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New Cryptands Synthesized by [2 + 3] Condensation and Reduction with or without Templates†

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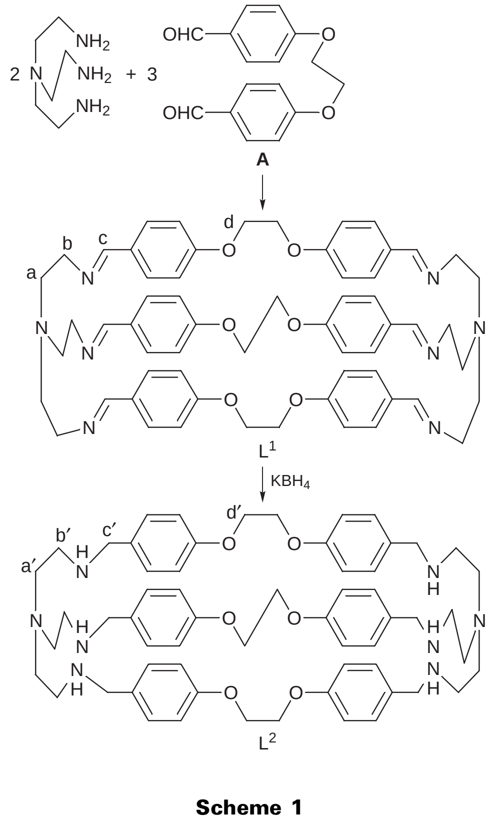
A Schiff base cryptand is synthesized in 65–75 and 20% yield, respectively, *via* one-step [2 + 3] condensation of a flexible dialdehyde with tris(2-aminoethyl)amine in the presence and absence of template; a polyoxa-aza cryptand is synthesized in 75% yield upon reduction of the Schiff base.

Characterized by distinctive receptor sites with hydrophilic, multi-dimentional and circular cavities, Schiff-base and polyaza cryptands are suitable as hosts for inorganic and organic guests. Owing to their special and novel structures, they provide impetus for chemists to design a large number of such compounds for use in many fields, such as molecular recognition, catalysis and transport.[1–3] Since the work of Jazwinski *et al.*,[4] many new Schiff-base and polyaza cryptands, in which nitrogen is the main heteroatom and which show special coordinative abilities toward transition metal elements, have been synthesized[5–7] by [2 + 3] condensation of dialdehydes and tris(2-aminoethyl)amine followed by reduction, in simple and high yield processes.



Scheme 1

Although Schiff-base and polyaza cryptands have such advantages mentioned above, some Schiff-bases readily polymerize in some solvents and the dialdehydes require rigid structures.[6] To circumvent these difficulties, high-dilution techniques and the use of templates such as alkali or transition metal ions are used to increase yields seldom, however, have rare earth elements[3] been used. We synthesized two new cryptands which contain not only nitrogen but also oxygen atoms by [2 + 3] condensation of a flexible dialdehyde **A** with tris(2-aminoethyl)amine both with and without template ions. The resulting cryptand L^1 upon reduction gave a high yield of saturated L^2 (Scheme 1). Dialdehyde **A** and tris(2-aminoethyl)amine were prepared as reported[8,9] and underwent [2 + 3] condensation to form L^1 in acetonitrile or corresponding cryptates in ethanol when templates were used. L^1 was obtained after removal of template ions from the cryptates and the yields were much higher than in the former method. Cryptand L^2 was obtained in 75% yield when L^1 was reduced with KBH_4 in methanol. IR spectra showed strong $\nu_{C=N}$ absorption of L^1 at 1644 cm^{-1} but exhibited no ν_{NH_2} or $\nu_{C=O}$ bands. After reduction, the bands due to C=N disappeared and a new N–H band emerged at 3297 cm^{-1}. Cryptand L^1 turned yellow after several weeks, and IR and ^1H NMR showed that it had decomposed. The solvents used in condensation are important in terms of obtained yields[6] and L^1 was not obtained in THF.

