Oxathia-macrobicyclic Diamines and their "Cryptates"

By B. DIETRICH, J. M. LEHN,* and J. P. SAUVAGE
(*Institut de Chimie, 1 rue Blaise Pascal, Strasbourg-67, France*)

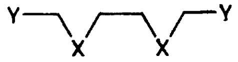
Summary The synthesis and complexation properties of new oxathia-macrobicyclic diamines are reported.

POLYOXA-MACROBICYCLIC diamines have been synthesized recently.[1,2] It has been found that these compounds are able to complex various metal cations, leading to a new class of complexes, called cryptates, in which the cation is included within the central molecular cavity of the macrobicyclic system.[1,2] The structure of these complexes has been confirmed recently by *X*-ray crystallography.[3]

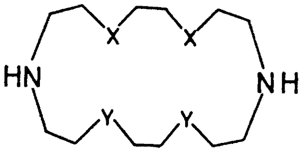
It is probable that one of the factors governing the stability of the cryptates, and thus the cation selectivity of a given polydentate bicyclic ligand, is the nature of the heteroatoms present in the three bridges of the macrobicyclic system.

The previously reported substances[1] contained only oxygen atoms in the bridges and nitrogen at the bridgeheads. We report here preliminary results about the synthesis and properties of the sulphur-oxygen-containing macrobicyclic diamines (V)—(VII).

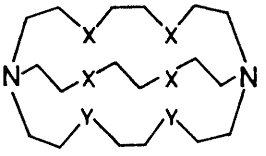
The synthetic procedure used was similar to that previously described.[1] Starting from the required dioxa- or dithia-diamine or dicarboxylic acid dichloride (I), the macrocyclic diamines (II,[1] m.p. 115—116°), (III, m.p. 47°), and (IV,[4] m.p. 125°) are obtained in 75, 55, and 45% yield, respectively, by condensation under high dilution conditions, followed by reduction (lithium aluminium hydride or diborane) of the diamides obtained. Condensation (high dilution) of these compounds with the required diacid dichloride (I) followed by reduction (diborane) of the intermediate diamides leads to the macrobicyclic diamines (V), (VI), and (VII) in 25, 20, and 7% yield, respectively from starting materials (I).



(I) X = O or S
Y = COCl or CH_2NH_2



(II) X = Y = O
(III) X = O,Y = S
(IV) X = Y = S



(V) X = O,Y = S
(VI) X = S,Y = O
(VII) X = Y = S
(VIII) X = Y = O

Compounds (V)—(VII) are solids [m.p. 78—80° (V); 86—87° (VI); 172° (VII)] whose solubility in water and in organic solvents decreases as the number of sulphur atoms increases [(VII) is insoluble and (VI) is only slightly soluble in water]. Assignment of their structures is based on the synthetic procedure used, on their analytical and spectral properties [n.m.r. spectra (see Figure), mass spectra], and on comparison with the previously described substance (VIII).[1]

It is not yet known if (V)—(VII) exist in a preferred conformation (of the *exo–exo*, *exo–endo*, or *endo–endo* type[1]) or as a mixture of conformations interconverting rapidly.

Like the hexaoxa-diamine (VIII),[1,2] compounds (V)—(VII) form complexes with various metal cations.† The ease of complex formation decreases along the series (V)—(VII) and only a few complexes of (VI) and (VII) have so far been obtained. The complexes are generally of 1 : 1 stoicheiometry (although complex anions are found in some cases); they are probably of the cryptate type,[2] the cation being held in the centre of the macrobicyclic molecular cavity of the *endo–endo* conformational isomer.[2,3]

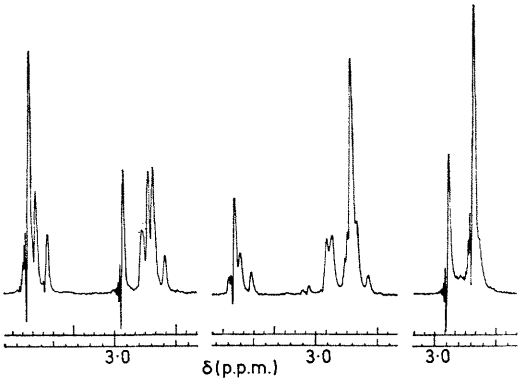


FIGURE. 60 *MHz N.m.r. spectra* ($CDCl_3$ *solutions*) *of compounds* (V), (VI), *and* (VII) (*from left to right*).

In the case of compounds (V) especially, the cryptate formation may be observed conveniently by n.m.r. spectroscopy when a suitable inorganic salt is added to a water or a chloroform solution of the ligand. The magnitude of the spectral changes from the parent diamine to the cryptate depends on the nature of the cation. For example, formation of the KSCN cryptate of (V) displaces principally the $N-CH_2$ resonances, whereas AgSCN or $Pb(SCN)_2$ cryptates show a strong displacement of several signals, especially of the $S-CH_2-CH_2-S$ singlet. Such specific changes may give an indication of the preferred complexing sites of a given cation in a given bicyclic ligand.

As examples, the formation of the following cryptates has been observed: (i) in chloroform: (V) + KSCN, $Ba(SCN)_2$, AgSCN, $TlNO_3$ *etc.*; (VI) + LiSCN, NaSCN, AgSCN; (ii) in water: (V) + NaCl, KSCN, RbCl, $TlNO_3$, AgSCN, $Ba(SCN)_2$, $Pb(SCN)_2$ *etc.* A complex of (VI) with $Co(SCN)_2$ has been isolated; it has 1 : 2 stoicheiometry, the structure probably being $[(VI),Co][Co(SCN)_4]$.

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† The monocyclic compounds (II),[1] (III), and (IV)[4] also form complexes with a number of metal cations, *e.g.* $[(III),Co(SCN)_2]$ has been obtained; see also refs. 1 and 4.

[1] B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Letters*, 1969, 2885.
[2] B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Letters*, 1969, 2889.
[3] B. Metz, D. Moras, and R. Weiss, *Chem. Comm.*, 1970, 217.
[4] D. St. C. Black and I. A. McLean, *Chem. Comm.*, 1968, 1004; *Tetrahedron Letters*, 1969, 3961.