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The Synthesis and the Coordination Characteristics of (Phosphinoamino)pyridines

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The new polydentate ligands 2-(diphenylphosphinoamino)pyridine (PAP), 2-(diphenylphosphinoamino)-4-methylpyridine (4PAP), and 2-(diphenylphosphinoamino)-6-methylpyridine (6PAP) and their thio and seleno derivatives have been synthesized and characterized. Coordination complexes of 4PAP and 6PAP have been isolated, *viz.*, (a) 1:1 metal–ligand complexes $MLCl_2$: (i) M = Co(II), Ni(II), Hg(II), Pd(II), L = 4PAP; (ii) M = Co(II), Ni(II), Pd(II), L = 6PAP; (b) 1:2 metal–ligand complexes, $ML_2X_2 \cdot nH_2O$: $Co(4PAP)_2Cl_2$, $Ni(4PAP)_2Cl_2 \cdot 2H_2O$, $[Ni(4PAP)_2](ClO_4)_2 \cdot 2H_2O$, $Hg(4PAP)Cl_2$, $Ag(4PAP)_2NO_3$, $[Ni(6PAP)_2](ClO_4)_2$; (c) $[Ni(4PAP)_2X](ClO_4)$, X = Cl, Br; (d) 1:3 metal–ligand complexes ML_3X_2: $[Ni(4PAP)_3](ClO_4)_2$. Physicochemical studies, including the measurement of conductivity, magnetic moment, solution molecular weight, and infrared, visible, and nuclear magnetic resonance absorption spectra, were performed on the complexes of Co(II) and Ni(II); their structures are discussed.

Coordination compounds based on an extremely wide variety of multidentate ligands have been reported in the recent literature; by far the greatest number of such ligands is based upon a skeleton of carbon atoms, bearing combinations of the donor atoms of groups V and VI. Variations in the structural features of the molecular skeleton of the ligand and in the "hard" or "soft" character[1] of the donor atoms provide a range of complexing and stereochemical characteristics. Thus, amino,[2] phosphino,[3] arseno,[4] thioether,[5] and seleno[6] donor sites and mixed combinations of these sites[3b,7–9] are to be found within flexible aliphatic polymethylene frameworks, as well as within relatively rigid *o*-phenylene derivatives.[10–16] Many Schiff base "mixed-donor" systems, also containing the atoms N, O, P, As, and S, have proven effective as chelating agents.[17] Ciampolini[18] and others have reviewed the physical data, particularly electronic spectra and magnetic data, pertaining to such complexes.

The contrasting smaller number of inorganic multidentate ligands is represented by hydrazines,[19] aminophosphines,[20] aminophosphine sulfides,[21] phosphonitrilic halides,[22] hydrazinophosphines,[23] hydrazinophosphine sulfides,[23b,c] thio-[24] and selenophosphates,[25] thio-[26] and selenoureas,[27] and organosilyl- and organostannylphosphines and -arsines.[28]

In this paper we describe the synthesis of a number of phosphinoaminopyridines (Figure 1, I–III) and their coordination complexes. Earlier work with *N*,*N*-

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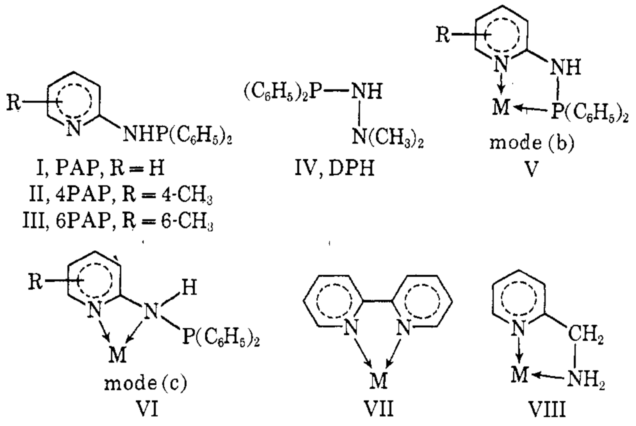

Figure 1.

dimethyl-*N*′-diphenylphosphinohydrazine[23c] (DPH, Figure 1, IV) showed that this system, based on a P–N–N skeleton, acts mostly as a unidentate ligand, with the phosphorus atom as the preferred donor site; in only two cases, Pd(DPH)Cl_2 and [Pd$(DPH)_2$Cl]ClO_4, was bidentate functionality observed, giving strained, four-membered, cyclic systems. The phosphinoaminopyridines, containing a P–N–C–N skeleton, may function (a) as unidentate ligands, using only one of the three basic centers, (b) as bidentate mixed ligands, using the P and the pyridine N atoms, or (c) as bidentate ligands, using the two N atoms (Figure 1, V and VI). Mode (b) would utilize the more basic pyridine nitrogen and phosphorus centers to establish five-membered rings, an advantage over DPH, where chelation is restricted to four-membered rings, and over (c), where a strained four-membered ring, utilizing the least basic NH site, is also required. In theory, the differing functionalities of the ligands may be distinguished by ir and nmr spectroscopy, since coordination by an NH or NH_2 group results in a change of ν(N–H) to longer wavelength[29] and a deshielding of the NH protons, relative to the uncoordinated situation.

