



Synthesis and characterization of Ni(II) complex with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium bromide

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Synthesis and Characterization of Ni(II) Complex with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium bromide

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Abstract. Nickel(II) complex have been synthesized by treating a 14-membered ring tetraaza macrocyclic compound, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium, bromide ($\text{Me}_6\text{N}_4\text{H}_4$)Br₂ with nickel acetate in methanol. The complex was characterized using elemental analysis, Fourier Transform Infrared (FTIR), Ultraviolet-Visible (UV-Vis), and single crystal diffraction (X-ray). The nickel atom coordinates through four nitrogen atoms in the ligand. Square planar geometry has been proposed for this complex.

Keywords: nickel(II) complex, macrocyclic, tetraaza

PACS: 80

INTRODUCTION

A 14-membered ring macrocyclic tetraaza compound was first discovered by Curtis in 1961 by metal template method when he attempted to recrystallize tris(ethylenediamine) nickel(II) in acetone [1]. Many similar reactions with other metals have also been reported by using the metal template ion method [2]. Less convenient method to prepare the complexes is by direct reaction of the tetraaza with metals. Tetraaza macrocyclic compound was synthesized by using template condensation of 4,4'-diaminodiphenylmethane, formaldehyde, *p*-anisidine and metal salts under refluxed condition for 24 hours in ethanol [3].

Tetraaza heterocyclic compounds are important compounds due to their potential industrial applications as radiotherapeutic [4], medical imaging [5], metals extraction [6] and possess biological activities such as antibacterial and antifungal [7]. Their properties as catalyst in various reactions has also been investigated [8]. The presence of four electron donor nitrogen atoms has attracted extensive study on their complexation with various metals. Their role in biological processes such as metalloenzyme, catalysis and photosynthesis has been the subject of long interest. Therefore, molecular design and coordination chemistry of macrocyclic tetraaza have received much attention till today.

The discovery of protonated tetraaza ligand, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium bromide in this laboratory allowed us to study the complexation with several metals by direct reaction in methanol [9]. In the present paper, the complexation with nickel acetate is described.

EXPERIMENTAL

Materials and Instrumentation

All chemical were of AR grade and use without purification. The solvent were distilled before use. The CHNS microelemental analysis were determined by using Carlo Erba Model Fison EA 1108 analyser. Infrared spectra were obtained using FTIR Perkin Elmer Model Spectrum 400 FT-IR/ FT-NIR & Spotlight 400 Imaging System in the spectral range of 4000-400 cm⁻¹. UV-Visible spectra were recorded with a UV 1800 Shimadzu. The single crystal X-ray study was conducted by using Single Crystal X-ray Diffractometer model Bruker SMART APEX CCD.

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Synthesis of $(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2$

$(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2$ was prepared by method described by Mohamad in 2012 [10]. To an acetone solution (30 cm^3) containing potassium bromide (0.01 mol), ethylenediamine (0.01 mol) was slowly added (FIGURE 1). The mixture was refluxed for 30 minutes. On cooling, the remaining ammonium bromide was filtered out and the filtrate was left at room temperature. After one day of evaporation, single crystals were obtained and washed with acetone.

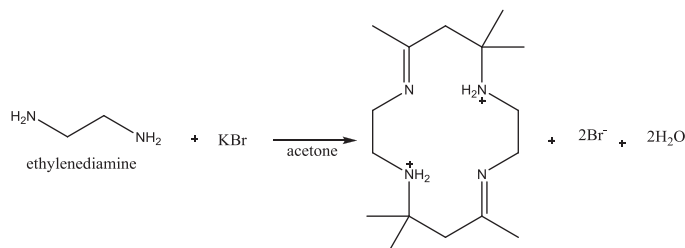


FIGURE 1. Preparation scheme of $(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2$.

Synthesis of $\text{Ni}-[(\text{Me}_6\text{N}_4\text{H}_4)]\text{Br}_2$ Complex

A solution of $\text{Ni}(\text{CH}_3\text{COO})_2$ (0.001mol) in methanol (10mL) and a solution of $(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2$ (0.001mol) in methanol (10mL) were mixed in round bottom flask (FIGURE 2). The mixture was then refluxed for 3 hours under constant stirring. The resulting clear solution was left for crystallization. After 4 days, the orange crystal form was washed with a small amount of methanol and dried at room temperature.

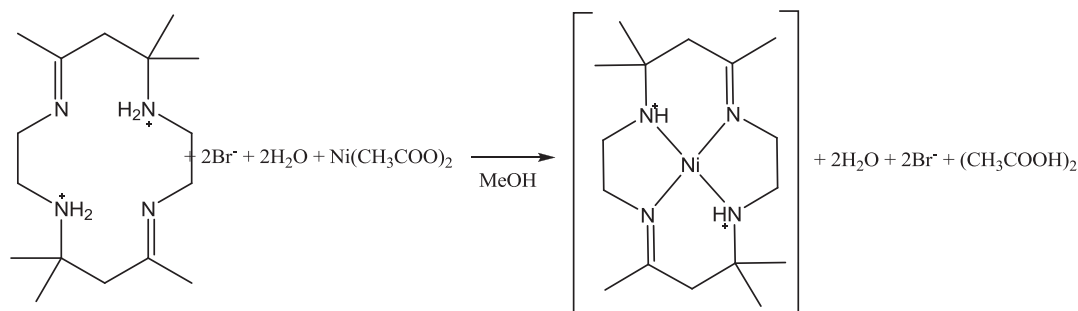


FIGURE 2. Synthesis scheme of $\text{Ni}-[(\text{Me}_6\text{N}_4\text{H}_4)]\text{Br}_2$ complex.

