Borneo International Journal eISSN 2636-9826; Vol. 7 (1); 2024; 1-8
Published by *Majmuah Enterprise*
www.majmuah.com

Synthesis and Structural Elucidation of Non-Functionalized Symmetrical Tetrakis-Imidazolium Dinuclear Silver(I) Di-*N*-Heterocyclic Carbene Complex

MUHAMMAD ZULHELMI NAZRI[1], MOHD RIZAL RAZALI[2] & NORAZAH BASAR[1,3]
[1]*Innovation Centre in Agritechnology for Advanced Bioprocessing (ICA), Universiti Teknologi Malaysia (Pagoh Campus), Eduhub Pagoh 84600 Pagoh, Johor, Malaysia*
[2]*School of Chemical Sciences, Universiti Sains Malaysia 11800 Minden, Penang, Malaysia*
3Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia 81310 Skudai, Johor Bahru, Malaysia
Email: mzulhelmin@utm.my | Tel: +606-9742859

Received: February 27, 2024
Accepted: March 07, 2024
Online Published: March 30, 2024

Abstract

This brief report outlines the synthesis and analysis of symmetrical dinuclear silver(I) di-*N*-heterocyclic carbene (NHC) complex, primarily derived from tetrakis-benzimidazolium salt. The symmetrical tetrakis-imidazolium salt was synthesized by reacting 1,2,4,5-tetrakis(bromomethyl)benzene with the imidazole moiety of **1·Br**. The salt was then transformed into the respective complex through an *in-situ* deprotonation reaction with Ag_2O, utilizing different salt-to-metal molar ratio, resulting in the establishment of dinuclear silver(I) di-NHC complex designated as **Ag1**. The structures of both the tetrakis-imidazolium (**1·Br**) salt and the silver(I) di-NHC complex **Ag1** were determined using a combination of spectroscopic techniques (FTIR, ^{1}H- and ^{13}C-NMR), CHN elemental analysis, and single crystal X-ray diffraction. The single crystal X-ray diffraction analysis of the macrocyclic complex **Ag1** suggests a crystalline structure resembling a cylinder. Further exploration on the application of the complex could be done in the future on as such the antimicrobial, anticancer, catalysis and many more.

Keywords: Imidazolium salt; Dinuclear Ag(I) complex; Macrocyclic; *N*-heterocyclic carbene

1. Introduction

In coordination chemistry, the macrocyclic effect is an important requirement for the design and synthesis of ligand motifs (Jakob et al., 2021). The macrocyclic ligand can be defined as a ligand with at least nine ring atoms, three of which are possible donor atoms usually contains a donor atom of neutral nitrogen, oxygen, or sulphur, that forms a continuous ring around a metal core and to be appeared forming extremely strong metal complexes due to macrocyclic effect (Bertrand et al., 2015). This macrocyclic effect stabilizes both the kinetic and thermodynamic properties of the system (Altmann et al., 2016). Hence, by integrating the *N*-heterocyclic carbene (NHC) chemistry, which has become a key component of current homogeneous catalysts, photoluminescent materials, and medicinal drugs, with macrocyclic ligand patterns has been shown to provide favorable scaffolds for transition metal coordination (Lescop, 2017).

A number of techniques have been used to synthesize cyclic polymers; ring-chain equilibration was the first approach used (De et al., 2019). The method of developing cyclic poly(decamethylene adipate) by polycondensing adipic acid and decamethylene glycol marked the beginning of the synthesis of cyclic polymers, validating an earlier theory put out by Jacobson and Stockmayer. These scientists suggested that the proportion of rings rises with dilution and molecular weight after incorporating ring formation into their models of the distribution of molecular species in polycondensates. Additionally, studies were carried out on ring-chain equilibration in the production of cyclic oligo- and poly(dimethyl siloxane). Advances in ring-chain equilibration have been extensively discussed in reviews and articles over the years, including discussions of the Jacobson and Stockmayer theory in addition to more recent ideas.

The NHCs are a new class of donors that could be used to build metallo-supramolecular structures that have M-C_{NHC} bonds in them (Wang et al., 2018). NHCs are useful auxiliary ligands that have garnered a lot of interest in the disciplines of coordination chemistry and organometallic research. Their robust δ-donor capabilities and reciprocal back donation from the metal *d*-orbital to the vacant *p*-orbital on the carbene carbon have led to the formation of stable M–C_{NHC} bonds, primarily utilized in homogeneous catalysts (Gutiérrez-Blanco et al., 2021; Rufino-Felipe et al., 2020). The silver(I), gold(I), copper(I), palladium(II), and nickel(II) react with poly-NHC ligands that contain a variety of functional groups, including pyridyl, phosphinyl, pyrazolyl, and quinolinyl groups, to produce the numerous poly-NHC metal complexes that have been described (Catalano et al., 2023; Narouz et al., 2019). The Ag-NHC family is one of these metal-NHC supramolecular structures that has attracted a lot of interest because of its attractive chemical,

structural, and photophysical characteristics as well as its frequent use as carbene transfer agents in the synthesis of other metal-NHC supramolecular structures (Yu et al., 2021).

This study focuses on the synthesis and structural analysis of a tetrakis-tetrabromide salt obtained by reacting 1,2,4,5-tetrakis(bromomethyl)benzene with the imidazole moiety. Upon treatment of these salts with Ag_2O, macrocyclic structures were formed, wherein two Ag(I) ions are coordinated between two dicarbene ligands.