Experimental Section

Materials.—2-Aminopyridine, 2-amino-4-methylpyridine, 2-amino-6-methylpyridine (Aldrich), diphenylchlorophosphine (K & K), potassium selenocyanate (Alfa), and sulfur were reagent grade chemicals and were used without further purification. Solvents were dried and distilled before use.

Physicochemical Measurements.—Electrical conductivities were measured at 25°, using a Radiometer (Copenhagen) conductivity meter, Type CDM2d, and a cell fitted with polished platinum electrodes. Magnetic moments were determined by the Faraday method. Visible and near-infrared absorption spectra were recorded with a Cary spectrophotometer, Model 14; infrared measurments were obtained with a Perkin-Elmer 457 instrument. Molecular weight measurements were determined using a Hitachi Perkin-Elmer osmometer, Model 115, and proton magnetic resonance data (pmr) with a Varian A-56/60 instrument.

Synthesis of Ligands. (a) **Preparation of 2-(Diphenylphosphinoamino)pyridine and Its 4-Methylpyridine and 6-Methylpyridine Analogs.**—To a stirred solution of 2-aminopyridine (0.2 mol) in dry benzene (50 ml), cooled to 0° and protected by an atmosphere of N_2, was added a benzene solution (20 ml) of diphenylchlorophosphine (0.1 mol), over a period of 30 min. After warming the mixture to room temperature for 15 min, the aminopyridine hydrochloride salt was filtered off, and the solvent was removed from the filtrate to yield crude 2-(diphenylphosphinoamino)pyridine, which was recrystallized from a hexane–benzene mixture.

2-(Diphenylphosphinoamino)-4-methylpyridine and 2-(diphenylphosphinoamino)-6-methylpyridine were prepared in a similar way, using 2-amino-4-methylpyridine and 2-amino-6-methylpyridine as bases. Yields were 75–80%; properties and analytical data are given in Table I, and pmr data, in Table II. Infrared spectra (in cm^{-1}; obtained using Nujol mulls): (i) 2-(diphenylphosphinoamino)pyridine: 3130 (b, m), 1597 (s), 1568 (s), 1303 (s), 1276 (w), 1152 (m), 1098 (m), 1051 (w), 1023 (w), 990 (m), 918 (s), 851 (w), 790 (w), 772 (s), 740 (m), 720 (m), 700 (s); (ii) 2-(diphenylphosphinoamino)-4-methylpyridine: 3110 (s), 1900 (w), 1820 (w), 1600 (s), 1560 (s), 1309 (m), 1275 (m), 1175 (s), 1122 (vw), 1098 (m), 1070 (w), 1037 (m), 1015 (w), 1000 (sh), 990 (w), 960 (m), 922 (w), 890 (sh), 868 (s), 858 (sh), 850 (sh), 810 (s), 770 (w), 758 (m), 740 (s), 725 (sh), 700 (s), 675 (w); (iii) 2-(diphenylphosphinoamino)-6-methylpyridine: 3260 (b, w), 1660 (w, b), 1580 (s, b), 1300 (m), 1200 (s), 1160 (w), 1122 (m), 1110 (sh), 1090 (sh), 1020 (w, b), 990 (w), 950 (w, b), 895 (m), 840 (w), 798 (s), 755 (m), 730 (s), 720 (s), 700 (s).

(b) **Preparation of 2-(Diphenylthiophosphinatoamino)pyridine and Its 4-Methylpyridine and 6-Methylpyridine Analogs.**—A mixture of the appropriate phosphinoaminopyridine and sulfur, in a 1:1 molar ratio, in benzene solution was heated under reflux until all the sulfur had dissolved. The oxidized product, obtained by evaporating the benzene, was recrystallized from a hexane–benzene solvent mixture. Yields were 70–80%; properties and analytical data are given in Table I. Ir spectra: (i) 2-(diphenylthiophosphinatoamino)pyridine: 1655 (w, b), 1598 (s), 1570 (m), 1300 (s), 1280 (w), 1210 (v, w), 1180 (v, w), 1150 (m), 1120 (w), 1104 (s), 1050 (w, b), 1022 (w), 995 (s), 970 (w), 950 (s), 935 (s), 860 (w), 805 (w), 780 (s), 774 (sh), 751 (sh), 751 (s), 743 (m); (ii) 2-(diphenylthiophosphinatoamino)-4-methylpyridine: 3090 (s), 1910 (w), 1828 (w), 1610 (s), 1570 (m), 1309 (s), 1270 (w), 1260 (s), 1240 (w), 1215 (w), 1190 (s), 1165 (w), 1109 (s), 1040 (m), 1020 (w), 995 (m), 960 (s), 930 (w), 882 (s), 854 (m), 812 (s), 770 (m), 760 (w), 748 (s), 725 (s), 715 (sh), 692 (s), 640 (s), 618 (m); (iii) 2-(diphenylthiophosphinatoamino)-6-methylpyridine: 3160 (m, b), 1650 (w, b), 1570 (s, b), 1298 (s), 1230 (w), 1153 (w), 1117 (w), 1100 (s), 1090 (sh), 1020 (m, b), 990 (w), 950 (w), 850 (s), 778 (s), 750 (m), 730 (sh), 720 (s), 705 (w), 690 (m), 633 (s).

