ELSEVIER

Inorganica Chimica Acta 228 (1995) 133–138

Inorganica Chimica Acta

Preparation of a flexible binucleating ligand, xylylene-bridged biscyclam α,α'-bis(1,4,8,11-tetraazacyclotetradecan-6-yl)-*p*-xylene and structure of its dinickel(II) complex

Hiroaki Kido *[,1], Makoto Takada, Masaaki Suwabe, Tadashi Yamaguchi, Tasuku Ito *

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Received 29 March 1994; revised 3 June 1994

Abstract

A binucleating ligand, xylylene-bridged biscyclam α,α'-bis(1,4,8,11-tetraazacyclotetradecan-6-yl)-*p*-xylene ((cyclam)$_2$-*p*-xyl) was prepared from α,α'-dichloro-*p*-xylene, diethylmalonate and 1,4,8,11-tetraazaundecane in three steps. The second step, aminolytic condensation of the tetraamine was critical. The ligand yielded a dinickel(II) complex [Ni$_2$(cyclam)$_2$-*p*-xyl](ClO$_4$)$_4\cdot$4H$_2$O. X-ray crystal analysis of the complex disclosed opposite and almost perpendicular occupation of the macrocycles to the bridging benzene ring through equatorial connection at the 6-carbons. Crystal data: tetragonal space group $P4_2$, $a = 15.251(2)$, $c = 9.821(2)$ Å, $V = 2284.3(6)$ Å^3, $Z = 2$. It is anticipated that conformational change in solution due to free rotation around the methylene carbon at the junction puts the macrocycles into face-to-face location with Ni–Ni distance of ~7.7 Å.

Keywords: Crystal structures; Electrochemistry; Nickel complexes; Binucleating ligand complexes; Azamacrocycle complexes; Dinuclear complexes

1. Introduction

Linking two saturated azamacrocycles at the carbon position to a rigid benzene ring through full free rotating tetrahedral methylene groups affords a flexible binucleating ligand as to mutual location of the macrocycles. They can approach each other very closely above one side of the benzene ring, even to the face-to-face position. Such a ligand with a pure hydrocarbon spacer, xylylene group, is expected to yield flexible homo- and heterobimetallic complexes with interesting properties due to metal–metal (M–M) interactions. These could also fix small molecules and anions between the metal ions at a preferred M–M distance and orientation of the macrocycles. Linkage of the spacer to a carbon atom (not to a ligating atom) and through a methylene group to the macrocycles also minimizes the electronic and steric effects of the substituent group in sustaining the natures of the original unlinked macrocycles.

Such a ligand has not been prepared, although a couple of complexes of xylylene bridged ligands, a Cu$^{I}_2$ complex of 1,4-bis(1-oxa-4,10-dithia-7-azacyclododecan-7-ylmethyl)benzene [1] and Ni$^{II}_2$ and Cu$^{II}_2$ complexes of 11,11′-*p*-xylylenebis(1,4,8,11-tetraazacyclotetradecane) [2] have been reported. However, they are connected at the nitrogen atom and the macrocycles are located rather distantly. An Ni$^{II}_2$ complex of connected tetraazamacrocycles with the isophthaloyl group, 6,6′-isophthaloylbis(5,7-dimethyl-1,4,8,11-tetraazacyclotetra-4,6-dienato)dinickel(II) iodide has been reported [3]. Linkage of trigonal carbonyl carbons to rather flat and unsaturated macrocycles affords a lower freedom of flexible movement to the ligand than that given with totally tetrahedral connection, as mentioned above. The well-studied macrocycle, cyclam [4], was also linked directly at the 6-C atoms to give bicyclam (6,6′-bi-1,4,8,11-tetraazacyclotetradecane) and its mixed Ni^{II}/Cu^{II} complex with a rather flat structure about the macrocycles [5]. Cyclam complexes have recently been paid attention because of their reactivity toward CO$_2$ [6,7].

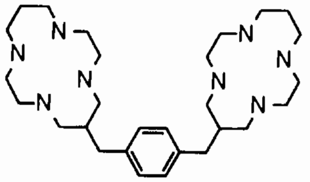
We have prepared a simple biscyclam ligand with potential proximity between the macrocycles, as mentioned above. Further we report the preparation and structure of the dinickel(II) complex of the ligand.

