

การสังเคราะห์ และโครงสร้างผลึกของสารประกอบเชิงซ้อนนิกเกิล (II) กับลิแกนด์เตตระอะซา  
วงขนาดใหญ่ 14 เหลี่ยม

Synthesis and Crystal Structure of Nickel(II) Complex With 14-Membered Tetraaza  
Macrocyclic Ligand

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บทคัดย่อ

สารประกอบเชิงซ้อน  $[\text{NiL}](\text{ClO}_4)_2$  ที่มีวงขนาด 14 เหลี่ยมถูกเตรียมจากการทำปฏิกิริยาของเอทิลีนไดเอมีน บิวทิลามีน ฟอรัลดีไฮด์ และโลหะนิกเกิล(II) เมื่อ L คือ 1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane โดย ลิแกนด์ เตตระอะซาที่มีวงขนาด 14 เหลี่ยม ประกอบด้วย บิวทิลามีน 2 โมเลกุลเป็นแขนด้านข้างได้ยื่นยื่นโครงสร้าง สารประกอบเชิงซ้อนด้วยเทคนิคทางสเปกโทรสโกปีและเทคนิคการเลี้ยวเบนรังสีเอกซ์บนผลึกเดี่ยวพบว่าสารประกอบ เชิงซ้อนดังกล่าวมีรูปทรงทางเรขาคณิตแบบสี่เหลี่ยมแบนราบโดยรอบไอออนนิกเกิล(II) ประกอบด้วยอะตอม ไนโตรเจน 4 อะตอม โดยแขนด้านข้างเป็นเอมีน 2 โมเลกุลอยู่ตรงข้ามกัน และมีแรงดึงดูดอย่างอ่อนระหว่างเปอร์ คลอเรต 2 ไอออนกับโลหะนิกเกิล(II) ในตำแหน่งทรานส์ซึ่งกันและกัน

คำสำคัญ: โครงสร้างผลึก วงขนาด 14 เหลี่ยม สารประกอบเชิงซ้อนนิกเกิล(II)

Abstract

The 14-membered macrocyclic complex,  $[\text{NiL}](\text{ClO}_4)_2$  has been prepared via the reaction of ethylenedi-amine, butylamine and formaldehyde in the presence of Ni(II) ion, as L = 1,8-dibutyl-1,3,6,8,10,13-hexaazacy clotetradecane. The ligand is a 14-membered tetraaza macrocycle having two butylamine pendant arm. The complex, investigated by spectroscopic and single crystal x-ray diffraction technique, supports the formation of square-planar complex with the Ni(II) ion located within a tetraaza macrocyclic containing four nitrogen atoms and two pendant amines coordinating on opposite sides of a plane defined by macrocycle and the Ni(II) ion. Two perchlorate ions coordinate weakly to the central Ni(II) in trans position.

**Keywords:** Crystal structure, 14-Membered Cycle, Nickel (II) complex

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## Introduction

Tetraaza macrocyclic complexes have been synthesized as models for metalloporphyrins, chlorophyll, metalloproteins, hemoglobin and vitamin B12 due to their intrinsic structure properties. There have been various applications of tetraaza macrocyclic complexes, such as antimicrobial, luminescent sensor, artificial restriction enzymes for cleaving DNA and RNA, magnetic and catalytic properties Metal template syntheses of macrocyclic ligands have been useful and effective method to obtain new macrocyclic ligands during the last three decades. The metal ions as templates and many macrocyclic ligands have been prepared by the condensation of formaldehyde with amide. Template synthesis of macrocyclic complexes is simple reaction as formaldehyde links between two amine moieties to form methylenediamine linkages ( $-N-CH_2-N-$ ). The methylenediamine linkage is unstable when it contains primary amines,  $R-NH_2$  in which R is either aromatic or aliphatic group, such as methylamine, propylamine and phenylethylamine, which can condense with formaldehyde to form a new N-C bond

In this work, the Ni(II) complex containing the 14-membered tetraaza macrocyclic ligands has been synthesized in a one-pot reaction involving nickel(II) chloride, ethylenediamine, formaldehyde and butylamine in 95% absolute ethanol.

