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Syntheses and Characterizations of Lactam Cyclophanes. Attempted Synthesis of a Lactam Catenane Using Hydrogen Bonds

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New cyclophanes having multilactam linkages were synthesized and characterized. One-pot coupling reaction of 2,6-pyridinedicarbonyl dichloride and a diamine gave a tetralactam, a hexalactam, and a octalactam in good yields. The TLC behaviour, the molecular symmetry shown by ^{1}H NMR spectrum, and the fragmentation patterns shown by FAB mass spectrum of the octalactam support its monocyclic structure.

Introduction

Catenane[1] is a new topological isomer in which two or more cyclic compounds are interlocked each other to give a [2]catenane or a [n]catenane as shown in Figure 1. Rotaxane[1] is another topological isomer in which a chain component is threaded into a cyclic component but the chain component cannot escape due to the bulky groups at both ends. The first catenane was synthesized using statistical method in an extremely low yield.[2] But recently the high yields of new catenanes have been reported using metal templation,[3] charge-dipole interactions as well as π-π interaction.[4] Other weak molecular interactions such as dipole-dipole, hydrogen bonding, electrostatic, and hydrophobic interactions could be also applied in catenane synthesis, which implies that molecular recognition phenomena can be applied in articulate manner for designing and synthesizing new functional topological isomers in much improved yields.[5]

Cyclophanes, cyclic compounds in which aromatic units are incorporated, are good candidates for organizing those weak molecular interactions to give fruitful results in catenane chemistry.[6] Cyclophanes usually provide a hydrophobic cavity surrounded by aromatic rings facing each other. They were developed to charge transfer complexes, enzyme mimics, organic hosts, molecular sensors and etc. Enzyme mimics based on cyclophanes are attractive, because the designs and syntheses are easily accessible, the conformation is stable structurally, and various functional groups could be introduced to benzene rings.[7] Also, cyclophane hosts have the

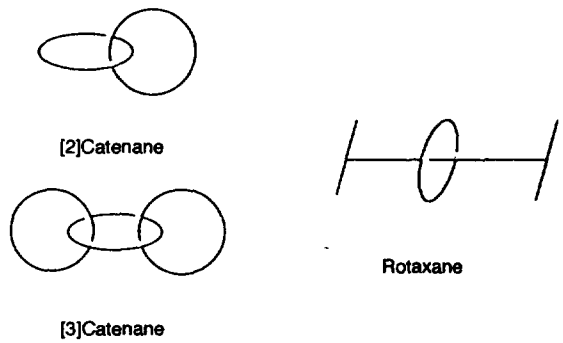
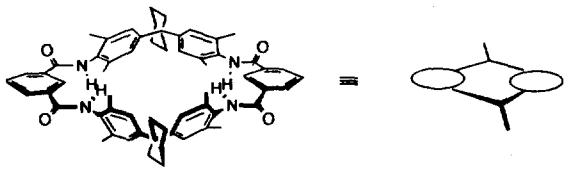
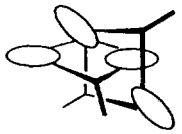


Figure 1. Illustration of Catenanes and Rotaxane.



Tetralactam 1



Octalactam Catenane 2 ([2]Catenane 2)

Figure 2. Reported Tetralactam and Octalactam Catenane.

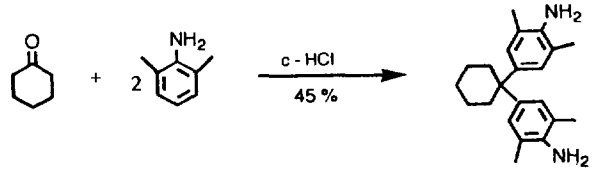
merit that their binding sites are easily controlled by incorporating the polar binding sites into their nonpolar binding sites in molecular cavity.[6,7b,8] In these regards, cyclophanes are versatile bases for a wide variety of new functional molecular mechanics.

