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Four- and Five-Coordinate Nickel(II) Complexes of the Flexible Triphosphine Bis(2-diphenylphosphinoethyl)phenylphosphine[1]

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The preparation of the ligand and the nickel complexes of the formulation Ni(DPP)X$_2$, where DPP is the new flexible triphosphorous ligand bis(2-diphenylphosphinoethyl)phenylphosphine, $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and X is Cl^-, Br^-, I^-, NCS^-, or CN^-, is described. Except for the Ni(DPP)(CN)$_2$ complex, which is a non-conductor in acetonitrile, the above complexes behave as uni-univalent electrolytes in acetonitrile. The implied existence of the cation, $[Ni(DPP)X]^+$, is confirmed by the isolation of the complexes $[Ni(DPP)X]B(C_6H_5)_4$, when equimolar amounts of the above nickel complexes and sodium tetraphenylborate are mixed in hot ethanol. The visible electronic absorption spectra of the two series of complexes $[Ni(DPP)X]B(C_6H_5)_4$ and Ni(DPP)X$_2$ in acetonitrile solution are quite similar, and are indicative of Ni^{II} in a planar, four-coordinate environment. Electronic spectra of the solid complexes Ni(DPP)X$_2$, taken at both 300°K and 77°K, show two ligand field bands in the visible region. These spectra are discussed in terms of five-coordinate structures in the solid state. The cyanide complex, Ni(DPP)(CN)$_2$, appears to be five-coordinate both in the solid state and in solution.

Introduction

A large number of five-coordinate, diamagnetic nickel(II) complexes have been characterized since 1965 with polydentate ligands that contain the heavier donor atoms such as phosphorus,[3,4] arsenic,[3-6] sulfur,[7] selenium,[8] antimony,[9] and combinations of mixed donor groups. However, until recently chelating aliphatic ligands containing more than two phosphorus atoms were quite rare.[10] As a part of our investigations into the factors that influence the structures and electronic ground states of five-coordinate complexes,[4,6-8] we were interested in determining the coordination geometry that would be favored by a P_3X_2 donor set when the ligand was a flexible chelating triphosphine. Thus, we began studies on the syntheses of several different types of aliphatic polyphosphines.

The compounds $ClCH_2CH_2P(C_6H_5)_2$ and $(C_6H_5)_2PCH_2CH_2P{<}^{C_6H_5}_{H}$ look attractive as intermediates to several polyphosphines, as one can imagine viable routes by the reaction of 2-chloroethyldiphenylphosphine[11] with the alkali metal salts of R_2PH and RPH_2 molecules. Unfortunately, $ClCH_2CH_2P(C_6H_5)_2$ had previously been obtained in only 2% yield,[12] and $(C_6H_5)_2PCH_2CH_2P{<}^{C_6H_5}_{H}$ was unknown. We have now developed satisfactory methods for syntheses of these two phosphines and have used them to prepare the triphosphine $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ (I) and the tetraphosphine $(C_6H_5)_2PCH_2CH_2\underset{Ph}{P}CH_2CH_2\underset{Ph}{P}CH_2CH_2P(C_6H_5)_2$ (II) in good yields (Equations 1-4).[13]

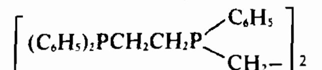
Recently King and Kapoor[14] reported the syntheses of I and II by an entirely different reaction.

$$(C_6H_5)_2PK + (excess)ClCH_2CH_2Cl \rightarrow (C_6H_5)_2PCH_2CH_2Cl + KCl \tag{1}$$

$$(C_6H_5)_2PCH_2CH_2Cl + C_6H_5PHNa \xrightarrow{\text{liq } NH_3/THF} (C_6H_5)_2PCH_2CH_2P(H)C_6H_5 + NaCl \tag{2}$$

$$(C_6H_5)_2PCH_2CH_2P(H)C_6H_5 \xrightarrow[\text{(b) } (C_6H_5)_2PCH_2CH_2Cl/THF]{\text{(a) BuLi/hexane}} \underset{\textbf{I}}{C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2} \tag{3}$$

$$(C_6H_5)_2PCH_2CH_2P(H)C_6H_5 \xrightarrow[\text{(b) } ClCH_2CH_2Cl]{\text{(a) BuLi/hexane}} \tag{4}$$



$$\left[(C_6H_5)_2PCH_2CH_2P{<}^{C_6H_5}_{CH_2-}\right]_2$$

II

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[4] G.S. Benner, W.E. Hatfield, and D.W. Meek, *Inorg. Chem.*, 3, 1544 (1964).

