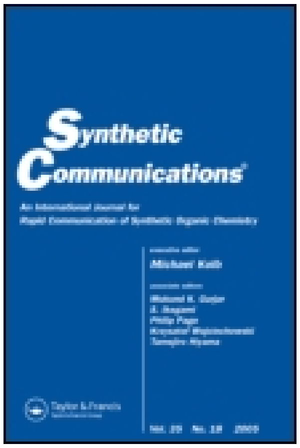


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

SYNTHESIS AND CHARACTERIZATION OF NEW POLYOXA-AZA CRYPTANDS

Jianjun Yu [a] & Rudong Yang [b]

[a] College of Chemistry and Chemical Engineering, Lanzhou University, Gansu, 730000, China

[b] College of Chemistry and Chemical Engineering, Lanzhou University, Gansu, 730000, China

Version of record first published: 16 Aug 2006.

To cite this article: Jianjun Yu & Rudong Yang (2002): SYNTHESIS AND CHARACTERIZATION OF NEW POLYOXA-AZA CRYPTANDS, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:20, 3113-3117

To link to this article: http://dx.doi.org/10.1081/SCC-120013721

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SYNTHETIC COMMUNICATIONS
Vol. 32, No. 20, pp. 3113–3117, 2002

SYNTHESIS AND CHARACTERIZATION OF NEW POLYOXA-AZA CRYPTANDS

Jianjun Yu and Rudong Yang*

College of Chemistry and Chemical Engineering,
Lanzhou University, Gansu, 730000, China

ABSTRACT

In this paper, two new polyoxa-aza cryptands were synthesized in high yield (70–80%) and characterized with elemental analyses, ^{1}H NMR, ^{13}C NMR, IR, and MS methods.

Macropolycyclic ligands have distinctive structures and properties, they as synthetic receptors for organic or inorganic cations, anions or neutral molecules play important roles in a number of areas in chemistry and biochemistry.[1–3] Thus they have potential applications in exploring new materials, analysis and separation of the rare earth ions, supramolecular devices, luminescent labels, fluorescent probes, magnetic resonance imaging and catalytic cleavage of RNA. In order to study the interaction between macropolycyclic ligands and rare earth ions, the present set of macrobicyclic cryptands were designed to include two and over metal ions inside the cavity, which is the area of considerable current interest. Macrobicyclic cryptands have not been used as extensively as the macrocyclic cryptands,

---

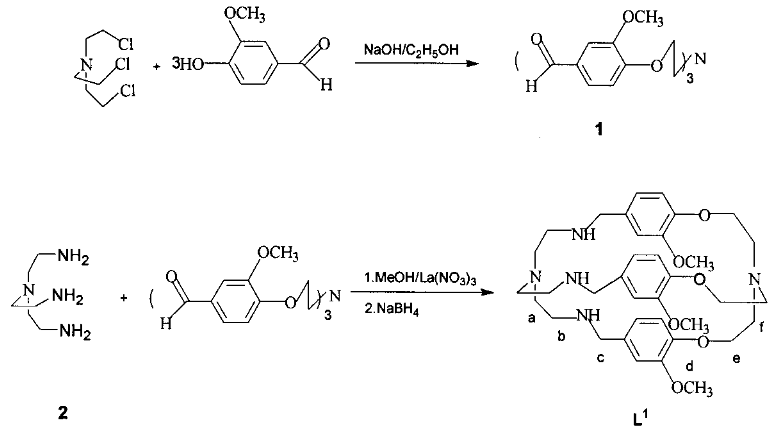
*Corresponding author. E-mail: yuwangs@public.lz.gs.cn

DOI: 10.1081/SCC-120013721
0039-7911 (Print); 1532-2432 (Online)

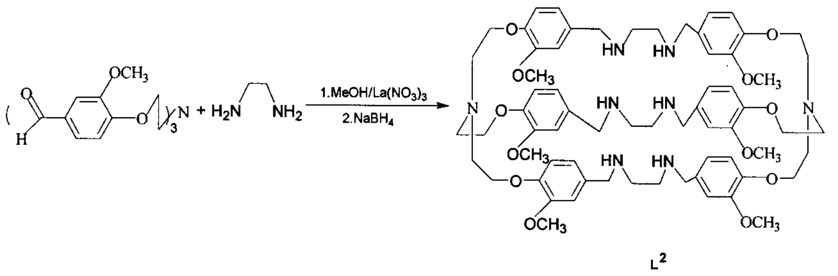
www.dekker.com

owing in part to difficulties associated with their synthesis.[4] The usual method of synthesis of these molecules involves linking of macrocycles through their functionalizable sites with spacers to delineate the central cavity of the compound. However, the method of synthesis starting from acyclic precursors, usually affords the desired cryptand in low yields. In this thesis, two polyoxa-aza cryptands (L^1 and L^2) were synthesized in high yield by [1 + 1] or [2 + 3] cyclocondensation and hydrogenation, where rare earth elements act as template. Synthesis process of the products were shown in Schs. 1 and 2.

