

CHAPTER II

Syntheses of diaza dioxo dithia *p*-tert-butylcalix[4]arenes as heavy metal ion receptors

2.1 Introduction

Crown ethers, discovered accidentally by Charles Pedersen in 1967, have attracted chemist's attention due to its selective metal-ion binding properties.³⁸ Metal cations are important pollutants in environment. They, therefore, should be removed. Many researchers pay an attention on waste treatment. Crown ethers are capable of binding alkali and alkaline earth metals using oxygen donors. Binding constants of crown ethers depend on size and charge density of cations. For instances, crown-5 prefers binding Na^+ to K^+ and Cs^+ while crown-6 is more favorable for K^+ .³⁹ Crown ethers not only form complexes with alkali or alkaline earth metals, but also transition metals. Dernimi and coworkers studied use of crown ethers such as benzo-15-crown-5 (A), dibenzo-18-crown-6 (B) and dicyclohexano-18-crown-6 (C) as extracting agents to remove lead from aqueous solution containing lead and other cations. It was found that Pb^{2+} was extracted with all crown ethers much more effectively than other transition metals; Ni^{2+} , Co^{2+} , Cu^{2+} , and Zn^{2+} .⁴⁰

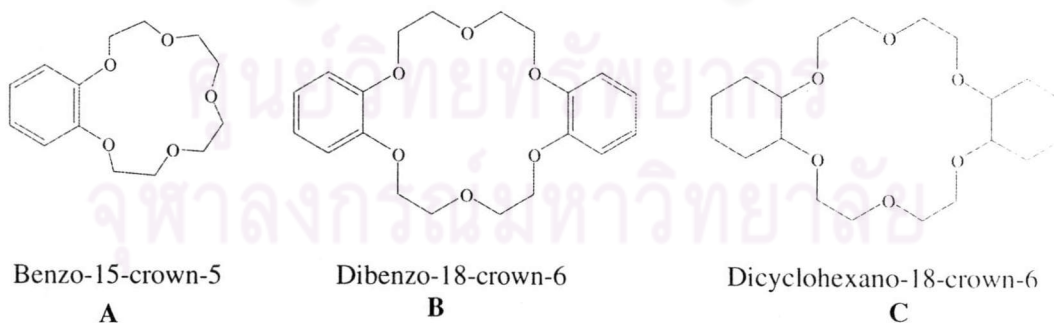
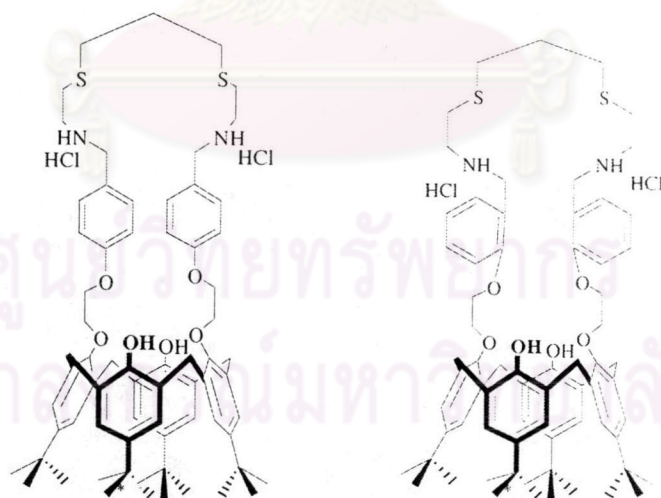


Figure 2.1.1 Crown ether derivatives

Recently, thiocrown ethers have found their applications as soft cation receptors⁴¹ and appealed researchers in environmental studies.⁴²⁻⁴³ By the HSAB concept, a so-called

coordination to each other.⁴⁴ Therefore molecules containing S-atom can bind strongly with heavy metal ions. However, not many thiacrown ethers were found in the literature due to the difficulty in handling and incorporating the S-atoms to the crown ether unit.⁴⁵⁻⁴⁹

Calixarenes are popular and extremely versatile host frameworks in supramolecular chemistry. The general strategy used to develop these molecules for sensing and separation of metal ions and organic molecules has relied on the modification of the upper and/or lower rims of the parent calixarenes.⁵⁰⁻⁵² Crown ether calix[4]arenes were designed by substitution of polyethylene glycol on phenolic OH groups of calix[4]arene.⁵³ They effectively formed complexes with alkali metals. Therefore, they were well-known extractants for alkali metal ions in environment as well as in biological system.⁵⁴ Our group has been working with derivatives of calix[4]arene. Navakun et al. has synthesized azathiol derivatives of calix[4]arenes and studied binding properties of these receptors with transition metals, Zn(II), Cd(II) and Hg(II), by potentiometric titrations. It was found that azathiol calix[4]arene selectively bind Hg(II).⁵⁵



para-azathiol calix[4]arene

ortho-azathiol calix[4]arene

Figure 2.1.2 Structure of azathiol calix[4]arene derivatives

It is our goal to synthesize a calix[4]arene derivative containing N-, O- and S-donors (**Figure 2.1.3**) and study its binding properties with heavy metals. Crown ether type

derivatives of calix[4]arene which possess sulfur donors are quite rare. It may be difficult in handling the mercaptan ligands due to their facile oxidizability to disulfide or polymerization.

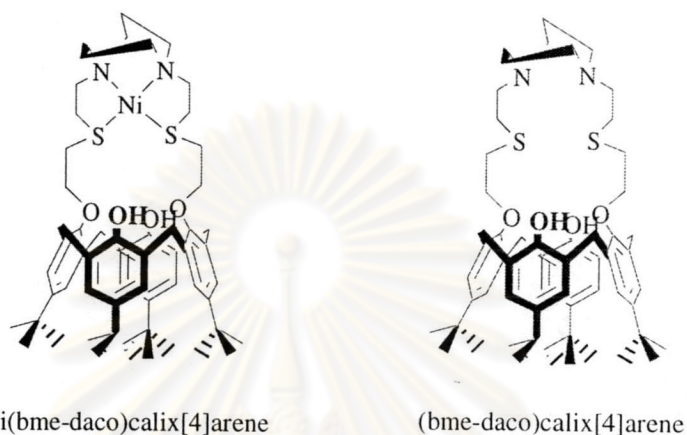
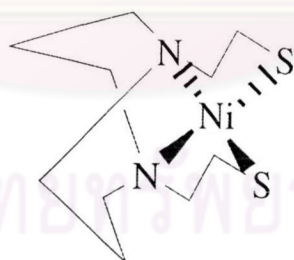