Especially π-stacking interactions combined with charge-dipole interaction of a cyclophane have been applied for the synthesis of unprecedented multi-catenanes, such as olympiads, by Stoddart *et al.*[4] Principally any kinds of noncovalent interactions could be used only if they act cooperatively to assemble substrates into an organized structure to lead to catenanes. Quite recently Hunter[9] and Vögtle[10] reported the synthesis of lactam catenanes such as **2** in Figure 2. Until now the mechanism of formation of these octalactam catenanes has not been addressed properly. But it has been assumed that "orthogonalization", the perpendicular preorganization of the catenane building blocks, enables the catenane formation. The orthogonalization is based on steric complementarity, hydrogen bonding between carbonyl oxygen atoms and amide protons, and π-π interactions between the benzene rings of host and guest subunits.

To elucidate the role of these interactions in the formation of lactam catenanes and to develop new functional cyclophanes based on lactam linkages, various lactam cyclophanes **7**, **8**, and **9** were designed and synthesized. These hosts could be used as template for a catenane synthesis. Also they could recognize neutral organic guest molecules using hydrogen bonds and aromatic stacking interactions converging into its cavity. The rigidity and preorganization of binding cavity formed by benzene units and amide groups incorporated into the macrocyclic system as well as the inward facing hydrogen bonding groups would lead to a strong and selective binding of the guests.

Results and Discussion

Synthesis of Lactam Macrocycles. Diamine **3** was prepared by acid-catalyzed condensation reaction with cyclohexanone and 2,6-dimethylaniline in 45% yield.[9] The synthesis of tetralactams **7**, **8**, and **9** is shown in Scheme 2. Diaminodiamides **4**, **5**, and **6** were obtained by coupling diamine **3** with the corresponding acid chlorides in 55.1%, 52.1%, and 54.0% yield, respectively. Acid chlorides were prepared from the corresponding dicarboxylic acids using thionyl chloride.



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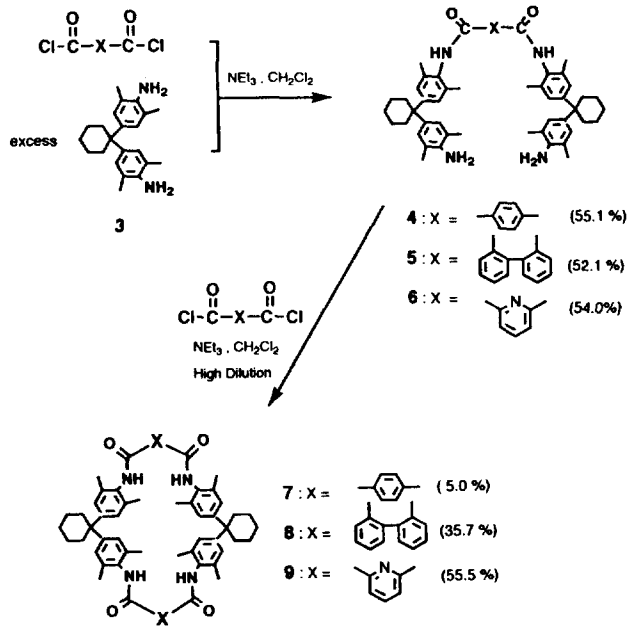
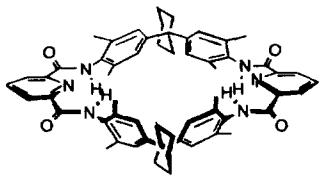
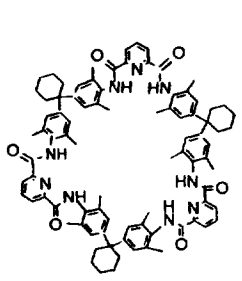
Scheme 1. Synthesis of Diamine **3**.



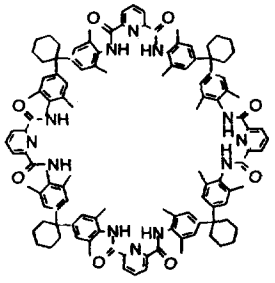
Scheme 2. Synthesis of Tetralactam Cyclophanes **7**, **8**, and **9**.



