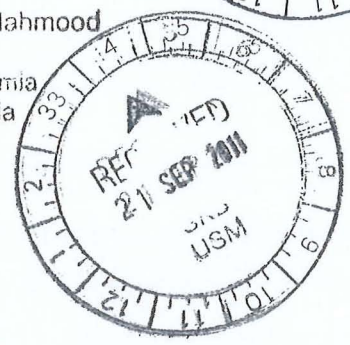
Prof Asma Ismail
Timbalan Naib Canselor Penyelidikan dan Inovasi
Universiti Sains Malaysia
11800 Pulau Pinang

12 Sept 2011

Melalui:

Prof Wan Ahmad Kamil Che Mahmod
Dekan, Pusat Pengajian Sains Kimia

Prof. Dr. Wan Ahmad Kamil Mahmood
Dekan
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia



Prof Norita Mohamed
Timbalan dekan Penyelidikan
Pusat Pengajian Sains Kimia

Yang berbahagia Prof

Laporan Akhir Geran RU.

Dengan segala hormatnya perkara di atas adalah di rujuk. Di sertakan di sini laporan akhir untuk geran penyelidikan RU seperti butir berikut:

Project Title	:	Silver Complexes of Cyclophanes and Their Analogues as Antimicrobial and Anticancer Agents.
Grant Number	:	304/PKIMIA/639001
Project Coordinator	:	Dr. Rosenani SMA Haque
Date of Commencement	:	14 May 2009
Date of Expiry	:	14 November 2011
Amount	:	RM100,000

2. Sebanyak 14 penerbitan telah di hasilkan untuk projek ini, Sila lihat lampiran.

Sekian, harap maklum dan saya harap pihak Prof dapat mempertimbangkan permohonan geran penyelidikan jangka pendek saya yang akan menyusul dalam masa terdekat.

Salam hormat.

Yang benar

Dr Rosenani S.M. Anwarul Haque
Pensyarah Kanan
Pusat Pengajian Sains Kimia

Dr. Rosenani S.M. Anwarul Haque
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia
11800 Pulau Pinang

UNIVERSITI SAINS MALAYSIA

UNIVERSITY RESEARCH GRANT FINAL REPORT
Geran Penyelidikan Universiti Laporan Akhir

A.	**PARTICULARS OF RESEARCH** / *MAKLUMAT PENYELIDIKAN:*
(i)	**Title of Research: Silver Complexes of Cyclophanes and Their Analogues as Antimicrobial and Anticancer Agents.** *Tajuk Penyelidikan:*
(ii)	**Account Number: 1001/PKIMIA/813023** *Nombor Akaun:*
B.	**PERSONAL PARTICULARS OF RESEARCHER** / *MAKLUMAT PENYELIDIK:*
(i)	**Name of Research Leader: Dr Rosenani bt. S.M. Anwarul Haque** *Nama Ketua Penyelidik:*
	Name of Co-Researcher 1. Assoc Prof Dr Amirul Al Ashraf Abdullah **2. Dr. Amutha Santhanam** *Nama Penyelidik Bersama:*
(ii)	**School/Institute/Centre/Unit : School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Minden, Penang.** *Pusat Pengajian /Institut/Pusat/Unit :*
C.	**Research Platform (Please tick (/) the appropriate box):** *Pelantar Penyelidikan (Sila tanda (/) kotak berkenaan):*

- [√] **A. Life Sciences** *Sains Hayat*
- [ ] **B. Fundamental** *Fundamental*
- [ ] **C. Engineering & Technology** *Kejuruteraan & Teknologi*
- [ ] **D. Social Transformation** *Transformasi Sosial*
- [ ] **E. Information & Communications Technology (ICT)** *Teknologi Maklumat & Komunikasi*
- [ ] **F. Clinical Sciences** *Sains Klinikal*
- [√] **G. Biomedical & Health Sciences** *Bioperubatan Sains Kesihatan*

D. **Duration of this research :**
Tempoh masa penyelidikan ini :

***Duration :** 30 Months
Tempoh :

From : 14 May 2009 **To** : 14 November 2011
Dari: *Ke :*

E. **ABSTRACT OF RESEARCH**

(An abstract of between 100 and 200 words must be prepared in **Bahasa Malaysia and in English**. This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Abstrak Penyelidikan
(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris**.
Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Please See Appendix 1.

F. **SUMMARY OF RESEARCH FINDINGS:**
Ringkasan dapatan Projek Penyelidikan

Please See Appendix 2.

G. **COMPREHENSIVE TECHNICAL REPORT:**
Laporan Teknikal Lengkap
Applicants are required to prepare a comprehensive technical report explaining the project.
(This report must be attached separately)
Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini.
[Laporan ini mesti dikepilkan]

Please See Appendix 3.

List the key words that reflectour research:
Senaraikan kata kunci yang mencerminkan penyelidikan anda:

English	Bahasa Malaysia
Silver(I) complexes	Kompleks argentum
Antimicrobial agents	Agen antimikrobial
Anticancer agents	Agen antitumor
N-Heterocyclic carbene	N-Heterosiklik carben

H. **a) Results/Benefits of this research**
Hasil Penyelidikan

No. *Bil:*	Category/Number: *Kategori/ Bilangan:*	Promised	Achieved
1.	**Research Publications (Specify target journals)** *Penerbitan Penyelidikan (Nyatakan sasaran jurnal)*	**At least 3 more, one on antimicrobial activities (J. Organomet. Chem) and 2 in structural reports (Acta cryst E)**	**14 publications.** **Please see Appendix 4**
2.	**Human Capital Development**		
	a. Ph. D Students	**3**	
	b. Masters Students	**3**	
	c. Undergraduates (Final Year Project)	**9**	
	d. Research Officers		
	e. Research Assisstants		
	f. Other: Please specify		
3.	**Patents** *Paten*		
4.	**Specific / Potential Applications** *Spesifik/Potensi aplikasin*	**The University of Western Australia (UWA)**	
5.	**Networking & Linkages** *Jaringan & Jalinan*		
6.	**Possible External Research Grants to be Acquired** *Jangkaan Geran Penyelidikan Luar Diperoleh*		

- Kindly provide copies/evidence for Category 1 to 6.

b) Equipment used for this research.
Peralatan yang telah digunakan dalam penyelidikan ini.

Items *Perkara*	Approved Equipment	Approved Requested Equipment	Location
Specialized Equipment Peralatan khusus			
Facility Kemudahan			
Infrastructure Infrastruktur			

- Please attach appendix if necessary.

I.	**BUDGET** / *BAJET*

Total Approved Budget : RM 100,000
Total Additional Budget : RM 0
Grand Total of Approved Budget : RM 100,000

Yearly Budget Distributed

Year 1 : RM 40,000
Year 2 : RM 60,000
Year 3 : RM

Additional Budget Approved

Year 1 : RM
Year 2 : RM
Year 3 : RM

Total Expenditure : RM 98896.84
Balance : RM 1,103.16

- **Please attach final account statement from Treasury** (attached)

Rosenani

Signature of Researcher
Tandatangan Penyelidik

12/9/11

Date
Tarikh

Dr. Rosenani S.M. Anwarul Haque
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia
11800 Pulau Pinang

H. **COMMENTS OF PTJ'S RESEARCH COMMITTEE**
KOMEN JAWATANKUASA PENYELIDIKAN PERINGKAT PTJ

General Comments:
Ulasan Umum:

The work has resulted in publication regarding synthesis and characterisation of proposed complexes. For continuing work, publications on studies on antimicrobial and anticancer ~~shot~~ activities are anticipated.

.....

Signature and Stamp of Chairperson of PTJ's Evaluation Committee
Tandatangan dan Cop Pengerusi Jawatankuasa Penilaian PTJ

Profesor Norita Mohamed
Timbalan Dekan
(Pengajian Siswazah dan Penyelidikan)
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia

Date : .....
Tarikh :.....

Signature and Stamp of Dean/ Director of PTJ
Tandatangan dan Cop Dekan/ Pengarah PTJ

Date : .....
Tarikh :.....

Prof. Dr. Wan Ahmad Kamil Mahmood
Dekan
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia

Purchase Requisition ▸ Purchase Order ▸ Suppliers ▸ Maintenance ▸ Financials ▸ Coda Info ▸ Reports ▸ Admin ▸

UserCode: SHEELA / USMPGLIVE / PKIMIA **Program Code: Votebook9100** **Current Program : Votebook (Header)**

Current Date : 19/08/2011 3:53:58 PM **Version: 13.92, Last Updated at 30/05/2011** **DB: 13.02, 9/27/2010 VB: 13.01, 3/14/2011** **Switch Language : English / Malay**

Wildcard : eg. Like 100%, Like 10%1, Like %1

Element 1: 1001 Element 2: % Element 4: PKIMIA

Element 5: 813023 Year: 2011

Detail	Excel	Budget Rule	Budget Control	Account Description	Budget Account Code	Roll over	Budget	Cash Received	Advanced	Commit	Actual	Available	Percentage
Detail	Excel	489	T	Projek Kumpulan Wang Uni Penyelidikan	1001.111.0.PKIMIA.813023	22,500.00	0.00	0.00	0.00	0.00	0.00	22,500.00	0.00%
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Detail	Excel	490	T	Projek Kumpulan Wang Uni Penyelidikan	1001.221.0.PKIMIA.813023	10,040.35	0.00	0.00	0.00	0.00	1,247.00	8,793.35	0.00%
Detail	Excel	490	T	Projek Kumpulan Wang Uni Penyelidikan	1001.223.0.PKIMIA.813023	4,000.00	0.00	0.00	0.00	0.00	0.00	4,000.00	0.00%
Detail	Excel	490	T	Projek Kumpulan Wang Uni Penyelidikan	1001.224.0.PKIMIA.813023	-50.00	0.00	0.00	0.00	0.00	60.00	-110.00	0.00%
Detail	Excel	490	T	Projek Kumpulan Wang Uni Penyelidikan	1001.227.0.PKIMIA.813023	-11,593.03	0.00	0.00	0.00	343.00	29,054.74	-40,990.77	0.00%
Detail	Excel	490	T	Projek Kumpulan Wang Uni Penyelidikan	1001.228.0.PKIMIA.813023	6,000.00	0.00	0.00	0.00	0.00	0.00	6,000.00	0.00%
Detail	Excel	490	T	Projek Kumpulan Wang Uni Penyelidikan	1001.229.0.PKIMIA.813023	3,048.45	0.00	0.00	0.00	2,100.00	0.00	948.45	0.00%
		490	T	SubTotal		11,445.77	0.00	0.00	0.00	2,443.00	30,361.74	-21,358.97	0.00%
Detail	Excel	493	T	Projek Kumpulan Wang Uni Penyelidikan	1001.552.0.PKIMIA.813023	-37.87	0.00	0.00	0.00	0.00	0.00	-37.87	0.00%
		493	T	SubTotal		-37.87	0.00	0.00	0.00	0.00	0.00	-37.87	0.00%
		9999		GrandTotal		33,907.90	0.00	0.00	0.00	2,443.00	30,361.74	1,103.16	0.00%

Appendix 3 Comprehensive Final Report

Contents

1. Project Overview
    - 1.1. Consortium Description
    - 1.2. Main Achievements
2. Project Objectives
3. Project Methodologies, Results and Achievements
    - 3.1. Metal-Based System Developments
    - 3.2. Methodologies
    - 3.3. Results and Discussion
    - 3.4. Achievements of Objectives
4. Out Looks
5. Conclusions

Project Details

Project Title	:	Silver complexes of cyclophanes and their analogues as antimicrobial and anticancer agents.
Grant Number	:	1001/PKIMIA/813023
Project Coordinator	:	Dr. Rosenani SM Anwarul Haque, PhD
Date of Commencement	:	14 May 2009
Date of Expiry	:	14 November 2011
Researchers Employed	:	3 PhD and 3 MSc. students
Allotted Fund	:	RM100,000
Number of Publications	:	12
% Utilization of Fund	:	100 %
Remarks	:	Successfully completed

1. Project Overview

1.1. Consortium Description

The Research University project (1001/PKIMIA/813023) is led by Dr. Rosenani SMA Haque as research leader and Assoc Prof Dr Amirul Al Ashraf Abdullah and Dr. Amutha Santhanam as co-researchers; followed by the assistance of a group of students to execute the project goals. All researchers worked under this project share a common mission, which is to conduct research on the application of formal methods for the development of novel metal-based coordination compounds with N-heterocyclic carbene (NHC) ligands as metal-based drugs. The researchers also have a long range objective of transforming the applications of formal methods from an academic research topic into a practice in pharmaceutical/medical sciences. The co-researchers from biology school and The Institute for Research in Molecular Medicine (INFORMM) have common background knowledge which facilitates collaborative work, and they bring in complementary expertise.

This project has also generated interests of a number of collaborators from USM and abroad. One student from this research group will be working in similar area as visiting student in The University of Western Australia (UWA) for 3 months starting September 2011 as collaboration with the UWA; a collaborator in The University of Mauritius is interested to perform theoretical studies on our complexes and recently a researcher from The National Institute of Technology-Karnataka, Surathkal, India has also approached the lead researcher for a collaboration. In USM, our external collaborators in the physics school contributed significantly in the structure analysis using single crystal X-ray diffraction technique that helped to get more insight into the structures of compounds; which led to the excellent achievements.

1.2. Main Achievements

In the project approach, the ligand systems are modeled as mimics of the biological entities with a well-defined dynamics. Preparation of novel Ag(I)-NHC complexes have been at the forefront of many research areas, however, the relevance to the biological systems haven't been fully explored yet. In this project, we have attempted to achieve confirmation, optimization, synthesis and design of NHC salts and their silver complexes, so that the resulting behaviors of the complexes are correct, optimal and relevant.

In this approach, we successfully synthesized and characterized a series of eight NHC ligands and their respective silver(I) complexes in moderate to good yields at low-to-moderate costs. Structures of many of the ligands and their corresponding silver(I) complexes have been determined by single crystal X-ray diffraction technique. All of the novel compounds are stable, not sensitive towards air and moisture and possessing structural relevance with the existing biological systems (a well-established system) to act as potent antimicrobial as well as anticancer agents. All of the Ag(I)-NHC complexes tested have shown exceptionally good antimicrobial property against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) biocides. The methods and results of the microbial activity is appended as **Appendix 5**. Anticancer activity screening of the prepared silver(I) complexes and their respective NHC salts is in progress at our very recent collaboration with The EMAN Testing and Research Laboratory, Department of Pharmacology, School of Pharmaceutical Sciences, USM.

Project Objectives

The following description of the objectives of this project has been undertaken:

This project intends to contribute to the solutions for the growing synthetic inorganic chemistry needs to design reliable and efficient metal-based systems for treatment of cancer. In particular, the project intends to provide novel methodologies and stable Ag(I)-NHC complexes for anticancer activities. This academic research outcome, in the form of novel compounds, the methods and the tools of which can be a basis for the next generation research practice of such systems. In addition to its technological contributions, this project invests actively in knowledge transfer to the many researchers working on analysis and design of silver complexes NHC. The main objectives of this project are listed as below.

1. To synthesize cyclophane and its analogues of bis-imidazolium/bis-benzimidazolium salts as precursors to NHC.
2. To synthesize and characterize silver(I) complexes of NHC
3. To study the antimicrobial and anticancer activities of the synthesized silver(I) complexes.

3. Project Methodologies, Results and Achievements

3.1. Metal-based system developments

This segment of report is to summarize the developments that took place within this project and put them in a larger scientific and technological context. The approach we took in designing stable Ag(I)-NHC compounds relevant to the anticancer systems are the nature of chelation, type of ligand consisting heterocyclic ring system and the nature of counter ions. We then move to the more specific goal of the project, viz., the design of cyclophane analogue periphery with imidazole or benzimidazole core provide suitable topology for the silver center. Moreover, it is expected that the academic propagation of this research results will influence and advance the field of synthetic organometallic chemistry of Ag(I)-NHC complexes and their use as anticancer agents. Considerable further work on applications of silver-based drugs, with alternative approaches, all in the context of case studies of greater orders of magnitude is needed to develop Ag(I)-NHC series into readily applicable anticancer drugs.

3.2. Methodologies

It is important to notice that the presence of sp^3 hybridized carbon and nitrogen atoms in ligand system provides more rigidity and robustness to the complexes derived from such systems. This rigidity factor is the main ease for the formation of stable silver(I)-NHC complexes. While working with the cyclophane analogue systems, we found an easier and novel method for the preparation of NHC imidazolium salts, which save valuable time and expensive solvents. As an example, in the preparation of 1,2–bis(allylimidazole-1-ylmethyl)benzene-bis(hexafluorophosphate) salt, we established a novel method of preparation for bis-carbene salts in good yields as follows.

A mixture of imidazole (0.9 g, 13.0 mmol) and sodium hydroxide (0.5 g, 12 mmol) in DMSO (5mL) was heated to 90 °C for 2 h, and then was cooled to room temperature. A solution of 1,2-bis(bromomethyl)benzene (1.5 g, 5.7 mmol) in DMSO (10 mL) was added to the mixture and heated slowly to 40 °C for 1 h with constant stirring. The resulting solution was poured into ice-cold water (40 mL). The precipitate was collected, washed with water, and recrystallized from methanol/water to give 1,2–bis(N-imidazole-1-ylmethyl)benzene [1] as a white solid (0.95 g, 79 %). Further, a mixture of [1] (0.5 g, 2.1 mmol) and allyl bromide (0.7 g, 6.1 mmol in acetonitrile (20 mL) was refluxed for 24 h. The solvent

was removed under reduced pressure to result pale-brown oil, which was converted directly to its corresponding hexafluorophosphate salt by metathesis reaction using KPF6 (0.76g, 4.0 mmol) in 20 ml of methanol. The precipitate formed was collected and washed with distilled water (2 × 5 ml), and recrystallized from acetonitrile to give colorless solid. (1.1g, 80 %). Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the salt solution in acetonitrile at room temperature.

3.3. Results and Discussion

In this section of the report, we are summarizing all the results which we have obtained during last two years with the aid of this project. A large part of organometallic chemistry, biology and pharmacology is concerned with designing suitable models of silver-carbon frameworks. By using these models, it is easy to validate the existing functioning of the biocatalysts and to choose between design alternatives in order to optimize the biological performance. The class of models advocated in this project has its origins in the domain often called organometallics whose goal is to prove that, the separate array of compounds, especially, silver-NHCs, in which silver-to-carbon bonding is possible and such compounds are useful in medicinal field as antimicrobial or anticancer agents. We strongly believe that the phenomena of silver-NHCs relevant to the biological systems come first and that it is more useful to understand them and devise novel models, whose semantics corresponds faithfully to these phenomena, rather than to rush and translate their study only on structural diversity factor. It is found in the literature that a large number of Ag(I)-NHCs are employed for the antimicrobial and anticancer activity and hence an attempt is made with Ag(I)-NHCs bearing cyclophane analogue ligand systems to get the similar results.

Under this headline, we designed, synthesized and successfully characterized many series of NHC salts and Ag(I)-NHC complexes (Figure 1). On the other hand, 3-benzyl-1-alkylimidazolium salts act as mono- and bis-carbene chelates towards Ag(I) are shown in Figure-2. Similarly, another set of bis-carbene imidazolium salts with aryl-alkyl spacer ligands and their Ag(I) complexes are shown in Figure-3. Prepared silver complexes examined for the antimicrobial tests are shown in Figure-4. Silver complexes depicted in Figure 4 shown excellent antimicrobial activity against *E. coli* and *S. aureus* bacterial stains even at Minimum Inhibition Concentration (MIC) level. The higher activity in case of complexes **1, 3** and **6**

are attributed to the direct cleavage of DNA of bacterial stain which further reduces the cell multiplication. The methods and results of antimicrobial tests are appended as separate leaf with the title Appendix 5. It is expected that, if a complex is acting as a strong growth inhibitor against bacterial stain, it is potentially useful as an anticancer agent. This insight led us to go with the *in vitro* DNA binding/cleavage and anticancer activity of the Ag(I) complexes which is in progress.

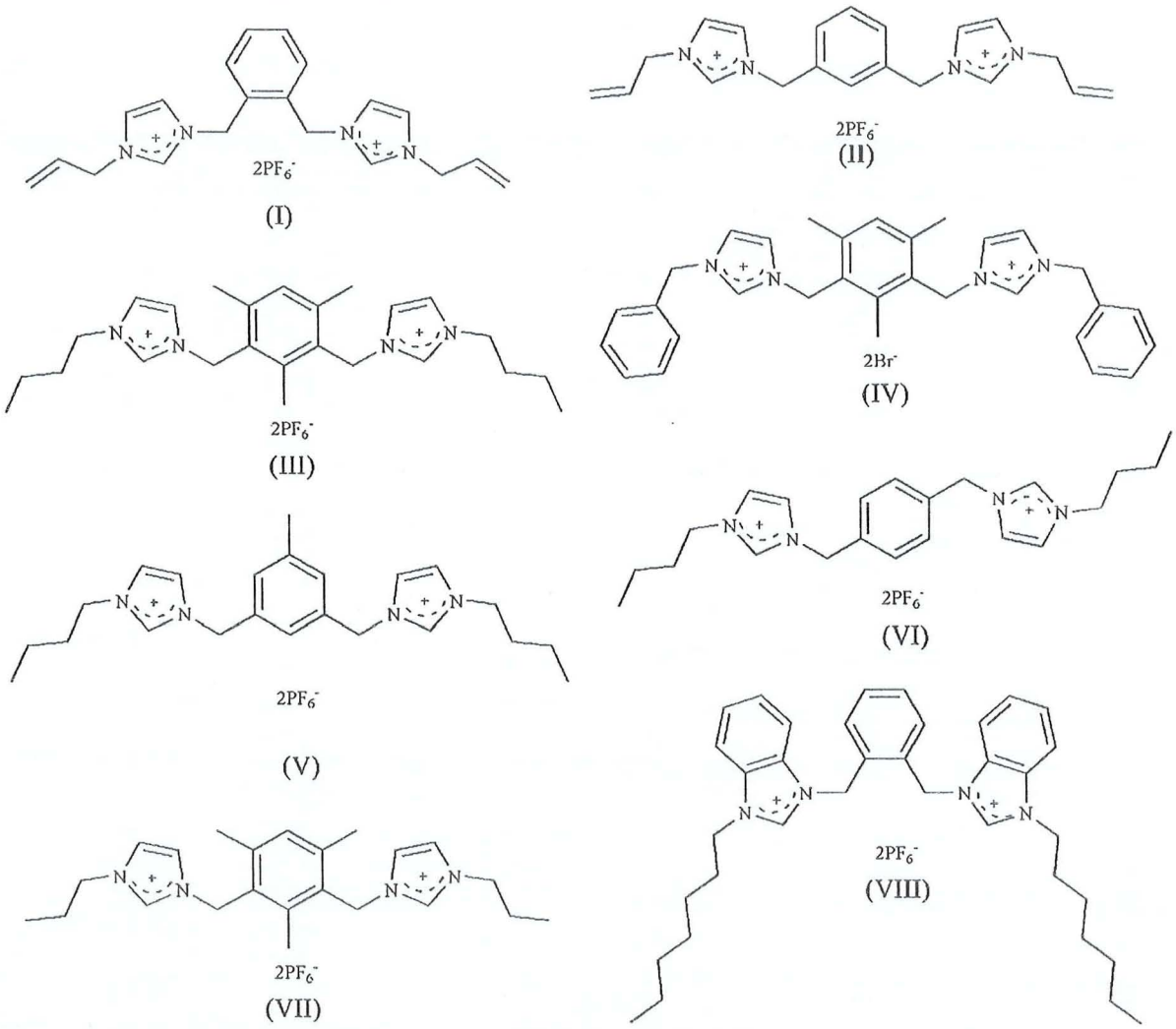


Figure 1. Synthesized NHC precursors of bis-carbene imidazolium/benzimidazolium salts.

