

Chemical Communications

NUMBER 6/1965

24 MARCH

The Molecular Structure of Dichloro-1,4,8,11-Tetra-azacyclotetradecanenickel(II)

By B. BOSNICH, R. MASON, P. J. PAULING, G. B. ROBERTSON, and M. L. TOBE

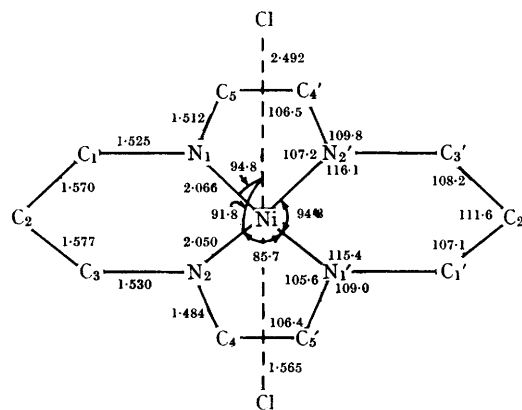
[*William Ramsey and Ralph Forster Laboratories, University College, London (B.B., P.J.P., and M.L.T.), and The Department of Chemistry, The University, Sheffield (R.M. and G.B.R.)*]

A NUMBER of complexes of 1,4,8,11-tetra-azacyclotetradecane^{1,2} with first-row transition-metal ions have been prepared recently^{3,4} and are of interest in connection with the stereochemical consequences of substitution in octahedral complexes. Complexes of nickel(II) halides with this secondary amine show interesting variations in magnetic properties⁴ and, together with the question of the conformation of the co-ordinated ligand, led to an X-ray analysis of the crystal structure of dichloro-1,4,8,11-tetra-azacyclotetradecanenickel(II).

The crystals are monoclinic with $a = 13.644$, $b = 8.355$ Å, $c = 6.541$ Å, $\beta = 104.58^\circ$; the space group is $P2_1/a$, the two molecules per unit cell of $C_{10}N_4H_{24}Cl_2Ni$ being required to be strictly centrosymmetric. The molecular structure is shown in the Figure and is the result of a least squares analysis of the three-dimensional data which has converged to a present discrepancy index of 0.047. Average standard deviations are 0.003 (Ni-Cl), 0.008 (Ni-N), 0.015 (C-C and C-N), and 0.06 Å (C-H and N-H).

The symmetry of the ligand field around the nickel ion is less than D_{4h} . Deviations from 90° of such bond angles as Cl-Ni-N are due to intramolecular non-bonded interactions between chlorine and hydrogen atoms, the positions of the latter

being directly determined by difference density syntheses; in particular, the chlorine atoms move away from hydrogens attached to carbon and towards those bonded to nitrogen. Moreover, the



bond lengths around the nickel ion show a tetrahedral distortion of approximately 0.15 Å which may be greater in the case of the diamagnetic di-iodo-complex, as a result of increased steric

¹ J. van Alphen, *Rec. Trav. chim.*, 1937, **36**, 343.

² H. Stetter and K. H. Mayer, *Chem. Ber.*, 1961, **94**, 1410.

³ B. Bosnich, C. K. Poon, and M. L. Tobe, in the press.

⁴ B. Bosnich, M. L. Tobe, and G. A. Webb, in the press.

interactions, so that there is a change-over from the ${}^3A_{2g}$ ground state of the dichloro-derivative (μ_{eff} 3.1 B.M. at 300° K) to a ${}^1A_{1g}$ state. Analyses of the crystal structures of the dibromo- and diiodo-complexes are in progress so as to confirm or disprove this view.

The results represent the first observation of the conformation of a six-membered chelate ring.

The 1,3-diaminopropane rings have a chair conformation while the ethylenediamine residues are *gauche*, their carbon atoms being equatorial substituents on the nitrogens of the 1,3-diaminopropane rings.

We thank Dr. P. B. Braun for making available an automatic diffractometer for data collection.

(Received, February 11th, 1965.)