Figure 2.1.3 Dithia diaza calix[4]arene as target molecules

In order to overcome this obstacle, a metal thiolate complex is used as a template for synthesizing macrocyclic compounds bearing sulfur donors.⁵⁶ A square planar nickel (II) thiolate, (bme-daco)Ni, containing two nitrogen and two sulfur donors was synthesized by the Darensbourg group.⁵⁷ (**Figure 2.1.4**)



Ni(bme-daco)

Figure 2.1.4 Structure of Ni(bme-daco)

The available lone pairs on the thiolatesulfurs of Ni(bme-daco) can also act as nucleophiles towards alkyl halides on calix[4]arene to produce a number of macrocyclic nickel complex macromolecules which possess interesting Ni^{III/I} redox potential. The Ni(II) ion can be removed from the complex by addition of excess KCN or NaCN salts. The free ligand containing s-donor atom thus can be obtained.

2.2 Experimental section

2.2.1 Synthesis part

2.2.1.1 General Procedure

2.2.1.1.1 Analytical Measurement

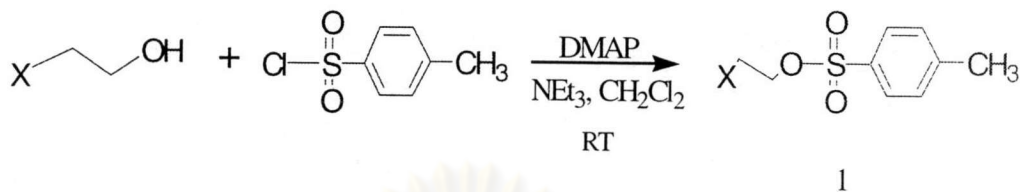
Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker ACF 200 MHz nuclear magnetic resonance spectrometer. All chemical shifts were recorded in part per million (ppm) using the residual proton or carbon signals in deuterated solvents as internal references. Mass results were carried out on Bruker Biflex MALDI-TOF Mass Spectrometer.

2.2.1.1.2 Materials

Unless otherwise stated, all materials and solvents were standard analytical grade, purchased from Fluka, BDH, Aldrich, Carlo Erba, Merck, J. T. Baker or Lab scan. They were used without further purification. Commercial grade solvents such as acetone, dichloromethane, hexane, methanol and ethyl acetate were purified by distillation. Acetonitrile and CH_2Cl_2 were dried over CaH_2 and freshly distilled under nitrogen prior to used. Column chromatography were carried out on silica gel (Kieselgel 60, 0.063-0.200 nm, Merck). Thin-layer chromatography (TLC) were performed on silica gel plates (Kieselgel 60 F₂₅₄, 1 mm, Merck)

2.2.1.2 Experimental procedure

2.2.1.2.1 Preparation of 1-bromo-2-*p*-sulfonyltolueneethane (1a)



1a : X = Br

1b : X = Cl

In a 2-necked round bottom flask, 2-bromoethanol (6.0 mL; 56.6 mmol), triethylamine (17.00 g; 16.8 mmol) and 4-dimethylaminopyridine (catalytic amount) were stirred in dichloromethane (200 mL) at room temperature. Toluene-4-sulfonylchloride (11.03g; 57 mmol) in dichloromethane (50 mL) was added dropwise into the reaction. The reaction mixture was stirred under N₂ at room temperature overnight. Subsequently, water (50mL) was added into the mixture, and the organic layer was separated. The organic layer was washed with 2 portions of 50 mL water. Finally, saturated NaHCO₃ in water was added and the organic phase was then separated. The organic solvent was removed by a rotary evaporator to obtain as yellow liquid in 13.59 g (86%).

Characterization data for (1a)

¹H-NMR spectrum (CDCl₃, 200 MHz): δ (in ppm)

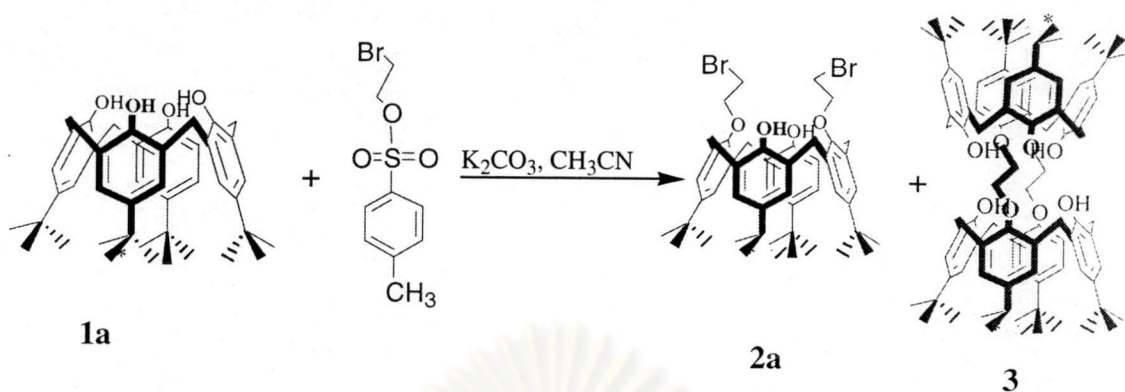
δ = 7.73 (d, *J* = 8.0 Hz, 2H, ArH_a), 7.26 (d, *J* = 7.8 Hz, 2H, ArH_b), 4.20 (t, *J* = 6.1 Hz, 2H, -OCH₂-), 3.39 (t, *J* = 6.2 Hz, 2H, BrCH₂), 2.36 (s, 3H, ArCH₃)

Characterization data for (1b)

¹H-NMR spectrum (CDCl₃, 200 MHz): δ (in ppm)

δ = 7.79 (d, *J* = 8.2 Hz, 2H, ArH_a), 7.38 (d, *J* = 5.6 Hz, 2H, ArH_b), 4.21 (t, *J* = 5.9 Hz, 2H, -OCH₂-), 3.63 (t, *J* = 5.9 Hz, 2H, BrCH₂), 2.44 (s, 3H, ArCH₃)

