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Folding of a Macrocyclic Ligand Induced by Hydrogenation of Part of the Ring: The effect of Rigidity in the System

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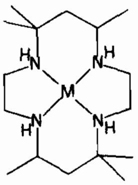
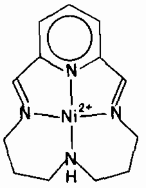
Hydrogenation of imine bonds in macrocyclic complexes is a well documented method of altering the degree of unsaturation in the ligands [1, 2].



I



II

Planar coordination of the macrocycles can be retained in complexes like (I) because of the flexibility of the aliphatic chelate rings; reasoning that is still valid with the more rigid produce from (II) [2, 3]. We wish to report the effect of hydrogenation on the two ligands, (III) and (IV) each containing two rigid components in the ring. The X-ray structure of the Mn(II) derivative of (III) has established a planar arrangement of the macrocycle's ligand. However on hydrogenation of the zinc complexes the macrocycles appear to fold.

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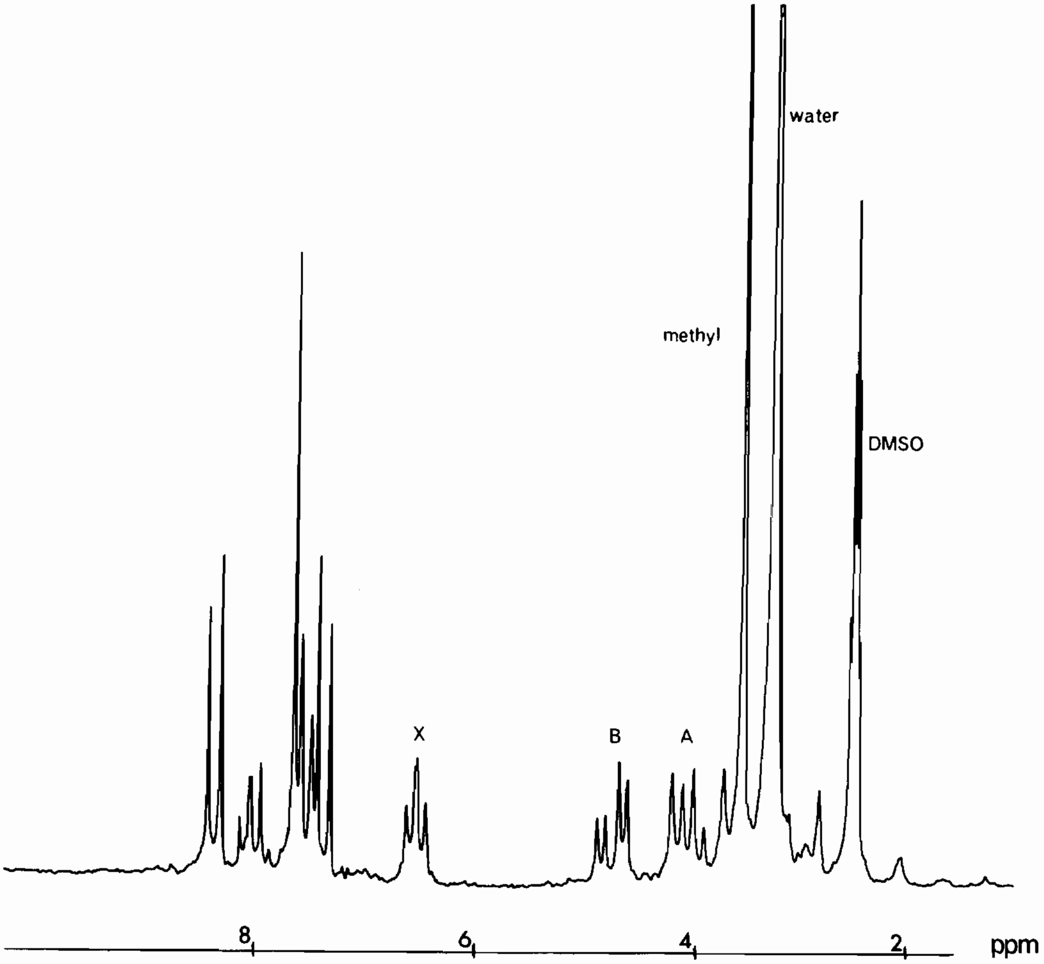
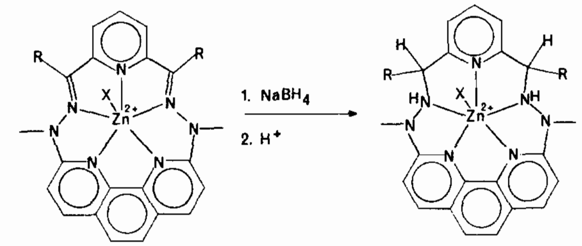


Fig. 1. N.m.r. spectrum of compound (V).



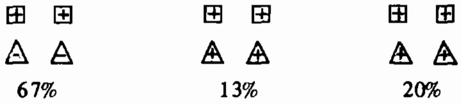
III R = H, X = Cl^-
IV R = Me.

V R = H,
VI R = Me.

Reaction of excess $NaBH_4$ with aqueous solutions of (III) and (IV), followed by acid work up, yield pale yellow solids, (V) and (VI) respectively. Analytical and conductivity data demonstrate that an axial ligand is retained in both complexes.

The ^1H n.m.r. spectrum of a solution of V in d^6-dimethylsulphoxide is shown in Figure 1. The geminal hydrogen atoms are inequivalent and form the AB part of an ABX spin system [4], the X atom being the vicinal hydrazine hydrogen. The two coordinating hydrazine nitrogens in (V) are asymmetric centres and the four possible optical isomers consist of two with N–H bonds on the same side of the macrocycle (*cis*), and two with these bonds on opposite sides (*trans*) of the ring. Molecular models indicate that planar coordination of the pentadentate ligand is possible only with the highly strained *trans* isomers: the rigid phenanthroline and pyridine rings on opposite sides of the sp^3 hybridised nitrogens cause the macrocycle to be folded in the *cis* isomers. The spectrum contains signals from only one of the isomer pairs, the allocation of signals being shown in Figure 1. The presence of the axial ligand by distinguishing between the two axial sites, enables an assignment to be made of the specific pair of optical isomers formed. Hydrogenation results in folding of the macrocycle as the product is the *cis* isomer pair. The coordination geometry about zinc(II) in (V) and (VI) should be between a pentagonal pyramid [5, 6] and an octahedron.

The compound (VI) contains four asymmetric centres and the n.m.r. spectrum is, as expected, more complicated than that of (V). Support for the notion that the only possible isomers formed have *cis* N–H bonds across the fold axis is provided by the spectrum. There are eight possible optical isomers having *cis* N–H bonds, and they fall into three categories for n.m.r. purposes. A schematic diagram of one member from each of these classes is given in Figure 2, along with their relative yields. These yields were measured from the areas under the high field methyl signals in the spectrum. The category with the highest yield has both methyl groups on the less hindered side of the macrocycle: *trans* hydrogenation has occurred across both hydrazone bonds.



□ represents a Nitrogen atom; △ represents a Carbon atom; + indicates that the hydrogen attached to this atom is above the plane of the paper, – that it is below the plane.

Figure 2. Possible optical isomers.

Acknowledgment

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