All rare earth elements (except Pm) can be used as templates to synthesize L^1 while several other ions such as K^+, Cu^{2+} and Zn^{2+} could also be used as templates, which formed more stable cryptates with L^1 than did the rare earth elements. No L^1 was obtained when K^+ and Na^+ were used as templates since the former in its cryptate could not be removed whilst the latter, which did not form a cryptate with L^1 simply led to polymerization. While L^1 is a good host for K^+ and transition metal elements it is less so for rare earth elements or Na^+ with DMF or DMSO solutions of the rare earth cryptates undergoing decomposition. L^2, however, is a good host for both rare earth and transition metal elements with DMF or DMSO solutions of the cryptates being stable. All cryptates of L^1 were stable in the air in contrast to L^1 itself.

Experimental

Syntheses of L^1 *by a High Dilution Method.*—Tris(2-aminoethyl)amine (1.0 mmol) in 50 ml of acetonitrile was added dropwise to a solution of dialdehyde **A** (1.5 mmol) in 450 ml of acetonitrile within 2 h at ambient temperature. Stirring for 24 h led to slow formation of a white powder which was collected by filtration and purified using a silica chromatographic column [MeOH–$CHCl_3$ (5:95)] to give L^1 in 20% yield (no mp evident from DTA–TG). δ_H (80 MHz, $CDCl_3$), 2.8 (br s, 12H, H^a), 3.5 (br s, 12H, H^b), 4.4 (s, 12H, H^d), 6.6 (d, 12H, C_6H_4), 6.7 (d, 12H C_6H_4), 7.6 (s, 6H, H^c) (Found: C, 70.35; H, 7.01; N, 11.07. $C_{60}H_{66}N_8O_6 \cdot 1.5H_2O$ requires C, 70.50; H, 6.80; N, 10.96%).

General Procedure for the Template Synthesis of L^1.—Solutions of dialdehyde **A** (1.5 mmol) and a nitrate salt of the template ion (1.2 mmol) in 150 ml of absolute ethanol were refluxed until the precipitate dissolved completely. Tris(2-aminoethyl)amine (1.0 mmol) in 30 ml of absolute ethanol was then added dropwise within 2 h and the solution cooled to ambient temperature. After stirring for 24 h, the solid formed was collected by filtration and dried *in vacuo*, to give the pure cryptate in 60–85% yield. To protect rare

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earth ions from hydrolysis, several ml of ethyl orthoformate was added. Ions such as La^{3+}, Sm^{3+}, Y^{3+}, Cu^{2+} and Zn^{2+} were removed from their cryptates by addition of 0.5 mol dm^{-3} sodium hydroxide, 1:1 aqueous ammonia or 0.5 mol dm^{-3} Na_2S giving precipitates which were separated from the solution by filtration. The precipitate was dissolved in methanol–chloroform (1:9) and after filtration, the filtrate was evaporated to dryness and a white solid formed. Recrystallization from $MeCN-CH_2Cl_2$ (1:1), gave pure L^1 (yield 65–75%).

Syntheses of L^2 by Reduction.—The L^1 (1 mmol) was mixed with KBH_4 (20 mmol) in 50 ml of absolute methanol, stirred for 30 min and refluxed for 3 h. Then the solvent was distilled off and precipitate was washed twice with water and dissolved in MeOH–$CHCl_3$ (1:4). After the remaining precipitate was filtered off the filtrate was evaporated completely to give L^2 which was recrystallized from $MeCN-MeOH-CH_2Cl_2$ (5:1:4) as a pure white power (yield 75%) (no mp was obtained). δ_H (80 MHz, $CDCl_3$) 2.3 (br s, 6H, –NH) 2.7 (br s, 12H, $H^{a'}$), 2.9 (br s, 12H, $H^{b'}$), 3.7 (br s, 12H, $H^{c'}$), 4.3 (br s, 12H, $H^{d'}$), 6.6 (d, 12H, benzene), 6.8 (d, 12H, benzene). δ_C [100 MHz, $CDCl_3$–CD_3OD (4:1)] 46.48 (6C, $C^{a'}$), 51.96 (6C, $C^{b'}$), 53.13 (6C, $C^{c'}$), 66.29 (6C, $C^{d'}$), 114.11 (12C), 128.65 (12C), 131.36 (6C), 157.16 (6C, aromatic) (Found: C, 70.87, H, 7.78; N, 10.84; $C_{60}H_{78}N_8O_6\cdot0.5H_2O$ requires C, 70.91; H, 7.84; N, 11.03%).

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