[5] G. Dyer, J.G. Hartley, and L.M. Venanzi, *J. Chem. Soc.*, 1293 (1965); G. Dyer and L.M. Venanzi, *ibid.*, 2771 (1965), and references contained therein.

[6] G.S. Benner and D.W. Meek, *Inorg. Chem.*, 6, 1399 (1967), and references contained therein.

[7] G. Dyer and D.W. Meek, *ibid.*, 4, 1398 (1965); L. Sacconi, *J. Chem. Soc. A*, 248 (1970); L. Sacconi and R. Morassi, *ibid.*, 575 (1970).

[8] G. Dyer and D.W. Meek, *ibid.*, 6, 149 (1967).

[9] B.R. Higginson, C.A. McAuliffe, and L.M. Venanzi, *Inorg. Chimica Acta*, 5, 37 (1971); C.A. McAuliffe and D.W. Meek, *ibid.*, 5, 270 (1971).

[10] W. Hewertson and H.R. Watson, *J. Chem. Soc.*, 1490 (1962).

In this paper we report the preparation and characterization of the tridentate phosphine, bis(2-diphenylphosphinoethyl)phenylphosphine (abbreviated D-PP). Also, its nickel(II) complexes are reported and discussed.

Experimental Section

All synthetic procedures were performed under a dry nitrogen atmosphere.

Reagents. Acetonitrile[15] and p-dioxane[16] were purified before use, and phenylphosphine[17] and potassium diphenylphosphide[18] were prepared according to literature methods. Tetrahydrofuran was purified by distillation from lithium aluminum hydride, and it was used within three days after distillation. 1,2-Dichloroethane was stirred overnight over anhydrous sodium sulphate and filtered through a medium porosity sintered-glass frit immediately prior to use.

2-Chloroethyldiphenylphosphine. The synthetic procedure of Struck and Shealy[12] was used, except that $KP(C_6H_5)_2$ was substituted for $LiP(C_6H_5)_2$ and a 30-40 molar excess of 1,2-dichloroethane was employed. Furthermore, after isolation of the crude product,[13] no attempt was made to distill it. The crude phosphine was isolated as a colorless liquid which solidified spontaneously to a white solid upon standing for a short period at room temperature. Mixing the crude 2-chloroethylphosphine with sulfur in benzene gave a 90% yield of 2-chloroethyldiphenylphosphine sulphide which was recrystallized from ethanol (m.p. 73°C, uncorr.).

Anal. Calcd. for $C_{14}H_{14}ClPS$: P, 11.05. Found: P, 10.80.

The infrared spectra of the phosphine and of the phosphine sulphide were essentially the same, except for an additional band at 610 cm^{-1} in the spectrum of the latter compound, which is assigned to the $P=S$ stretching frequency. A pmr spectrum of the phosphine suphide showed two unresolved multiplets centered at τ 7.00 and 6.15 (methylene protons), and a larger multiplet centered τ 2.17 (phenyl protons). The integrated intensity ratio of phenyl protons to methylene protons was 4.95 to 2, in good agreement with the theoretical ratio of 5 to 2.

No further purification of the 2-chloroethyldiphenylphosphine was attempted, and the crude product was used in the synthetic step below.

Bis(2-diphenylphosphinoethyl)phenylphospine. Liquid ammonia (75 ml) and dry THF (150 ml) were transferred to a 50 ml, three-neck, round bottom flask immersed in a Dry Ice-acetone cold bath. The flask was fitted with a Dry Ice-acetone reflux condenser that was protected with a calcium chloride drying tube, mechanical stirrer, and an addition funnel fitted with a nitrogen inlet tube. The solvent mixture was held at −78°, and 1.04 g (45 mmole) of sodium was added. The mixture was stirred for ½ hr., after which 4.95 g (45 mmole) of phenylphosphine was added slowly. A golden yellow color persisted after complete reaction of the phenylphosphine, signifying the presence of the salt, C_6H_5PHNa. A solution of 11.2 g (45 mmole) of 2-chloroethyldiphenylphosphine in dry THF was added dropwise to the C_6H_5PHNa solution. After the mixture was stirred for one hour, the cold bath was removed and the ammonia was allowed to evaporate slowly. The resulting THF solution was cooled to 0°C (ice-water bath), and 28.1 ml of a 1.6 *M* hexane solution of butyl lithium were added, producing a deep red solution of $(C_6H_5)_2PCH_2CH_2P(Li)C_6H_5$. A dry THF solution of 11.2 g (45 mmole) 2-chloroethyldiphenylphosphine was added to the phosphide solution dropwise. The resulting mixture was allowed to warm slowly to room temperature and stirred for an additional 2 hrs. A small amount of ethanol was added to destroy any excess phosphide, and the solvent was removed under vacuum on a rotary evaporator. The solid residue was treated with water and then chloroform. The two liquid layers were separated, the water layer was washed twice with chloroform and the combined organic fractions were dried overnight over anhydrous sodium sulphate. The chloroform solution was filtered, and the solvent was removed under vacuum on a rotary evaporator. The infrared spectrum of the white solid showed a weak band at 2280 cm^{-1}, which was assigned to the P–H stretching frequency. This crude material was washed with ether, filtered and dried; the resulting white, air-sensitive solid showed no evidence of the P–H moiety (*vide infrared*).

