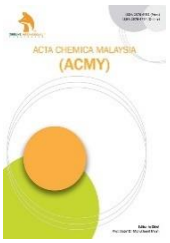
ZIBELINE INTERNATIONAL™ PUBLISHING

ISSN: 2576-6724 (Print)
ISSN: 2576-6732 (Online)
CODEN: ACMCCG

Acta Chemica Malaysia (ACMY)

DOI: http://doi.org/10.26480/acmy.01.2024.13.18



RESEARCH ARTICLE

SYNTHESIS AND STRUCTURAL ELUCIDATION OF SYMMETRICAL TETRAKIS-IMIDAZOLIUM DINUCLEAR SILVER(I) DI-*N*-HETEROCYCLIC CARBENE COMPLEX

Muhammad Zulhelmi Nazri[a,b*] and Mohd Rizal Razali[b]

[a,b]Innovation Centre in Agritechnology for Advanced Bioprocessing (ICA), Universiti Teknologi Malaysia (Pagoh Campus), Eduhub Pagoh 84600 Pagoh, Johor, Malaysia
[b]School of Chemical Sciences, Universiti Sains Malaysia 11800 Minden, Penang, Malaysia
**Corresponding Author Email: mzulhelmin@utm.my*

ARTICLE DETAILS

Article History:

Received 10 January 2024
Revised 13 February 2024
Accepted 17 March 2024
Available online 23 March 2024

ABSTRACT

This brief report outlines the synthesis and analysis of symmetrical dinuclear Ag(I) di-*N*-heterocyclic carbene (NHC) complexes, primarily derived from tetrakis-benzimidazolium salts. The symmetrical tetrakis-imidazolium salt was synthesized by reacting 1,2,4,5-tetrakis(bromomethyl)benzene with the imidazole moiety of **1·Br**. These salts were then transformed into their respective complexes through an in-situ deprotonation reaction with Ag_2O, utilizing different salt-to-metal molar ratios, resulting in the establishment of dinuclear Ag(I) di-NHC complexes designated as **Ag1**. The structures of both the tetrakis-imidazolium (**1·Br**) salts and the Ag(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.

KEYWORDS

Imidazolium salt; Dinuclear silver(I) complex; Macrocyclic; NHC

1. INTRODUCTION

In coordination chemistry, the macrocyclic effect is an important requirement for the design and synthesis of ligand motifs (Cabbiness and Margerum, 1969). 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). 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, C., 2017).

Several methodologies have been utilized in the synthesis of cyclic polymers, initially employing ring-chain equilibration (Gan et al., 2018). The synthesis of cyclic polymers commenced with the generation of cyclic poly (decamethylene adipate) through the polycondensation reaction of adipic acid and decamethylene glycol, thus corroborating a previous concept proposed by Jacobson and Stockmayer. These researchers integrated ring formation into their models of molecular species distribution in polycondensates, proposing that the proportion of rings increases with dilution and molecular weight. Furthermore, investigations into the synthesis of cyclic oligo- and poly(dimethyl siloxane) were conducted concerning ring-chain equilibration. Throughout the years, numerous reviews and publications have elaborated on advancements in ring-chain equilibration, encompassing discussions on the Jacobson and Stockmayer theory alongside newer concepts.

NHCs have emerged as a novel class of potential donors for constructing metallo-supramolecular structures characterized by M-C_{NHC} bonds (Sinha and Hahn, 2017). Serving as valuable ancillary ligands, NHCs have attracted significant attention in the fields of organometallic and coordination chemistry 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 (Danopoulos et al., 2019; Rufino-Felipe et al., 2020). Numerous poly-NHC metal complexes have been reported, synthesized by reacting Ag(I), Au(I), Cu(I), Pd(II), and Ni(II) with poly-NHC ligands containing various functional groups such as pyridyl, phosphinyl, pyrazolyl, and quinolinyl groups (Botubol-Ares et al., 2021; Narouz et al., 2019; Mondal et al., 2019). Among these metal-NHC supramolecular structures, the Ag-NHC family has garnered significant attention due to its frequent use as carbene transfer agents in the synthesis of other metal-NHC supramolecular structures, along with its appealing chemical, structural, and photophysical properties (Lu et al., 2018; Yu et al., 2021; Liu and Chen, 2012).

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.

