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The Preparation of 1,4,8,11-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetra-azacyclotetradecane and its Complexes with Na(I), Cu(II) and Ni(II)

ROBERT W. HAY and DAVID M. S. CLARK

Chemistry Department, University of Stirling, Stirling FK9 4LA, U.K.

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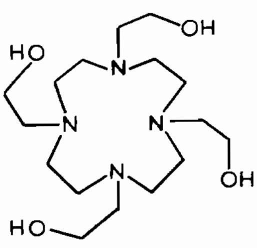
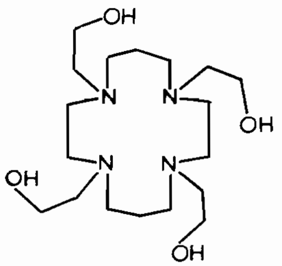
Dale and coworkers [1] have reported the preparation of 1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetra-azacyclododecane(I) by the reaction of ethylene oxide with cyclen at 0 °C in aqueous solution.



(I) = A



(II)

The ligand uses a varying number of ligating side-arms for the complexation of alkali cations leading to penta-, hepta-, and octa-coordination for Li^+, Na^+ and K^+ respectively, and to tetrahedral encapsulation of a water molecule. The crystal structures of $(A)(LiCl)_2(H_2O)_2$ [2] and $(A)\cdot H_2O$ [3] have been published. The present publication discusses the preparation of the cyclam derivative (II), where cyclam = 1,4,8,11-tetra-azacyclotetradecane, and its interaction with Na(I), Cu(II) and Ni(II).

Experimental

Cyclam was prepared as described by Barefield and Wagner [4].

1,4,8,11-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetra-azacyclotetradecane was prepared as follows. Cyclam (1 g) was dissolved in water (*ca.* 25 cm^3). The solution was cooled to 0 °C in an ice bath and ethylene oxide (6 cm^3) added. The mixture was stirred at 0 °C for 2 hr. The initially formed solid hydrate or clathrate of ethylene oxide dissolved during this time to give a clear solution. The solvent was removed on a rotatory evaporator to give a yellowish oily residue. Refrigeration overnight gave colourless crystals of the tetrakis(2-hydroxyethyl)derivative, which were filtered off, washed with water and air dried, m.p. 112 °C. *Anal.* Calcd for $C_{18}H_{40}N_4O_4\cdot H_2O$: C, 54.80; H, 10.22; N, 14.20; H_2O, 4.56%. Found: C, 54.70; H, 10.35; N, 14.36; H_2O, 4.8%. The water content was determined by TGA. The IR spectrum (KBr disc) lacks the νNH bands which occur in cyclam at 3182 and 3265 cm^{-1}; but gives a sharp band at 3420 cm^{-1} assigned to νOH. The ^{13}C nmr spectrum is fully consistent with the expected structure ($CDCl_3$ solvent and TMS reference) giving signals at 25.49δ ($-CH_2-\mathit{C}H_2-CH_2-$), 49.50$\delta$ ($-\mathit{C}H_2-CH_2$), 52.18δ ($\mathit{C}H_2-CH_2-\mathit{C}H_2$), 55.89$\delta$ ($\mathit{C}H_2-N$), 59.55δ ($\mathit{C}H_2-N$). The latter four signals are of approximately equal intensity and are of roughly twice the intensity of the 25.49δ signal.

NMR measurements were carried out with a Bruker WP80 instrument. ^{23}Na measurements were made at 21.2 MHz.

Results and Discussion

Reaction of ethylene oxide (oxiran) with cyclam in aqueous solution at 0 °C readily gives the tetrakis-(2-hydroxyethyl)-cyclam(II) in reasonable yield.