The white solid obtained above was mixed with sulfur in benzene to give an essentially quantitative yield of the trisulphide of bis(2-diphenylphosphinoethyl)phenylphosphine. The latter compound was obtained as a powdery, white solid which was washed with hot ethanol, filtered, and dried *in vacuo* (m.p. 226-8°C, uncorr.).

Infrared spectra of the triphosphine and of its trisulphide were similar except for a three component band (620, 607, and 600 cm^{-1}) in the $P=S$ stretching region of the latter compound. A pmr spectrum of the trisulphide showed two unresolved multiplets centered at τ 7.67 (methylene protons) and τ 2.50 (phenyl protons). The integrated intensity ratio of the phenyl protons to the methylene protons was 24.8 to 8, in excellent agreement with the theoretical value of 25 to 8.

Preparation of the Complexes. Both types of complexes, $Ni(DPP)X_2$ and $[Ni(DPP)X]B(C_6H_5)_4$, except where $X=CN^-$, were prepared by a general procedure; the specific case of $X=I^-$ is described in detail below.

$Ni(DPP)I_2$. A chloroform solution of 0.30 g (0.56 mmole) of bis(2-diphenylphosphinoethyl)phenylphosphine was added to 0.18 g (0.56 mmole) of anhydrous nickel(II) iodide in ethanol. The deep purple solution was stirred for 1 hr at room temperature, the solvent was removed on a rotary evaporator, and the

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(11) *Caution*: 2-chloroethyldiphenylphosphine is closely related to the nitrogen mustards. Its toxic properties have been described.[12]

(12) R.F. Struck and Y.F. Shealy, *J. Med. Chem.*, 9, 414 (1966).

(13) J.C. Cloyd, Jr., and D.W. Meek, unpublished data (1969).

(14) R.B. King and P.N. Kapoor, *J. Am. Chem. Soc.*, *91*, 5191 (1969).

(15) T.D. DuBois and D.W. Meek, *Inorg. Chem.*, *8*, 146 (1969).

(16) K. Issleib and D. Jacob, *Chem. Ber.*, *94*, 187 (1961).

(17) F. Pass and H. Schindlbauer, *Monatsch. Chem.*, *90*, 148 (1959).

(18) K. Issleib and Mobius, *Chem. Ber.*, *94*, 102 (1961).

residue was dissolved in dichloromethane and filtered. An equal volume of ethanol was added to the filtrate and the dichloromethane was allowed to evaporate slowly. Deep purple, pyramidal crystals separated; these crystals were collected on a filter, washed with ether and dried *in vacuo*. The complex analyzed for the solvate, Ni(DPP)$I_2 \cdot \frac{1}{2}CH_2Cl_2$.

The colors and recrystallization procedures for the other complexes are described below. The yields of the recrystallized complexes varied from 50 to 70%.

Ni(DPP)Cl_2. An equal volume of t-butylchloride was added to the dichloromethane solution of the complex; the dichloromethane subsequently evaporated slowly and red-brown needles separated.

Ni(DPP)Br_2. The complex was dissolved in ethanol and the volume of the solution was reduced to 5 ml. This concentrated solution was kept at –10°C for 3 days; red-brown needles separated.

Ni(DPP)$(NCS)_2$. This complex was dissolved in ethanol, and then the solution was gradually concentrated by heating it on a hotplate. Deep, red crystals were deposited and collected.