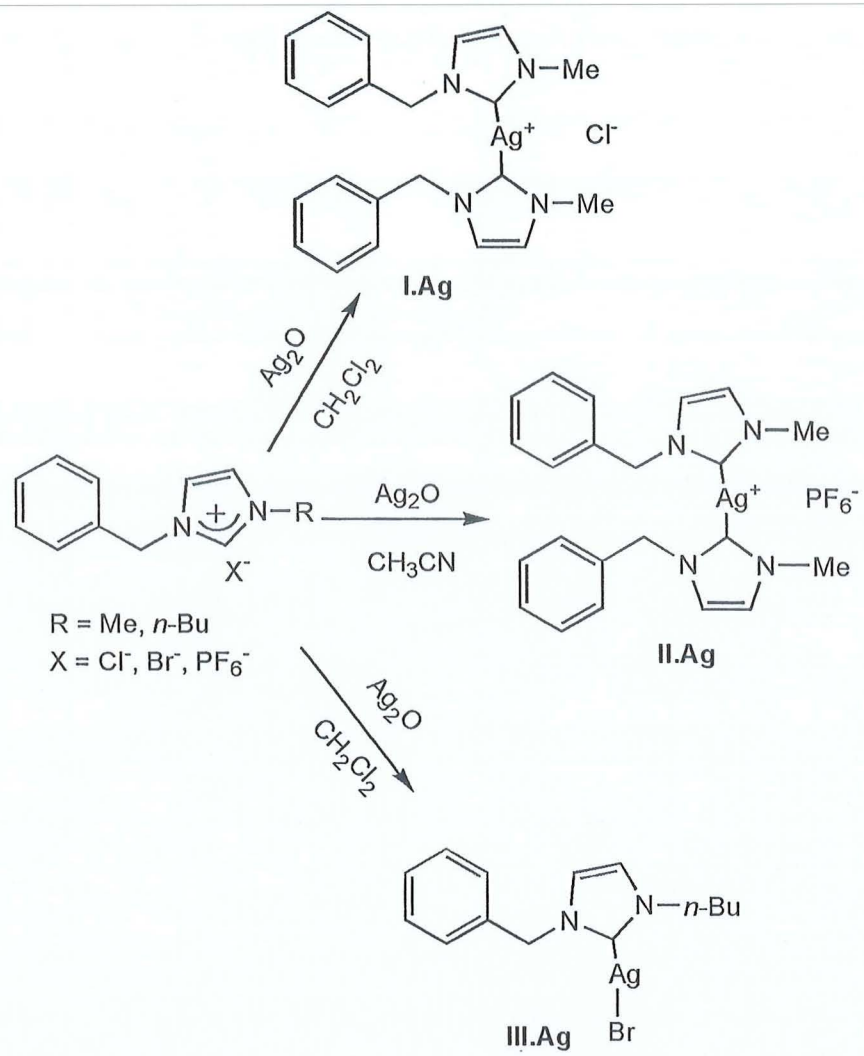
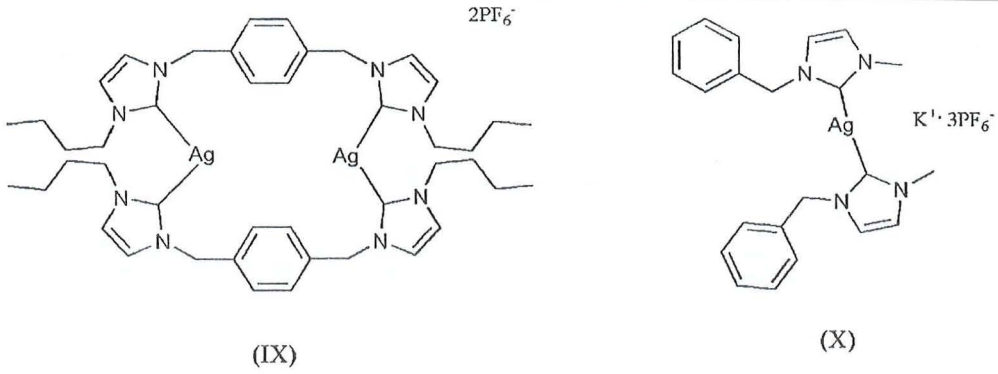


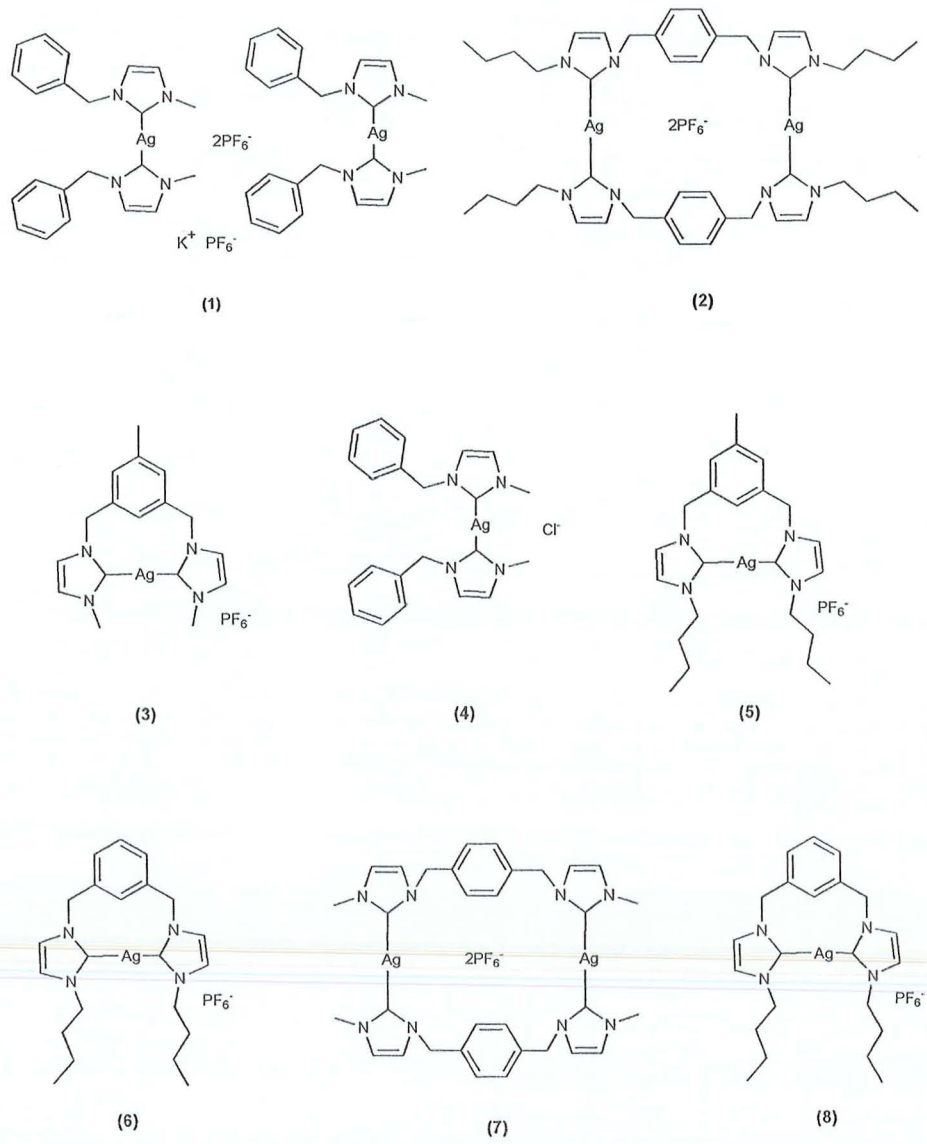
Figure 2. 3-Benzyl-1-alkylimidazolium salts act as mono-carbene chelates towards Ag(I).

In the preliminary investigations of antimicrobial studies using mono and bis-carbene silver(I) complexes, it was found that the complexes are moderate-to-most active towards bacterial strains. To proceed, we planned to go with the *in-vitro* anticancer studies on six different cell-lines viz., Human colon cancer cells (HCT 116), Human adino carcinoma cells (HT 29), Human breast cancer cells (MCF -7 and MDA MA), Human prostate cancer cells (PC 3), Human liver cancer lines (Hep G2), Normal fibrobalster cancer cells (CCD-Co 18) and Human vein endothelial cells (HUVEC) by collaboration with EMAN center in USM. Second concern for scheduling focuses on anticancer activities is the biocompatibilities of the designed silver(I) mono-carbene systems and their solubility in common organic solvents.



(IX) (X)

Figure 3: Cyclophane analogues of mono and bis-carbene imidazolium salts based Ag(I) complexes.



(1) (2) (3) (4) (5) (6) (7) (8)

Figure 4. Silver(I) complexes examined for antimicrobial activity against *E. coli* and *S. aureus*.

Overall, the project moves towards this goal along several tracks that the more profound biological investigations are needed to call these as silver-based drugs in the future days. Indeed much of the project's resources are being spent on synthesis and their structural characterizations using analytical and single crystal X-ray analyses. A second direction of the project aims to improve understanding about the mode of action with the help of 3-dimemtional structure-activity-relationship (3D-SAR) of the silver(I) complexes and their resemblance, both structural and functional, with standard drugs available in the market.

3.4. Achievement of the Objectives

The objectives of this project have been met with many interesting outcomes. We believe the most important discovery is achieved in the last year, i.e. a very good abstraction on microbial studies of silver complexes. It is obvious, that the first contribution (careful designs of NHC salts and their corresponding Ag complexes) significantly improves the prospects of the second. And we hope will get success in the design and synthesis of silver-based drugs for cancer treatment.

In order to mention the done things, a series of eight NHC-ligands of cyclophane analogues bearing imidazole or benzimidazole core were prepared and successfully characterized using various analytical techniques. Using these ligand systems, a series of eight silver(I) complexes were prepared and successfully characterized. All the prepared silver complexes are examined for the antibacterial screening against different microbes viz., *E. coli* and *S. aureus* using disc diffusion and viable colony count method. Finally, the anticancer screening of these complexes is about to complete and yet few more research articles will be communicated in the nearest future gathering the results of this project.

4. Outlooks

The project enabled us to prepare and characterize a series of cyclophane analogues with mono and bis-imidazolium/benzimidazolium salts and their respective Ag(I) complexes. The initial screening of all the Ag(I)-NHC complexes for antimicrobial activity shown excellent results as strong growth inhibitors against biocides viz., *E. Coli* and *S. aureus* strains. The complexes are scheduled to be analyzed further for DNA binding/cleavage and anticancer activity using different cell lines.

5. Conclusions

The antimicrobial study of prepared Ag(I)-NHC complexes was very inspiring to the project, in particular during the last half of the tenure. It exposed at the same time the DNA binding/cleavage and anticancer study of the silver(I) complexes was most notably concerning complexity issues; perhaps, we defended the situation more clearly with the available antimicrobial results. However, the in progress work adds still more insights to call the prepared series of complexes as anticancer agents. With exception of the new abstraction reported here, one can safely state that a full comprehension of the study on silver(I)-NHC complexes having cyclophane analogues ligands was achieved after about 30 months. Consequently, the interest of the consortium shifted to harder and unresolved challenges of other issues of the prepared compounds like DNA binding/cleavage, anticancer activity, etc., arise at the end and the related work is in progress. Concerning the original goals of this project, important parts were achieved already in the first half of the project. In summary, the project on silver complexes of cyclophanes and their analogues can be considered a success, a proof that the use of knowledge can lead to new insights into a complex problem.

Abstract

Novel silver complexes of N-heterocyclic carbene (NHC) backbone are synthesized in good yields at low-to-moderate costs. All compounds are characterized with the help of various spetro-analytical and single crystal X-ray diffraction techniques. Prepared Ag(I)-NHC complexes of cyclophane analogues are studied for antimicrobial and anticancer activity, which found great importance in biological and bio-catalytical research. All of the novel compounds are stable solids, non-sensitive towards air and moisture and possessing structural relevance with the existing anticancer systems. In a preliminary investigation on biocides, viz., bacterial and fungal stains, few of the Ag(I)-NHC complexes show remarkable activity that evidences their anticancer nature.

Bahasa Malaysia

Kompleks perak novel N-heterosiklik karbena telah disintesis dalam kadar hasil yang baik pada kos rendah-sederhana. Semua sebatian ini dicirikan dengan bantuan pelbagai teknik spetro-analisis dan kristal tunggal pembelauan X-ray. Kompleks Ag(I)-NHC analog siklofen yang disediakan telah dikaji untuk aktiviti anti-mikrobial dan anti-kanser, yang mengambil tempat penting dalam penyelidikan biologi dan bio-catalytikal. Kesemua sebatian novel ini adalah pepejal yang stabil, tidak sensitif terhadap udara dan lembapan dan mempunyai kaitan struktur dengan sistem anti-kanser yang sedia ada. Dalam siasatan awal mengenai biosid, iaitu, bakteria dan kulat noda, sebahagian dari kompleks Ag(I)-NHC menunjukkan aktiviti yang luar biasa, satu pameran untuk sifat antikanser mereka.

Appendix 2 Research Findings

The findings of the project meet project's expectations and led the way to explore N-heterocyclic (NHC) ligands for the preparation of biologically active silver(I) complexes. The preliminary biological activity results of the prepared silver-NHC complexes shows promising application as silver-based drugs for the treatment of cancer. In precise, the findings of the project are listed below.

1. Silver complexes of NHC are synthesized and characterized.
2. In the series of eight silver complexes, five are successfully characterized by using single crystal X-ray diffraction techniques.
3. A wide range of spectro-analytical techniques viz., ^{1}H and ^{13}C NMR, elemental analysis, FT-IR, etc., are used for structural elucidation of the non-crystalline complexes.
4. Among eight silver complexes, six show remarkable antimicrobial activity against biocides viz., *E. coli* and *S. aureus* even at the minimum inhibitory concentrations level.
5. All silver complexes which shown good antimicrobial activity will be screened for the anticancer activity on different cell-lines.

Appendix 4 Publications

1. Haque, R. A.; Ghdhayeb, M. Z.; Abdallah, H. H.; Quah, C. K.; Fun, H.-K., 1,3-Bis[(3-allylimidazol-3-ium-1-yl)methyl]benzene bis(hexafluoridophosphate). *Acta Cryts.* **2011,** E67, o80-o81.

2. Haque, R. A.; Ghdhayeb, M. Z.; Hemamalini, M.; Fun, H.-K., 2,4-Bis[(3-allylimidazolium-1-yl)methyl]mesitylene bis(hexafluoridophosphate). *Acta Cryts.* **2011,** E67, o2068.

3. Haque, R. A.; Ghdhayeb, M. Z.; Hemamalini, M.; Fun, H.-K., 3,30-Diallyl-1,10-[o-phenylenebis(methylene)] diimidazol-3-ium bis(hexafluorophosphate). *Acta Cryts.* **2011,** E67, o2529–o2530.

4. Haque, R. A.; Iqbal, M. A.; Hemamalini, M.; Fun, H.-K., 3,3□-[1,2-Phenylenebis(methylene)]bis(1-heptylbenzimidazolium) dibromide monohydrate. *Acta Cryts.* **2011,** E67, o1814–o1815.

5. Haque, R. A.; Salman, A. W.; Guan, T. S., Synthesis and Characterization of New Silver(I)- and Mercury(II)-n-heterocyclic Carbene Complexes. *Aust. J. Basic & Appl. Sci.* **2011,** In press.

6. Haque, R. A.; Salman, A. W.; Guan, T. S.; Abdallah, H. H., New N-heterocyclic carbene mercury(II) complexes: close mercury-arene interaction. *Journal of Organomet. Chem* **2011,** In Press.

7. Haque, R. A.; Salman, A. W.; Hemamalini, M.; Fun, H.-K., 2,4-Bis[(3-butylimidazol-3-ium-1-yl)- methyl]-1,3,5-trimethylbenzene bis(hexafluorophosphate). *Acta Cryts.* **2011,** E67, o562–o563.

8. Haque, R. A.; Salman, A. W.; Hemamalini, M.; Fun, H.-K., Bis(1-benzyl-3-methylimidazolium-jC2)- mercury(II) bis(hexafluoridophosphate). *Acta Cryts.* **2011,** E67, m1242–m1243.

9. Haque, R. A.; Salman, A. W.; Nadarajan, P.; Hemamalini, M.; Fun, H.-K., 3,3□-Dibenzyl-1,1□-(2,4,6-trimethyl-m-phenylenedimethylene) diimidazol-3-ium dibromide. *Acta Cryts.* **2011,** (E67), o643.

10. Haque, R. A.; Salman, A. W.; Whai, C. K.; Quah, C. K.; Fun, H.-K., Potassium bis[bis(1-benzyl-3-methylimidazolium) silver(I)] tris(hexafluoridophosphate). *Acta Cryts.* **2011,** E67, m97-m98.

11. Haque, R. A.; Washeel, A.; Nasri, S. F.; Yeap, C. S.; Fun, H.-K., 3,30-Di-n-butyl-1,10-(p-phenylenedimethylene) diimidazolium bis(hexafluorophosphate). *Acta Cryts.* **2010,** E66, o824-o825.

12. Haque, R. A.; Washeel, A.; Teoh, S. G.; Hemamalini, M.; Fun, H.-K., Bis{1,4-bis[(3-butylimidazolium-1-yl)- methyl]benzene}silver(I) bis(hexafluoridophosphate). *Acta Cryts.* **2010,** E66, m1286–m1287.

13. Haque, R. A.; Washeel, A.; Teoh, S. G.; Quah, C. K.; Fun, H.-K., 3,5-Bis(3-butylimidazolium-1-ylmethyl)-toluene bis(hexafluorophosphate). *Acta Cryts.* **2010,** E66, o2797–o2798.

14. Iqbal, M. A.; Haque, R. A.; Sulaiman, S.; Izzati, T., Synthesis, characterization, and theoretical studies of xylyl linked bisimidazoliumand bisbenzimidazolium salts. *Journal of Chemistry* **2011,** 2, (1), 17-24.

Appendix 5

Methods and results of antimicrobial tests against microbes

Antimicrobial test of silver(I) complexes against *Escherichia coli* and *Staphylococccus aureus* using disc diffusion and viable colony count method

Materials

Silver samples, dimethylsulphoxide (DMSO), nutrient agar, nutrient broth, *Escherichia coli* (*E.coli*), *Staphylococcus aureus* (*S.aureus*)

Methods

The stock solution of all compounds was prepared by using dimethylsulphoxide (DMSO). For disc diffusion method, a loop of the bacterial strain was inoculated into the nutrient broth and was incubated for 16 hours at 37°C. About 50 µl of the suspension was applied uniformly on the surface of the nutrient agar plate before placing the antimicrobial assay discs on the plate (4 per plate) and different volumes of silver samples (3 µl, 6 µl, 9 µl and 12 µl) were loaded on the discs. The plates were incubated at 37°C for 24 hours. After that, the average zone of inhibition was measured with a ruler with up to 1 mm resolution. For viable cell count method, the concentration of the tested compound were 100 µg ml^{-1}, 200 µg ml^{-1}, 400 µg ml^{-1} and 800 µg ml^{-1}. The bacterial strain was inoculated into the nutrient broth and was incubated for 16 hours at 37°C. After the serial dilution (10^7 CFU/ml) was done, about 60 µl of bacterial suspension was transferred into the universal bottles containing 3 ml of nutrient broth followed by silver suspension. The incubation was carried out for 5 hours at 37°C and 50 µl of culture was uniformly spread on the nutrient agar which was incubated at 37°C for 24 hours. The incubation of the culture in the universal bottles was continued for 24 hours. MIC was determined based on the lowest concentration of the silver samples that inhibit the growth of bacterial strain. For growth inhibitory concentrations, the presence of viable microorganisms was tested and the lowest concentration causing bactericidal effect was reported as MBC.

Table 1.0: Antimicrobial activity of the silver samples against *Escherichia coli* (Gram negative bacteria) by disc diffusion method

Sample	Diameter (mm)			
	3 µl	6 µl	9 µl	12 µl
1	20 ± 0	22 ± 1	25 ± 1	26 ± 1
2	10 ± 1	12 ± 0	14 ± 1	14 ± 1
3	11± 1	13 ± 0	14 ± 0	15 ± 0
4	8 ± 0	9 ± 0	10 ± 0	11 ± 1
5	8 ± 0	9 ± 1	10 ± 0	11 ± 0
6	13 ± 1	15 ± 0	17 ± 1	18 ± 1
7	12 ± 0	14 ± 1	17 ± 0	18 ± 0
8	10 ± 0	12 ± 1	12 ± 0	14 ± 0

According to this result, the antimicrobial activity of sample 1 is the highest and showed good inhibition against the bacteria. The sensitivity of the Gram negative bacteria increases as the volume of the silver suspensions increases. *E.coli* depicted highest resistance against sample 4 and 5.

Table 1.1: Antimicrobial activity of the silver samples against *Staphylococcus aureus* (Gram positive bacteria) by disc diffusion method

Sample	Diameter (mm)			
	3 µl	6 µl	9 µl	12 µl
1	27 ± 1	29 ± 1	30 ± 1	31 ± 0
2	10 ± 1	12 ± 0	15 ± 0	15 ± 0
3	17 ± 0	18 ± 0	19 ± 0	22 ± 1
4	9 ± 1	10 ± 0	10 ± 1	11 ± 1
5	9 ± 0	10 ± 1	11 ± 0	12 ± 0
6	15 ± 0	16 ± 1	17 ± 1	20 ± 1
7	13 ± 1	15 ± 0	16 ± 1	18 ± 0
8	9 ± 1	15 ± 0	16 ± 0	16 ± 1

Based on the table, sample 1 showed good antimicrobial activity against Gram positive bacteria compared with other samples. The diameter of the zone of inhibition increases as the volume of sample increases. Sample 4 and 5 showed the lowest antimicrobial activity against the Gram positive bacteria.