RESULT AND DISCUSSIONS

Synthesis of $(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2$

The tetraaza salt was obtained as white crystalline solid with the melting point of $115.4\text{-}116.9^\circ\text{C}$. The yield was 70%. The infrared spectrum showed the stretching frequency of azomethine $\text{C}=\text{N}$ and $\text{C}-\text{N}$ bands at 1665 cm^{-1} and 1225 cm^{-1} , respectively. The bands at 3468 cm^{-1} (sharp) and 3045 cm^{-1} (broad) are due to the primary amino and $\text{C}-\text{H}$ stretchings, respectively. The high primary amino stretching than the normal value indicates the presence of protonated primary amino group. The microelemental analysis data is in good agreement with the calculated molecular formula of $\text{C}_{16}\text{H}_{40}\text{N}_4\text{O}_3\text{Br}_2$ (experiment $\text{C}=40.2 \text{ H}=8.3 \text{ N}=11.6$; calculated $\text{C}=40.2 \text{ H}=7.9 \text{ N}=11.1$). UV-*Vis* spectrum shows a maximum absorption at 236 nm ($\epsilon=1.82 \text{ M}^{-1}\text{cm}^{-1}$). The salt crystallized in triclinic system with space group $\text{P}\bar{1}$, $a=8.290(3) \text{ \AA}$, $b=8.655(3) \text{ \AA}$, $c=8.809(3) \text{ \AA}$, $\alpha=72.797(6)^\circ$, $\beta=75.373(6)^\circ$, $\gamma=66.593(6)^\circ$, $Z=2$, 1.452 Mg/m^3 and $V=547.4(3) \text{ \AA}^3$.

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Synthesis of Ni-[(Me₆N₄H₄)]Br₂ Complex

The reaction of the heterocyclic ligand with nickel(II) acetate gave orange solid crystal. The yield was 80% with melting point of 283.4- 284.5°C. The microelemental analysis data is in agreement with the formula of C₁₆H₃₄N₄O₂Br₂Ni (experimental: C= 36.2 H= 6.8 N= 8.3%; calculate: C= 36.7 H= 6.7 N= 8.6%). The IR band at 1639 cm⁻¹ (sharp) is due to the stretching frequency of C=N bond. The $\nu(\text{C-N})$ is in the region of 1271 cm⁻¹. The band in the region of 3049 cm⁻¹ corresponds to C-H stretching. The slight shift of $\nu(\text{C=N})$ and N-H stretching band at 3339 cm⁻¹ were indicated the coordination between the nickel and nitrogen atoms.

The electronic spectrum of the Ni(II) complex showed band at λ_{max} of 436.5 nm ($\epsilon = 70.1 \text{ M}^{-1}\text{cm}^{-1}$) is assigned to d-d transition [11]. The chemical and spectroscopic data is supported by the molecular structural study. The complex have a monoclinic system with space group P2(1)/c, $a = 8.0589(5) \text{ \AA}$, $b = 15.5951(10) \text{ \AA}$, $c = 8.9142(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 100.046(2)^\circ$, $\gamma = 90^\circ$, $Z = 4$ Mg/m³ and $V = 1103.15(12) \text{ \AA}^3$. The nickel atom is coordinated to four nitrogen atoms in a square planar geometry (FIGURE 3).

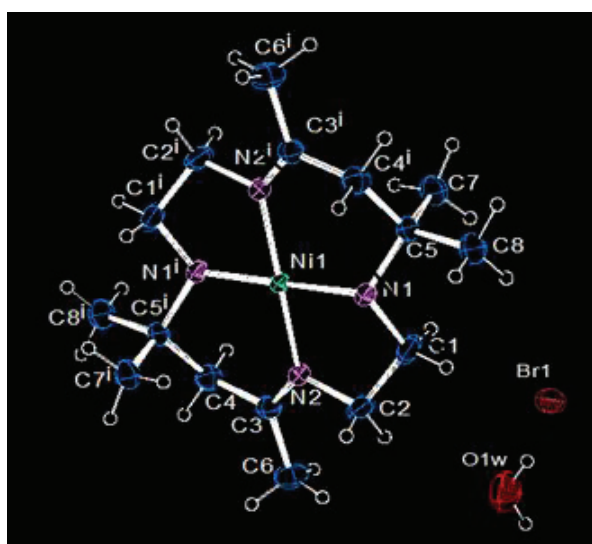


FIGURE 3. The ORTEP drawing of Ni-(Me₆N₄H₄)]Br₂ drawn at 50% probability ellipsoid.

CONCLUSION

The formation of the Ni-(Me₆N₄H₄)]Br₂ complex involves the deprotonation of the protonated nitrogen atoms of the ligand. Electronic spectra data support that the Ni-(Me₆N₄H₄)]Br₂ complex have square-planar geometry. The infrared spectrum showed the nickel atom coordinated to the ligand through four nitrogen atoms. The chemical analysis is supported by the x-ray crystallography study.

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