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Four- vs. Five-Coordination of Nickel(II) with Certain Tertiary Phosphorus Ligands

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Infrared and electronic spectral data are presented and discussed for the following complexes: $NiL_3(CN)_2$ and $NiL_2(CN)_2$ ($L = (CH_3)_3P$, $(CH_3)_2POCH_3$, $CH_3P(OCH_3)_2$, or $P(OCH_3)_3$), $(NiL_5)(ClO_4)_2$ ($L = (CH_3)_2POCH_3$, $CH_3P(OCH_3)_2$, or $P(OCH_3)_3$), and $\{Ni[(CH_3)_3P]_4\}(BF_4)_2$. The five-coordinate complexes are believed to have a trigonal-bipyramidal structure in both solid and solution on the basis of their infrared and electronic spectra. Equilibria of the following type are found in solutions of the five-coordinate complexes: $NiL_3(CN)_2 \rightleftarrows NiL_2(CN)_2 + L$ and $NiL_5^{2+} \rightleftarrows NiL_4^{2+} + L$. Isosbestic points have been observed in the ultraviolet–visible spectra of these solutions. Electronic factors (nature of the metal–ligand bond) which favor the formation of five-coordinate complexes over four-coordinate complexes are discussed on the basis of their electronic spectra.

Introduction

Numerous four- and five-coordinate complexes have been isolated from reactions of Ni(II) salts with monodentate phosphorus ligands: tertiary phosphines,[2,3] secondary phosphines,[4] fluorophenylphosphines,[5] and phosphites.[6]

Most of the five-coordinate complexes have been reported to be dissociatively unstable with respect to a four-coordinate complex and free ligand. Equilibrium constants and thermodynamic data have been reported for $NiL_2(CN)_2 + L \rightleftarrows NiL_3(CN)_2$.[5,7]

The instability of these five-coordinate $NiL_3(CN)_2$ complexes has been related to both steric and electronic effects, but no clear attempt has been made at characterizing the electronic effects.[5,8]

In this study an attempt was made to minimize the steric factors by utilizing "small"[9] monodentate ligands. It has been possible to relate the observed coordination number of some nickel cyanide complexes to electronic effects, i.e., the nature of the metal–ligand bond. To accomplish this the series of ligands $(CH_3)_3P$, $(CH_3)_2POCH_3$, $CH_3P(OCH_3)_2$, and $P(OCH_3)_3$ was chosen for reaction with $Ni(ClO_4)_2{\cdot}6H_2O$, $Ni(BF_4)_2{\cdot}6H_2O$, and $Ni(CN)_2$. (Those complexes of $P(OCH_3)_3$ pertinent to this study have been prepared previously,[5,10] and the complexes of $(CH_3)_3P$ were reported while this research was in progress.)[11]

The following five-coordinate complexes have been isolated and investigated in this study: $NiL_3(CN)_2$ (L = all of the ligands in the above series) and $(NiL_5)(ClO_4)_2$ ($L = P(OCH_3)_3$,[6] $CH_3P(OCH_3)_2$, $(CH_3)_2POCH_3$). A number of four-coordinate complexes have also been isolated: *cis*-$NiL_2(CN)_2$ ($L = (CH_3)_2POCH_3$, $CH_3P(OCH_3)_2$), *trans*-$Ni[(CH_3)_3P]_2(CN)_2$,[11] and $Ni[(CH_3)_3P]_4(BF_4)_2$.

Relative stabilities of the five-coordinate complexes toward their corresponding four-coordinate complexes were investigated by optical absorption studies. The following types of equilibria were found to be present in solution