2. Materials and Methodology

Materials and instruments

Without any additional purification, all chemicals and solvents were obtained from commercial providers and used as it is. Melting points were determined using a Stuart Scientific SMP-1 (UK) instrument. A PerkinElmer Series II, 2400 microanalyzer was used for elemental studies. Using a PerkinElmer FTIR Microscope Spotlight 200, FTIR spectra were obtained between 4000 and 600 cm ^{1}. Bruker 500 MHz Ascend spectrometers were used to record nuclear magnetic resonance (NMR) spectra in DMSO-d_6 at room temperature. The TMS was used as an internal reference.

Synthesis of imidazole substituted tetrakis-tetrabromide salt with 1,2,4,5-tetrakis(bromomethyl)benzene, 1·Br

The mixture of 1,2,4,5-tetrakis(bromomethyl)benzene (0.50 g, 1.11 mmol) was reacted with imidazole (0.37 g, 4.50 mmol) in 30 mL of acetonitrile. The resulting mixture was refluxed at 80 – 100 °C and stirred for 24 hours. The white precipitate appears in the round bottom flask was removed and washed with acetonitrile (2 × 5 mL) and diethyl ether (2 mL) before air dried. Salt **1·Br** obtained as colorless needles-like crystals after removal of the solvents within 2 days in the fume cupboard. **Yield**: 0.68 g (80 %), **MP**: 277 - 278 °C. **FTIR** (ATR, cm^{-1}): 3143 (Csp^2-H stretching); 3044, 2946 (Csp^3-$H_{aliphatic}$ stretching); 1468 -1367 (C-N stretching). **^{1}H NMR** (500 MHz, d_6-DMSO) in δ ppm: 3.87 (4H, s, 2 × N-C**H**$_2$-Ar); 5.63 (4H, s, 2 × N-C**H**$_2$-Ar); 7.41 (1H, s, Ar-**H**); 7.71 (2H, s, 2 × imidazole-**H**); 9.20 (4H, s, 4 × NC**H**N). **^{13}C NMR** (125 MHz, d_6-DMSO) in δ ppm: 36.47 (N-**C**H$_2$-Ar); 49.14 (N-**C**H$_2$-Ar); 122.86, 124.26 (Ar-**C**); 132.69, 134.63 (imidazole-**C**); 137.24, 137.37 (N**C**HN). Anal. Calc. for $C_{32}H_{32}N_8Br_4$: C, 72.70; H, 6.10; N, 21.20%. Found: C, 72.35; H, 6.38; N, 21.53%

Synthesis of imidazole substituted silver(I)-NHC complex with 1,2,4,5-tetrakis(bromomethyl)benzene, Ag1

A mixture comprising Ag_2O (0.36 g, 1.55 mmol) and **1·Br** (0.30 g, 0.39 mmol) was stirred in methanol (15 mL) for 48 hours at room temperature in darkness, followed by filtration through Celite. The resulting clear filtrate was transformed into the hexafluorophosphate salt by adding KPF_6 (0.30 g, 1.63 mmol). The mixture was stirred for 3 hours and then left to stand overnight. The white precipitate obtained was washed with distilled water (2 x 5 mL) and air-dried. Single crystals suitable for single-crystal diffraction studies were obtained by diffusing diethyl ether into a solution of the **Ag1** complex in acetonitrile at room temperature. **Yield**: 0.40 g (56 %), **MP**: 300 - 302 °C. **FTIR** (ATR, cm^{-1}): 3147 (Csp^2-H stretching); 2976 (Csp^3-$H_{aliphatic}$ stretching); 1439 (C-N stretching). **^{13}C NMR** (125 MHz, d_6-DMSO) in δ ppm: 39.52 (N-**C**H$_2$-Ar), 51.31 (N-**C**H$_2$-Ar); 121.71, 121.75, 122.06, 122.74, 124.05, 124.09, 133.50 (Ar-**C**); 133.78, 136.45, 140.01 (imidazole-**C**); 180.62, 180.74, 182.19, 182.30 ($C_{carbene}$-Ag, $J_{C\text{-}Ag107}$ = 181.25 Hz; $J_{C\text{-}Ag109}$ = 210.00 Hz). Anal. Calc. for $C_{32}H_{28}Ag_2N_8P_2F_{12}$: C, 52.91; H, 3.81; N, 15.14%. Found: C, 52.61; H, 3.46; N, 15.27%

X-ray crystallography refinement

A Bruker-Smart ApexII-2009 CCD diffractometer fitted with a graphite monochromator and employing Mo-Kα radiation (λ = 0.71073 Å) was used to collect data on single crystal X-ray diffraction. For the complex, data collection was place at room temperature. The APEXII software suite's SAINT application was used for integration. Direct approaches were used to derive solutions via SHELXS-2014. The full-matrix least-squares method was then used iteratively to refine the solutions against F^2 using SHELXL-2014. SHELX used the X-seed application as a graphical user interface.

