ONE-POT SYNTHESIS OF TROPOCORONANDS HAVING HETEROATOMS IN LINKER CHAINS AND RELATED PODANDS[1]

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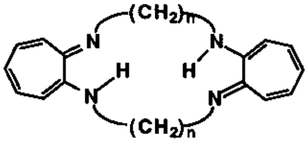
Abstract - Treatment of benzo[*b*]cyclohepta[*e*][1,4]oxazine (**4**) with 1.2 equiv. of dipropylenetriamine (**5a**) in ethanol at 80 °C gave 6,7,8,9,11,12,13,20,21,22,23,25,26,27-tetradecahydrodicyclohepta[*b*,*m*][1,4,8,12,15,19]hexaazacyclodocosine (**7a**). Similar reactions of **4** with *N*,*N*-bis(3-aminopropyl)methylamine (**5b**), bis(3-aminopropyl) ether (**5c**), 1,2-bis(2-aminoethoxy)ethane (**6b**), and cystamine (**6c**) afforded similar tropocoronands (**7b**, **7c**, **8a**, and **8b**), respectively, while the reactions of **4** with an excess of these amines gave the corresponding tropopodands (**11a**, **11b**, **11c**, **12a**, and **12b**). The reaction of **4** with diethylenetriamine (**6a**) yielded tricyclic compound (**10**) *via* bicyclic pyrazino compound (**9**). A single-crystal X-ray diffraction analysis of the nickel(II)-complex (**13**) obtained from **7a** was made.

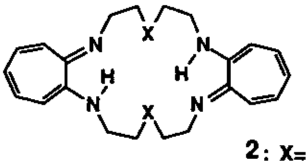
Previously, one of us, (T.N.) and his co-workers synthesized tropocoronands containing two aminotroponeimine units bridged by polymethylenes (**1**, n=2-6) or heteroatom-containing linker chains (**2**, X=O,S).[2] These crown-type compounds had been synthesized from reactive troponoids and α,ω-diaminoalkanes *via*

Dedicated to Professor Alan R. Katritzky on the occasion of his 65th birthday.

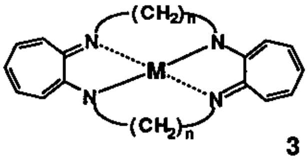
ditropones and then bis-enol ethers under high dilution conditions.[2] Although several interesting physicochemical properties were revealed for their transition metal complexes (**3**),[3] the overall yields of **1** were only 12-23%, and a more convenient synthetic method has been anticipated.



1



2: X=O,S

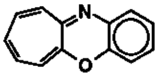


3

Recently, we reported a very convenient, one-pot synthesis of **1** by the reaction of **4** with α,ω–diaminoalkanes through an intermolecular heterocycle exchange reaction[4] in high yields without using a high dilution technique.[5] We wish to report here the synthesis of various tropocoronands having heteroatoms in the linker chains by the use of aforementioned method.[5]

Results and Discussion

Treatment of a solution of **4** with amines (1:1.2 - 6) in absolute ethanol at 80 °C for 20-30 h under an inert atmosphere yielded orange crystals or oils as the main products.[6] These showed similar uv absorption maxima



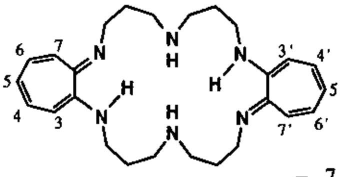
4

$H_2N\text{-}(CH_2)_3\text{-}X\text{-}(CH_2)_3\text{-}NH_2$

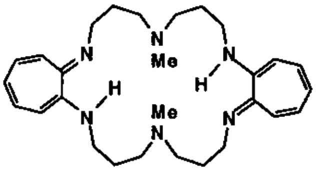
5a : X=NH
5b : X=NMe
5c : X=O

$H_2N\text{-}(CH_2)_2\text{-}X\text{-}(CH_2)_2\text{-}NH_2$

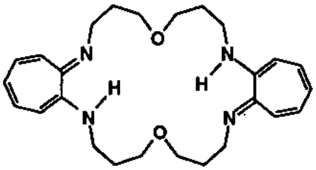
6a : X=NH
6b : X=O(CH$_2$)$_2$O
6c : X=S-S



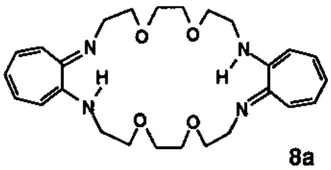
7a[7]