2.2.1.2.2 Preparation of 25,27-Bisbromoethyl-*p*-*tert*-butylcalix[4]arene (2a)



Into a 250 mL two-necked round bottom flask, a suspension of *p*-*tert*-butylcalix[4]arene (0.68 g, 1.0 mmol) and K_2CO_3 (4.0 g, 28.89 mmol) was stirred in dry CH_3CN (100 mL) for 1 h. A solution of 1-bromo-2-tosylethane (0.605g., 2.30 mmol) in dry CH_3CN (50 mL) was subsequently added dropwise. The mixture was stirred and refluxed under nitrogen overnight. The reaction was allowed to cool to room temperature and the solvent was evaporated to dryness under reduced pressure to afford a crude product. Water was added into the mixture and the organic layer was partitioned. The organic phase was extracted twice with water. The organic layer was then dried over anhydrous sodium sulfate and the solvent was removed to yield a yellow residue. The product was separated on a silica gel column using a 40% mixture of hexane and dichloromethane as eluant to obtain provide a white powder of dibromoethyl-calix[4]arene (2a) and calix[4]arene dimer (3) in 0.187 g, (23%) and 0.554 g, (41%) respectively.

Characterization data for (2a)

1H -NMR spectrum ($CDCl_3$, 200 MHz): δ (in ppm)

$\delta = 7.05$ (s, 4H, *H*ArR), 6.93 (s, 2H, *HO*Ar), 6.78 (s, 4H, *H*ArOH), 4.27 (t, $J = 6$ Hz, 4H, $ArOCH_2CH_2Br$), 3.83 (t, $J=6$ Hz, 4H, $ArOCH_2CH_2Br$), 4.32 and 3.32 (dd, $J = 13$ Hz, 8H, AB system) 1.28 (s, 18H, $ROArC(CH_3)_3$), 0.94 (s, 18H, $HOArC(CH_3)_3$)

Elemental Analysis: Anal Calcd For $C_{44}H_{62}O_4Br_2$: C, 66.82; H, 7.24

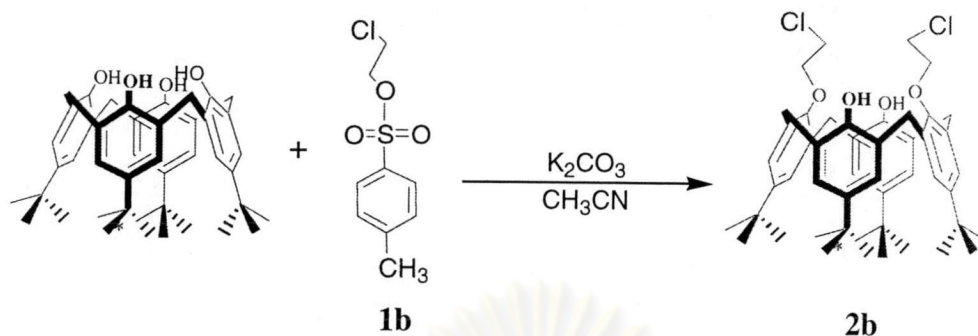
Found: C, 66.99; H, 7.19

Characterization data for (3)

1H -NMR spectrum ($CDCl_3$, 200 MHz): δ (in ppm)

$\delta = 7.64$ (s, 2H, *HO*Ar), 7.00 (s, 4H, *m*-*H*ArOR), 6.85 (s, 4H, *m*-*H*ArOH), 4.60 (s, 8H, OCH_2CH_2O), 4.51 and 3.35 (dd, $J = 12.7$ Hz, 8H, AB system), 1.25 (s, 18H, $ROArC(CH_3)_3$), 0.98 (s, 18H, $HOArC(CH_3)_3$)

2.2.1.2.3 Preparation of 25,27-Bischloroethyl-*p*-*tert*-butylcalix[4]arene (**2b**)



In a 250 mL two-necked round bottom flask, a suspension of *p*-*tert*-butylcalix[4]arene (0.68 g, 1.0 mmol) and KCO_3 (4.0 g, 28.89 mmol) was stirred in dry CH_3CN (100 mL) for 1 h. A solution of 1-chloro-2-tosylateethane (**1b**) (0.503 g, 2.30 mmol) in dry CH_3CN (50 mL) was subsequently added dropwise. The mixture was stirred and refluxed under nitrogen atmosphere overnight. The reaction was allowed to cool to room temperature and evaporated to dryness under reduced pressure to give a crude product. Water was added into the mixture and the organic layer was partitioned. The organic phase was extracted twice with water. The organic layer was then dried over anhydrous sodium sulfate and the solvent was removed to yield a yellow residue. The product was obtained by addition of methanol into the dichloromethane solution. Dichloroethyl-calix[4]arene (**2b**) precipitated as a white solid in 0.486 g (67%).

Characterization data for (**2b**)

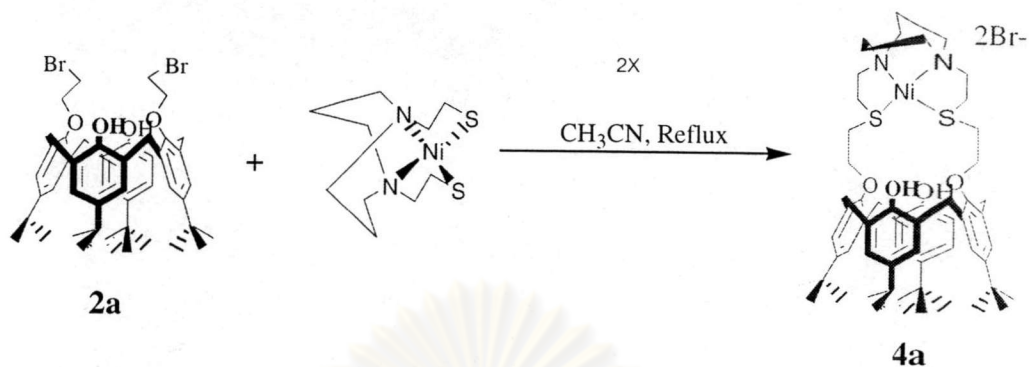
$^1\text{H-NMR}$ spectrum (CDCl_3 , 200 MHz): δ (in ppm)

