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Synthesis of Cryptands Having Tritopic Receptor Sites by [2+3] Schiff Base Condensation Using Cs(I) Ion as the Template

Kaliappa G. Ragunathan, Rameshwer Shukla, Swati Mishra and Parimal K. Bharadwaj*

Department of Chemistry, Indian Institute of Technology Kanpur,
Kanpur, 208016, INDIA

Abstract: Synthesis of two tritopic receptors L^1 and L^2 by [2+3] Schiff base condensation of trialdehyde 1 or 2 and 1,2-diaminobenzene followed by reduction with $NaBH_4$ are reported. The reactions undergo smoothly in presence of Cs(I) ion as the template.

Macropolycyclic ligands as synthetic receptors for organic or inorganic cations, anions or neutral molecules play an important role in a number of areas in chemistry as well as biochemistry[1]. Our research efforts[2] in this area involve manipulation of the binding sites and the macropolycyclic architecture with the ultimate aim to effect (i) specificity in the recognition processes as well as (ii) cooperative binding of different substrates leading to catalysis so as to mimic some of the active sites of metalloenzymes. Moreover, receptors having multi-metal binding capability can be used to study metal-metal interaction(s) which might lead to molecular magnets[3], molecular wires[4] and molecular switches[5]. We report here the synthesis of two hetero-tritopic receptors L^1 and L^2 to realize some of our objectives. Recently, an all-nitrogen cryptand with three receptor sites has been shown to accommodate three Ag(I) ions inside the cavity[6].

The synthetic scheme for the cryptand L^1 is shown in fig.1. The tripodal trialdehyde 1 is prepared by the reaction of tris(2-chloroethyl)amine hydrochloride and sodium salt of

4-hydroxybenzaldehyde in 75% yield as a pale brown solid[7]. This trialdehyde and 1,2-diaminobenzene undergo [2+3] Schiff base condensation in presence of Cs(I) ion as the template and *insitu* reduction of the resulting Schiff base with $NaBH_4$ afforded the desired cryptand in 35% yield[8]. The intermediate Schiff base is stable only for a few hours and could not be isolated in pure form. Also, in absence of the Cs(I) ion, a mixture of products of indefinite composition formed. We did not probe any other metal ion instead of Cs(I) as the template. A similar synthetic strategy is follwed[8] for the preparation of L^2 except that in place of 4-hydroxybenzaldehyde, 2-hydroxybenzaldehyde is used to have the corresponding ortho-isomer of the trialdehyde 1. The yield in this case

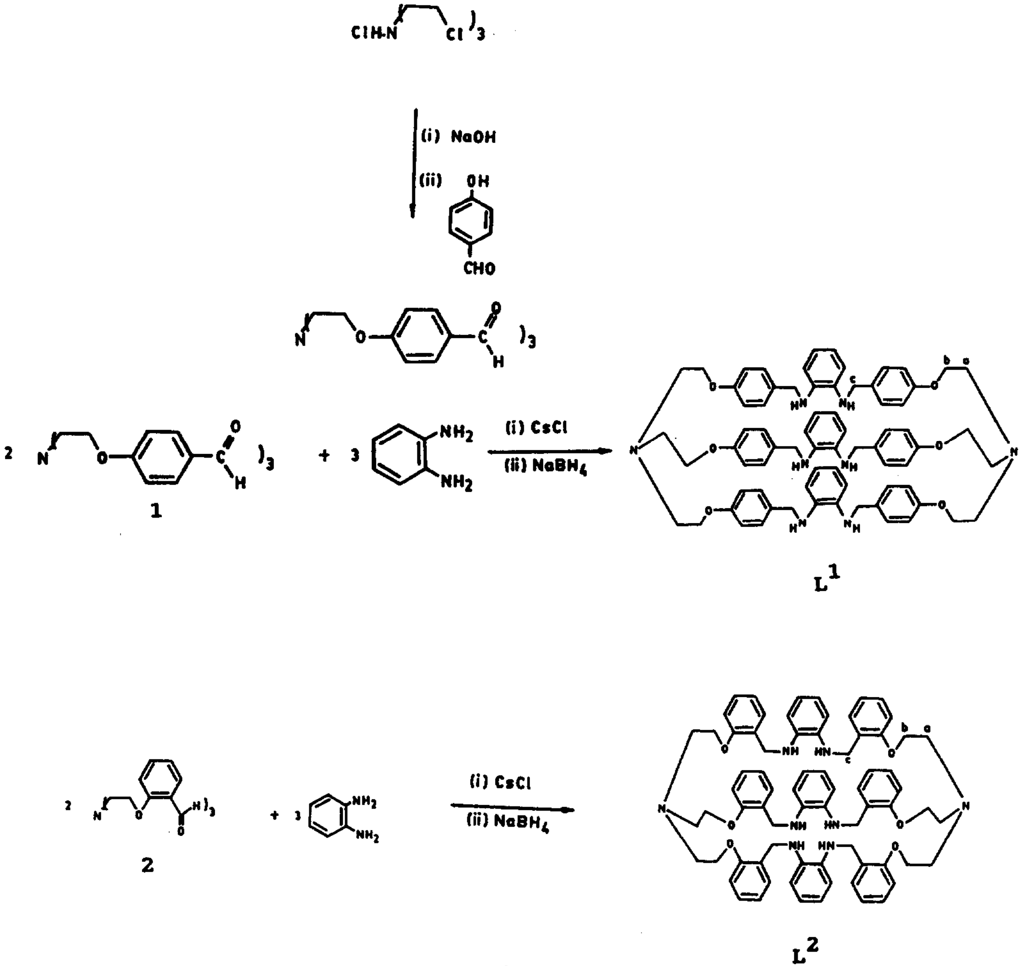

Fig. 1

was 30%. We had earlier reported the synthesis of a hetero-ditopic cryptand with this trialdehyde[9].

