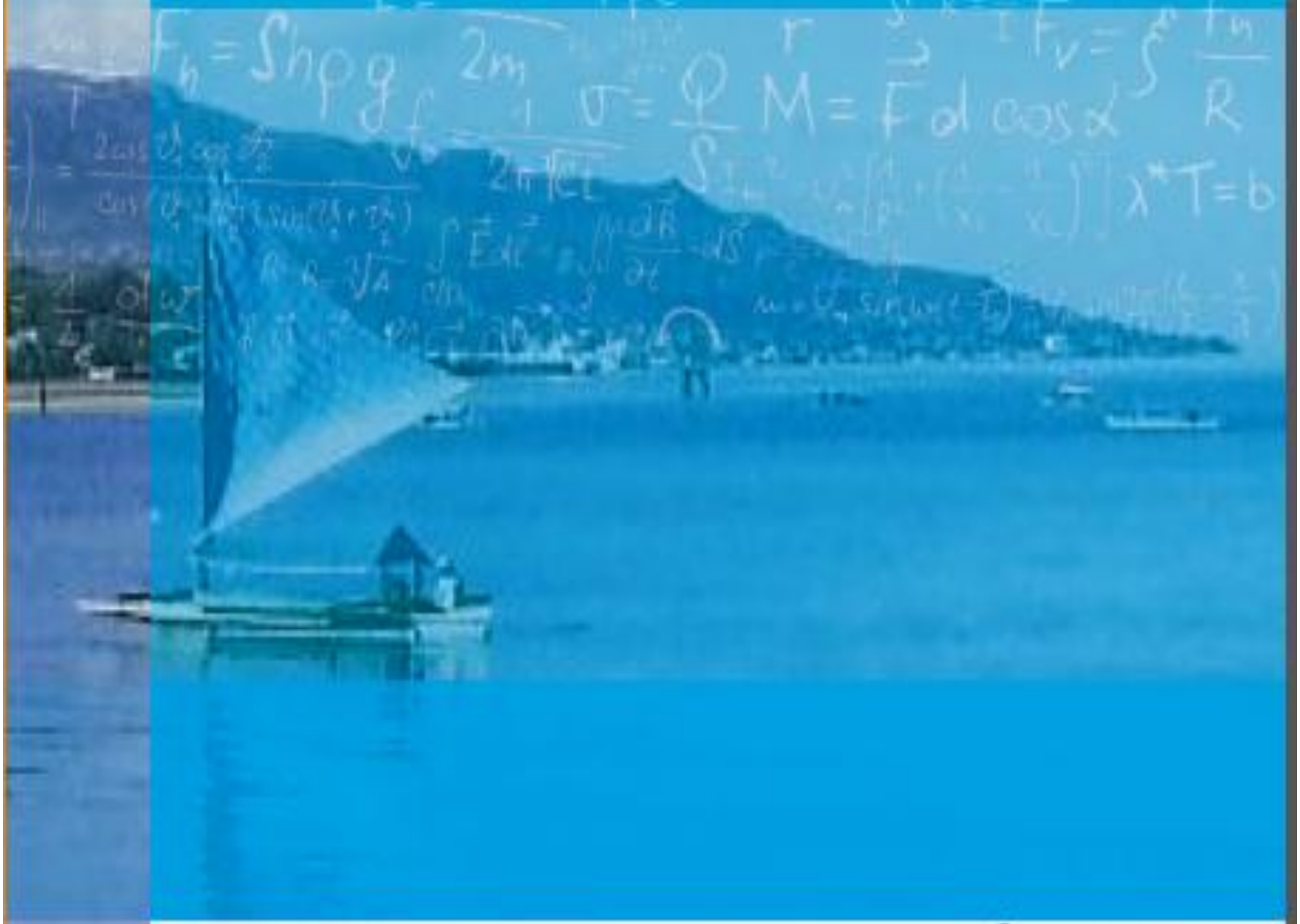
Basic Science
for Sustainable Marine Development

PROCEEDING
INTERNATIONAL SEMINAR 2015

Ambon, 3-4 June 2015



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Welcoming Address by The Organizing Committee

The honorable, the rector of Pattimura University
The honorable, the vice rector of academic affair, Pattimura University
The honorable, the vice rector of administration and financial affair, Pattimura University
The honorable, the vice rector of planning, cooperation and information affair, Pattimura University
The honorable, all the deans in Pattimura University
The honorable, the key note speakers and other guests.