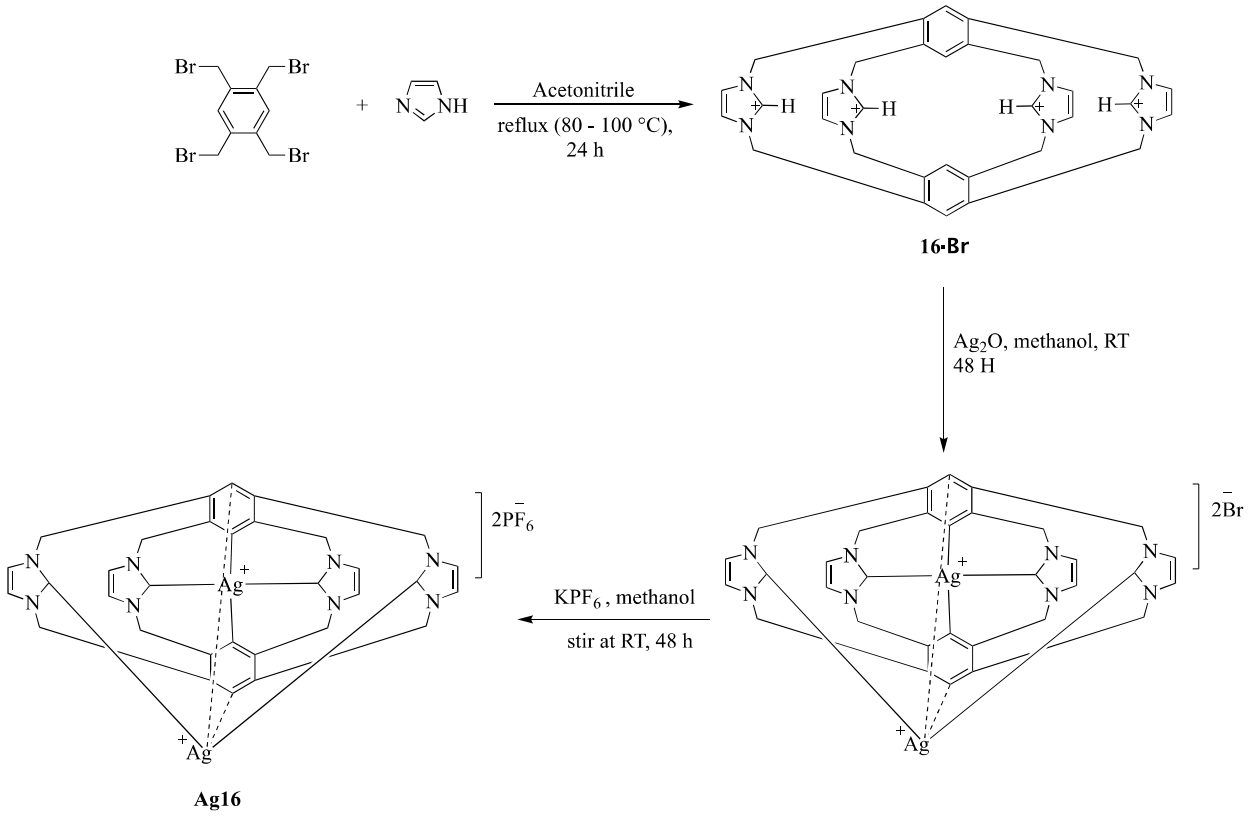
3. Results and discussion

Synthesis

The **Scheme 1** outlines the conversion of imidazolium salt, **1·Br** to its corresponding silver(I) di-NHC complex, **Ag1**. The *N*-substituted imidazole underwent a reaction with 1,2,4,5-tetrakis(bromomethyl)benzene in acetonitrile, yielding the respective tetrakis-imidazolium bromide salt, **1·Br**, in appreciable yield. This salt exhibits good solubility in

common organic solvents such as acetonitrile, DMSO, and methanol, while being insoluble in diethyl ether, petroleum ether, and hexane. Subsequently, the dinuclear silver(I)-NHC complex, **Ag1** was obtained as a white precipitate by treating of 1 equivalent of compound **1·Br** with 4 equivalents of Ag_2O in methanol, stirred at room temperature for 48 hours. The Ag(I)-NHC complex of **Ag1** shows solubility in diethyl ether, benzene, hexane, and water, but it is soluble in polar organic solvents including acetonitrile, DMSO, and DMF.

*Scheme 1 The synthesis procedure of silver(I)-NHC complex, **Ag1** from imidazolium salt, **1·Br**.*



The FTIR Analysis

The FTIR spectra of the non-functionalized tetrakis-imidazolium salt, **1·Br** and its respective dinuclear silver(I) di-NHC complex, Ag1, exhibited bands of medium intensity within the range of 3143 – 3147 cm^{-1}, assigned to Csp^2-H stretching, while the bands at 3044 – 2936 cm^{-1} corresponded to aliphatic Csp^3-H vibrations in both the salt and the complex, respectively. A sharp and strong intensity band at 1559 cm^{-1} indicated the presence of C=N moiety attributed to the imidazolium ring. Upon complexation with Ag(I) ions, the aforementioned bands shifted to 1454 cm^{-1}, indicative of C-N stretching, a characteristic observation for the complex itself (Atif et al., 2020; Babamale et al., 2022).

