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THE CRYSTAL STRUCTURE OF 7R(S),14S(R)-5,5,7,12,12,14-HEXAMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECANENICKEL(II) CHLORIDE DIHYDRATE

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The crystal structure of the title coumpound has been determined by the X-ray diffraction method. The nickel(II) ion is surrounded square-planarly by four nitrogen atoms of the macrocyclic ligand. The strong hydrogen-bond networks prevent the coordination of chloride ions and water molecules, yielding a diamagnetic nickel(II) complex.

The macrocyclic ligand, 7R(S),14S(R)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (hereafter abbreviated as meso-Me_6[14]ane) forms with a nickel(II) ion complexes of the types [Ni(meso-Me_6[14]ane)]$X_2 \cdot 2H_2O$ and [NiX_2(meso-Me_6[14]ane)] ($X = Cl^-$, Br^-, I^-).[1,2] The ligand meso-Me_6[14]ane is constrained by the steric requirements to coordinate in a single plane.[3] As revealed by the electronic spectra and the magnetic properties, the orange dihydrate, [Ni(meso-Me_6[14]ane)]$X_2 \cdot 2H_2O$, is a square-planar four coordinate complex having a singlet ground state, whereas the violet anhydride [NiX_2(meso-Me_6[14]ane)] is a pseudo-octahedral six coordinate complex having a triplet ground state.[1] Our recent study revealed that the solid, orange, diamagnetic dihydrate is converted upon heating to violet, paramagnetic anhydride [NiX_2(meso-Me_6[14]ane)].[2] Conversely, the solid, violet, paramagnetic anhydrous chloro- and bromo-complexes readily revert to [Ni(meso-Me_6[14]ane)]$X_2 \cdot 2H_2O$ unless they are carefully protected from moisture. Of particular interest is the fact that two molecules of water are taken up to produce a diamagnetic nickel(II) ion. Judging from the electronic spectra and the magnetic data, water molecules do not coordinate to a nickel(II) ion, although H_2O has considerable coordinating ability compared with halide ions. Spatial restrictions are not involved since the H_2O molecule is much smaller than Br^-. In an attempt to determine the role played by water to produce a diamagnetic nickel(II) ion, the structural investigation of [Ni(meso-Me_6[14]ane)]$Cl_2 \cdot 2H_2O$ by the single-crystal X-ray diffraction method has been carried out.

The crystals used for X-ray work were prepared from the perchlorate salts[3] by ion exchange (Dowex 1X8). The crystals are triclinic with the space group $P\bar{1}$, a = 8.833(1), b = 8.721(1), c = 8.212(1) Å, α = 86.79(1), β = 100.41(1), γ = 118.61(1)° (Mo K_α, λ = 0.7107 Å), and Z = 1. The structure was solved by the heavy atom method and refined to give an R-value of 0.031 for the 3018 independent reflections collected by an automated four-circle diffractometer (Philips PW 1100). A perspective drawing of the complex is presented in Fig. 1 together with the packing mode. Figure 2 shows the arrangement of the complex cation, chloride ions, and water molecules as viewed perpendicularly to the coordination plane. The nickel(II) atom which is required to lie on a center of symmetry is surrounded by four secondary nitrogen atoms of the macrocyclic ligand, yielding a square-planar, diamgnetic nickel(II) complex. The Ni-N bond distances are 1.957(1) and 1.961(1) Å for N(1) and N(2), respectively, and are in the normal range expected for a low-spin nickel(II) complex. The maclocyclic ligand adopts the most stable conformation : the six-membered chelate rings take the chair form with the C(5)-CH_3 bonds in equatorial positions ; the five-membered rings are in the gauche conformation. The chloride ions and the oxygen atoms of the water of crystallization are not located near the fifth or sixth coordination site but are situated just above and below the amine nitrogen atoms with respect to the coordination plane. All the positions of the hydrogen atoms were found from a difference systhesis and were refined. There appear to be four hydrogen bonds of importance in the structure, i.e., N(1)-H--Cl [3.261(2) Å], N(2)-H--O [2.948(3) Å], O-H--Cl [3.149(2) Å], and O-H--Cl' [3.175(2) Å]. These bonds are drawn as broken lines in Fig. 1. It should be emphasized that all hydrogen atoms involved in these hydrogen bonds lie very close to the respective lines joining the donor and acceptor atoms. Furthermore, one of the lone pairs of the oxygen atom is directed specifically toward the N(2)-H bond. These results suggest that the hydrogen bond networks are tight and strong enough to prevent the coordination of the water molecules and chloride ions, yielding thereby a diamagnetic nickel(II) complex.

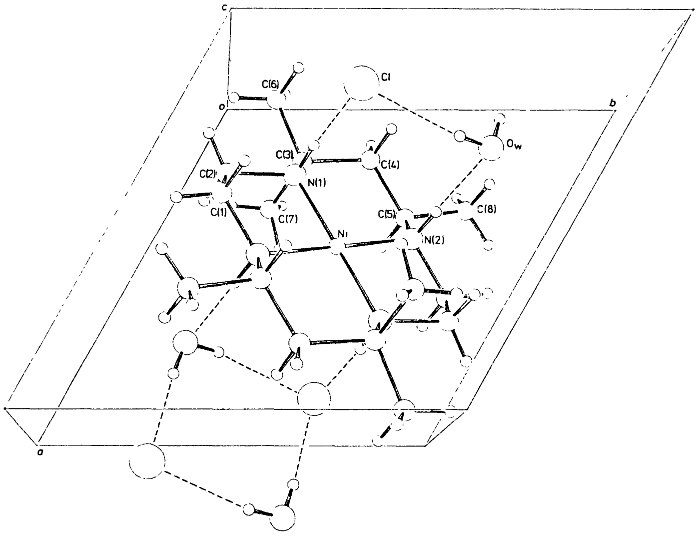

Fig. 1 The crystal structure of $[Ni(meso\text{-}Me_6[14]ane)]Cl_2\cdot 2H_2O$

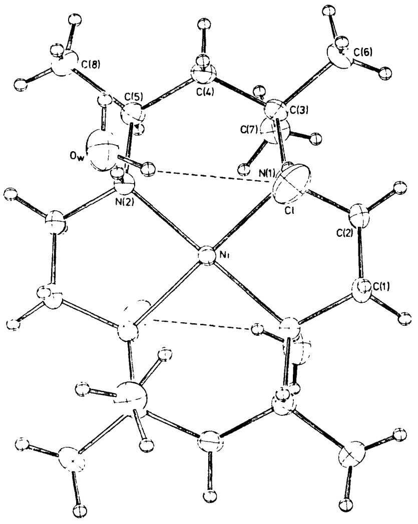

Fig. 2 The structure as viewed perpendicularly to the coordination plane

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