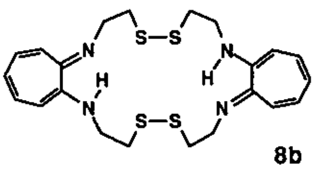
7b



7c

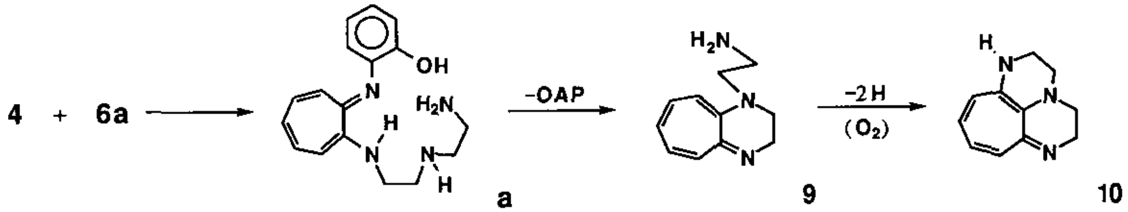


8a

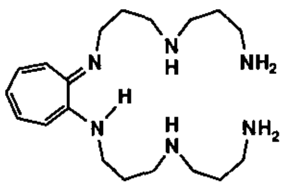


8b

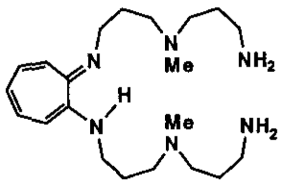
to the previously known tropocoronands and podands^{2,5} and the structures were determined on the basis of nmr, mass spectra, and elemental analysis (see Experimental section). The reaction of **4** with dipropylenetriamine (**5a**) in a 1:1.2 ratio gave orange crystalline precipitates (mp 198-200 °C) of coronand (**7a**). Compound (**7a**) showed uv absorption maxima at 260 (log ε 4.57), 325 (3.94), 346 (4.23), 357 (4.28), 378 (4.04), and 400-500 nm (4.14-3.05) which resemble to those of **1**, and ^{1}H nmr signals at δ=1.98 (m), 2.83 (t), and 3.36 (t) (8:8:8 proton ratio) due to methylene protons of symmetrical linker chains and at δ=6.14 (t), 6.27 (d), and 6.75 (dd) (2:4:4) due to five adjacent protons on the two seven-membered rings. The high resolution mass spectrum of **7a** gave a molecular ion peak at m/z 434.3174 closely agreeable with 434.3157 (M$^+$) calcd for $C_{26}H_{38}N_6$. From these spectra, the structure of **7a** was determined as 6,7,8,9,11,12,13,20,21,22,23,25,26,27-tetradecahydrodicyclohepta[*b,m*][1,4,8,12,15,19]hexaazacyclodocosine. Similar reactions of **4** with *N,N*-bis (3-aminopropyl) methylamine (**5b**), bis (3-aminopropyl) ether (**5c**), 1,2-bis (2-aminoethoxy)ethane



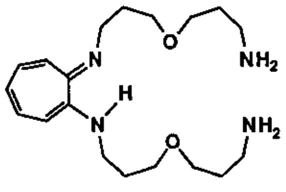
Scheme 1



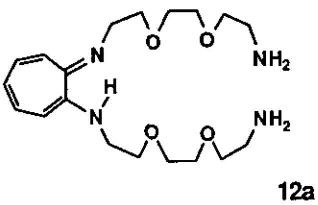
11a



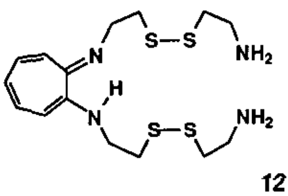
11b



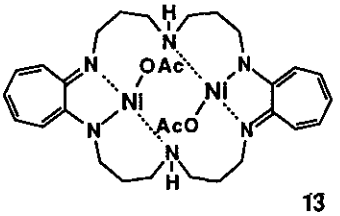
11c



12a



12b



13

(**6b**), and cystamine (**6c**) afforded tropocoronands (**7b**, **7c**, **8a**, and **8b**), respectively. However, the reaction of **4** with diethylenetriamine (**6a**) afforded bicyclic pyrazino compound (**9**). No tropocoronand (**2**: X=O) was produced under these reaction conditions. In the reaction of **4** with **6a** the initially formed intermediate **a** cyclized at imino-position in the chain to give pyrazino derivative (**9**) extruding *o*-aminophenol (**OAP**) under the anaerobic conditions. Compound (**9**) afforded easily dehydrogenated product (**10**) (Scheme 1). The reaction of **4** with those amines in a 1:4-6 ratio gave the corresponding podands (**11a**, **11b**, **11c**, **12a**, and **12b**).