$$NiL_3(CN)_2 \rightleftarrows NiL_2(CN)_2 + L$$

$$NiL_5{}^{2+} \rightleftarrows NiL_4{}^{2+} + L$$

Experimental Section

Materials. $Ni(CN)_2{\cdot}4H_2O$ was prepared according to a method previously given;[12] the blue solid was dehydrated to buff-colored $Ni(CN)_2$ by heating at 150° under vacuum for approximately 5 hr. The salts $Ni(ClO_4)_2{\cdot}6H_2O$ and $Ni(BF_4)_2{\cdot}6H_2O$ were obtained from G. Frederick Smith Chemical Co., Columbus, Ohio, and Alfa Inorganics, Beverly, Mass., respectively. Methyldichlorophosphine was received from the Department of the Army, Edgewood Arsenal, Edgewood, Md., as a gift, and it was used without further purification. The dehydrating agent, 2,2-dimethoxypropane was obtained from Eastman Kodak Co., Rochester, N.Y. Trimethylphosphine was purchased from Strem Chemicals, Inc., Danvers, Mass., and converted to the silver iodide complex[13] which was stored at about −20° in a stoppered flask. The ligand $CH_3P(OCH_3)_2$ was prepared according to the method of Maier;[14] however, CH_3PCl_2 was used as the starting material. The observed boiling point (bp_{300} 60–61°) for $CH_3P(OCH_3)_2$ agreed well with the literature value.[14] The ligand $(CH_3)_2POCH_3$ was prepared by heating a 1:1 molar mixture of $(CH_3)_2PN(CH_3)_2$[15] and CH_3OH at 65° for 1 hr and then distilling the product at bp_{760} 58–59°. The reactant $(CH_3)_2PN(CH_3)_2$ was prepared by two methods: a reaction sequence outlined by Burg and Slota,[15] which gave very poor yields, and heating $(CH_3)_2PCl$[16] with 2 mol of $(CH_3)_2NH$ in Na-dried diethyl ether at −78° under a nitrogen atmosphere. The $(CH_3)_2NH$ was slowly added through an addition funnel with a pressure-equalizing side arm. The reaction flask was also equipped with a very efficient stirrer and a Dry Ice condenser. After complete addition of $(CH_3)_2NH$, the reaction mixture was allowed to come slowly to room temperature with stirring, the amine hydrochloride was filtered off under suction, and the product was distilled (bp_{760} 95–100°). The direct reaction of $(CH_3)_2PCl$ or CH_3PCl_2 with CH_3OH in the presence of base gave very poor yields of the phosphinite and phosphonite. The ^{1}H NMR spectrum of $CH_3P(OCH_3)_2$ consists of two doublets at 1.13 ppm (CH_3, J_{PCH} = 8.5 Hz) and at 3.52 ppm (OCH_3, J_{POCH} = 11.1 Hz) with integrated intensities of 1:2, respectively. Similarly, the spectrum of $(CH_3)_2POCH_3$ consists of two doublets at 1.19 ppm (CH_3, J_{PCH} = 6.0 Hz) and at 3.32 ppm (OCH_3, J_{POCH} = 13.5 Hz) with intensities of 2:1, respectively.

$Ni[CH_3P(OCH_3)_2]_3(CN)_2$. To 2.2 g (20 mmol) of $Ni(CN)_2$ suspended in 50 ml of acetone and cooled in ice water was added 5.4 g (50 mmol) of $CH_3P(OCH_3)_2$ all at once. The solution was stirred for approximately 10 hr, filtered under nitrogen, and concentrated under vacuum to give a dark red solution. Red-orange crystals formed when the solution was cooled to −78°. These crystals were filtered, rapidly washed with −78° acetone, and dried in a stream of dry nitrogen.

Anal. Calcd for $C_{11}H_{27}N_2O_6P_3Ni$: C, 30.35; H, 6.22; P, 21.39; N, 6.44. Found: C, 30.21; H, 6.11; P, 21.48; N, 6.63.

$Ni[CH_3P(OCH_3)_2]_2(CN)_2$. This yellow complex often appeared as an impurity in the preceding five-coordinate complex. Treatment of $Ni[CH_3P(OCH_3)_2]_3(CN)_2$ with anhydrous ethyl ether as reported earlier[10] produces a yellow powder which is insoluble in acetone and diethyl ether. The five-coordinate complex is also converted to yellow $Ni[CH_3P(OCH_3)_2]_2(CN)_2$ by pumping under a good vacuum for 1 hr or more.

Anal. Calcd for $C_8H_{18}N_2O_4P_2Ni$: C, 29.35; H, 5.52; P, 18.95; N, 8.57. Found: C, 28.95; H, 5.17; P, 18.95; N, 8.50.

$Ni[(CH_3)_2POCH_3]_3(CN)_2$. To 1.1 g (10 mmol) of $Ni(CN)_2$ suspended in 50 ml of acetone and cooled in ice water was added 2.8 g (30 mmol) of $(CH_3)_2POCH_3$ all at once. After several hours of stirring (magnetic), the solution was filtered, concentrated under vacuum, and cooled to give red-orange crystals. Attempts at recrystallization in the presence of excess ligand yielded mostly the four-coordinate complex; repeated attempts at obtaining a satisfactory elemental analysis were unsuccessful. This complex could, however, be identified in the solid state by both infrared and electronic spectroscopy.

$Ni[(CH_3)_2POCH_3]_2(CN)_2$. This yellow complex consistently appeared as an impurity in the preceding five-coordinate complex and could be isolated from its solutions. Also, by allowing $Ni(CN)_2$ to react with $(CH_3)_2POCH_3$ in a molar ratio of 1:2 or less and in a manner similar to the above, the complex could be prepared easily.

Anal. Calcd for $C_8H_{18}N_2O_2P_2Ni$: C, 32.61; H, 6.13; P, 21.08; N, 9.53. Found: C, 33.04; H, 6.11; P, 19.78; N, 9.69.

$Ni[(CH_3)_3P]_3(CN)_2$. A 50-ml acetone suspension of 0.44 g (4.0 mmol) of $Ni(CN)_2$ was cooled with liquid nitrogen and evacuated on a high-vacuum line. The ligand $P(CH_3)_3$, 0.91 g (12 mmol), liberated from the AgI complex by heating, was condensed onto this frozen suspension and the mixture allowed to warm to room temperature. Stirring (magnetic) was initiated as soon as possible, and a dark red solution resulted. After the solution had been stirred for about $^1/_4$ hr, it was removed from the vacuum line, filtered, concentrated, and cooled to −78° to give red-orange crystals. Alternatively, the acetone solution may be evaporated to dryness and the resulting red-orange powder recrystallized from *n*-hexane or diethyl ether.

