Five-co-ordinate Complexes of Bivalent Nickel with Monodentate Ligands

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WHEREAS examples of five-co-ordinate nickel(II) complexes with polydentate ligands are becoming more and more common,[1] examples of the corresponding complexes with monodentate ligands remain relatively rare.[2] Furthermore, of the few known examples of five-co-ordinate nickel(II) complexes with monodentate ligands, most dissociate in solution, usually into four-co-ordinate species. We now report an example of a dissociatively stable, five-co-ordinate nickel(II) complex containing only monodentate ligands.

When an ethanolic slurry of anhydrous nickel cyanide is heated under reflux with diethoxyphenylphosphine there is obtained an orange, crystalline complex (m.p. 105°) which has the correct elemental analysis for $[PhP(OEt)_2]_3Ni[CN]_2$. This compound is readily recrystallized from hexane and has a molar conductance of approximately zero in nitromethane solutions. The complex is diamagnetic, and molecular-weight determinations indicate that it does not dissociate to any appreciable extent in acetone solution.

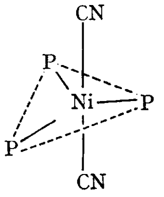
The ultraviolet spectrum of $[PhP(OEt)_2]_3Ni[CN]_2$ in ethanol solution shows two ligand-field bands ($\lambda_{max} = 350$ mμ, log $\epsilon = 3{\cdot}5$ with a shoulder $\lambda_{max} = 415$ mμ, log $\epsilon = 3{\cdot}4$) with energy positions which are characteristic of d^8, low-spin, trigonal-bipyramidal structures.[3]

There are three possible isomeric structures for a trigonal-bipyramidal $MP_3(CN)_2$ complex, (I), (II), and (III). The infrared spectrum of $[PhP(OEt)_2]_3$-$Ni[CN]_2$ (KBr plaque) shows only one sharp absorption ($\lambda_{max} = 4{\cdot}75$ μ) attributable to the $C{\equiv}N$ stretching motion of the cyanide groups.

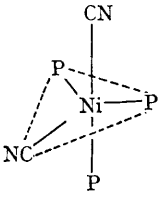
This behaviour is consistent with structure (I), a trigonal-bipyramidal structure with the cyanide groups occupying the *trans*-axial positions.

Preliminary evidence suggests that the complex produced by the reaction of nickel cyanide with dimethoxyphenylphosphine in methanol also produces a five-co-ordinate complex.

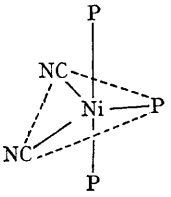
In contrast, we find that ethoxydiphenylphosphine and n-propyloxydiphenylphosphine react to produce four-co-ordinate nickel cyanide complexes. The behaviour of these latter complexes in solution is quite interesting, for it would appear that in the presence of an excess of phosphine they are converted into the more highly coloured five-co-ordinate species. Examination of the ultraviolet spectrum of $[\mathrm{Pr^nOPPh_2}]_2\mathrm{Ni[CN]_2}$ in n-propanol solution reveals that as n-propyloxydiphenylphosphine is added to the solution, two new absorption bands appear ($\lambda_{\max} = 360$ mμ with a shoulder $\lambda_{\max} = 455$ mμ). The intensities of these absorption bands reach a maximum (log $\epsilon = 3{\cdot}7$ and $3{\cdot}3$ respectively) as the mole ratio of added phosphine to $[\mathrm{Pr^nOPPh_2}]_2\mathrm{Ni[CN]_2}$ approaches 1000:1.



(I)



(II)



(III)

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