Table 1.2: Minimum inhibition concentration (MIC) and minimum bactericidal concentration (MBC) of silver samples against *E.coli* (Gram negative bacteria) and *S.aureus* (Gram positive bacteria)

Samples	*E.coli* (μg ml^{-1})		*S.aureus* (μg ml^{-1})	
	MIC	MBC	MIC	MBC
1	100	200	100	200
2	200	400	200	400
3	200	400	100	200
4	200	400	200	400
5	200	400	200	400
6	200	400	100	200
7	200	400	200	400
8	200	400	200	400

The MIC values for silver samples against both Gram positive and Gram negative are in the range of 100-200 μg ml^{-1} and the MBC values are in the range of 200-400 μg ml^{-1}. Sample 1 showed bactericidal activity against both Gram positive and Gram negative bacteria at even 200 μg ml^{-1}. Sample 3 and 6 showed bactericidal effect against Gram positive bacteria at 200 μg ml^{-1} but the activity was only revealed at 400 μg ml^{-1} against Gram negative bacteria.

Table 1.3: Colony forming unit per ml (CFU/ml) of different concentrations of silver samples against *E.coli*

Samples	CFU/ml (10^5)			
	Concentration (μg ml^{-1})			
	100	200	400	800
1	8 ± 1	0	0	0
2	13 ± 1	5 ± 1	0	0
3	15 ± 1	5 ± 1	0	0
4	17 ± 1	8 ± 1	0	0
5	16 ± 1	7 ± 1	0	0
6	13 ± 1	4 ± 1	0	0
7	14 ± 1	6 ± 1	0	0
8	15 ± 1	9 ± 1	0	0

The colony forming unit per ml (CFU/ml) decreases as the concentration of the silver samples increases. No viable colony of *E.coli* was observed for sample 1 at concentration of 200 μg ml^{-1}.

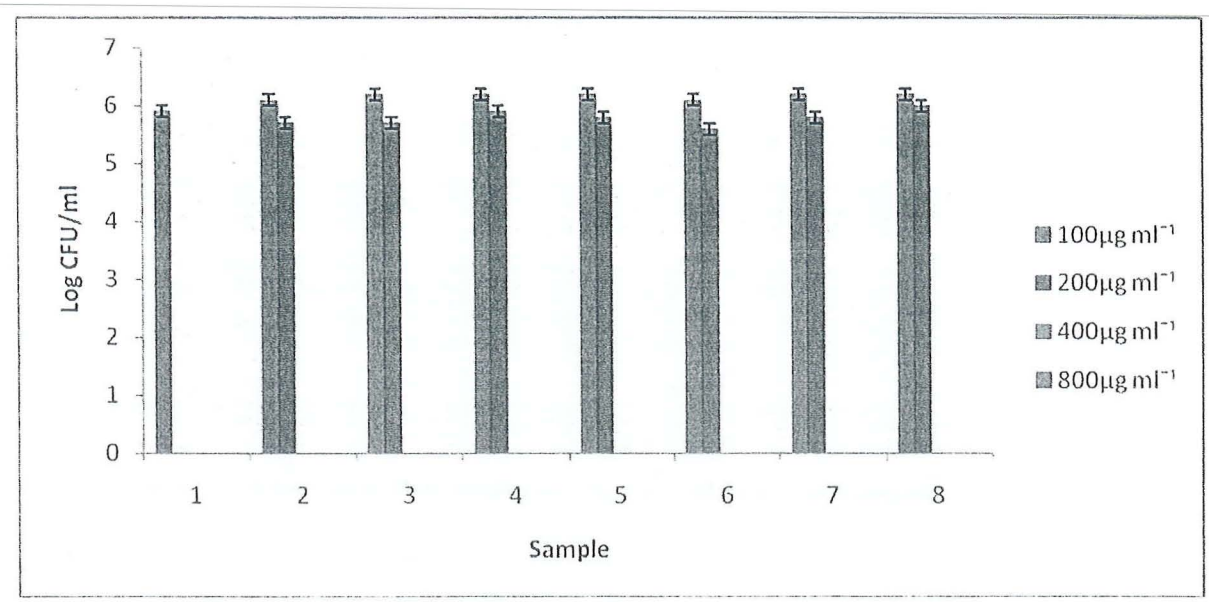


Fig 1.0: Cell count of *E.coli* after treated with different concentrations of silver samples

Table 1.4: Colony forming unit per ml (CFU/ml) of different concentrations of silver samples against *S.aureus*

CFU/ml (10^5)				
Samples	Concentration (µg ml^{-1})			
	100	200	400	800
1	5 ± 1	0	0	0
2	12 ± 1	5 ± 1	0	0
3	13 ± 1	0	0	0
4	16 ± 1	8 ± 1	0	0
5	15 ± 1	5 ± 1	0	0
6	11 ± 1	0	0	0
7	12 ± 1	6 ± 1	0	0
8	14 ± 1	5 ± 1	0	0

According to the table, all the samples exhibited bacteriostatic and bactericidal effect against Gram positive bacteria. Sample 1, 3 and 6 depicted bactericidal effect even at 200 µg ml^{-1} compared with other samples.

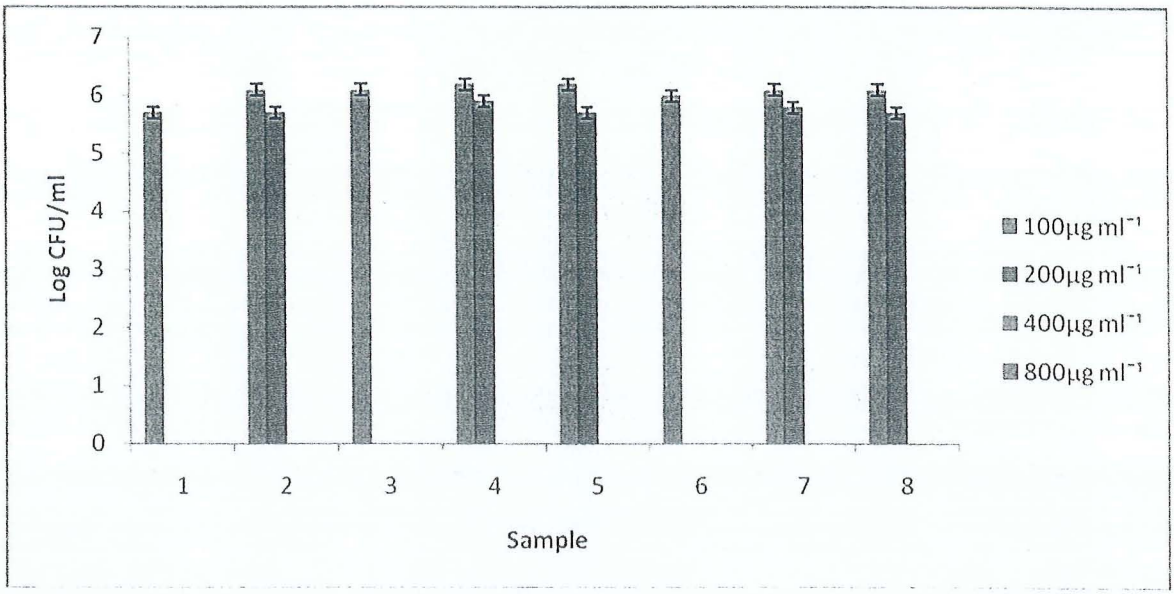


Fig 1.1: Cell count of *S.aureus* after treated with different concentrations of silver samples

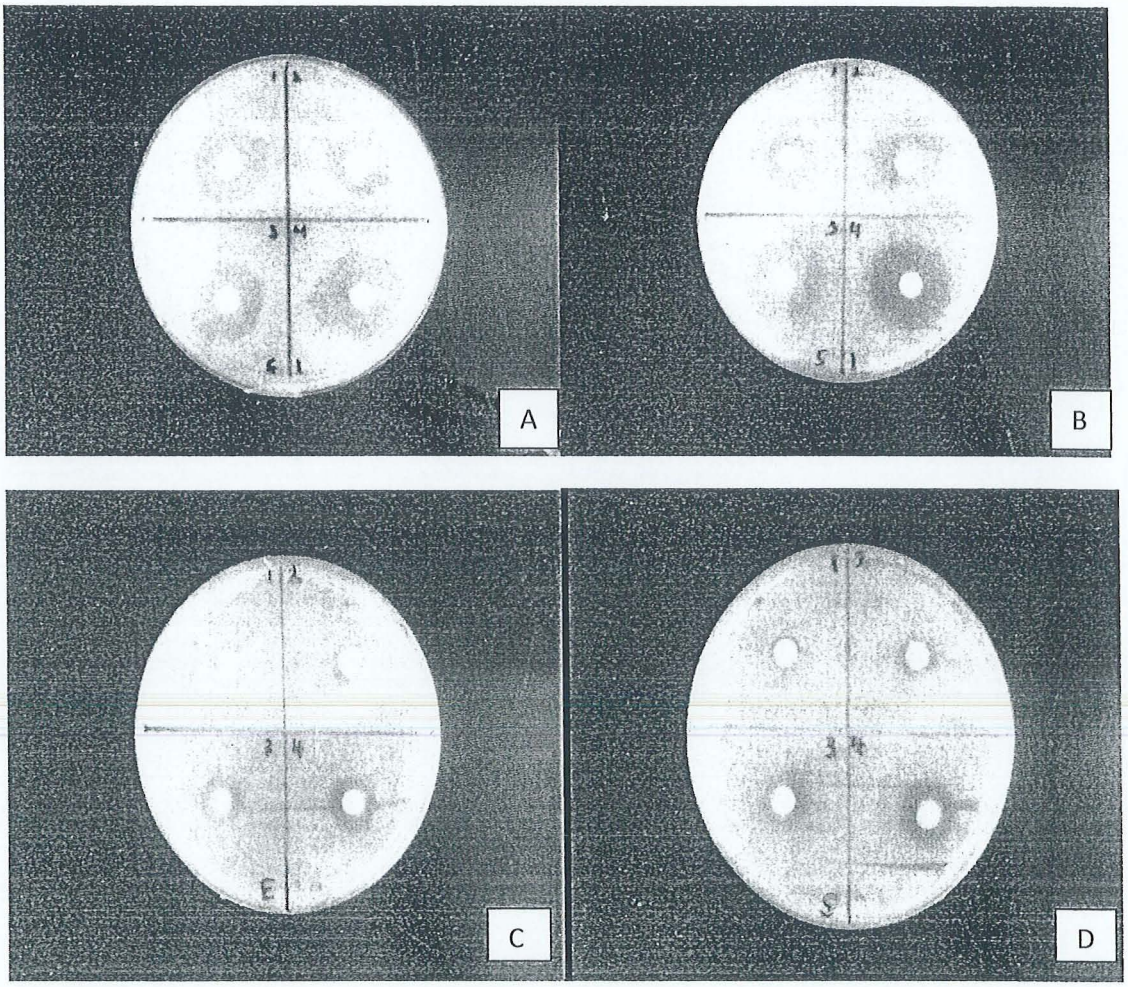


Fig 1.2: Antimicrobial activity of sample 1 and 4 against *E.coli* (A & C) and *S.aureus* (B & D)

Sample	
1	KA1-Ag
2	BUF-Ag
3	M2-Ag
4	Benzmin-Ag
5	Bu2-Ag
6	Bu3-Ag
7	M1-Ag
8	Zmc5-Ag

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New *N*-heterocyclic carbene mercury(II) complexes: Close mercury–arene interaction

Rosenani A. Haque*, Abbas Washeel Salman, Teoh Siang Guan, Hassan Hadi Abdallah

School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM Penang, Malaysia

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ABSTRACT

Mononuclear mercury complexes (**1**, **2**, and **3**) bearing bis-*N*-heterocyclic carbene (NHC) ligands of the form $[(NHC)_2\text{-}\mu\text{-}Hg]^{+2}$ have been prepared and structurally characterised. The complexes were derived from three bis-imidazolium salts as precursors to NHC; either 1,3-bis(*N*-methylimidazolium-1-ylmethyl) benzene bis(hexafluorophosphate) (**I**·$2PF_6$), 1,3-bis(*N*-butylimidazolium-1-ylmethyl)benzene bis(hexafluorophosphate) (**II**·$2PF_6$) or 3,5-bis(*N*-butylimidazolium-1-ylmethyl)toluene bis(hexafluorophosphate) (**III**·$2PF_6$) treated with mercury(II) acetate. Interestingly X-ray crystal structure analysis revealed a close interaction between the Hg metal centre with one carbon atom of the aryl linker in addition to coordination with two NHCs.

1. Introduction

The use of *N*-heterocyclic carbene (NHC) ligands is now widespread in modern organometallic synthesis [1]. NHC has attractive properties such as stability, ease of handling, compatibility with metals in low- and high-oxidation states, and stability of its complexes because of a strong metal-ligand binding. Studies have reported NHC complexes with a large number of transition metals [2] showing several interesting applications, most importantly in the area of catalysis [3], as well as in antimicrobial and anti-mitochondrial biological studies [4].

The work in our laboratory is inspired by previous work in the Baker's laboratory [5] where the corresponding author was part of the group. The group is actively working with xylyl-linked NHCs and their metal complexes, both in NHCs forming part of a macrocyclic structures (cyclophanes) and in their analogues, wherein bis(NHC) ligands contain only one xylyl linker (non-cyclophane structures) [5].

Baker et al. reported a series of well-defined NHC-metal complexes with these ligands bearing a broad range of coordination modes, Chart 1 [5,6]. For example, two NHCs chelating a single metal forming either a dimeric (**4** and **5**) or a monomeric structure (**6**–**9**); two NHCs and an arene, which constitute part of a single cyclophane macrocyclic structure, simultaneously binding to one metal center (**10**); and a pincer complex where binding involves the NHCs and the additional groups when an additional donor atom is included (**11**).

In 1968, Wanzlick and Schönherr successfully synthesised the first mercury-NHC complex via direct reaction of an imidazolium salt with mercury(II) acetate [7]. Despite being the earliest example of NHC-metal complexes, mercury-NHC complexes have received little attention compared with other metals. Similarly, their applications have not been widely explored. Baker et al. reported the first syntheses of mercury-NHC complexes derived from imidazolium-linked cyclophanes (e.g., **6** and **7**, Chart 1), as well as their use for redox–transmetallation chemistry, wherein the reaction of an NHC-mercury(II) complex with a palladium(0) source results in an NHC-palladium(II) complex [5c].

Although transmetallation involving silver(I)-NHC complexes is now a routine method for the synthesis of other metal-NHC complexes, this is the first reported example of a (redox) transmetallation reaction involving a mercury-NHC complex [5c].

We have been interested in the chemistry of mercury(II)-NHC complexes due to their potential use as carbene transfer reagents. In actively dealing with both mercury- and silver-NHC complexes in our laboratory, we found that obtaining different coordination geometry of silver(I) and mercury(II) complexes starting from the same ligand is possible. For example, silver(I) and mercury(II) complexes made from an NHC-linked *meta*-xylyl cyclophane produce different geometry of complexes [5b]. We have shown that

* Correspondence author. Tel.: +604 653 3578.
E-mail address: rosenani@usm.my (R.A. Haque).

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performance of mercury-NHC complexes is comparable to that of their silver counterparts in carbene transfer reactions [5b,5c]. Hence, the use of mercury complexes as NHC-transfer agents potentially may complement the silver transfer method, thereby perhaps allowing different geometries of complexes to be prepared via transfer method, depending on whether one starts with silver- or mercury-NHC.

In this study, we report the synthesis and characterisation of three new mercury(II) complexes derived from *meta*-xylylene linked bis-imidazolium salts. These complexes exhibit unique binding behavior previously observed only in our mercury complexes, where the mercury metal is bonded to two NHCs and exhibit close interaction with one carbon atom of the aryl group [5b].

2. Results and discussion

2.1. Synthesis of imidazolium salts

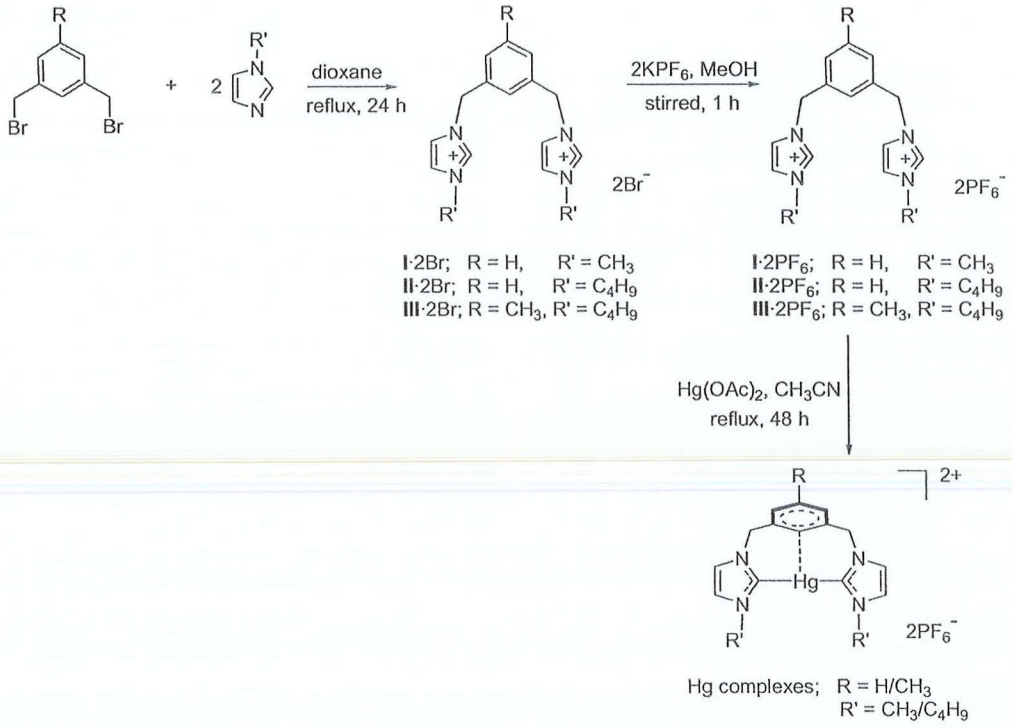
The imidazolium salts **I**·2Br, **II**·2Br, and **III**·2Br were prepared using the procedure of Dias and Jin [8], followed by conversion to their hexafluorophosphate salts to give **I**·2PF_6, **II**·2PF_6, and **III**·2PF_6, respectively (Scheme 1). A reaction of either 1,3-bis(bromomethyl) benzene or 3,5-bis(bromomethyl)toluene with two equivalent of either *N*-methylimidazole or *N*-butylimidazole in 1,4-dioxane under reflux for 24 h, followed by conversion to their corresponding PF_6 salts by metathesis reaction with KPF_6 resulted in **I**·2PF_6 as a white precipitate (72% yield), **II**·2PF_6 as colorless crystals (92% yield) and **III**·2PF_6 as off-white crystals (79% yield). Conversion from bromide to hexafluorophosphate counter-ions is for easier handling and solubility. As bromides, the compound's solubility is limited to solvents such as methanol, water, and dimethyl sulfoxide (DMSO), whereas as PF_6, the salts are soluble in common organic solvents including acetone, acetonitrile, and DMSO; facilitating isolation and characterization steps.

The ^{1}H NMR spectra of the prepared imidazolium salts **I**, **II**, and **III** in their PF_6 form in CD_3CN show the signals expected for common imidazolium salt [9]. The imidazolium proton H2′ signal (NC*H*N) appeared at δ 8.5–8.6 range and the benzylic protons appeared at δ 5.3–5.4, both as singlets. In the ^{13}C NMR spectra, the signal for C2′ was observed at δ 135–136 range.

2.2. Synthesis of mercury(II)-NHC complexes

Mercury(II) complexes **1**, **2**, and **3** were prepared by reaction of the imidazolium salts **I**·2PF_6, **II**·2PF_6, and **III**·2PF_6 with excess mercury (II) acetate in acetonitrile at 80–90 °C for 48 h (Scheme 1). After recrystallisation utilising acetonitrile, complexes **1** and **2** were obtained as white solids, whereas complex **3** was off-white solid in 54%, 50%, and 54% yield, respectively. During workup, residual mercury(II) acetate was removed by repeated washings of the crude product with water.

The ^{1}H NMR data for the complexes in CD_3CN show the full absence of the imidazolium H2′ signal; a common occurrence attributed to deprotonation of the acidic proton of the heterocycles [5c] and coordination with the metal. The signals caused by the benzylic protons display sharp couple o doublets for all complexes, indicative of some conformational rigidity in the solution. The benzylics, arene, and imidazolium H4′/H5′ signals of the complexes are shifted slightly downfield compared with those of their respective salts. There is a significant downfield shift (approximately 0.5 ppm) for the proton on the carbon atom in the aryl rings which closely interacts with the mercury metal, compared with the same proton in the uncoordinated salts. In the ^{13}C NMR spectra, carbene carbon bond to mercury appear at 173.5, 172.6, and 172.8 for **1**, **2**, and **3**, respectively, consistent with the literature [9]. In



Scheme 1. Synthesis of imidazolium salts **I**, **II**, and **III** and their corresponding mercury complexes.

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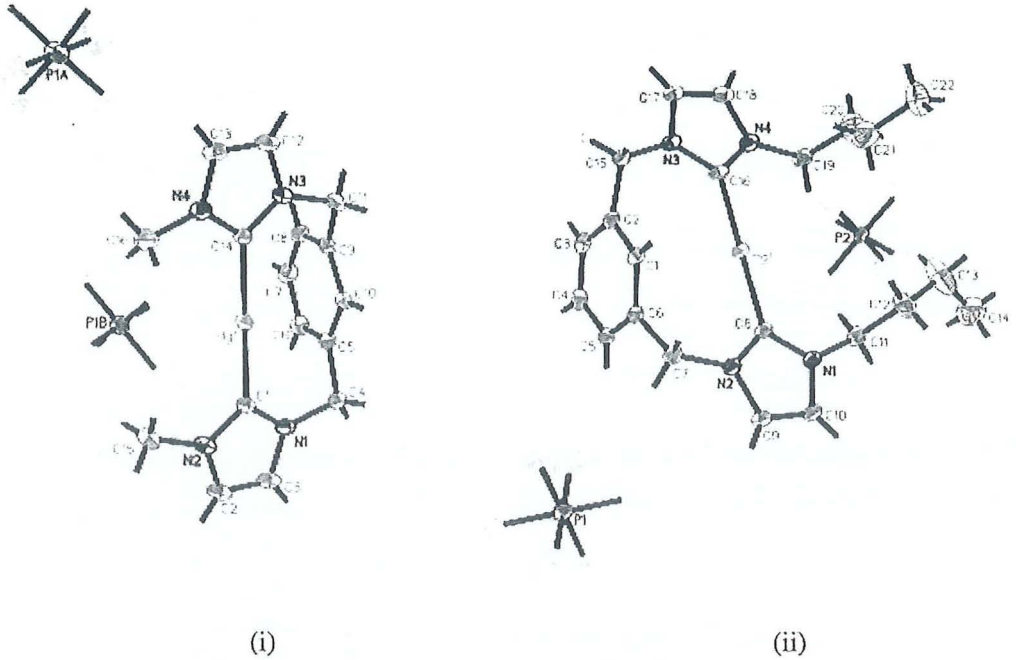

Fig. 1. (i) Cation 1 and (ii) Cation 2 with two independent PF_6^- anions, showing 30% probability displacement ellipsoids; hydrogen atoms are omitted for clarity.

addition, there are downfield shift (approximately 2.0–4.0 ppm) for the carbon atom in arene rings that have interacted with mercury. No C–Hg couplings were observed, although large C–Hg couplings between 2700 and 3300 Hz have been reported in the literature for mercury-NHC complexes [10]. This is not unusual as we also did not observe any C–Hg couplings in our previously reported Hg-NHC complexes [5b,c].

