

## [3]-Cryptates: Metal Cation Inclusion Complexes with a Macrotricyclic Ligand

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**Summary** A novel macrotricyclic ligand (I) has been synthesized and the formation of mono and binuclear-complexes of the [3]-cryptate type with various metal cations has been observed.

MACROHETEROCYCLIC ligands of natural or synthetic origin complex various metal cations especially of the alkaline and alkaline-earth types.<sup>1</sup> It has been shown recently that macroheterobicyclic molecules may form inclusion complexes (termed "cryptates")<sup>2,3</sup> which display higher stabilities and selectivities (in the same solvent) than the natural and synthetic macrocycles.<sup>4</sup>

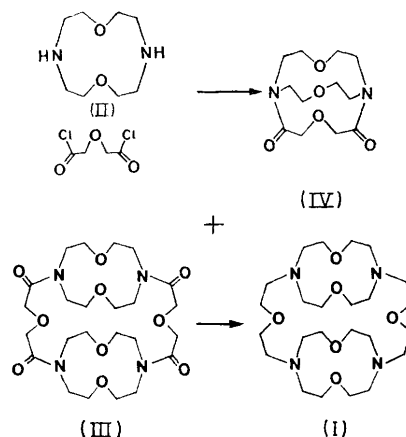
We report here the synthesis and some properties of a tetra-azahexaoxa-macrotricyclic ligand (I), which forms inclusion complexes of the [3]-cryptate type† with various metal cations.

Condensation, in high dilute conditions, of the macrocyclic diamine (II)<sup>4</sup> with diglycolic acid dichloride<sup>2</sup> affords a dimer (30%) together with the macrobicyclic monomer (IV) (ca. 10%).<sup>5</sup>

The dimer is the macrotricyclic tetramide (III) (which crystallizes with two molecules of chloroform; m.p. 243–246°) formed by the condensation of two molecules of the diamine (II) with two acid chloride molecules. (III) may be converted into the tetramine (I) (m.p. 54–55°) by reduction with diborane and subsequent hydrolysis.<sup>2,4</sup> The spectral and analytical data of (I), (II), and (IV)<sup>5</sup> agree with the proposed structures. The formation of a macrotricyclic tetramide of type (III) containing C<sub>9</sub> chains between any two nitrogens and no ether oxygens, has also been described recently.<sup>6</sup>

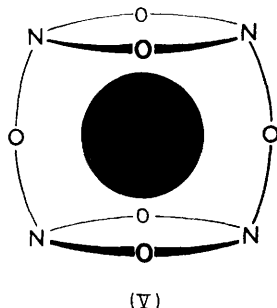
† A more general terminology extending the original "cryptate" denomination<sup>2</sup> of bicyclic complexes to mono-<sup>1</sup> and to polycyclic-systems could be [1]-, [2]-, [3]-, [n]-cryptates for metal cation inclusion complexes formed by macrocyclic, macrobicyclic, -tricyclic, -n-cyclic ligands.

The <sup>1</sup>H 250 MHz n.m.r. spectrum of (I) (in CDCl<sub>3</sub>) displays two CH<sub>2</sub>-N triplets (relative areas 1:2) and two CH<sub>2</sub>-O triplets (relative area 1:2). The 25 MHz noise-decoupled Fourier-transform <sup>13</sup>C n.m.r. spectrum of (I) (CDCl<sub>3</sub>) shows two CH<sub>2</sub>-N <sup>13</sup>C signals at high field and two CH<sub>2</sub>-O signals at low field (relative areas 2:1 within each group).



When solid RbI is added to a CDCl<sub>3</sub> solution of (I) rapid changes occur in the <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra and a new compound is formed. The <sup>1</sup>H spectrum now contains ill-resolved CH<sub>2</sub>-O signals and the CH<sub>2</sub>-N pattern shows that, while the CH<sub>2</sub>-N protons in the bridges remain equivalent, the CH<sub>2</sub>-N protons in the twelve-membered

rings have become non equivalent, displaying a geminal coupling of 14 Hz. The  $^{13}\text{C}$  n.m.r. spectrum of this new compound contains four peaks which are appreciably shifted from their original positions in (I). Isolation and analysis of this compound shows that it is a 1:1 complex between (I) and RbI. The symmetry properties deduced from the n.m.r. spectra and the stoichiometry of the complex favour a structure in which the rubidium cation is contained in the central molecular cavity defined by the two rings and the two bridges of compound (I); this is shown schematically in (V), where the tricyclic ligand (I) is in its most extended form (cavity length of about 6 Å) and the cation is arbitrarily located in the centre.†



The non-equivalence of the  $\text{CH}_2$  protons of the two rings point to the much greater rigidity of the ligand in the cryptate, due to the inclusion of the cation, as compared to the free ligand where the chemical shifts may be averaged by exchange of the 'inside' and 'outside' faces of each ring system.