---

* Corresponding authors.

[1] Present address: Department of Industrial Chemistry, College of Engineering, Nihon University, Koriyama 963, Japan.

SSDI 0020-1693(94)04165-R



$(cyclam)_2$-*p*-xyl

Recently, we reported an extensive dinucleating ligand comprised of two dimethylcyclams bridged with an *ortho*-xylylene group and its dinickel(II) and dizinc(II) complexes with a cofacial ring arrangement due to axial positioning of the xylylmethyl to the macrocycles [8].

2. Experimental

2.1. Materials

Ethylenediamine, 1,3-dibromopropane, α,α'-dichloro-*p*-xylene and diethylmalonate were of reagent grade from Wako. The borane–tetrahydrofuran complex in THF was purchased from Aldrich. 1,4,8,11-Tetraazaundecane (2,3,2-tet) was prepared from ethylenediamine and 1,3-dibromopropane on the basis of the reported procedure for 3,2,3-tet [9]. 6-Benzyl-1,4,8,11-tetraazacyclotetradecane (benzylcyclam) [10] and its Ni^{II} complex [11] were prepared by procedures reported in the literature.

2.2. Apparatus

^1H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra in $CDCl_3$ or DCl (20wt.%) in D_2O were recorded precisely with a JEOL GSX-270.

2.3. Preparations

2.3.1. α,α'-Bis[bis(ethylcarboxy)methyl]xylene (1)

To sodium ethoxide solution in ethanol (sodium 34.5 g (1.5 mol) + anhydrous ethanol 750 ml), diethylmalonate (250 g, 1.5 mol) was added dropwise with vigorous stirring for 30 min. To the resulting turbid solution, α,α'-dichloro-*p*-xylene (131.5 g, 0.75 mol) was added portionwise (10 g/10 min) and the mixture was refluxed for 10 h with stirring. After removing NaCl by filtration at room temperature, the filtrate was concentrated by rotary evaporation to an oily residue, from which NaCl was again removed by extraction using water and ether. The ether layer was distilled after drying (Na_2SO_4) to give colorless oil of **1** (53 g, 17%) at ~200 °C under reduced pressure ($\sim 5 \times 10^{-3}$ mmHg). The product was checked by ^1H NMR ($CDCl_3$): δ 1.19 (12H, t, $-OCH_2CH_3$), 3.18 (4H, d, $-CH_2-$), 3.61 (2H, t, $-CH-$), 4.13 (8H, q, $-OCH_2CH_3$), 7.11 (4H, s, $-C_6H_4-$); ^{13}C NMR ($CDCl_3$): δ 13.72 ($-OCH_2CH_3$), 34.00 ($-CH_2-$), 53.12 ($-CH-$), 61.08 ($-OCH_2CH_3$), 128.70 ($-C_6H_4-$), 136.08 ($-C_6H_4-$), 168.49 (CO).

2.3.2. α,α'-Bis(1,4,8,11-tetraazacyclotetradecan-5,7-dione-6-yl)-p-xylene (2)

1 (66.3 g, 0.15 mol) and 1,4,8,11-tetraazaundecane, 2,3,2-tet (48 g, 0.3 mol) were gently refluxed under high dilution conditions in anhydrous ethanol (3 l) for 7 days under a slow stream of N_2. Rotary evaporation at 30–40 °C of the resulting viscous solution to 1/10–1/20 in volume resulted in a white precipitate, which was filtered and washed with a small amount of cold ethanol and with ether. The white powder, **2** (yield 1.7 g, 2.4%), was confirmed to be pure by ^1H NMR (DCl/D_2O): δ 1.87 (4H, q, $-CH_2-$), 2.9–3.6 (30H, m, four $-CH_2-$, $-CH-$), 7.01 (4H, s $-C_6H_4-$); ^{13}C NMR (DCl/D_2O): δ 22.19, 37.96, 45.36, 46.88 (four $-CH_2-$), 34.34 ($-CH_2-C_6H_4-$), 56.36 ($-CH-$), 129.77, 136.79 ($-C_6H_4-$), 172.75 (CO).