Ni(DPP)$(CN)_2$. To Ni(DPP)I_2, prepared as described above, was added two equivalents of potassium cyanide in methanol. The color of the solution changed immediately from deep purple to pastel red. The solvent was removed under vacuum and the red solid was dissolved in dichloromethane and filtered. To this solution was added 10 ml of dimethylformamide and the dichloromethane was evaporated by warming the solution on a hot plate. The DMF was removed slowly under vacuum until the volume of the solution was approximately 1 ml, where red needle-shaped crystals precipitated. These crystals were collected on a filter, washed with ether and dried *in vacuo*.

The [Ni(DPP)X]$B(C_6H_5)_4$ complexes were prepared by adding one equivalent of sodium tetraphenylborate to ethanol solutions of the Ni(DPP)X_2 complexes described above. The solvent was removed *in vacuo* and the solid was dissolved in dichloromethane. The resulting solutions were filtered and crystals were obtained as described below.

[Ni(DPP)X]$B(C_6H_5)_4$; X = I^- and Br^-. To the dichloromethane solution of the complex was added 25 ml of ethanol. The volume of the solution was reduced to 20 ml by warming it on a hotplate and on cooling, red (I^-) or orange (Br^-) needles separated; these were collected and dried *in vacuo*.

[Ni(DPP)X]$B(C_6H_5)_4$; X = Cl^- and SCN^-. An equal volume of t-butylchloride was added to the dichloromethane solution. The dichloromethane was allowed to evaporate slowly and orange platelets (Cl^- and SCN^-) were deposited.

[$Ni_2(DPP)_2(CN)_3$]$B(C_6H_5)_4$. Equimolar amounts of [Ni(DPP)$(CN)_2$] and $NaB(C_6H_5)_4$ were combined in ethanol. Concentrating the volume of the solution resulted in the precipitation of feathery red crystals. These were collected and recrystallized from ethanol.

[Pd(DPP)I]I. Palladium(II) chloride (0.99 g, 0.560 mmole) and LiCl (0.0476 g, 1.12 mmole) were dissolved in ethanol (30 ml) at room temperature. To this solution was added NaI (0.42 g, 2.8 mmole) in ethanol (20 ml). The resultant deeply colored solution was stirred as DPP (0.300 g, 0.560 mmole) in chloroform (20 ml) was added. The resulting yellow solution was concentrated nearly to dryness *in vacuo*, the residue was dissolved in dichloromethane (20 ml), and the solution was filtered. Ethanol (20 ml) was added and the volume was reduced to 10 ml. The flask was stoppered and kept at –10° for two days. Orange needles crystallized at –10° over a two-day period; these were collected and recrystallized from 5 ml of cold (–10°) ethanol (yield, 0.25 g, 50%).

Spectral, Conductance, and Magnetic Measurements. These were obtained as described previously.[19] Solid state electronic spectra at 77°K were obtained as Nujol mulls immersed in liquid nitrogen in a quartz dewar.

Results and Discussion

The Ligand Bis(diphenylphosphinoethyl)phenylphosphine. A synthesis of the ligand bis(diphenylphosphinoethyl)phenylphosphine (abbreviated DPP) in 16% yield was first reported by Hewertson and Watson;[10] a different synthesis was reported recently by King and Kapoor.[14] Our synthetic route, which differs from the two cited above, was developed concurrently with that of King and Kapoor and gives comparable yields of ~80%. Both methods are far superior to the route used by Hewertson and Watson[10]

The three steps in our synthesis are illustrated in Equations 1-3. The 2-chloroethyldiphenylphosphine produced in the first step has been reported previously,[12] but it was isolated in only a 2% yield after distillation. The low yield may have resulted from the self-quaternization of the phosphine at the temperature required for distillation. In order to minimize formation of 1,2-bis(diphenylphosphino)ethane, we employed a large excess of 1,2-dichloroethane, and the potassium diphenylphosphide was added very slowly with vigorous stirring. A slight excess of C_6H_5PHNa was always employed in the second step to favor the complete reaction of 2-chloroethyldiphenylphosphine. Phenylphosphine was added to the sodium liquid ammonia solution until a golden yellow color persisted, indicating that all the sodium had reacted to form C_6H_5PHNa. Addition of ethanol at the end of the reaction converted the excess C_6H_5PHNa to $C_6H_5PH_2$. The boiling point of phenylphosphine is approximately 25° at 0.3 torr and the excess $C_6H_5PH_2$ is removed conveniently *via* vacuum distillation after the reaction is completed. The secondary-tertiary-diphosphine $(C_6H_5)_2PCH_2CH_2PHC_6H_5$ reacts with butyllithium in THF at 0°C to give $(C_6H_5)_2PCH_2CH_2P(Li)C_6H_5$. The white solid that was isolated after the last step of the synthesis always contained an impurity that was indicated by an absorption in the P–H stretching region of the infrared spectrum. By washing the solid quickly with ether one

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(19) T.D. DuBois and D. W. Meek, *Inorg. Chem.*, *6*, 1395 (1967).