Anal. Calcd for $C_{11}H_{27}N_2P_3Ni$: C, 38.95; H, 7.97; P, 27.41; N, 8.26. Found: C, 38.53; H, 8.02; P, 26.59; N, 8.12.

$Ni[(CH_3)_3P]_2(CN)_2$. Prolonged evacuation of $Ni[(CH_3)_3P]_3(CN)_2$ or extraction of impure $Ni[(CH_3)_3P]_3(CN)_2$ with *n*-hexane several times produced a yellow solid which could be recrystallized from an acetone–diethyl ether mixture (10:1).

Anal. Calcd for $C_8H_{18}N_2P_2Ni$: C, 36.50; H, 6.85; P, 23.60; N, 10.65. Found: C, 36.39; H, 6.88; P, 23.41; N, 10.43.

$\{Ni[CH_3P(OCH_3)_2]_5\}(ClO_4)_2$. A solution of 0.73 g (2.0 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ and acetone–2,2-dimethoxypropane[17] (10 ml each) was stirred at room temperature for $^1/_2$ hr. Then 1.25 ml (>10 mmol) of $CH_3P(OCH_3)_2$ was added all at once to give an orange precipitate and a similarly colored solution. The solution was stirred for $^1/_4$ hr and filtered, and the solid was washed well with diethyl ether and dried under vacuum. The compound could be recrystallized from a very concentrated acetone solution.

Anal. Calcd for $C_{15}H_{45}Cl_2O_{18}P_5Ni$: C, 22.55; H, 5.64; P, 19.42; Cl, 8.90. Found: C, 22.42; H, 5.63; P, 19.06; Cl, 8.94.

$\{Ni[(CH_3)_2POCH_3]_5\}(ClO_4)_2$. This compound was prepared in a manner identical with that described above for $\{Ni[CH_3P(OCH_3)_2]_5\}(ClO_4)_2$.

Anal. Calcd for $C_{15}H_{45}Cl_2O_{13}P_5Ni$: C, 25.08; H, 6.27; P, 21.55; Cl, 9.88. Found: C, 25.27; H, 6.19; P, 21.47; Cl, 10.08.

$\{Ni[(CH_3)_3P]_4\}(BF_4)_2$. The air over a 25-ml solution of absolute ethanol and 0.34 g (1.0 mmol) of $Ni(BF_4)_2 \cdot 6H_2O$ was evacuated on a high-vacuum line and the solution was cooled with liquid nitrogen. Trimethylphosphine (0.30 g, 4.0 mmol) was added to this solution as above. A pale red solid formed as this mixture was allowed to warm to room temperature and stirred. The solution was removed from the vacuum line and filtered, and the solid was washed well with diethyl ether and dried under vacuum. The complex dissolves in ethanol only very slowly to give a yellow solution, in acetonitrile to give a purple solution which eventually becomes colorless upon standing, and in acetone to give a red solution which rapidly decomposes to give a nearly colorless solution.

Anal. Calcd for $C_{12}H_{36}B_2F_8P_4Ni$: C, 26.80; H, 6.70; P, 23.10. Found: C, 26.65; H, 6.56; P, 22.98.

Physical Measurements. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were obtained in Nujol mulls by use of either a Beckman Model 12 grating spectrophotometer or a Perkin-Elmer Model 225 grating spectrophotometer. Reflectance spectra were obtained by use of a Bausch and Lomb Spectronic 600 with $BaSO_4$ as the diluent and reference. Spectra in the solid state were also obtained with a Cary Model 14 spectrophotometer and a Nujol mull of the compound which was "painted" onto filter paper.[18] Nujol alone on filter paper was used in the reference beam. These "filter paper cells" were simply taped to the wall of the cell compartment nearest the detector; however, little difference in the spectra was noted when the opposite wall was used. Spectra were also recorded by use of Nujol mulls mounted between quartz windows. In the visible region, almost identical spectra were obtained by the two methods; however, in the ultraviolet region the resolution was very poor when quartz windows were used. Solution ultraviolet–visible spectra were recorded with Unicam Model SP-800B and Cary Model 14 spectrophotometers using CH_2Cl_2 which was previously dried by refluxing over CaH_2. Solutions were prepared under nitrogen and placed in stoppered cells in order to minimize evaporation while the spectra were recorded at various temperatures. A thermostated methanol–water bath (±0.10°) was attached to the spectrophotometer so that spectra could be recorded at different temperatures.

Table I. Cyanide Stretching Frequencies of $NiL_3(CN)_2$ and $NiL_2(CN)_2$ in Nujol

	ν_{CN}, cm^{-1}	
L	$NiL_3(CN)_2$	$NiL_2(CN)_2$
$(CH_3)_3P$	2097	2106
$(CH_3)_2POCH_3$	2100	2129, 2113
$CH_3P(OCH_3)_2$	2104	2122, 2103
$P(OCH_3)_3$^{a}	2125	2149, 2144, 2127, 2122

^{a} See ref 10.

