การสังเคราะห์สารประกอบ 25,27-[เอ็น,เอ็น′-ได-((2-เอทอกซี)เบนซิล)โพรพิลีนไดเอมีน]-26,28-ไดเมทอกซี-พารา-เทอร์เชียรี-บิวทิลคาลิก[4]ซารีน ไดไฮโดรคลอไรด์ และการทดสอบความเป็นเบสและการเกิดสารประกอบเชิงซ้อนกับโลหะแทรนซิชันไอออนบางชนิด

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SYNTHESIS OF 25,27-[*N,N'*-DI-((ETHOXY)BENZYL)PROPYLENEDIAMINE]-26,28-DIMETHOXY-*p-tert*-BUTYLCALIX[4]ARENE DIHYDROCHLORIDE AND INVESTIGATION OF ITS BASICITY AND COMPLEXATION WITH SOME TRANSITION METAL IONS

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การสังเคราะห์สารประกอบ 25,27-[เอ็น,เอ็น′-ได-((2-เอทอกซี)เบนซิล)โพรพิลีนไดเอมีน]-26,28-ได-เมทอกซี-พารา-เทอร์เชียรี-บิวทิลคาลิก[4]ซารีน ไดไฮโดรคลอไรด์ (**7**, **L**.2HCl) ซึ่งเป็นอนุพันธ์แอมโมเนียมของสารประกอบไดเอซาคาลิก[4]ซารีนเตรียมโดยการเมทิลเลทฟีนอกซีออกซิเจนของไดอัลดีไฮด์คาลิก[4]ซารีนด้วย CH_3I หลังจากนั้นนำสารประกอบ methylated dialdehyde ไปทำปฏิกิริยากับ 1,3-ไดอะมิโนโพรเพน ได้สารประกอบซิฟเบส ซึ่งนำไปรีดิวซ์ด้วย $NaBH_4$ และโปรโตเนทด้วย 2% HCl ใน CH_3OH นำสารประกอบ **L**.2HCl ไปศึกษา conformational isomerism โดยวิธีโปรตอนเอ็นเอ็มอาร์สเปกโตรสโกปี โปรตอนเอ็นเอ็มอาร์สเปกตรัมของ **L**.2HCl ใน $CDCl_3$ และใน DMSO-d_6 แสดงให้เห็นว่าคาลิก[4]ซารีนมีการจัดตัวแบบโครงรูปผสม อย่างไรก็ดี เอ็นเอ็มอาร์สเปกตรัมใน CD_3OD บ่งบอก ถึงโครงรูปแบบโคน เมื่อค่อยๆเติม CD_3OD ลงในสารละลาย $CDCl_3$ ของ **L**.2HCl พบว่าพันธะไฮโดรเจนระหว่างโมเลกุลของ $CD_3O\boldsymbol{H}$ กับ $CH_3\boldsymbol{O}$Ar-*t*-C_4H_9 ยึดโครงรูปของคาลิก[4]ซารีนให้อยู่ในรูปโคน การทดลองที่อุณหภูมิต่างๆกันของ **L**.2HCl ในสารละลายผสม $CD_3OD/CDCl_3$ แสดงถึงกลไกการเคลื่อนที่ที่อาจเป็นไปได้ของวงเฟนนิลและบ่งบอกว่าโครงรูปแบบ pinched cone จะเกิดขึ้นที่อุณหภูมิ –40 °C

นอกจากนี้ได้มีการศึกษาหาค่าคงที่ของการรับโปรตอนของ **L** โดยวิธีโพเทนชิโอเมทริกไทเทรชัน (potentiometric titration) ใน $1x10^{-2}$ M $Bu_4NCF_3SO_3$ ในเมทานอล พบว่าค่า Log K_1 (Log K_2) ของการรับโปรตอนตัวแรก (ตัวที่สอง) คือ 10.06 (6.67), 9.97 (6.75), 9.61 (6.64), 9.75 (6.77) และ 9.69 (6.68) ที่อุณหภูมิ 20, 23, 25, 27 และ 30 °C ตามลำดับ ค่าฟังก์ชันทางเทอร์โมไดนามิก ΔH_1, ΔH_2, ΔS_1 และ ΔS_2 ที่คำนวณได้สำหรับการรับโปรตอนตัวแรกและตัวที่สอง มีค่าเป็น –67 kJ/mol, 3 kJ/mol, -38 kJ/mol·K และ 137 KJ/mol·K ตามลำดับ ในการศึกษาการเกิดสารประกอบเชิงซ้อนของ **L** กับไอออนของ Zn^{2+} และ Cu^{2+} ด้วยวิธีเดียวกัน พบว่า **L** ไม่เกิดสารประกอบเชิงซ้อนกับไอออนทั้งสองชนิด

ภาควิชาเคมี ..... **ลายมือชื่อนิสิต**.....