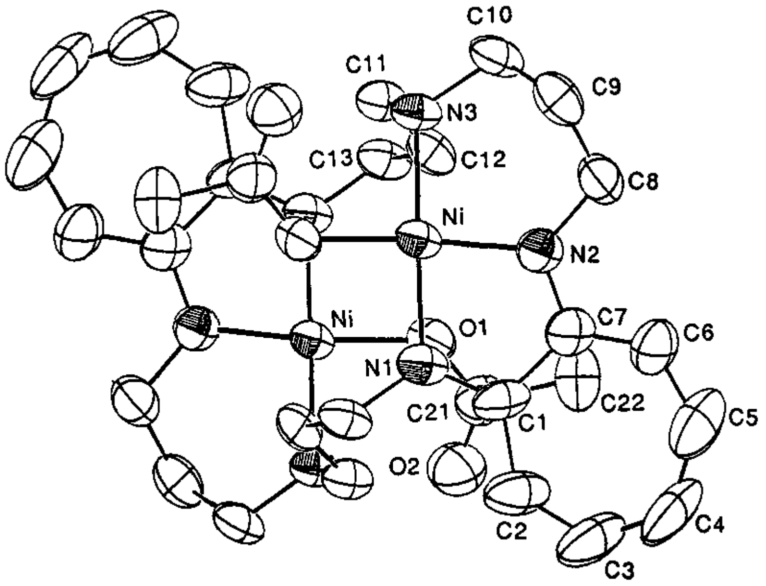
We then tried to synthesize metal complexes from ligand (**7a**) with nickel acetate tetrahydrate. The crystals of **13** recrystallized from a dichloromethane-ethanol solution are rhombohedral system with cell dimensions of a=23.985(5), c=14.990(7)Å, V=7466(4)Å^3, Z=9 in hexagonal system, and stable in the air over months. ORTEP drawing of **13** elucidated by an X-ray diffraction analysis is shown in Figure 1.[8] Selected bond

Table 1. Selected bond distances (Å) and angles (°) of **13**.

Ni-Ni	4.652(2)	C2-C3	1.38(2)	C9-C10	1.52(2)
Ni-N1	1.884(8)	C3-C4	1.37(2)	C10-N3	1.48(1)
Ni-N2	1.852(8)	C4-C5	1.39(2)	C3-C11	1.48(1)
Ni-N3	1.945(8)	C5-C6	1.37(2)	C11-C12	1.51(1)
Ni-O1	1.897(7)	C6-C7	1.40(2)	C12-C13	1.56(1)
Ni-C1	1.32(1)	C7-N2	1.33(1)	C21-C22	1.51(2)
C1-C2	1.42(2)	N2-C8	1.46(1)	O1-C21	1.30(1)
C1-C7	1.47(1)	C8-C9	1.51(2)	O2-C21	1.22(1)
N1-Ni-N2	82.6(3)	Ni-O1-C21	128.1(7)	C4-C5-C6	130.1(13)
N1-Ni-N3	168.9(3)	N1-C1-C2	124.4(9)	C5-C6-C7	131.1(11)
N1-Ni-O1	92.0(3)	N1-C1-C7	111.8(8)	C6-C7-N2	121.6(10)
N2-Ni-N3	96.5(3)	N2-C8-C9	111.7(9)	C7-N2-C8	119.1(8)
N2-Ni-O1	173.6(3)	N3-C11-C12	112.8(8)	C8-C9-C10	110.0(9)
N3-Ni-O1	89.5(3)	C1-C7-N2	111.9(9)	C9-C10-N3	112.3(9)
Ni-N1-C1	116.0(6)	C1-C7-C6	126.4(10)	C10-N3-C11	112.9(7)
Ni-N2-C7	115.9(7)	C1-C2-C3	130.6(11)	C11-C12-C13	113.8(8)
Ni-N2-C8	125.0(7)	C2-C3-C4	131.6(13)	O1-C21-O2	126.0(10)
Ni-N3-C10	120.0(6)	C2-C1-C7	123.7(9)	O1-C21-C22	113.3(10)
Ni-N3-C11	107.5(6)	C3-C4-C5	125.6(3)	O2-C21-C22	120.7(11)

distances and angles are listed in Table 1. The numberings given in Figure 1 and Table 1 is arbitrary. Two nickel (II) atoms, coodinated in a planer fashion, are 4.652Å apart, and bind two AcO groups situated on opposite sides of the seven-membered ring. Complex (**13**) is centrosymmetrical structure with dinuclear units.

