

Template synthesis of a hetero-ditopic cryptand with three naphthyl side groups: Synthesis and characterisation of Cu(II) and Ni(II) cryptates

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Abstract. A new hetero-ditopic cryptand with naphthyl side groups has been synthesized by tripod-tripod Schiff base condensation of a tripodal trialdehyde with *tris*(2-aminoethyl)amine in presence of Cs(I) ion. This cryptand reacts readily with Cu(II) and Ni(II) salts forming mononuclear cryptates. The Cu(II)-cryptate can accept a molecule of H₂S which is tightly bound to the metal ion forming a CuN₄S complex. The electronic spectral characteristics are indicative of the presence of Cu–SH₂ bond.

Keywords. Macrobicyclic cryptand; template synthesis; transition metal cryptates.

Imposition of a desired coordination geometry on to metal ions has important bioinorganic relevance (Vallee and Williams 1968). Such an imposition is effected on the metal ions at the intrinsic active sites (Solomon *et al* 1992) of metalloenzymes.

The new cryptand (L) is synthesized by tripod-tripod Schiff base condensation of the trialdehyde (A) and *tris*(2-aminoethyl)amine (B) followed by NaBH₄ reduction (figure 1). Previously, we reported the synthesis of an analogous cryptand following the same synthetic strategy (Ragunathan and Bharadwaj 1992). The present cryptand is synthesized to study whether the naphthyl side groups can effectively shield the cavity from outside interference and thus can effect unusual coordination of metal ion inside the cavity. The trialdehyde is synthesized in 65% yield by treating 2-hydroxynaphthalene-1 carbaldehyde (3 mmoles) with *tris*(2-chloroethyl)amine (1 mmol) in presence of KOH (3 mmoles) in 50 dm³ of refluxing ethanol. m.p. 138–140°C (uncorrected); IR 1660 cm⁻¹ (C=O stretching); 80 MHz ¹H-NMR (CDCl₃, SiMe₄, ppm): 3.2(*t*, 6H, NCH₂); 4.3(*t*, 6H, OCH₂), 7.5(*m*, 18H, aromatic) and 10.9(*s*, 3H, CHO).

The trialdehyde (1 mmol) and CsCl (1 mmol) were dissolved in a mixture of 150 dm³ of MeOH and 50 dm³ of THF at 40°C. To this solution was added dropwise a solution of *tris*(2-aminoethyl)amine (1 mmol) in 150 dm³ of MeOH over a period of 5 h under an argon blanket. The reaction went smoothly at 40°C. After a total of 8 h, the Schiff base that formed was reduced *in situ* with NaBH₄. Upon removal of solvents and treatment with water, the pale yellow product was extracted with CHCl₃. The cryptand is purified by column chromatography on neutral alumina (CHCl₃–MeOH). The product was obtained as a high viscous pale yellow liquid. Yield 52%. ¹H-NMR (400 MHz, CDCl₃, ppm): 2.4(*t*, 6H, a); 2.7(*t*, 6H, b); 3.4(*t*, 6H, e); 4.2(*s*, 6H, c); 4.3(*t*, 6H, d) and 7.6(*m*, 18H, aromatic). ¹³C-NMR (100 MHz, CDCl₃, ppm): 43.0(3C, a); 48.2(3C, e); 54.9(3C, b);

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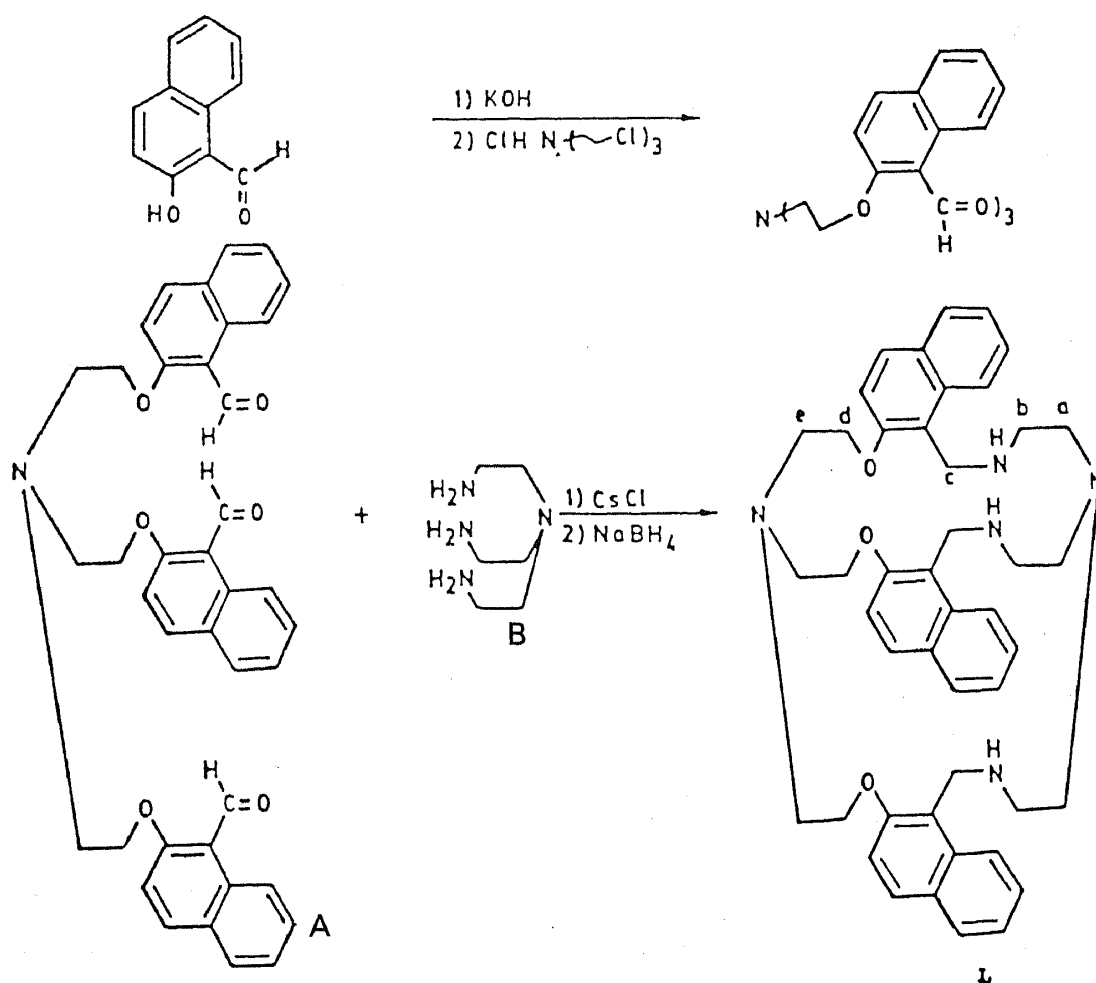


