

Crystal Structure of a Macrocyclic Tetraaminenickel(II) Complex

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CRYSTALS of the perchlorate salt of the α -form of the macrocyclic nickel(II) complex, 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,8,10,14-tetraenenickel(II)¹ [hereafter referred to as the *cis*-tetene nickel(II) complex], $[\text{C}_{16}\text{H}_{28}\text{N}_4\text{Ni}^{\text{II}}]^{2+}$, prepared by oxidation of the *cis*-diene complex,² $[\text{C}_{16}\text{H}_{32}\text{N}_4\text{Ni}^{\text{II}}]^{2+}$, are orthorhombic with $a = 10.62$, $b = 11.18$, and $c = 18.81$ Å. $D_0 = 1.59$ g.cm.⁻³; for $Z = 4$, $D_m = 1.59$ g.cm.⁻³. Systematic absences uniquely indicate the centrosymmetric space group, $Pbcn$, which requires this tetene complex to lie on either a crystallographic centre of symmetry or a crystallographic twofold axis.³ A three-dimensional analysis involving Patterson and Fourier techniques has located the 16 nonhydrogen atoms ($R = 0.25$ for 1230 independent reflections). Although a detailed discussion of this structure must await completion of a least squares refinement, several important points can now be made:

- (1) The crystallographic twofold axis lies in the approximate plane of the complex (Fig. 1), thus requiring this isomer of the tetene to possess the *cis* arrangement of

gem-dimethyl and imine groups. (Note that if the crystallographic twofold axis were *perpendicular* to the approximately planar complex, the *trans* arrangement would be required.) This assignment of geometrical isomers is in agreement with *X*-ray studies of the diene.^{4,5}

- (2) The observed bond distances and angles (Fig. 1) confirm the ring structure predicted for the *cis*-tetene complex on the basis of infrared spectra and chemical analysis. That is, there are four imine groups, as evidenced by short carbon-nitrogen bonds [$\text{C}_8\text{-N}_2$, $\text{C}_2\text{-N}_1$: 1.27 Å. (av.)] and trigonal bond angles about C_8 , N_2 , C_2 , and N_1 .
- (3) As expected from the structure and relative rigidity of the tetene heterocycle, the co-ordination about the nickel atom appears to be significantly distorted from square planarity. First, the $\text{N}(1)\text{-Ni-N}(2)$ angle (96°) of the six-membered rings is larger than the average N-Ni-N angle (85°) in the five-membered rings formed by the ethylenediamine and ethylenediimine

residues. Secondly, the ethylenediamine residue is in the *gauche* configuration and this twisting of the C(1)—C(1') bond out of the plane of the Ni, N(2), and N(2') atoms is accompanied by a similar but smaller deviation from this plane by the attached nitrogen atoms, N(1) and N(1'). The

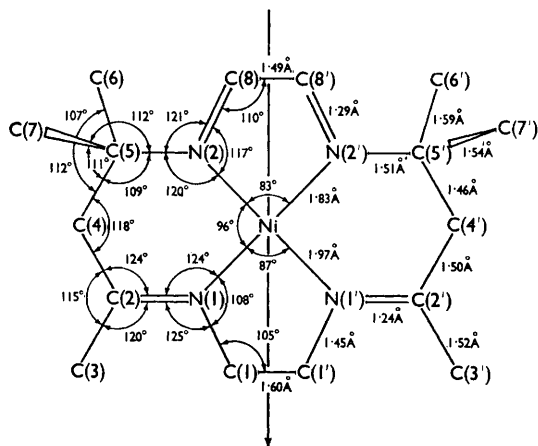


FIGURE 1

Bond distances and angles in the *cis*-tetene Ni^{II} cation (e.s.d. 0.02 Å).

result is a slight tetrahedral distortion from square planar co-ordination about the nickel atom. Third, the Ni—N distances in the planar ethylenediamine group appear to be significantly shorter than the corresponding Ni—N distances in the twisted ethylenediamine residue (1.83 as against 1.97 Å). This difference might be explained in terms of strengthening of the Ni—N(2) bonds by delocalization within the planar five-membered ring formed by the nickel atom and ethylenediamine residue.

- (4) The packing of the perchlorate salt of the *cis*-tetene Ni^{II} complex (Fig. 2) shows there is no direct interaction between Ni^{II} atoms and the perchlorate ions. Instead the

nickel complex cations lie nearly perpendicular to the *a* axis with two perchlorate ions sandwiched between two cations, the latter being related by a unit cell translation. Although a perchlorate interaction

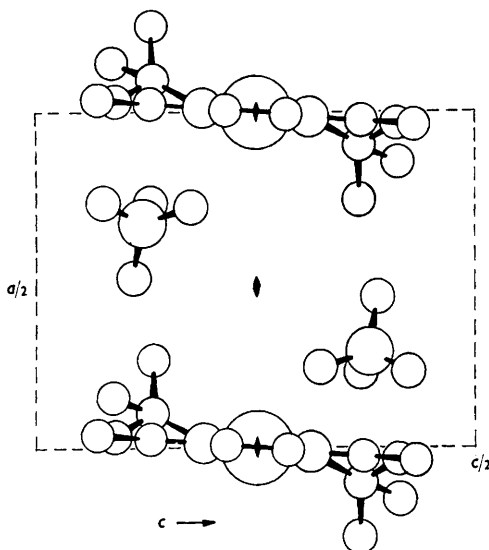


FIGURE 2

Unit cell packing.

with the cation is suggested by the fact that one oxygen [O(1)] of the perchlorate ion is pointed towards one of the methyls [C(7)] of each *gem*-dimethyl group, the methyl—oxygen distance [C(7) ··· O(1) = 3.26 Å] is not significantly less than that expected for van der Waals packing (CH₃ ··· O = 3.4 Å).⁶ Of the oxygen atoms in the ClO₄⁻ ion, only O(1) is rigidly fixed in the crystal; the other three oxygens appear to be vibrating about the Cl—O(1) bond (three distinct but smeared peaks are observed).

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¹ N. F. Curtis, *Chem. Comm.*, preceding Communication.

² N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc. (A)*, 1966, 1015.

³ "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1952, p. 149.

⁴ M. F. Bailey and I. E. Maxwell, *Chem. Comm.*, to be published.

⁵ J. Dunitz and B. T. Kilbourn, private communication.

⁶ L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1960.