$\delta = 7.07$ (s, 4H, *H*ArOR), 7.00 (s, 2H, *HO*Ar), 6.78 (s, 4H, *H*ArOH), 4.30 (t, $J=6\text{Hz}$, 4H, ArOCH₂CH₂Cl), 4.00 (t, $J=6\text{Hz}$, 4H, ArOCH₂CH₂Cl), 4.30 and 3.41 (dd, $J=13\text{Hz}$, 8H, AB system) 1.30 (s, 18H, RArC(CH₃)₃), 0.95 (s, 18H, HOArC(CH₃)₃)

Elemental Analysis: Anal Calcd For $\text{C}_{44}\text{H}_{62}\text{O}_4\text{Cl}_2$: C, 74.49; H, 8.04

Found: C, 74.57; H, 7.90

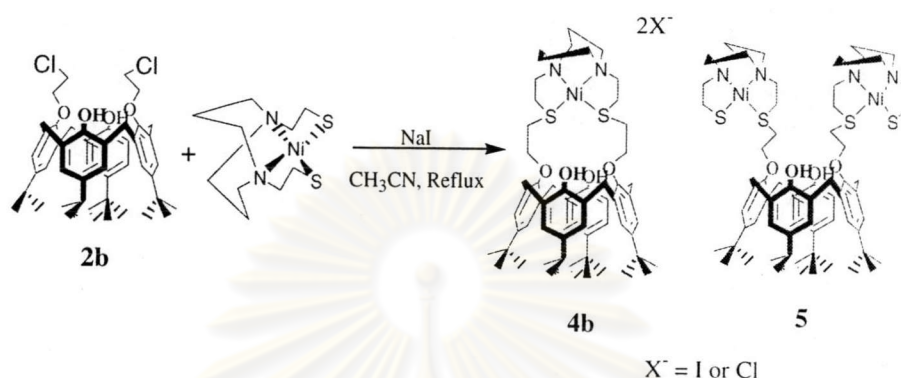
2.2.1.2.4 Preparation of 25,27-*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctane ethyl-*p-tert*-butylcalix[4]arene (**4a**)



In a 250 mL two-necked round bottle flask equipped with a magnetic bar and a reflux condenser, dibromoethyl-calix[4]arene (**2a**) (0.50 g., 0.70 mmol) in dry CH₃CN (20 mL) were stirred. The purple acetonitrile solution of Ni(dme-daco) (0.233, 0.80 mmol) was added dropwise. The mixture was refluxed for 18 h. The solution gradually changed from purple to dark red. The mixture was then evaporated to dryness under reduce pressure. Water was added into the mixture and the organic layer was partitioned twice with water. The organic phase was dried over sodium sulfate anhydrous and the solvent was removed by a rotary evaporator. The mixture was separated on a silica gel column with a mixture of 15% methanol and dichloromethane providing in order the yellowish green of Ni(bme-daco)calix[4]arene-Br₂ (**4a**) in 0.145g (18%).

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2.2.1.2.5. Preparation of 25,27-*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctane ethyl-*p*-*tert*-butylcalix[4]arene (**4b**)



In a 250 mL two-necked round bottle flask equipped with a magnetic bar and a reflux condenser, dichloroethyl-calix[4]arene (**2b**) (0.50 g., 0.70 mmol) and NaI (catalytic amount) in dry CH₃CN (20 mL) were stirred. The purple acetonitrile solution of Ni(dme-daco) (0.233, 0.80 mmol) was added dropwise. The mixture was refluxed for 48 h. The solution gradually changed from purple to dark red. The mixture was then evaporated to dryness under reduce pressure. Water was added into the mixture and the organic layer was partitioned twice with water. The organic phase was dried over sodium sulfate anhydrous and the solvent was removed by a rotary evaporator. The mixture was separated on a silica gel column with a mixture of 15% methanol and dichloromethane providing in order the yellowish green of Ni(bme-daco)calix[4]arene (**4b**) in 0.072 g. an unidentified green complex and the bisNi(bme-daco)calix[4]arene (**5**) in 0.35 g.

Characterization data for (4)

$^1\text{H-NMR}$ spectrum (CDCl_3 , 200 MHz): δ (in ppm)

$\delta = 7.04$ (s, 4H, *HArOH*), 6.82 (s, 2H, *OH*), 6.70 (s, 4H, *HArOR*), 4.05 (br, m, 8H-*OCH₂CH₂S-* and *-NCH₂CH₂S-*), 3.8-3.63 (br, 4H, *-NCH₂CH₂CH₂N-*), 3.54 (br, m, 8H, *-NCH₂CH₂CH₂N-*), 3.20 and 4.30 (dd, 8H, $J = 13$ Hz, AB system), 2.13 (br, m, 4H, *-OCH₂CH₂S-*), 1.93 (br, m, 4H, *-NCH₂CH₂S-*), 1.29 (s, 18H, *HOArC(CH₃)₃*), 0.87 (s, 18H, *ROAr(C(CH₃)₃)*)

MALDI-TOF mass spectrum: $\text{C}_{58}\text{H}_{82}\text{O}_4\text{S}_2\text{N}_2\text{I}_2\text{Ni} = 935.5$ ($[\text{M-NiI}]^+$) m/z .

UV-vis (λ_{max}): 281 nm

Elemental Analysis:

Anal Calcd. For $\text{C}_{58}\text{H}_{82}\text{O}_4\text{S}_2\text{N}_2\text{Br}_2\text{Ni}\cdot 2\text{H}_2\text{O}$: C, 58.54; H, 7.28; N, 2.35%

Found: C, 58.08; H, 7.05; N, 2.22%

Characterization data for (5)

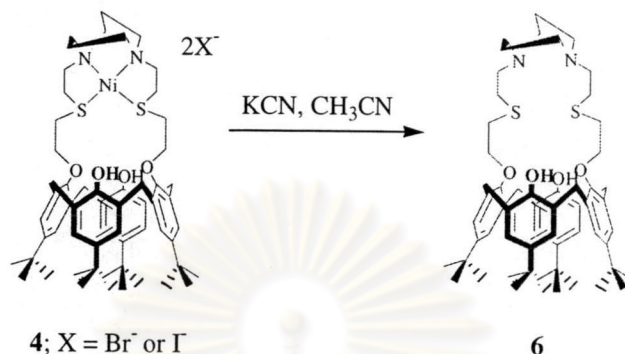
$^1\text{H-NMR}$ spectrum (CDCl_3 , 200 MHz): δ (in ppm)

$\delta = 7.10$ (s, 4H, *HArOH*), 6.60 (s, 4H, *HArOR*), 5.77 (s, 2H, *OH*), 4.40-1.48 (br, 56H, *-OCH₂CH₂SCH₂CH₂NCH₂CH₂CH₂N-* and AB system), 1.36 (s, 18H, *HOArC(CH₃)₃*), 0.82 (s, 18H, *ROArC(CH₃)₃*).

