Nickel(II) Complexes of Two New Phosphorus–Nitrogen Macrocyclic Ligands

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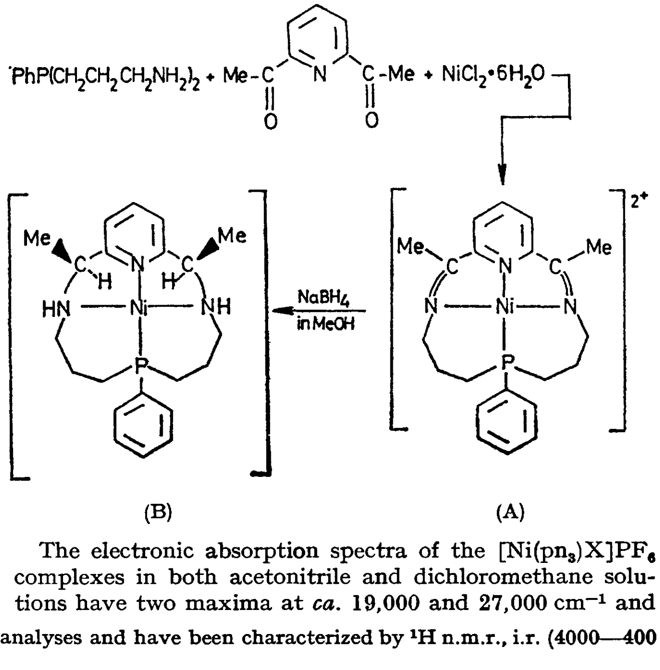
Summary The first tetradentate macrocyclic ligands containing a phosphine donor have been characterized as their four- and five-co-ordinate nickel(II) complexes.

DURING the past ten years co-ordination chemists have extensively investigated the condensation of amines with aldehydes and ketones in the presence of metal ions.[1] Reactions of co-ordinated ligands under the influence of the template effect have produced many new macrocycles containing four nitrogen, oxygen, or sulphur atoms or combinations of these donor atoms. Conspicuously absent from the list of donor atoms incorporated into macrocyclic ligands are phosphorus and arsenic. We now report two new tetradentate macrocyclic ligands that contain a phosphine donor.

Refluxing an ethanolic solution containing bis-(3-aminopropyl)phenylphosphine,[2] 2,6-diacetylpyridine, and $NiX_2 \cdot 6H_2O$ (X = Br, I), followed by addition of NH_4PF_6, results in the crystallization of five-co-ordinate complexes $[Ni(pn_3)X]PF_6$,† where pn_3 = the phosphorus–nitrogen macrocycle 2,12-dimethyl-7-phenyl-3,11,17-triaza-7-phosphabicyclo[11,3,1]heptadecapent-1(17),2,11,13,15-ene. When X = Cl the above reaction produces the four-co-ordinate complex $[Ni(pn_3)](PF_6)_2$. The five-co-ordinate complex $[Ni(pn_3)Cl]PF_6$ may be obtained easily, however, by using an ethanolic solution of "$NiCl(PF_6)$" as the original source of nickel(II). The purple, five-co-ordinate complexes are diamagnetic and uni-univalent electrolytes in acetonitrile (Λ_M = 140—148 cm^2 ohm^{-1} mol^{-1}). The i.r. spectra are all very similar and show a weak C=N absorption at 1620 cm^{-1} and no peaks due to $-NH_2$ or C=O groups. The i.r. spectra, along with the ^{1}H n.m.r. spectra, indicate that the Schiff base condensation was successful. Formation and reduction of the macrocycle are shown in the Scheme.



(B) (A)

The electronic absorption spectra of the $[Ni(pn_3)X]PF_6$ complexes in both acetonitrile and dichloromethane solutions have two maxima at *ca.* 19,000 and 27,000 cm^{-1} and

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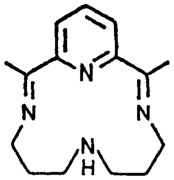
† All compounds described in this report had satisfactory microanalyses and have been characterized by ^{1}H n.m.r., i.r. (4000—400 cm^{-1}), and electronic absorption spectroscopy.

may be interpreted in terms of a trigonal-bipyramidal arrangement of donor atoms around nickel. A trigonal-bipyramidal co-ordination geometry implies that the pn_3 macrocycle is sufficiently flexible to fold around the metal and accommodate the structural preference of a low-spin nickel(II) complex. The electronic spectra of the solid complexes at 77 K differ significantly from the spectra obtained from solutions and resemble the solid state spectrum of $[Ni(L)Br]Br{\cdot}H_2O$, which is known to have a distorted structure intermediate between a trigonal bipyramid and a square pyramid.[3]

L =



Reduction of the imine groups in the macrocycle pn_3 has been accomplished with both $NaBH_4$ in ethanol solution and $PtO{-}H_2$. The yellow crystalline compound $[Ni(pn_3H_4)](PF_6)_2$‡ that results from the BH_4^- reduction of (A) has a new i.r. absorption at 3225 cm^{-1} (ν_{N-H}), is diamagnetic, and is a di-univalent electrolyte in acetonitrile ($\Lambda_M = 286\ cm^2\ ohm^{-1}\ mol^{-1}$). This square-planar complex also readily adds iodide ion in ethanol to give a five-co-ordinate complex of the reduced macrocycle, *i.e.* $[Ni(pn_3H_4)I]PF_6$, which is rose coloured, diamagnetic and a 1 : 1 electrolyte.

The ^1H n.m.r. spectrum of $[Ni(pn_3H_4)](PF_6)_2$ in $(CD_3)_2SO$, recorded at both 60 and 100 MHz, exhibits a doublet at τ 8·50 (J_{HCCH} 7·0 Hz) which is assigned to the methyl resonance. The equivalence of the two methyl groups in pn_3H_4 suggests that this macrocycle is the *meso* form (B).

The reduced ligand pn_3H_4 has been removed from nickel by refluxing $[Ni(pn_3H_4)](PF_6)_2$ for 2—3 h in water with a large excess of cyanide ion. The resulting solution was extracted with benzene and treated with elemental sulphur to form the solid phosphine sulphide derivative Spn_3H_4. The i.r. and ^1H n.m.r. spectra of Spn_3H_4 are consistent with the proposed macrocyclic structure and the mass spectrum provides confirmation as it gives the parent ion peak at $m/e = 387$ as the most intense peak.

The related N_4 macrocycle, L, generally gives tetragonal, paramagnetic complexes with nickel halides.[3] In contrast, this work indicates that substitution of just one phosphorus donor into the L ring significantly alters the spin state and the type of complex that is formed. Further work is directed toward preparing other macrocycles containing polyphosphine donor groups.

(*Received*, *25th February* 1974; *Com.* 233.)

‡ The fully reduced ligand is abbreviated pn_3H_4 to show the incorporation of four hydrogen atoms.

[1] The following review articles summarize the large number of papers published on macrocyclic ligands: D. H. Busch, *Helv. Chim. Acta, Fasciculus extraordinarius Alfred Werner*, 1967, 174; N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3; D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Adv. Chem. Series*, 1971, **100**, 44; L. F. Lindoy and D. H. Busch, in 'Preparative Inorganic Reactions,' ed. Jolly, vol. 6, p. 1, Interscience, New York, 1972.

[2] B. A. Arbuzov, G. M. Vinokurava, and I. A. Aleksandrov, *Izvest. Akad. Nauk S.S.R., Old. Khim. N.*, 1962, 290.

[3] J. L. Karn and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1149; E. B. Fleischer and S. W. Hawkinson, *Inorg. Chem.*, 1968, **7**, 2312.