Results and Discussion

Five-coordinate complexes of the type $NiL_3(CN)_2$ (L = $(CH_3)_3P$,[3] $(CH_3)_2POCH_3$, $CH_3P(OCH_3)_2$, $P(OCH_3)_3$[10]) are produced when $Ni(CN)_2$ is allowed to react with an excess of the ligands in acetone. The corresponding $NiL_2(CN)_2$ complexes are prepared by subjecting the five-coordinate complexes to high vacuum at room temperature or by allowing $Ni(CN)_2$ to react with these ligands in a 1:2 molar ratio. Complexes of the type $(NiL_5)(ClO_4)_2$ (L = $(CH_3)_2POCH_3$, $CH_3P(OCH_3)_2$, $P(OCH_3)_3$)[6] are isolated from acetone–2,2-dimethoxypropane solutions of $Ni(ClO_4)_2 \cdot 6H_2O$ and excess ligand. When L = $(CH_3)_3P$ no five-coordinate complex could be isolated. However, the complex $Ni[(CH_3)_3P]_4(BF_4)_2$ was prepared when $Ni(BF_4)_2 \cdot 6H_2O$ was allowed to react with $(CH_3)_3P$ in ethanol solutions, similar in manner to the preparation of $Ni[(CH_3)_3P]_4(ClO_4)_2$.[3]

Infrared Spectra. Complexes of $Ni(CN)_2$ which were prepared in this study permit easy assignment of the cyanide stretching vibration. The mull infrared spectrum of each $NiL_3(CN)_2$ (L = $(CH_3)_3P$, $(CH_3)_2POCH_3$, $CH_3P(OCH_3)_2$, $P(OCH_3)_3$[10]) complex consists of one sharp absorption (Table I), consistent with a trigonal-bipyramidal structure with the cyanide groups in trans apical positions. Infrared spectral data in the cyanide region for the corresponding $NiL_2(CN)_2$ complexes are also presented in Table I. When L = $(CH_3)_2POCH_3$ or $CH_3P(OCH_3)_2$, two cyanide stretching frequencies are observed, and when L = $(CH_3)_3P$, only one is observed. We interpret these data in terms of a cis square-planar geometry for the complexes of $(CH_3)_2POCH_3$ and $CH_3P(OCH_3)_2$ and a trans square-planar arrangement for the complex of $(CH_3)_3P$. When L = $P(OCH_3)$, four cyanide stretching frequencies are observed, and it has been postulated[10] that a dimer is present in the solid state, which contains both bridging and terminal cyanides.

Electronic Spectra. Nickel Cyanide Complexes. The band maxima in the electronic spectra for both the four- and five-coordinate $Ni(CN)_2$ complexes are listed in Table II for both solids and CH_2Cl_2 solutions, along with the effect of adding excess ligand.

For each four-coordinate complex in solution, there is a very intense absorption in the region 290–300 mμ. The presence of this absorption (290–300 mμ) in the solution spectra of the five-coordinate complexes and the absence of this absorption in the solid spectra and solution spectra with excess ligand of the five-coordinate complexes suggest that the band is due to the four-coordinate complexes. The spectra of the $(CH_3)_3P$ complexes in Figure 1 are typical. The rather constant position of this band in all the spectra of the four-coordinate complexes suggests that it is a Ni → π* CN charge-transfer band.[8]

Absorption spectra of the five-coordinate complexes in solution show isosbestic points as the temperature is varied (0–30°), as shown in Figure 2 for $Ni[P(OCH_3)_3]_3(CN)_2$. When excess ligand is added to these solutions (and also to the reference cell), the same isosbestic points are observed[10] and the band near 300 mμ is suppressed. These results suggest that an equilibrium is present in solutions of the five-coordinate complexes

$$NiL_3(CN)_2 \rightleftarrows NiL_2(CN)_2 + L$$

Table II. Electronic Spectral Data for $NiL_3(CN)_2$ and $NiL_2(CN)_2$ Complexes

Compd	Absorptions, mμ: Solid state	Absorptions, mμ: CH_2Cl_2	Absorptions, mμ: CH_2Cl_2, excess ligand
$Ni[P(OCH_3)_3](CN)_2$	260, 395 b	297, 355, 420 sh	355, 420 sh
$Ni[P(OCH_3)_3]_2(CN)_2$	260, 345 sh, 420 sh	297, 345 sh, 420 sh	355, 420 sh
$Ni[CH_3P(OCH_3)_2]_3(CN)_2$	255, 325 sh, 420 sh	297, 325, 415 sh	325, 415 sh
$Ni[CH_3P(OCH_3)_2]_2(CN)_2$	265, 335 sh, 430 sh	297, 325 sh, 415 sh	325, 415 sh
$Ni[(CH_3)_2POCH_3]_3(CN)_2$	350 sh, 440 sh	294, 345, 430 sh	345, 430 sh
$Ni[(CH_3)_2POCH_3]_2(CN)_2$	275, 335 sh, 440 sh	295, 335 sh, 440 sh	345, 430 sh
$Ni[(CH_3)_3P]_3(CN)_2$	395	290, 300 sh, 390, 455 sh	390, 455 sh
$Ni[(CH_3)_3P]_3(CN)_2$	293, 345	290, 300 sh, 370 sh	390, 455 sh