Figure 1. Synthetic scheme for the cryptand L.

55.1(3C, c); 68.7(3C, d) and 114.2, 122.1, 123.8, 124.0, 127.1, 129.0, 129.7, 134.3, 147.0 and 154.8 (aromatic). FAB-mass: $m/z = 710 [L]^+$.

Any Cu(II) or Ni(II) salt readily forms the mononuclear cryptate. The recognition site for the metal ion is at the tren-end of the cavity. The crystal structures of Cu(II) and Ni(II) complexes of similar cryptands (unpublished work of P Ghosh, D Chand and P K Bharadwaj) show that the metal ion always occupies the tren-end of the cavity. The ligand superstructure imposes a distorted tetrahedral geometry onto the Cu(II) ion, surmounting the ligand field driven tendency of CuN₄ to form square planar complexes. The ligand field bands of the Cu(II)-complex agree well with those of X-ray crystallographically characterised pseudotetrahedral CuN₄ chromophores (Yokoi and Addison 1977; Knapp *et al* 1990) as well as our Cu(II)-cryptates. Similarly, the spectrum of the mononuclear Ni(II)-cryptate matches closely that of the pseudotetrahedral NiN₄ complex (Knapp *et al* 1990). Examples of pseudotetrahedral NiN₄ complexes are rare in the literature. However, the exact coordination geometry of the two cryptates can be ascertained from their crystal structural studies. The RT magnetic moment ($\mu_{\text{eff}}/\mu_{\text{B}}$) for the cupric cryptate is 2.1 and is consistent with a discrete Cu(II)-complex. For the Ni(II)-cryptate it is 3.0 which is attributable to a coordination geometry having a flattened tetrahedral symmetry (Hill *et al* 1982).

The Cu(II)-cryptate exhibits a broad isotropic ESR signal with $g_{av} = 2.06$ both at 298 and 77 K. In MeCN at RT, however, an axial signal corresponding to the $d_{x^2-y^2}$ ground state is obtained. The g_{\parallel} value of 2.13 is within the range for a pseudotetrahedral CuN_4 complex (Blumberg and Peisach 1974) while the A^{Cu} value ($60 \times 10^{-4} \text{ cm}^{-1}$) is the smallest reported to date for a tetracoordinate complex of Cu(II). On cooling to 77 K, both the g_{\parallel} and the A^{Cu} values increase ($g = 2.19$; $A^{Cu} = 91 \times 10^{-4} \text{ cm}^{-1}$), which is due to conformational changes in the ligand superstructure and leads to a change in the coordination symmetry.

The Cu(II)-cryptate shows secondary recognition. When a stream of dry H_2S gas is bubbled through an acetone solution of the cryptate for 5 min, no precipitate was observed; instead the solution turned green from the original blue colour. The green solid isolated gives two peaks at m/z 873 and 772 that correspond to the liberation of one and two perchlorate ions respectively from the complex, $[L = Cu(II)(H_2S)](ClO_4)_2$. The infrared spectrum of the solid cryptate shows a weak absorption at 2490 cm^{-1} which is not present in the parent compound. Bonding of S (of H_2S) to the metal ion is revealed by the appearance of a new band at λ_{max} of 440 nm ($\epsilon_{max} = 450 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). This band is attributable (Kuehn and Taube 1976; Kuehn and Isied 1980) to the LMCT transition involving H_2S and the Cu(II) ion. The magnetic moment number at 301 K is 2.09 indicative of a discrete mononuclear Cu(II)-cryptate. EPR spectrum of the solid complex at 298 K is anisotropic with $g_{av} = 2.07$ which becomes axial at 77 K. The solution spectra in MeCN at 295 K show a typical four-line signal with $g_{av} = 2.07$ and $A^{Cu} = 65 \times 10^{-4} \text{ cm}^{-1}$. At 77 K, the signal is highly rhombic with the values: $g_1 = 2.17$, $g_2 = 2.07$, $g_3 = 2.03$ and the hyperfine coupling is not well-resolved.

In summary, a new cryptand has been synthesized on a Cs(I) template in high yields. It shows a definite recognition site for Cu(II) and Ni(II). The donor atoms are able to impose a pseudotetrahedral geometry onto Cu(II) and Ni(II) ions. The Cu(II)-cryptate is found to bind one H_2S molecule. Crystallisations of the complexes are in progress. Their structures along with detailed spectroscopic studies will be reported.

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