Spin-state Isomerism in a Five-co-ordinate Nickel(II) Complex

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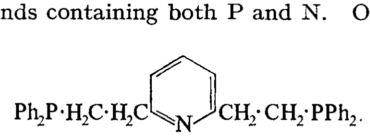
FIVE-CO-ORDINATE nickel(II) compounds may be low-spin or high-spin. The former usually contain polarisable donor atoms such as P or As,[1] whereas in the high-spin complexes the ligand donor atoms are generally N or O.[2] In order to investigate compounds having ground states close to the "magnetic cross-over" we have synthesised several new ligands containing both P and N. One such ligand is terdendate 2,6-di-(β-diphenylphosphinoethyl)pyridine (PNP). Reaction of PNP with NiX_2 (X = Cl, Br, or I) yielded crystalline brown complexes of formula, $Ni(PNP)X_2$. The bromide and iodide are low-spin with temperature-independent paramagnetism (t.i.p.) of *ca.* 250 × 10^{-6} and *ca.* 300 × 10^{-6} c.g.s.u., respectively (99—294°K). The chloride, on the other hand, has a moment of 3·14 B.M. at 294°K which falls, reversibly, to 1·30 B.M. at 99°K. The susceptibilities are independent of field strength. We believe that in this compound there exists a thermal equilibrium between singlet and triplet states. Spin-state isomerism has been suggested[3] previously to account for the room temperature moment of 1·29 B.M. found[3,4] for the five-co-ordinate complex, $Ni(PHPh_2)_3I_2$. However, this has yet to be proved; susceptibilities of this order (692 × 10^{-6} c.g.s.u.) can arise from t.i.p. plus a small amount of paramagnetic impurity.



("PNP")

Monomeric five-co-ordinate structures are assigned to the $Ni(PNP)X_2$ complexes on the basis of their physical properties. All three are isomorphous. The i.r. spectra show that the pyridine nitrogen atom is co-ordinated. The solid-state electronic spectra of the low-spin bromide and iodide cannot be accounted for in terms of a square-planar configuration; instead, the spectra are very similar to those of other low-spin nickel(II) complexes of known five-co-ordinate structure;[4] *e.g.* in $Ni(PNP)I_2$, maxima occur at 22,800, 17,400, and 12,300 cm.$^{-1}$. In the chloride the visible bands (25,700, 18,800, and 13,200 cm.$^{-1}$) are of lower intensity and there is also an extra weaker band at $\sim$7500 cm.$^{-1}$. In polar solvents such as ethanol or nitromethane the three compounds show a strong band at 19,000—22,000 cm.$^{-1}$ with little or no absorption at lower energies. All are uni-univalent electrolytes in nitromethane (Λ 77—86 ohm^{-1} at 25°). In 1,2-dichloroethane or acetone the spectra indicate the presence of both square-planar and five-co-ordinate species in equilibrium.

$$[Ni(PNP)X_2] \rightleftharpoons [Ni(PNP)X]^+ + X^-$$

Added $[AsMePh_3]X$ or $[NEt_4]X$ shifts the equilibrium to the left. Molecular-weight measurements in 1,2-dichloroethane at 37° confirmed that $Ni(PNP)Cl_2$ is partially dissociated (Formula *M* 633, observed *M* 507). Further confirmation for the structural assignments is provided by the observation that the chloro-complex is diamagnetic in ethanol, and by the successful isolation of the perchlorate salts of the square-planar complex cations, $[Ni(PNP)Cl]^+$ and $[Ni(PNP)Br]^+$, which have electronic spectra almost identical with those of $Ni(PNP)Cl_2$ and $Ni(PNP)Br_2$, respectively, in ethanol.

TABLE

Temp. (°K)	294·2	269·5	244·0	217·9	192·4	167·8	143·6	118·5	99·3
$10^6 \chi_M$(c.g.s.u.)[a] for $Ni(PNP)Cl_2$	4149	4299	4299	4218	3974	3584	3054	2509	2129

[a] Corrected for diamagnetism of ligands.

An explanation of the magnetic behaviour of $Ni(PNP)Cl_2$ in terms of a configurational equilibrium can be ruled out by the observation[5] that there was no change in the 299°K *X*-ray diffraction pattern, except that caused by anisotropic thermal expansion coefficients, on cooling to 77°K. An antiferromagnetic exchange mechanism is similarly irreconcilable with the properties of the three compounds.

With $N\alpha = 250 \times 10^{-6}$ c.g.s.u. and $\mu_{eff} = 3{\cdot}4$ B.M. for the high-spin form, application of the theory of Ballhausen and Liehr,[6] for a Maxwell–Boltzmann distribution between singlet and triplet states, yields an energy separation ΔE, which decreases monotonically with increase in temperature, *i.e.* from 203 cm.$^{-1}$ at 99°K to -103 cm.$^{-1}$ at 294°K. From this it appears that the ground state is a singlet below about 250°K and a triplet above this temperature. A variation of ΔE with temperature, noted previously for a distorted octahedral nickel(II) complex,[7] is not unexpected since lattice expansion must influence the ligand field parameters to some extent. Further properties of these, and of an isomeric series of complexes, will be reported more fully elsewhere.

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[1] See, for example: G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1964, 1293; G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, 1964, **3**, 1544.

[2] See, for example: M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41; 45; S. M. Nelson and J. Rodgers, *ibid.*, 1967, **6**, 1390.

[3] J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, 1966, **5**, 879.

[4] R. G. Hayter, *Inorg. Chem.*, 1963, **2**, 932.

[5] J. A. C. Marples, private communication.

[6] C. J. Ballhausen and A. D. Liehr, *J. Amer. Chem. Soc.*, 1959, **81**, 538.

[7] S. L. Holt, R. J. Bouchard, and R. L. Carlin, *J. Amer. Chem. Soc.*, 1964, **86**, 519.