*Figure 2 The FTIR spectra of **1·Br** as representative for the tetrakis-imidazolium salt.*

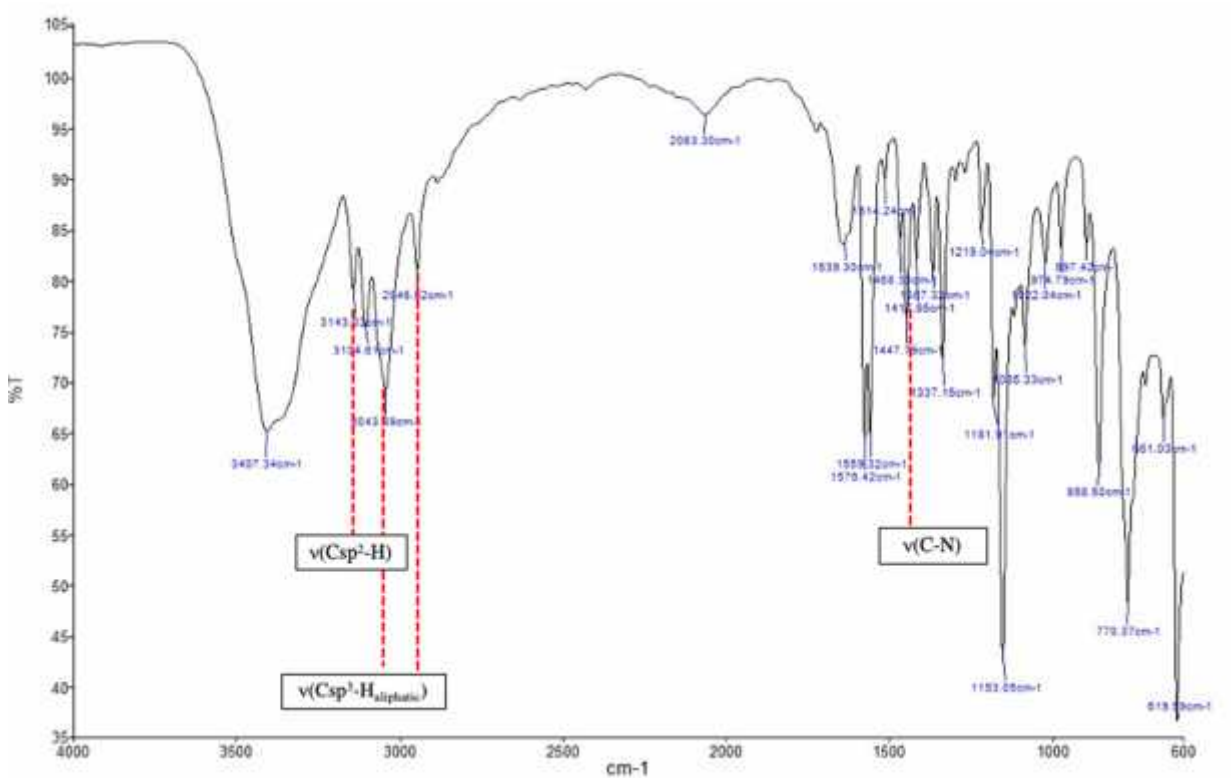
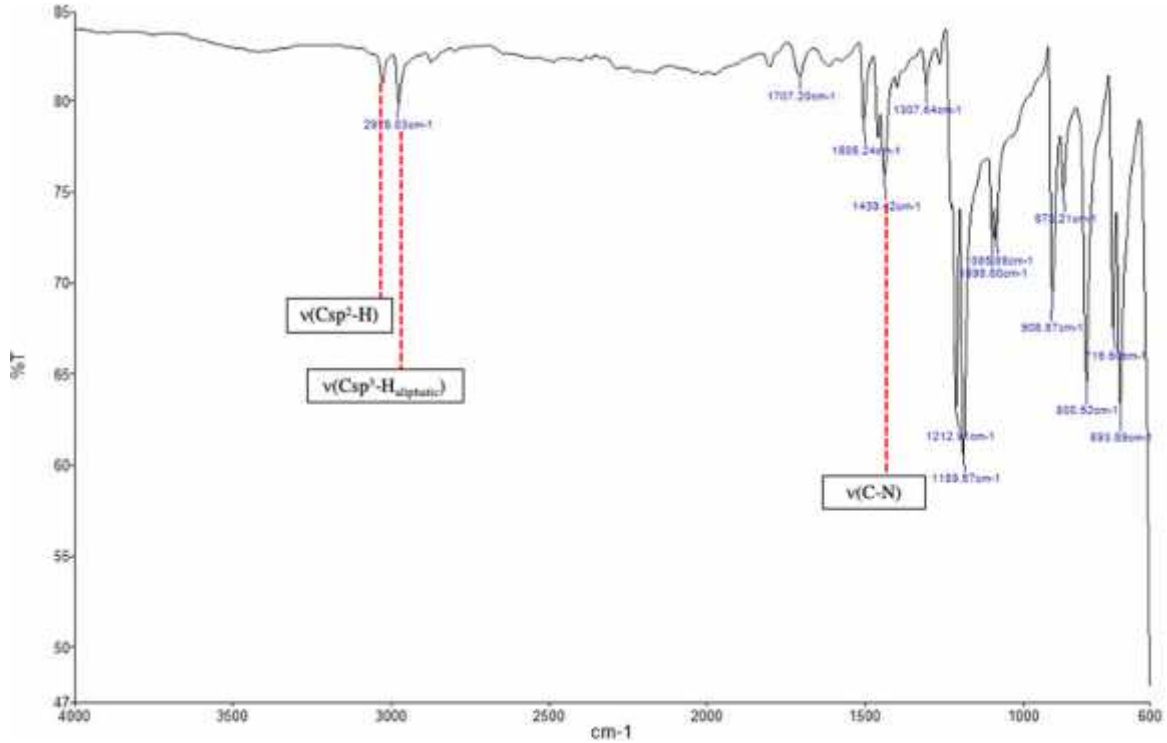


