

Complexation of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium bromide with copper salts

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Complexation of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium Bromide with Copper Salts

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Abstract. Copper complexes have been synthesized with 14-membered macrocyclic 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium bromide ($\text{Me}_6\text{N}_4\text{H}_4$) Br_2 as ligand having six methyl groups and two double bonds located in diagonal position. These complexes were characterized by microelemental analysis, Fourier Transform Infrared (FTIR) and Ultraviolet-Visible (UV-VIS) spectroscopies. The chemical analysis and spectroscopic data is supported by chemical crystallographic study showed that one of the synthesized copper complex with CuCl_2 consists of $[\text{Cu}(\text{Me}_6\text{N}_4\text{H}_2)]$ dication, two bromide counter anions and 2 water molecules of crystallisation. Thermogravimetry Analysis (TGA) showed that the complex is stable up to about 200°C before gradually decomposed up to 400°C.

Keywords: Tetraaza, Macrocyclic, Copper Complexes
PACS: 80

INTRODUCTION

The chemistry of transition metal complexes of tetraaza macrocyclic ligands is an area that has attracted considerable interest. These compounds exhibit a range of characteristic properties that useful as antibacterial, antifungal, or for other biological applications such as biological models for researching insufficiently examined metal proteins. In addition, these types of complexes have been used as catalysts in oxidation and epoxidation processes. Other than that, tetraaza macrocyclic complexes can be used in reduction of CO_2 , as good corrosion inhibitors, for the capture and concentration of CO_2 by electrochemically modulated complexation. Transition metal complex like copper have been reported as active catalyst for alkene oxidation since it is cheap and less toxic [1].

In 1961, macrocyclic tetraaza with 14-membered ring, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-diene ($\text{Me}_6\text{N}_4\text{H}_2$) was unexpectedly obtained by Curtis and his co-worker from an attempt to crystallized tris(ethylenediamine)nickel(II) in acetone [2]. The discovery allowed the synthesis of several complexes of similar ligand with various metals by the templation method. On the contrary, our group have obtained the same macrocyclic but with two protonated amine ($\text{Me}_6\text{N}_4\text{H}_4$) X_2 also by accident without involving metal salts [3]. Therefore, this allow the extensive research in order to study the reaction of the protonated macrocyclic with metal salts in the periodic table.

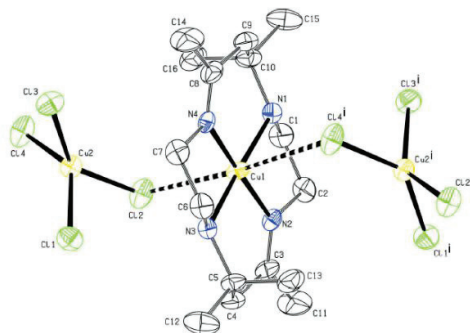


FIGURE 1. Structure of $[\text{C}_{16}\text{H}_{32}\text{N}_4.\text{Cu}(\text{CuCl}_4)]_n$ at the probability of 50% ellipsoid.

Previously, several complexes involving the neutral $[\text{Me}_6\text{N}_4\text{H}_2]$ with copper such as $[\text{CuBr}(\text{Me}_6\text{N}_4\text{H}_2)]\text{Br} \cdot 2\text{H}_2\text{O}$ [4], $[\text{Cu}(\text{Me}_6\text{N}_4\text{H}_2)]\text{ClO}_4$ [5] and $[\text{CuI}(\text{Me}_6\text{N}_4\text{H}_2)]\text{H}_2\text{O}$ [6] have been reported. However, our first copper complex

was obtained from the reaction of protonated [(Me₆N₄H₄)Cl₂] with [CuCl₄]²⁻ resulting in the formation of polymeric structure of catena-poly[[5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,7-diene)copper(II)]-μ-chlorido [dichlorocuprate(II)-μ-chlorido] [7]. FIGURE 1 shows the ORTEP drawing of the complex. The central copper atom, CuI was weakly linked with two Cl atoms from the [CuCl₄]²⁻ anion.

In this paper, complexation of various copper salts, CuCl₂, CuBr₂ and CuSO₄ with protonated tetraaza ligand, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium bromide and its thermal stability are reported. Both ligand and complexes have been characterized by using various physico-chemical techniques such as the microelemental analysis (carbon, hydrogen and nitrogen), Fourier Transform Infrared (FTIR), Ultraviolet-Visible (UV-VIS), Thermogravimetry Analysis (TGA), and X-ray Crystallography.

EXPERIMENTAL

The complexes were synthesized by refluxing 1:1 mixture of metal salts and macrocyclic ligand in methanol for 3 hours at 100°C. The metal salts used in this experiment were CuCl₂ (**MC1**), CuBr₂ (**MC2**) and CuSO₄ (**MC3**). Then, the mixture was filtered and left to evaporate at room temperature. Some crystals were obtained after four days.