Quick Response Code	Access this article online	
	Website: www.actachemicamalaysia.com	**DOI:** 10.26480/acmy.01.2024.13.18

Cite the Article: Muhammad Zulhelmi Nazri and Mohd Rizal Razali (2024). Synthesis and Structural Elucidation of Symmetrical Tetrakis-Imidazolium Dinuclear Silver(I) Di-*N*-Heterocyclic Carbene Complex. *Acta Chemica Malaysia, 8(1): 13-18.*

2. Materials and Methods

2.1 Materials and Instruments

All chemicals and solvents were procured from commercial suppliers and utilized without further purification. Melting points were determined using a Stuart Scientific SMP-1 (UK) instrument. Elemental analyses were conducted employing a PerkinElmer Series II, 2400 microanalyzer. FTIR spectra were acquired using a PerkinElmer FTIR Microscope Spotlight 200 within the range of 4000 – 600 cm^{-1}. Nuclear magnetic resonance (NMR) spectra were recorded in DMSO-d_6 on Bruker 500 MHz Ascend spectrometers at room temperature, with TMS serving as an internal standard.

2.3 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 **16·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%

2.4 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%

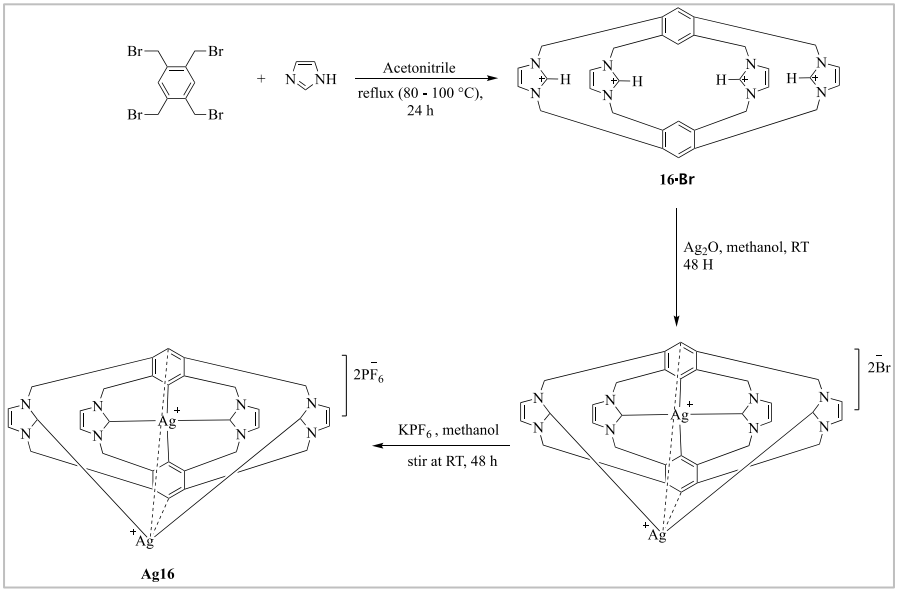
2.5 X-Ray Crystallography Refinement

Single crystal X-ray diffraction data were gathered using a Bruker-Smart ApexII-2009 CCD diffractometer equipped with a graphite monochromator utilizing Mo-Kα radiation (λ = 0.71073 Å). Data collection for the complex occurred at room temperature. Integration was performed utilizing the SAINT program within the APEXII software suite. Solutions were derived employing direct methods via SHELXS-2014, followed by iterative refinements using the full-matrix least-squares method against F^2 with SHELXL-2014 (Wisconsin, 2005; Sheldrick, 2008). The X-seed program served as a graphical interface for SHELX.

3. Result and Discussion

3.1 Synthesis

Scheme 1 outlines the conversion of imidazolium salt, **1·Br** to its corresponding Ag(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 Ag(I)-NHC complex, **Ag1** was obtained as a white precipitate by treating 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** is soluble in polar organic solvents such as acetonitrile, DMSO, and DMF, but exhibits insolubility in diethyl ether, benzene, hexane, and water.



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

3.2 The FTIR Analysis

The FTIR spectra of the non-functionalized tetrakis-imidazolium salt **1·Br** and its respective dinuclear Ag(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 – 2946 cm^{-1} corresponded to aliphatic Csp^3-H vibrations in both the salt and the complex. A sharp and strong intensity band at 1559 cm^{-1} indicated the presence of the 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 (Babamale et al., 2022; Loh et al., 2019).

3.3 The ^{1}H and ^{13}C NMR analysis

The synthesis of tetrakis-imidazolium salt, **1·Br**, and the corresponding dinuclear Ag(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. Apart from these changes, all other peaks remained consistent with no significant alterations observed in either the salt nor the complex.