2.3.3. α,α'-Bis(1,4,8,11-tetraazacyclotetradecan-6-yl)-p-xylene, $(cyclam)_2$-p-xyl (3)

1.12 g (2 mmol) of **2** were dissolved in 200 ml of borane–tetrahydrofuran complex, '1.0 M' solution in tetrahydrofuran from Aldrich, and the mixture was stirred for 1 h under N_2 atmosphere at ice bath temperature, and then refluxed for 24 h. To the resulting turbid solution, 12 ml of 6 N HCl were added to decompose unreacted borane, and then 200 ml of water were added to obtain a clear solution, which was concentrated by rotary evaporation to half its volume to form a white precipitate, which was removed by filtration and washed thoroughly with chloroform. The filtrate was evaporated to half its volume after alkalizing (pH > 11) with saturated KOH solution in methanol to yield a turbid solution, which was extracted with chloroform together with the chloroform washings mentioned above. The organic layer was dried with Na_2SO_4 and evaporated to dryness to yield a white powder, **3** (yield 0.4 g, 40%), which was checked by ^1H NMR: δ 2.20 (4H, q, $-CH_2-$), 3.1–3.6 (38H, m, six $-CH_2-$, $-CH-$), 7.26 (4H, s); ^{13}C NMR: δ 21.17, 36.10, 42.31, 43.15, 43.97 ($-CH_2-$, $-CH-$), 34.79 ($-CH_2-C_6H_4-$), 130.49, 136.62 ($-C_6H_4-$).

No residual peaks other than those of the solvents were recorded for **1**, **2** and **3**.

2.3.4. $[Ni_2(cyclam)_2\text{-}p\text{-}xyl](ClO_4)_4 \cdot 4H_2O$, α,α'-Bis(1,4,8,11-tetraazacyclotetradecane-6-yl)-p-xylene dinickel(II) perchlorate tetrahydrate

This was prepared by the standard method [11]. The ligand **3** (150 mg, 0.3 mmol) was dissolved in hot ethanol (10 ml), mixed with a ethanol solution of nickel perchlorate hexahydrate (220 mg, 0.6 mmol), and heated at 60–80 °C for 1 h to yield a yellowish orange precipitate, which was filtered after cooling at room temperature.

Table 1
Crystallographic data for $[Ni_2(cyclam)_2$-p-$xyl](ClO_4)_4 \cdot 4H_2O$

Formula	$C_{28}H_{62}N_8O_{20}Cl_4Ni_2$
a (Å)	15.251(2)
c (Å)	9.821(2)
V (Å^3)	2284.3(6)
Z	2
Formula weight	1090.1
Space group	$P4_2$ (No. 77)
T (°C)	20
ρ_{obs} (g cm^{-3})	1.595
ρ_{calc} (g cm^{-3})	1.585
μ (cm^{-1})	11.4
Transmission coefficient	0.940–0.992
R	0.056
R_w	0.070

Table 2
Atomic positional and equivalent thermal parameters for the complex cation of $[Ni_2(cyclam)_2$-p-$xyl](ClO_4)_4 \cdot 4H_2O$

Atom	x	y	z	B_{eq}
Ni	0.73901(5)	0.18757(5)	0.0030	2.87(3)
N(1)	0.7462(6)	0.1015(5)	−0.1435(9)	3.6(4)
N(4)	0.7340(5)	0.2726(5)	−0.1373(8)	2.8(3)
N(8)	0.7364(5)	0.2774(5)	0.147(1)	3.5(4)
N(11)	0.7408(5)	0.1005(5)	0.144(1)	3.5(3)
C(2)	0.7134(7)	0.1425(6)	−0.264(1)	4.4(5)
C(3)	0.7609(8)	0.2370(7)	−0.264(1)	4.5(5)
C(5)	0.7818(7)	0.3594(7)	−0.116(1)	3.9(4)
C(6)	0.7644(4)	0.4068(4)	0.008(2)	3.3(3)
C(7)	0.7935(6)	0.3548(6)	0.136(1)	2.9(4)
C(9)	0.7532(7)	0.2293(7)	0.284(1)	3.9(4)
C(10)	0.7172(8)	0.1459(8)	0.281(1)	5.0(5)
C(12)	0.6961(8)	0.0150(7)	0.132(1)	4.4(5)
C(13)	0.7252(5)	−0.0325(4)	0.004(2)	4.9(3)
C(14)	0.6971(7)	0.0152(7)	−0.121(1)	5.1(6)
C(15)	0.8083(4)	0.4978(4)	−0.002(2)	3.8(3)
C(16)	0.9075(4)	0.4985(3)	0.012(2)	3.2(3)
C(17)	0.9538(6)	0.4990(6)	0.128(1)	3.2(4)
C(18)	0.9546(7)	0.4997(7)	−0.113(1)	4.2(5)

$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{11}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{12}bb^*cc^* \cos\alpha)$.