Tetralactam 9



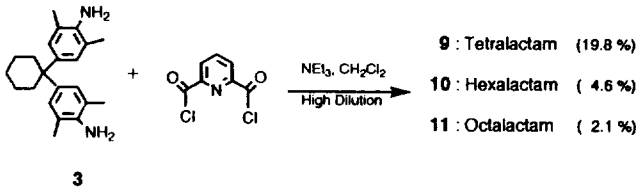
Hexalactam 10



Octalactam 11

Figure 3. Structures of Lactam Macrocyclophanes.

The syntheses of tetralactams **7**, **8**, or **9** were carried out by coupling diaminodiamide **4**, **5**, or **6** with the corresponding acid chlorides under high dilution conditions. Simultaneous addition of CH_2Cl_2 solution of **4**, **5**, or **6** and triethylamine



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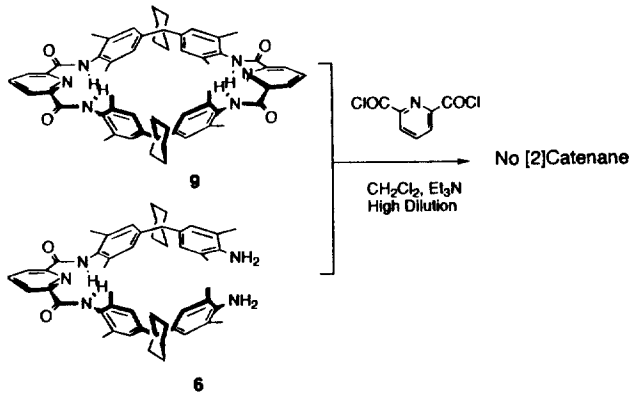
Scheme 3. One-Pot Synthesis of Three Lactam Cyclophanes **9**, **10**, and **11**.



9

6

Scheme 4. Attempted Template Synthesis of a [2]Catenane.

and of CH_2Cl_2 solution of the corresponding acid chloride to a large amount of CH_2Cl_2 solution at room temperature followed by purification of the crude mixture by column chromatography yielded tetralactam cyclophanes **7**, **8**, and **9** in 5.0%, 35.7%, and 55.5% yield, respectively. In case of X=pyridinyl, octalactam **11** was also obtained in 10% yield. One-pot coupling reaction between diamine **3** and 2,6-pyridinedicarbonyl dichloride in high dilution condition gave tetralactam **9**, hexalactam **10**, and octalactam **11** in 19.8%, 4.6%, and 2.1% yield respectively as shown in Scheme 3.

Attempted Template Synthesis of a [2]Catenane. In an attempt to improve the yield of tetralactam cyclophane **1** starting from isophthaloyl dichloride and diamine **3** in a stepwise manner similar to the Scheme 2, Hunter isolated a octalactam [2]catenane **2** together with a tetralactam and a octalactam.[9] In this case it is proposed that the intermolecular hydrogen bonds between two diaminodiamides (the same structure as **6** except that a pyridine unit is substituted by a benzene unit) in a orthogonal fashion result in a self-templation effect. When the same trial was attempted using terephthaloyl dichloride, 2,2'-biphenyldicarbonyl dichloride, or 2,6-pyridinedicarbonyl dichloride and the corresponding diaminodiamide **4**, **5**, or **6**, no isolable [2]catenane was observed (the second step reaction in Scheme 2). CPK molecular model examinations show that tetralactam **7** and **9** could be interlocked to give [2]catenane without any steric difficulty, but **8** could not. In case of tetralactam **7**, the relatively low yield is attributable to the difficulty in isolating **7** from other unisolable side products due to the strong polarity of product (R_f=0.25 from 2% MeOH in CH_2Cl_2 on SiO_2), the proximity of side products in TLC behaviour and the weak solubility of reaction mixture. Surprisingly tetralactam **9** was quite soluble and easily isolated from

