NEW MACROCYCLIC POLYTHIOETHERS

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The synthesis of macrocyclic polyethers (1) has received recent attention in an extensive study by Pedersen (2) involving the formation of a wide variety of types containing three or more ring oxygen atoms. A number of those cyclic polyethers, containing five to ten oxygen atoms have been found to form stable complexes with salts of the alkali and alkaline earth elements: these appear to be salt-polyether complexes formed by ion-dipole interaction between the cation and the ring oxygen atoms and their stability depends among other factors upon the relative positions of the oxygen atoms. Some polyethers also form complexes with transition elements (2,3): for example, a planar polyether with six oxygen atoms has been shown (3) to act as a bis-tridentate ligand in its formation of cobalt complexes.

Whereas the macrocyclic polyether (I) (2) tends to be planar in its metal complexes, the corresponding thioether analog (II) can be expected from models to accommodate the six octahedral valence positions of a transition metal ion. Also, the coordinating ability of ether oxygen is slightly weaker than that of thioether sulphur (4), so that macrocyclic polythioethers could form metal salts and complexes more readily than polyethers.

We now report the synthesis of three new macrocyclic thioethers, including the hexathioether (II), which have been designed in an attempt to satisfy some or all of the octahedral sites of a suitable transition metal.
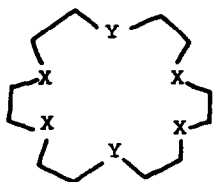
(I) : X = Y = O

(II) : X = Y = S

(III) : X = S, Y = O

(IV) : X = S, Y = NH
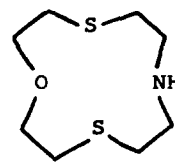
(V)

The hexathioether (II) and the tetrathioether (III) have been synthesised as white, crystalline solids [(II); m.p. 89–90° (31%) : (III); m.p. 50° (7%)] by reaction of 1,2-dibromoethane with the disodium salt of 3-thiapentane-1,5-dithiol and 3-oxapentane-1,5-dithiol respectively, in ethanol at high dilution. The yield of (II) was surprisingly high and this 18-membered ring appears to be geometrically favourable. The proposed structures were confirmed by analytical and osmometric data and the appearance of molecular ions at m/e 360 and 328 in the respective mass spectra. The methylene protons of (II) appeared as a sharp singlet at τ 7.20 in the n.m.r. spectrum (CDCl$_3$, 60MHz). In the n.m.r. spectrum (CDCl$_3$, 60MHz) of (III), the methylene splitting pattern was more complex, showing a multiplet centred at τ 7.2 (16H: methylene protons adjacent to sulphur) and a triplet at τ 6.31, J = 6.5 cps (8H: methylene protons adjacent to oxygen). By comparison, the n.m.r. spectrum (CDCl$_3$, 60MHz) of the previously reported (5) macrocycle (IV) showed a methylene multiplet resonance centred at τ 7.2 (24H).

The polythioether (II) behaves as a sexadentate ligand – apparently the first all-sulphur sexadentate – and readily yielded complexes [M(ligand)](picrate)$_2$ (M = Ni, Co), which were characterised by elemental analysis. They exhibited visible absorption spectra compatible with octahedral coordination and showed magnetic moments of 2.35 B.M. (Ni) and 3.01 B.M. (Co) at 18.5°. By contrast, it has not been possible to obtain nickel and cobalt complexes of (III).

In general, for macrocyclic sexadentates with four sulphur donor atoms in an equatorial plane, there are two possible configurations (A) and (B) for their metal complexes.
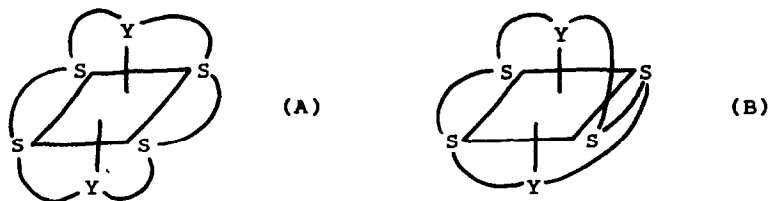
In acting as a sexadentate ligand, the thioether (II) must give complexes of·
configuration (A). On the other hand, if (III) were to act as a sexadentate,
it would give complexes of configuration (B).

Despite the difference in coordinating strength of oxygen and sulphur
donor atoms, it would appear from the above results that configuration (A) is
geometrically less strained than configuration (B) for an 18-membered macrocycle,
thus suggesting a preference for this configuration in the complexes (5) of the
flexible thioether (IV). However, a 20-membered macrocycle has been shown (6)
to give complexes of configuration (B), but these can be decomposed easily.

The 12-membered dithioether (V) has also been designed for octahedral
coordination, but in this case only four donor atoms are available. This
macrocycle (V) has been prepared as a white, crystalline solid, m.p. 64° (18%)
by the reaction of the disodium salt of 3-oxapentane-1,5-dithiol with
di-(2-bromoethyl)amine (7) in ethanol at high dilution. Elemental analysis
coupled with the appearance of a molecular ion at m/e 207 in the mass spectrum
provided firm evidence for the proposed cyclic structure (V). The n.m.r.
spectrum (CCl_4, 60MHz) showed a multiplet from τ 6.9 to τ 7.2 (13H: methylene
protons adjacent to nitrogen and sulphur, together with the amino proton) and a
triplet at τ 6.17, J = 5 cps (4H: methylene protons adjacent to oxygen).
Infrared absorption at 3255 and 3230 cm^{-1} indicated the presence of some
hydrogen bonding of the amino proton. .

Thioether (V) readily formed metal complexes with octahedral metal
ions : it reacted with nickel (II) chloride and cobalt (II) chloride and bromide
to give the emerald green Ni(ligand)Cl_2 and the purple Co(ligand)X_2 (where X =
Cl, Br). These complexes were characterised by elemental analysis and were
found to exhibit visible spectra characteristic of octahedral complexes. Also,

conductance measurements in nitromethane established that the complexes were non-electrolytes. The two N-H infrared stretching vibrations in the free ligand were replaced by a single absorption at about 3170 cm^{-1} in the metal complexes.

From geometrical considerations, it is clear that (V) should have a non-planar distribution of its four donor atoms and that the above octahedral complexes should be represented by a configuration in which the two unidentate groups are cis.

Such a configuration has been found (8) for complexes of the analogous compound with four nitrogen donors, whereas larger four-nitrogen macrocycles (9) give complexes both of this configuration and the corresponding trans arrangement, where the four donor atoms lie in a plane.

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