*Figure 3 The FTIR spectra of **Ag1** as representative for the dinuclear silver(I) di-NHC complex.*



Borneo International Journal eISSN 2636-9826; Vol. 7 (1); 2024; 1-8
Published by *Majmuah Enterprise*
www.majmuah.com

The ^{1}H- and ^{13}C-NMR Analysis

The synthesis of tetrakis-imidazolium salt, **1·Br**, and the corresponding dinuclear silver(I) di-NHC complex, **Ag1**, was monitored using ^{1}H and ^{13}C NMR spectroscopy across the range of δ 0 – 11 and δ 0 – 200 ppm, respectively. In the ^{1}H NMR spectrum of **1·Br**, a sharp singlet peak at δ 9.20 ppm attributed to the acidic proton of the imidazolium rings (NC**H**N) was observed, consistent with previous findings. Furthermore, a single peak at δ 3.87 ppm was assigned to the proton of the methylene (N-C**H**$_2$-Ar) unit of the outer part of the imidazolium salt. Additionally, the resonance for the protons of the methylene unit (N-CH$_2$-Ar) within the tetrakis-imidazolium salt, **1·Br**, appeared as a singlet at δ 5.63 ppm. The aromatic protons and imidazole protons were observed as singlets at δ 7.41 - 7.71 ppm and δ, respectively. The formation of complexes was confirmed by the complete disappearance of the acidic (NC**H**N) proton in the complex, **Ag1**, consistent with previous reports. Conversely, the ^{1}H NMR spectrum of the **Ag1** complex displayed signal broadening, indicative of high flexibility in the complex structure, consistent with prior observations.

In the ^{13}C NMR spectrum of tetrakis-imidazolium salt **1·Br**, a peak was observed at δ 137.24 – 137.37 ppm, corresponding to the imidazolium carbon (N**C**HN). However, upon formation of the Ag(I) complex, **Ag1**, a doublet of doublet peaks appeared in the range of δ 180.62 – 182.30 ppm, indicating C$_{carbene}$-Ag bonds. These peaks are attributed to the carbon of the carbene coordinated with two isotopes of silver, ^{107}Ag and ^{109}Ag, with average coupling constants of 181.25 and 210.00 Hz, respectively. The observed variety in the C-Ag peak positions is attributed to the fluxional characteristics of the complex (Şahin et al., 2021). Apart from these changes, all other peaks remained consistent with no significant alterations observed in either the salt, nor the complex.

*Figure 4 The representative ^{1}H NMR spectra (d_6-DMSO, 500 MHz) of **1·Br** as representative for the tetrakis-imidazolium salt.*

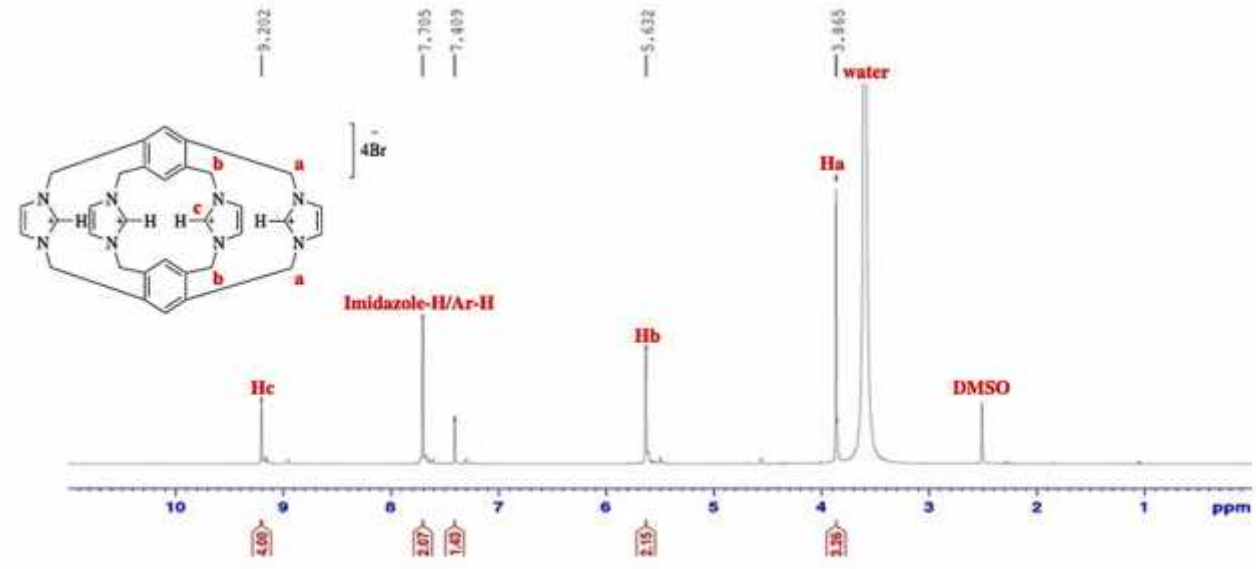


*Figure 5 The ^{13}C NMR spectra (d_6-DMSO, 125 MHz) of **1·Br** as representative for the tetrakis-imidazolium salt.*