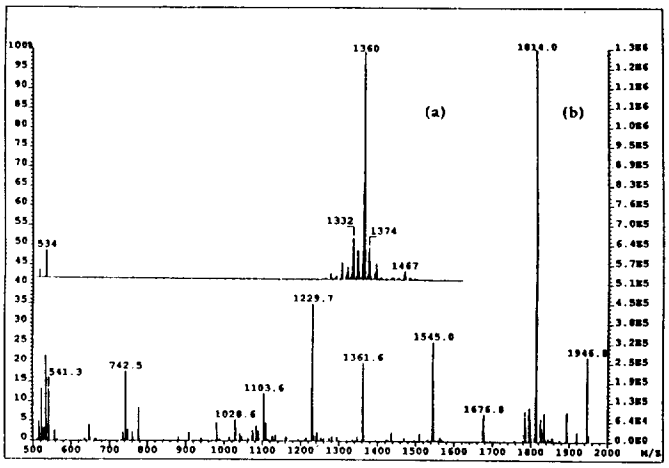


Figure 4. FAB Mass Spectra of (a) Hexalactam **10** (Above) and (b) Octalactam **11** (Below) (Ionized by 35 KeV Cs^+ Ion Beam in Thioglycerol).

octalactam **11** which was obtained in 10% yield in the same reaction. One-pot trial shown in Scheme 3 in high dilution condition also afforded only macrocyclophanes **9**, **10**, and **11** which were successfully isolated in 19.8%, 4.6%, and 2.1% yield respectively owing to their high solubilities and reasonable R_f differences. To maximize the templation effect, if there were any, tetralactam **9** and diaminodiamide **6** was first mixed together in CH_2Cl_2 and then coupled with 2,6-pyridinedicarbonyl dichloride in high dilution condition (Scheme 4), but disappointingly only tetralactam **9** together with a trace of octalactam **11** was observed.

Characterization of Lactam Cyclophanes. ^1H NMR, IR, and FAB mass spectra of tetralactam **7**, **8**, and **9** are identical to those anticipated from their structures. The patterns of ^1H NMR spectra and of FAB mass spectra of tetralactam **9** and hexalactam **10** are quite similar to each other.

Octalactam **11** has the same molecular weight as that of anticipated catenane and it was observed at 1814 (M^+, 100%) on FAB mass spectrum. There are several rationales against that octalactam **11** might be a catenane rather than a monocycle. At first R_f values (SiO_2, eluent is a 3 : 97 mixture of MeOH and CH_2Cl_2) of lactams **9**, **10**, and **11** were 0.32, 0.29, and 0.26, which manifests that its polarity increases as its size increases and that there is no striking structural abnormality among them. Hunter observed that catenane **2** is much less polar than anticipated due to the intramolecuar hydrogen bonds between two cyclic subunits presumably in orthogonal fashion.[9] It moves even faster than tetralactam **1** on SiO_2. Secondly ^1H NMR spectra of lactams **9**, **10**, and **11** were quite similar except that the peaks of larger cycle were a little bit broader than those of smaller cycle, which implies that each structural components in these cycles were equivalent and had retained their symmetry in solution. If octalactam **11** were in catenane structure, its ^1H NMR spectrum should be much more complex than that of tetralactam **9** due to the nonequivalencies of several sets of protons and the changes in chemical shifts arising from the shielding or deshielding effects of aromatic units. Thirdly the fragmentation patterns observed in FAB mass spectrum of octalactam **11** supported its monocyclic structure. Figure 4 shows the

FAB mass spectra of hexalactam **10** and octalactam **11** taken in thioglycerol matrix using Cs^+ ion beam. Tetralactam **9** (M^+ : 908, 100%) gave a similar mass spectrum as that of hexalactam **10** (M^+ : 1360, 100%). Usually a catenane gives no or very weak fragments peaks between M^+ and $M^+/2$ peaks because of the easy cleavage of a cycle.[11] But octalactam **11** gave many prominent peaks between 1814 (M^+) and 908 ($M^+/2$). The peak at 1946 was assumed as that of $M+Cs^+$. Also $M^+/2$ peak of a catenane used to be very strong because of its high population, but that of lactam **11** didn't even appear. Based on those analyses it was concluded that lactam **11** is a monocycle.