MALDI-TOF mass spectrum: $\text{C}_{68}\text{H}_{102}\text{O}_4\text{S}_4\text{N}_4\text{I}_2\text{Ni}_2 = 1412.1$ ($[\text{M-I}]^+$) m/z . and 1227.2 ($[\text{M-NiI}_2]^+$) m/z .

UV-vis (λ_{max}): 244 nm

2.2.1.2.5 Preparation of 25,27-*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctaneethyl-*p*-*tert*-butylcalix[4]arene (6)



In a 25 mL two-necked round bottle flask equipped with a magnetic bar and a reflux condenser, 25,27-*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctaneethyl-*p*-*tert*-butylcalix[4]arene(4) and KCN were heated in 5 mL acetonitrile until the color changes from purple solution to yellow solution. The reaction was cooled to room temperature and filtered to remove solids. The filtrate solution was concentrated by a rotary evaporator to afford the yellow solid in 92% yield.

Characterization data for (6)

¹H-NMR spectrum (CDCl₃, 200 MHz): δ (in ppm)

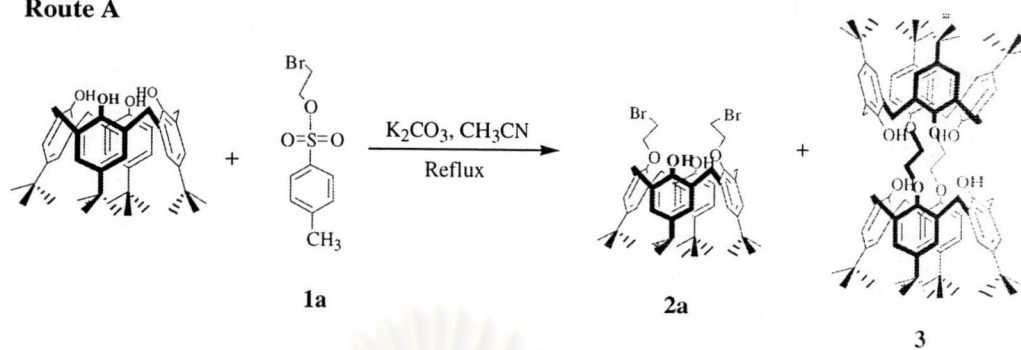
δ = 7.03 (s, 4H, HArOH), 6.93 (s, 2H, OH), 6.77 (s, 4H, HArOR), 4.32-1.68 (br, 36H, -OCH₂CH₂SCH₂CH₂NCH₂CH₂CH₂N- and AB system), 1.31 (s, 18H, HOArC(CH₃)₃), 0.96 (18H, ROArC(CH₃)₃)

2.3 Results and Discussion

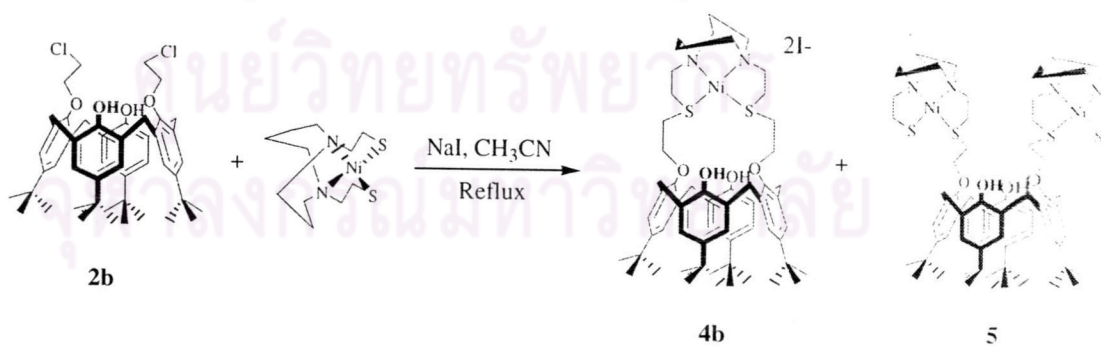
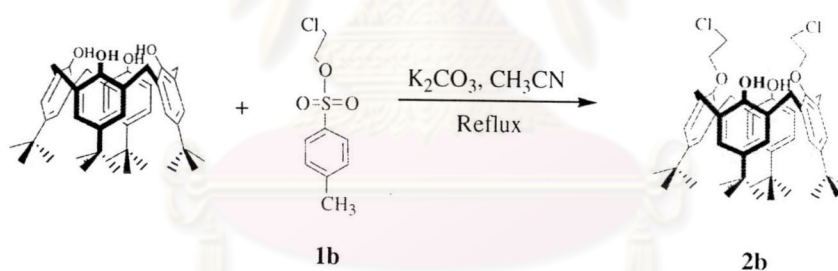
2.3.1 Synthesis and Characterization of Ni(bme-daco)calix[4]arene derivatives