DMF was the traditional solvent in the synthesis of compound **1**. However, methanol and ethanol were chosen for our synthesis process, because the higher yields (>90%) than those reactions in DMF were gotten.[5]



Scheme 1.



Scheme 2.

The conditions is as follows in the synthesis of cryptands L^1: To avoid collision of reactants, (1) The temperature should be the room temperature and not over 25°C; (2) **2** should be dropped into the systems to keep a low concentration of reactants. And, for reactions between two compounds having three opening bond respectively, templating metal ions is very important to make them near and react with each other. For the easier removal of rare earth ion at the end of reactions, rare earth ion were usually chosen for templating metal ion, instead of base metal. No water appeared in reactions, otherwise rare earth ion would undergo hydrolysis.

Since linear diamine release the cyclic strain, templating ion is not necessary in the synthesis of cryptands L^2. Yield of L^2 is lower than that of L^1, probably because the reaction took place in three different molecules, which led to more by-products.

In summary, we reported the facile synthesis of two new macrobicyclic cryptands (Schs. 1 and 2) in high yields. They are both stable. Currently, studies in function of the cryptands are in progress, especially in their electrochemical and fluorescent characteristics. The studies for their recognition characteristics towards neutral molecules, anions and cations are also in progress. The results will be reported later.

EXPERIMENTAL

Elemental analyses were determined with the Elementar Vario EL elemental analyzers. The IR spectra were obtained on the Nicolet FT-170 SX model FT-IR spectrophotometer, using KBr pellets. Melting point were measured with the X_4 microscopic melting point apparatus by Beijing third Optical Instrument Factory and the thermometer used in determination process was not calibrated. ^{1}H NMR spectra were measured with Bruker AC-80 NMR and ^{13}C NMR spectra were obtained with Bruker AM-200 NMR. The FAB-MS date were obtained with the VG 2BA-HS model MS.

The rare earth oxide were bought from Shanghai Yuelong Chemical Factory and were at least of 99.99% purity. Rare earth (III) nitrates were prepared according to the literature method.[6]

3-Methoxy-4-hydroxybenzaldehyde (A.P) and triethanolamine (A.R.) were purchased from Shanghai Chemical Reagent third Factory.

Other reagents used in experiments were all purified as need.[7]

Tri{[2-(2′-methoxy-4′-oxomethyl-phenyl)-oxy]-ethyl}amine 1: 3-Methoxy-4-hydroxybenzaldehyde (4.56 g, 30 mmol) and *tris*(2-chloroethyl)amine hydrochloride (2.41 g, 10 mmol) and anhydrous potassium carbonate were dissolved in 100 mL ethanol and stirred for 12 h at reflux. Then 100 mL of water added. The yellow precipitate was formed immediately, filtered off, recrystallized twice with ethanol, dried under reduced pressure and a white crystal was obtained (95% yield), m.p. 82–84°C. IR spectrum gave a strong band of $\nu_{C=O}$ at 1713 cm^{-1}. Satisfactory elemental analysis of C, 65.34; H, 5.99; N, 2.50 were obtained (**$C_{30}H_{33}O_9N$** requires C, 65.34; H, 5.99; N, 2.54). ^1H NMR (80 MHz, $CDCl_3$) δ_H: 3.3 (t, $J = 6.0$ Hz, 6H, NCH_2), 3.9 (s, 9H, OCH_3), 4.3 (t, $J = 6.0$ Hz, 6H, OCH_2), 6.8–7.4 (m, 9H, aromatic), 9.7 (s, 3H, CHO).