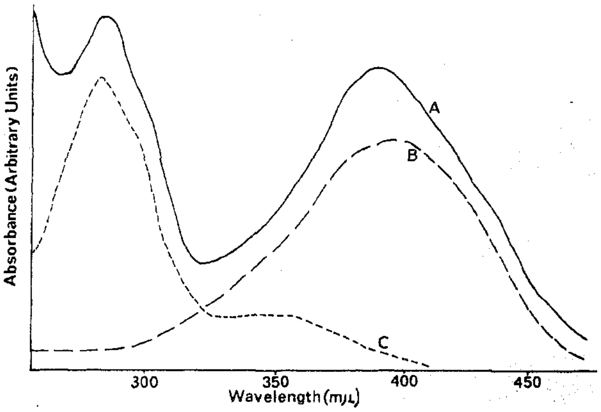

Figure 1. Absorption spectra: (A) $Ni[(CH_3)_3P]_3(CN)_2$ in CH_2Cl_2; (B) solid-state $Ni[(CH_3)_3P]_3(CN)_2$; (C) $Ni[(CH_3)_3P]_2(CN)_2$ in CH_2Cl_2.

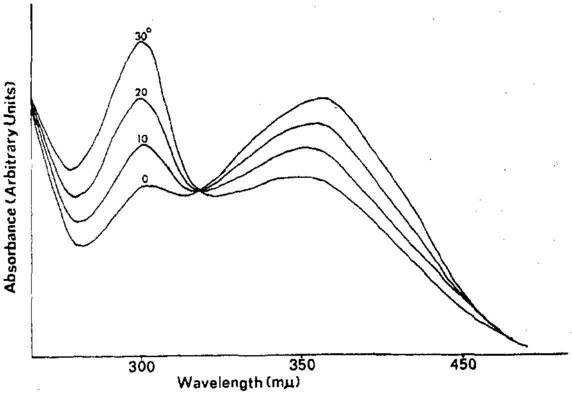

Figure 2. Effect of temperature on the ultraviolet-visible spectrum of $Ni[P(OCH_3)_3]_3(CN)_2$ in CH_2Cl_2.

This equilibrium is also consistent with the observation that the four-coordinate complexes can be easily isolated from solutions of the five-coordinate complexes. It can also be noted (Figure 2) that the bands due to the five-coordinate complexes (325–455 mμ) increase in intensity as the temperature is decreased, while the bands assigned to the four-coordinate complex (290–300 mμ) decrease. Thus, the equilibrium shifts toward the five-coordinate complex with a decrease in temperature.[10]

The five-coordinate complexes show an intense absorption in the visible region, with a low-energy shoulder (325–455 mμ), assigned to the $(e'')^4(e')^4 \rightarrow (e'')^4(e')^3(a_1)^1$, ν_1, transition in complexes of D_{3h} symmetry.[19] Venanzi and coworkers[20] have discussed the splitting of this band in solution spectra in terms of a dynamic Jahn–Teller distortion of excited states and the splitting in the solid spectra in terms of a molecular ground-state distortion. A dipole-forbidden transition, $(e'')^4(e')^4 \rightarrow (e'')^3(e')_4(a_1)^1$, ν_2, of low intensity is expected at shorter wavelength than ν_1, but overlapping of intense ultraviolet absorptions and the above allowed absorptions prohibits accurate assignment of its position. These assignments are in agreement with similar assignments which have been made for other five-coordinate Ni(II) complexes of tertiary phosphorus ligands.[19]

Table III. K_{inst} for $NiL_3(CN)_2$ Complexes at 25°

L	$10^4 K_{inst}$, M	ϵ, M^{-1} cm^{-1}
$(CH_3)_3P$	2.5	2390
$(CH_3)_2POCH_3$	0.4	2480
$CH_3P(OCH_3)_2$	0.5	2506
$P(OCH_3)_3$	1.7	2756

The band assignments that are proposed above assume that these five-coordinate complexes have trigonal-bipyramidal structures (D_{3h}) in the solid state and in solution. However, it may be argued that these spectra are those of a square-pyramidal complex (C_{4v}), since three spin-allowed transitions are predicted for these complexes.[21] The proof of this argument would rest in the low-temperature solution electronic spectra, as the three bands in C_{4v} symmetry are independent of temperature, and the two low-energy bands (325–455 mμ) would persist at low temperature (~77°K) and not coalesce to a single absorption as they do in D_{3h} symmetry.[20] We have made the band assignments on the basis of a trigonal-bipyramidal structure. It is predominant in those complexes of Ni(II) with monodentate ligands whose structures have been determined,[22-25] is predicted by ligand–ligand repulsion theories,[26] and is consistent with the infrared spectra.