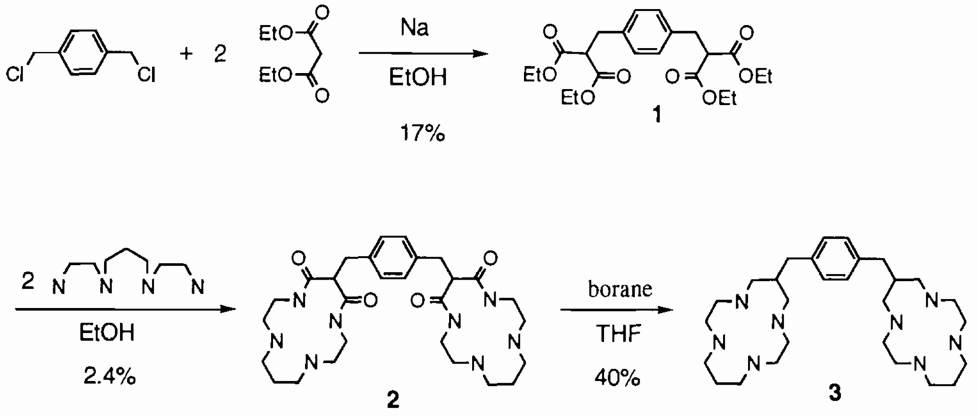
Table 3
Selected bond distances (Å) and angles (°) for $[Ni_2(cyclam)_2$-p-$xyl](ClO_4)_4 \cdot 4H_2O$

Bond distances			
Ni–N(1)	1.950(8)	C(2)–C(3)	1.61(1)
Ni–N(4)	1.893(8)	C(5)–C(6)	1.44(2)
Ni–N(8)	1.971(8)	C(6)–C(7)	1.55(2)
Ni–N(11)	1.920(8)	C(6)–C(15)	1.54(1)
N(1)–C(2)	1.43(1)	C(9)–C(10)	1.39(2)
N(1)–C(14)	1.53(1)	C(12)–C(13)	1.52(2)
N(4)–C(3)	1.42(1)	C(13)–C(14)	1.49(2)
N(4)–C(5)	1.53(1)	C(15)–C(16)	1.52(1)
N(8)–C(7)	1.47(1)	C(16)–C(17)	1.33(2)
N(8)–C(9)	1.55(1)	C(16)–C(18)	1.43(2)
N(11)–C(10)	1.55(1)	C(17)–C(17)	1.41(2)
N(11)–C(12)	1.48(1)	C(18)–C(18)	1.39(2)
Bond angles			
N(1)–Ni–N(4)	85.8(3)	N(1)–C(2)–C(3)	103.4(8)
N(1)–Ni–N(8)	177.3(3)	N(4)–C(3)–C(2)	102.3(8)
N(1)–Ni–N(11)	93.8(2)	N(4)–C(5)–C(6)	117.8(8)
N(4)–Ni–N(8)	92.7(2)	C(5)–C(6)–C(7)	112.0(5)
N(4)–Ni–N(11)	178.4(3)	C(5)–C(6)–C(15)	109(1)
N(8)–Ni–N(11)	87.8(3)	C(7)–C(6)–C(15)	113(1)
Ni–N(1)–C(2)	107.3(6)	N(8)–C(7)–C(6)	107.6(7)
Ni–N(1)–C(14)	116.5(7)	N(8)–C(9)–C(10)	110(1)
C(2)–N(1)–C(14)	108.8(8)	N(11)–C(10)–C(9)	109.7(9)
Ni–N(4)–C(3)	111.4(6)	N(11)–C(12)–C(13)	110.8(8)
Ni–N(4)–C(5)	118.3(6)	C(12)–C(13)–C(14)	111.4(6)
C(3)–N(4)–C(5)	108.4(8)	N(1)–C(14)–C(13)	113.3(9)
Ni–N(8)–C(7)	119.5(6)	C(6)–C(15)–C(16)	115.6(5)
Ni–N(8)–C(9)	107.0(6)	C(15)–C(16)–C(17)	127(2)
C(7)–N(8)–C(9)	110.2(7)	C(15)–C(16)–C(18)	115(2)
Ni–N(11)–C(10)	108.3(6)	C(17)–C(16)–C(18)	117.8(5)
Ni–N(11)–C(12)	123.0(7)	C(16)–C(17)–C(17)	122.0(7)
C(10)–N(11)–C(12)	111.0(8)	C(16)–C(18)–C(18)	120.2(6)