Figure 1. ORTEP diagram of **13**.



EXPERIMENTAL

General methods: The melting points were determined with aYanagimoto MP-3S melting-point apparatus and were uncorrected. The ir and uv spectra were measured by using Shimadzu IR-450 and UV-265FS spectrophotometers, respectively. The nmr spectra were measured in $CDCl_3$ with a JEOL JNM-GX270 (270 MHz for ^1H and 67.8 MHz for ^{13}C) spectrometer using TMS as an internal standard. The assignments of all signals were made by employing a first-order analysis with the aid of a decoupling technique. The mass spectra were taken on a JEOL JMS-DX300 mass spectrometer at 70 eV. The tlc analyses and column chromatography were carried out with Merck Kieselgel 60F-254 plates and Wako gel C-200 using benzene-methanol and methanol-NaCl aq (1:1) as an eluent.

6,7,8,9,10,11,12,13,20,21,22,23,24,25,26,27-Hexadecahydrodicyclohepta[*b*,*m*][1,4,8,12,

15,19]hexaazacyclodocosine (7a): A solution of **4** (200 mg, 1.02 mmol) and **5a** (160 mg, 1.22 mmol) in absolute ethanol (2 ml) was heated at 80 $^{\circ}$C for 30 h under an argon atmosphere. After having been set aside overnight at 0-5 $^{\circ}$C, the orange precipitates which formed were combined with the second crop isolated by silica gel column chromatography and washed with cold methanol to give, upon recrystallization from chloroform-methanol, **7a** as yellow crystals (133 mg, 60%); mp 198-200 $^{\circ}$C; uv λ max (MeOH) 260 (log ε 4.57), 325 (3.94 sh), 346 (4.23), 357 (4.28), 378 (4.04), 414 (4.14), 434 (4.04 sh), 459 (3.78), 506 nm (3.05); ir (KBr) ν: 3200 cm^{-1}; ^{1}H nmr (270 MHz, $CDCl_3$) δ 1.98 (8H, m, CH_2), 2.83 (8H, t, J=7 Hz, CH_2), 3.36 (8H, t, J=7 Hz, CH_2), 6.14 (2H, t, J=9.5 Hz, H-5,5'), 6.27 (4H, d, J=11 Hz, H-3,3',7,7'), 6.75 (4H, dd, J=11 and 9.5 Hz, H-4,4',6,6'); ms (70eV) m/z 434 (M^{+}, 100%), 348 (17%), 271 (14%), 259 (19%), 230 (22%), 216 (35%), 190 (36%), 175 (42%). Found: m/z 434.3174. Calcd for $C_{26}H_{38}N_6$: M, 434.3156.

10,24-Dimethyl-6,7,8,9,12,13,20,21,22,23,26,27-11*H*,25*H*-dodecahydrodicyclohepta[*b,m*][1,4,8,12,15,19]hexaazacyclodocosine (7b): A solution of **4** (200 mg, 1.02 mmol) and **5b** (180 mg, 1.24 mmol) in absolute ethanol (2 ml) was heated at 80 $^{\circ}$C for 30 h under an argon atmosphere. After having been set aside overnight at 0-5 $^{\circ}$C, the oily precipitate which formed was dissolved in chloroform and chromatographed as described above to give **7b** (120 mg, 51%) as orange oil; uv λ max (MeOH) 261 (log ε 4.15), 348 (3.80), 361 (3.84), 424 (3.80), 461 (3.44), 510 nm (2.70); ir (KBr) ν: 3210 cm^{-1}; ^{1}H nmr (270 MHz, $CDCl_3$) δ 1.88 (8H, m, CH_2), 2.44 (8H, s, NCH_3), 2.47 (8H, m, CH_2), 3.30 (8H, m, CH_2), 5.85 (2H, br, NH), 6.11 (2H, t, J=9.6 Hz, H-5,5'), 6.25 (4H, d, J=11.0 Hz, H-3,3',7,7'), 6.71 (4H, dd, J=11.0 and 9.6 Hz, H-4,4',6,6'); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 27.68 (t, CH_2), 42.33 (q, CH_3), 44.47 (t, CH_2), 55.71 (t, CH_2), 110.25 (d, C-3,7), 117.69 (d, C-5), 133.05 (d, C-4,6), 152.98 (s, C-1,2); ms (70eV) m/z 462 (M^{+}, 17%), 195 (100%). Found: m/z 462.3485. Calcd for $C_{28}H_{42}N_6$: M, 462.3468.

