Complexes of Nickel(II) Cyanide with Ditertiary Phosphines and their Reduction to Nickel(I) Derivatives

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NICKEL(I) compounds are rare and the few which are in the oxidation state +1 have not been obtained by straightforward reduction from Ni^{II} to Ni^{I}.[1,2] The reduction of the ditertiary phosphine complexes of nickel(II) with sodium naphthalenide or $NaBH_4$ has previously been reported to yield the nickel(0) complexes $Ni(diph)_2$ (diph = ditertiary phosphine).[3]

We now find that complexes of nickel(I) of composition $Ni(diph)_{1\cdot5}(CN)$ [diph = 1,4-bis(diphenylphosphino)propane (dpp) or 1,4-bis(diphenylphosphino)butane (dpb)] can be obtained by reduction of the corresponding complexes of nickel(II), $Ni(diph)_{1\cdot5}(CN)_2$. The latter compounds have been obtained as red crystalline products by addition of water to a solution of the ligand diphosphine in ethanol containing $Ni(diph)(NCS)_2$ and KCN. The electronic spectra of these diamagnetic complexes show that the nickel(II) atoms are 5-co-ordinate.[4] To account for the 5-co-ordination and the stoicheiometry, the complexes $Ni(diph)_{1\cdot5}(CN)_2$ are best formulated as binuclear units

$$[(CN)_2(diph)Ni(diph)Ni(diph)(CN)_2]$$

with each of the two nickel atoms bound to one chelating diphosphine and the third diphosphine bridging the two metal atoms. The molecular weight of $Ni(dpb)_{1\cdot5}(CN)_2$ determined cryoscopically in $C_2H_4Cl_2$ is 1150 for a solution 1·4% by weight (calculated for a dimer, 1500), showing that the binuclear species are partially dissociated in this solvent.

Careful reduction with $NaBH_4$ of these complexes suspended in ethanol yields yellow products which analyse as $Ni(diph)_{1\cdot5}CN$. The reduction of the 4-co-ordinate bromide derivatives $Ni(diph)Br_2$ (even in the presence of the diphosphine) cannot be so easily controlled and did not yield the nickel(I) complexes. It thus appears that the presence in the molecule of CN^- groups stabilizes the +1 oxidation state. The reduction to Ni^I can also be observed in the case of the complexes with tertiary phosphines $Ni(PR_3)_2(CN)_2$. However purification from by-products is more difficult and we did not obtain reasonably pure samples.

The magnetic moments of the compounds $Ni(diph)_{1\cdot5}(CN)$ determined by the Gouy method are in the range 2·0—2·3 B.M., as expected for a d^9 configuration with a small orbital contribution. The infrared spectra in Nujol show a sharp peak at 2100—2105 cm.$^{-1}$ assigned to the CN^- stretching, and do not show any evidence in the 1700—2200 cm.$^{-1}$ region of absorption attributable to hydridic hydrogens. The complexes are fairly stable in the solid state in an argon atmosphere and decompose more or less rapidly in the common organic solvents. The electronic reflectance spectrum of $Ni(dpp)_{1\cdot5}(CN)$ displays a distinct shoulder at about 23,000 cm.$^{-1}$. The reflectance spectrum of $Ni(dpb)_{1\cdot5}(CN)$ shows a broad absorption band at about this frequency. Both spectra are comparable with those given by the square complexes of Ag^{II} with bipyridyl[5] suggesting that the nickel(I) complexes have a similar structure. (The compounds $Ni(PPh_3)_3X$ are reported to be tetrahedral).[2] The complexes $Ni(diph)_{1\cdot5}(CN)$ should also be formulated as binuclear species

$$[(CN)(diph)Ni(diph)Ni(diph)(CN)]$$

with a planar arrangement of three phosphorus atoms and one cyanide group around the nickel atom.

The visible spectra in CH_2Cl_2 are initially very similar to the reflectance spectra however they undergo a rapid change owing to the decomposition of the complexes. If the latter are dissolved in CH_2Cl_2 containing diphosphine, the initial spectrum remains practically unaltered. This behaviour suggests that the decomposition observed in solution is probably due to solvolysis. The existence of solvated species in which one tertiary phosphine is replaced by one solvent molecule has already been reported for the analogous complexes of rhodium(I) and nickel(I) with tertiary phosphines.[2,6]

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