(c) **Preparation of 2-(Diphenylselenophosphinatoamino)pyridine and Its 4-Methylpyridine and 6-Methylpyridine Analogs.**—Using the procedure of Nicpon and Meek,[30] a stirred solution of the appropriate phosphinoaminopyridine (about 0.01 mol) in warm acetonitrile (20 ml) was treated with a warm solution of potassium selenocyanate (0.01 mol) in the same solvent (20 ml). A white precipitate of potassium cyanide was formed. After 15 min the solution was filtered, and the filtrate was evaporated to dryness. The residue was washed with distilled water and ether and dried. Yields were 60–70% (see Table I). Ir spectra: (i) 2-(diphenylselenophosphinatoamino)pyridine: 1598 (m), 1575 (m), 1300 (s), 1270 (w), 1180 (vw), 1150 (m), 1102 (s), 1050 (w, b), 1022 (w), 993 (s), 950 (s), 938 (s), 800 (w), 780 (s), 772 (sh), 750 (s), 740 (m), 733 (w), 710 (m), 700 (m), 680 (s), 545 (s); (ii) 2-(diphenylselenophosphinatoamino)-4-methylpyridine: 3080 (s, b), 1925 (w), 1820 (w), 1610 (s), 1500 (s), 1309 (s), 1278 (w), 1245 (w), 1183 (s), 1107 (s), 1032 (m), 1020 (m), 1000 (m), 960 (s), 930 (w), 875 (s), 860 (w), 850 (w), 809 (s), 755 (s), 749 (s), 715 (s), 705 (m), 695 (m), 620 (m), 542 (s); (iii) 2-(diphenylselenophosphinatoamino)-6-methylpyridine: 1590 (sh), 1570 (s), 1298 (s), 1238 (m), 1175 (w), 1155 (w), 1117

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TABLE I

PROPERTIES AND ANALYTICAL DATA FOR DERIVATIVES OF AMINOPYRIDINES

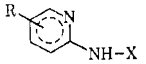
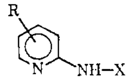
		Analytical data, %					
		C		H		N	
	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found
R = H; X = $(C_6H_5)_2P$–, PAP	125–129	73.4	73.2	5.44	5.48	10.1	9.90
R = H; X = $(C_6H_5)_2P(S)$–	125	65.8	64.7	4.88	4.90	9.03	9.00
R = H; X = $(C_6H_5)_2P(Se)$–	147	57.2	56.2	4.24	4.30	7.84	7.80
R = 4-CH_3; X = $(C_6H_5)_2P$–, 4PAP	132	73.9	73.6	5.87	5.70	9.58	9.10
R = 4-CH_3; X = $(C_6H_5)_2P(S)$–	137	66.6	66.4	5.29	5.24	8.63	8.70
R = 4-CH_3; X = $(C_6H_5)_2P(Se)$–	148	58.2	58.1	4.62	4.70	7.56	7.62
R = 6-CH_3; X = $(C_6H_5)_2P$–, 6PAP	108	73.9	73.3	5.87	5.82	9.58	9.45
R = 6-CH_3; X = $(C_6H_5)_2P(S)$–	136	66.6	65.9	5.29	5.20	8.63	8.64
R = 6-CH_3; X = $(C_6H_5)_2P(Se)$–	153	58.2	58.2	4.62	4.62	7.56	7.58

TABLE II

PROTON MAGNETIC RESONANCE DATA[a] FOR SUBSTITUTED AMINOPYRIDINES

	NH or NH_2	CH_3
R = H; X = H	5.25	...
R = H; X = $P(C_6H_5)_2$	4.15	...
R = H; X = $P(S)(C_6H_5)_2$	...	...
R = H; X = $P(Se)(C_6H_5)_2$	...	...
R = 4-CH_3; X = H	5.62	7.80
R = 4-CH_3; X = $P(C_6H_5)_2$	4.65	7.80
R = 4-CH_3; X = $P(S)(C_6H_5)_2$	...	7.95
R = 4-CH_3; X = $P(Se)(C_6H_5)_2$	...	7.90
R = 6-CH_3; X = H	5.06	7.65
R = 6-CH_3; X = $P(C_6H_5)_2$	4.65	7.65
R = 6-CH_3; X = $P(S)(C_6H_5)_2$	...	7.75
R = 6-CH_3; X = $P(Se)(C_6H_5)_2$	...	7.75

[a] τ values, using solutions in $CDCl_3$, with $Si(CH_3)_4$ as internal standard.