6,7,8,9,12,13,20,21,22,23,26,27-Dodecahydro-11*H*,25*H*-dicyclohepta[*f,q*][1,12,5,8,16,19]dioxatetraazacyclodocosine (7c): The reaction of **4** with **5c** (mole ratio, 1:1.2) was conducted in a manner similar to that described above for **7b**, giving **7c** in 91% yield as orange oil; uv λ max (MeOH) 259 (log ε 4.53), 349 (4.21), 358 (4.21), 381 (4.03 sh), 415 (4.14), 463 (3.73 sh), 517 (3.21 sh), 638 nm (2.73 sh); ir (KBr) ν: 3240 cm^{-1}; ^{1}H nmr (270 MHz, $CDCl_3$) δ 1.99 (8H, m, CH_2), 3.39 (8H, t, J=6.5 Hz, CH_2), 3.55 (8H, t, J=6.5 Hz, CH_2), 4.80 (2H, br, NH), 6.11 (2H, t, J=9.5 Hz, H-5,5'), 6.28 (4H, d, J=11 Hz, H-3,3',7,7'), 6.72 (4H, m, J=11 and 9.5 Hz, H-4,4',6,6'); ms (70eV) m/z 436 (M^+, 100%), 363 (20%), 131 (65%). Found: m/z 436.2814. Calcd for $C_{26}H_{36}N_2O_2$: M, 436.2836.

7,8,10,11,13,14,22,23,25,26,28,29-Dodecahydro-*6H*,*21H*-dicyclohepta[*h*,*t*][1,4,13,16,7,10,19,22]tetraoxatetraazacyclotetraicosine (8a): The reaction of **4** with **6b** (mole ratio, 1:1.2) was conducted in a manner similar to that described above for **7b**, giving **8a** in 35% yield as orange crystal; mp 158-165 °C; uv λ max (MeOH) 259 (log ε 4.38), 349 (4.04), 360 (4.05), 410 (3.97), 420 (3.96), 458 (3.68, sh), 509 nm (3.17, sh); ir (KBr) ν: 3230 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 3.48 (8H, t, J=5.5 Hz, NCH_2), 3.78 (8H, s, OCH_2CH_2O), 3.90 (8H, t, J=5.5 Hz, OCH_2), 6.15 (2H, t, J=9.5 Hz, H-5,5'), 6.26 (4H, d, J=11.0 Hz, H-3,7,3',7'), 6.75 (4H, dd, J=11.0 and 9.5 Hz, H-4,6,4',6'); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 46.40 (t, CH_2), 70.74 (t, CH_2), 71.03 (t, CH_2), 110.44 (d, C-3,7), 117.97 (d, C-5), 133.11 (d, C-4,6), 153.35 (s, C-1,2); ms (70eV) m/z 468 (M^+, 68%), 393 (26%), 221 (50%), 131 (100%). Found: m/z 468.2707. Calcd for $C_{26}H_{36}N_4O_4$: M, 468.2734.

7,8,11,12,20,21,24,25-Octahydro-*6H*,*19H*-dicyclohepta[*f*,*p*][1,2,11,12,5,8,15,18]tetrathiatetraazacycloicosine (8b): A solution of **4** (200 mg, 1.02 mmol) and **6c** (163 mg, 1.07 mmol) in methanol (2 ml) was sealed in a small tube and heated for 5 h at 80 °C. After having been set aside overnight at 0-5 °C, the brown precipitates which formed were collected and washed with cold methanol to give, upon recrystallization (chloroform-methanol), **12** as orange crystals (212mg, 87%); mp 61-63 °C; uv λ max (MeOH) 257 (log ε 4.54), 348 (4.16), 362 (4.20), 418 (4.26), 463 nm (3.85); ir (KBr) ν: 3200 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 2.99 (8H, m, SCH_2), 3.60 (8H, m, NCH_2),5.62 (2H, br, NH), 6.18 (2H, t, J=9.5 Hz, H-5,5'), 6.28 (4H, d, J=11 Hz, H-3,3',7,7'), 6.74 (4H, m, J=11 and 9.5 Hz, H-4,4',6,6'); ms (70 eV) m/z 476 (M^+, 4%), 238 (28%), 204 (75%), 145 (92%), 131 (100%). Anal. Calcd for $C_{22}H_{28}N_4S_4$: C, 55.43; H, 2.10 ; N: 11.75. Found: C, 55.31; H, 2.37; N,11.52.