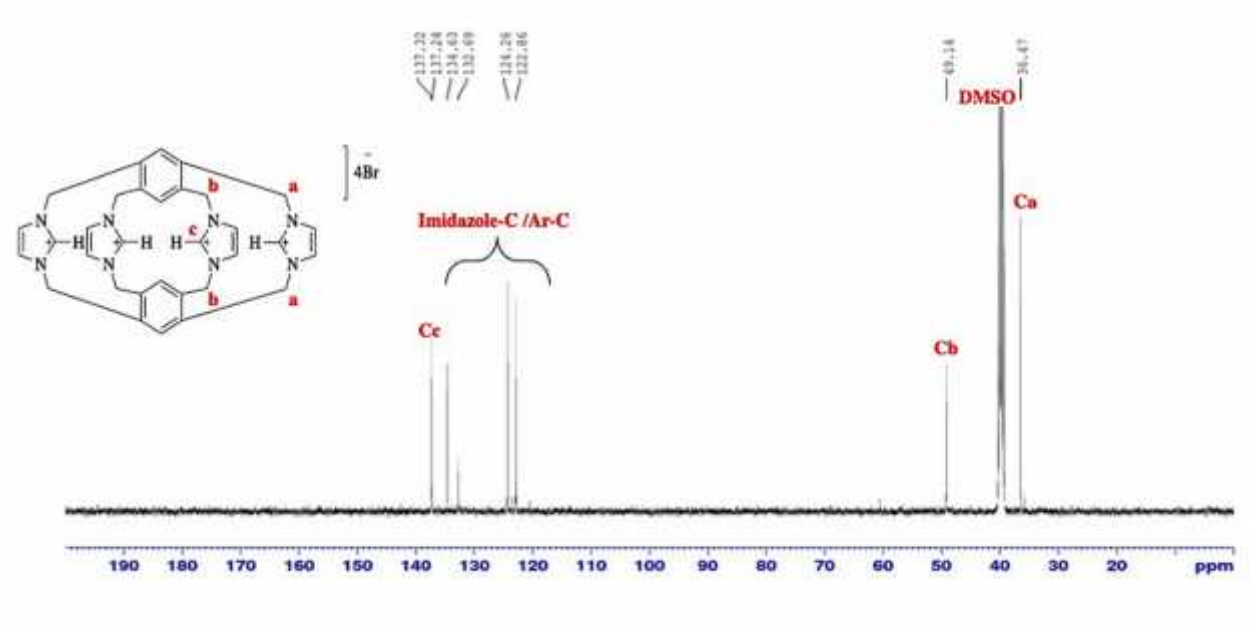


*Figure 6 The ^{13}C NMR spectra (d_6-DMSO, 125 MHz) of **Ag1** as representative for the dinuclear silver(I) di-NHC complex.*

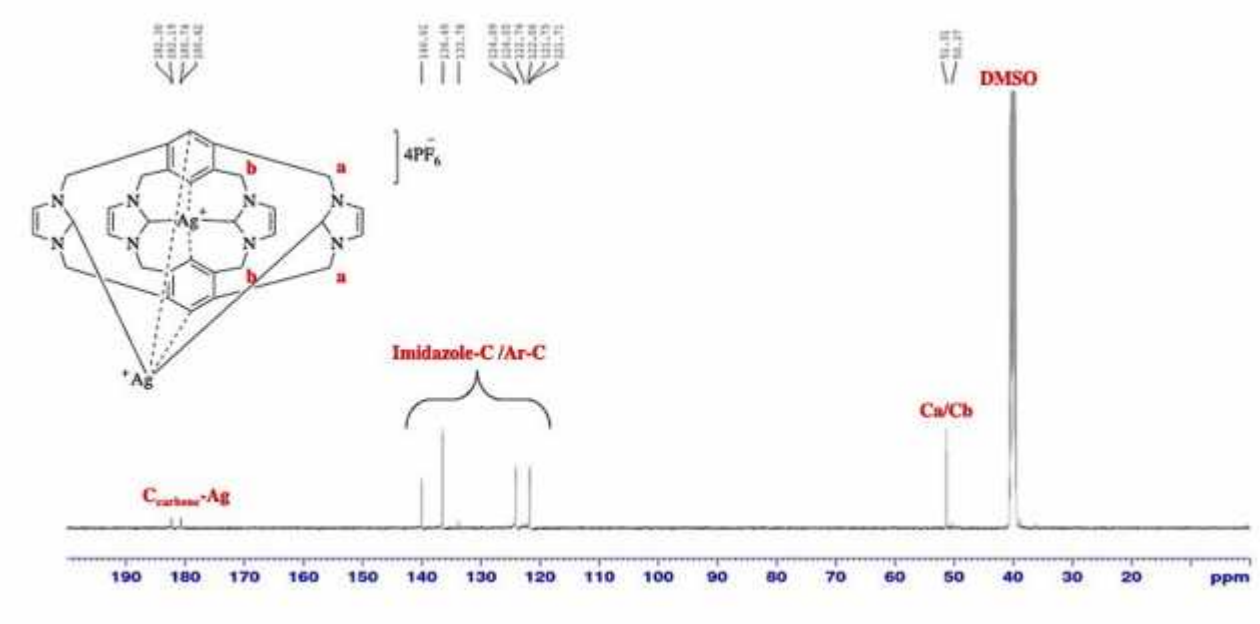
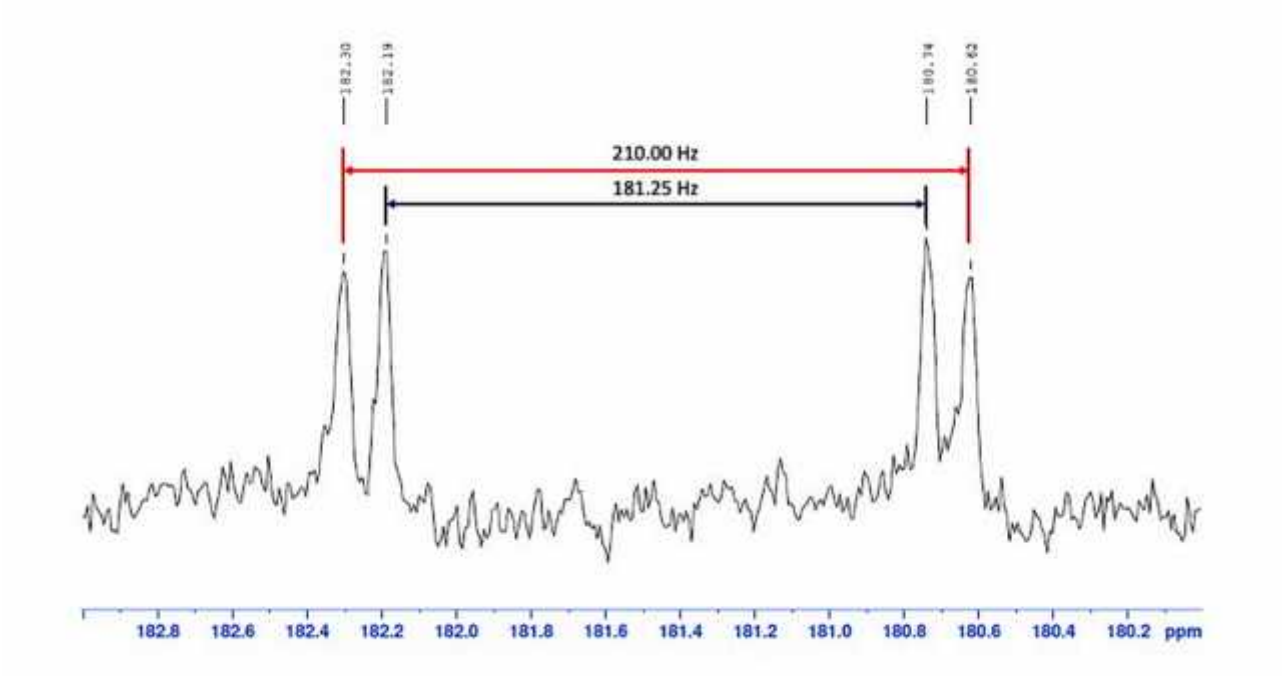


