Geometrical and Optical Isomerism in a Macrocyclic Schiff Base Nickel(II) Complex: Unambiguous Assignment of Isomers from Crystal Structure Analysis

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FROM the synthesis of the novel macrocyclic square-planar Ni^{II} complex, hexamethyl-1,4,8,11-tetra-azacyclotetradecadiene nickel(II) (hereafter referred to as the diene complex), Curtis and co-workers[1] have reported the isolation of three isomeric forms, designated $A\alpha$, and $A\beta$, and B. The A and B isomers are non-interconvertible, whereas $A\alpha$ and $A\beta$ are interconvertible in solution,[1] the position and rate of attainment of equilibrium being a function of solvent, temperature, and pH. The A–B isomerism was attributed to *cis–trans*-arrangements of the imine groups in the heterocycle[1] (the *trans*-diene is shown in Figure 1), although an unambiguous assignment of geometrical isomers based on chemical evidence alone was not possible. Curtis also suggested that the interconvertible $A\alpha$–$A\beta$ isomerism is due to various conformational arrangements of the complexed tetradentate heterocycle.[1] A subset of the possible ring conformations is the group of three optical isomers [*meso*, (+), and (−)] which differ in the configurations about the two optically active secondary nitrogen atoms, as shown in Figures 1 and 2.

X-Ray studies in this laboratory have conclusively proven that (a) the A isomers possess the *trans*-configuration of the two imine groups, and (b) the $A\alpha$–$A\beta$ isomerism arises from the asymmetry at the two tetrahedral nitrogen atoms in the diene complex. That is, our X-ray work has unambiguously shown that the $A\alpha$ form is a racemic mixture of (+)–(−) *trans*-diene isomers (approximate C_2 symmetry) whereas the $A\beta$ form is the *meso-trans*-diene isomer (exactly C_i symmetry). Further it is inferred that the B form is a racemic mixture of (+)–(−) *cis*-diene isomers, the formation of the *meso*-form of the *cis*-diene being sterically hindered.

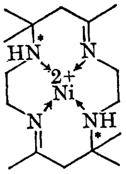

FIGURE 1. Trans-*diene.*

Our X-ray work confirms the results of concurrent n.m.r. studies by Busch and co-workers[2] from which they infer a *trans*-arrangement of the imine groups in the $A\alpha$ and $A\beta$ isomers. Further, they have succeeded in a partial optical resolution of the SCN^- derivative of the $A\alpha$ isomer.[2]

Crystals of the perchlorate salt of the $A\beta$ isomer of the diene complex $[C_{16}H_{32}N_4Ni^{II}(ClO_4)_2]$[1] are monoclinic with unit cell dimensions: $a = 9{\cdot}65$, $b = 10{\cdot}76$, $c = 10{\cdot}90$ Å and $\beta = 99°55'$. $D_c = 1{\cdot}59$ g.cm.$^{-3}$; for $Z = 2$, $D_m = 1{\cdot}60$ g.cm.$^{-3}$. Systematic absences uniquely indicate the centrosymmetric space group, $P2_1/C$ which locates the $A\beta$ complex at a crystallographic centre of symmetry. We can therefore conclude that the $A\beta$ isomer is the *meso* form of the *trans*-diene; *i.e.*, (a) the imine groups are *trans* to one another in the ring, and (b) one N–H group is above, the other below the approximate plane of the complex, as required for the *meso* form of the *trans*-diene (Figure 2).

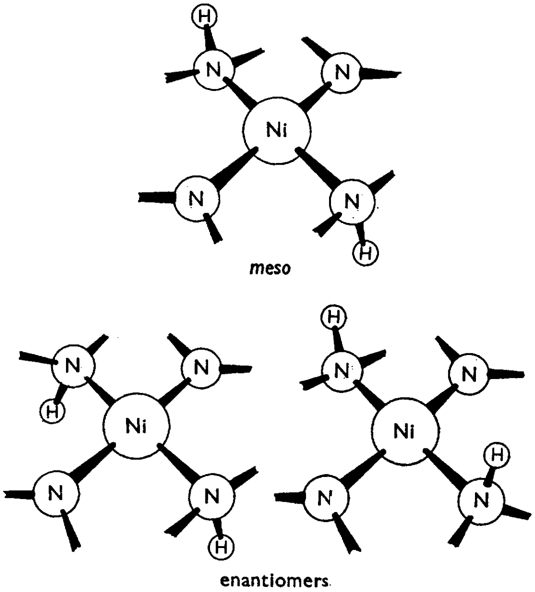

FIGURE 2. *Optical isomers of the* trans-*diene.*

Crystals of the perchlorate salt of the $A\alpha$ isomer of the diene complex $[C_{16}H_{32}N_4Ni^{II}(ClO_4)_2]$ are orthorhombic, space group *Pbca* with $a = 19{\cdot}73$, $b = 17{\cdot}01$ and $c = 13{\cdot}69$ Å., $D_m = 1{\cdot}56$ g.cm.$^{-3}$ for $Z = 8$, $D_c = 1{\cdot}58$ g.cm.$^{-3}$. From three-dimensional intensity data the 31 nonhydrogen atoms have been located ($R = 0{\cdot}28$ for 2072 reflections), and the following structural details are of interest:

(1) Both the *gem*-dimethyl groups and the imine groups [N(2)–C(6), N(4)–C(14) : 1·32 Å. (av.)] are *trans* to one another in the ring[5] this conclusively proves that the *A* isomers of the diene involve a *trans*-configuration of imine groups (Figure 3).