RESULTS AND DISCUSSIONS

The reaction of the tetraaza ligand with copper salts gave purple solid crystal. The yield, melting point, formula weight, colour and microelemental analysis data are shown in TABLE (1). The microelemental analysis data showed an agreement with the formula of C₁₆H₃₆N₄O₂Br₂Cu.

TABLE (1). Microelemental analysis data, yield, melting point, formula weight and colour of complexes.

Complex	Colour	Yield (%)	Expt. value (Calc.value) %			Melting point (°C)
			C	H	N	
MC1	Purple	65	31.0 (31.0)	5.0 (6.8)	11.4 (9.0)	208.0- 208.3
MC2	Purple	88	23.2 (28.7)	5.1 (5.7)	7.8 (8.4)	225.4- 225.8
MC3	Purple	70	34.2 (28.9)	7.0 (7.2)	9.5 (8.5)	199.6- 200.4

For the infrared analysis, the prominent IR spectral bands of the complexes are presented in TABLE (2). A band observed in the region of 1164-1171 cm⁻¹ was the characteristic of ν(C-N). The complexes exhibit a C=N absorption in the range of 1632-1670 cm⁻¹ indicated the presence of azomethine group in the compound. Absorption band in the region of 2968-2973 cm⁻¹ corresponds to the methyl groups (-CH). In the complexes, N-H band were observed at 3395-3431 cm⁻¹ indicates the coordination to the metal through the four nitrogen atoms in the macrocyclic ring.

TABLE (2). IR spectral data of the complexes.

Complex	Vibration (cm ⁻¹)			
	N-H(amine)	C-H (methyl)	C-N (imine)	C=N (azomethine)
MC1	3395.1	2973.9	1169.7	1662.9
MC2	3431.1	2969.8	1164.4	1670.8
MC3	3424.4	2968.7	1171.4	1632.7

The electronic spectra (TABLE (3)) of the copper complexes showed two bands in which may reasonably be assigned to the π → π* and d-d transition, respectively. The magnetic moments of the complexes further support the electronic spectra. The magnetic moment of the complexes suggest square-planar geometry and the values are

corresponding to one unpaired electron in the complexes of macrocyclic tetraaza. Thus, confirmed that the complexes formed are paramagnetic.

TABLE (3). Magnetic moments and electronic spectral bands (nm).

Complexes	μ_{eff} (B.M)	Band position $\pi \rightarrow \pi^*$ (nm)	Band position d-d (nm)
MC1	2.45	245	518
MC2	2.31	237	520
MC3	2.01	269	516

Compound MC1 was successfully crystallized and analysed by using Bruker APEX-II CCD fitted with Mo K α radiation. FIGURE 2 shows the molecular structure with numbering scheme. Like its ligand, the asymmetric unit consists of symmetrically generated Cu-ring, one bromo and one water molecule. The central Cu atom is coordinated to four tetraaza nitrogen atoms in a distorted square planar geometry. Two hydrogen atoms of the protonated amino in the ligand were deprotonated but the bromo anions and two water molecules of crystallization remain in the complex salt. The compound crystallized in monoclinic crystal system with space group P21/c, $a=8.0453(8)$, $b=15.6095(19)$, $c=8.9229(10)$ Å, $\alpha=90$, $\beta=99.844(4)$, $\gamma=90^\circ$, $V=1104.1(2)$ Å³ and $Z=2$.

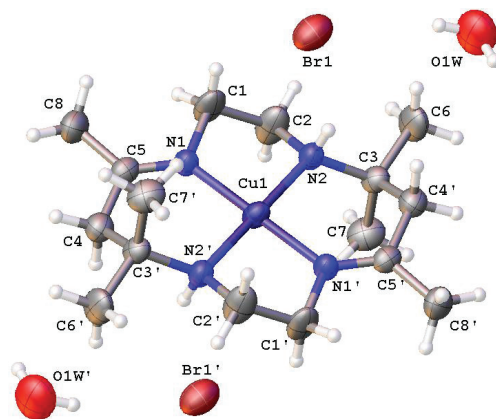


FIGURE 2. The ORTEP drawing of $[\text{Cu}(\text{Me}_6\text{N}_4\text{H}_2)].\text{Br}_2.2\text{H}_2\text{O}$ drawn at 50% probability ellipsoid.

Thermogravimetric study (TGA) showed that the MC1 is stable up to 170 °C after the first mass loss due to the removal of water of crystallisation. A gradual mass loss of 34% occurred up to 400 °C before gradually decomposed to give most likely CuO. Unlike MC1, the complexes of MC2 and MC3 possessed few stages of mass loss before finally decomposed above 400°C.

CONCLUSION

Three new macrocyclic tetraaza complexes using copper salts were successfully synthesized and analysed. The structure of $[\text{Cu}(\text{Me}_6\text{N}_4\text{H}_2)].\text{Br}_2.2\text{H}_2\text{O}$ demonstrated four-coordination geometry, monoclinic system with space group P21/c. The antibacterial studies of the complexes will be carried out in the near future.

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