(w), 1100 (s), 1020 (m), 990 (m), 950 (w), 850 (s), 780 (s), 850 (s), 728 (m), 718 (sh), 705 (m), 697 (sh), 690 (m), 550 (s) (abbreviations: s, strong; w, weak; m, medium; sh, shoulder; b, broad; vw, very weak).

General Procedures for Preparation of Complexes. (a) **1:1 Metal Ligand Complexes, $MLCl_2$:** (i) **M = Ni(II), Co(II), Hg(II), Pd(II); L = 4PAP;** (ii) **M = Co(II), Ni(II), Pd(II); L = 6PAP.**—The ligand 4PAP (0.146 g) in solution in acetone (15 ml) was added with stirring to a solution of cobalt chloride (0.065 g) in 50:50 acetone–dimethoxypropane (10 ml). The mixture was heated, reduced in volume, and cooled; precipitation was effected by adding small quantities of ether. The product, $Co(4PAP)Cl_2$, was recrystallized from acetone or from a dichloromethane–ether solvent mixture; yield 70–80%.

Other members were prepared in a similar way, using appropriate metal chlorides and ligands in 1:1 molar ratios; for $Ni(4PAP)Cl_2$, the most satisfactory procedure involved the addition of a solution of ligand in dichloromethane to a 50:50 ethanol–dimethoxypropane solution of $NiCl_2 \cdot xH_2O$.

(b) **1:2 Metal–Ligand Complexes. $ML_2X_2 \cdot nH_2O$: $Co(4PAP)_2Cl_2$, $Ni(4PAP)_2Cl_2 \cdot 2H_2O$, $Ni(4PAP)_2(ClO_4)_2 \cdot 2H_2O$, $Hg(4PAP)_2Cl_2$, $Ag(4PAP)_2(NO_3)$, $Ni(6PAP)_2(ClO_4)_2$.**—The procedure was similar to that outlined above, except that the appropriate metal salt and ligand were mixed in a 1:2 molar ratio. The products were recrystallized from acetone or dichloromethane–ether mixtures, giving 60–70% yields, except for $Ni(6PAP)_2(ClO_4)_2$, where yields of only 20% were obtained.

(c) **$Ni(4PAP)_2X(ClO_4)$, X = Cl, Br.**—To a solution of $[Ni(4PAP)_2](ClO_4)_2 \cdot 2H_2O$ (0.219 g) in acetone (30 ml) was added sodium chloride (0.0147 g) dissolved in an acetone–water mixture. Solvent was removed under vacuum, giving solid $[Ni(4PAP)_2Cl](ClO_4)$, which was recrystallized from acetone or dichloromethane–ether mixture; yield 50–60%.

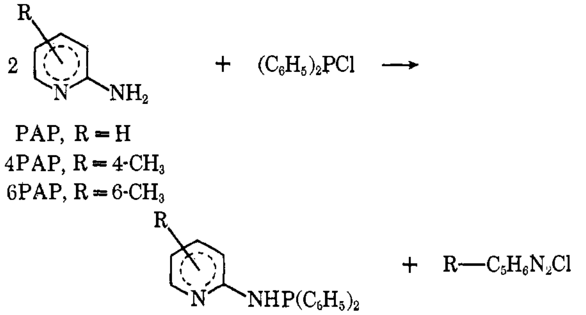
$[Ni(4PAP)_2Br](ClO_4)$ was prepared in a similar way, using sodium bromide and $[Ni(4PAP)_2](ClO_4)_2$ in a 1:1 molar ratio.

(d) **1:3 Metal–Ligand Complexes, ML_3X_2: $Ni(4PAP)_4(ClO_4)_2$.**—A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0·121 g) in acetone–dimethoxypropane (10 ml) was added to a solution of ligand 4PAP (0.292 g) in acetone (20 ml); the mixture was warmed, concentrated by vacuum evaporation, and treated with a small volume of ether to yield a mauve precipitate of $[Ni(4PAP)_3](ClO_4)_2$, which was recrystallized from an acetone–ether solvent pair; yield 70–75%.

Attempts to prepare 1:3 metal–ligand complexes with Co(II) and with the ligand 6PAP were unsuccessful.

Results and Discussion

The phosphinoaminopyridine ligands were synthesized according to



(1)

The reaction involves aminolysis of the P–Cl bond and salt formation between the basic aminopyridine (used in a 2:1 molar ratio with $(C_6H_5)_2PCl$) and the liberated HCl molecule. A possible rearrangement of the product according to

$$R'NHP(C_6H_5)_2 \longrightarrow R'N{=}P(H)(C_6H_5)_2 \quad (R' = RC_5H_3) \qquad (2)$$

is precluded on the basis of infrared and nmr evidence. Bands in the ν(N–H stretch) region were observed for 4PAP (3110 cm^{-1}) and for 6PAP (3260 cm^{-1}), while ν(P–H), in the 2200–2300-cm^{-1} region, was absent in all cases. Similarly, pmr spectra revealed the N–H protons, the shielding of the proton being less, as expected, in 4PAP and 6PAP (τ_{NH} 4.65) than in PAP itself (τ_{NH} 4.15) (see Table II). The phosphinoaminopyridines were further characterized by oxidation with sulfur to thiophosphinato derivatives and by reaction with potassium selenocyanate[30] to yield the corresponding selenophosphinato derivatives. The stretching vibrations ν(P=S) and ν(P=Se) were observed at 640[31] and at 540–550 cm^{-1},[30] respectively, comparable to the values in known compounds. Melting point data and