2.3. Structural studies

The molecular structure of the imidazolium salt **III**·$2PF_6$ was determined by X-ray diffraction studies and have been published elsewhere [11].

Mercury(II) complexes **1**, **2** and **3**: X-ray studies reveal the mercury atom is coordinated to two carbene carbons of the imidazolium rings in linear arrangement for all the complexes [Fig. 1(i) and (ii), 2 (i)]. There is a close interaction between the Hg centre and one of the carbon atoms of the aryl linker ring [Hg–C(arene) bond distances [2.742(2) for **1**; 2.750(5) for **2**; and 2.724(13) Å for **3**], but the distance is not sufficiently short to be indicative of a significant bonding interaction. However the distances are much shorter than the sum of van der Waals radii of the respective elements (rvdw(C) = 1.70 Å, rvdw(Hg) = 1.55 Å) = 3.25 Å for C···Hg interaction [12]. This kind of close interaction was observed in the previously reported Hg-cyclophane complexes by Baker et al. (Hg–C(arene) bond distances of 2.7–2.8 Å [5a]. In contrast, Gabbai et al. [13] reported a much longer Hg–benzene carbon distances of around 3.16 Å to 3.24 Å for a triad of Hg-benzene sandwiched compounds. Recently Baker et al. reported a rare chelating [(η^1–NHC)$_2$: η^6-arene] binding mode for a ruthenium(II) NHC complex where Ru–C(xylylene ring) bond distances are around 2.09 Å to 2.33 Å [5d]. Therefore, we feel that the C-arene bond distances in mercury complexes **1**, **2** and **3** are best described as "close interaction" and since so far we only observe this in Hg-NHC

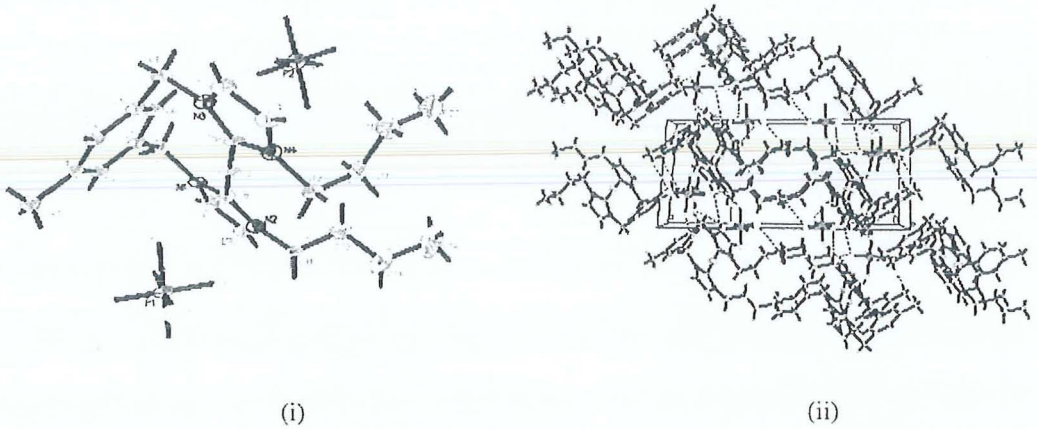

Fig. 2. Cation 3 (i) showing 30% probability displacement ellipsoids and the crystal packing (ii) showing the C-H…F hydrogen bonds as dashed lines.

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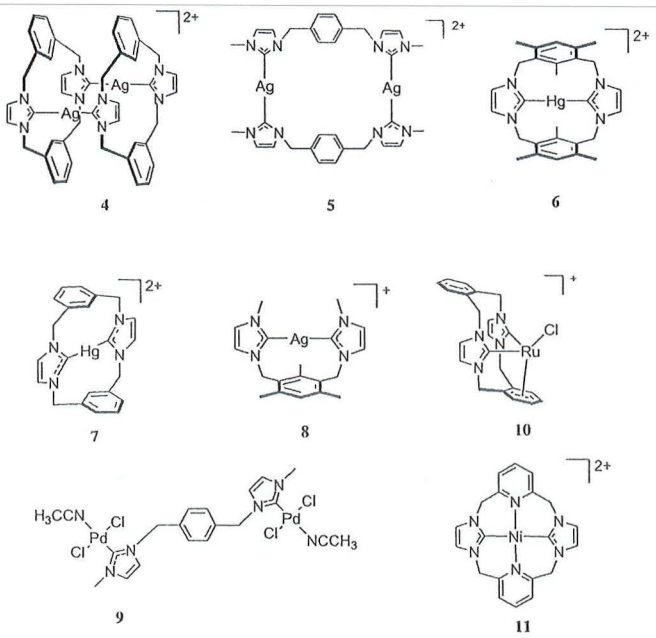

Chart 1. NHC-metal complexes with a variety of ligands showing a broad range of coordination modes.

complexes. We are inclined to regard it as quite unique for Hg-NHC chemistry. The Hg–C(carbene) bond lengths (in the range of 2.06–2.07 Å) are consistent with other mercury complexes reported so far in the literature [14, 15]. The C–Hg–C plane is perpendicular to the plane of the aryl ring in all cases [Hg(1)–C(10)-C(5) = 90.39(14)°; Hg(1)–C(10)-C(9) = 91.91(15)° for **1**, Hg(1)–C(1)-C(2) = 89.8(3)°; Hg(1)–C(1)-C(6) = 89.8(3)° for **2**; and Hg(1)-C(6)–C(1) = 90.5(8)°; Hg(1)-C(6)-C(5) = 90.1(8)° for **3**]. The coordination geometry of the mercury is linear, with a C–Hg–C bond angle of 179.29(10)° for **1**, 179.5(2)° for **2**, and 177.4(5)° for **3**. This linear coordination is commonly observed for Hg-NHC complexes [16,7,10a,14b]. In all the complexes, the hexafluorophosphate anions link the cations with a three-dimensional network via the intermolecular hydrogen bonding C–H...F [Fig. 2(ii)]. Crystal data, selected bond lengths and angles for Complexes **1**, **2**, and **3** are listed in Tables 1–4, respectively.

3. Experimental section

Nuclear magnetic resonance spectra were recorded on Bruker 400 MHz Ultrashield™ and Bruker Avance 300 MHz spectrometers at ambient temperature. The instruments are available at The School of Chemical Sciences, Universiti Sains Malaysia (USM). ^{1}H and ^{13}C NMR peaks are labeled as singlet (s), doublet (d), triplet (t) and multiplet (m), Chemical shifts were referenced with respect to solvent signals. Elemental analysis was carried out on a Perkin Elmer series II, 2400 microanalyzer available at The School of Chemical Sciences, USM. X-ray diffraction data were taken with Bruker SMART APEX2 CCD area-detector diffractometer available at The School of Physics, USM. Chemicals and solvents were used as received without further purifications.

3.1. Synthesis of 1,3-bis(N-methylimidazolium-1-ylmethyl)benzene bis(hexafluorophosphate) (I·2PF$_6$)

First, *N*-methylimidazole (0.6 g, 7.6 mmol) was added to a stirred solution of 1,3-bis(bromomethyl)benzene (1.0 g, 3.8 mmol) in 20 mL of 1,4-dioxane. The mixture was refluxed at 100 °C for 24 h. The sticky product was isolated by decantation, and then washed with fresh 1,4-dioxane (2 × 5 mL) and diethyl ether (2 × 3 mL). The resulting bromide salt was converted directly to its hexafluorophosphate counterpart by metathesis reaction using KPF_6 (1.1 g, 7.6 mmol) in 20 mL of methanol. The mixture was stirred for 1 h and was left to stand overnight. The white precipitate was collected and washed with distilled water (2 × 5 mL), then left to dry at ambient temperature. Yield: 1.5 g (72%), m.p.: 153–154 °C. ^{1}H NMR (400 MHz, CD_3CN): δ 3.85 (6H, s, 2 × *N*-CH_3), 5.36 (4H, s, 2 × benzylic CH_2), 7.39 (1H, t, Ar-H), 7.43 (2H, t, 2 × imidazolium H5′), 7.45 (2H, t, 2 × imidazolium H4′), 7.51 (1H, s, Ar-H), 7.53 (2H, d, 2 × Ar-H) and 8.54 (2H, s, 2 × imidazolium H2′); $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN): δ 36.38 (*N*-CH_3), 52.7 (CH_2), 122.7, 124.5 (imidazolium C5′ and C4′), 129.1, 129.6, 130.5, 135.2 (Ar-C) and 136.6 (imidazolium C2′). Anal. Calc. for $C_{16}H_{20}N_4F_{12}P_2$: C, 34.42, H, 3.61, N, 10.04%. Found: C, 34.56, H, 3.20, N, 10.21%.

3.2. Synthesis of 1,3-bis(N-butylimidazolium-1-ylmethyl)benzene bis(hexafluorophosphate) (II·2PF$_6$)

This compound was prepared in a manner analogous to that for (I·2PF$_6$), only with *N*-butylimidazole instead of *N*-methylimidazole.

Table 1
Crystal data and structure refinement details for Complexes **1**, **2**, and **3**.

	1	2	3
Formula	C_{23} H_{32} Hg N_4F_{12} P_2	C_{22} H_{30} Hg N_4 $F_{12}P_2$	C_{16} H_{18} Hg $N_4F_{12}P_2$
Formula Weight	855.06	841.03	756.87
Crystal System	Triclinic	Triclinic	Triclinic
Space group	P-1 (No. 2)	P-1 (No. 2)	P-1 (No. 2)
a, b, c [Å]	8.9620(3), 9.0342(3), 20.1252(8)	8.8904(4), 9.2120(4), 19.1703(9)	8.2759(1), 9.6744(1), 15.9721(2)
α, β, γ [deg]	90.374(2), 96.279(2), 114.637(2)	76.464(1), 86.338(1), 65.077(1)	91.517(1), 104.447(1), 13.938(1)
V [Ang**3]	1469.76(9)	1383.18(11)	1120.00(3)
Z	2	2	2
D(calc)[g/cm**3]	1.932	2.019	2.244
Mu(MoKa)[/mm]	5.443	5.782	7.127
F(000)	832	816	720
Crystal Size[mm]	0.09 × 0.16 × 0.46	0.12 × 0.23 × 0.38	0.13 × 0.29 × 0.29
Temperature (K)	293	293	293
Radiation [Å]	MoKa 0.71073	MoKa 0.71073	MoKa 0.71073
θ Min-Max [Deg]	2.0, 28.5	2.5, 27.5	2.3, 35.0
Dataset	−12:12; −12:12; −27:27	−11:11; −11:11; −24:24	−13:13; −15:15; −25:25
Tot.; Uniq. Data	26,089; 7328	24,962; 6234	39,929; 9829
R(int)	0.046	0.027	0.031
Nref; Npar	7328; 370	6234; 372	9829; 410
R, wR_2, S	0.0811, 0.2147, 1.30	0.0304, 0.1258, 1.20	0.0257, 0.0610, 1.02

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Table 2
Selected bond lengths (Å) and angles (°) for cation **1**.

Hg(1)–C(1)	2.067(3)	Hg(1)–C(14)	2.070(3)	Hg(1)–C(10)	2.742(2)
N(1)–C(1)	1.343(3)	N(1)-C(3)	1.381(4)	N(1)-C(4)	1.477(3)
N(2)-C(2)	1.372(4)	N(2)–C(15)	1.463(4)	N(2)–C(1)	1.337(3)
N(3)–C(14)	1.347(3)	N(3)–C(12)	1.378(4)	N(3)–C(11)	1.488(4)
N(4)–C(14)	1.339(4)	N(4)–C(16)	1.460(4)	N(4)–C(13)	1.370(5)
C(1)-Hg(1)–C(10)		90.35(9)	C(10)-Hg(1)–C(14)		89.46(9)
C(1)-Hg(1)–C(14)		179.29(10)	Hg(1)–C(10)-C(5)		90.39(14)
Hg(1)–C(10)-C(9)		91.91(15)	Hg(1)–C(1)-N(2)		126.54(19)
Hg(1)–C(1)–N(1)		26.65(19)	Hg(1)–C(14)-N(3)		127.5(2)
Hg(1)–C(14)-N(4)		126.0(2)	Hg(1)–C(10)–H(10A)		88.00

Table 4
Selected bond lengths (Å) and angles (°) for cation **3**.

Hg(1)-C(6)	2.724(13)	Hg(1)-C(8)	2.070(16)	Hg(1)-C16	2.058(15)
N(1)-C(8)	1.354(19)	N(1)-C(7)	1.486(18)	N(1)-C(9)	1.38(2)
N(2)–C(10)	1.38(2)	N(2)-C(8)	1.350(19)	N(2)–C(11)	1.46(2)
N(3)–C(17)	1.38(2)	N(3)–C(16)	1.358(17)	N(3)–C(15)	1.491(18)
N(4)–C(19)	1.477(19)	N(4)–C(16)	1.332(19)	N(4)–C(18)	1.39(2)
C(6)-Hg(1)-C(8)		90.4(5)	C(6)-Hg(1)–C(16)		90.3(5)
C(8)-Hg(1)–C(16)		177.4(5)	Hg(1)-C(6)–H(6A)		117.00
Hg(1)-C(6)–C(1)		90.5(8)	Hg(1)-C(6)-C(5)		90.1(8)
Hg(1)-C(8)–N(1)		126.5(10)	Hg(1)-C(8)-N(2)		126.5(11)
Hg(1)–C(16)-N(4)		126.1(10)	Hg(1)–C(16)-N(3)		127.3(10)

Compound **II**·$2PF_6$ was obtained as colorless crystals. Yield: 2.2 g (92%), m.p.: 94–96 °C ^{1}H NMR (400 MHz, CD_3CN): δ 0.96 (6H, t, 2 × CH_3), 1.35 (4H, sextet, 2 × CH_2), 1.85 (4H, quintet, 2 × CH_2), 4.15 (4H, t, 2 × *N*-CH_2), 5.35 (4H, s, 2 × benzylic CH_2), 7.38 (2H, t, 2 × imidazolium H5′), 7.43 (2H, t, 2 × imidazolium H4′), 7.45–7.55 (4H, m, 4 × Ar-H) and 8.54 (2H, s, 2 × imidazolium H2′); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): δ 13.0 (CH_3), 19.3 (CH_2), 31.8 (CH_2), 49.9 (*N*-CH_2), 52.8 (CH_2), 122.8, 123.2 (imidazolium C5′ and C4′), 129.3, 129.7, 130.5, 135.9 (Ar-C) and 135.2 (imidazolium C2′). Anal. Calc. for $C_{22}H_{32}N_4F_{12}P_2$: C, 41.13; H, 5.02; N, 8.72%. Found: C, 41.02, H, 4.91, N, 8.53%.

3.3. Synthesis of 3,5-bis(N-butylimidazolium-1-ylmethyl)toluene bis(hexafluorophosphate) (*III*·$2PF_6$)

This salt has been described in a previous study [11] and was prepared in a manner analogous to that for (**I**·$2PF_6$), only with 3,5-bis(bromomethyl)toluene instead of 1,3-bis(bromomethyl) benzene. Compound **III**·$2PF_6$ was obtained as light-beige crystals. Yield: 1.9 g (79%), m.p.: 96–98 °C. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the salt solution in acetonitrile at ambient temperature. ^{1}H NMR (400 MHz, CD_3CN): δ 0.95 (6H, t, 2 × CH_3), 1.35 (4H, sextet, 2 × CH_2), 1.85 (4H, quintet, 2 × CH_2), 2.38 (3H, s, Ar-CH_3), 4.15 (4H, t, 2 × *N*-CH_2), 5.30 (4H, s, 2 × benzylic CH_2), 7.22 (1H, s, Ar-H), 7.265 (2H, s, 2 × Ar-H), 7.39 (2H, t, imidazolium H5′), 7.44 (2H, t, imidazolium H4′) and 8.58 (2H, s, 2 × imidazolium H2′); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): δ 13.0 (CH_3), 19.4 (CH_2), 20.6 (Ar-CH_3) 31.8 (CH_2), 49.9 (*N*-CH_2), 52.8 (CH_2), 122.8, 123.2 (imidazolium C5′ and C4′), 126.38, 130.35, 135.15, 140.85 (Ar-C), 136.1 (imidazolium C2′) and 135.9 (Ar-CH_3). Anal. Calc. for $C_{23}H_{34}N_4F_{12}P_2$: C, 42.08; H, 5.22; N, 8.53%. Found: C, 42.05; H, 5.09; N, 8.34%.

3.4. Synthesis of 1,3-Bis(3-methylimidazolium-1-ylmethyl) benzenemercury(II) bis(hexafluorophosphate) (*1*)

Mercury acetate (0.2 g, 0.6 mmol) was added to a solution of **I**·$2PF_6$ (0.3 g, 0.5 mmol) in 40 mL of acetonitrile. The mixture was refluxed for 48 h, after which the solvent was removed under reduced pressure. The white residue was washed with distilled water and recrystallised from acetonitrile to produce a white solid, (0.2 g), 54%, m.p.: 267–269 °C. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a solution of the complex in acetonitrile at ambient temperature. ^{1}H NMR (400 MHz, CD_3CN): δ 3.85 (6H, s, 2 × *N*-CH_3), 5.36 (4H, d, J = 13.6 Hz, 2 × benzylic C*H*H), 5.66 (4H, d, J = 13.6 Hz, 2 × benzylic CH*H*), 7.43 (2H, d, J = 1.6 Hz, 2 × imidazolium H5′), 7.66 (2H, d, J = 1.6 Hz, 2 × imidazolium H4′), 7.68 (2H, d, J = 2.0 Hz, 2 × Ar-H), 7.76 (1H, t, Ar-H) and 8.12 (1H, s, Ar-H); $^{13}C\{^1H\}$ (100 MHz, CD_3CN): δ 39.5 (*N*-CH_3), 54.4 (CH_2), 125.2, 126.3 (imidazolium C5′ and C4′), 132.1, 132.4, 134.6, 136.3 (Ar-C) and 173.5 (C2′-Hg). Anal. Calc. for $C_{16}H_{18}N_4F_{12}P_2Hg$: C, 25.39; H, 2.40; N, 7.40%. Found: C, 25.28; H, 2.21; N, 7.15%.

3.5. Synthesis of 1,3-Bis(3-butylimidazolium-1-ylmethyl) benzenemercury(II) bis(hexafluorophosphate) (*2*)

Complex **2** was prepared similar to complex **1** except using **II**·$2PF_6$. Colorless crystals Yield: 0.3 g (50%), m.p.: 285–287 °C. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a solution of the complex in acetone/ethanol at ambient temperature. ^{1}H NMR (400 MHz, CD_3CN): δ 0.94 (6H, t, 2 × CH_3), 1.33 (4H, sextet, 2 × CH_2), 1.83 (4H, quartet, 2 × CH_2), 4.08 (4H, t, 2 × CH_2), 5.37 (4H, d, J = 13.6 Hz, 2 × benzylic C*H*H), 5.676 (4H, d, J = 13.6 Hz, 2 × benzylic CH*H*), 7.49 (2H, d, J = 1.6 Hz, 2 × imidazolium H5′), 7.68 (2H, d, J = 1.6 Hz, 2 × imidazolium H4′), 7.73 (2H, d, J = 2.004 Hz, 2 × Ar-CH), 7.78 (1H, t, Ar-H) and 8.07 (1H, s, Ar-H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 13.19 (CH_3), 19.88 (CH_2), 32.84 (CH_2), 53.39 (*N*-CH_2), 54.39 (CH_2), 123.75, 126.70 (imidazolium C5′ and C4′), 131.30, 132.72, 134.84, 136.33 (Ar-C) and 172.64 (C2′-Hg). Anal. Calc. for $C_{22}H_{30}N_4F_{12}P_2Hg$: C; 31.42, H; 3.60, N; 6.66%. Found: C; 31.83, H; 3.10, N; 6.57%.

3.6. Synthesis of 3,5-Bis(3-butylimidazolium-1-ylmethyl) toluenemercury(II) bis(hexafluorophosphate) (*3*)

Complex **3** was prepared similar to complex **1** except using **III**·$2PF_6$. An off-white solid, Yield: 0.28 g (54%) m.p.: 256–258 °C. Crystals suitable for X-ray studies were obtained by slow evaporation of a solution of the salt in acetonitrile/water at ambient temperature. ^{1}H NMR (400 MHz, CD_3CN): δ 0.84 (6H, t, 2 × CH_3), 1.22 (4H, sextet, 2 × CH_2), 1.73 (4H, quartet, 2 × CH_2), 2.3 (3H, s, Ar-CH_3), 4.08 (4H, t, 2 × CH_2), 5.32 (4H, d, J = 13.6 Hz, 2 × benzylic C*H*H), 5.605 (4H, d, J = 13.6 Hz, 2 × benzylic CH*H*), 7.49 (2H, d, J = 2.0 Hz, 2 × imidazolium H5′), 7.526 (2H, s, 2Ar-H), 7.68 (2H, d, J = 2.0 Hz, 2 × imidazolium H4′) and 7.83 (1H, s, Ar-H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 13.20 (CH_3), 19.89 (CH_2), 20.93 (Ar-CH_3) 32.89 (CH_2), 53.36 (*N*-CH_2), 54.34 (CH_2), 123.74, 126.56 (imidazolium C5′ and C4′), 128.17, 133.34, 136.15 (Ar-C), 146.07 (Ar-CH_3) and

Table 3
Selected bond lengths (Å) and angles (°) for cation **2**.