## Experimental

### Materials and Method

$NiCl_2 \cdot 6H_2O$ , ethylenediamine, formaldehyde, butylamine and perchloric acid were all purchased from commercial source and used as received. Caution! Perchlorate salts of metal complexes are potentially explosive. Only a small amount material should be prepared, and it should be handled with care. IR spectra ( $4000 - 400\text{ cm}^{-1}$ ) were recorded with FT - IR spectrometer as a KBr disk. The visible spectra were recorded with a Shimadzu Lambda-1600 UV - Vis spectrophotometer in DMSO. Single crystal suitable for x-ray crystallographic analyses were obtained by the slow evaporation of solvent from the acetonitrile : ethanol solution of complex at room temperature. X-ray data for complex were collected at 293 K on a Bruker SMART APEX CCD area-detector diffractometer with graphite monochromated  $Mo\ K\alpha$  - radiation ( $\lambda = 0.71073\text{ \AA}$ ). The data integration and reduction were processed with SAINT software. An empirical absorption correction was applied to the collected reflections with SADABS program The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the International Tables for x-ray crystallography. All the structure was solved by the direct method using SHELXS-97 program [1] and was refined on  $F^2$  by the full-matrix least-squares technique using the SHELXL-97 program. Figures were drawn using Mercury - 3.0 [2] and Diamond - 3.0 [3]

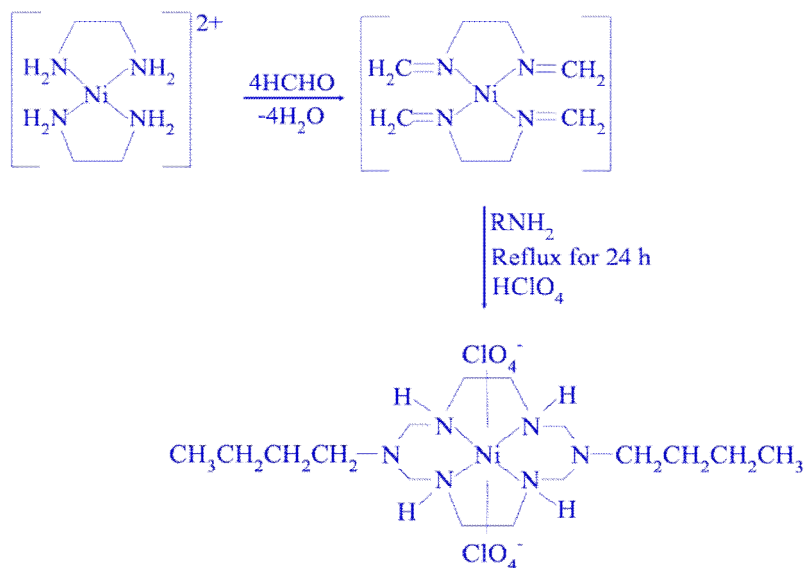
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### Synthesis of $[\text{NiL}](\text{ClO}_4)_2$

To a 95% absolute ethanol (10 mL) of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (2.3058 g, 10 mmol) were added 99% ethylenediamine (1.3 mL, 20 mmol) in 95% absolute ethanol (10). After the mixture was completely clear blue solution then, added 37% formaldehyde (2.2 mL, 40 mmol), with stirring until the mixture was completely dark blue solution and then butylamine (2 mL, 20 mmol) was added with continuous stirring. The mixture of reactants was refluxed for 24 h and the yellow solution was cooled to room temperature and filtered to remove any insoluble solids. After the amount of concentrated perchloric acid have been added dropwise, the mixture was filtered and stored at room temperature to form yellow solids. Yield:  $\approx 67\%$ . The product was purified by recrystallization from acetonitrile : absolute ethanol in mole ratio 1 : 1. The physical properties and analytical x-ray data are given in Table 1.