The failure of catenane formation from diaminodiamides **4** or **5** is presumably due to the geometric as well as steric difficulties for the orthogonal templation prior to cyclization. In case of diaminodiamide **6** the intramolecular hydrogen bonds are possible between the pyridine nitrogen and a amide hydrogen which presumably causes the intrinsically weak intermolecular hydrogen bond and eventually no catenane formation. Also the dipole-dipole repulsion between pyridine nitrogen and carbonyl oxygens fixes these two hetroatoms in s-trans position, which eventually prohibit an across double hydrogen bonds. CPK molecular model study shows the across double hydrogen bonds between tetralactam **9** and threaded diaminodiamide **6** might be very crucial in an attempted template synthesis as shown in Scheme 4.

The amide carbonyl oxygens of lactams could orient inward forming somewhat potential metal ion binding site. But no mentionable results were observed from ion selective electrode experiments yet.

Conclusion

New tetralactam cyclophanes were obtained in good yields using high dilution reaction and their structures were identified. The TLC behaviour, the simple symmetry shown by ^1H NMR spectrum, and the fragmentation patterns on FAB mass spectrum of octalactam **11** manifested its monocyclic structure. For the formation of a lactam catenane similar to **2** it is concluded that the self templation in proper geometry (in the lactam case, orthogonal geometry) assembled by the organized noncovalent molecular interactions is crucial.

Experimental

Chemicals were reagent grade (Aldrich), and used as received. Solvents were distilled from calcium chloride, and dichloromethane was distilled two times. All anhydrous reactions were conducted under an argon atmosphere. The ^1H NMR spectra were measured on either a Bruker AW-80 (80 MHz) or a Gemini-300 (300 MHz) spectrometer. Spectra were referenced to deuterated solvents (300 MHz) or TMS (80 MHz, 0.0 ppm). Melting points were measured on a electrothermal 9100 apparatus and are uncorrected. FAB^+ mass spectra were obtained with VG70-VSEQ spectrophotometer in thioglycerol matrix using Cs^+ ion beam. Infrared spectra were recorded on a Mattson 3000 FT-IR spectrometer. Gravity column chromatography was performed on E. Merck silica gel 60 (70-230 mesh ASTM). Thin-layer chromatography was done on plastic sheets silica gel 60 F_{254} (E. Merck, 0.2 mm).

1,1-Bis(4-amino-3,5-dimethylphenyl)cyclohexane (3). A mixture of 2,6-dimethylaniline (30 mL), cyclohexanone (12.6 mL), and conc. HCl (30 mL) was refluxed for 48 h. Additional 30 mL of conc. HCl was added with stirring and the mixture was refluxed for 5 d. The products were taken up in 300 mL of water and basified with 1 N NaOH. After extraction with 600 mL of $CHCl_3$, the organic layer was washed with water, brine and then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was recrystallized from a mixture of CH_2Cl_2 and hexane. The crystals were filtered and dried *in vacuo* (17.4 g, 45%): mp 180-181 ℃; FT-IR (KBr) 3364 (NH) cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 1.55 (br s, 10H, CH_2), 2.10 (br s, 12H, ArCH_3), 3.35 (br s, 4H, NH_2), 6.78 (s, 4H, Ar*H*).

Terephthaloyl Diaminodiamide (4). Terephthaloyl dichloride (0.5 g, 2.46 mmol) was dissolved in 300 mL of dry dichloromethane and the solution was transferred to a dropping funnel. It was added dropwise to a reaction vessel containing a solution of 4.96 g (15.4 mmol) of **3**, 1.53 mL of triethylamine, and 50 mL of dry dichloromethane over a period of 2 h under an argon atmosphere at RT. The reaction mixture was stirred for a further 24 h. The reaction mixture was washed with water and then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was column chromatographed on silica gel with 1% MeOH in CH_2Cl_2. The best portions were collected and concentrated. The residue was recrystallized from a mixture of CH_2Cl_2 and hexane to afford 1.05 g (55.1%) of product: mp 270-270.9 ℃; FT-IR (KBr) 3300 (NH), 1647 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 1.49 (br s, 12H), 2.05 (s, 12H), 2.17 (br s, 20H), 4.3 (s, 4H), 6.75 (s, 4H), 7.0 (s, 4H), 8.06 (s, 2H), 8.30 (s, 2H), 9.74 (s, 2H); FAB^+ MS (thioglycerol), m/e 775 (M^+, 100%).