The product was purified by Sephadex C-25 chromatography; a yellowish orange band was eluted with 0.5 M NaCl aqueous solution, which gave a light purple powder by evaporation. After several times of desalting from an aqueous solution of the complex ion with ethanol, yellowish orange crystals of $[Ni_2(cyclam)_2$-p-$xyl](ClO_4)_4 \cdot 4H_2O$ (170 mg, 56%) were obtained by addition of an excess of sodium perchlorate. *Anal.* Calc. for $C_{28}H_{62}N_8O_{20}Cl_4Ni_2$: C, 30.85; H, 5.74; N, 10.28%. Found: C, 30.27; H, 5.28; N, 10.37%.

2.4. Crystal structure determination

An orange needle of $[Ni_2(cyclam)_2$-p-$xyl](ClO_4)_4 \cdot 4H_2O$ (0.8×0.25×0.15 mm) obtained from 0.5 mM aqueous $NaClO_4$ (0.1 M) solution was attached to a glass fiber and mounted on a Rigaku AFC-7S diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation. Cell constants were obtained from a least-squares refinement using the setting angles of 25 reflections in the range $27.2 < 2\theta < 29.7°$. Based on the systematic absence ($00l$: $l \neq 2n$) and the successful solution of the structure, the space group was determined to be $P4_2$ (No. 77). The data were corrected for Lorentz and polarization effects. Crystallographic and other experimental data are listed in Table 1 and Table S1 (see Section 4). The structure was solved by automatic Patterson analysis [12] and expanded using DIRDIF92 [13]. The non-hydrogen atoms were refined anisotropically. Hydrogen atom coordinates except those of the water molecules were calculated and fixed at those positions. Full-matrix least-squares refinement based on 1901 observed reflections ($I > 3.0\sigma(I)$) and 279 variable parameters was converged smoothly with unweighted and weighted agreement factors of $R = 0.056$ and $R_w = 0.070$, respectively. Final atomic positional and thermal parameters are listed in Table 2. Selected interatomic distances and angles are listed in Table 3.



Scheme 1.

All the calculations were performed using the teXsan crystallographic software package [14].

3. Results and discussion

3.1. Preparation of the ligand

Preparation was carried out in the sequence shown in Scheme 1, according to the method of Tabushi et al. for 6-benzyl-1,4,8,11-tetraazacyclotetradecane (benzylcyclam) [10], and that of Fabbrizzi et al. for 6,6′-bi-1,4,8,11-tetraazacyclotetradecane (bicyclam) [5,15]. The crucial process is the second step, aminolytic condensation of the aliphatic tetraamine with the tetraethyl ester **1** to give the double-ring macromolecule **2** in low yield. Gentle reflux and careful evaporation of the reaction mixture as mentioned in Section 2 resulted in a rather viscous solution from which the product was precipitated. Vigorous refluxing and fast or complete evaporation of the solution formed a rubber-like solid which is insoluble in organic solvents such as ethanol and acetone. In the preparation of benzylcyclam [9] and bicyclam [5], the yields for the corresponding process were 30% under ordinary and high dilution (concentration of the ester 0.05 mol/l) conditions, respectively, but such solidification was not reported. In the present preparation, in spite of high dilution ([**1**] = 0.05 mol/l), some polymerization seems to take place. It is considered to be caused by 'wrong' ring formation of 2,3,2-tet between different $-CH_2CH(COOEt)_2$ substituent groups across the benzene ring leaving two free −COOEt groups, which may facilitate polymerization by intermolecular aminolytic condensation. Simple intermolecular condensation seems to be slow, since efficient ring formation was accomplished for benzylcyclam, even under ordinary concentration. Such cross-condensation may not take place for bicyclam presumably because of the almost opposite directions of the $-CH_2CH(COOEt)_2$ groups. Such undesirable reactions and insufficient recovery of the product restrained by such solidification reduce the yield of **2**. Chromatographic separation of the product is expected to improve the yield, but further dilution of the reaction mixture may not be effective, since the undesirable reaction is initiated by the intramolecular process as considered.