Estimates of the equilibrium constants, or instability constants (K_{inst}), for the system

$$NiL_3(CN)_2 \overset{K_{inst}}{\rightleftharpoons} NiL_2(CN)_2 + L$$

have been obtained for these five-coordinate complexes. These calculations were facilitated by the large spectral differences between four- and five-coordinate complexes. The extinction coefficient (ϵ) for the intense visible absorption of each five-coordinate complex was determined from the absorption maxima observed when extremely large excesses of ligand were added to solutions of the five-coordinate complexes of known concentration. These values of ϵ were then used to calculate the concentration of five-coordinate complex present at equilibrium with no added ligand, and the difference between this concentration and the initial concentration was taken as the four-coordinate complex concentration and the dissociated ligand concentration, also at equilibrium. The calculated instability constants are recorded in Table III along with the calculated ϵ's. The uncertainty in these values is such that $(CH_3)_2POCH_3$ and $CH_3P(OCH_3)_2$ may be interchanged, but it is definite that these constants follow the order $(CH_3)_3P > P(OCH_3)_3 > CH_3P(OCH_3)_2 \sim (CH_3)_2POCH_3$. Surprisingly, there is no regular order in K_{inst} paralleling the systematic change in the nature of these phosphorus derivatives. This particular order, however, is observed elsewhere. The band maxima (Table II) for the allowed d–d transitions are in approximately the same order indicating that the $(CH_3)_3P$ complex has the weakest ligand field interaction. The large extinction coefficients that are obtained for these five-

Table IV. Absorption Spectral Data for $(NiL_5)(ClO_4)_2$ and $(NiL_4)(BF_4)_2$ Complexes

Compd	Absorptions, mμ		
	Solid state	CH_2Cl_2	CH_2Cl_2, excess ligand
$\{Ni[P(OCH_3)_3]_5\}(ClO_4)_2$	305 sh, 404, 465 sh	300 sh, 404, 450 sh	300 sh, 412, 470 sh
$\{Ni[CH_3P(OCH_3)_2]_5\}(ClO_4)_2$	320 sh, 425 b	310 sh, 415, 475 sh	300, 445, 525 sh
$\{Ni[(CH_3)_2POCH_3]_5\}(ClO_4)_2$	320 sh, 440, 525 sh	290 sh, 425 b	310, 470, 560 sh
$\{Ni[(CH_3)_3P]_4\}(BF_4)_2$	300, 400	290, 400 sh, 490	300 sh, 570, 650 sh

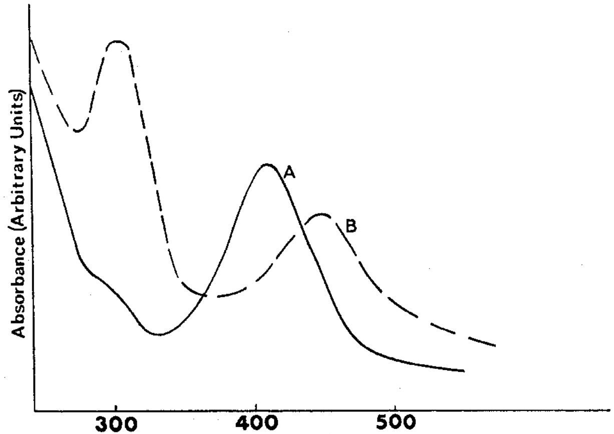

Figure 3. Absorption spectra in CH_2Cl_2: (A) $\{Ni[CH_3P(OCH_3)_2]_5\}(ClO_4)_2$; (B) $\{Ni[CH_3P(OCH_3)_2]_5\}(ClO_4)_2$ plus added $CH_3P(OCH_3)_2$.

coordinate complexes are similar to previous observations[2,19] and demonstrate the strong mixing of ligand and metal orbitals in these complexes. The above ligand order is also found in the ligand-exchange rates of the five-coordinate complexes in solution.[27]

Electronic Spectra. $(NiL_5)(ClO_4)_2$ and $(NiL_4)(BF_4)_2$ Complexes. The band maxima in the solid-state and solution spectra of the five-coordinate $(NiL_5)(ClO_4)_2$ (L = $(CH_3)_2POCH_3$, $CH_3P(OCH_3)_2$, $P(OCH_3)_3$[6]) complexes and the four-coordinate $Ni[(CH_3)_3P]_4(BF_4)_2$ complex are presented in Table IV. The ultraviolet–visible spectra of the five-coordinate complexes in the solid state and in solution to which ligand has been added (see later) are similar to those reported for $\{Ni[P(OCH)_3(CH_2)_3]_5\}(ClO_4)_2$,[6,28] which is trigonal bipyramidal, according to a three-dimensional X-ray crystal structure analysis.[25] Assignment of the bands in the five-coordinate complexes is accomplished by assuming a similar structure and by analogy with the assignments in the $NiL_3(CN)_2$ complexes. The low-energy absorption bands in the spectra of these complexes (400–560 mμ) are split and are assigned to the $(e'')^4(e')^4 \rightarrow (e'')^4(e')^3(a_1)^1$, ν_1, transition (D_{3h} symmetry).[21] The high-energy band (300–320 mμ) is assigned to the dipole-forbidden $(e'')^4(e')^4 \rightarrow (e'')^3(e')^4(a_1)^1$, ν_2, transition.