Table I. Analytical and Conductance Data on the DPP Complexes.

Compound [a]	Color	Λ_M [b]	Analyses %C Calcd.	Found	%H Calcd.	Found	% Halogen Calcd.	Found
$Ni(DPP)Cl_2$	Red	120	61.48	61.41	5.01	5.12	10.68	10.90
$Ni(DPP)Br_2$	Red	126	54.23	54.05	4.42	4.37	21.22	21.45
$Ni(DPP)I_2 \cdot 0.5CH_2Cl_2$	Purple	119	46.58	46.42	3.85	3.75	28.53	28.32 [c]
$Ni(DPP)(NCS)_2$	Red	123	60.95	60.72	4.69	4.54	3.95	3.80 [d]
$Ni(DPP)(CN)_2$	Red	1.90	67.01	67.02	5.15	4.91	4.34	4.29 [d]
$[Ni(DPP)Cl]B(C_6H_5)_4$	Orange	94.2	73.49	73.31	5.64	5.49	3.74	4.01
$[Ni(DPP)Br]B(C_6H_5)_4$	Orange	97.0	70.20	70.21	5.38	5.38	8.05	8.31
$[Ni(DPP)I]B(C_6H_5)_4$	Red	111	67.02	66.88	5.14	5.00	12.21	12.22
$[Ni(DPP)NCS]B(C_6H_5)_4$	Orange	91.6	73.01	73.09	5.50	5.54	3.30	3.56 [e]
$[Ni_2(DPP)_2(CN)_3]B(C_6H_5)_4$	Red	93.0	72.04	71.01	5.47	5.37	2.65	2.55 [d,f]
$Pd(DPP)I_2$	Red	130	45.64	45.75	3.72	3.51	28.36	28.33
$DPPS_3$	White	—	64.74	64.67	5.27	5.30	15.25	15.51 [e]

[a] DPP is the ligand bis(2-diphenylphosphinoethyl)phenylphosphine, $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$. [b] Molar conductance values (cm²/ohm-mole) on freshly prepared ~$10^{-3}M$ solutions in acetonitrile. Uni-univalent electrolytes in this solvent exhibit conductance values in the range 140-160 cm²/ohm-mole.[20] [c] Total halogen. [d] Nitrogen analysis. [e] Sulfur analysis. [f] Phosphorus analysis; Calcd., 11.73; Found, 11.40.

Table II. Electronic Spectral Data on the DPP Complexes.

Complex	Solution In Acetonitrile cm⁻¹ (ε_{max})	In Dichloromethane cm⁻¹ (ε_{max})	Solid State At ~298°K cm⁻¹	At 77°K cm⁻¹
$Ni(DPP)I_2 \cdot 0.5CH_2Cl_2$	22,350 (1860) [a,b] 35,090 (22,020) 40,820 (34,860)	15,700 (288) 21,300 (1840) 28,600 (7660) 34,500 (27,930)	15,380S 20,200 27,800	15,200 20,650 28,200
$Ni(DPP)Br_2$	23,530 (2970) 35,090 (21,030)	16,700S[c] (183) 23,150 (3070) 35,100 (18,810)	17,200S 22,900 28,600	18,500 23,100 27,800
$Ni(DPP)Cl_2$	24,100 (3450)	16,700S (100) 23,800 (3410) 34,850 (17,400)	18,180S 23,530 27,780	18,700 23,800 27,800
$Ni(DPP)(NCS)_2$	24,550 (4220) 35,700 (24,270)	18,200S (325) 23,800 (3950) 35,700 (19,740)	22,450B 29,400	19,200S 22,750 29,600
$Ni(DPP)(CN)_2$	24,400 (1850) 32,300S (7600) 40,000S (23,600)	24,400 (1830) 32,300S (7000) 40,000S (23,000)	26,600B 30,800	22,750 29,600
$[Ni_2(DPP)_2(CN)_3]B(C_6H_5)_4$	25,6000S (4120) 37,740 (43,790)	23,550 (4600) 31,250S (10,700) 37,050 (40.640)	22,800B	23,100 31,800
$[Ni(DPP)I]B(C_6H_5)_4$	23,530 (2430) 34,780 (22,770)			
$[Ni(DPP)Br]B(C_6H_5)_4$	23,700 (3200) 35,090 (20,880)			
$[Ni(DPP)Cl]B(C_6H_5)_4$	24,100 (3550)			
$[Ni(DPP)NCS]B(C_6H_5)_4$	24,690 (4020) 36,040 (23,040)			
$Pd(DPP)I_2$	25,650S (2800) 28,600 (3600) 35,350 (23,00)			

