

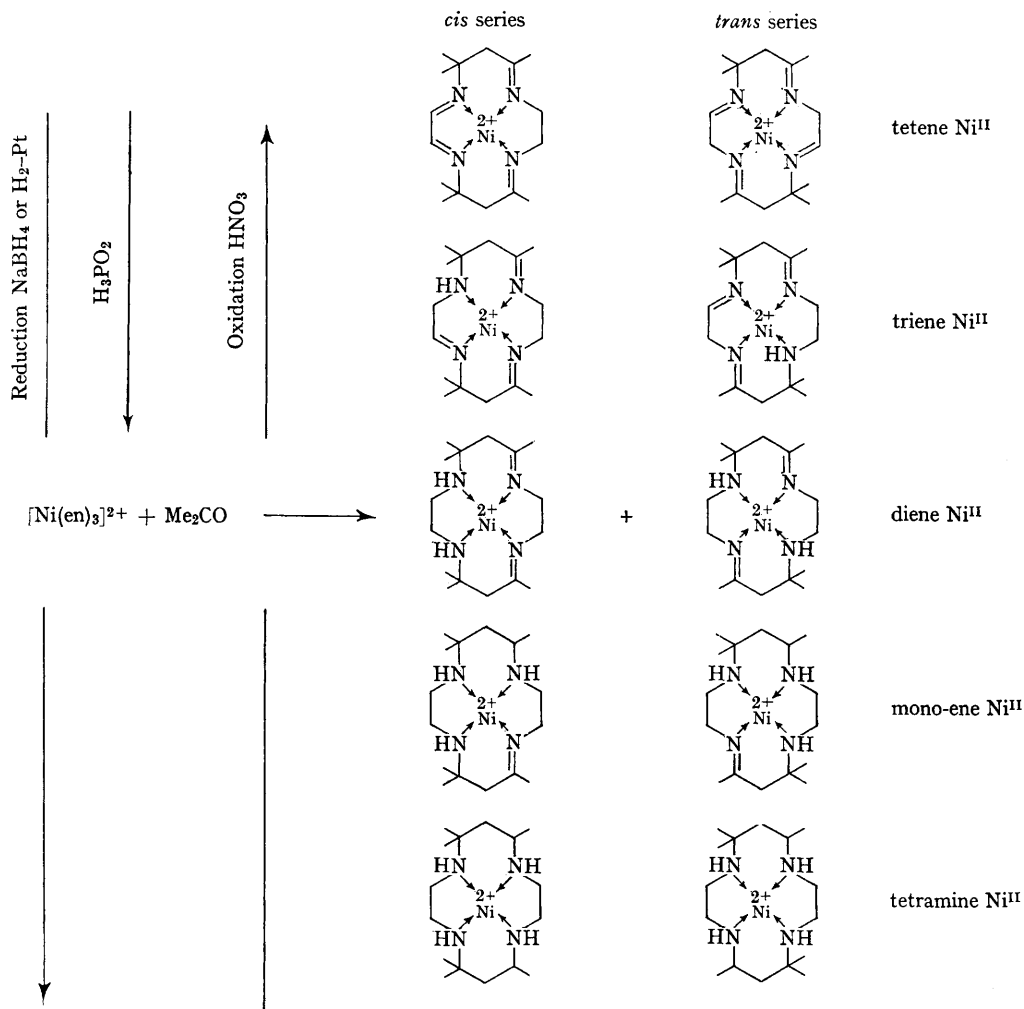
Nickel(II) Complexes of Two Isomeric Cyclic Tetra-amines and Dehydro-derivatives with One to Four Imine Donor Groups

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THE nickel(II) complexes of the heterocycles 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclo-tetradeca-4,14-diene (*cis*-diene Ni^{II}) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclo-tetradeca-4,11-diene (*trans*-diene Ni^{II}), which have

two secondary amine and two imine donor groups, are formed by reaction of trisdiaminoethane-nickel(II) with acetone.¹ These can be reduced stepwise to give first the tri-amine-mon-imine complexes *cis*- and *trans*-triene Ni^{II} and then



the cyclic tetra-amine complexes *cis*- and *trans*-tetramine Ni^{II} .² The diene complexes are oxidised by nitric acid to give the cyclic tetra-imine complexes (5,7,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,8,10-14-tetra-ene)nickel(II) (*cis*-tetene Ni^{II}) and (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-3,7,10,14-tetraene)nickel(II) (*trans*-tetene Ni^{II}). These may be partially reduced, using hypophosphorus acid, to give the mono-amine-tri-imine complexes (5,7,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,8,14-triene)-nickel(II) (*cis*-triene Ni^{II}) and (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-3,7,14-triene)nickel(II) (*trans*-triene Ni^{II})—further reduction yields the diene starting material,

indicating that the imine groups with an α -hydrogen are preferentially reduced. The molecular structures of the perchlorate salts have been confirmed by X-ray crystallography for *cis*-diene Ni^{II} ,³ racemic *trans*-diene Ni^{II} ,⁴ and *cis*-tetene Ni^{II} .⁵ Infrared spectral band frequencies of the main functional groups (perchlorate salts) are $\nu(\text{NH})$, $\sim 3200 \text{ cm}^{-1}$, $\nu(\text{CH})$, vinyl hydrogen of tri- and tet-enes, $\sim 3070 \text{ cm}^{-1}$, $\nu(\text{C:N})$, $\sim 1660 \text{ cm}^{-1}$ for α -methyl and $\sim 1675 \text{ cm}^{-1}$ for α -hydrogen C:N groups.

The complex cations are all stable in acid solution, but the tetene, and to a lesser extent the triene complexes, are unstable in basic solution.

With anions of low co-ordinating ability, such

as perchlorate, the complex cations form diamagnetic salts. With anions of higher co-ordinating ability some triplet ground state pseudo-octahedral derivatives are formed (*e.g.*, all except *cis*-diene Ni^{II} form triplet ground state dithiocyanato-derivatives⁶). Several of the complex cations form derivatives with the heterocycle buckled to accommodate a chelate, particularly of the type [*trans*-diene Ni]₂C₂O₄(ClO₄)₂.⁷ The main factor determining whether triplet ground state "octahedral" or diamagnetic square planar derivatives are formed by anions of high ligand field strength appears to be the amount of interference between the ring methyl substituents and the fifth and sixth co-ordination sites. This varies with ring conformation, which depends on the numbers of amine and imine groups, and on the configurations of the asymmetric carbon and

nitrogen centres present. The metal-ion spectra of the complexes indicate that there is little variation in the ligand field strength of the heterocycle when amine and imine donor groups are interchanged, all having ligand field strengths comparable with bisdiaminoethane.

The tetra-amines have two asymmetric carbon centres and occur as non-interconvertible racemic and *meso* forms.² Many of the complex cations occur as interconvertible isomeric forms because of restricted inversion about asymmetric nitrogen centres present.^{1,6} The tetene complexes each occur as two interconvertible isomeric forms, and stabilisation of different ring conformations by steric hindrance, although apparently improbable, is suggested as an explanation pending crystallographic studies of a pair of these isomers.

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³ J. Dunitz and B. T. Kilbourn, private communication.

⁴ M. F. Bailey and I. E. Maxwell, *Chem. Comm.*, 1966, in the press.

⁵ I. E. Maxwell and M. F. Bailey, following Communication.

⁶ N. F. Curtis and Y. M. Curtis, *Austral. J. Chem.*, 1966, 19, 1423; *J. Chem. Soc. (A)*, 1966, 1653; L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, to be published.