Synthesis of *Tris*(2-aminoethyl)amine 2: synthesized as methods in literature.[8]

Synthesis of cryptand (L^1): *tris*(2-Aminoethyl)amine (1.0 mmol, 0.146 g) in 50 mL of absolute methanol was added dropwise into 100 mL absolute methanol, in which **1** (1.0 mmol, 0.551 g) and rare earth nitrates (2.0 mmol) were dissolved, within 4 h at ambient temperature. After stirring for 24 h, the Schiff base was formed and hydrogenated in situ by stirring at room temperature for 12 h with $NaBH_4$. Then 20 mL of 1 : 1 ammonia solution was added into the liquor and rare earth ion was precipitated and filtered off. Finally, the solvent was evaporated to almost dryness and the residue was shaken with 80 mL of water, the cryptand was extracted from the aqueous medium with $CHCl_3$ (3 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated completely to obtain the desired product L^1 (70% yield). L^1 was a white powder [Found: C, 66.50; H, 8.07; N, 10.98; **$C_{36}H_{51}O_6N_5$** requires C, 66.56; H, 7.86; N, 10.79]; ^1H NMR (80 MHz, DMSO) δ_H: 3.0 (t, $J = 5.0$ Hz, 6H, a), 3.4 (t, $J = 5.0$ Hz, 12H, b and f), 3.7 (s, 9H, d), 4.0 (t, $J = 5.0$ Hz, 6H, e), 4.4 (s, 6H, c), 5.1 (brs, 3H, -NH), 6.7–7.0 (m, 12H, benzene); ^{13}C NMR (50 MHz, DMSO) δc: 53.95 (3C, a), 55.45 (6C, b and f), 62.78 (6C, c and d), 67.47 (3C, e), 110.86 (3C, benzene), 112.99 (3C, benzene), 118.60 (3C, benzene), 135.28 (3C, benzene), 146.89 (3C, benzene), 148.87 (3C, benzene); FAB-MS *m/z*: 650 $[L^1 + H]^+$.

Synthesis of cryptand (L^2): The ethylene diamine (3 mmol, 0.18 g) was dissolved in 20 mL of absolute methanol at room temperature. The solution was added dropwise into a solution of **1** (1.0 mmol) dissolved in 100 mL absolute methanol within 6 h at room temperature, then stirred for 24 h. The yellow Schiff base was formed and hydrogenated with $NaBH_4$ by stirring for 2 h at 10°C. After the solvent was distilled off under reduced pressure, the residue was shaken with 50 mL of water and extracted with $CHCl_3$ (3 × 30). Then the aqueous medium was removed, the organic layer was dried over anhydrous Na_2SO_4 and evaporated. The desired product (L^2) was obtained (68% yield). L^2 was a white powder [Found: C, 66.67; H, 7.48; N, 9.63; **$C_{66}H_{90}O_{12}N_8$** requires C, 66.78; H, 7.59; N, 9.44]; ^1H NMR (80 MHz, $CDCl_3$) δ_H: 1.9 (brs, 12H, NH), 2.9 (m, 12H, $-NHCH_2-$), 3.2 (t, $J = 6.0$ Hz, 12H, $N(CH_2)_3$), 3.8 (s, 18H, OCH_3), 3.9 (t, $J = 6.0$ Hz, 12H, $-OCH_2-$), 4.6 (s, 12H, Ar), 6.7–7.3 (m, 24H, benzene); FAB-MS *m/z*: 1187 $[L^2 + H]^+$.

ACKNOWLEDGMENT

The National Education Committee's Doctoral Foundation of China (9573005) financially supported this work.

REFERENCES

1. Lehn, J.M. *Supramolecular Chemistry*; VCH: Weinheim, 1995.
2. Ragunathan, K.G.; Bharadwaj, P.K. Tetrahedron Lett. **1992**, *33*, 7581.
3. Lehn, J.M. Acc. Chem. Res. **1978**, *11*, 49.
4. Krakowiak, K.E.; Bradshaw, J.S.; Dalley, N.K.; Zhu, C.Y.; Yi, G.L.; Curtis, J.L.; Li, D.; Izatt, R.M. J. Org. Chem. **1992**, *57*, 3166.
5. Ma, Z.; Yang, R.D.; Yan, L. Chin. Chem. Lett. **1999**, *10*, 995.
6. Wendland, W.W. Anal. Chim. Acta **1956**, *15*, 435.
7. Zhang, G.C.; Tan, Z. *Experiment of Fine Organic Chemistry*. Publishing House of Lanzhou University, 2000, pp. 13–30.
8. Kimura, S.; Young, S.; Collman, J.P. Inorg. Chem. **1970**, *9*, 1183.

Received in Japan July 16, 2001

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016