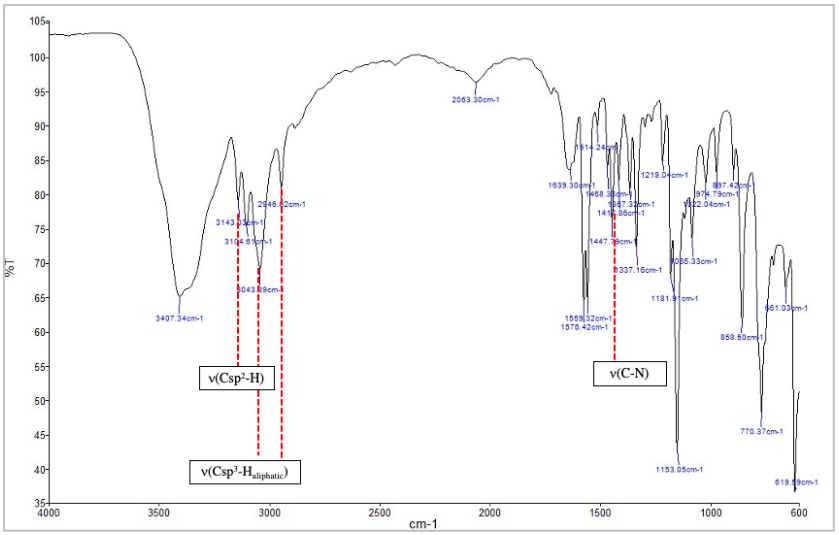


Figure 2: The FTIR spectra of **1·Br** as representative for the tetrakis-imidazolium salt.

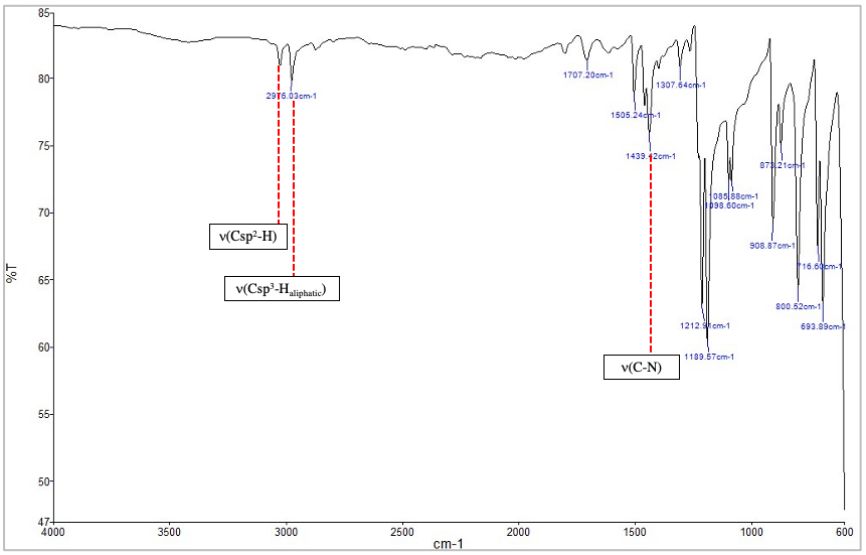


Figure 3: The FTIR spectra of **Ag1** as representative for the dinuclear Ag(I) di-NHCcomplex.