Hg(1)–C(1)	2.067(3)	Hg(1)-C(8)	2.067(7)	Hg(1)–C(16)	2.079(7)
N(1)–C(1)	1.343(3)	N(1)-C(8)	1.354(8)	N(1)–C(11)	1.477(8)
N(2)-C(2)	1.372(4)	N(2)-C(8)	1.337(8)	N(2)-C(7)	1.502(8)
N(3)–C(14)	1.347(3)	N(3)–C(15)	1.480(8)	N(3)–C(16)	1.354(8)
N(4)–C(14)	1.339(4)	N(4)–C(19)	1.469(8)	N(4)–C(16)	1.331(8)
C(1)-Hg(1)-C(8)		90.2(2)	C(1)-Hg(1)–C(16)		90.3(2)
C(8)-Hg(1)–C(16)		179.5(2)	Hg(1)–C(1)-C(2)		89.8(3)
Hg(1)–C(1)-C(6)		89.8(3)	Hg(1)-C(8)-N(2)		127.0(4)
Hg(1)-C(8)–N(1)		127.0(4)	Hg(1)–C(16)-N(3)		125.9(5)
Hg(1)–C(16)-N(4)		126.8(4)	Hg(1)–C(1)–H(1A)		117.00

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172.79 (C2′-Hg). Anal. Calc. for $C_{23}H_{32}N_4F_{12}P_2Hg$: C; 32.31, H; 3.77, N; 6.55%. Found: C; 32.34, H; 3.27, N; 6.21%.

4. Conclusion

In conclusion, three novel Hg-NHC complexes of the type $[(NHC)_2\text{-}\mu\text{-}Hg]^{+2}$ were prepared. The complexes display interesting bonding motif confirmed through X-ray studies. This type of metal-carbene bonding, along with close interactions of the metal to the aryl ring in the vicinity of the structure, is becoming quite unique for Hg-NHC chemistry. Further studies need to be conducted to assess whether other metals display this kind of behavior or if this behavior is exclusive to mercury complexes.

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AppendixA. Supplementary material

Crystallographic data for structural analysis have been deposited in the Cambridge Crystallographic Data Center, CCDC 799587 for **III.2PF$_6$** and 820354, 820355, 820356 for the complexes **1-3**. These data can be obtained free of charge from CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.07.032

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Synthesis, characterization, and theoretical studies of xylyl linked bis-imidazolium and bis-benzimidazolium salts

*Muhammad Adnan Iqbal[a], Rosenani A. Haque[a], Shukri Sulaiman[b] Titia Izzati[b]

[a]*School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM Penang, Malaysia*

[b]*School of Distance Education, Universiti Sains Malaysia, 11800 USM Penang, Malaysia*

(*mai10_che022p@student.usm.my, *adnan_chem38@yahoo.com)

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Abstract: Xylyl linked bis-imidazolium and bis-benzimidazolium salts were synthesized and characterized by spectroscopic techniques (NMR & FT-IR) and microanalysis. Density functional theory was used to calculate the binding free energies for acidic protons of both types of ligands and compared with the NMR results. The findings of this study provides a better understanding for the formation of free carbenes and therefore have potential applications to predict the complex formation reactions as well as to assess strength of coordination bonds with metals for imidazole and benzimidazole based ligands.

Key Words: Imidazolium salts, Benzimidazolium salts, Density functional theory

1. Introduction:

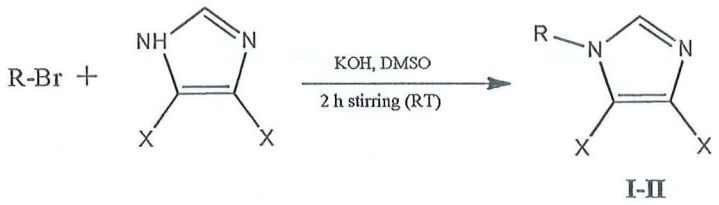
The use of *N*-heterocyclic carbene (NHC) ligands is increasing rapidly in the organometallic and inorganic coordination chemistry [1]. This increase in popularity of these complexes is due to their potential catalytical ability, as evidenced by growing research in this area [2]. Every year, a number of new NHC ligands are reported all around the world in which the main body of information is accumulated on imidazole based NHCs whereas their benzannulated counterparts are relatively unexplored [1, 3-6]. Benzimidazole compounds are of chemical and biological interest [7]. The activity associated with benzimidazole containing compounds has widely been studied which proves them as good Analgesic and anti-inflammatory agents [8], Antimicrobial and Anthelmentic agents [9], Anti-Ulcer agents [10], Gastric [H^+-K^+] AT phase inhibitory agents [11], and Anti-hypertension Agents [12]. In view of above, we synthesized imidazole and benzimidazole-based NHC ligands (**III** and **IV**, *Scheme 1*) and a theoretical study was performed to predict the formation and stability of their respective complexes.

The salts were synthesized by dual step synthesis. In the 1st step, respective alkyl halides (*i*-Pr & *n*-Pr bromides) were attached either to imidazole or benzimidazole according to modified method developed by Starikova *et al.* [13]. In the 2nd step *N*-substituted imidazole and benzimidazoles were linked to *ortho*-xylene dibromide and *meta*-xylene dibromide respectively using dioxane as a reaction medium (*Scheme 1*).

The structures of respective ligands (**III** and **IV**) were constructed by ChemBioDraw Ultra 12.0 and theoretical calculations were performed using the Gaussain 03 softwear package [14]. The ligands

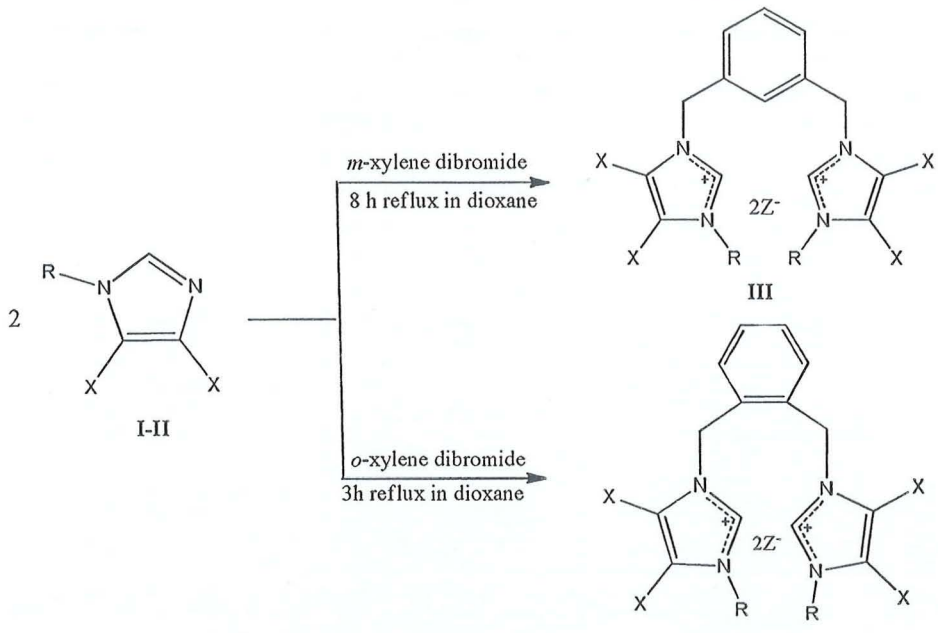
(**III** and **IV**) were examined using DFT with beck's three parameters hydride method B3LYP to optimize the structures with the 6-31g basis set. GaussianView software was used for visualization to examine the structures and other related properties.

Step 1



I-II

Step 2



I-II

III

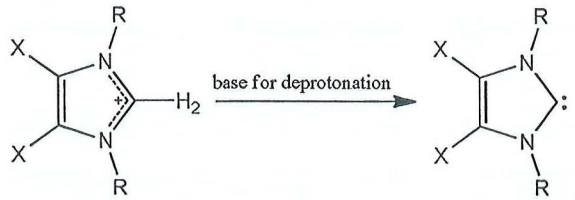
IV

I (R = n-Pr, XX = CH=CH-CH=CH), **II** (R = *i*-Pr, X = H),
III (R = n-Pr, XX = CH=CH-CH=CH, Z = PF_6) and
IV (R = i-Pr, X = H, Z = Br)

Scheme 1: Dual step synthesis of *bis*-imidazolium and *bis*-benzimidazolium salts (**III-IV**).

2. Results and discussion:

A free *N*-heterocyclic carbene is generated by removing an acidic proton (H_2) from an azolium ion and as a result, in its ground state, it keeps two non-bonding electrons, paired in sp^2 orbital which are utilized to form coordinate bond with metals (*Scheme 2*).



an imidazolium/benzimidazolium ion **V-VI** a free carbene

Scheme 2: Deprotonation of acidic proton (H2) to form a NHC [**V** (X = H4/H5), **VI** (X = CH=CH-CH=CH)].

Electronic and steric factors affect the stability of these carbenes (lone pair). The electronic contribution is generally believed to be the main stabilizing factor, and involves electron donation from the *N*-heteroatoms to the vacant p-orbital [15] facilitating carbene lone pair to be available for coordinate bonding. The substitution of electron withdrawing groups either at the *N*-heteroatoms or at H4 & H5 (see *Fig. 1*) may affect the strength of NHC to form organometallic compounds as well as inorganic complexes. Substitution of benzene at H4 & H5 decreases electron donation from *N*-heteroatom to vacant p-orbital resultantly decreasing the coordination ability of benzimidazole based NHCs as compared to imidazolium-based NHCs (*see Fig. 1*).

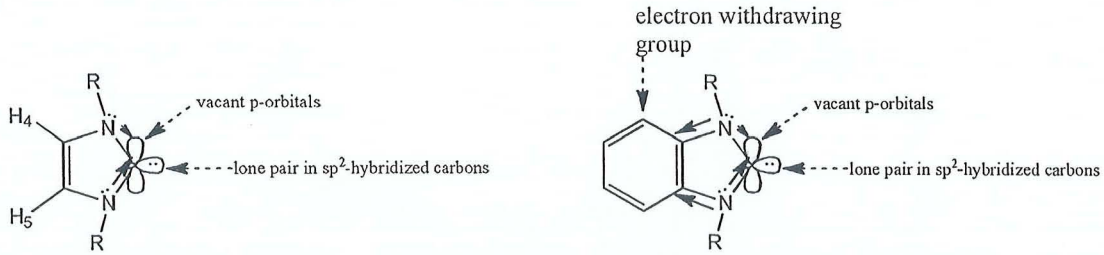


Fig. 1: Orbital view of imidazolium and benzimidazolium-based NHC showing electron donations.

The lower coordination ability of benzimidazolium-based NHCs may be one of the contributing factors to the unpopularity of this type of NHCs as compared to the imidazolium-based NHCs. In this work we tried to study these differences using NMR results and theoretical calculations. The acidic proton signal for imidazole based salt **IV** was observed at 9.22 whereas for benzimidazole based salt **III** at relatively downfield (10.06, *see Fig. 3*). This difference may be due to the presence of an electron withdrawing (phenyl) group at the H4 and H5 positions of the imidazolium ring. Theoretical calculations performed for the respective salts also support this argument.

In this study, the binding free energies for **III** and **IV** are estimated based on simulation results from single molecule. From a more intrinsic view, we analyzed the binding free energies between acidic protons of **III** and **IV**, and investigated the conformational characteristics involved in these processes. Gao Yi and Zeng, X.C mentioned that the hydrogen binding energies were evaluated in general with the

formula $E_{binding}$=E(compound+H_2)-E(H_2)-(compound) [16].The calculated free energies reflected the experimental observations, the energy contributions and their roles in binding **III** and **IV** without hydrogens are clear. We observed that the contributions of internal energies are quite big and hence non bonded interactions play dominant role. The results show that binding energy for hydrogen in **III** is lower than the binding energy for hydrogen in **IV** (*see Table1*). This fact proves that the C-**He** bond in **III** is weaker than C-**Hd** bond in **IV** molecule. One of the difficulties faced in discussing the reactivity of **III** and **IV** in terms of dipolar interactions is the fact that for most of the interesting highly reactive ligand the dipoles are unknown. Although the dipole moment of an energy-minimized structure could give an indicative value, it has to be realized that in a (neat) solution more conformations than just the minimum-energy structure are present and that the average dipole moment could differ significantly from the dipole of the energy minimized structure. Therefore, we calculated the dipoles as the Boltzmann-averaged dipole moment (*see Table1*).

The findings of our study serve as a complement to experimental observations, which provide clues on reactivity of **III** and **IV** for controlling the interactions. HOMO and LUMO characteristics for strong electron donating substituent and strong electron withdrawing substituent are show in *Fig.2*. The resonance in benzimidazole based salts has been highlighted by showing the unhybridized p-orbitals. Electronegativity (X) indicates the acidity of a compound. This value was calculated by equation [17] below:

$$X=(I-A)/2$$

$$I : \text{ionization energy} = -E_{HOMO}$$

$$A : \text{electron affinity} = -E_{LUMO}$$

From *Table1*, the elimination addition of strong electron withdrawing hydrogen has given the electronegativity value of 247.624kJ/mol to the benzimidazole which indicates that it is the highest acidity. The magnetic shield was calculated for both of the compounds, specifically for carbons and hydrogens. *Fig. 2* shows that the acidic protons are more deshielded as compared to other protons in each salt as well as the carbons attached to the same hydrogens. The deshielding is more in benzimidazole based salts.

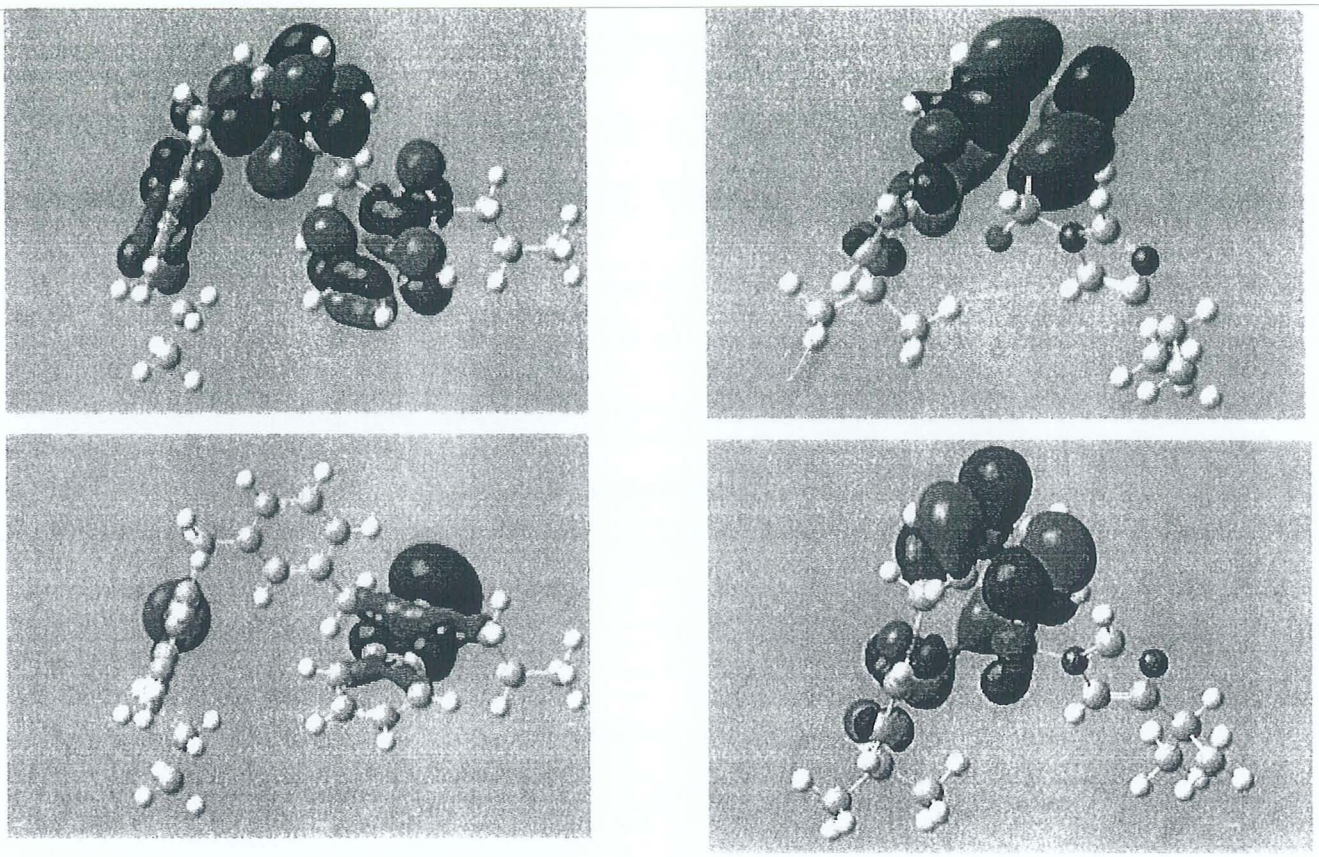


Figure 2: HOMO and LUMO characteristics for strong electron donating substituent and strong electron withdrawing substituent.

Table 1: Chemical characteristics for **III** and **IV**.

Parameter		III	III-H	IV	IV-H
ENERGY	(kJ/mol)	-3425979,608	-3422770,795	-2617748,148	-2614430,115
BINDING ENERGY	(kJ/mol)	-3207,637891		-3316,857116	
DIPOLE MOMENT	(Debye)	3,4582	3,1845	4,8300	6,7913
POINT GROUP		C1	C1	C1	C1
HOMO	(kJ/mol)	-405,5346904	-531,584933	-229,0748526	-233,9582821
LUMO	(kJ/mol)	-33,58014172	-36,33691645	-81,810572	-84,17352177
ELECTRONEGATIVITY	(kJ/mol)	185,9773	247,6240	73,6321	74,8924

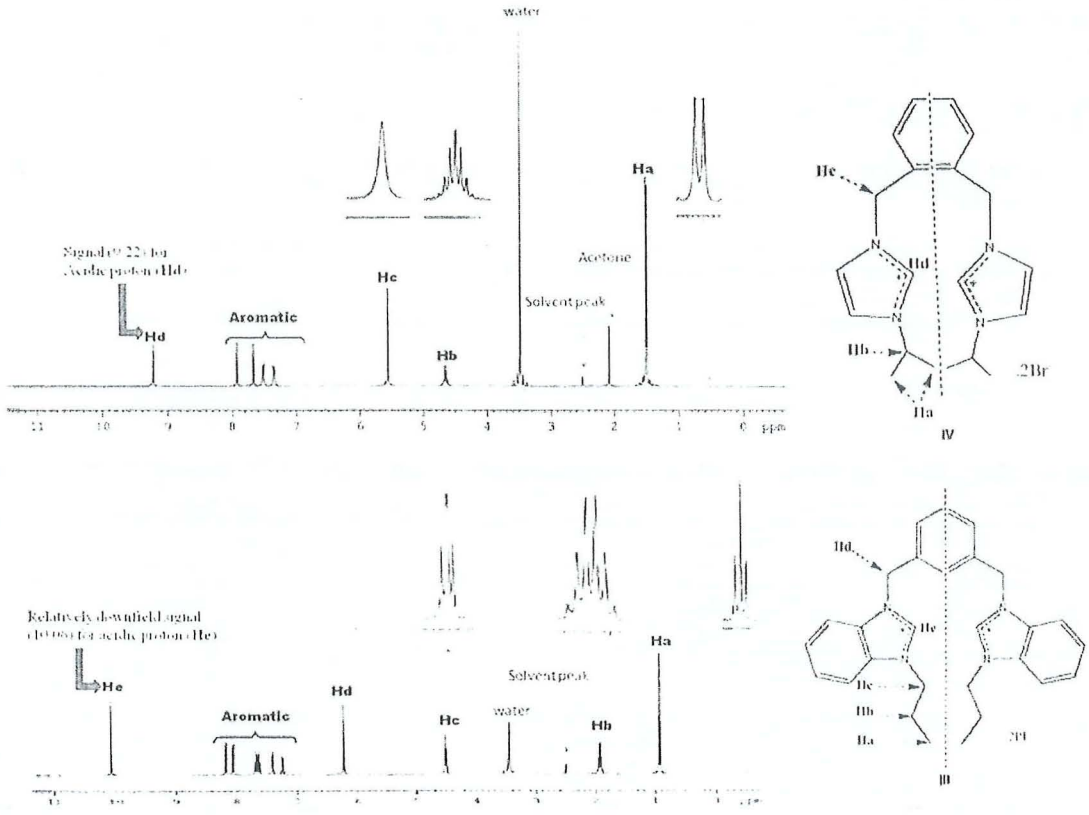


Figure 3: ^{1}H NMR spectrum highlighting the signals for acidic protons for salts III & IV (400 MHz, d_6-DMSO).

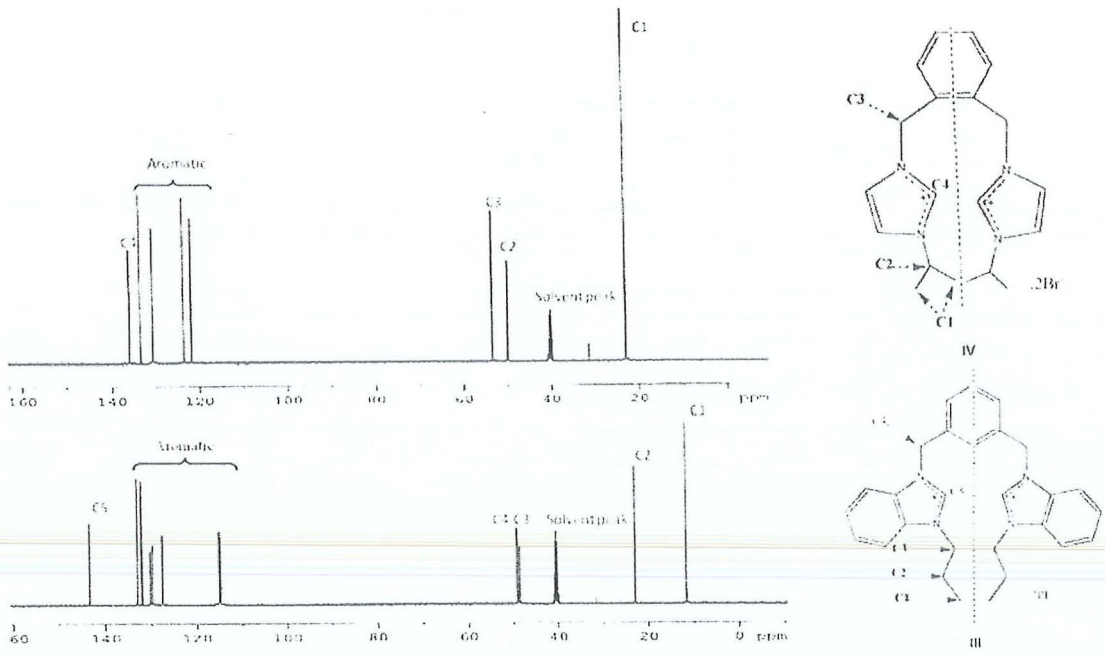


Figure 4: ^{13}C NMR spectrum for salts (**III** & **IV**). The signal for C5 in **III** is relatively downfield as compare to C4 in **IV**. This also proves the deshielding is due to an electron withdrawing group at H4 & H5 substitution (100 MHz, d_6-DMSO).