Isosbestic points are obtained in the solution spectra of $\{Ni[P(OCH_3)_3]_5\}(ClO_4)_2$ and $\{Ni[CH_3P(OCH_3)_2]_5\}(ClO_4)_2$, when the temperature is varied (0–30°) ($\{Ni[(CH_3)_2POCH_3]_5\}(ClO_4)_2$ decomposes rapidly in CH_2Cl_2 and isosbestic points were not observed). Therefore, an equilibrium similar to that found in the $NiL_3(CN)_2$ complexes is proposed

$$NiL_5^{2+} \rightleftarrows NiL_4^{2+} + L$$

Further evidence for this equilibrium is given by the observation that the solution spectra of the five-coordinate complexes are altered by addition of ligand (Figure 3). The positions of the low-energy bands shift to lower energies when ligand is added to approximately the positions of the absorptions in the solid-state spectra (Table IV). This shift indicates that the four- and five-coordinate bands overlap to a large extent. Indeed, the solution spectrum of $\{Ni[(CH_3)_2POCH_3)_5\}(ClO_4)_2$ closely resembles the spectrum of the four-coordinate complex $\{Ni[(CH_3)_3P]_4\}(BF_4)_2$ inasmuch as the five-coordinate species is probably largely dissociated in solution according to the preceding equilibrium.

$Ni[(CH_3)_3P]_4^{2+}$ was the only NiL_4^{2+} complex which could be isolated. Its solution and solid-state spectra are similar (Table IV) and similar to other square-planar Ni(II) complexes.[21] Addition of excess $(CH_3)_3P$ gives a dark blue solution whose spectrum resembles those of the five-coordinate complexes in this work (Table IV) and also that of the blue complex $[Ni(TAP)Br]ClO_4$ (TAP = $P(CH_2CH_2As(CH_3)_2)_3$).[29]

It is worthwhile to comment further on the associative nature of $Ni[(CH_3)_3P]_4^{2+}$ in solution. When the tetrafluoroborate salt is dissolved in CH_3CN, a dark purple solution results. Addition of a large amount of diethyl ether causes trace amounts of a blue solid to be precipitated with a ν_{CN} at ~2300 cm^{-1}, indicating a coordinated CH_3CN group.[30] The proposed five-coordinate complex present in solution when excess $(CH_3)_3P$ is added to $Ni[(CH_3)_3P]_4^{2+}$ has not been isolated, however. The dark blue solution that forms when excess ligand is added rapidly fades to pale yellow, and addition of diethyl ether to this solution causes precipitation of a pale yellow solid. Moreover, when diethyl ether is added to the initial blue solution, the same yellow solid is obtained. Attempts at recrystallization inevitably produced light green solutions indicative of solvated Ni(II). Elemental analyses of the compound were inconsistent and offered no information about it. Nevertheless, it is tempting to speculate that this light yellow complex is a Ni(0) complex of $(CH_3)_3P$. The complex $Ni[(CH_3)_3P]_4$ has been prepared and its color is light yellow.[9] The mechanism for its formation in this work might be considered to be similar to that used for preparation of nickel(0) phosphite complex,[31,32] in which excess ligand causes reduction of Ni(II) to Ni(0) and the excess ligand is oxidized.

The order of increasing ligand field strength in NiL_5^{2+} complexes is $(CH_3)_3P < (CH_3)_2POCH_3 < CH_3P(OCH_3)_2 < P(OCH_3)$ (Table IV). This order of ligand field splitting closely parallels the stability of the five-coordinate complexes. The isolable $P(OCH_3)_3$ complex appears to be stable in solution, and its absorption spectrum is affected very little upon the addition of ligand.

Electronic Effects in Five-Coordinate Complexes. In five-coordinate d^8 complexes with trigonal-bipyramidal structures, four of the five filled metal d orbitals can be used in π bonding, if π-acceptor ligands are available.[8] In square-planar, d^8 complexes, only three metal ion d orbitals can be used in π bonding for reasons of symmetry.[8] Thus, a good π-acceptor ligand would favor the formation of a five-coordinate complex over a four-coordinate complex. In the ligands considered in this study, the π-acceptor ability would be expected to decrease in the order $P(OCH_3)_3 > CH_3P(OCH_3)_2 > (CH_3)_2POCH_3 > (CH_3)_3P$.[33] The more electronegative OCH_3 groups would have the effect of lowering the energy of the empty phosphorus 3d oribtals, thus enhancing their π-acceptor character.[34] At the same time the OCH_3 groups should withdraw electron density from the phosphorus atom and produce a contracted and more stable σ-donor orbital, which would be less suited for σ bonding to the relatively more expanded Ni 4s and 4p orbitals.[8] Since ligands which bond to these s and p orbitals in preference to d orbitals favor the five-coordinate structure, the tendency toward fivefold coordination should decrease in the order $(CH_3)_3P > (CH_3)_2POCH_3 > CH_3P(OCH_3)_2 > P(OCH_3)_3$, according to σ-bonding arguments.[5,8]