Cyclen has a small hole size and gives *cis*-complexes with metal ions such as Co(III) (r = 52 pm) and Rh(III) [5]. Copper(II) gives the square pyramidal complex $[Cu(cyclen)NO_3]NO_3$ in which the copper atom lies 0.5 Å above the plane of the four nitrogen donors [6]. The 14-membered ring of cyclam provides a larger hole size, thus $[Co(cyclam)(ClO_4)_2]$ has planar coordination to S = ½ Co(II) with perchlorate oxygen atoms completing a tetragonally elongated octahedral arrangement [7]. The complexes *trans*-$[Ni(cyclam)Cl_2]$ [8] and $[Cu(cyclam)](ClO_4)_2$ [9] involve planar coordination of the nitrogen donors. A preliminary report of the structures of $[Li(cyclam)]ClO_4$ and $[Li_2(cyclam)](ClO_4)_2$ has appeared [10] indicating that the nitrogen atoms of $[Li(cyclam)](ClO_4)_2$ are crystallographically equivalent. The alkali metal cations have the following ionic radii Li^+ (60 pm) Na^+ (95 pm), K^+ (133 pm) [11] and the formation of complexes with tetrakis(2-hydroxyethyl)cyclam is expected.

Complexation with Na^+ was monitored by ^{23}Na NMR using Dy^{3+} as a shift reagent. The NMR measurements involved concentric sample tubes. The inner tube containing 100 mM NaCl in D_2O, and the outer tube 10 mM ligand, 50 mM NaCl and 10 mM $DyCl_3$ in H_2O. The instrument was locked on the D_2O signal. Under these conditions the outer tube signal is shifted −0.45 ± 0.07 ppm with respect to the inner tube signal (Fig. 1).

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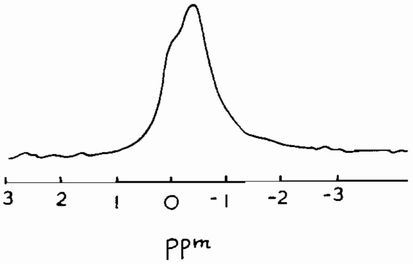
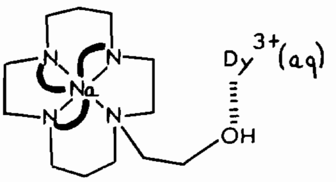


Fig. 1. ^{23}Na spectrum at 21.2 MHz. The right hand signal occurs with 10 mM ligand, 50 mM MaCl and 10 mM $DyCl_3$ in H_2O (outer tube). The left hand signal is due to 100 mM NaCl in D_2O (inner tube).

These results would be consistent with the formation of a complex of type (III), in which three of the 'arms' are ligated to Na^+ and the free arm interacts with Dy^{3+}. Such a hepta coordinate complex with Na^+ and tetrakis(hydroxyethyl)cyclen has been characterised in the solid state [1]. Tris(hydroxyethyl)cyclam can transfer sodium across a $CHCl_3$ membrane, using the U-tube technique [13]. One arm of the U-tube contained an aqueous solution of sodium 2,4-dinitrophenolate and the ligand, and the other arm water. The two arms being separated by $CHCl_3$. Transfer of the coloured sodium salt across the membrane occurred over several days.



(III)

A copper(II) complex can be readily prepared by mixing ethanolic solutions of the ligand and copper(II) perchlorate. Cooling in ice gives the crystalline complex, which has λmax 630 nm in ethanol solvent. The copper(II) complex dissociates rapidly in acidic or basic solution, in marked contrast to the behaviour observed with the copper(II) derivative of cyclam which dissociates extremely slowly. The observed lability is similar to that of the copper(II) complex of tetrakis(cyanoethyl)cyclam which is also labile in acidic solution [12].

The nickel(II) complex forms relatively slowly (minutes) on mixing ethanolic solutions of the ligand and nickel(II) perchlorate (1:1 mole ratio). The complex has a typical octahedral spectrum (ethanol solvent) with the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (O_h) occurring at 17000 cm^{-1} and the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition at 27,300 cm^{-1}.

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