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TABLE III

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF COMPLEXES OF 2-(DIPHENYLPHOSPHINOAMINO)-4-METHYLPYRIDINE (4PAP) AND 2-(DIPHENYLPHOSPHINOAMINO)-6-METHYLPYRIDINE (6PAP)

				Analytical data,[b] %							
				C		H		N		M	
	Color	Conductivity[a]	ν(N–H), cm^{-1}	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Ni(4PAP)_3(ClO_4)_2$	Mauve	40	3140	57.1	56.8	4.53	4.61	7.40	7.44	5.17	5.14
$Ni(4PAP)_2(ClO_4)_2 \cdot 2H_2O$	Yellow	40	3170	49.2	48.7	4.12	4.30	6.38	6.50	6.69	6.54
$Ni(4PAP)_2Cl_2 \cdot 2H_2O$	Light blue	4 37[c]	3150	57.6	57.1	5.06	5.02	7.47	7.60	7.82	7.65
$Ni(4PAP)_2Cl_2 \cdot H_2O$	Pink	3	...	59.1	58.8	4.92	5.10	7.65	7.50	...	...
$[Ni(4PAP)_2Cl](ClO_4)$	Light blue	...	3180	55.6	54.8	4.36	4.39	7.19	7.17	7.54	7.50
$[Ni(4PAP)_2Br](ClO_4)$	Deep blue	31	3180	52.6	53.0	4.13	4.10	6.81	6.70	7.13	7.02
$Ni(4PAP)Cl_2$	Pink	Insol	...	51.1	51.6	4.02	4.67	6.63	6.62	...	...
$Ni(6PAP)_2(ClO_4)_2$	Orange-yellow	44	3200	51.3	51.1	3.99	4.10	6.65	6.69	6.97	6.90
$Ni(6PAP)Cl_2$	Green	Insol	3200	51.2	50.4	4.07	4.02	6.64	6.70	13.8	13.9
$Co(4PAP)_2Cl_2$	Brown	...	3150	60.5	59.1	4.76	4.70	7.84	7.80	8.26	8.15
$Co(4PAP)Cl_2 \cdot 1.5H_2O$	Green	3	3140	48.3	48.0	4.45	4.16	6.23	6.30	13.1	13.1
$Co(6PAP)_2(ClO_4)_2 \cdot 5H_2O$	Blue	...	...	46.0	46.4	4.72	4.75	6.01	6.20	6.32	6.42
$Co(6PAP)Cl_2$	Deep green	2	3230	51.2	50.1	4.02	4.21	6.63	6.65	13.9	13.8
$Pd(4PAP)Cl_2$	Salmon	2	3100	41.3	40.3	3.62	3.30	5.39	5.30	20.3	20.0
$Pd(6PAP)Cl_2 \cdot H_2O$	Yellow	2	3180	44.3	43.2	3.89	3.60	5.74	5.50	21.8	21.3
$Ag(4PAP)_2NO_3$	White	23	3140	57.3	57.4	4.50	4.70	9.28	9.19	14.3	14.1
$Hg(4PAP)Cl_2$	White	2	3140	38.3	38.0	3.05	3.20	4.97	4.91	...	...
$Hg(4PAP)_2Cl_2$	White	3	3070	50.5	50.7	4.01	4.00	6.55	6.43	...	...

[a] Conductivities (mhos cm^{-2} mol^{-1}) were measured on 10^{-3} *M* solutions in nitrobenzene. [b] Analyses were performed by F. Pascher, Mikroanalytisches Laboratorium, 53 Bonn, Germany. [c] Measured in solution in ethanol; a 10^{-3} *N* solution of $(C_2H_5)_4NClO_4$ in ethanol gives a value of 48. Typical conductivity values in nitrobenzene for 1:1 and 2:1 electrolytes are 33 and 40–60, respectively: J. R. Hall, M. R. Litzow, and R. A. Plowman, *Aust. J. Chem.*, **18**, 1331 (1965).

analytical results for these new compounds are given in Table I.

Complexes of Ni(II) with 4PAP.—With the ligand 4PAP and Ni(II) and on the bases of conductivity, magnetic susceptibility, and ir–visible spectroscopic measurements, we identified the species $Ni(4PAP)_3^{2+}$, $Ni(4PAP)_2^{2+}$, $Ni(4PAP)_2L^+$, $Ni(4PAP)_2L_2$, and $Ni(4PAP)Cl_2$, representing possible six-, five-, and four-coordination for the central metal atom. The N–H band occurs at 3110 cm^{-1} for 4PAP, and at 3100–3180 cm^{-1} in its complexes (Table III), a small change taken as evidence against coordination by this site.