***N*-[2-[(7-Amino-4-azaheptyl)amino]-2,4,6-cycloheptatrienylidene]-4-aza-1,7-heptanediamine (11a):** A mixture of **4** (100 mg, 0.51 mmol) and **5a** (408 mg, 3.11 mmol) in absolute ethanol (1.5 ml) was heated at 80 °C for 30 h under an argon atmosphere. After concentration in vacuo, the residue dissolved in chloroform was washed with aqueous 20% NaOH and water, dried over magnesium sulfate and then concentrated in vacuo to give **11a** (129 mg, 73% yield) as orange oil; uv λ max (MeOH) 250 (log ε 4.19), 266 (4,13 sh), 343 (3.86), 357 (3.84), 407 (3.81), 437 (3.57 sh), 460 nm (3.24 sh); ir (neat) ν: 3350 and 3260 cm^{-1}; ^{1}H nmr (270 MHz, $CDCl_3$) δ 1.64 (4H, m, CH_2), 1.94 (4H, m, CH_2), 2.48 (6H, br, NH), 2.70 (4H, m, CH_2NH_2), 2.77 (8H, m, CH_2NH), 3.38 (4H, m, CH_2NHAr), 6.14 (1H, t, J=9.5 Hz, H-5), 6.29 (2H, d, J=11.0 Hz, H-3,7), 6.75 (2H, dd, J=9.5 and 11.0 Hz, H-4,6); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 30.46, 33.90, 40.56, 44.49, 47.96, 48.31, 110.22, 117.74, 133.00, 153.06; ms (70eV) m/z 348 (M^+, 15%), 324 (8 %), 274 (10%), 247 (100%). Found: m/z 348.2971. Calcd for $C_{19}H_{36}N_6$: M, 348.2999.

***N*-[2-[(7-Amino-4-methylazaheptyl)amino]-2,4,6-cycloheptatrienylidene]-4-methylaza-1,7-heptanediamine (11b):** The reaction of **4** (100 mg, 0.51 mmol) with **5b** (452 mg, 3.10 mmol), as described above, gave **11b** (151 mg, 78%) as orange oil; uv λ max (MeOH) 260 (log ε 4.19), 347 (3.89), 358 (3.92), 379 (3.68 sh), 415 (3.78), 460 nm (3.38 sh); ir (neat) ν: 3350 and 3200 cm^{-1}; ^{1}H nmr (270 MHz, $CDCl_3$) δ 1.61 (4H, m, CH_2), 1.89 (4H, m, CH_2), 2.23 (6H, s, CH_3), 2.40 (4H, m, CH_2),2.47 (4H, m, CH_2), 2.72 (4H, m, CH_2), 3.33 (4H, m, CH_2), 6.12 (1H, t, J=9.5 Hz, H-5), 6.28 (2H, d, J=11.0 Hz, H-3.7), 6.78 (2H, dd, J=11.0 Hz and 9.5 Hz, H-4.6); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 27.81 (t), 31.15 (t), 40.67 (t), 42.33 (q), 44.40 (t), 55.61 (t), 55.81 (t), 110.07 (d), 117.55 (d), 132.89 (d), 152.93 (d); ms (70 eV) m/z 376 (M^+, 11%), 275 (15%), 261 (45%), 129(100%). Found: m/z 376.3337. Calcd for $C_{21}H_{40}N_6$: M, 376.3312.

***N*-[2-[(7-Amino-4-oxaheptyl)amino]-2,4,6-cycloheptatrienylidene]-4-oxa-1,7-heptanediamine (11c):** The reaction of **4** (100 mg, 0.51 mmol) with **5c** (411 mg, 3.11 mmol), as described above, gave **11c** (105 mg, 59%) as orange oil; uv λ max (MeOH) 260 (log ε 4.25), 344 (3.95 sh), 348 (3.96), 358 (3.96), 378 (3.75 sh), 415 (3.83), 459 nm (3.42 sh); ir (neat) ν: 3350 and 3257 cm^{-1}; ^{1}H nmr (270 MHz, $CDCl_3$) δ 1.72 (4H, m, CH_2), 2.00 (4H, m, CH_2), 2.79 (4H, m, CH_2NH_2), 3.39 (4H, m, CH_2N), 3.50 (4H, m, CH_2O), 3.75 (4H, m, CH_2O), 6.10 (1H, t, J=10 Hz, H-5), 6.29 (2H, d, J=10 Hz, H-3,7), 6.73 (2H, m, H-4,6); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 30.33 (t), 33.51 (t), 39.64 (t), 43.30 (t), 68.97 (t), 69.12 (t), 110.18 (d), 117.74 (d), 132.98 (d), 153.11 (s).; ms (70 eV) m/z 350 (M^+, 5%), 248 (100%). Anal. Calcd for $C_{19}H_{34}N_4O_2$: C, 65.11; H, 9.78; N, 15.98. Found: C, 64.82; H, 10.05; N, 15.83.