We have to thank The Almighty God for the blessings that allow this International seminar can be held today. This is the first seminar about MIPA Science in which the Faculty of MIPA Pattimura University becomes the host. The seminar under the title Basic Science for Sustainable Marine Development will be carried out on 3 June 2015 at Rectorate Building, the second floor. There are 250 participants from lecturers, research institute, students, and also there are 34 papers will be presented.

This International seminar is supported by the amazing people who always give financial as well as moral supports. My special thanks refer to the rector of Pattimura University, Prof. Dr. Thomas Pentury, M.Si, and the Dean of MIPA Faculty, Prof. Dr. Pieter Kakissina, M. Si. I also would like to express my deepest gratitude to Dr. Kotaro Ichikawa, the director of CSEAS Kyoto University, Prof. Bohari M. Yamin, University of Kebangsaan Malaysia, Prof. Dr. Budi Nurani Ruchjana (Prisident of Indonesian Mathematical Society/Indo-MS), Dr. Ir. A. Syailatua, M.Sc (Director of LIPI Ambon), and Hendry Ishak Elim, PhD as the key note speakers. We expect that this international seminar can give valuable information and contribution especially in developing basic science for sustainable marine development in the future.

Last but not least, we realize that as human we have weaknesses in holding this seminar, but personally I believe that there are pearls behind this seminar. Thank you very much.

Chairman
Dr. Netty Siahaya, M.Si.

Opening Remarks
By Dean of Mathematic and Natural Science Faculty

I express my deepest gratitude to The Almighty God for every single blessing He provides us especially in the process of holding the seminar until publishing the proceeding of International Seminar in celebrating the 17th anniversary of MIPA Faculty, Pattimura University. The theme of the anniversary is under the title Basic Science for Sustainable Marine Development. The reason of choosing this theme is that Maluku is one of five areas in Techno Park Marine in Indonesia. Furthermore, it is expected that this development can be means where the process of innovation, it is the conversion of science and technology into economic value can be worthwhile for public welfare especially coastal communities.

Having the second big variety of biological resources in the world, Indonesia is rich of its marine flora and fauna. These potential resources can be treated as high value products that demand by international market. Basic science of MIPA plays important role in developing the management of sustainable marine biological resources.

The scientific articles in this proceeding are the results of research and they are analyzed scientifically. It is expected that this proceeding can be valuable information in terms of developing science and technology for public welfare, especially people in Maluku.

My special thanks refer to all researchers and reviewers for your brilliant ideas in completing and publishing this proceeding. I also would like to express my gratefulness to the dies committee-anniversary of MIPA Faculty for your creativity and hard working in finishing this proceeding, God Bless you all.

Dean of Mathematic and Natural Science Faculty

Prof. Dr. Pieter Kakisina, M.Si.

Contents

Papers

Complexation and Structural Studies of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazayclotetradeca-7,14-dienium Bromide Complexes with Copper Salts

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ABSTRACT

Both Copper chloride and sulfate reacted with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetracyclotetradeca-7,14-dienium bromide ($(Me_6N_4H_4)Br_2$) to give the same complexes of $[(Me_6N_4H_2)Cu]Br_2.2H_2O$. The copper atom is coordinated to the tetraaza nitrogen atoms in a square planar environment. The two amino nitrogen atoms were deprotonated. The two bromine anions remained as counter anion for the complex. Copper chloride gave complex of $[(Me_6N_4H_2)BrCu]Br.2H_2O$. The coordination sphere consists of the tetraaza nitrogen atoms and one bromo in a square pyramidal geometry. Contrary to $CuCl_2$ copper bromide reacted to give slightly different of $[(Me_6N_4H_2)Cu(II)]$ $[(Me_6N_4H_2)(H_2O)_2Cu(II)][Br_3Cu(I)]_2$. One of the tetraaza-Cu cation has two water molecules coordinated to the copper in a distorted octahedral geometry. The counter anion of tribromocupperate indicates that the reaction also involve a reduction of $CuBr_2$. On the other hand ammonium terrachloroferrate(II) gave a complex of $[(Me_6N_4H_2)Cu(II)][Cl_4Cu(II)]$ indicating the reaction involved complexation and deprotonation but tetrachlorocopperate is the counter anion instead of bromo.

