pH-induced Co-ordination Geometry Change in a Macrocyclic Nickel(II) Complex

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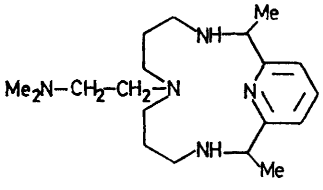
Summary The co-ordination geometry of the Ni^{II} complex with the new macrocyclic ligand L, which contains a side chain, is controlled by the pH of the solution, the square-planar yellow diamagnetic form and the octahedral blue paramagnetic one being stable below and above pH 6·3, respectively.

IN most macrocyclic ligands described in the literature the co-ordinating atoms are an integral part of the cyclic structure.[1] There are, however, a few macrocyclic ligands which, besides the donor groups of the ring, have additional ligand functions attached to a side chain.[2] Such compounds are less rigid in regard to the geometrical requirement of the co-ordinated metal ion and so are especially interesting for structural studies. We report here an example of a new macrocyclic ligand of this type and of the pH-induced change in structure and electronic properties of its Ni^{II} complex.



L

Condensation of *NN*-bis(3-aminopropyl)-*N'N'*-dimethylethylenediamine with 2,6-diacetylpyridine in the presence of Ni^{II} ions and subsequent reduction of the imine groups yields Ni^{II} complexes of L.[3] Of the 14 possible isomers[4] we were able to isolate, by chromatography on Sephadex ionic exchanger SP-C25, three components, (A), (B), and (C), which were eluted in that order with 0·4M sodium acetate at pH 5. The major component (B) was crystallized as a triperchlorate $NiLH(ClO_4)_3$.† Its i.r. spectrum between 2700 and 2300 cm^{-1} shows the typical intercombination bands for an ammonium ion,[5] indicating that one of the amino groups is protonated. The triperchlorate absorbs at 480 nm as a solid and at 476 nm in acetone solution. The electronic absorption is assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition for square planar Ni^{II} complexes.[6] In agreement with this the complex was found to be diamagnetic by n.m.r. techniques.

Addition of 2,6-lutidine to a solution of (B) in acetone gave a blue-violet product, which analysed as $NiL(ClO_4)_2$.† The i.r. spectrum shows no intercombination bands and the electronic absorption spectrum in acetone is typical for triplet state, hexaco-ordinate Ni^{II}. The three bands, which occur at 758, 634, and 367 nm, are assigned to the components of $^3A_{1g} \rightarrow {}^3T_{1g}(F)$ and to the transition $^3A_{1g} \rightarrow {}^3T_{1g}(P)$, respectively.[6]

The colour change from yellow to blue also takes place in aqueous solution when the pH is increased to > 7. Spectrophotometric titration of (B) with NaOH yields a pK_a of 6·29 at 25 °C and $I = 0{\cdot}5$ M. The reversible acid–base equilibrium and the concomitant colour change can be explained by a pH-dependent structural rearrangement. At pH $< 6{\cdot}3$, where the dimethylamino group is protonated, the Ni^{II} ion is surrounded by the four nitrogen donor atoms of the macrocycle in a square planar geometry similar to that of the unsubstituted parent compound $Ni(CRH)(ClO_4)_2$.[4,7] Deprotonation of the dimethylammonium group at pH $> 6{\cdot}3$ produces a potential ligand which can co-ordinate to one of the axial positions whereby an octahedral species is formed. The pH-induced structural change in this Ni^{II} complex is a consequence of the unique combination of the rigid and kinetically stable structure of the macrocycle and the flexible and kinetically labile group of the side chain.

This is similar in some respects to the structural changes induced by external conditions when metal ions are co-ordinated to proteins. The tyrosine 248 residue in carboxypeptidase is free and is *ca.* 10 Å apart from the active Zn^{II} ion in the crystals, but is co-ordinated to the metal ion when the protein is dissolved.[8] Tyrosine 248, located in a flexible part of the protein chain, can approach the metal ion in a similar way as the dimethylamino group of L does. The pH-controlled spectral and geometrical change of the Ni^{II} complex with L also resembles that observed for Co^{II} carbonic anhydrase where, through a pH increase, the visible spectrum dramatically changes from one typical for tetrahedral geometry to one thought to reflect pentaco-ordination.[9]

(*Received*, 7*th October* 1976; *Com.* 1140.)

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† Satisfactory elemental analyses were obtained.

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