### Results and Discussion

The tetraaza macrocyclic complex has been synthesized in a one – pot reaction involving Nickel chloride, ethylenediamine, formaldehyde and butylamine as shown in Scheme 1. The synthesized complex is found to be air stable and insoluble in water, but soluble in some polar solvents, for instance MeCN, DMF and DMSO. The analytical data of the complexes and some physical properties are summarized in Table 1.



Where L = 1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane

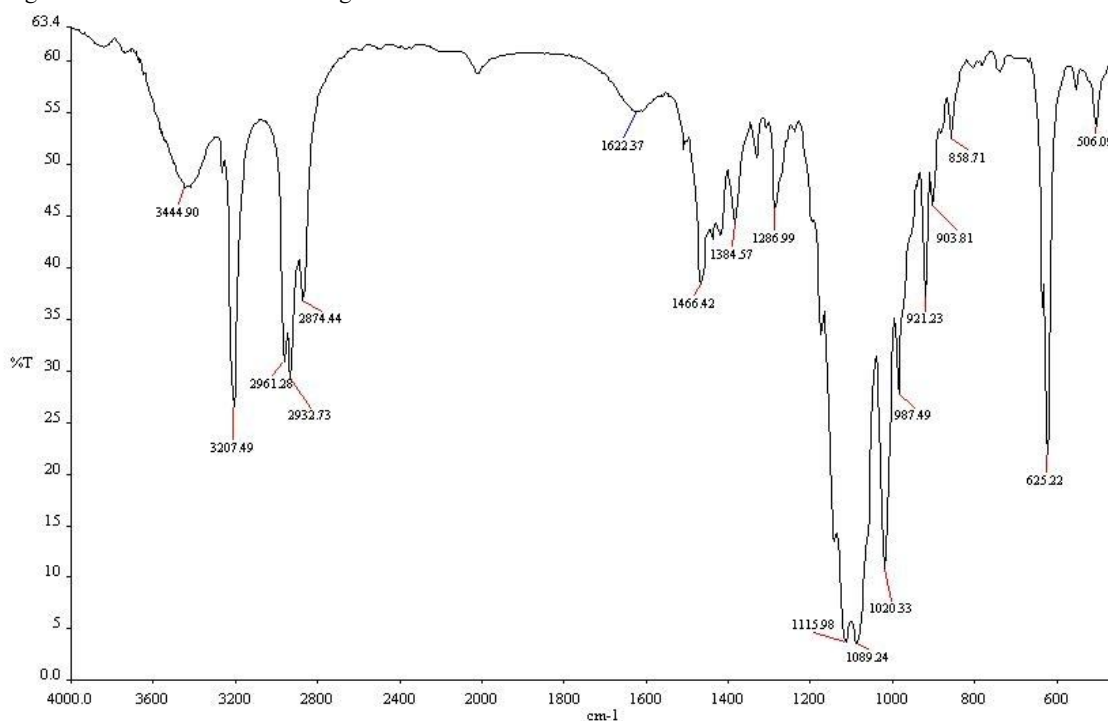
**Scheme 1.** Synthesis of  $[\text{NiL}](\text{ClO}_4)_2$

**Table 1.** Physical properties and analytical data of nickel(II) complexes containing tetraaza macrocyclic ligands

Complex	Reaction	Empirical formula	Melting point (°C)	Colour
[NiL](ClO <sub>4</sub> ) <sub>2</sub>	NiCl <sub>2</sub> •6H <sub>2</sub> O + 2C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> + 4CH <sub>2</sub> O + 2C <sub>4</sub> H <sub>11</sub> N <sub>2</sub> + HClO <sub>4</sub>	C <sub>16</sub> H <sub>38</sub> O <sub>8</sub> N <sub>6</sub> Cl <sub>2</sub> Ni	~ 223	yellow