The stability of the $NiL_3(CN)_2$ complexes toward the corresponding $NiL_2(CN)_2$ complexes decreases in the order $(CH_3)_2POCH_3 \sim CH_3P(OCH_3)_2 > P(OCH_3)_3 > (CH_3)_3P$ (Table III). This does not reflect the order predicted by either π-acceptor or σ-donor arguments alone but suggests that the stability of five-coordinate $NiL_3(CN)_2$ complexes is determined by a combination of these two effects.[8]

The proposed stability of the NiL_5^{2+} complexes relative to the corresponding NiL_4^{2+} complexes decreases in the order predicted by π-bonding arguments alone: $P(OCH_3)_3 > CH_3P(OCH_3)_2 > (CH_3)_2POCH_3 > (CH_3)_3P$. However, in this case ligand steric effects may be important. Cone angles of $(CH_3)_3P$ and $P(OCH_3)_3$ are 118 and 107°, respectively.[9] In $NiL_3(CN)_2$ trigonal-bipyramidal complexes each phosphine has an available ligand cone angle of nearly 120° and steric interactions should not be important. In NiL_5^{2+} complexes, however, the ligands are considerably more crowded, and steric effects could dominate the dissociation to NiL_4^{2+}.

Registry No. $Ni[CH_3P(OCH_3)_2]_3(CN)_2$, 55299-05-3; $Ni[CH_3P(OCH_3)_2]_2(CN)_2$, 55299-04-2; $Ni[(CH_3)_2POCH_3]_3(CN)_2$, 55299-03-1; $Ni[(CH_3)_2POCH_3]_2(CN)_2$, 55299-02-0; $Ni[(CH_3)_3P]_3(CN)_2$, 54515-54-7; $Ni[(CH_3)_3P]_2(CN)_2$, 38889-86-0; $\{Ni[CH_3P(OCH_3)_2]_5\}(ClO_4)_2$, 55299-01-9; $\{Ni[(CH_3)_2POCH_3]_5\}(ClO_4)_2$, 55298-99-2; $\{Ni[(CH_3)_3P]_4\}(BF_4)_2$, 55298-97-0; $Ni[P(OCH_3)_3]_3(CN)_2$, 21007-23-8; $Ni[P(OCH_3)_3]_2(CN)_2$, 55299-08-6; $\{Ni[P(OCH_3)_3]_5\}(ClO_4)_2$, 55009-50-2.

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Proton Magnetic Resonance Temperature Studies of Four- and Five-Coordinate Transition Metal Complexes with Tertiary Phosphorus Ligands

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The temperature dependence of the proton NMR spectra is reported for the complexes $NiL_3(CN)_2$ ($L = (CH_3)_3P$, $(CH_3)_2POCH_3$, $CH_3P(OCH_3)_2$, $P(OCH_3)_3$), $Ni[(CH_3)_3P]_2(CN)_2$, $\{Ni[P(OCH_3)_3]_5\}(ClO_4)_2$, $\{Co[P(OCH_3)_3]_5\}ClO_4$, $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$, and $\{Ni[CH_3P(OCH_3)_2]_5\}(ClO_4)_2$. Each of these five-coordinate complexes is in equilibrium in solution with a four-coordinate complex and free ligand, with a ligand-exchange rate which can be varied with temperature. The proton NMR spectra are similar for all complexes: a doublet at fast exchange rates, a sharp singlet at intermediate rates, and a multiplet at slow exchange rates. The doublets are simply $^{31}P-^{1}H$ coupling; however, the coupling constants and chemical shifts are an average of complexed and free ligand in solution. Decoupling of phosphorus and hydrogen nuclei at intermediate exchange rates is believed due to a spin-exchange mechanism for which strong $^{31}P-^{31}P$ coupling is necessary. Multiplets at slow exchange rates are due to $^{31}P-^{31}P$ coupling. J_{PCH} is found to be of opposite sign in complexed and free ligand, while J_{POCH} has the same sign. Qualitative rates of ligand exchange follow the order $(CH_3)_3P > P(OCH_3)_3 > CH_3P(OCH_3)_2 > (CH_3)_2POCH_3$. In the metal complexes of the type ML_5^{n+}, where $L = P(OCH_3)_3$, the rate follows the order $Co^+ > Rh^+ > Ni^{2+}$.

Introduction

In the previous paper[2] we reported on some five-coordinate complexes of the types $NiL_3(CN)_2$ and $(NiL_5)(ClO_4)_2$ where L is a tertiary phosphorus ligand. These complexes were shown by absorption spectral studies to dissociate in solution, and equilibria like $NiL_3(CN)_2 \rightleftarrows NiL_2(CN)_2 + L$ and $NiL_5^{2+} \rightleftarrows NiL_4^{2+} + L$ were proposed.

The equilibria cause intermolecular ligand exchange, and we have now undertaken the study of the temperature-dependent proton NMR spectra. The complexes studied are $NiL_3(CN)_2$ ($L = (CH_3)_3P$, $(CH_3)_2POCH_3$, $CH_3P(OCH_3)_2$, $P(OCH_3)_3$), $(NiL_5)(ClO_4)_2$ ($L = CH_3P(OCH_3)_2$, $P(OCH_3)_3$),