INTRODUCTION

Among the tetraaza macrocyclic compounds 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($Me_6N_4H_2$) is quite unique as it was discovered by from the recrystalization of bis(ethylenediamine)Ni in acetone (Curtis and House, 1961). Since then several metal complexes were synthesized by the same method. The Cambridge data base search has indicated 31 structures of copper-($Me_6N_4H_2$) complexes and most of them are salt types with counter anions from simple halogen (Podberezskaya et al., 1986; Yamin et al., 2012), to complicated and bulky groups such as (μ_6-oxo)- dodecakis(μ_2-oxo)hexaoxo-hexa-tungsten (Lu et al.,1999). Most of the complexes reported were prepared by templation method. Therefore mechanistic and kinetic studies of the complexation are not simple to be carried out. The dissociation of the complexes in acid or basic solution have been investigated quite extensively (Hyldtoft et al., 1989; Kasprzyk et al., 1982; Monsted et al., 1993). However, the availability of the macrocyclic ligand in our laboratory enable us to study the complexation by one pot synthesis. In this paper the complexation of $(Me_6N_4H_4)Br_2$ salt with copper acetate, copper chloride, copper sulfate, copper bromide and ammonium tetrachlorocuprate are presented.

Experimental

Preparation of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclotetradeca-7,14-diene Salts

The macrocyclic ligand $C_{16}H_{38}N_4O_2Br_2$ was synthesised by mixing ammonium bromide (0.9794g, 0.01 mol) and ethylenediamine (0.601g, 0.01 mol) in acetone at 80°C under constant stirring for 2 h. The solution was then filtered and left overnight at room temperature. After 3 days crystalline solid was obtained.

Complexation of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclotetradeca-7,14-diene with copper salts

The complex was synthesised by stirring a 1:1 mixture of the ligand and copper salts in methanol or water for 2 hours. The solution was then left to evaporate at room temperature. The copper salts used in the study are copper acetate, copper chloride , copper sulphate, copper bromide and ammonium tetrachlorocuprate.

RESULTS AND DISCUSSION

Macrocyclic Ligand

The ligand was obtained as white crystalline solid, yield 65% and melting point of 113.4-125.3°C. The microelemental analysis data is in agreement with the formula of $C_{16}H_{40}N_4O_3Br_2$. (expt C=38.9 H=7.5 N=11.6; cal C=40.2 H=7.9 N=11.1). The salt is soluble in water, methanol, ethanol, chloroform and dimethyl sulfoxide. The infrared spectrum showed the presence of the azomethine C=N and C-N stretching bands at 1667 and 1228cm^{-1}, respectively. The bands at 3468 cm^{-1} (sharp) and 3012 cm^{-1} (broad) are due to the primary amino N-H_2 and water OH stretchings, respectively. The high primary amino N-H stretching than the normal value of 3260 cm^{-1} indicates the presence of protonated NH_2 group. ^1H NMR spectrum showed the presence of methyl proton at 2.06 ppm and protonated amine at 4.89ppm. The methylene protons are at 1.49ppm. The ^{13}C NMR confirmed the formation of azomethine and C-N bond with the chemical shifts of 175.87ppm and 58.35ppm respectively. Ultra-violet visible spectrum shows a maximum absorption peak around 238nm (ε=22500) corresponding to $\pi \rightarrow \pi^*$ electronic transitions of azomethine chromophore. The chemical structure was supported by chemical crystallographic study (Ismail, 2012) showing the two protonated amine at diagonal position of the tetraaza group (Fig.1).

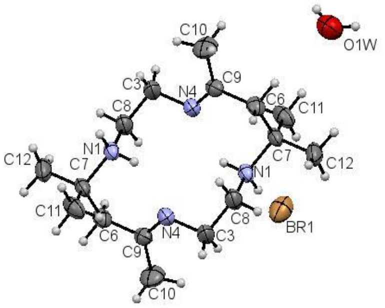

Fig 1. Molecular structure of $C_{16}H_{38}N_4O_2Br_2$ ligand drawn at 50% probability ellipsoids

Synthesis of Copper Complexes

The complexes of the ligand ($Me_6N_4H_4)Br_2$ with copper acetate, copper chloride, copper sulfate, copper bromide and ammonium tetrachlorocuprate in methanol at reflux temperature gave the corresponding complexes in moderate yield (65-88%) . The complexes are coloured, stable in air and partially soluble in common solvents. The micro elemental analysis data of all the complexes were in agreement with its theoretical value based on X-ray studies.