The pmr absorptions for N–H protons in our complexes could not be detected, partly due to the low concentrations available and partly due to band broadening associated with the quadrupolar relaxation of the nitrogen nucleus.[32]

The purple complex $[Ni(4PAP)_3](ClO_4)_2$ behaves as a bi-univalent electrolyte in solution in nitrobenzene (Table III); in this and in all other perchlorate salts, infrared bands at 1100 and 625 cm^{-1} indicate anionic perchlorate groups.[33] The electronic absorption bands, characteristic of the d–d transitions for an octahedral complex,[34] may be assigned as $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (19,000 cm^{-1}) and $^3A_{2g} \rightarrow {}^3T_{2g}$ (12,660 cm^{-1}), with an intense charge-transfer band overlapping the region of the third transition, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (see Figure 2). Magnetic susceptibility data (Table IV) provide additional evidence in support of the octahedral configuration; thus 4PAP is functioning as a bidentate ligand, *via* its pyridine N and P atoms, forming five-membered chelate complexes. The position of 4PAP in the spectrochemical series is shown in Table V; it develops a ligand field strength similar to that of 2,2′-bipyridine[35] but stronger than that of 2-picolylamine[36] both of which are bifunctional "homoligands," based on two nitrogen atom donors forming five-membered chelate structures (see Figure 1, VII and VIII).

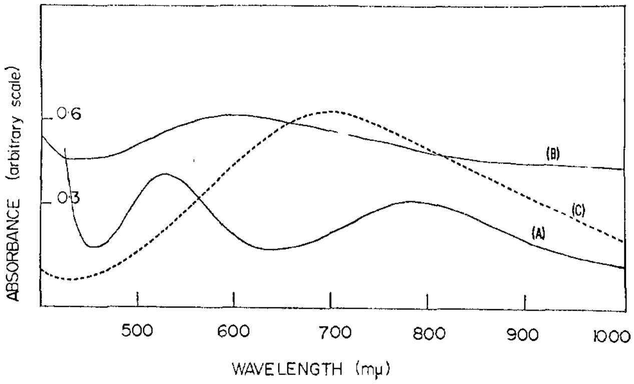

Figure 2.—Electronic transmittance spectra of Nujol mulls of (A) $[Ni(4PAP)_3](ClO_4)_2$ and (B) $[Ni(4PAP)_2Br](ClO_4)$ and the solution spectrum of (C) $[Ni(4PAP)_2Br](ClO_4)$ in nitrobenzene.

In the absence of coordinating ligands, the yellow compound $Ni(4PAP)_2(ClO_4)_2 \cdot 2H_2O$ is obtained from the reaction of $Ni(ClO_4)_2$ (1 mol) and 4PAP (2 mol) in solution in acetone. The complex, a bi-univalent electrolyte in nitrobenzene, is ionic in the solid state as well. Since the compound is diamagnetic, both octahedral

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[32] J. W. Emsley, J. Feeney, and L. H. Sutcliffe in "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1967, p 26.

[33] (a) A. Turco and C. Pecile, *Nature (London)*, **191**, 66 (1961); (b) J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964); (c) M. F. Farona and A. Wojcicki, *ibid.*, **4**, 1402 (1965).

[34] F. A. Cotton and G. Wilkinson in "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1967.

[35] K. Sone and M. Kato, *Naturwissenschaften*, **45**, 10 (1958).

[36] S. Utsuno and K. Sone, *Bull. Chem. Soc. Jap.*, **37**, 1028 (1964).

TABLE IV

MAGNETIC AND SPECTRAL CHARACTERISTICS OF THE COMPLEXES OF Ni(II) AND Co(II) WITH THE LIGANDS 4PAP AND 6PAP

	μ_{eff}, BM	Electron spectrum, cm^{-1}	Solvent	Postulated structure[a]
$[Ni(4PAP)_3](ClO_4)_2$	3.05	18,980 (80, ν_2), 12,660 (66, ν_1)	CH_2Cl_2	Octahedral
$[Ni(4PAP)_2](ClO_4)_2 \cdot 2H_2O$	Diam	25,000	Nujol	Square planar
$Ni(4PAP)_2Cl_2 \cdot 2H_2O$ (blue)	2.84	17,540 (160)	Ethanol	Tetrahedral[b]
$Ni(4PAP)_2Cl_2 \cdot 2H_2O$	3.12	20,000 (450, ν_2), 13,700 (60, ν_1)	$C_6H_5NO_2$	Six-coordinate
$[Ni(4PAP)_2Cl]ClO_4$	...	17,400 (170)	Acetone	...
$[Ni(4PAP)_2Br]ClO_4$	3.09	16,800 (900)[b]	$C_3H_5NO_2$	...
		17,400	Nujol	
$Ni(4PAP)Cl_2$	2.96	20,000 (200, ν_2), 16,120 (100, ν_1)	Acetone	Octahedral
$Co(4PAP)_2Cl_2$	2.55	21,740, 14,500, 13,150, 7005	Nujol	Square pyramidal
$Co(4PAP)Cl_2 \cdot 1.5H_2O$	4.49	16,830 (190), 15,620, 14,920 (ν_3), 7460 (ν_2)	CH_2NO_2	Tetrahedral
$Co(6PAP)_2(ClO_4)_2 \cdot 5H_2O$	4.60	18,520, 17,240, 15,748 (ν_3), 8330 (ν_2)	Nujol	Tetrahedral
$[Ni(6PAP)_2](ClO_4)_2$	Diam	21,740	Nujol	Square planar
$Ni(6PAP)Cl_2$	3.12	14,700 (ν_2), 9175 (ν_1)	Nujol	Six-coordinate, polymeric