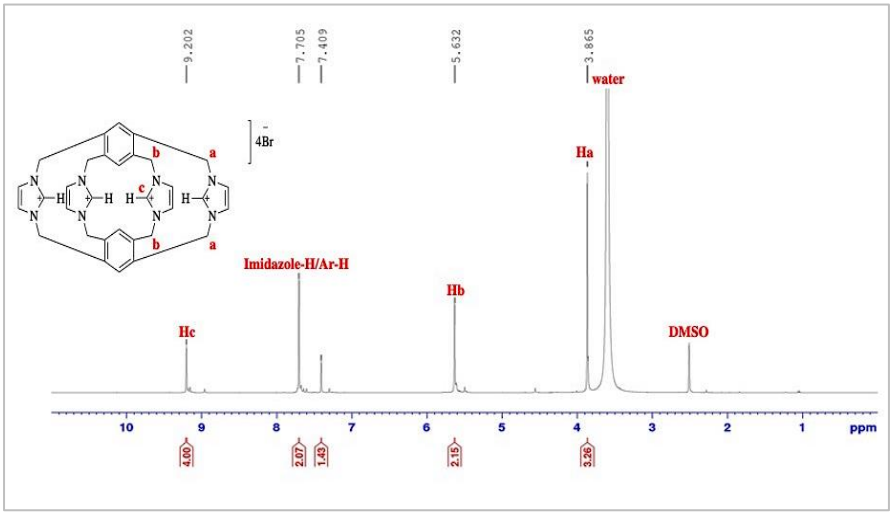


Figure 4: The representative ^{1}H NMR spectra (d_6-DMSO, 500 MHz) of **1·Br** as representative for the tetrakis-imidazolium salt.

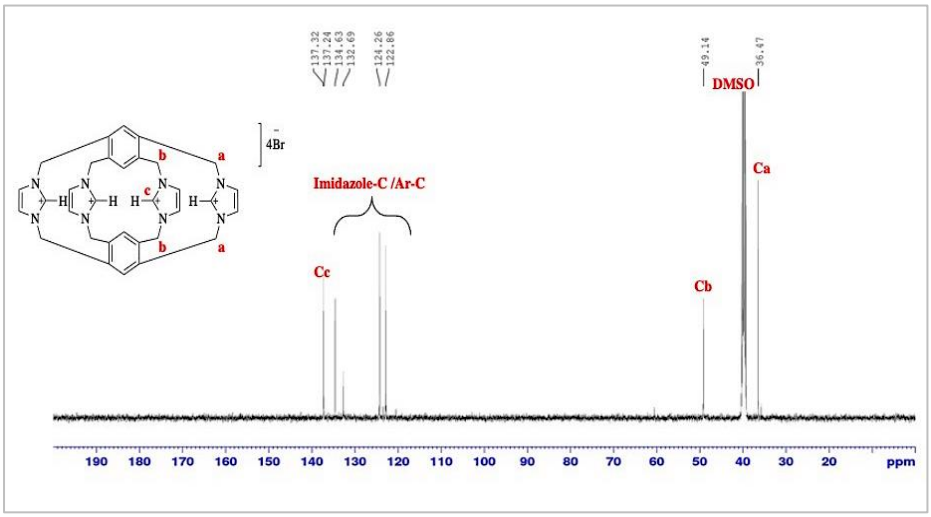


Figure 5: The ^{13}C NMR spectra (d_6-DMSO, 125 MHz) of **1·Br** as representative for the tetrakis-imidazolium salt.

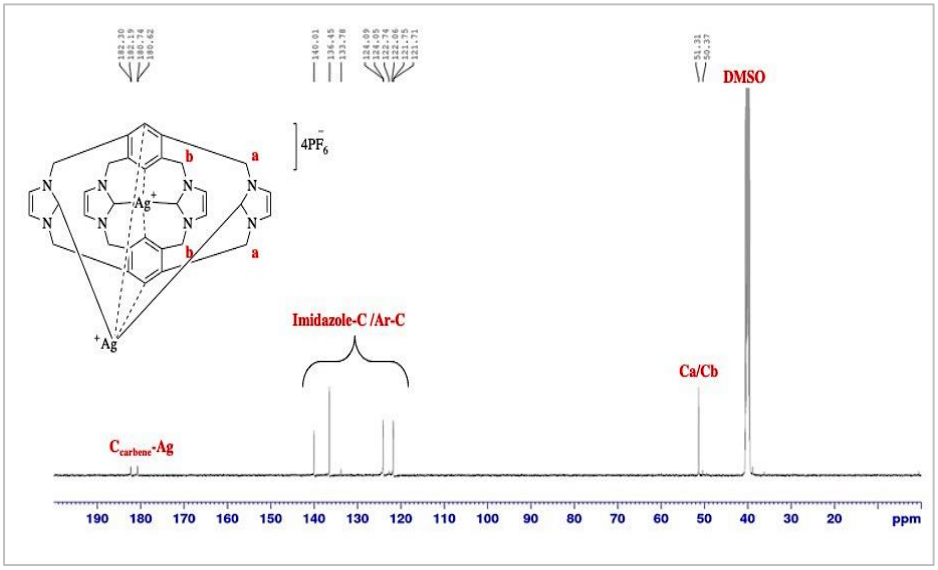


Figure 6: The ^{13}C NMR spectra (d_6-DMSO, 125 MHz) of **Ag1** as representative for the dinuclear Ag(I) di-NHC complex.

