X-Ray Crystal Structure of *meso*-Chloroaqua-6,16-dimethyl-1,5,9,13-tetra-azacyclohexadeca-6,16-dienenickel(II) Chloride

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Summary The stereochemistry of a sixteen-membered cyclic ring nickel(II) complex has been determined.

THE well known reaction of $[Ni(en)_3]^{2+}$ with acetone to obtain the macrocyclic square-planar nickel(II) complex, hexamethyl-1,4,8,11-tetra-azacyclotetradecadienenickel(II), $Ni(ct)^{2+}$, yields three isomeric forms designated as Aα, Aβ, and B.[1] These have been unambiguously identified by crystal structure analysis as the *rac-trans*, *meso-trans*, and *rac-cis* conformers, respectively.[2-4] The *meso-cis* conformer has not been reported in this fourteen-membered ring system and arguments based on conformational analysis have been given to explain the absence of this conformer.[4]

The same results were obtained independently by a ^1H n.m.r. study[5,6] and a similar suggestion was advanced that the strained, eclipsed five-membered chelate rings result in limited stability of the *meso-cis* conformer and hence account for its absence.[6]

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We report here the crystal structure determination of the *meso-cis* conformer in an analogous sixteen-membered ring system. The existence of this conformer is the result of increased ring size and flexibility, and illustrates an important difference between fourteen- and sixteen-membered ring systems. ^{1}H n.m.r. studies[7] have shown that the two isomers, *meso-cis* and *rac-cis*, are interconvertible. Their physical properties have also been characterized.[8] The existence of a *trans* isomer is currently being investigated.

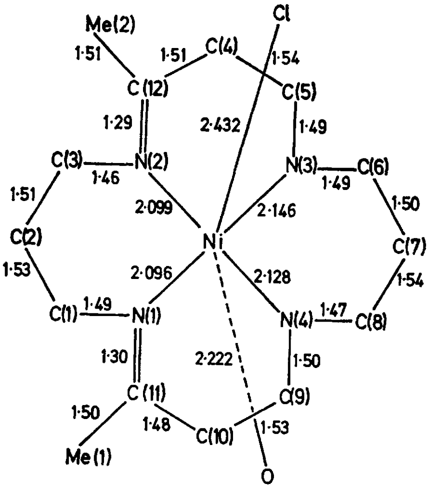

Figure 1

The reaction between methyl vinyl ketone and trimethylenediamine monohydrochloride in the presence of nickel(II) acetate yields[8] a macrocyclic square-planar nickel(II) complex, 6,16-dimethyl-1,5,9,13-tetra-azacyclohexadeca-6,16-dienenickel(II), (I). Blue needle crystals of the chloroaqua chloride of (I) were obtained by evaporating an acetonitrile solution containing the blue anhydrous dichloro-derivative of (I).

Crystal data: $C_{14}H_{30}Cl_2N_4NiO$; $M = 400{\cdot}0$, monoclinic, $a = 15{\cdot}394(1)$, $b = 7{\cdot}668(1)$, $c = 17{\cdot}974(1)$ Å, $\beta = 119{\cdot}81(1)^\circ$; $U = 1841{\cdot}2$ Å^3, $Z = 4$, $D_c = 1{\cdot}44$; space group, $P2_1/c$. 1465 reflections were observed out of 1721 collected up to 2θ equals 40° by a Hilger–Watts four-circle computer operated diffractometer (Mo-K_α radiation, Zr filtered), using ω–2θ scanning mode. No corrections were made for absorption or extinction. The structure was solved by direct methods using symbolic addition and subsequently refined anisotropically using diagonal least-squares to a reliability factor R of 0·048. The pseudo-octahedral cation is shown in the Figures. Figure 1 gives the bond distances; Figure 2 shows the bond angles and heights of the atoms with respect to the plane consisting of the four nitrogen atoms. The estimated standard deviations are 0·002(Ni–Cl), 0·005(Ni–O, Ni–N), and 0·01 Å (C–C, C–N). The nickel(II) atom is hexaco-ordinated with Cl(1) together with a water molecule filling the two apical positions of the pseudo-octahedron, [∠Cl(1)–Ni–O 177·8°). The anion, Cl(2), holds the molecules together through a hydrogen-bond network, [Cl(2)–N(4), 3·40; Cl(2)–O, 3·08 in the same molecule, and Cl(2)-O, 3·09 Å to an adjacent molecule]. The 1,3-diaminopropane ring containing the two amines [N(3), N(4)] is in a chair conformation, while the other ring containing the two imines [N(1), N(2)] is in a twist conformation.

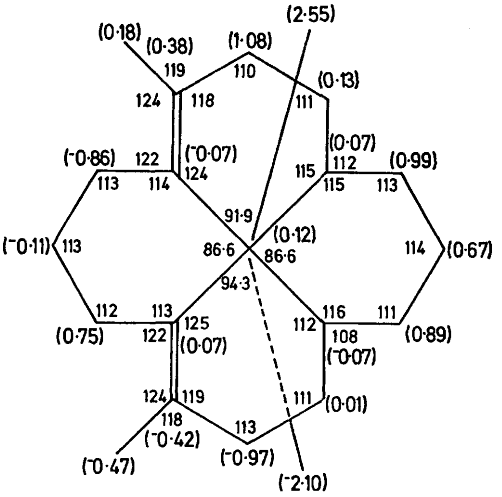

Figure 2

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