[a] Calculated on the basis of the unsolvated species. [b] Molar absorptivity given in parentheses. [c] S, shoulder on a more intense absorption. [d] B, a broad band.

can remove the impurity and obtain the triphosphine,

The Nickel(II) Complexes. Mixing equimolar amounts of nickel(II) salts with the ligand DPP produces deeply colored solutions from which the complexes $Ni(DPP)X_2$ may be isolated. In general, these compounds have high solubility in common organic solvents (e.g., ethanol, dichloromethane). The iodide and thiocyanate complexes may be crystallized conveniently from ethanol solutions at room temperature, but isolation of the bromide complex requires a cold (−10°), concentrated ethanol solution. The chloride complex was isolated from a solvent mixture of dichloromethane and t-butylchloride. A pure cyanide complex was isolated only from a concentrated DMF solution.

When ethanol solutions of $NaB(C_6H_5)_4$ and $Ni(DPP)X_2$ (except X = CN) are combined, the original color of the solutions become somewhat less intense, and the complexes $[Ni(DPP)X]B(C_6H_5)_4$ are obtained (Table I). In the case of the cyanide complex, $Ni(DPP)(CN)_2$ the analytical data for the red crystals that were isolated from the reaction with sodium tetraphenylborate suggest a dinuclear formulation, $[Ni_2(DPP)_2(CN)_3]B(C_6H_5)_4$.

Both series of complexes $[Ni(DPP)X_2]$ and $[Ni(DPP)X]B(C_6H_5)_4$ are diamagnetic and exhibit conductance values typical of uni-univalent electrolytes in acetonitrile solutions (Table I). The low conductance values for $[Ni(DPP)X]X$ (Table I) can be attributed to the relatively low specific conductance of the large cation $[Ni(DPP)X]^+$.[20] The values are even lower for the $[Ni(DPP)X]B(C_6H_5)_4$ complexes, which is consistent with the presence of two relatively immobile ions, $[Ni(DPP)X]^+$ and $B(C_6H_5)_4^-$. The electronic absorption spectra of the $Ni(DPP)X_2$ and the $[Ni(DPP)X]B(C_6H_5)_4$ complexes in acetonitrile are essentially identical (Table II, Figure 1) and indicate a four-coördinate nickel(II) in a planar environment. The energy value of the single, intense absorption compares favorably to other four-coordinate nickel(II) complexes containing similar sets of donors.[21]

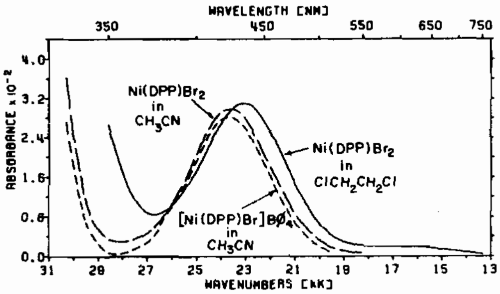

Figure 1. Solution electronic spectra of $[Ni(DPP)Br_2]$ in $ClCH_2CH_2Cl$ (———) and CH_3CN (— —); $[Ni(DPP)Br]B(C_6H_5)_4$ in CH_3CN (- - - -).

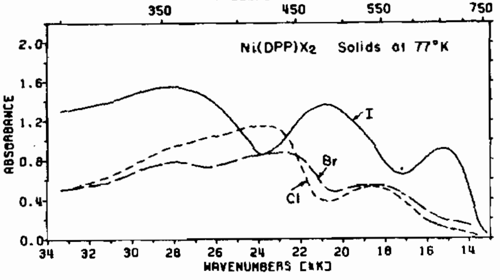

Figure 2. Solid state electronic spectra of $[Ni(DPP)X_2]$ as Nujol mulls at 77°K; X=I (———); X=Br (— —), X=Cl (- - - -). The absorbance scale is arbitrary.