3. Experimental

General procedure: The IR spectra were recorded on a Perkin Elmer system 2000 spectrometer in KBr for solids and on Thallium bromide disks for liquids. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 and 300 instruments from solutions in d_6-DMSO. The melting points were assessed by using Stuart Scientific SMP-1 (UK). The CHN microanalyses were carried out by using a Perkin Elmer 2400 LS Series CHN/S analyser.

Synthesis of compounds: *N*-substituted imidazole (**I**) and benzimidazole (**II**) compounds were synthesized and purified according to the modified method by starikova et al [13] whereas the respective salts (**III** & **IV**) were synthesized by refluxing the reactants in dioxane.

3,3'-(1,3-phenylenebis(methylene))bis(1-propyl-1H-benzoimidazolium) (III.2PF$_6$): *N*-Propylbenzimidazole (0.01M) was added dropwise in a vigorously stirred solution of 1,3-bis(bromomethylene)benzene (0.005M, 1.319g) in 30 ml of dioxane and refluxed for 8 h. The product settled as a sticky brownish fluid at bottom of the flask. The upper layer was decanted and the product was washed with fresh dioxane (3 × 5 ml). The resulting bromide salt was converted directly to its hexaflourophosphate counterpart by metathesis reaction using KPF_6 (0.965g, 0.005 M) in 50 mL of methanol/water mixture (1:1). The mixture was stirred for 3 h. The white precipitates were filtered and washed with distilled water (2 × 5 mL), then dried in oven at 80 °C for 6 h. White powder. Yield: 1.76 g (49.29 %), mp.: 240–244 °C. **^{1}H NMR** (400 MHz, d_6-DMSO): δ 0.938 (6H, t, 2 × CH_3), 1.94 (4H, sext., 2 × CH_2), 4.51 (4H, t, 2 × N-CH_2-R), 7.40 – 8.19 (12H, Ar-H 12 × CH), 10.06 (2H, s, 2 × NCHN); **$^{13}C\{^{1}HNMR\}$**100 MHz, d_6-DMSO: 11.07 (CH_3), 22.98 (CH_2), 48.67 (N-CH_2-R), 49.02 (N-CH_2-Ar), 114.84, 115.04, 126.74, 127.55, 127.64, 129.67, 130.22, 132.00, 132.12, 132.99 (Ar-C) and 143.43 (NCHN). **FT-IR** (KBr): υ (cm^{-1}); 3461, 3380 ($N_{benzimi}$-C_{aliph}); 3018 (C-H_{arom}); 2929, 2863 (C-H_{aliph}). Anal. Cal. for $C_{28}H_{32}F_{12}N_4P_2$: C, 47.07, H, 4.51, N, 7.84 %. Found: C, 46.92, H, 4.48, N, 7.55 %.

3,3'-(1,3-phenylenebis(methylene))bis(1-*i*-propyl-1H-imidazolium) (VI.2Br): *N-i*-Propylimidazole (0.01M) was added dropwise in a vigorously stirring solution of 1,2-bis(bromomethylene)benzene (0.005M, 1.319g) in 30 ml of dioxane and refluxed at 100 °C. White precipitates started to float in solvent within 30 minutes. Reaction mixture was refluxed for 3 h. The product was filtered and washed with fresh dioxane (3 × 5 ml) and air-dried for 24 h. Beige colored lumps. Yield: 1.20 g (49.58 %), mp.: 142–146 °C. **^{1}H NMR** (400 MHz, d_6-DMSO): δ 1.51(6H, d, 4 × CH_3), 4.65 (2H, hept., *i*-Pr 2 × CH), 5.56 (4H, s, 2 × N-CH_2-Ar), 7.33 – 7.36 (4H, Ar-H 4 × CH), 7.66 (2H, s, 2 × H4/H5), 7.92 (2H, s, Ar 2 × H4/H5) and 9.22 (2H, s, 2 × NCHN); **$^{13}C\{^{1}HNMR\}$**100 MHz, d_6-DMSO: 23.01 (CH_3), 49.99 (CH_2), 53.45 (i-Pr-CH), 121.75, 123.54, 130.65, 130.67, 133.49 (Ar-C) and 136.06 (NCHN). **FT-IR** (KBr): υ (cm^{-1}); 3439 ($N_{benzimi}$-C_{aliph}); 3173, 3092 (C-H_{arom}); 2981,

2929, 2848 (C-H_{aliph}). Anal. Cal. for $C_{20}H_{28}Br_2N_4$: C, 49.60, H, 5.83, N, 11.57 %. Found: C, 48.92, H, 5.48, N, 11.51 %.

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Synthesis and Characterization of New Silver(I)- and Mercury(II)-n-heterocyclic Carbene Complexes

Rosenani A. Haque, Abbas Washeel Salman, Teoh Siang Guan

School of Chemical Sciences, Universiti Sains Malaysia, Minden 11800, Penang, Malaysia.

Abstract: New silver(I)- and mercury(II)-N-heterocyclic carbene (NHC) complexes were prepared from the reaction of the imidazolium salts with silver(I) oxide and mercury(II). The prepared complexes were characterized by ^{1}H and ^{13}C NMR, elemental analysis (CHN) and X-ray crystallography for on of the silver complexes. The metal centers are coordinated either by two NHCs giving the general formula (M-μ-L_2, where M = silver or mercury, L = NHC), or by one NHC and on bromide.

Key words: imidazolium salts; NHC complexes, Ag(I), Hg(II); synthesis; ^{1}H NMR, ^{13}C NMR.

INTRODUCTION

N-heterocyclic carbenes (NHCs) are cyclic carbenes that are usually derived from the deprotonation of imidazolium salts. NHCs have the ability to bond to both hard and soft metals making them more versatile ligand than phosphines (Herrmann and Kocher, 1997). The first investigation for the NHC chemistry was by Wanzlick in the early of 1960s (Wanzlick and Kleiner, 1961; Wanzlick, 1962 and Wanzlick *et al.*, 1963). In 1968, Öfele (Öfele, 1968) and Wanzlick (Wanzlick and Schonherr, 1968) were reported independently the synthesis and isolation of chromium and mercury NHC complexes. After the isolation of the first stable carbene by Arduengo (Arduengo *et al.*, 1991), NHCs have become an important area of research. Mercury-NHC complexes have received little attention compared with other metals in spite of being the earliest example of metal-NHC. The family of silver-NHC complexes has been receiving continuous attention (Zhou *et al.*, 2008). Silver-NHC complexes have been used successfully as transfer agents in the transmetallation reactions (Wang and Lin, 1998, and Çetinkaya *et al.*, 2006) to make other metal-NHC complexes. Also, the biological activity of many Ag-NHC complexes as antimicrobial (Youngs *et al.*, 2007; Özdemir *et al.*, 2010 and Özdemir *et al.*, 2010) and anticancer (Youngs, *et al.*, 2008 and Youngs *et al.*, 2011) agents has been confirmed. We have been interested in the chemistry of metal-NHC complexes due to their wide and diverse application. Herein, we present the synthesis and characterization of a range of new silver- and mercuy-NHC complexes.

Experimental:

Material and Measurements:

NMR spectra were recorded on Bruker 400 MHz Ultrashield™ and Avance 300 MHz spectrometers at ambient temperature. ^{1}H and ^{13}C NMR peaks are labeled as singlet (s), doublet (d), triplet (t) and multiplet (m). Chemical shifts were referenced with respect to solvent signals. Elemental analysis was carried out on a PerkinElmer series II, 2400 microanalyzer. Solvents were used as received without further purifications.

Synthesis of 1-methyl-3-benzylimidazolium chloride (I)

To a solution of 1-methylimidazole (1.0 g, 12.17 mmol) in 25 ml of dioxane, benzyl chloride (1.55 g, 12.22 mmol) was added. The mixture was stirred for 10 min then refluxed for overnight. The resulted solution was cooled using ice bath to get thick brown oil which was recrystallized from dichloromethane to give the product as brown oil in 88.0 %. ^{1}H NMR (400 MHz, D_2O): δ 3.72 (3H, s, N-CH_3), 5.21 (2H, s, benzylic CH_2), 7.23-7.34 (5H, m, 5 × Ar-H), 7.27 (1H, s, imidazolium H5), 7.31 (1H, s, imidazolium H4) and 8.58 (1H, s, imidazolium H2); $^{13}C\{1H\}$ NMR (100 MHz, D_2O): δ 36.08 (N-CH_3), 53.14 (benzylic CH_2) 122.55, 124.11 (imidazolium C5 & C4), 128.98, 129.65, 129.71 (4 × Ar-C) and 133.96 (imidazolium C2).

Synthesis of 1-methyl-3-benzylimidazolium hexafluorophosphate (II):

To a solution of **I** (1.0 g, 4.79 mmol) in a 10 ml of methanol, KPF_6 (0.9 g, 4.89 mmol) in 10 ml of

Corresponding Author: Rosenani A. Haque, School of Chemical Sciences, Universiti Sains Malaysia, Minden 11800, Penang, Malaysia
Tel: +604-653-3578, E-mail: rosenani@usm.my

methanol was added. The mixture was stirred for 1 h then left standing for overnight. The white precipitate was filtered, washed with distilled water several times and recrystallized from acetonitrile to give the final product as white solid in 93.8 %, m.p = 133-134 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 3.86 (3H, s, N-CH_3), 5.42 (2H, s, benzylic CH_2), 7.39-7.44 (5H, m, 5 × Ar-H), 7.7 (1H, t, imidazolium H5), 7.78 (1H, t, imidazolium H4) and 9.2 (1H, s, imidazolium H2); ^{13}C{1H} NMR (100 MHz, d_6-DMSO): δ 36.71 (N-CH_3), 52.75 (benzylic CH_2) 123.2, 124.86 (imidazolium C5 & C4), 129.13, 129.62, 129.87, 135.67 (4 × Ar-C) and 137.51 (imidazolium C2).

Synthesis of 1-butyl-3-benzylimidazolium Bromide (III):

To a solution of 1-butylimidazole (1.0 g, 8.05 mmol) in 30 ml of acetonitrile, benzyl bromide (1.4 g, 8.2 mmol) was added. The solution was stirred for 10 min then refluxed for overnight. The solvent was removed under vacuum giving the product as brown oil in 95.8 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.76 (3H, t, CH_3), 1.19 (2H, sextet, CH_2), 1.73 (2H, quintet, CH_2), 4.15 (2H, t, N-CH_2), 5.17, 5.46 (2H, s, benzylic CH_2), 7.19 (2H, d, J = 2.4 Hz, 2 × Ar-H), 7.2 (1H, t, Ar-H), 7.37 (2H, t, Ar-H), 7.40 (1H, t, imidazolium H5), 7.45 (1H, t, imidazolium H4) and 10.14 (1H, s, imidazolium H2); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 13.72 (CH_3), 19.70 (CH_2), 32.32 (CH_2), 50.13 (N-CH_2), 53.33 (benzylic CH_2) 122.56, 122.88 (imidazolium C5 & C4), 129.30, 129.59, 133.72 (4 × Ar-C) and 136.63 (imidazolium C2).

Synthesis of I.Ag:

Ag_2O (0.4 g, 1.7 mmol) was added to a solution of **I** (0.5 g, 2.4 mmol) in 30 ml of dichloromethane. The round bottom flask was wrapped with aluminum foil to exclude the light and the mixture was stirred for overnight. A clear solution with a black suspension was obtained. The suspension was filtered through a celite to give a clear solution. The solvent was removed under vacuum to give a grey precipitate, which recrystallized from dichloromethane giving the complex as light-grey crystals in 71.08 %. m.p = 142-144 °C ; ^{1}H NMR (300 MHz, d_6-DMSO): δ 3.77 (6H, s, N-CH_3), 5.31 (4H, s, benzylic CH_2), 7.29-7.35 (10H, m, 10 × Ar-H), 7.45 (2H, d, J = 1.2 Hz, imidazolium H5) and 7.53 (2H, d, J = 1.2 Hz imidazolium H4), ^{13}C{1H} NMR (100 MHz, d_6-DMSO): δ 39.05 (N-CH_3), 54.89 (benzylic CH_2) 123.02, 124.15 (imidazolium C5 & C4), 128.46, 128.84, 129.62, 138.19 (4 × Ar-C) and 179.86 (C2 -Ag). Anal. Cal. For $C_{22}H_{24}Ag\ N_4Cl.\ 2(CH_2Cl_2)$: C, 43.83; H, 4.29; N, 8.52 %. Found: C, 44.08; H, 4.40; N, 9.10 %.

Synthesis of II.Ag:

The experimental part and x-ray crystallography of this complex has been reported elsewhere (Rosenani *et al.*, 2011), ^{1}H NMR (300 MHz, d_6-DMSO): δ 3.76 (6H, s, N-CH_3), 5.31 (4H, s, benzylic CH_2), 7.26-7.33 (10H, m, 10 × Ar-H), 7.44 (2H, d, J = 1.8 Hz imidazolium H5) and 7.54 (2H, d, J = 1.8 Hz imidazolium H4), ^{13}C{1H} NMR (100 MHz, d_6-DMSO): δ 39.0 (N-CH_3), 54.83 (benzylic CH_2) 123.19, 124.08 (imidazolium C5 & C4), 128.43, 128.86, 129.63, 138.17 (4 × Ar-C) and 180.57 (C2 -Ag). Anal. Cal. For $K(Ag(C_{11}H_{12}N_2)_2)_2(PF_6)_3$: C, 38.33; H, 3.51; N, 8.13 %. Found: C, 38.27; H, 2.94; N, 8.23 %.

Synthesis of III.Ag:

Ag_2O (0.3 g, 1.3 mmol) was added to a solution of **III** (0.6 g, 2.0 mmol) in 40 ml of dichloromethane. The round bottom flask was wrapped with aluminum foil to exclude the light and the mixture was stirred for overnight. A clear solution with black suspension was obtained. The mixture was filtered using the celite and the solvent removed under vacuum to give thick brown oil which recrystallized from dichloromethane giving the product as dark-brown oil in 84.55 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (3H, t, CH_3), 1.31 (2H, sextet, CH_2), 1.77 (2H, quintet, CH_2), 4.08 (2H, t, N-CH_2), 5.25, 5.28 (2H, s, benzylic CH_2), 6.97 (1H, d, J = 1.6 Hz imidazolium H5), 7.03 (2H, d, J = 1.6 Hz imidazolium H4), 7.21 (2H, d, J = 7.4 Hz, 2 × Ar-H), 7.3 (2H, t, 2 × Ar-H) and 7.32 (1H, t, Ar-H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 14.04 (CH_3), 20.10 (CH_2), 33.85 (CH_2), 52.25 (N-CH_2), 55.99 (benzylic CH_2) 121.69, 121.81 (imidazolium C5 & C4), 128.15, 128.91, 129.45, 136.15 (4 × Ar-C), 181.21 (C2 -Ag).

Synthesis of II.Hg:

$Hg(OAc)_2$ (0.35 g, 1.09 mmol) was added to a solution of **II** (0.6 g, 1.88 mmol) in 40 ml of acetonitrile. The mixture was refluxed at 80-90°C for 20 h. A clear solution was resulted. The solvent was removed under vacuum to give a white powder which was washed with distilled water (3 × 5 ml) and recrystallized from acetonitrile to give the complex as a colorless crystals in 62.4 %, m.p = 267-270 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 3.95 (6H, s, N-CH_3), 5.55 (4H, s, benzylic CH_2), 7.26-7.4 (10H, multiple, Ar-H), 7.76 (2H, d, J

= 2.0 Hz imidazolium H5) and 7.78 (2H, d, J = 2.0 Hz imidazolium H4); 13C{1H} NMR (75.3 MHz, d_6-DMSO): δ 38.80 (N-CH_3), 54.24 (benzylic CH_2), 124.86, 126.52 (imidazolium C5 & C4), 128.6, 129.35, 129.8, 136.75 (4 × Ar-C) and 176.15 (C2 -Hg). Anal. Cal. For $C_{22}H_{24}N_4HgP_2F_{12}$: C, 31.65; H, 2.90; N, 6.71 %. Found: C, 32.17; H, 2.48; N, 6.89 %.

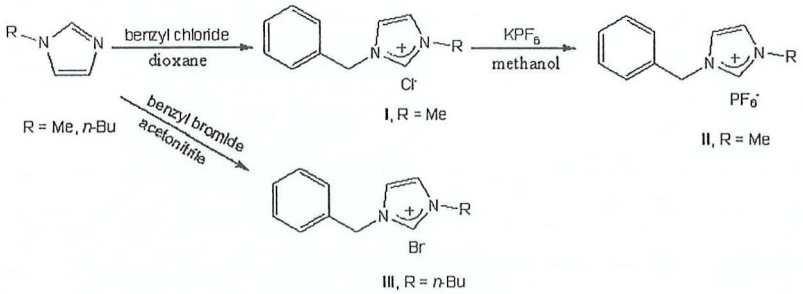
Synthesis of III.Hg:

Hg(OAc)2 (0.4 g, 1.25 mmol) was added to a solution of **III** (0.7 g, 2.37 mmol) in 40 ml of acetonitrile. The mixture was refluxed at 80-90°C for 20 h. The solvent was removed under vacuum to give a white powder which was washed with distilled water (3 × 3 ml) and recrystallized from acetonitrile giving the complex as white crystals in 68.22 %, m.p = 253-254 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 0.9 (6H, t, CH_3), 1.27 (4H, sextet, CH_2), 1.75 (4H, quintet, CH_2), 4.23 (4H, t, N-CH_2), 5.48 (4H, s, benzylic CH_2), 7.32-7.45 (10H, m, 10 × Ar-H), 7.7 (2H, d, J = 2.0 Hz imidazolium H5) and 7.76 (2H, d, J = 2.0 Hz imidazolium H4). ^{13}C{1H} NMR (75.3 MHz, d_6-DMSO): δ 14.31 (CH_3), 19.87 (CH_2), 33.37 (CH_2), 51.10 (N-CH_2), 54.10 (benzylic CH_2) 124.23, 124.67 (imidazolium C5 & C4), 129.0, 129.27, 129.68, 136.7 (4 × Ar-C) and 175.22 (C2 -Hg). $C_{28}H_{26}N_4HgBr_2$: C, 42.62; H, 4.60; N, 7.10 %. Found: C, 42.28; H, 4.33; N, 6.94 %.

RESULTS AND DISCUSSION

Synthesis of the Imidazolium Salts:

The imidazolium salts **I, II** and **III** were prepared as described in scheme 1. Reaction of 1-methylimidazole with one equivalent of benzyl chloride in dioxane afforded **I** as brown oil in 88.0%. A part of **I** was converted to its corresponding hexafluorophosphate counterpart by metathesis reaction using KPF_6 in methanol giving **II** as a white solid in 93.8%. The salt **III** was prepared by reaction of 1-butylimidazole with one equivalent of benzyl bromide in acetonitrile to give the salt as brown oil in 95.8 %. The salts **I** and **III** were soluble in most of the organic solvents as well as the water, while salt **II** was soluble in many of the solvents except methanol, ethanol, diethyl ether and water.



Scheme. 1: The synthesis of the imidazolium salts **I, II** and III

The ^{1}H NMR data for the prepared imidazolium salts show the common signals for imidazolium salts (Hahn *et al.*, 2009 and Fahlbusch *et al.*, 2009). The signals of H2′ proton appeared at δ 8.58 for **I**, δ 9.2 for **II** and δ 10.14 for **III** as singlet peaks (Figure 1). The benzylic protons appeared at δ 5.21 for **I** and δ 5.42 for **II** as singlet peaks, while appeared as couple of peaks for **III** at δ 5.17 and δ 5.46. In the ^{13}C NMR spectra, the C2′ signals for the salts were appeared at δ 133.96 for **I**, δ 137.51 for **II** and δ 136.63 for **III**.

Synthesis of the Complexes:

Scheme 2 shows the typical synthesis of the silver- and mercury-NHC complexes. The reaction of the imidazolium salts **I, II** and **III** with access of Ag_2O resulted the complexes in different forms. Complexes **I.Ag** and **II.Ag** were obtained in crystal forms in 71.08 % and 70.3 % yield, respectively, while complex **III.Ag** was obtained as dark-brown liquid in 84.55 %.

The ^{1}H NMR spectra were shown the fully absence of the imidazolium H2′ signals, this attributed to the deprotonation of those protons and formation of the complexes (Özdemir *et al.*, 2010; Özdemir *et al.*, 2010; Baker *et al.*, 2009 and Lin *et al.*, 2009). The complexation was confirmed by the ^{13}C NMR spectra which shown the signals of C′-Ag at δ 179.86 for **I.Ag**, δ 180.57 for **II.Ag** and 181.21 for **III.Ag** (Figure 2), consistent with the literature (Liu *et al.*, 2006 and Liu *et al.*, 2006).

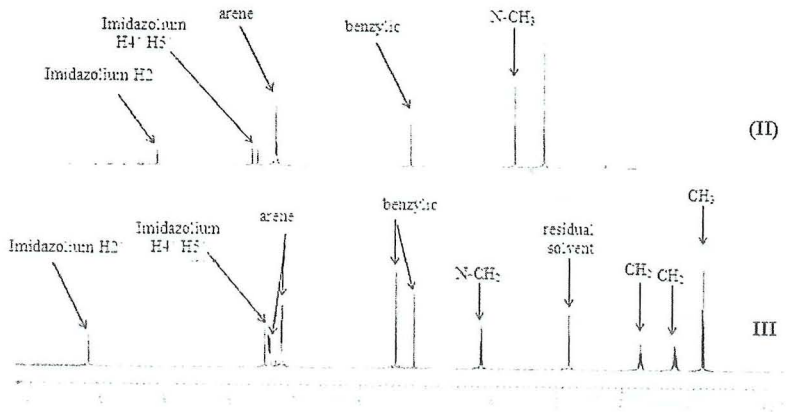
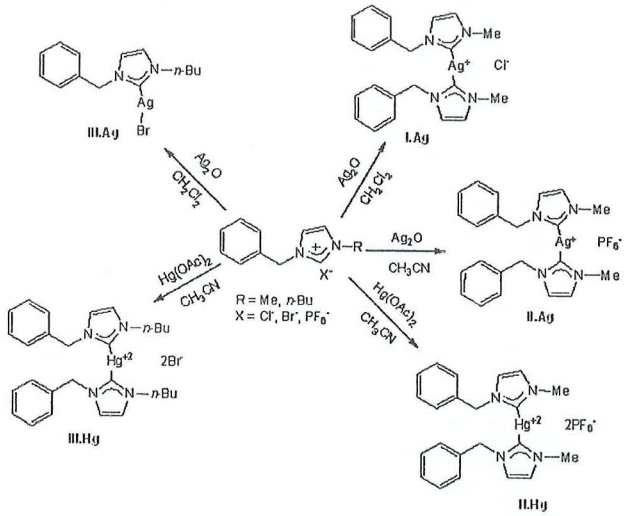


Fig. 1: ^{1}H NMR spectra for the salts **II** and **III**.



Scheme. 2: Synthesis of the silver and mercury complexes.