### Infrared spectra

The preliminary identification of [NiL](ClO<sub>4</sub>)<sub>2</sub> complex was done from their IR spectra in Figure 1. There are IR frequencies of the macrocyclic complex to be shown the presence of sharp band in the 3207 cm<sup>-1</sup> region, assignable to the coordination of secondary amine stretching mode. The absence of a band in the regions 1720 – 1740 cm<sup>-1</sup>, which is characteristic  $\nu$ (C=O) carbonyl of aldehyde moiety, further confirms the condensation. In the regions 1384 – 1466 cm<sup>-1</sup> and 2874 – 2961 cm<sup>-1</sup>, respectively, the  $\nu$ (C - N) and  $\nu$ (C - H) modes are found. In addition it is apparent that there is considerable broadening and splitting in the region centered around 1100 cm<sup>-1</sup> with two peaks at 1089 and 1115 cm<sup>-1</sup> in which these regions are assigned to perchlorate ions. An important feature is the appearance of a new band of peak intensity at 506 cm<sup>-1</sup> attributable to  $\nu$ (Ni - N) which assigns for the involvement of nitrogen in coordination.



**Figure 1.** The IR spectrum of [NiL](ClO<sub>4</sub>)<sub>2</sub> complex

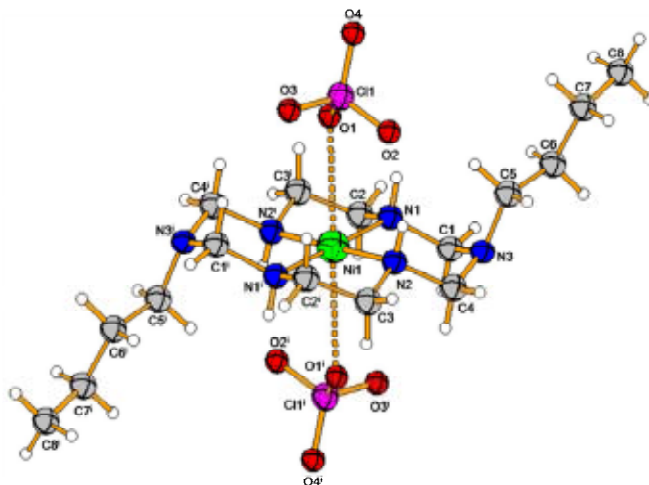
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### Crystal structure description of $[\text{NiL}](\text{ClO}_4)_2$

The ORTEP drawing view of the molecular structure and labelling scheme are given in Figure 2. Crystallographic data are given in Table 2. The complex crystallizes in the triclinic and space group  $P\bar{1}$ . In the cation, the Ni(II) ion is coordinated by four secondary amine nitrogen atoms of the macrocyclic ligand  $[\text{NiL}]^{2+}$  and the coordination geometry about Ni(1) is a square-planar. The macrocyclic secondary amine adopts trans-II configuration with six-membered macrocyclic rings adopting chair conformations. These pendant butyl groups are similar to those reported for the nickel(II) complex [4]. The average Ni-N (macrocyclic) bond length of 1.9310(18) Å is close to the ca. 1.92 Å of other square-planar macrocyclic nickel complex [4]. The Ni-N bond lengths are 1.9306(18) to 1.9315(18) Å and the bite angle of five and six-membered chelate rings are 87.04(8) and 92.96(8)°, respectively. These values are similar to those in the related macrocyclic Ni(II) complex. The average C-N bond length involving bridgehead tertiary nitrogen atom N(3) is 1.427(3) Å, which is shorter than the normal C-N single bond length [1.469(14) Å]. Large C-N-C angle involving N(3) are found to be in the range 110.83(18) - 111.15(19)°. Similar shortening of the bond length and flattening of the bond angles involving uncoordinated tertiary amine have been observed for other complexes [5].