We took an attempt to synthesize a calix[4]arene derivatives containing a macrocyclic N-, O- and S-atom donors to be able to form complexes with soft metals such as Ag^+ , Pb^{2+} , Hg^{2+} , Zn^{2+} and Cu^{2+} .⁵⁸ Ni(bme-daco) synthesized by the Darensbourg's group⁵⁷ was used as a precursor for N- and S- atom donors and as a nucleophile. Dibromoethylcalix[4]arene (**2a**) and dichloroethylcalix[4]arene (**2b**) were employed as a precursor for an O-atom donor as well as an alkylating agent. The synthetic methodology for Ni(bme-daco) ethylcalix[4]arene (**4**) is represented in **Scheme 2.3.1**. In order to synthesize dibromoethylcalix[4]arene (**2a**), 1-bromo-2-tosylateethane (**1a**) was prepared from the reaction of 2-bromoethanol with *p*-toluenesulfonylchloride in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine (DMAP). The nucleophilic substitution reaction between *p*-*tert*-butylcalix[4]arene and 2 equivalents of **1a** in the presence of K_2CO_3 in CH_3CN provided the mixture of products which were separated on a silica gel column using 40% mixture of hexane and dichloromethane as eluent. This resulted in dibromoethylcalix[4]arene (**2a**) and calix[4]arene dimer (**3**) in 23% and 41%, respectively. This synthetic route gives a copious amount of by-product, calix[4]arene dimer (**3**) since both Br and Ots are good leaving groups. Nucleophilic substitution by *p*-*tert*-butylcalix[4]arene can thus occur at both ends of **1a**. This side reaction results in calix[4]arene dimer (**3**). To improve the yield of Ni(bme-daco)ethylcalix[4]arene (**4**), dichloroethylcalix[4]arene (**2b**) was obtained by the reaction between 2 equivalents of 1-chloro-2-tosylateethane (**1b**), which was prepared by the same method as **1a**, and *p*-*tert*-butylcalix[4]arene in the presence of K_2CO_3 in CH_3CN . Dichloroethylcalix[4]arene (**2b**) precursor was obtained by precipitating with methanol in dichloromethane in 67% yield (**Scheme 2.3.1**).

Route A



Route B



Scheme 2.3.1 Pathway of synthesis dithia diaza calix[4]arene (4)

Both dibromoethylcalix[4]arene (**2a**) and dichloroethylcalix[4]arene (**2b**) were characterized by $^1\text{H-NMR}$ spectrum and elemental analysis. NMR spectrum of compounds **2a** and **2b** possess 2 triplet signals of $-\text{OCH}_2\text{CH}_2\text{X}$ at approximately 4.00 and 4.30 ppm for **2b** and 3.83 and 4.27 ppm for **2a**. In contrast, calix[4]arene dimer (**3**) has 1 singlet signal of $-\text{OCH}_2\text{CH}_2\text{O}-$ at 4.60 ppm because of the symmetrical structure of bridging ethylene glycol between two calix[4]arenes. Nevertheless, all of calix[4]arene units in **2a**, **2b** and **3** are in cone conformation that can be identified from the appearance of the ArCH_2Ar signals as two doublets having J -coupling constants around 13 Hz. (spectrum shown in **Figures 2.3.1** and **2.3.2**)

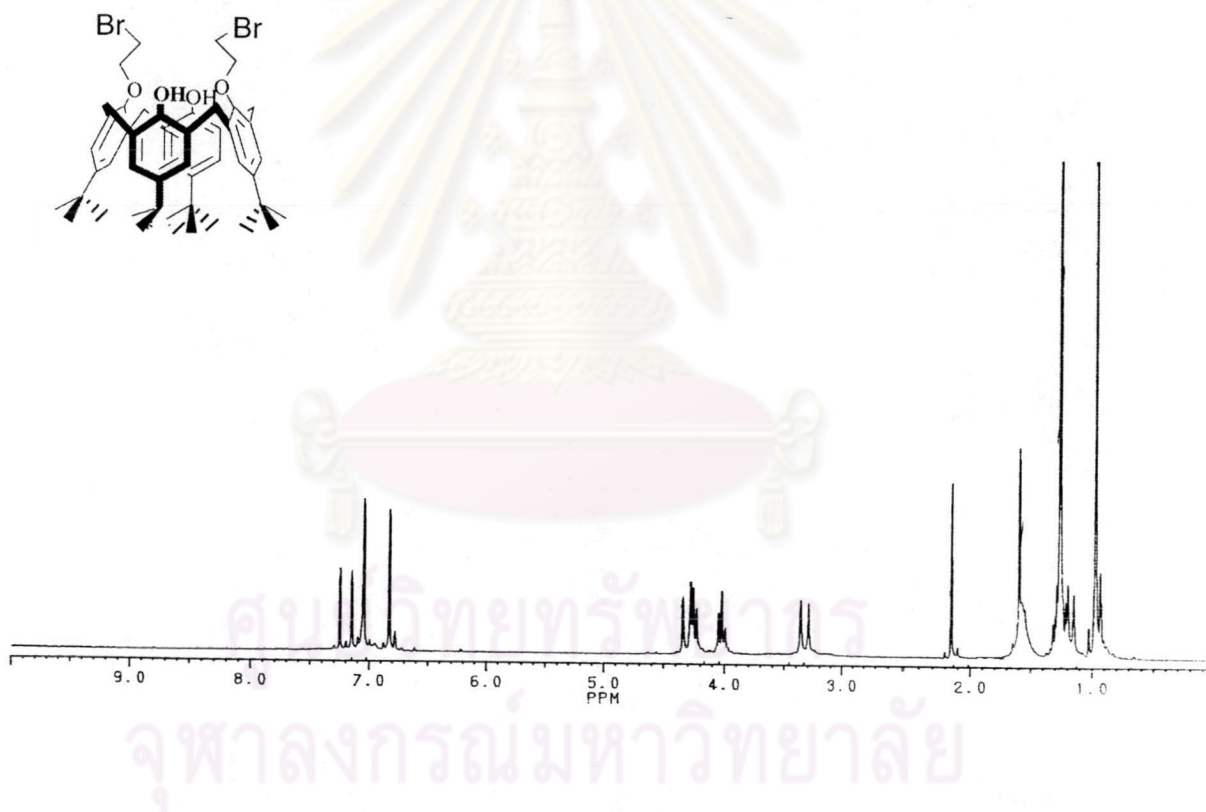


Figure 2.3.1 $^1\text{H-NMR}$ spectrum of Bisbromoethylcalix[4]arene (**2a**) in CDCl_3 with 200 MHz

