optimization and mechanistic biological studies are recommended to explore its full therapeutic potential.

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