Diphenic Diaminodiamide (5). A mixture of diphenic acid (0.6 g, 2.48 mmol), thionyl chloride (10 mL), benzene (20 mL), and DMF (0.5 mL) was refluxed for 12 h. Thionyl chloride was evaporated under reduced pressure and 20 mL of benzene was added and then evaporated, which was repeated three times. The residue was dissolved in 40 mL of dry dichloromethane and the solution was transferred to a dropping funnel. This solution was added dropwise to a mixture of 4.98 g (15.5 mmol) of **3**, 1.3 mL of triethylamine, and 100 mL of dry dichloromethane over a period of 2 h with stirring under an argon atmosphere at RT. The reaction mixture was acidified with 100 mL of 2 N HCl, washed with water, brine and then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The product was purified by column chromatography (silica gel, 1% MeOH in CH_2Cl_2). The best fractions were collected, concentrated, and then recrystallized from a mixture of CH_2Cl_2 and hexane to give a white powder (1.1 g, 52.1%): mp 199.8-200.9 ℃; FT-IR (KBr) 3363 (NH), 1639 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (br s, 12H), 1.94 (br s, 12H), 2.13 (br s, 20H), 2.18 (s, 4H), 6.81 (s, 4H), 6.86 (s, 4H), 7.27 (br s, 4H), 7.44 (t, 2H), 7.67 (t, 2H), 8.24 (s, 2H); FAB^+ MS (thioglycerol), m/e 983 ($M+Cs^+$, 47%), 852 (MH^+, 100%).

Pyridinyl Diaminodiamide (6). A mixture of pyridine dicarboxylic acid (0.41 g, 2.45 mmol), thionyl chloride (10 mL), benzene (20 mL), and DMF (0.5 mL) was refluxed for 12 h. Thionyl chloride was evaporated under reduced pressure and 20 mL of benzene was added and then evaporated, which was repeated three times. The product was dissolved

in 40 mL of dry dichloromethane and the solution was transferred to a dropping funnel. It was added dropwise to a mixture of 4.94 g (15.3 mmol) of **3**, 1.4 mL of triethylamine, and 60 mL of dry dichloromethane over a period of 2 h with stirring under an argon atmosphere at RT. The reaction mixture was washed with water, brine and then dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel gravity column (0.5% MeOH in CH_2Cl_2) and the best fractions were collected, concentrated. It was recrystallized from a mixture of CH_2Cl_2 and hexane to give 1.03 g (54%) of product: mp 170.3-171.8 ℃; FT-IR (KBr) 3361 (NH), 1632 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.26 (s, 4H), 1.54 (br s, 8H) 2.15-2.25 (m, 32H), 3.45 (s, 4H), 6.91 (s, 4H), 7.02 (s, 4H), 8.14 (t, 1H), 8.51 (d, 2H), 8.98 (s, 2H).

Terephtaloyl Tetralactam (7). Terephthaloyl diaminodiamide **4** (0.5 g, 0.645 mmol) and 0.2 mL of triethylamine were dissolved in 130 mL of dry dichloromethane and the solution was transferred to a dropping funnel. A mixture of 0.131 g (0.645 mmol) of terephthaloyl dichloride and 130 mL of dry dichloromethane was transferred to another identical dropping funnel. These two solutions were added dropwise to 600 mL of dry dichloromethane over a period of 28 h with stirring at RT under an argon atmosphere.. The reaction mixture was then stirred for a further 12 h. The mixture was acidified with 100 mL of 2 N HCl. The organic phase was washed with water, brine and then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The crude product was chromatographed on silica gel gravity column (0.5% MeOH in CH_2Cl_2) and the best fractions were collected, concentrated. The residue was recrystallized from a mixture of CH_2Cl_2 and hexane to afford 28 mg (5%) of product: mp 210-230 ℃ dec; FT-IR (KBr) 3300 (NH), 1637 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.85 (br s, 4H), 1.25-1.60 (two br s, 24H), 2.15 (s, 8H), 2.25 (s, 8H), 6.79 (s, 4H), 7.05 (s, 4H), 7.40 (d, 4H), 7.65 (d, 4H); FAB^+ MS (thioglycerol), m/e 1037 ($M+Cs^+$, 29%), 906 ($M+H^+$, 100%).