The $[Ni(DPP)X]^+$ cation has approximately C_{2v} microsymmetry, and the electronic absorption band may be assigned to the orbitally allowed transition $^1A_1 \rightarrow {}^1A_1(d_{z^2} \rightarrow d_{x^2-y^2})$.

In less polar solvents, such as 1,2-dichloroethane and dichloromethane (Table II), the electronic spectra of the $Ni(DPP)X_2$ complexes differ somewhat from those obtained in acetonitrile solutions (Figure 1). An intense band is present above 20,000 cm^{-1}, but shifted slightly to lower energies as compared to the absorption of the corresponding complex in acetonitrile; also, a much weaker band is observed between 15,000 cm^{-1} and 20,000 cm^{-1} (Table II, Figure 1). In the solid state (Nujol mulls) at room temperature (Table II and Figure 2), the spectral features are comparable to those observed in the non-polar solvents. On the other hand, the solid state spectra at 77°K show two distinct maxima (Figure 2).

In the solid state the electronic spectral features of these $Ni(DPP)X_2$ complexes closely resemble those of the known square-pyramidal $[Ni(diars)(triars)]^{2+}$ [22] and $Ni(dap)(CN)_2$ (dap = $C_6H_5P[CH_2CH_2CH_2As(CH_3)_2]_2$ [23] complexes. Assuming two coordinated halides, the $Ni(DPP)X_2$ complexes would posses C_s microsymmetry, thus there would be four spin-allowed transitions, $^1A' \rightarrow {}^1A'(d_{z^2} \rightarrow d_{x^2-y^2})$, $^1A' \rightarrow {}^1A''(d_{xz} \rightarrow d_{x^2-y^2})$, $^1A' \rightarrow {}^1A''(d_{yz} \rightarrow d_{x^2-y^2})$, and $^1A' \rightarrow {}^1A'(d_{xy} \rightarrow d_{x^2-y^2})$. Two of these transitions ($d_{z^2} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow {}_{x^2-y^2}$) are also orbitally allowed and would be expected to give the two most intense electronic absorptions. Addition of a fifth ligand to the planar $[Ni(DPP)X]^+$ cations would affect the relative energy of the d_{z^2} orbital more than any other 3*d*-orbital. The destablization of the d_{z^2} orbital is shown in Figure 3, and the qualitative diagram of d-orbital energy levels may be used to assign the single band in the four-coordinate $[Ni(DPP)X]^+$ and the two bands in the five-cordinate $Ni(DPP)X_2$ complexes. The E_{max} values for the two transitions span comparable energy values for the splitting of the d-orbitals in the complexes $[Ni(diars)_2X]^+$.[22] Taking into account that 6-member chelate rings would exert a smaller ligand field than analogous 5-member chelates,[24] the donor set in $Ni(DPP)X_2$ should be com-

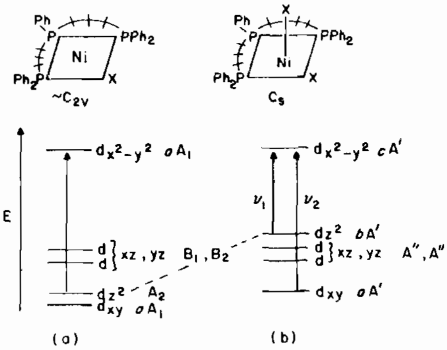

Figure 3. d-orbital energy levels for the (a) four-coordinate C_{2v} $[Ni(DPP)X]^+$ and for the (b) five-coordinate C_s $[Ni(DPP)X_2]$ complexes.

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Table III. Electronic Spectral (cm^{-1}) and Conductance Values of Solutions of $Ni(DPP)X_2$ Plus Excess $C_6H_5P(CH_3)_2$

X	E_{max} for $Ni(DPP)X_2$	E_{max} for $Ni(DPP)X_2 + C_6H_5P(CH_3)_2$ [a]	E_{max} for $Ni[C_6H_5P(CH_3)_2]_3X_2$ [b]	Λ_M [c] cm^2/ohm-mole
Cl	23,800 (3410)	19,500 (1000)	15,050 (482) 22,750S	131
Br	23,150 (3070)	19,200 (1250)	15,150 (950) 20,700 (554)	164
I	21,300 (1840)	18,700 (1650)	15,400 (1085) 22,200	146

[a] The ratio of $C_6H_5P(CH_3)_2/Ni(DPP)X_2$ is ~100 for the iodide and bromide, and ~10 for the chloride. [b] Data taken from reference 25. [c] The molar conductance values are given for freshly prepared ~$10^{-3}M$ acetonitrile solutions, where ion-pairing would be minimized. In order to correlate the conductance data obtained in acetonitrile with the concentration dependent spectral data obtained in dichloromethane, the spectra were obtained on the acetonitrile solutions also. Essentially the same spectral data were observed in both dichloromethane and acetonitrile.

parable to that in $[Ni(diars)_2X]^+$, even though the ligand DPP contains three phosphorus donors and forms two chelate rings.