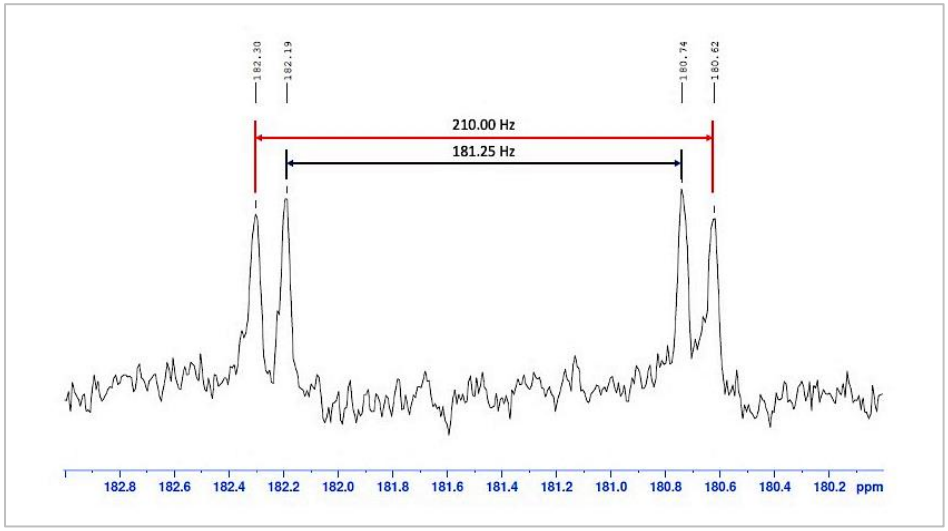


Figure 7: The expansion of the ^{13}C NMR spectrum of the Ag(I)-NHC complex, **Ag1**, recorded in d_6-DMSO at 125 MHz, reveals the distinct resonance signals corresponding to the two types of $C_{carbene}$-Ag bonds, serving as clear evidence of successful complexation.

3.4 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).

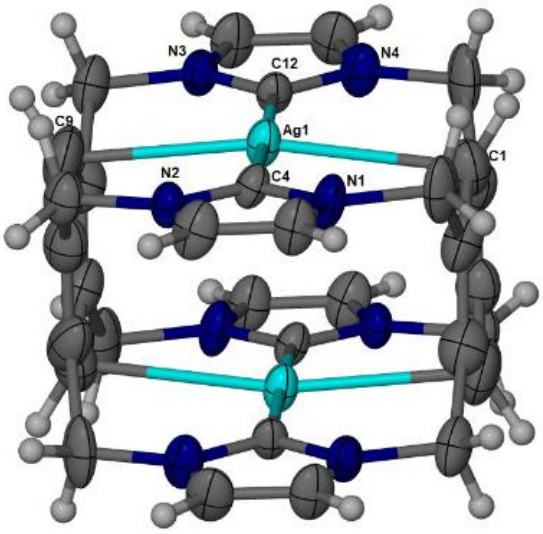


Figure 8: The crystal structure of the macrocyclic Ag(I)-NHC complex, **Ag1**, exhibits a cylinder-type architecture.

4. Conclusion

In summary, the tetrakis-imidazolium salt, 1·Br along with its **Ag(I)** di-NHC complex, **Ag1** were also synthesized. All synthesized tetrakis-imidazolium salt and their **Ag(I)** di-NHC complexes were characterized by several spectroscopic techniques including FTIR, ^{1}H- and ^{13}C-NMR spectroscopies and CHN elemental analysis. Meanwhile, through the single crystal X-ray diffraction studies, has suggest complex the macrocyclic complex of **Ag1** has cylinder-type structure.

Acknowledgement

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.

Declaration of Competing Interest

We would like to declare that there is no conflict of interest in publishing this work.

References

Altmann, P. J., Weiss, D. T., Jandl, C., and 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), Pp. 1597-1605.

Babamale, H. F., Khor, B. K., Chear, N. J. Y., Haque, R. A., and Yam, W., 2022. The first tetrafluorinated azobenzene-imidazolium ionic conjugates as potential thermotropic liquid crystalline drugs: self-assembly properties and cytotoxic effects. Journal of Molecular Structure, Pp. 132470.