The formation of similar 1:1 cryptate complexes of (I) with NaI, NaCl, KI,  $\text{KNO}_3$ , RbI, CsI,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{La}(\text{NO}_3)_3$ ,  $\text{AgNO}_3$ ,  $\text{TlNO}_3$ , and  $\text{PbCl}_2$  has been observed

† The possibility of an unsymmetrical location of the cation in some complexes will be discussed in a later publication.

<sup>1</sup> R. J. P. Williams, *Quart. Rev.*, 1970, **24**, 331; M. R. Truter and C. J. Pedersen, *Endeavour*, 1971, **30**, 142; C. J. Pedersen and H. K. Frensdorff, *Angew. Chem.*, 1972, **84**, 16.

<sup>2</sup> B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Letters*, 1969, 2885.

<sup>3</sup> B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Letters*, 1969, 2888.

<sup>4</sup> J. M. Lehn and J. P. Sauvage, *Chem. Comm.*, 1971, 440; and unpublished results.

<sup>5</sup> J. Cheney and J. M. Lehn, *J.C.S. Chem. Comm.*, 1972, 487.

<sup>6</sup> H. E. Simmons, C. H. Park, R. T. Uyeda, and M. F. Habibi, *Trans. N.Y. Acad. Sci.*, 1970, II, **32**, 521.

<sup>7</sup> D. E. Fenton, M. Mercer, N. S. Poonia, and M. R. Truter, *J.C.S. Chem. Comm.*, 1972, 66.

by n.m.r. spectroscopy. Several of these have been isolated and characterized [ $\text{RbI}$ ,  $\text{CsI}$ ,  $\text{Ba}(\text{SCN})_2$ ].

The stability constants ( $\log K_s$ ,  $1 \text{ mol}^{-1}$ ) of the 1:1 cryptates of ligand (I) with the alkali metal cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  range between 1 and 1.7 in water and are equal respectively to ( $\pm 0.2$ ) 4.5, 5.8, 6.2,  $> 6.0$  in methanol, as determined by means of cation specific electrodes. The  $\text{Ag}^+$  1:1 complex of (I) has  $\log K_s = 6.0$  in water and  $> 9.5$  in methanol. Stability and selectivity of these complexes are thus lower than in the case of the [2]-cryptates.<sup>4</sup>

With  $\text{AgNO}_3$  and  $\text{TlO}_2\text{CH}$  in  $\text{CDCl}_3$  or water, further spectral changes are observed when more salt is added to the 1:1 complex until a 1:2 stoichiometry is reached; no significant changes are observed beyond this point. The 1:2 (I) +  $2(\text{AgNO}_3)$  complex has been isolated and characterized. The general features of its  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra in  $\text{D}_2\text{O}$  solution are analogous to those of [(I),  $\text{Rb}^+$ ]- $\text{I}^-$  in  $\text{CDCl}_3$ . Thus the symmetry of the two complexes should be the same, implying that the two  $\text{Ag}^+$  cations are both either outside or inside the molecular cavity. Since the spectral data also show that cation exchange is very slow and since the [(I),  $2\text{Ag}^+$ ]( $\text{NO}_3^-$ )<sub>2</sub> complex is found to be very stable {stability constant larger than  $10^6$   $1 \text{ mol}^{-1}$  in methanol with respect to [(I),  $\text{Ag}^+$ ] $\text{NO}_3^-$  +  $\text{AgNO}_3$ }, we favour a structure where both silver cations are contained in the molecular cavity each being co-ordinated to the two nitrogen atoms and to the two oxygen atoms of one of the twelve-membered rings and both cations sharing the oxygen sites in the bridges (for a similar situation see ref. 7).

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