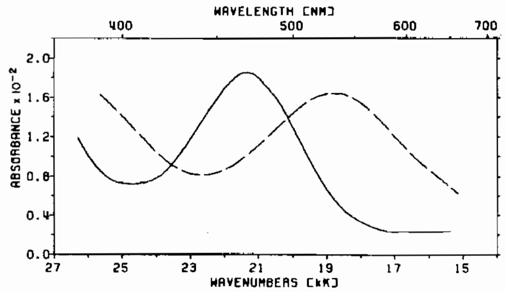

Figure 4. Solution (CH_2Cl_2) electronic spectra of $[Ni(DPP)I_2]$ (———) and $[Ni(DPP)I_2]$ plus ~100-fold molar excess of $C_6H_5P(CH_3)_2$ (— — —).

The $[Ni(DPP)(CN)_2]$ complex is diamagnetic and a non-conductor in acetonitrile. The electronic spectra in acetonitrile and in the solid state are essentially identical and are indicative of low-spin, square-pyramidal nickel(II). In the C≡N stretching region of the infrared spectrum, the cyanide complex has two sharp absorptions at 2110 and 2100 cm^{-1} (Nujol mulls; in dichloromethane solution the peaks occur at 2120 and 2113 cm^{-1}), which is consistent with a square-pyramidal structure and one apical cyanide. The fact that $Ni(DPP)(CN)_2$ is a monomeric non-conductor and remains pentacoordinate in acetonitrile further attests to the strong tendency of cyanide to promote five-coordination in nickel-phosphine complexes.[25]

In an attempt to prepare the planar complex $[Ni(DPP)CN]B(C_6H_5)_4$, a red, crystalline compound was isolated that had elemental analyses consistent with the dinuclear formulation $[Ni_2(DPP)_2(CN)_3]B(C_6H_5)_4$. This complex is diamagnetic and a uni-univalent electrolyte in acetonitrile. The infrared CN stretching frequency (Nujol mull) occurs at 2100 cm^{-1} (weak); in dichloromethane solution this absorption occurs at 2121 cm^{-1}. The visible electronic spectra in solution (acetonitrile and dichloromethane) and the solid state (Nujol mulls at ~300°K and 77°K) do not differ significantly from the corresponding spectra of $[Ni(DPP)(CN)_2]$. It is concluded that the cation in $[Ni_2(DPP)_2(CN)_3]B(C_6H_5)_4$ probably possesses a dinuclear, pentacoordinate structure, but the exact nature of this complex cannot be determined unambiguously from these data.

The infrared spectrum (Nujol mull) of $[Ni(DPP)(NCS)_2]$ in the C≡N stretching region exhibits two strong absorptions at 2070 cm^{-1} and 2100 cm^{-1}. In acetonitrile solution the positions and integrated absorption values (A) are 2086 cm^{-1} ($A = 1.99 \times 10^4$ M^{-1} cm^{-2}) and 2086 cm^{-1} ($A = 7.22 \times 10^4 M^{-1}$ cm^{-2}), indicative of ionic and N-bonded thiocyanate, respectively. The solid state electronic spectra of this compound at 77°K exhibits a maximum at 22,750 cm^{-1} with a shoulder at 19,200 cm^{-1} The electronic spectra, along with the infrared data indicate that the thiocyanate complex exhibits the smallest tendency of all the $[Ni(DPP)X_2]$ complexes to become pentacoordinate.

The $Pd(DPP)I_2$ complex is diamagnetic, a uni-univalent electrolyte in acetonitrile, and exhibits electronic spectra consistent with four-coordinate, planar palladium(II). The four-cordinate Pd^{II} complexes with DPP would be expected on the basis that the Ni^{II} complexes (except for the cyanide) tended to ionize in solution to give the four-coordinate $[Ni(DPP)X]^+$ ions. Also, the higher ligand fields exhibited by palladium and by four-coordinate complexes as compared to analogous five-coordinate complexes makes the four-coordinate species $[Pd(DPP)I]I$ preferred over the pentacoordinate $Pd(DPP)I_2$ complex.

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