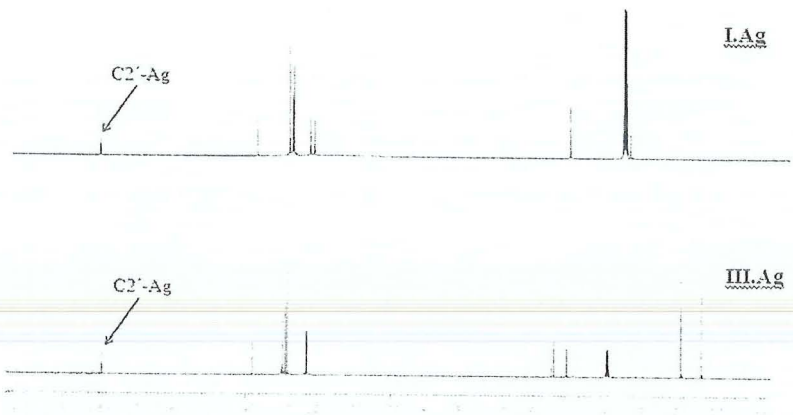


Fig. 2: ^{13}C NMR for **I.Ag** and **III.Ag**.

The reaction of the imidazolium salts **II** and **III** with excess of $Hg(OAc)_2$ in acetonitrile for 20 h produced the complexes as solid powders. The complexes were not soluble in water, so the residual of mercury acetate was removed by washing of the crude product with plenty of water. After recrystallization using acetonitrile, complexes **II.Hg** and **III.Hg** were obtained as colorless crystals for **II.Hg** and white crystals for **III.Hg** in 62.4 % and 68.2 % yield, respectively.

The ^1H NMR spectra for the mercury complexes shown the absence of the imidazolium H2′ signals which attributed to the successful complexation (Baker *et al.*, 2009; Baker *et al.*, 2009 and Xu *et al.*, 2009). The peaks for the C2′-Hg in the ^{13}C NMR spectrum appeared at δ 176.15 and δ 175.2 respectively (Figure 3), which is characteristic for a metal carbene signal (Xu *et al.*, 2009).

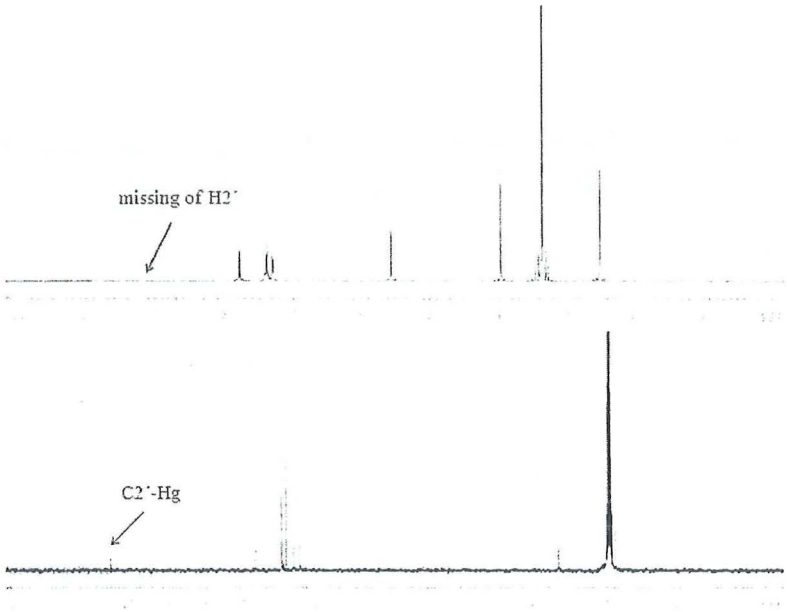


Fig. 3: ^1H and ^{13}C NMR for **II.Hg.**

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1,3-Bis[(3-allylimidazol-3-ium-1-yl)-methyl]benzene bis(hexafluoridophosphate)

Rosenani A. Haque,[a] Mohammed Z. Ghdhayeb,[a] Hassan H. Abdallah,[a] Ching Kheng Quah[b]‡ and Hoong-Kun Fun[b]*§

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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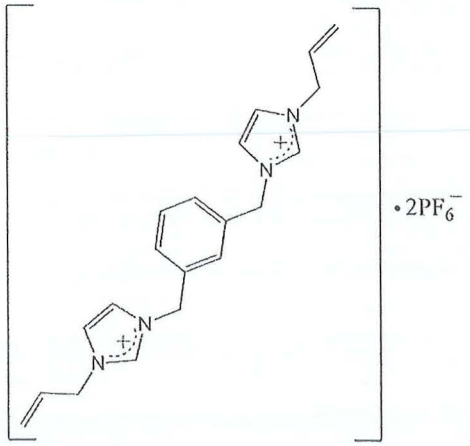
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; disorder in main residue; R factor = 0.108; wR factor = 0.201; data-to-parameter ratio = 12.1.

In the title compound, $C_{20}H_{24}N_4^{2+}\cdot 2PF_6^-$, the ethene and 3-allylimidazolium moieties of the cation are disordered over two positions with refined site occupancies of 0.664 (19): 0.336 (19) and 0.784 (7):0.216 (7), respectively, whereas four F atoms of one hexafluoridophosphate anion and all atoms in the other hexafluoridophosphate anion are disordered over two positions with refined site occupancies of 0.764 (5):0.2365) and 0.847 (9):0.153 (9), respectively. The benzene ring is inclined at angles of 78.2 (3), 81.3 (4) and 73.9 (12)° with the 1*H*-imidazol-3-ium ring and the major and minor components of the disordered 1*H*-imidazol-3-ium ring, respectively. In the crystal, the hexafluoridophosphate anions link the cations into two-dimensional networks parallel to (001) *via* intermolecular C—H···F hydrogen bonds. The crystal structure is further consolidated by π–π [centroid–centroid distance = 3.672 (3) Å] and C—H···π interactions.

Related literature

For general background to and the biological activity of carbene derivatives, see: Yang & Nolan (2001); Böhm *et al.* (2000); Jafarpour & Nolan (2001); Bourissou *et al.* (2000); Herrmann *et al.* (1996, 1997); Arduengo *et al.* (1991); Danopoulos *et al.* (2002); Dias & Jin (1994); Caballero *et al.* (2001); Thompson *et al.* (1999); Melaiye *et al.* (2005). For bond-length data, see: Allen *et al.* (1987). For a related structure, see: Haque *et al.* (2010).



Experimental

Crystal data

$C_{20}H_{24}N_4^{2+}\cdot 2PF_6^-$
M_r = 610.37
Monoclinic, $P2_1/c$
a = 9.8748 (4) Å
b = 9.9098 (3) Å
c = 26.124 (1) Å
β = 101.138 (2)°
V = 2508.27 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.28 mm^{-1}
T = 296 K
0.25 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.921, T_{max} = 0.924
35601 measured reflections
5217 independent reflections
4324 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.108
$wR(F^2)$ = 0.201
S = 1.14
5217 reflections
431 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*2 and *Cg*3 are the centroids of the N3*A*/N4*A*/C15*A*–C17*A* and N3*B*/N4*B*/C15*B*–C17*B* rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3*A*···F7*A*^{i}	0.93	2.40	3.276 (6)	156
C5—H5*A*···F5^{ii}	0.93	2.51	3.320 (6)	146
C8—H8*A*···F11*A*^{iii}	0.93	2.27	3.107 (8)	150
C10—H10*A*···F7*A*	0.93	2.25	3.130 (6)	158
C16*A*—H16*A*···F6^{iii}	0.93	2.48	3.407 (9)	172
C20*A*—H20*A*···*Cg*2	0.93	2.89	3.489 (11)	123
C20*B*—H20*C*···*Cg*3	0.93	2.84	3.44 (5)	124

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x, y-1, z$; (iii) $x+1, y, z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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§ Thomson Reuters ResearcherID: A-3561-2009.

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2,4-Bis[(3-allylimidazolium-1-yl)methyl]-mesitylene bis(hexafluoridophosphate)

Rosenani A. Haque,[a] Mohammed Z. Ghdhayeb,[a] Madhukar Hemamalini[b] and Hoong-Kun Fun[b]*‡

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

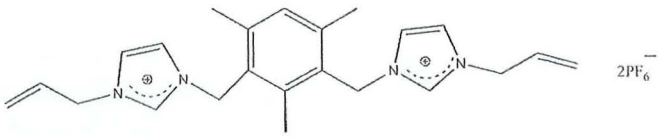
Received 25 June 2011; accepted 9 July 2011

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.046; wR factor = 0.117; data-to-parameter ratio = 25.1.

In the title molecular salt, $C_{23}H_{30}N_4^{2+}\cdot 2PF_6^-$, the central benzene ring of the cation makes dihedral angles of 89.80 (8) and 85.23 (7)° with the pendant imidazole rings. In the crystal, the cations and anions are linked by numerous C—H···F hydrogen bonds, thereby forming a three-dimensional network.

Related literature

For further details of imidazol-2-ylidenes, see: Arduengo *et al.* (1991); Scott & Nolan (2005); Scholl *et al.* (1999). For a related structure, see: Villegas *et al.* (2005). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{23}H_{30}N_4^{2+}\cdot 2PF_6^-$
M_r = 652.45
Monoclinic, $P2_1/n$
a = 11.9269 (4) Å
b = 19.1480 (6) Å
c = 12.4233 (4) Å
β = 103.479 (1)°
V = 2759.04 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 100 K
0.67 × 0.29 × 0.15 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.845, T_{max} = 0.961
67401 measured reflections
9961 independent reflections
8004 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.117
S = 1.05
9961 reflections
397 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.94 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···F3^{i}	1.00 (2)	2.49 (2)	3.411 (2)	153.1 (18)
C1—H2B···F7^{ii}	1.01 (2)	2.47 (2)	3.480 (2)	173.7 (18)
C3—H3A···F6^{ii}	0.97	2.53	3.3303 (17)	140
C3—H3B···F2^{i}	0.97	2.48	3.4151 (17)	161
C4—H4A···F8^{iii}	0.93	2.37	3.248 (2)	157
C5—H5A···F4^{iv}	0.93	2.34	3.0754 (16)	136
C5—H5A···F12^{iii}	0.93	2.52	3.1110 (18)	122
C6—H6A···F6^{ii}	0.93	2.31	3.1005 (16)	143
C14—H14A···F9^{iv}	0.97	2.45	3.401 (2)	167
C15—H15A···F6^{ii}	0.93	2.42	3.1873 (16)	139
C16—H16A···F8^{iv}	0.93	2.46	3.3113 (19)	152
C17—H17A···F3	0.93	2.53	3.2000 (18)	129
C18—H18B···F4^{ii}	0.97	2.54	3.2398 (17)	129
C18—H18B···F6^{ii}	0.97	2.50	3.3781 (17)	150

Symmetry codes: (i) $x, y, z-1$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+1, -y, -z$; (iv) $-x+1, -y, -z+1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5934).

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‡ Thomson Reuters ResearcherID: A-3561-2009.

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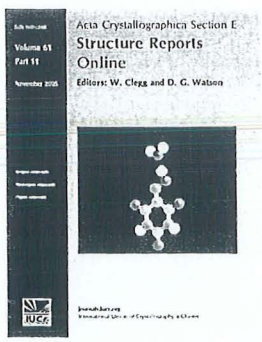
3,3′-Diallyl-1,1′-[*o*-phenylenebis(methylene)]diimidazol-3-ium bis(hexafluorophosphate)

Rosenani A. Haque, Mohammed Z. Ghdhayeb, Madhukar Hemamalini and Hoong-Kun Fun

Acta Cryst. (2011). E**67**, o2529–o2530



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3,3′-Diallyl-1,1′-[*o*-phenylenebis(methylene)]diimidazol-3-ium bis(hexafluorophosphate)

Rosenani A. Haque,[a] Mohammed Z. Ghdhayeb,[a] Madhukar Hemamalini[b] and Hoong-Kun Fun[b]*‡

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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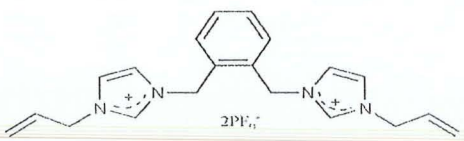
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; disorder in solvent or counterion; R factor = 0.049; wR factor = 0.142; data-to-parameter ratio = 29.3.

In the cation of the title molecular salt, $C_{20}H_{24}N_4^{2+}\cdot 2PF_6^-$, the central benzene ring makes dihedral angles of 84.19 (7) and 79.10 (7)° with the pendant imidazole rings. In one of the hexafluorophosphate anions, the six F atoms are disordered over two sets of sites, with an occupancy ratio of 0.842 (3):0.158 (3). In the crystal, the cations and anions are linked by numerous C—H···F hydrogen bonds, thereby forming a three-dimensional network.

Related literature

For applications and properties of *N*-heterocyclic carbenes, see: Bielawski & Grubbs (2000); Herrmann *et al.* (1998); Yeung *et al.* (2011); Jokic *et al.* (2010); Yu *et al.* (2010); Esteruelas *et al.* (2003). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{20}H_{24}N_4^{2+}\cdot 2PF_6^-$
M_r = 610.37
Triclinic, $P\overline{1}$
a = 7.3151 (3) Å
b = 12.4913 (4) Å
c = 13.8569 (5) Å
α = 101.810 (1)°
β = 94.603 (1)°
γ = 91.424 (1)°
V = 1234.27 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 100 K
0.82 × 0.61 × 0.48 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.801, T_{max} = 0.874
38348 measured reflections
10789 independent reflections
9422 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.142
S = 1.05
10789 reflections
368 parameters
15 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.91 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4A···F5^{i}	0.93	2.44	3.2625 (17)	148
C9—H9A···F8A^{ii}	0.93	2.38	3.303 (3)	171
C10—H10A···F2^{iii}	0.93	2.47	3.2429 (18)	141
C14—H14A···F3	0.97	2.41	3.3065 (16)	154
C14—H14B···F9A^{ii}	0.97	2.42	3.224 (2)	140
C15—H15A···F5	0.93	2.51	3.2100 (15)	132
C17—H17A···F12A^{iv}	0.93	2.42	3.279 (2)	154
C18—H18B···F1^{ii}	0.97	2.55	3.349 (2)	140
C19—H19A···F12A^{v}	0.93	2.50	3.364 (2)	155
C20—H20A···F8A^{vi}	0.93	2.40	3.158 (3)	139
C20—H20B···F1^{vii}	0.93	2.45	3.267 (2)	146

Symmetry codes: (i) $-x+2, -y+1, -z$; (ii) $x+1, y, z$; (iii) $x, y-1, z$; (iv) $-x+2, -y+1, -z+1$; (v) $x+1, y+1, z$; (vi) $-x+1, -y+1, -z+1$; (vii) $-x+2, -y+2, -z+1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

RAH thank Universiti Sains Malaysia for the FRGS fund (203/PKIMIA/671115), short term grant (304/PKIMIA/639001) and RU grants (1001/PKIMIA/813023 and 1001/PKIMIA/811157). HKF and MH thank the Malaysian Government and Universiti Sains Malaysia for the Research University Grant No. 1001/PFIZIK/811160. MH also thanks Universiti Sains Malaysia for a post-doctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6386).

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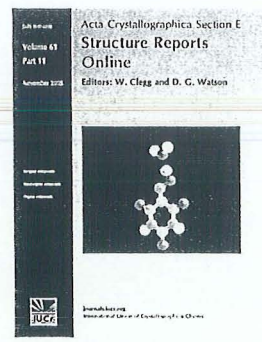
3,3′-[1,2-Phenylenebis(methylene)]bis(1-heptylbenzimidazolium) dibromide monohydrate

Rosenani A. Haque, Muhammad Adnan Iqbal, Madhukar Hemamalini and Hoong-Kun Fun

Acta Cryst. (2011). E**67**, o1814–o1815



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3,3′-[1,2-Phenylenebis(methylene)]bis(1-heptylbenzimidazolium) dibromide monohydrate

Rosenani A. Haque,[a] Muhammad Adnan Iqbal,[a] Madhukar Hemamalini[b] and Hoong-Kun Fun[b]*‡

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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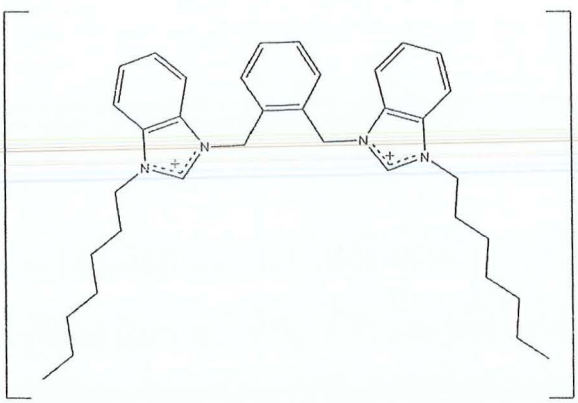
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.032; wR factor = 0.077; data-to-parameter ratio = 29.3.

In the title salt, $C_{36}H_{48}N_4^{2+}\cdot 2Br^-\cdot H_2O$, the central benzene ring makes dihedral angles of 84.77 (9) and 69.92 (7)° with the adjacent imidazole rings. In the crystal, one of the heptyl groups is disordered over two sets of sites with an occupancy ratio of 0.474 (5):0.526 (5). In the crystal, the cations, anions and water molecules are connected *via* intermolecular O—H···Br, C—H···Br and C—H···O hydrogen bonds, forming a three-dimensional network.

Related literature

For details and applications of *N*-heterocyclic carbenes (NHCs), see: Winkelmann & Navarro (2010); Kascatan-Nebioglu *et al.* (2007); Teyssot *et al.* (2009); Herrmann *et al.* (1995); Choi *et al.* (2001); Kumar & Kumar (2009). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



‡ Thomson Reuters ResearcherID: A-3561-2009.

Experimental

Crystal data

$C_{36}H_{48}N_4^{2+}\cdot 2Br^-\cdot H_2O$
M_r = 714.62
Triclinic, $P\overline{1}$
a = 8.8494 (1) Å
b = 14.7170 (3) Å
c = 16.0838 (2) Å
α = 115.705 (1)°
β = 105.380 (1)°
γ = 91.946 (1)°
V = 1792.83 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.29 mm^{-1}
T = 100 K
0.39 × 0.18 × 0.16 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.469, T_{max} = 0.715
50860 measured reflections
12945 independent reflections
10091 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.077
S = 1.02
12945 reflections
442 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.84 e Å^{-3}
$\Delta\rho_{min}$ = −0.75 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···Br1	0.84 (3)	2.50 (3)	3.3271 (17)	169 (2)
O1W—H2W1···Br2	0.79 (3)	2.54 (3)	3.3280 (14)	177 (3)
C1—H1A···Br1^{i}	0.95	2.80	3.6093 (15)	144
C3—H3A···Br2^{ii}	0.95	2.92	3.7866 (16)	153
C5—H5A···Br2^{iii}	0.95	2.89	3.8162 (17)	167
C8—H8A···Br2^{iv}	0.99	2.93	3.9117 (16)	172
C15—H15A···Br2^{iv}	0.99	2.72	3.6809 (19)	165
C15—H15B···Br1^{iv}	0.99	2.80	3.7842 (15)	170
C18—H18A···O1W^{v}	0.95	2.46	3.187 (2)	133
C20—H20A···Br2	0.95	2.76	3.6602 (16)	158
C22—H22A···Br1^{i}	0.95	2.70	3.5577 (15)	150
C23—H23A···Br2^{i}	0.99	2.89	3.7836 (14)	151
C23—H23B···Br2^{ii}	0.99	2.81	3.7285 (17)	154

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z+1$; (iii) $x, y, z+1$; (iv) $-x, -y+1, -z+1$; (v) $x-1, y, z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

RAH thanks Universiti Sains Malaysia (USM) for the FRGS fund (203/PKIMIA/671115), short term grant (304/PKIMIA639001), and RU grants (1001/PKIMIA/811157) and (1001/PKIMIA/823082). MAI is grateful to (IPS) USM for financial support [fellowship: USM.IPS/JWT/1/19 (JLD 6)]. HKF and MH thank the Malaysian Government and UUSM for the Research University Grant No. 1001/PFIZIK/811160. MH thanks USM for a post-doctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2732).

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2,4-Bis[(3-butylimidazol-3-ium-1-yl)-methyl]-1,3,5-trimethylbenzene bis(hexafluorophosphate)

Rosenani A. Haque,[a] Abbas Washeel Salman,[a] Madhukar Hemamalini[b] and Hoong-Kun Fun[b]*‡

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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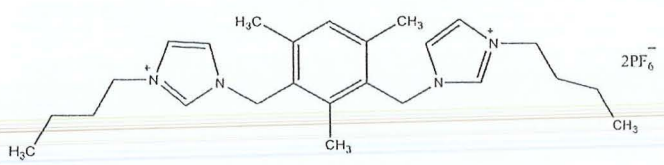
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.055; wR factor = 0.135; data-to-parameter ratio = 19.4.

In the title molecular salt, $C_{25}H_{38}N_4^{2+}\cdot 2PF_6^-$, one of the butyl groups and four F atoms in the basal plane of one of the PF_6^- octahedra are disordered over two sets of sites, with occupancy ratios of 0.704 (5):0.296 (5) and 0.71 (3):0.296 (5), respectively. The central benzene ring makes dihedral angles of 85.17 (12) and 81.97 (12)° with the terminal imidazole rings. In the crystal, cations and anions are linked together *via* intermolecular C—H···F hydrogen bonds forming a three-dimensional network.

Related literature

For applications of *N*-heterocyclic carbenes, see: Tryg *et al.* (2005); Herrmann (2002); Tominaga *et al.* (2004); Magill *et al.* (2001); Arduengo *et al.* (1991); Herrmann & Kocher (1997); Herrmann *et al.* (1998); McGuinness *et al.* (1999). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{25}H_{38}N_4^{2+}\cdot 2PF_6^-$
M_r = 684.53
Monoclinic, $P2_1/n$
a = 12.3851 (2) Å
b = 19.6516 (3) Å
c = 12.7586 (2) Å
β = 104.698 (1)°
V = 3003.66 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 100 K
0.39 × 0.17 × 0.12 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.911, T_{max} = 0.971
34854 measured reflections
8766 independent reflections
5113 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.135
S = 1.03
8766 reflections
453 parameters
177 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···F5^{i}	0.97	2.45	3.312 (3)	149
C5—H5A···F9A^{ii}	0.93	2.35	3.235 (9)	159
C6—H6A···F6^{ii}	0.93	2.51	3.248 (3)	136
C6—H6A···F12^{ii}	0.93	2.54	3.145 (3)	123
C7—H7A···F4^{iii}	0.93	2.32	3.140 (3)	146
C15—H15A···F10A^{iv}	0.97	2.54	3.103 (9)	117
C15—H15A···F11^{iv}	0.97	2.50	3.353 (3)	147
C19—H19B···F6^{iii}	0.97	2.54	3.327 (3)	138

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y, -z+1$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+1, -y, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

RAH thanks Universiti Sains Malaysia for the FRGS fund (203/PKIMIA/671115), short-term grant (304/PKIMIA/639001) and RU grants (1001/PKIMIA/813023 and 1001/PKIMIA/811157). AWS thanks Universiti Sains Malaysia for the RU grant (1001/PKIMIA/843090). HKF and MH thank the Malaysian Government and Universiti Sains Malaysia for the Research University grant No. 1001/PFIZIK/811160. MH also thanks Universiti Sains Malaysia for a post-doctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ5098).