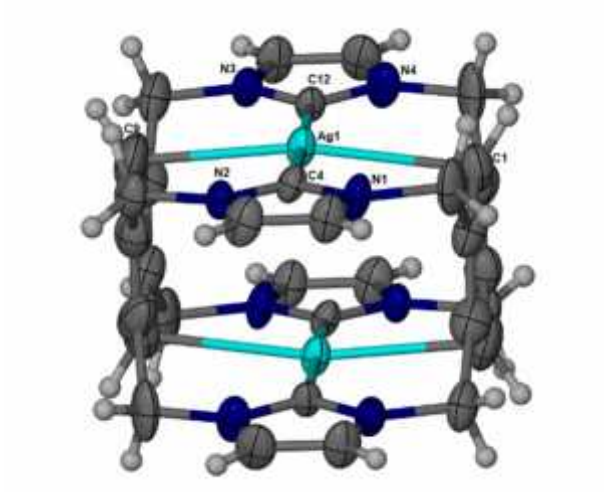
*Figure 7 The expansion of the ^{13}C NMR spectrum of the silver(I)-NHC complex, **Ag1**, recorded in d_6-DMSO at 125 MHz, reveals the distinct resonance signals corresponding to the two types of $C_{carbene}$-Ag bonds, serving as clear evidence of successful complexation.*



X-ray Crystallography Analysis

On the other hand, the crystal structure of complex **Ag1** is successfully obtained by slow diffusion of diethyl ether into a solution of the **Ag1** complex in acetonitrile at room temperature. **Figure 8** depicted the crystal structure of complex **Ag1** as cylinder-type structure. The complex of **Ag1** exists as dinuclear complexes, with each Ag(I) ion display an unprecedented coordination mode to the cyclic ligand. Each Ag(I) is four coordinated, bonded through two carbon carbene atoms and two benzene ring carbons. The entire structure is stabilized with the present of weak argentophilic interaction between the two adjacent Ag(I) ions and p-p interaction. The distances between Ag(I) and the carbon atoms lie in the agreeable with the reported structures (Slimani et al., 2020).

*Figure 8 The crystal structure of the macrocyclic silver(I) di-NHC complex, **Ag1**, exhibits a cyclinder-type architecture.*



4. Conclusions

In conclusion, the silver(I) di-NHC complex of **Ag1** and the tetrakis-imidazolium salt **1·Br** were also synthesized. The Ag(I) di-NHC complexes and generated tetrakis-imidazolium salts were all studied using FTIR, ^{1}H- and ^{13}C-NMR spectroscopies, and CHN elemental analysis, among other spectroscopic methods. Concurrently, single crystal X-ray diffraction experiments have suggested that the **Ag1** macrocyclic complex has a shape akin to a cylinder. Nevertheless, the complex can be further study as antimicrobial and anticancer agent as published by various researchers.