Table 1. Elemental analysis and melting point data of copper complexes with ligand L= $(Me_6N_4H_4)Br_2$

Complexes	**Colour**	**Yield (%)**	**Experimental (theoritical)**			**Meting point (°C)**
			C	**H**	**N**	
$Cu(OAc)_2$-L(I)	Purple	65	34.9(35.3)	7.1(7.4)	10.1(10.3)	201.2-202.0
$CuCl_2$-L(II)	Purple	88	28.2(28.7)	5.1(5.7)	7.6(8.4)	208.1-208.6
$CuSO_4$-L(III)	Purple	70	28.2(28.9)	7.0(7.2)	9.5(8.5)	199.6-200.4
$CuBr_2$-L(IV)	Purple	73	23.2(28.7)	5.1(5.7)	7.8(8.0)	225.4-225.8
NH_4Cl_4-L(V)	Purple	78	33.9(34.7)	6.3(6.5)	9.8(10.1)	203.3-204.1

L- $(Me_6N_4H_2)$

The N-H (amine), C-H (methyl), C-N (imine), and C=N (azomethine) stretching frequencies. In IR spectra showed significant shifts compare to the free ligand indicating the coordination between copper and the nitrogen atoms. The important vibrations are shown in Table 2.

Table 2. FTIR stretching frequencies for the complexes

Complex	**Stretching frequencies (cm^{-1})**			
	N-H (amine)	**C-H (methyl)**	**CN (imin)**	**C=N (azomethine)**
(I)	3395.1	2975.2	1169	1162.7
(II)	3158.4	2973.9	1169	1662.9
(III)	3148.8	2969.8	1164	1670.8
(IV)	3158.7	2973.6	1169	1662.6
(V)	3424.4	2968.7	1171	1632.7

The UV-VIS analysis showed the presence of the azomethine chromophore and *d-d* transition of copper. The d-d transition of copper acetate for example is shown by the maximum absorption wavelength of about 772 nm. Upon complexation with tetraaza the λ_{max} is shifted to higher energy (about 519 nm) indicating a strong splitting or high crystal field stabilization energy (Table 3). The magnetic susceptibility values indicate the complexes are paramagnetic and therefore no NMR signals was observed.

Table 3. UV-VIS and μ_{eff} data for the synthesised complexes

Complexes	**μ_{eff}**	**Transition $\pi \rightarrow \pi^*$**	**Transition d-d**
(I))	2.45	246.0	519.0
(II))	2.31	237.5	520.5

(III)	2.40	242.5	516.5
(IV)	2.35	350.5	-
(V)	2.01	234.0	519.0

The x-ray structure of the complexes are very useful to support and provide more structural information of the complex. Some of the complexes are not analogous and not easy to predict. Fortunately all the five complexes were successfully obtained in crystalline form and their structures are discussed below.

The complex (I) possess molecular structure where copper coordinated to the nitrogen of the tetraaza and deprotonation of the two imino nitrogen (Ismail, 2012). One bromo anion is coordinated to the central copper atom and made it a square pyramidal geometry. Another bromine anion remains as counter anion to the tetraza complex (Fig.2). The stoichiometry of the reaction can be written as $(Me_6N_4H_4)Br_2 + Cu(OAc)_2 \rightarrow [(Me_6N_4H_2)BrCu]Br + 2CH_3COOH$. Similar complex was reported by

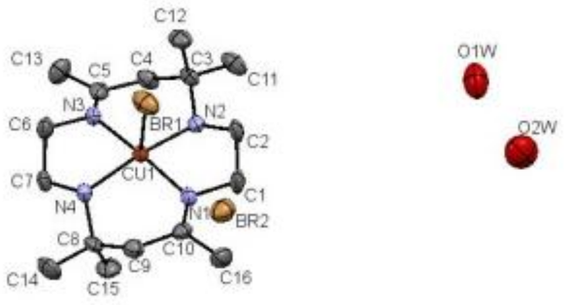

Figure 2. Molecular structure of complex (I). $[(Me_6N_4H_2)BrCu]Br.2H_2O$ drawn at 50% probability ellipsoids. Hydrogen are omitted for clarity.

Figure 3. shows the structure of the complex (II) prepared from the reaction of ligand with $CuCl_2$.The complexation reaction also involved the coordination of copper to four tetraaza nitrogen atoms and deprotonation of the two amino nitrogen atoms (Huddin et al., 2014). The bromine anion is not coordinated to the central copper. The stoichiometric equation can be written as;

$(Me_6N_4H_4)Br_2 + CuCl_2 \rightarrow [(Me_6N_4H_2)Cu]Br_2 + 2HCl$.

The complex took away two water molecules during crystallization.