The cryptand L^1 was found to be more stable compared to L^2.The cryptands form mononuclear cryptates[10] with Cu(II), Ni(II), Co(II) and Fe(III), when the metal perchlorate salts and the ligand were mixed in 1:1 ratio in methanol at RT. The UV-VIS and EPR spectroscopic data suggest that the metal ion might be occupying the center of the cavity bonded to six nitrogen donor atoms. However, only single crystal X-ray structures can provide unambiguous pictures. Ligating behaviour of these cryptands towards non-transition metal ions as well as organic molecules is being probed.

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References and Notes

1. Lehn, J. M. *Angew. Chem. Int. Ed. Engl.* 1988,27, 90-112. Lehn, J.M. in *Perspectives in Coordination Chemistry,* Williams, A. F.; Floriani,C.; Merbach, A. F. Eds., V.C.H., New York, 1992, pp. 447 - 462. Cram, D. J. *Nature*, 1992, 356, 29-36.
2. Ragunathan, K.; Bharadwaj, P.K. *J. Chem. Soc. Dalton Trans.*, 1992, 1653-1356. Ragunathan, K.; Bharadwaj P.K. *Proc. Indian Acad.Sci (Chem Sci.)* 1993, 105, 215-217.
3. Carlin, R. L. in *"Magnetochemistry"* Springer Verlag, Berlin, 1986.
4. Lehn,J. M. *Angew. Chem. Int. Ed. Engl.* 1992, 29, 1304 - 1319.
5. Launy, J.-P. Ed., *"Molecular Electronics"*, *New J.Chem.*,Special issue, 1991, 15, pp. 95-232. Balzani,V.; Scandola, F. in *"Supramolecular Photochemistry "*, Ellis Horwood, New york, 1991.
6. Mendoza,J.; Mesa,E.; Redriquez-Ubis,J.; Vazquez,P; Vogtle,F,; Windscheif,P.; Rissanen,K.; Lehn,J.M.; Lilienbaumn,D.; Ziessel,R. *Angew. Chem. Int. Ed. Engl.*, 1991, 30, 1331-1334.
7. Sodium salt of 4-hydroxybenzaldehyde was prepared by adding NaOH (4 mmoles) to a solution of 4-hydroxybenzaldehyde (3 mmoles)in ethanol (50 ml) and stirring at RT for 1/2 h. To this solution, tris(2-chloro ethyl)amine hydrochloride (1 mmol) was added and refluxed for 3 h. The reaction mixture was cooled to RT and added to water when the product crashed out as pale brown solid which was collected by filtration, washed with cold ethanol and finally air-dried to obtain the trialdehyde 1 in 75% yield. m.pt.81°C. IR spectrum gives a strong

band at 1670 cm^{-1}(C=O). ^{1}H-NMR (80 MHz, $CDCl_3$, ppm): 3.1 (t, $3NCH_2$), 4.2 (t, $3OCH_2$), 7.5 (dd, 12H, aromatic) and 10.9 (s, 3CHO).
The trialdehyde 2 was prepared as reported in ref. 9.

8. CsCl (0.5 mmoles) and the trialdehyde 1 (1 mmol) were dissolved in methanol (250 ml) at 40°C. To this stirred solution was added a solution of 1,2-diaminobenzene (1.5 mmoles) dissolved in methanol (200 ml) in a dropwise manner over a period of 5 h. The temperature of the reaction mixture was maintained at 40°C. After the addition was over, the reaction mixture was stirred at 40°C for an additional 3 h. period. The Schiff base that formed was reduced *insitu* by refluxing for 4 h with $NaBH_4$.Then methanol was removed at low pressure in a rotary evaporator.The residue obtained first shaken with water and extracted with chloroform.The chloroform layer was dried over anhydrous Na_2SO_4 and removal of the solvent gave a light yellow oily liquid. ^{1}H-NMR (80 MHz, $CDCl_3$, ppm): 3.27 (t, 6H, a), 4.03 (t, 6H, b), 4.48 (s, 6H, c) and 6.78 (m, 36H, aromatic). ^{13}C-NMR (20.1 MHz, $CDCl_3$, ppm): 54.5 (3c, a), 64.8 (3c, b), 67.1 (3C, c), 113.7, 116.9, 120.4, 128.6, 133.5, and 158.4 (aromatic carbons). The cryptant L^2 was prepared by follwing the above procedure from the trialdehyde 2 and 1,2-diaminobenzene.
^{1}H-NMR (80 MHz, $CDCl_3$, ppm): 3.06 (t,6H, a), 4.15 (t, 6H, b), 4.51 (s, 6H, c) and 7.0 (m, 36H, aromatic). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): 54.0 (3C, a), 61 (3C, b), 66 (3C, c), 112.0, 116.5, 120.5, 122.0, 123.0. 129.0, 130.0, 131.0, 132.0 and 156.5 (aromatic carbons).The FAB-mass spectrum of L^1 and L^2 did not show the molecular ion peak due to fragmentation.

9. Ragunathan,K.; Bharadwaj, P. K. *Tetrahedron Lett.*, **1992**, 7581-7584.

10. All are solids and gave satisfactory elemental analyses.

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