Although the total yield of the objective compound **3** is low, it was obtained in gram-scale from easily obtainable starting materials.

3.2. Preparation and properties of the complex

For checking the ligation of the biscyclam **3**, the dinickel(II) complex was prepared as the perchlorate salt by the standard method [11]. $[Ni_2(cyclam)_2$-*p*-xyl$](ClO_4)_4 \cdot 4H_2O$ gave a d–d absorption peak at 450 nm ($\epsilon = 109$ M^{-1} cm^{-1}) in water. The λ_{max} value is the same as that for the corresponding mononuclear complex $[Ni(benzylcyclam)](ClO_4)_2$ and the molar extinction coefficient (ϵ) is slightly more than double ($\epsilon = 51$ M^{-1} cm^{-1}). Cyclic voltammograms of the bis complex (0.5 mM) were recorded under N_2 and CO_2 at the scan rate 100 mV s^{-1}, using glassy carbon, saturated calomel and Pt wire electrodes for working, reference and counter electrodes, respectively, in 0.1 M $NaClO_4$ aqueous solution (Fig. 1). Under N_2, a single couple of reductive and oxidative peaks was observed at −1.5(7) and −1.4(8) V versus SCE, respectively, corresponding to $Ni^{I/II}$ ($E_{1/2} = -1.5(3)$ V). No splitting of the wave was observed. These results indicate that there is no interaction between the Ni^{II} centers. Under CO_2 a more intense reductive current with onset at −1.2(5) V was recorded. The intensity of current and the onset voltage are very close under identical conditions to those reexamined for $[Ni(cyclam)]^{2+}$ (1.0 mM), for which electrocatalytic reduction of CO_2 to CO has been verified [6a]. Since the concentration of the Ni^{II} center of the bis complex corresponds to 1.0 mM, no cooperative effect of the centers was shown. The products of the reduction have not been checked.

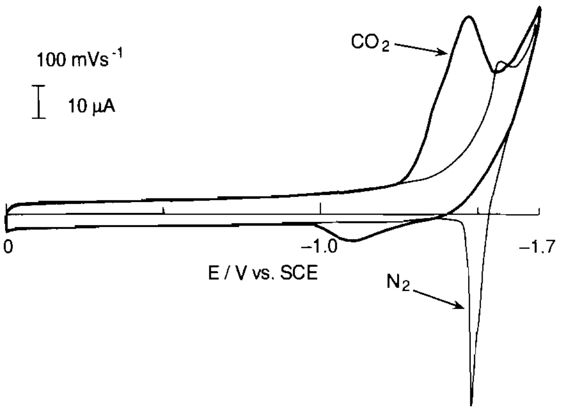
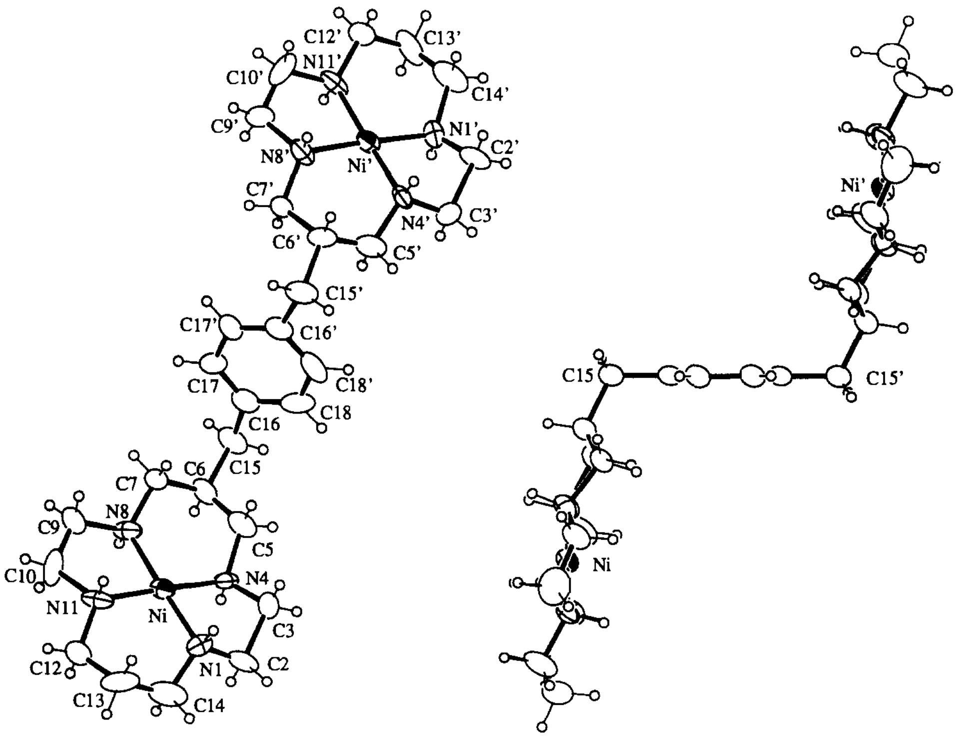