สาขาวิชาเคมี ..... **ลายมือชื่ออาจารย์ที่ปรึกษา**.....

ปีการศึกษา2541 ..... **ลายมือชื่ออาจารย์ที่ปรึกษาร่วม**.....

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SUDARATH VERAVONG : SYNTHESIS OF 25,27-[*N,N'*-DI-((ETHOXY)BENZYL) PROPYLENEDIAMINE]-26,28-DIMETHOXY-*p-tert*-BUTYLCALIX[4]ARENE DIHYDROCHLORIDE AND INVESTIGATION OF ITS BASICITY AND COMPLEXATION WITH SOME TRANSITION METAL IONS, THESIS ADVISOR ASSOC. PROF. VITHAYA RUANGPORNVISUTI, Dr. rer. nat., THESIS CO-ADVISOR : ASSIST. PROF. THAWATCHAI TUNTULANI, Ph.D. 112 pp. ISBN 974-331-216-1.

25,27-[*N,N'*-di-((ethoxy)benzyl)propylenediamine]-26,28-dimethoxy-*p-tert*-butylcalix[4]arene dihydrochloride (7, **L.2HCl**), an ammonium derivative of diaza calix[4]arene, was prepared by methylating phenoxy oxygen of dialdehyde calix [4]arene with CH_3I. The methylated dialdehyde was then reacted with 1,3-diaminopropane to give a Schiff base compound which was then reduced with $NaBH_4$ and protonated with 2% HCl in CH_3OH. The conformational isomerism of **L.2HCl** was studied by ^1H NMR spectroscopy. ^1H NMR spectra of **L.2HCl** in $CDCl_3$ and in DMSO-d_6 showed that the calix[4]arene moiety orientated in mixed conformations. However, the ^1H NMR spectrum in CD_3OD indicated cone conformation. Gradual additions of CD_3OD into a $CDCl_3$ solution of **L.2HCl** revealed that intermolecular hydrogen bonding between methanol and CH_3OAr-*t*-C_4H_9 held the calix[4]arene framework in cone conformation. Variable temperature experiments of **L.2HCl** in a mixed solvent of $CD_3OD/CDCl_3$, implied a possible mechanism of phenyl ring movement and suggested that a pinched cone conformation was preferred at –40 °C

In addition, protonation constants of **L** were calculated in methanolic solution of $1x10^{-2}$ M $Bu_4NCF_3SO_3$ by potentiometric titration. Log K_1 (Log K_2) values of the first protonation (second protonation) were 10.06 (6.67), 9.97 (6.75), 9.61 (6.64), 9.75 (6.77) and 9.69 (6.68) at 20, 23, 25, 27 and 30 °C, respectively. Calculated thermodynamic functions, ΔH_1, ΔH_2, ΔS_1 and ΔS_2 for the first and second protonations were –67 kJ/mol, 3 kJ/mol, -38 kJ/mol·K and 137 kJ/mol·K, respectively. Complexation studies of **L** with Zn^{2+} and Cu^{2+} ions by the same method showed that **L** could not form complexes with both ions.

ภาควิชา เคมี ลายมือชื่อนิสิต Sudarath Veravong

สาขาวิชา เคมี ลายมือชื่ออาจารย์ที่ปรึกษา

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α_c	degree of formation
β_n	overall stoichiometric stability constant for ML_n
°C	degree Celcius
ΔG	free energy change
ΔH	enthalpy energy change
ΔS	entropy change
e_i	error associated with the i^{th} component
E	observed potential (e.m.f.)
E°	standard potential
ϕ	degree of complex formation
γ	activity coefficient
ln	logarithm to base e
log	logarithm to base 10
M	metal
μ	ionic strength
ML	mononuclear complex
n	(in association with ligand) number of ligands in a complex
$\bar{n}$	complex formation function
o	experimental observations
$\prod$	product
$\bar{p}$	protonation formation function
pX	$-\log_{10}[X]$
$\sum$	sum
T	absolute temperature
[ ]	concentration
$[\ ]_T$	total concentration

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