[a] Most reasonable structures, consistent with observed data, are given. [b] A spectrum measured by Dr. D. L. Goodgame was as follows: 28,000, 16,800, 11,350 (sh), 9850 (sh), 8000–8400 (sh) cm^{-1}, plus weak bands at 7000–5000 cm^{-1}.

TABLE V

10*Dq* VALUES FOR VARIOUS OCTAHEDRAL, TRIS-CHELATED NiL_3^{2+} COMPLEXES

L[a]	10*Dq*, cm^{-1}	Ref	L[a]	10*Dq*, cm^{-1}	Ref
mepic	10,200	*b*	8-dmaq	12,500	*f*
pma	10,900	*c*	4PAP	12,660	*g*
en	11,136	*d*	bipy	12,670	*h*
plc	11,628	*e*			

[a] Abbreviations: mepic, 6-methyl-2-aminomethylpyridine; pma, *N*-methyl-2-(aminomethyl)pyridine; en, ethylenediamine; pic, 2-picolylamine; 8-dmaq, 8-dimethylarsinoquinoline; 4PAP, 2-(diphenylphosphino)-4-methylpyridine; bipy, 2,2′-bipyridine. [b] S. Utsuno, *J. Inorg. Nucl. Chem.*, **32,** 1631 (1970), [c] S. Utsuno and K. Sone, *Bull. Chem. Soc. Jap.*, **40,** 105 (1967). [d] C. K. Jørgensen, *Acta Chem. Scand.*, **8,** 1497 (1954). [e] S. Utsuno and K. Sone, *Bull. Chem. Soc. Jap.*, **37,** 1028 (1964). [f] G. A. Barclay, M. A. Collard, C. M. Harris, and J. V. Kingston. *J. Chem. Soc. A*, 1684, 830 (1969). [g] This work. [h] K. Sone and M. Kato, *Naturwissenschaften*, **45,** 10 (1958).

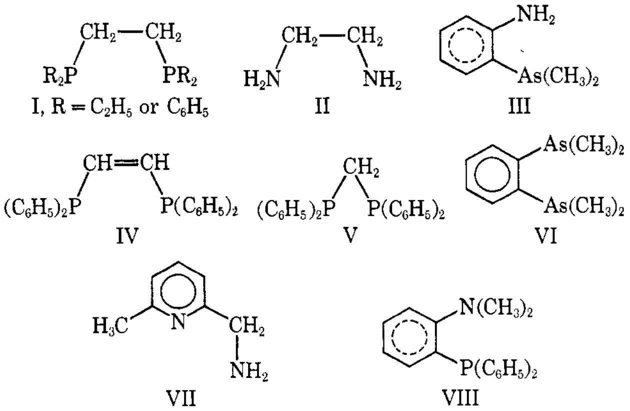

Figure 3.

and tetrahedral configurations are precluded, leading to a planar structure. The electronic absorption spectrum of solid $[Ni(4PAP)_2](ClO_4)_2 \cdot 2H_2O$, consisting of a band at 25,000 cm^{-1} ($^1A_1 \rightarrow {}^1B_2$) near an intense charge-transfer band, is typical of square-planar d^8 species.[37] Comparable square-planar complexes $Ni(L)_2^{2+}$, with L as a five-membered chelating ligand, are formed by ethylenediamine,[38] by 1,2-bis(diphenyl- and diethylphosphino)ethane,[3c,h] and by *o*-(dimethylarsino)aniline;[38b] these systems represent "hard" (NN), "soft" (PP), and "mixed" (AsN) donor atom combinations, respectively (see Figure 3, I–III). However the "hard" (NN) donor atom combination in 2,2′-bipyridine (dipy, Figure 1, VII) gives rise to paramagnetic $Ni(dipy)_2(ClO_4)_2$.[39] The ligands 4PAP and 2-picolylamine are structurally similar (Figure 1, II and VIII) but with PN and NN donor sites, respectively. The complex $[Ni(2\text{-picolylamine})_2](ClO_4)_2$, however, is apparently too unstable to be isolated, undergoing a facile conversion into an octahedral, six-coordinate complex.[40] Thus 4PAP is a better ligand, in that it does coordinate sufficiently strongly to give diamagnetic $[Ni(4PAP)_2](ClO_4)_2$, a four-coordinate complex, stable against facile conversion to the six-coordinate structure.