Fig. 1. Cyclic voltammograms of $[Ni_2(cyclam)_2\text{-}p\text{-}xyl](ClO_4)_4 \cdot 4H_2O$ (0.5 mM) under N_2 and CO_2 in 0.1 M $NaClO_4$ aqueous solution.

3.3. *Structure of the complex*

ORTEP drawings of $[Ni_2(cyclam)_2\text{-}p\text{-}xyl]^{4+}$ are shown in Fig. 2. The complex ion has a two-fold rotational axis passing across the benzene ring and bisecting the C(17) and C(17′), and C(18) and C(18′) bonds. Two cyclam rings stick out in entirely opposite directions from the benzene ring, and are parallel to each other. The xylylene group is an equatorial substituent to the macrocycles. The Ni(II) ion sits in the hole of the cyclam ring to give a typical square-planar four-coordinate geometry. The cyclam ring adapts stereochemically the most stable chair/gauche/chair/gauche conformation, so-called '*trans* III' type [16]. All the bond distances and angles are within the normal range (see Table 3). As shown in the side view in Fig. 2, we can assume a mean plane defined by all the non-hydrogen atoms with the macrocycle($NiC_{10}N_4$). The mean plane stands and is untwisted to the benzene face. It inclines to the outside by 10.0°. The NiN_4 face slanting to the mean plane by 12.9° is almost perpendicular (87.2°) to the central ring. Two perchlorates are located right above and below the NiN_4 face ($Ni \cdots O = 3.19$, 3.29 Å), and a water molecule is situated between the anions (see Section 4).

In the solid state, the bimetallic site is far separated and independent. Studies with a molecular model based on the solid structure afford a rough idea of the molecular structure of the bimetallic complex in solution. When the benzene ring is fixed for convenience, the macrocycles can move about by free rotations around two C–C bonds; one is between 1-C (or 4-C) of $-C_6H_4-$ and benzyl-C, and the other is between benzyl-C and 6-C of the macrocycle. The first rotation results in *cis* and *trans* conformers with respect to the benzene ring, as shown in Fig. 3. In the second rotation the distance and orientation between the macrocycles varies greatly in the *cis* conformer, since the mean plane of the macrocycle is slanted to the second C–C bond by 15.8°. In the most proximate position, the planes stand nearly vertical to the benzene moiety in a face-to-face location with an M–M distance of ~7.7 Å. In this case, the MN_4 planes tilted by 12.9° to the mean plane are almost vertical to the bridging ring (87.2°) and are roughly



Top view

Side view

Fig. 2. ORTEP drawing of $[Ni_2(cyclam)_2\text{-}p\text{-}xyl]^{4+}$.