(2) The two *gem*-dimethyl groups are above the approximate plane of the macrocycle. This arrangement of *gem*-dimethyl groups requires that the two secondary N–H groups be below the ligand plane giving rise to the optically active (±)-form of the *trans*-diene complex (Figure 2).

(3) An unexpected feature of this structure is the apparent hydrogen bonding between the two perchlorate ions and the two secondary nitrogens (Figure 3). The N(1) · · · O(3) and N(3) · · · O(6) distances are 2·97 and 2·98 Å., respectively, indicative of two moderately strong N–H · · · O bonds.[3] In the infrared spectrum of crystals of this compound, however, there is no apparent modification of the N–H or Cl–O stretches.[4]

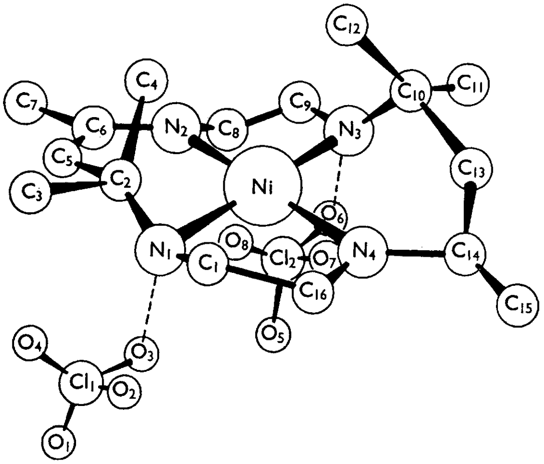

FIGURE 3. *Configuration and perchlorate interaction of the* (±)-trans-*dieneNi*^{II} *cation.*

On the basis of these *X*-ray studies it is predicted that the *B* isomer of the diene complex involves a *cis*-arrangement of the two imine groups.* Again optical isomerism [(±)- and *meso*] is possible, but it would appear from stereochemical considerations that the (±)-form (with one N–H above, the other below the ligand plane—C_2 symmetry) is the preferred configuration. Models show that in the *meso* form of the *cis*-diene complex (both N–H's above, both *gem*-dimethyls below the plane—C_s symmetry) the *gem*-dimethyl groups crowd one another. Chemical evidence also supports the hypothesis that the *B* isomer is a racemic mixture of the (±)-form of the *cis*-diene, as

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* A complete three-dimensional *X*-ray analysis[6] (M. F. Bailey and I. E. Maxwell, *Chem. Comm.*, 1966, 883) of an oxidized derivative of the *B* diene complex (the *B* tetene) has conclusively shown that the *B* isomers involve a *cis*-arrangment of imine groups.

both the $A\beta$ and the B isomers of the diene can hydrogen bond *via* the secondary N–H to two SCN^- ions (one on each side of the macrocyclic plane), whereas the $A\alpha$ diene can hydrogen bond to only one SCN^- ion.[5] (In the $A\alpha$ diene a second SCN^- would have to H-bond on the same side of the macrocyclic plane as the first; presumably SCN^-–SCN^- repulsions prevent this.) A recent *X*-ray study of the *cis*-diene Ni^{II} complex by Ryan, Kilbourn, and Dunitz[6] has confirmed this hypothesis.

The isolation of optical isomers of these complexes is made possible by the slow rate of interconversion at room temperature in both aqueous ($A\alpha \rightarrow A\beta$) and acetone solution ($A\beta \rightarrow A\alpha$).[1] As the interconversion is inhibited by acid[2] and catalyzed by base it is evident that the rate-determining step for inversion about the tetrahedral nitrogen atoms is deprotonation of the co-ordinated secondary nitrogen atoms. Recent n.m.r. studies of multidentate aminecobalt(III) complexes by Sargeson and co-workers[7] also provide evidence of restricted inversion at metal-co-ordinated secondary nitrogen atoms due to the inert nature of the secondary N–H bond.

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[2] L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, to be published.
[3] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", Freeman & Co., 1960, p. 289.
[4] N. F. Curtis, private communication.
[5] N. F. Curtis and Y. Curtis, *J. Chem. Soc.*, (*A*), 1966, in the press.
[6] R. R. Ryan, B. T. Kilbourn, and J. D. Dunitz, private communication.
[7] A. Sargeson, 3rd National Convention of the Royal Australian Chemical Institute, Coordination and Metal-Organic Chemistry Division Symposium, Canberra, August 1966.