Correlation of Spectroscopic Properties and Crystal Structure of Two Closely Related Five-co-ordinate Complexes of Nickel(II) Cyanide with Monodentate Heterocyclic Phosphine Ligands

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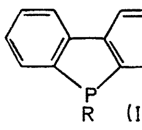
Summary Dicyanotris-(9-methyl-9-phosphafluorene)nickel(II) and dicyanotris-(9-ethyl-9-phosphafluorene)nickel(II) have tetragonal pyramidal and trigonal bipyramidal configurations, respectively, in the solid state, though in solution they have the same structure.

FIVE-CO-ORDINATE complexes of the d^7 and d^8 metals having trigonal bipyramidal, tetragonal pyramidal, and intermediate configurations[1,2] are now known. It has been suggested that the geometry of such complexes is determined by a delicate balance of various factors, such as ligand-field stabilisation energy,[3] valence shell electron-pair repulsions,[4] steric requirements of the ligands,[5] and packing requirements in the crystal lattice.

The electronic structures and energy levels in such compounds have been studied,[6,7] but few correlations of spectroscopic properties and crystal structure have been made.

It has recently been shown that 9-alkyl-9-phosphafluorenes, alternatively named 5-alkyldibenzophospholes (I; R = Me or Et) form a series of five-co-ordinate complexes of the type $(phos)_3MX_2$ (M = Ni^{II}, X = Cl, Br, I, NCS, CN; M = Pd^{II}, X = Br; M = Pt^{II}, X = Br, SCN; M = Co^{II}, X = Br).[8] These are stable in the solid state, but undergo partial and reversible dissociation in certain solvents.


(I)

$[(C_{13}H_{11}P)_3Ni(CN)_2]$ (II)

$[(C_{14}H_{13}P)_3Ni(CN)_2]$ (III)

Two closely related diamagnetic compounds, dicyanotris-(9-methyl-9-phosphafluorene)nickel(II) (II) and dicyanotris-(9-ethyl-9-phosphafluorene)nickel(II) (III) show, however, striking spectroscopic differences in the solid state. The complex (II) (mull) shows absorption bands at 18,750sh, 27,000, 31,200, and 35,500 cm.$^{-1}$, whereas the complex (III) shows bands at 23,000, 30,500, and 35,000 cm.$^{-1}$. The i.r. spectrum of (II) (mull) in the C≡N stretching region shows sharp absorptions of unequal intensity at 2118, 2108, and 2102 cm.$^{-1}$, whereas (III) shows one sharp absorption at 2118 cm.$^{-1}$.

In dichloromethane solutions, however, (II) and (III) show identical spectra, having an absorption band at 24,000 cm.$^{-1}$

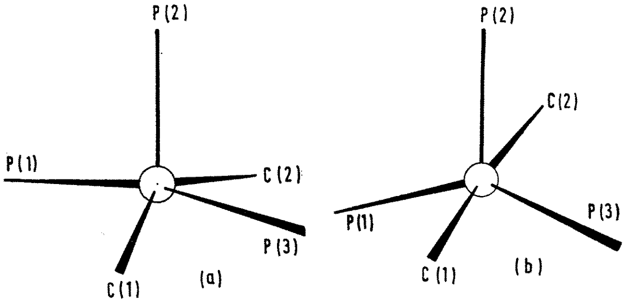


FIGURE. *Stereochemistry of nickel atom in the complexes* (II) *and* (III) *respectively*; (a) *tetragonal pyramid*; (b) *trigonal bipyramid, drawn from a stereogram of the observed bond angles.*

This strong evidence that the complexes (II) and (III) have different structures in the solid state (but become identical in solution when released from crystal lattice restraints) has now been independently confirmed by *X*-ray crystal structure analysis. A preliminary report[8] shows that the methyl complex (II) has the tetragonal pyramidal configuration, the four apices of the square being occupied alternately by a phosphine molecule and a cyano-group; the nickel atom lies centrally above the horizontal square, and the third phosphine molecule P(2) occupies the apical position (Figure, a). The ethyl complex (III), however, has the trigonal bipyramidal configuration, in which the three phosphine molecules occupy the equatorial positions and the two cyano groups the apical positions (Figure, b), in which the trigonal axis is approximately horizontal).

The evidence for these structures may be summarised.

Crystal Data

For the methyl complex (II): $C_{41}H_{33}N_2NiP_3$, $M = 705{\cdot}4$, triclinic $P\bar{1}$, $a = 15{\cdot}57$, $b = 11{\cdot}23$, $c = 12{\cdot}21$ Å, $\alpha = 118{\cdot}30°$ $\beta = 108{\cdot}13$, $\gamma = 90{\cdot}63°$, $V = 1753$ Å^3, $Z = 2$, $D_m = 1{\cdot}33$, $D_c = 1{\cdot}34$.

A linear diffractometer, with balanced filters, was used to collect 3399 independent reflections of intensity $>4\sigma(I)$, observable with molybdenum K_α radiation. Least-squares refinement, which is continuing, gives a current R factor of 13%.

For the ethyl complex (III): $C_{44}H_{39}N_2NiP_3$, $M = 747{\cdot}5$, monoclinic $P2_1/b$, $a = 11{\cdot}67$, $b = 26{\cdot}50$, $c = 15{\cdot}02$ Å, $\gamma = 125{\cdot}5°$, $V = 3781$ Å^3, $Z = 4$, $D_m = 1{\cdot}33$, $D_c = 1{\cdot}31$.

A four-circle diffractometer, with balanced filters, was used to collect 2412 independent reflections of intensity $>2\sigma(I)$, observable as above with molybdenum K_α radiation. Least-squares refinement, which is also continuing, gives a current R factor of 11%.

The stereochemistry of the nickel atom in the two molecules may be seen from the Table. Column b shows the approximation of the angles to the idealised values 180°, 120°, and 90° for trigonal bipyramid and the approximate equal lengths of the equatorial nickel–phosphorus bonds. The contrasting values in column a are consistent with a tetragonal pyramidal structure which has an apical phosphorus–nickel bond longer than the other two nickel–phosphorus bonds.

Bond angles (*degrees*) *and bond lengths* (Å)

	(Figure, a)	(Figure, b)
C(1)–Ni–C(2)	140·2°	176·7°
P(1)–Ni–P(2)	100·6	121·5
P(1)–Ni–P(3)	161·3	126·5
P(2)–Ni–P(3)	98·2	112·0
C(1)–Ni–P(1)	86·6	89·8
C(1)–Ni–P(2)	107·7	89·6
C(1)–Ni–P(2)	87·9	93·4
C(2)–Ni–P(1)	85·6	88·2
C(2)–Ni–P(2)	112·0	93·7
C(2)–Ni–P(3)	87·2	85·8
P(1)–Ni	2·177 Å	2·247 Å
P(2)–Ni	2·321	2·261
P(3)–Ni	2·178	2·252
C(1)–Ni	1·817	1·820
C(2)–Ni	1·857	1·855

It is noteworthy that the ethyl complex (III) is spectroscopically similar to the five-co-ordinate complexes of nickel(II) cyanide with certain phosphite and phosphonite esters: for these complexes a *trans*-trigonal-bipyramidal structure with cyano-groups in the apical positions has been suggested.[7]

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