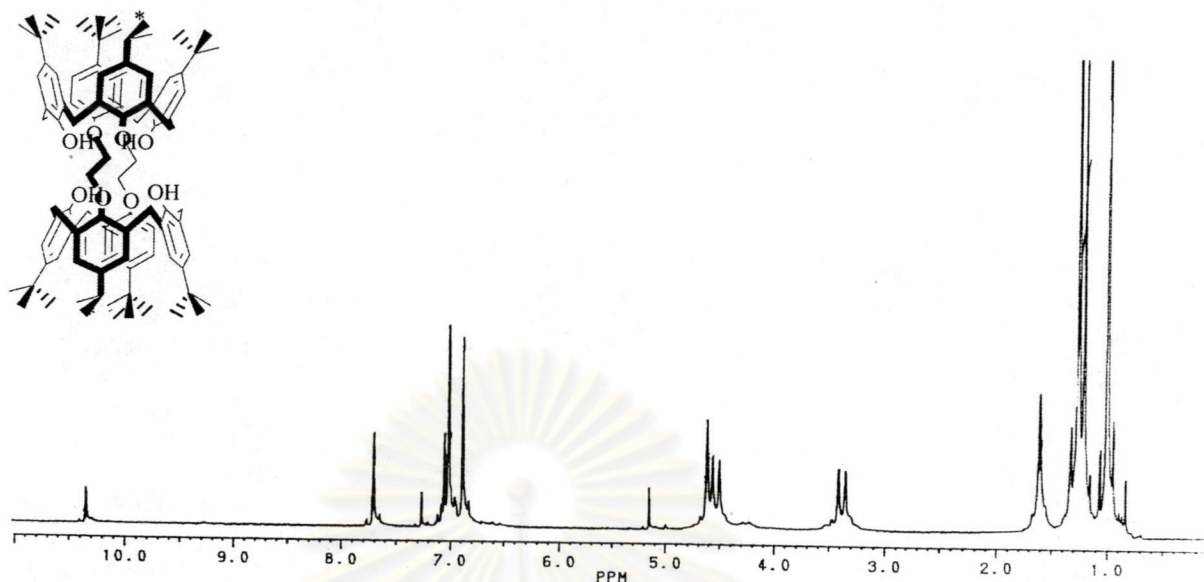


Figure 2.3.2 $^1\text{H-NMR}$ spectrum of calix[4]arene dimer (**3**) in CDCl_3 with 200 MHz

The alkylation of the metallo nucleophile $\text{Ni}(\text{bme-daco})$ with dichloroethylcalix[4]arene (**2b**) are shown in **Scheme 2.3.1**. The solution of dichloroethylcalix[4]arene (**2b**) was stirred with NaI acting as a catalyst. The exchange of Cl^- by I^- facilitates the nucleophilic substitution reaction to take place. Subsequently, the purple solution of $\text{Ni}(\text{bme-daco})$ was added dropwise into the reaction and the reaction mixture was allowed to reflux under nitrogen atmosphere for 48 hours. The solution gradually turned dark red. The mixture was then separated on silica gel column using a mixture of 15% methanol and dichloromethane as eluent to afford the yellowish green Ni calix[4]arene complex (**4b**) in 11% yield, an unidentified green complex and the bis Ni -calix[4]arene complex (**5**) in 35% yield. In the case of unidentified green complex, the result of MALDI-TOF MS showed a molecular ion peak at 1026.0 m/z , which matched closely to the molecular mass of the one arm substituted complex shown at 1029.56 m/z corresponding to $[\text{C}_{58}\text{H}_{82}\text{O}_4\text{N}_2\text{S}_2\text{NiCl}]^+$. Nonetheless, no other evidences supported the MS result because $^1\text{H-NMR}$ spectrum is too broad to deduce the structure. Moreover, the distribution of the products depends extremely on the concentration of reagents for **route B**. More concentration increased the yield of bis Ni -calix[4]arene complex (**5**) and decreased that of Ni -calix[4]arene (**4b**). On the other hand, a reaction of $\text{Ni}(\text{bme-daco})$ and dibromoethylcalix[4]arene (**2a**) in CH_3CN

was refluxed under nitrogen for 48 hours resulting in higher yield (18%) of the green Ni-calix[4]arene complex (**4a**). As illustrated in of **route A**, it is not necessary to put NaI into reaction since bromide atom is labile enough to undergo nucleophilic substitution reaction; therefore, the concentration of the reaction has no influence on the appearing of bisNi(bme-daco).

Ni-calix[4]arene complex (**4**) and BisNi-calix[4]arene (**5**) were characterized by $^1\text{H-NMR}$ and MALDI-TOF MS. Their $^1\text{H-NMR}$ spectra were broad in $\sim 2\text{-}4$ ppm due to the effect of the paramagnetic contribution from the nickel centers. Some characteristic of the complexes can, however, be deduced when compared the integral ratio of proton signals appearing in the range of 2-4 ppm belonging to the segment of Ni(bme-daco), $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}-$, the methylene bridges between the phenolic units and the ethylene bridges on the lower rim of calix[4]arene. According to $^1\text{H-NMR}$ spectrum of the Ni-calix[4]arene (**4**), the existence of AB system in the region of 3-4 ppm indicated that the complex is in cone conformation. The integral ratio of the signals of aromatic protons of calix[4]arene component and the proton signals in 1.93-4.30 region possessing the methylene bridge (8H), $-\text{CH}_2-$ in the part of Ni(bme-daco) (12H) and the ethano bridges displacing OH moiety (16H) is 8:36 implying to Ni-calix[4]arene (**4**) in 1:1 proportion of Ni(bme-daco) and calix[4]arene framework (**Figure 2.3.3**). In addition, the result of MALDI-TOF MS of compound (**4**) showed a molecular ion peak at 935.5 m/z, which corresponds to its molecular mass when stripped off NiI_2 . Usually, the thiolate is a better donor comparing to the thioether. It is assumed that the complex can readily lose the nickel ion to produce a free ligand. In the case of bisNi-calix[4]arene (**5**), $^1\text{H-NMR}$ spectrum exhibits the integral ratio between the aromatic protons of calix[4]arene and the proton signals in 1.48-4.40 region as 8:56. This indicates that the complex contains 1 building block of calix[4]arene and 2 units of Ni(bme-daco) on hydroxy group (**Figure 2.3.4**). Mass spectrum show two molecular ion peaks at 1412.1 and 1227.2 m/z corresponding to the $[\text{C}_{68}\text{H}_{102}\text{O}_4\text{N}_4\text{S}_4\text{Ni}_2]^+$ ion and the $[\text{C}_{68}\text{H}_{103}\text{O}_4\text{N}_4\text{S}_4\text{Ni}]^+$ ion, respectively. These results thus agree with the proposed structures of Nicalix[4]arene (**4**) and bisNicalix[4]arene