Diphenic Tetralactam (8). Diphenic diaminodiamide **5** (0.5 g, 0.587 mmol) and 0.2 mL of triethylamine were dissolved in 130 mL of dry dichloromethane and the solution was transferred to a dropping funnel. A mixture of 2,2′-biphenyldicarbonyl dichloride (0.16 g, 0.587 mmol) and 130 mL of dry dichloromethane was placed in another identical dropping funnel. These two solutions were added drowise to 600 mL of dry dichloromethane over a period of 8 h with stirring at RT under an argon atmosphere. The mixture was then stirred for a further 26 h. The mixture was acidified with 100 mL of 2 N HCl. The organic phase was washed with water, brine and then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The product was purified by silica gel gravity column (0.5% MeOH in 99.5% CH_2Cl_2) and then recrystallized from a mixtire of CH_2Cl_2 and hexane to give a off-white powder (0.22 g, 35.7%): mp 300 ℃ dec; FT-IR (KBr) 3369 (NH), 1586 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.9 (br s, 2H), 1.29 (br s, 6H), 1.40 (br s, 4H), 1.58 (s, 8H), 1.85 (s, 8H), 2.05 (br s, 2H), 2.25 (br s, 2H), 6.77 (s, 8H), 7.3 (m, 8H), 7.45 (m, 8H), 7.68 (m, 4H), 8.23 (s, 4H); FAB^+ MS (thioglycerol), m/e 1189 ($M+Cs^+$, 100%), 1057 (M^+, 60%).

One-Pot Synthesis of Tetralactam (9), Hexalactam (10), Octalactam (11). A solution of 1.90 g (5.99 mmol) of **3**, 2.1 mL of triethylamine, and 130 mL of dry dichloromethane was placed in a dropping funnel. A mixture of 2,6-pyridinedicarbonyl dichloride (1.22 g, 5.99 mmol) and 130 mL of dry dichloromethane was placed in another identical dropping funnel. These two solutions were added dropwise to 600 mL of dry dichloromethane over a period of 27 h with stirring at RT under an argon atmosphere. The reaction mixture was then stirred for a further 21 h. The mixture was washed with 100 mL of 1 N HCl two times. The organic phase was washed with water, brine and then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel with 0.5% MeOH in CH_2Cl_2. The best fractions corresponding to each lactam were collected and concentrated. The products were recrystallized from a mixture of CH_2Cl_2 and hexane to afford tetralactam **9** (1.07 g, 19.8%), hexalactam **10** (0.251 g, 4.6%), octalactam **11** (0.116 g, 2.1%), respectively. The step-wise synthesis (Coupling of **6** and 2,6-pyridinedicarbonyl dichloride, Scheme 2) similar to the synthesis of tetralactam **7** or **8** afforded 55.5% of tetralactam **9** and 10% of octalactam **11**: Tetralactam **9**: mp >380 ℃ dec.; FT-IR (KBr) 3359 (NH), 1639 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.52 (br s, 4H), 1.57 (s, 8H), 1.64 (br s, 4H), 2.14 (br s, 20H), 2.29 (s, 8H), 7.01 (s, 8H), 8.18 (t, 2H), 8.50 (d, 4H), 8.96 (s, 4H); FAB^+ MS (thioglycerol), m/e 908 ($M+H^+$, 100 %): Hexalactam **10**: mp >316.4 ℃ dec.; FT-IR (KBr) 3374 (NH), 1647 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.58 (br s, 30H), 2.28 (s, 36H), 7.05 (s, 12H), 8.14 (t, 3H), 8.50 (d, 6H), 8.97 (s, 6H); FAB^+ MS (thioglycerol), m/e 1360 (M^+, 100%); Octalactam **11**; mp >308 ℃ dec; FT-IR (KBr) 3385 (NH), 1639 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.58 (br s, 4H), 1.26 (s, 8H), 1.58 (br s, 44H), 2.22 (s, 32H), 7.01 (s, 16H), 8.12 (t, 4H), 8.47 (d, 8H), 8.96 (s, 8H); FAB^+ MS (thioglycerol), m/e 1946 ($M+Cs^+$, 22%), 1814 (M^+, 100%).