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Bis(1-benzyl-3-methylimidazolium-κC^2)-mercury(II) bis(hexafluoridophosphate)

Rosenani A. Haque,[a] Abbas Washeel Salman,[a] Madhukar Hemamalini[b] and Hoong-Kun Fun[b]*‡

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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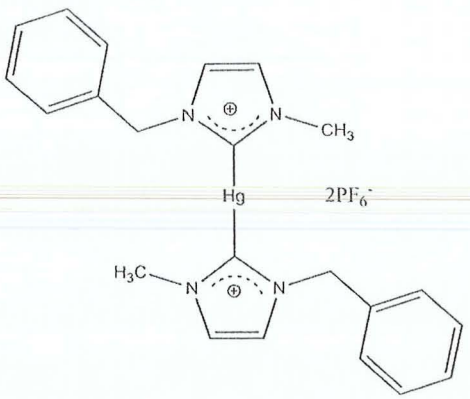
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.008 Å; R factor = 0.032; wR factor = 0.087; data-to-parameter ratio = 12.6.

The asymmetric unit of the title complex, $[Hg(C_{11}H_{12}N_2)_2](PF_6)_2$, consists of one bis(1-benzyl-3-methylimidazolium)-mercury(II) cation, one half of the cation and an additional Hg^{II} atom, which lies on an inversion centre, and three hexafluoridophosphate anions. The Hg^{II} atoms exist in a linear coordination geometry [C—Hg—C = 178.9 (2) and 180°] formed by two carbene C atoms from the imidazole rings. In the crystal, the cations and anions are connected *via* C—H···F hydrogen bonds, forming a three-dimensional network.

Related literature

For details of *N*-heterocyclic carbenes, see: Herrmann (2002); Arduengo *et al.* (1991); Herrmann *et al.* (1998); McGuinness *et al.* (1999); Wanzlick & Schönherr (1968). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$[Hg(C_{11}H_{12}N_2)_2](PF_6)_2$
M_r = 834.98
Monoclinic, $P2_1/c$
a = 15.1260 (17) Å
b = 10.3044 (11) Å
c = 26.398 (3) Å
β = 102.275 (2)°
V = 4020.5 (8) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 5.97 mm^{-1}
T = 100 K
0.34 × 0.32 × 0.05 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.233, T_{max} = 0.751
23876 measured reflections
7062 independent reflections
5985 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.087
S = 1.06
7062 reflections
559 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.71 e Å^{-3}
$\Delta\rho_{min}$ = −2.05 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10A···F15^{i}	0.93	2.32	3.240 (7)	171
C11—H11C···F6^{ii}	0.96	2.55	3.375 (7)	144
C13—H13A···F7^{i}	0.93	2.43	3.355 (7)	175
C18—H18A···F5^{ii}	0.97	2.50	3.282 (6)	138
C18—H18B···F13^{ii}	0.97	2.45	3.111 (6)	125
C21—H21A···F12^{iii}	0.93	2.51	3.351 (6)	150
C29—H29B···F17^{iv}	0.97	2.48	3.125 (7)	123
C31—H31A···F11^{iv}	0.93	2.43	3.271 (6)	150

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, y+1, z$; (iii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x, -y+1, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

RAH and AWS thank Universiti Sains Malaysia (USM) for the FRGS fund (203/PKIMIA/671115), short term grant (304/PKIMIA/639001) and RU grants (1001/PKIMIA/813023 and 1001/PKIMIA/811157). AWS thanks Universiti Sains Malaysia (USM) for the RU grant (1001/PKIMIA/843090). HKF and MH thank the Malaysian Government and Universiti Sains Malaysia for the Research University Grant No. 1001/PFIZIK/811160. MH also thanks Universiti Sains Malaysia for a post-doctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2765).

‡ Thomson Reuters ResearcherID: A-3561-2009.

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3,3′-Dibenzyl-1,1′-(2,4,6-trimethyl-*m*-phenylenedimethylene)diimidazol-3-ium dibromide

Rosenani A. Haque,[a] Abbas Washeel Salman,[a] Paremala Nadarajan,[a] Madhukar Hemamalini[b] and Hoong-Kun Fun[b]*‡

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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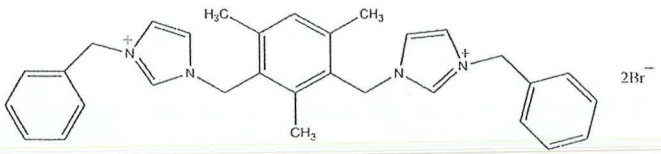
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.040; wR factor = 0.101; data-to-parameter ratio = 25.2.

In the title molecular salt, $C_{31}H_{34}N_4^{2+}\cdot 2Br^-$, the central benzene ring makes dihedral angles of 80.47 (12) and 82.78 (12)° with the adjacent imidazole rings. The dihedral angle between the two terminal phenyl rings is 79.16 (13)°. In the crystal, the cations and anions are linked *via* C—H···Br hydrogen bonds, forming supramolecular chains along the c axis.

Related literature

For applications of *N*-heterocyclic carbenes (NHCs), see: Winkelmann & Navarro (2010); Papini *et al.* (2008); Marion *et al.* (2007); Burstein & Glorius (2004); Sohn *et al.* (2004); Grasa *et al.* (2002); Singh & Nolan (2005). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{31}H_{34}N_4^{2+}\cdot 2Br^-$
M_r = 622.44
Monoclinic, $P2_1/c$
a = 8.9851 (2) Å
b = 12.8044 (2) Å
c = 25.6419 (5) Å
β = 102.611 (1)°
V = 2878.90 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.84 mm^{-1}
T = 100 K
0.49 × 0.43 × 0.21 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.337, T_{max} = 0.585
32884 measured reflections
8490 independent reflections
6550 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.101
S = 1.04
8490 reflections
337 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7A···Br2	0.97	2.90	3.754 (2)	147
C7—H7B···Br1^{i}	0.97	2.92	3.787 (2)	149
C8—H8A···Br2	0.93	2.81	3.496 (3)	132
C10—H10A···Br1^{i}	0.93	2.74	3.565 (2)	148
C18—H18B···Br2^{ii}	0.97	2.74	3.702 (2)	172
C19—H19A···Br1^{i}	0.93	2.74	3.553 (2)	147
C21—H21A···Br2^{iii}	0.93	2.83	3.603 (3)	141

Symmetry codes: (i) $x+1, y, z$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $x+1, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

RAH thanks Universiti Sains Malaysia (USM) for the FRGS fund (203/PKIMIA/671115), short term grant (304/PKIMIA/639001) and RU grants (1001/PKIMIA/813023 and 1001/PKIMIA/811157). AWS thanks USM for the RU grant (1001/PKIMIA/843090). HKF and MH thank the Malaysian Government and USM for the Research University grant No. 1001/PFIZIK/811160. MH also thanks Universiti Sains Malaysia for a post-doctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2422).

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Potassium bis[bis(1-benzyl-3-methylimidazolium)silver(I)] tris(hexafluoridophosphate)

Rosenani A. Haque,[a] Abbas Washeel Salman,[a] Choong Kah Whai,[a] Ching Kheng Quah[b]‡ and Hoong-Kun Fun[b]*§

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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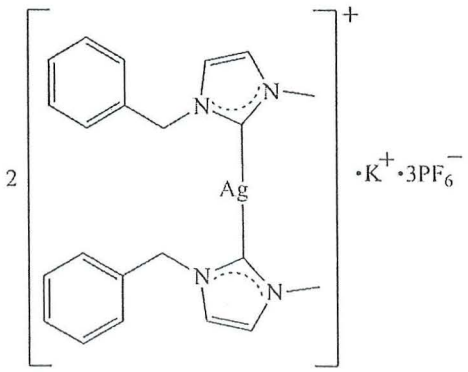
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.035; wR factor = 0.124; data-to-parameter ratio = 20.2.

In the title compound, $K[Ag(C_{11}H_{12}N_2)_2]_2(PF_6)_3$, the 12-coordinate potassium cation lies on a crystallographic twofold axis and one of the hexafluorophosphate anions is generated by $\bar{1}$ symmetry. In the complex cation, the Ag^I ion is coordinated by two C atoms; the two imidazolium rings are orientated at a dihedral angle of 8.14 (14)°. In the 1-benzyl-3-methylimidazolium units, the dihedral angles between imidazolium and phenyl rings are 80.47 (15) and 76.53 (14)°. The F atoms of the general-position hexafluorophosphate anion are disordered over two sets of sites in a 0.767 (17):0.233 (17) ratio. In the crystal, the hexafluorophosphate anions link the cations into three-dimensional networks *via* intermolecular C—H···F hydrogen bonds and are further consolidated by π–π stacking [centroid–centroid distances = 3.5518 (15) Å] interactions.

Related literature

For general background to and the biological activity of carbene derivatives, see: Lee *et al.* (2001); Bourissou *et al.* (2000); Herrmann & Köcher (1997); Hermann *et al.* (1996); Zhou *et al.* (2008); Wang & Lin (1998); Lin & Vasam (2007); Ray *et al.* (2007); Özdemir *et al.* (2010); Medvetz *et al.* (2008). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986). For related structures, see: Haque *et al.* (2010*a*,*b*). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$K[Ag(C_{11}H_{12}N_2)_2]_2(PF_6)_3$
M_r = 1378.65
Monoclinic, $C2/c$
a = 19.917 (2) Å
b = 23.047 (2) Å
c = 11.5787 (12) Å
β = 103.108 (3)°
V = 5176.4 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.04 mm^{-1}
T = 100 K
0.49 × 0.42 × 0.17 mm

Data collection

Bruker SMART APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.632, T_{max} = 0.847
66454 measured reflections
7528 independent reflections
7058 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.124
S = 1.11
7528 reflections
372 parameters
51 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.91 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ag1—C12	2.092 (2)	Ag1—C1	2.093 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14A···F1^{i}	0.93	2.45	3.285 (5)	149
C15—H15A···F6	0.97	2.51	3.204 (5)	129
C15—H15B···F4^{i}	0.97	2.51	3.415 (7)	156
C22—H22A···F6^{ii}	0.96	2.42	3.171 (5)	135

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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§ Thomson Reuters ResearcherID: A-3561-2009.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5767).

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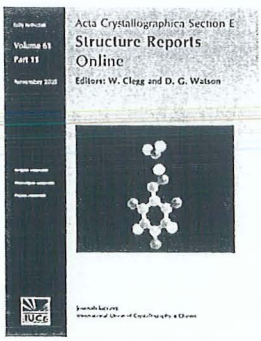
3,3′-Di-*n*-butyl-1,1′-(*p*-phenylenedimethylene)diimidazolium bis(hexafluorophosphate)

Rosenani A. Haque, Abbas Washeel, S. Fatimah Nasri, Chin Sing Yeap and Hoong-Kun Fun

Acta Cryst. (2010). E**66**, o824–o825



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3,3′-Di-*n*-butyl-1,1′-(*p*-phenylenedimethylene)diimidazolium bis(hexafluorophosphate)

Rosenani A. Haque,[a] Abbas Washeel,[a] S. Fatimah Nasri,[a] Chin Sing Yeap[b]‡ and Hoong-Kun Fun[b]*§

[a]School of Chemical Science, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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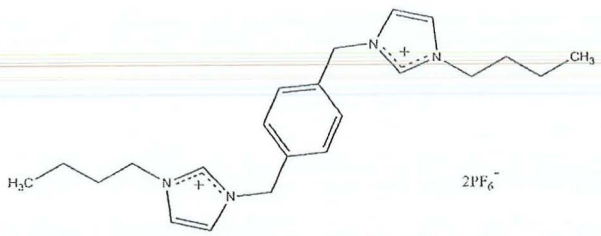
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.121; data-to-parameter ratio = 29.2.

The asymmetric unit of the title *N*-heterocyclic carbene compound, $C_{22}H_{32}N_4^{2+}\cdot 2PF_6^-$, consists of one half of the *N*-heterocyclic carbene dication and one hexafluorophosphate anion. The dication lies across a crystallographic inversion center. The imidazole ring is twisted away from the central benzene ring, making a dihedral angle of 76.23 (6)°. The hexafluorophosphate anions link the cations into a three-dimensional network *via* intermolecular C—H···F hydrogen bonds. A weak C—H···π interaction further stabilizes the crystal structure.

Related literature

For background to *N*-heterocyclic carbenes, see: Arduengo *et al.* (1991); Papini *et al.* (2008). For applications of *N*-heterocyclic carbene derivatives, see: Meyer *et al.* (2009); Barnard *et al.* (2004); Lin & Vasam (2007). For a related structure, see: Washeel *et al.* (2010). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{22}H_{32}N_4^{2+}\cdot 2PF_6^-$
M_r = 642.46
Monoclinic, $P2_1/c$
a = 8.9802 (5) Å
b = 17.8421 (10) Å
c = 9.3637 (5) Å
β = 113.233 (1)°
V = 1378.64 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 100 K
0.37 × 0.25 × 0.20 mm

Data collection

Bruker APEX Duo CCD area detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.910, T_{max} = 0.950
21938 measured reflections
5550 independent reflections
4750 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.121
S = 1.10
5550 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

Table 1. Hydrogen bond geometry (Å, °). *Cg*1 is the centroid of the C1–C3,C1*A*–C3*A* benzene ring.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1*A*···F3^{i}	1.004 (17)	2.532 (18)	3.3945 (14)	143.8 (15)
C4—H4*A*···F4^{i}	0.97	2.52	3.3516 (14)	144
C4—H4*B*···F2^{ii}	0.97	2.45	3.3497 (14)	153
C7—H7*A*···F1^{iii}	0.93	2.36	2.8798 (13)	115
C8—H8*B*···F6^{iv}	0.97	2.49	3.3537 (13)	148
C8—H8*A*···*Cg*1^{v}	0.97	2.84	3.7376 (12)	154
C8—H8*A*···*Cg*1^{vi}	0.97	2.84	3.7376 (12)	154

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, y-1, z$; (iii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (v) $x-1, y, z$; (vi) $-x, -y, -z+1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2739).

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Bis{1,4-bis[(3-butylimidazolium-1-yl)-methyl]benzene}silver(I) bis(hexafluoridophosphate)

Rosenani A. Haque,[a] Abbas Washeel,[a] Siang Guan Teoh,[a] Madhukar Hemamalini[b] and Hoong-Kun Fun[b]*‡

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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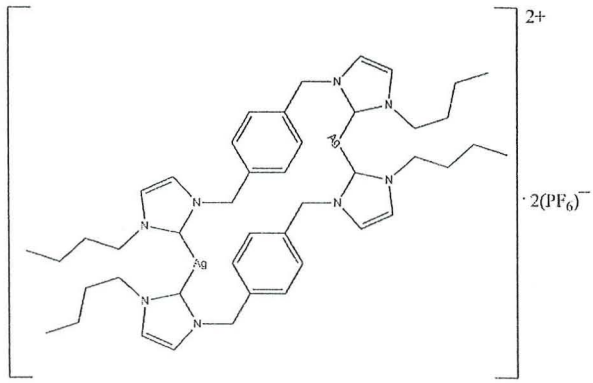
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.007 Å; R factor = 0.051; wR factor = 0.161; data-to-parameter ratio = 23.1.

The asymmetric unit of the title complex, $[Ag_2(C_{22}H_{30}N_4)_2](PF_6)_2$, consists of one Ag^I ion, one 1,4-bis[(3-butylimidazolium-1-yl)methyl]benzene ligand and one discrete hexafluoridophosphate anion. The formula unit is generated by an inversion center. The unique Ag^I ion is coordinated by two C atoms of two heterocyclic carbene ligands in an essentially linear geometry. In the crystal structure, cations and anions are linked through weak C—H···F hydrogen bonds, forming a three-dimensional network.

Related literature

For applications of *N*-heterocyclic carbenes, see: Tryg *et al.* (2005); Herrmann (2002); Herrmann *et al.* (1998); McGuinness *et al.* (1999); Tominaga *et al.* (2004); Magill *et al.* (2001); Yongbo *et al.* (2008); Garrison & Youngs (2005); Kascatan-Nebioglu *et al.* (2007); Özdemir *et al.* (2010); Medvetz *et al.* (2008); Catalano & Malwitz (2003). For a related structure, see: Chen & Liu (2003). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$[Ag_2(C_{22}H_{30}N_4)_2](PF_6)_2$
M_r = 1206.68
Triclinic, $P\overline{1}$
a = 11.3636 (15) Å
b = 11.4119 (15) Å
c = 11.9918 (15) Å
α = 63.528 (2)°
β = 89.335 (2)°
γ = 65.811 (2)°
V = 1241.7 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.94 mm^{-1}
T = 100 K
0.24 × 0.14 × 0.08 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.806, T_{max} = 0.930
25433 measured reflections
7142 independent reflections
6512 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.161
S = 1.16
7142 reflections
309 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 3.16 e Å^{-3}
$\Delta\rho_{min}$ = −1.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···F3^{i}	0.93	2.42	3.251 (6)	149
C5—H5A···F1^{ii}	0.93	2.52	3.392 (6)	157
C7—H7B···F5^{ii}	0.97	2.44	3.367 (6)	160
C11—H11A···F6^{iii}	0.97	2.44	3.364 (7)	159
C11—H11B···F2^{iv}	0.97	2.38	3.129 (7)	134

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x-1, y, z$; (iv) $-x+1, -y, -z+1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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3,5-Bis(3-butylimidazolium-1-ylmethyl)toluene bis(hexafluorophosphate)

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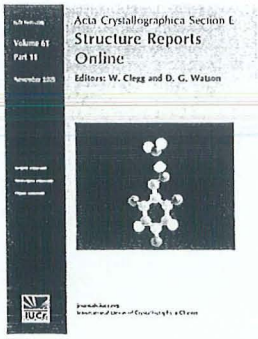

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3,5-Bis(3-butylimidazolium-1-ylmethyl)-toluene bis(hexafluorophosphate)

Rosenani A. Haque,[a] Abbas Washeel,[a] Siang Guan Teoh,[a] Ching Kheng Quah[b]‡ and Hoong-Kun Fun[b]*§

[a]School of Chemical Sciences, University Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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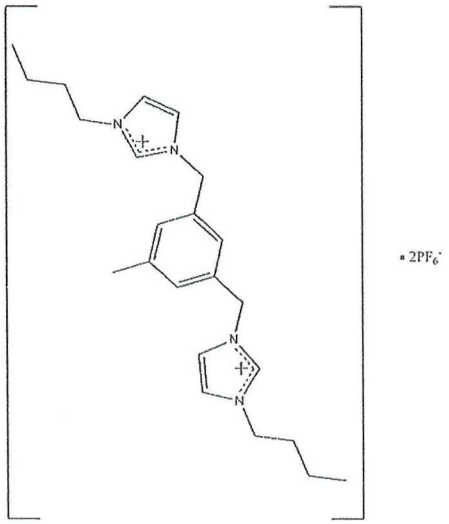
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.046; wR factor = 0.122; data-to-parameter ratio = 23.2.

In the title compound [systematic name: 3,3′-Dibutyl-1,1′-(5-methyl-*m*-phenylenedimethylene)diimidazol-1-ium bis(hexafluoridophosphate)], $C_{23}H_{34}N_4^{2+}\cdot 2PF_6^-$, the imidazole rings are inclined at angles of 68.06 (7) and 75.05 (8)° with respect to the central benzene ring. In the crystal, molecules are linked into one-dimensional columns along [010] *via* weak intermolecular C—H···F hydrogen bonds. The crystal structure is further consolidated by weak C—H···π(arene) interactions. One of the *n*-butyl groups is disordered over two sites with refined occupancies of 0.694 (5) and 0.306 (5). In addition, four of the F atoms of one of the PF_6^- cations are disordered over two sites with occupancies of 0.64 (3) and 0.36 (3).

Related literature

For general background to imidazoline-2-ylidenes, see: Arduengo *et al.* (1991). For the organometallic and coordination chemistry of *N*-heterocyclic carbene ligands, see: Chen *et al.* (2002); Zhou *et al.* (2008); Hahn & Jahnke (2008); Danopoulos *et al.* (2007); Bourissou *et al.* (2000); McGuinness & Cavell (2000); Garrison *et al.* (2001). For catalytic studies related to organic synthesis, see: Cavell & McGuinness (2004); Liu *et al.* (2007). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986). For standard bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{23}H_{34}N_4^{2+}\cdot 2PF_6^-$
M_r = 656.48
Monoclinic, $P2_1/c$
a = 9.6207 (1) Å
b = 11.1801 (1) Å
c = 27.9277 (3) Å
β = 102.416 (1)°
V = 2933.66 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 100 K
0.49 × 0.20 × 0.14 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.890, T_{max} = 0.967
45569 measured reflections
10399 independent reflections
7294 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.122
S = 1.03
10399 reflections
448 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C1–C6 phenyl ring.

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8*A*···F4	0.93	2.42	3.0154 (16)	121
C8—H8*A*···F5	0.93	2.39	3.2700 (16)	157
C16—H16*A*···F3	0.93	2.31	3.1941 (16)	160
C16—H16*A*···F4	0.93	2.45	3.1677 (16)	134
C21*A*—H21*B*···F4	0.97	2.49	3.196 (2)	130
C3—H3*A*···F12^{i}	0.93	2.44	3.3147 (16)	157
C5—H5*A*···F9*A*^{ii}	0.93	2.55	3.420 (8)	156
C7—H7*A*···F10*A*^{ii}	0.97	2.51	3.427 (6)	158
C9—H9*A*···F12^{iii}	0.93	2.48	3.2805 (17)	144
C12—H12*A*···F3^{iv}	0.97	2.53	3.3358 (18)	140
C18—H18*A*···F8*A*^{v}	0.93	2.38	3.148 (11)	140
C22*A*—H22*C*···*Cg*1^{vi}	0.96	2.76	3.535 (3)	138
C23—H23*B*···*Cg*1^{vii}	0.96	2.59	3.487 (2)	155
C22*B*—H22*E*···*Cg*1^{vi}	0.96	2.86	3.637 (8)	139

Symmetry codes: (i) $x-1, y+1, z$; (ii) $x-1, y, z$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (v) $-x+1, -y+2, -z+2$; (vi) $x+1, y, z$; (vii) $-x, -y+2, -z+2$.

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§ Thomson Reuters ResearcherID: A-3561-2009.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5143).

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