(5). We have tried to characterize both compounds by elemental analysis but the results are not acceptable. Possibly, it has the influence of the mixed counter ions of Cl^- and I^- , which take place from the preparation procedure involving both Cl^- and I^- . However, the elemental analysis result of Nicalix[4]arene (**4a**) having 2 atoms of Br^-

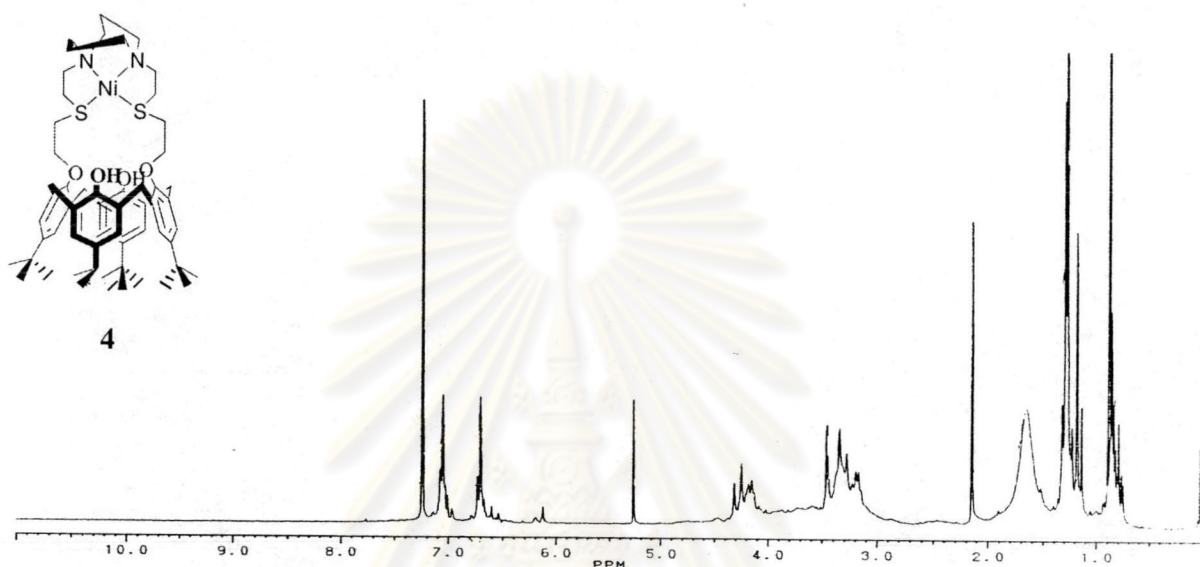


Figure 2.3.3 $^1\text{H-NMR}$ spectrum of Ni(bme-daco)ethylcalix[4]arene(**4**) in CDCl_3 with 200 MHz

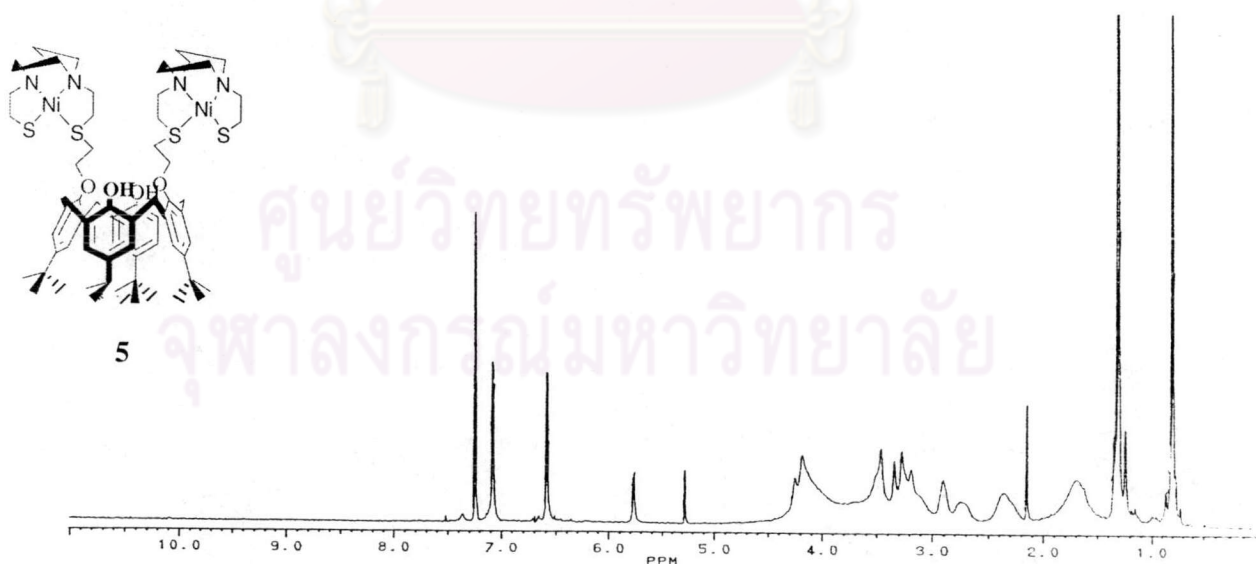


Figure 2.3.4 $^1\text{H-NMR}$ spectrum of BisNi(bme-daco)ethylcalix[4]arene(**5**) in CDCl_3 with 200 MHz

as counter anions agrees with the proposed structure accompanied with 2 water molecules. Moreover, the $^1\text{H-NMR}$ spectrum of Nicalix[4]arene (**4a**) is broader than that of Nicalix[4]arene (**4b**). We presumed that the geometry of Ni-complex converted from square planar geometry (diamagnetic) with Γ to distorted tetrahedral geometry (paramagnetic) with Br^- .⁵⁹ Upon addition of excess KCN into the solution of Ni-calix[4]arene (**4**) in CH_3CN resulted in immediate decolorization of the yellowish green solution.(Scheme 2.3.2) Upon working up the free ligand was obtained **6** in 92%.



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