Attempted Template Synthesis of a [2]Catenane (Scheme 4). Diaminodiamide **6** (30 mg, 0.039 mmol), tetralactam **9** (35 mg, 0.039 mmol), and triethylamine (0.1 mL) were dissolved in 120 mL of dry dichloromethane. 2,6-Pyridinedicarbonyl dichloride (7.9 mg, 0.039 mmol) in 30 mL of dry dichloromethane was added dropwise to this solution over a period of 6 h with stirring at RT under an argon atmosphere. After additional 12 h stirring, the reaction mixture was acidified with 2 N HCl. The organic phase was washed with water, brine and then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The extensive TLC study of the residue using the authentic samples revealed that the major product was tetralactam **9** with a trace amount of octalactam **11** (<5%).

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High Pressure Synthesis and Physical Properties of the Solid Solution, $SrLaAl_{1-x}Ni_xO_4(0<x<1)$

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A complete solid solution ($SrLaAl_{1-x}Ni_xO_4$) between insulating $SrLaAlO_4$ and metallic $SrLaNi(III)O_4$ oxides were prepared under high oxygen pressure (1.5 kbar, 800 ℃). They have tetragonal K_2NiF_4-type structure in all the solid solution range. Compared with lattice parameters of the same solid solution prepared under normal condition (1 bar, 1200 ℃), large decrease in the *c*-parameter was induced by high pressure treatment while no noticeable variation of the *a*-parameter was observed. Although marked changes of structural parameters, magnetic susceptibilities, and electron paramagnetic resonance spectra were consistently occurred before and after $x=0.5$, overall behaviors were essentially the same with those of solid solution prepared under normal condition. Such a phenomenon is explained by assuming the formation of partially filled narrow $\sigma^*_{x^2-y^2}$ band for $x>0.5$. Lattice contraction along the *c*-axis by high pressure treatment seems not to broaden this band. Particularly, the continuous absorption characteristic of a high free carrier concentration for $x>0.5$ and the absence of Ni-O in-plane stretching mode in the infrared absorption spectra supports this picture. However, the conductivities increasing with temperature for all solid solution suggest that some localization character, of probably Anderson type, remains for $x>0.5$.

Introduction

Layered perovskite-type oxides of the general formula A_2BO_4 have been intensively studied because they exibit typical two-dimensional magnetism,[1~3] metal-insulator transition,[4~6] and superconductivity.[7~9] The large variety of the properties that these compounds with so-called K_2NiF_4-type structure show is derived from the possibility of synthesis of multicomponent layer-type compounds. Partial substitution of cations in *A* and *B* positions, for example, gives rise to the $A_{2-y}A'_yB_{1-x}B'_xO_{4-\delta}$. The probability of solid solution formation in the entire compositional range is very high when the cation (A or B) is substituted by another cation (A′ or B′) with the same charge and a similar ionic radius.[10] In contrast, when there is a large difference in charge and/or ionic radius, ordered structures are formed and only certain compositions are allowed. In addition, this type of compounds are good candidates for the stabilization of a mixed or unusual oxidation states with anisotropic electronic configuration.[11~13]

Several studies have been carried out on the physical properties of the perovskite and the layered perovskite compounds with K_2NiF_4-type structure containing Ni(III). Although