***N*-[2-[(8-Amino-3,6-dioxaoctyl)amino]-2,4,6-cycloheptatrienylidene]-3,6-dioxa-1,8-octanediamine (12a):** The reaction of **4** (100 mg, 0.51 mmol) with **6b** (607 mg, 4.10 mmol), as described above, gave **12a** (173 mg, 89%) as orange oil; uv λ max (MeOH) 255 (log ε 3.94), 345 (3.87 sh), 358 (3.87), 408 (3.79), 562 (3.56 sh), 540 (3.25 sh), 494 nm (2.16 sh); ir (neat) ν: 3360 and 3260 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 2.30 (4H, br, NH_2), 2.87 (4H, m, CH_2N), 3.51 (8H, m, CH_2O), 3.65 (4H, m, CH_2O), 3.70 (4H, m, CH_2O), 3.83 (4H, t, J=6.3 Hz, CH_2N), 6.17 (1H, t, J=9.5 Hz, H-5), 6.31 (2H, d, J=11.0 Hz, H-3,7), 6.76 (2H, dd, J=9.5 and 11.0 Hz, H-4,6); ms (70eV) m/z 382 (M^+, 2%), 264 (100%). Anal. Calcd for $C_{19}H_{34}N_4O_4$: C, 59.66; H, 8.96; N, 14.65. Found: C, 59.38; H, 9.23; N, 14.41.

***N*-[2-[(6-Amino-3,4-dithiahexyl)amino]-2,4,6-cycloheptatrienylidene]-3,4-dithia-1,6-hexanediamine (12b):** A solution of **4** (100 mg, 0.51 mmol) and **6c** (532 mg, 3.50 mmol) in absolute methanol (2 ml) was heated in a small, sealed tube under argon atmosphere at 80 °C for 3 h. After concentration in vacuo, the residue dissolved in chloroform was washed with aqueous 20% NaOH and water, dried over magnesium sulfate and then concentrated in vacuo to give **12b** (96 mg, 48%) as orange oil; uv λ max (MeOH) 262 (log ε 4.11), 346 (3.79), 359 (3.81), 378 (3.65 sh), 408 (3.70), 458 nm (3.31 sh); ir (neat) ν: 3350 and 3260 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 2.28 (4H, br, NH_2), 2.76 (4H, t, J=6.2 Hz, CH_2NH_2), 2.99 (4H,t, J=6.2 Hz, SCH_2), 3.04 (4H, t, J=6.2 Hz, SCH_2), 3.66 (4H, t, J=6.2 Hz, CH_2N), 6.22 (1H, t, J=9.5 Hz, H-5), 6.31 (2H, d, J=10.5 Hz, H-3,7), 6.80 (2H, dd, J=10.5 Hz and 9.5 Hz, H-4,6); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 38.79 (t), 40.54 (t), 42.46 (t), 45.52(t), 110.77 (d), 118.70 (d), 133.36 (d), 152.98 (s). Anal. Calcd for $C_{15}H_{26}N_4S_4$: C, 46.12; H, 6.71; N, 14.34. Found: C, 45.87; H, 6.98; N, 14.13.

The Reaction of 4 with Diethylenetriamine (6a)

1-(2-Aminoethyl)-2,3-dihydro-1*H*-cyclohepta[*b*]pyrazine (9): A solution of **4** (200 mg, 1.02 mmol) and **6a** (124 mg, 1.20 mmol) in absolute ethanol (2 ml) was similarly heated at 80 °C for 30 h. The reaction solution was passed through a silica gel column with methanol-NaCl aq (1:1) to give **9** (129 mg, 67%): Orange oil, (picrate, decomp. 180 °C); uv λ max (MeOH) 258 (log ε 4.27), 367 (3.83), 427 nm (3.83); ^1H nmr (270 MHz, DMSO-d_6) δ 3.28 (2H, t, J=5 Hz, CH_2), 3.36 (4H, s, CH_2), 3.62 (2H, t, J=5 Hz, CH_2), 5.94 (1H, d, J=10 Hz, H-9), 6.01 (1H, dd, J=10 and 8 Hz, H-7), 6.38 (1H, d, J=12 Hz, H-5), 6.41 (1H, t, J=10 Hz, H-8), 6.52 (1H, dd, J=12 and 8 Hz, H-6); ms (70 eV) m/z 189 (M^+, 100%). Found: m/z 189.1277. Calcd for $C_{11}H_{15}N_3$: M, 189.1265.