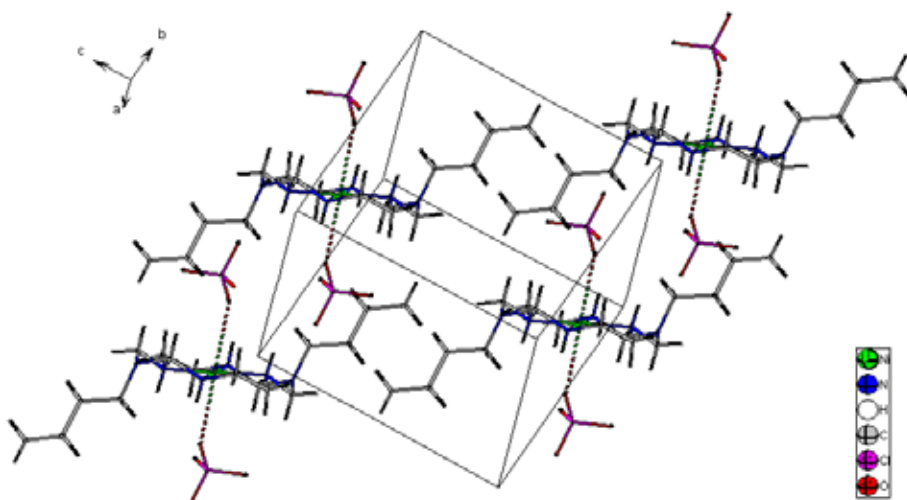
**Table 2.** Crystal data and structure refinement for Ni(II) complex.

Identification code	Ni(II) complex
Empirical formula	$\text{C}_{16}\text{H}_{38}\text{Cl}_2\text{N}_6\text{NiO}_8$
Formula weight	572.13
Temperature	293(2) K
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a, b, c	8.2987(5), 8.4300(5), 10.1648(6) Å
$\alpha, \beta, \gamma$	92.2540(10)°, 94.8790(10)°, 117.3230(10)°
Volume (Å <sup>3</sup> )	627.01(6)
Z	1
$\rho_{\text{calc}}$ (g/cm <sup>-3</sup> )	1.515
Crystal size (mm)	0.27 x 0.126 x 0.107
Final R indices [I > 2σ(I)]	R1 = 0.0315, wR2 = 0.0898
R indices (all data)	R1 = 0.0328, wR2 = 0.0911



**Figure 2.** ORTEP view of the molecular structure (showing 50% thermal ellipsoids), along with the atomic numbering scheme.

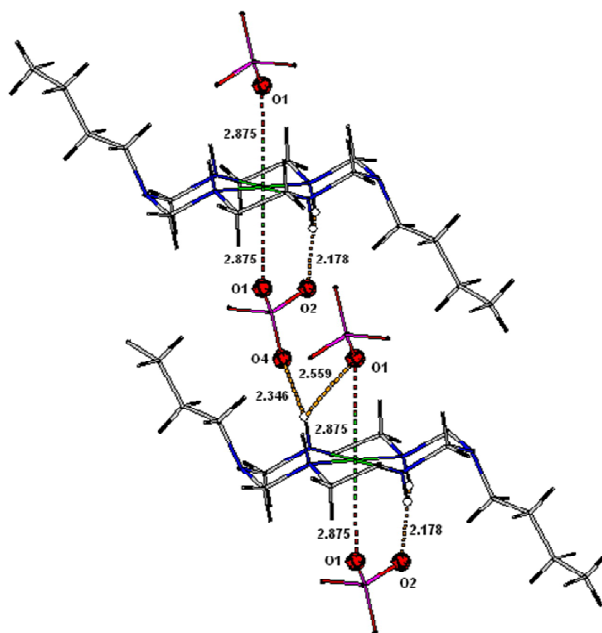
The bond angles in perchlorate ion at O-Cl(1)-O are found to be in the range of  $106.3(2) - 113.08(15)^\circ$  while bond distances, Cl-O are found to be in the range  $1.408(2)$  to  $1.432(2)$  Å. The perchlorate ion indicates at lengthening of the Cl – O bonds involving O(1), which were weakly coordinated to the Ni atom [Ni(1) – O(1) =  $2.875(35)$  Å]. The Cl(1) – O(1) bond length was  $1.408(2)$  Å, which was significantly shorter than the average of the other three Cl – O bonds,  $1.432(2)$  Å.