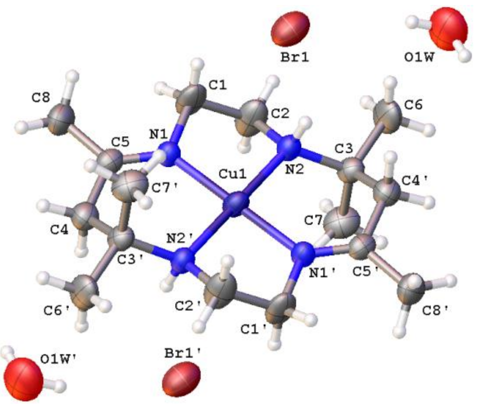

Figure 3. Molecular structure of complex (II), $[(Me_6N_4H_2)Cu]Br_2.2H_2O$ drawn at 50% probability ellipsoids

The complex (III) obtained from the reaction with copper sulfate showed similar chemical analysis and spectroscopic data with complex (II). The X-ray study also revealed similar unit cell as complex (II) confirming of the same structure. The reaction of the ligand with $CuBr_2$ (Huddin et al., 2014) was thought to be different than $CuCl_2$ due to the possibility for the speciation in solution. Bromide is known to form tribromocopperate anion as counter anion to two tetraaza-cu complex cations (Fig.4). Two possible structures can be suggested. If the Cu-tetraaza complexes are dication then the two anions should be $[Br_3Cu(I)]^{2-}$ to balance the total charge of the cation. Alternatively, if the cation possess Cu(I) then the two anions are$[Br_3Cu(II)]^{-}$. Both structures consists of mixed oxidation states. Further studies such as magnetic and XPS spectroscopy can assist in the identification.

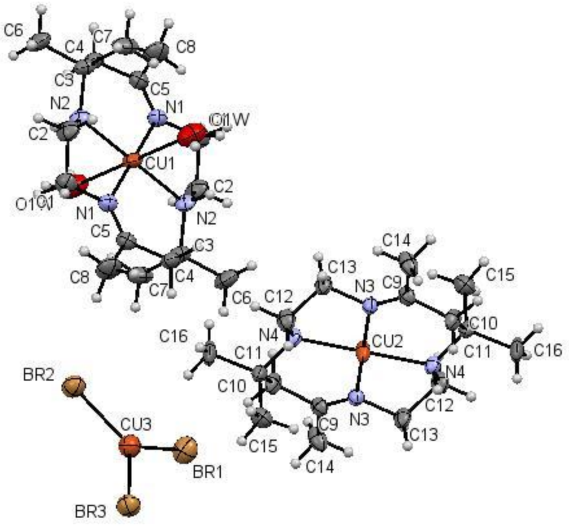

Figure 4. Molecular structure of complex (IV), $[(Me_6N_4H_2)Cu(II)]$ $[(Me_6N_4H_2)(H_2O)_2Cu(II)][Br_3Cu(I)]_2$ drawn at 50%probability ellipsoids

The reaction with ammonium tetrachlorocuprate (Ismail, 2012) also showed no involvement of bromo ion in the complex formation. Instead tetrachlorocuprate became the counter anion (Fig.5). The copper atom coordinated to the tetraaza macrocycle in a square planar environment. In this complexation the reaction involved complexation and deprotonation12. The reaction can be written as $(Me_6N_4H_4)Br_2$ + $2(NH_4)_2[CuCl_4]$ →[$(Me_6N_4H_2Cu(II)][CuCl_4]$ + $2(NH_4)Br$ + 2HCl + Cl_2.

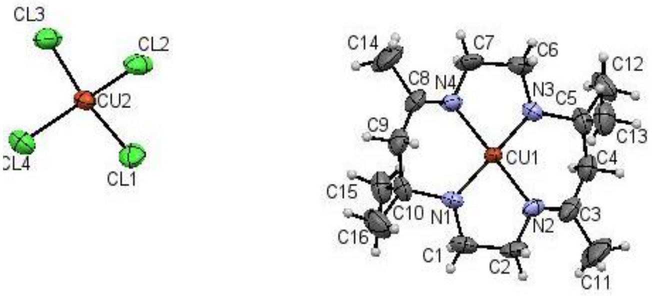

Figure 5. Molecular structure of complex (V), $[(Me_6N_4H_2)Cu(II)][Cl_4Cu(II)]$, drawn at 50% probability ellipsoids

CONCLUSIONS

Contrary to the templation reaction, protonated Curtis salt formed complexes with copper salts involved protonation and depend on the type of salts. Complex (I), (II) and (III) retained the bromo anion as counter anion in the complex. However, in complex (I) one of the bromo anion coordinated to the metal. In complex (II) and (III) only complexation and deprotonation occurred and the two bromo anions remained in the complex. $CuBr_2$ reacted with the ligand to give complex(IV) consisting of two dications and aa new copper species of $[CuBr_3]^{2-}$. On the other hand, ammonium tetrachlorocopperate gave one Cu-tetraaza complex and balanced by the tetrachlorocopperate.

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