Bertrand, B., Citta, A., Franken, I. L., Picquet, M., Folda, A., Scalcon, V., Rigobello, M. P., Gendre, P. L., Casini, A., and Bodio, E., 2015. Gold(I) NHC-based homo- and heterobimetallic complexes: synthesis, characterization and evaluation as potential anticancer agents. JBIC Journal of Biological Inorganic Chemistry, 20(6), Pp. 1005-1020

Botubol-Ares, J. M., Cordón-Ouahhabi, S., Moutaoukil, Z., Collado, I. G., Jiménez-Tenorio, M., Puerta, M. C., and Valerga, P., 2021. Methylene-linked Bis-NHC half-sandwich ruthenium complexes: binding of small molecules and catalysis toward ketone transfer hydrogenation .Organometallics, 40(6), Pp. 792-803.

Cabbiness, D. K., and Margerum, D. W., 1969. Macrocyclic effect on the stability of copper(II) tetramine complexes. Journal of the American Chemical Society, 91(23), Pp. 6540-6541.

Danopoulos, A. A., Simler, T., and Braunstein, P., 2019. *N*-heterocyclic carbene complexes of copper, nickel, and cobalt. Chemical reviews, 119(6), Pp. 3730-3961.

Gan, M. M., Liu, J. Q., Zhang, L., Wang, Y. Y., Hahn, F. E., and Han, Y. F., 2018. Preparation and post-assembly modification of metallosupramolecular assemblies from poly(*N*-heterocyclic carbene) ligands. Chemical reviews , 118(19), Pp. 9587-9641.

Haziz, U. F., Haque, R. A., Amirul, A. A., and Razali, M. R., 2021. Synthesis, structural analysis and antibacterial studies of bis-and open chain tetra-*N*-heterocyclic carbene dinuclear silver(I) complexes. Journal of Molecular Structure, 1236, Pp. 130301.

Lescop, C., 2017. Coordination-driven syntheses of compact supramolecular metallacycles toward extended metallo-organic stacked supramolecular asse mblies. Accounts of Chemical Research, 50(4), Pp. 885-894.

Liu, X., Chen, W., 2012. Pyridazine-based N-heterocyclic carbene complexes and ruthenium-catalyzed oxidation reaction of alkenes . Organo metallics, 31(18), Pp. 6614-6622.

Loh, Y. L., Haziz, U. F., Haque, R. A., Amirul, A. A., Aidda, O. N., and Razali, M. R., 2019. The effect of short alkane bridges in stability of bisbenzimidazole-2-ylidene silver(I) complexes: synthesis, crystal structure and antibacterial activity. Journal of Coordination Chemistry, 72(5-7), PP. 894-907.

Lu, T., Wang, J. Y., Shi, L. X., Chen, Z. N., Chen, X. T., and Xue, Z. L., 2018. Synthesis, structures and luminescence properties of amine-bis(*N*-heterocyclic carbene) copper(I) and silver(I) complexes. Dalton Transactions, 47(19), Pp. 6742-6753.

Mondal, A., Tripathy, R. K., Dutta, P., Santra, M. K., Isab, A. A., Bielawski, C. W., Kisan, H. K., Chandra, S. K. Dinda, J., 2019. Ru (II)-based antineoplastic: A "wingtip" N-heterocyclic carbene facilitates access to a new class of organometallics that are cytotoxic to common cancer cell lines. Applied Organometallic Chemistry, 33(1), e4692.

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. and Crudden, C. M., 2019. Robust, highly luminescent Au_{13} superatoms protected by *N*-heterocyclic carbenes. Journal of the American Chemical Society, 141(38), Pp. 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, 121 364.

Sheldrick, G. M., 2008. A short history of SHELX, Acta Crystallographica Section A: Foundations of Crystallography, 64(1), Pp. 112-122.

Sinha, N., and Hahn, F. E., 2017. Metallosupramolecular architectures obtained from poly-*N*-heterocyclic carbene ligands. Accounts of Chemical Research, 50(9), Pp. 2167-2184.

Slimani, I., Chakchouk-Mtibaa, A., Mellouli, L., Mansour, L., Ozdemir, I., Gürbüz, N., and 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, Pp. 2058-2070.

Ul Huda, N., Islam, S., Zia, M., William, K., i Abbas, F., Umar, M. I., Iqbal. M. A., and Mannan, A., 2019. Anticancer, antimicrobial and antioxidant potential of sterically tuned bis-*N*-heterocyclic salts. Zeitschrift für Naturf orschung C, 74(1-2), Pp. 17-23.

Wisconsin, 2005. ApexII, Bruker AXS Ltd., Madison,

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, Pp. 157614.