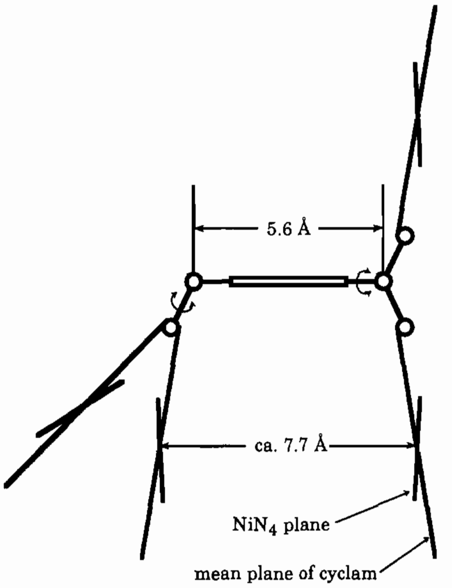


Fig. 3. Schematic illustration for the conformational change of $[Ni_2(cyclam)_2\text{-}p\text{-}xyl]^{4+}$, on the basis of the side view (Fig. 2), and by means of a molecular model.

parallel to each other. The second rotation of one macrocycle to the fixed one increases the M–M distance by ~2 Å. In the analogs bridged with *meta*- and *ortho*-xylylene groups, the M–M distance would be much reduced.

Some complexes of the ligand show interesting properties and reactivity specific of binucleation. The *cis*-conformer can fix a small molecule or an anion as a bridged ligand which would synergetically stabilize the conformer.

4. Supplementary material

Tables S1–S5, listing detailed crystallographic data, full atomic positional parameters, anisotropic thermal parameters, interatomic distances and bond angles, Fig. S1 showing the packing diagram of $[Ni_2(cyclam)_2\text{-}p\text{-}xyl](ClO_4)_4 \cdot 4H_2O$ (6 pages), and observed and calculated structure factors (7 pages) are available from author H.K.

Acknowledgements

This work was supported by a Grand-in-Aid for Scientific Research (No. 04241102 and No. 50020500) from the Ministry of Education, Science and Culture, Japan. We thank Mr T. Kajiwara and Mr S. Kawabata for his experimental assistance.

References

[1] J.E. Bulkowski, P.L. Burk, M.-F. Ludmann and J.A. Osborn, *J. Chem. Soc., Chem. Commun.*, (1977) 498.
[2] R. Schneider, A. Biesen and T.A. Kaden, *Helv. Chim. Acta, 69* (1986) 53.
[3] (a) N. Matsumoto, A. Hirano and A. Ohyoshi, *Bull. Chem. Soc. Jpn., 56* (1983) 891; (b) N. Matsumoto, M. Koikawa, N. Baba and H. Okawa, *Bull. Chem. Soc. Jpn., 65* (1992) 258.
[4] G.A. Melson (ed.), *Coordination Chemistry of Macrocyclic Compounds,* Plenum, New York, 1979.
[5] L. Fabbrizzi, L. Montagna, A. Poggi, T.A. Kaden and L.C. Siegfried, *Inorg. Chem., 25* (1986) 2671.
[6] (a) M. Beley, J.-P. Collin, R. Ruppert and J.-P. Sauvage, *J. Am. Chem. Soc., 108* (1986) 7461; (b) J.-P. Collin, A. Jouaiti and J.-P. Sauvage, *Inorg. Chem., 27* (1988) 1986.
[7] M. Kato and T. Ito, *Inorg. Chem., 24* (1985) 504, 509; *Bull. Chem. Soc. Jpn., 59* (1986) 285.
[8] T. Kajiwara, T. Yamaguchi, H. Kido, S. Kawabata, R. Kuroda and T. Ito, *Inorg. Chem., 32* (1993) 4990.
[9] E.K. Barefield, F. Wagner, A.W. Herlinger and A.R. Dahl, *Inorg. Synth., 16* (1976) 222.
[10] I. Tabushi, Y. Taniguchi and H. Kato, *Tetrahedron Lett., 12* (1977) 1049.
[11] B. Bosnich, M.L. Tobe and G.A. Webb, *Inorg. Chem., 4* (1965) 1109.
[12] *SAPI: Fan Hai-Fu,* structure analysis programs with intelligent control, Rigaku Corporation, Tokyo, Japan, 1991.
[13] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits and C. Smykalla, *DIRDIF92: the DIRDIF program system, Tech. Rep.,* Crystallography Laboratory, University of Nijmegen, Netherlands, 1992.
[14] *teXsan: Crystal Structue Analysis Package,* Molecular Structure Corporation, Woodlands, TX, 1985, 1992.
[15] L. Fabbrizzi, F. Forlimi, A. Perotte and B. Seghi, *Inorg. Chem., 23* (1984) 807.
[16] B. Bosnich, C.K. Poon and M.L. Tobe, *Inorg. Chem., 4* (1965) 1102.