1*H*-2,3,4,5-Tetrahydro-1,3a,6-triazacyclohepta[*de*]naphthalene (10): A solution of **9** in ethanol was refluxed for 2 h under argon atmosphere and then concentrated in vacuo, to quantitatively give **10**: Orange oil (picrate, mp 113-115 °C); uv λ max (MeOH) 250 (log ε 4.23), 298 (4.02), 317 (3.88), 345 (3.42 sh), 388 (3.87), 470 nm (3.54); ^{1}H nmr (270 MHz, DMSO-d_6) δ 3.44 (4H, m, CH_2), 3.54 (4H, m, CH_2), 6.95 (2H, m, H-8,9), 7.19 (2H, m, H-7,10), 9.10 (1H, br, NH); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 46.5 (t), 126.7 (d), 128.2 (s), 129.2 (d), 144.8 (s); ms 187 (M^+, 100%), 186 (73), 172 (12), 159 (27), 145 (25), 131 (28). Found: m/z 187.1118. Calcd for $C_{11}H_{13}N_3$: M, 187.1109.

μ-[6,7,8,9,10,11,12,13,20,21,22,23,24,25,26,27-Hexadecahydrodicyclohepta[*b,m*][1,4,8,12,15,19]hexaazacyclodocosinato-N^6,N^9,N^{13},N^{16},N^{20},N^{24}]bis(acetatonickel(II)) (13): To **7a** (40 mg, 0.092 mmol) in dichloromethane (30 ml) was added nickel(II) acetate tetrahydrate (58 mg, 0.233 mmol) in ethanol (16 ml), and the mixture was stirred for 10 min. After most of the dichloromethane had been removed on a water bath, the solution was set aside overnight at room temperature, resulting in the formation of black precipitates. These were collected and recrystallized from dichloromethane-ethanol to give **13** (53 mg, 86% yield) as dark brown plates; decomp. 290 °C; uv λ max (MeOH) 256 (log ε 4.62), 308 (4.32 sh), 337 (4.38), 407 (4.23), 460 (4.08), 492 (3.92 sh), 536 nm (3.22). Anal. Calcd for $C_{30}H_{42}N_6O_4Ni_2$: C, 53.13; H, 6.14; N, 12.79. Found: C, 53.41; H, 6.27; N, 12.63.

A crystal with dimensions ca. 0.5 × 0.3 × 0.2 mm^3 was used for data collection, using graphitemonochromated Mo Kα radiation (λ=0.71069Å). 2171 reflections ($2\theta \leq 60°$; h -28->28, k 0->28, l 0->17) were observed of which 1851 unique reflections with $|F| \geq 4\sigma(|F|)$ were used for structure determination. Intensities were corrected for Lorentz and polarization effects but not for absortion and extinction. Unit cell dimensions were obtained from least-squares fit of 14 2θ values (20<2θ<24°). Structure has been solved by direct method using MULTAN 78.[9] Coordinates of Ni atom and a six-membered chelating part of macrocycle were obatined from E map. From succesive Fourier maps all other non-H atoms could be located. Parameters for H-atoms were obtained from calculation. Atomic scattering factors used were from literature.[10] Structure refinement and characterzation were carried out using UNICS III program system[11] on a FACOM M-360 computer at

Josai University. R 0.101, R_w 0.069 for 2171 independent reflections. Observed and calculated structure amplitudes, final atomic coordinates, anisotropic thermal parameters, parameters for H-atoms, and bond distances and angles not given in the paper will be obtained from the author on request.

ACKNOWLEDGEMENT

We thank Prof. Hirosi Yamamoto (Okayama Univ.) and Dr. Teruo Kurihara (Josai Univ.) for their helpful advice, Mr. Hitoshi Fukada for the elemental analysis and Mr. Hideyuki Mitsuhashi for the measurement of the mass spectra (Analytical Center of Josai Univ.).

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Received, 29th September, 1993