**Figure 3.** Unit cell diagrams of  $[\text{NiL}](\text{ClO}_4)_2$ , Ni (green) atoms are shown as small spheres of arbitrary radii.

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A view of hydrogen bonds is present in the structure as shown in Figure 4. Selected bond lengths and angles for hydrogen bonding are summarized in Table 3.



**Figure 4.** View of the N-H...O hydrogen bonding in structure  $[\text{NiL}](\text{ClO}_4)_2$ .

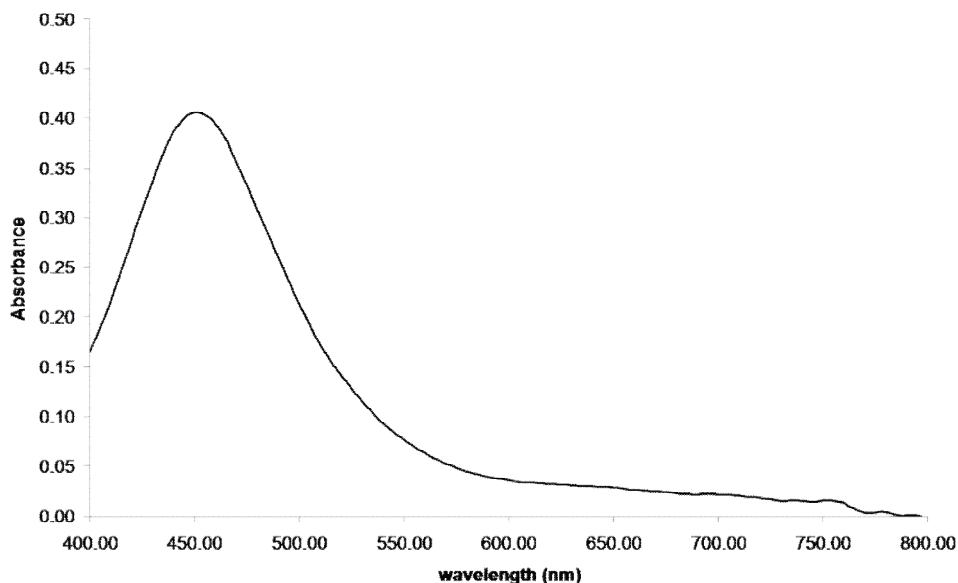
**Table 3.** Selected hydrogen bonds for  $[\text{NiL}](\text{ClO}_4)_2$  [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(2)#1	0.894(17)	2.177(19)	3.030(3)	159(2)
N(1)-H(1)...O(4)#2	0.878(17)	2.35(2)	3.031(3)	135(2)
N(1)-H(1)...O(1)	0.878(17)	2.56(2)	3.134(3)	124(2)

#1 -x+1,-y+1,-z #2 -x+1,-y+2,-z

### Visible spectra

The electronic spectral data (Figure 5.) of yellow complex,  $[\text{NiL}](\text{ClO}_4)_2$  which is soluble in DMSO show absorption with the  $\lambda_{\text{max}} = 452 \text{ nm}$  which means assigned to d – d transition of Ni(II) ions.



**Figure 5.** The visible spectrum of  $[\text{NiL}](\text{ClO}_4)_2$

### Conclusions

In this work, a novel 14 membered tetraaza macrocyclic complex has been synthesized in a one – pot reaction by ethylenediamine, butylamine, formaldehyde and nickel(II) chloride. The formation of the proposed macrocyclic framework has been confirmed by the appearance of secondary amine bands in the IR and corresponding crystal structure in the single crystal x-ray diffraction analysis and visible studies. The Ni(II) ion has square-planar coordination by four nitrogen atoms of the macrocyclic ligand, with weakly coordinated perchlorate ions in *trans* position.

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