Acknowledgments

The authors thank the Ministry of Higher Education Malaysia for Fundamental Research Grant Scheme with the project code of FRGS/1/2019/STG01/USM/03/2.

References

Altmann, P. J., Weiss, D. T., Jandl, C., & Kühn, F. E. (2016). Exploring Coordination Modes: Late Transition Metal Complexes with a Methylene-bridged Macrocyclic Tetra-NHC Ligand. *Chemistry - An Asian Journal*, *11*(10), 1597–1605.

Atif, M., Bhatti, H. N., Haque, R. A., Iqbal, M. A., Ahamed Khadeer, M. B., & Majid, A. M. S. A. (2020). Synthesis, Structure, and Anticancer Activity of Symmetrical and Non-symmetrical Silver(I)-*N*-Heterocyclic Carbene Complexes. *Applied Biochemistry and Biotechnology*, *191*(3), 1171–1189.

Babamale, H. F., Khor, B. K., Chear, N. J. Y., Haque, R. A., & Yam, W. S. (2022). The First Tetrafluorinated Azobenzene-imidazolium Ionic Conjugates as Potential Thermotropic Liquid Crystalline Drugs: Self-assembly Properties and Cytotoxic Effects. *Journal of Molecular Structure*, *1255*.

Bertrand, B., Citta, A., Franken, I. L., Picquet, M., Folda, A., Scalcon, V., Rigobello, M. P., Le Gendre, P., Casini, A., & Bodio, E. (2015). Gold(I) NHC-based Homo- and Heterobimetallic Complexes: Synthesis, Characterization and Evaluation as Potential Anticancer Agents. *Journal of Biological Inorganic Chemistry*, *20*(6), 1005–1020.

Catalano, A., Mariconda, A., Sinicropi, M. S., Ceramella, J., Iacopetta, D., Saturnino, C., & Longo, P. (2023). Biological Activities of Ruthenium NHC Complexes: An Update. In *Antibiotics* (Vol. 12, Issue 2). MDPI.

De, S., Udvardy, A., Czégéni, C. E., & Joó, F. (2019). Poly-*N*-Heterocyclic Carbene Complexes with Applications in Aqueous Media. In *Coordination Chemistry Reviews* (Vol. 400). Elsevier B.V.

Gutiérrez-Blanco, A., Dobbe, C., Hepp, A., Daniliuc, C. G., Poyatos, M., Hahn, F. E., & Peris, E. (2021). Synthesis and Characterization of Poly-NHC-Derived Silver(I) Assemblies and their Transformation into Poly-Imidazolium Macrocycles. *European Journal of Inorganic Chemistry*, *2021*(25), 2442–2451.

Jakob, C. H. G., Muñoz, A. W., Schlagintweit, J. F., Weiß, V., Reich, R. M., Sieber, S. A., Correia, J. D. G., & Kühn, F. E. (2021). Anticancer and Antibacterial Properties of Trinuclear Cu(I), Ag(I) and Au(I) Macrocyclic NHC/Urea Complexes. *Journal of Organometallic Chemistry*, *932*.

Lescop, C. (2017). Coordination-Driven Syntheses of Compact Supramolecular Metallacycles toward Extended Metallo-organic Stacked Supramolecular Assemblies. *Accounts of Chemical Research*, *50*(4).

Narouz, M. R., Takano, S., Lummis, P. A., Levchenko, T. I., Nazemi, A., Kaappa, S., Malola, S., Yousefalizadeh, G., Calhoun, L. A., Stamplecoskie, K. G., Häkkinen, H., Tsukuda, T., & Crudden, C. M. (2019). Robust, Highly Luminescent Au13 Superatoms Protected by *N*-Heterocyclic Carbenes. *Journal of the American Chemical Society*, *141*(38), 14997–15002.

Rufino-Felipe, E., Valdés, H., Germán-Acacio, J. M., Reyes-Márquez, V., & Morales-Morales, D. (2020). Fluorinated *N*-Heterocyclic carbene complexes. Applications in Catalysis. *Journal of Organometallic Chemistry*, *921*.

Şahin, N., Üstün, E., Tutar, U., Çelik, C., Gürbüz, N., & Özdemir, İ. (2021). Antimicrobial Activity, Inhibition of Biofilm Formation, and Molecular Docking Study of Novel Ag-NHC Complexes. *Journal of Organometallic Chemistry*, *954–955*.

Slimani, I., Chakchouk-Mtibaa, A., Mellouli, L., Mansour, L., Ozdemir, I., Gürbüz, N., & Hamdi, N. (2020). Novel *N*-Heterocyclic Carbene Silver(I) Complexes: Synthesis, Structural Characterization, Antimicrobial and Cytotoxicity Potential Studies. *Journal of the Brazilian Chemical Society*, *31*(10), 2058–2070.

Wang, Y. S., Feng, T., Wang, Y. Y., Hahn, F. E., & Han, Y. F. (2018). Homo- and Heteroligand Poly-NHC Metal Assemblies: Synthesis by Narcissistic and Social Self-Sorting. *Angewandte Chemie - International Edition*, *57*(48), 15767–15771.

Yu, J., Ye, S., Shi, Y., Liao, H., & Wang, D. (2021). Thermally Formation and Luminescent Performance of Silver Nanoclusters Confined within LTA Zeolites. *Journal of Alloys and Compounds*, *857*.