The addition of a coordinating ligand L, such as halide ion, to yellow $Ni(4PAP)_2^{2+}$, yields blue $Ni(4PAP)_2L^+$ (L = Br, Cl), infrared evidence indicating a noncoordinated, anionic ClO_4^- group. The bromo compound is much deeper in color than the chloro derivative, and band maxima, in the 17,000-cm^{-1} region, are consistent with the spectrochemical series. The blue species become yellow on standing in solution in nitrobenzene or nitromethane, presumably due to further ionization to $Ni(4PAP)_2^{2+}$ and Br^- or Cl^-.

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(37) A. T. Phillip, *Aust. J. Chem.*, **22,** 259 (1969).

(38) (a) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2552 (1963); (b) B. Chiswell, R. A. Plowman, and K. Verrall, *Inorg. Nucl. Chem. Lett.*, **5,** 649 (1969).

(39) C. M. Harris and E. D. McKenzie, *J. Inorg. Nucl. Chem.*, **29,** 1047 (1967).

(40) G. J. Sutton, *Aust. J. Chem.*, 74 (1960).

For $Ni(4PAP)_2Br^+$, the main bands occur at 28,000 and 16,800 cm^{-1}, with shoulders at 11,350, 9850, and 8000 cm^{-1}. Weak bands at 7000–5000 cm^{-1} were attributed to vibrations of the organic ligand. (See Figure 2, B and C. In addition, a detailed spectrum of $[Ni(4PAP)_2Br]ClO_4$ was obtained for us by Dr. D. L. Goodgame.) The maxima and shoulders of the main band are similar in energy to those reported by Ciampolini and Nardi[41] for high-spin, pentacoordinated $[Ni(trenMe)X]X'$ complexes; the intensity of the visible band, however, is much higher than normally found among five-coordinated complexes of Ni(II), being more characteristic of tetrahedral Ni(II). (We are grateful to one of the referees for pointing out this inconsistency.) Additional evidence in support of a tetrahedral structure, *viz.*, a relatively intense band at 7000–8000 cm^{-1} [34] and a magnetic moment of the order 3.5–4.2 BM,[34] was lacking. Thus a choice between a five-coordinate configuration (two chelating 4PAP ligands, plus one halogen) or a four-coordinate configuration (one chelating and one monodentate 4PAP ligand, plus one halogen) cannot be made.

Derivatives of the type $Ni(4PAP)_2L_2\cdot xH_2O$ were obtained in two forms: blue, paramagnetic (2.84 BM) $Ni(4PAP)_2Cl_2\cdot 2H_2O$, a 1:1 electrolyte in ethanol, with an electronic absorption spectrum in solution similar to that of $Ni(4PAP)_2Cl^+$; pink, paramagnetic (3.12 BM) $Ni(4PAP)_2Cl_2\cdot H_2O$, a nonelectrolyte in nitrobenzene, with a d–d spectrum (Table IV) characteristic of octahedral d^8 species.[34] The two forms are interconvertible as in

$$\underset{\text{blue}}{[Ni(4PAP)_2Cl]Cl\cdot 2H_2O} \xrightleftharpoons[\text{alcohol}]{\text{heat, 105°, 1 hr, in acetone, nitromethane, or nitrobenzene}} \underset{\text{pink}}{[Ni(4PAP)_2Cl_2]\cdot H_2O}$$

A similar dependence on solvent polarity is observed for complexes of 2-picolylamine.[40]

The complex $Ni(4PAP)Cl_2$, containing only 1 mol of ligand, is too insoluble for conductivity studies, but magnetic susceptibility (2.96 BM) and spectroscopic data (bands at 20,000, 16,000, 7500, and 8600 cm^{-1}) are consistent for an octahedral structure, presumably achieved through polymerization.

Complexes of Co(II) with 4PAP.—The ligand 4PAP appears to complex less effectively with Co(II) than with Ni(II); thus attempts to prepare $Co(4PAP)_3X_2$ always gave a brown precipitate of $Co(4PAP)_2Cl_2$. The color of the latter compound slowly changes to green, a process which can be completed in a few hours by heating at 100° or by treating with warm organic solvents; the resulting solutions have spectra identical with that of $Co(4PAP)Cl_2$, indicating the loss of one 4PAP ligand.

Magnetic susceptibility data for $Co(4PAP)_2Cl_2$ (2.55 BM) are consistent with three possible structures for d^7 Co(II) complexes—square planar, spin-paired tetragonal, and square pyramidal.[42] Complexes $Co(L_2)X_2$ of Co(II) with similar magnetic moments are formed by *o*-phenylenebis(dimethylarsine)[15b] (Figure 3, VI), *o*-(dimethylarsino)aniline[38a] (Figure 3, III), and 1,2-bis(diphenylphosphino)ethane[43] (Figure 3, I). A square-pyramidal structure has been proposed for $Co[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Br_2$;[3d] its electronic spectrum is similar to that of $Co(4PAP)_2Cl_2$ (see Figure 4), suggesting similar structures for the two cases; this structure transforms into and is therefore less stable than the pseudotetrahedral arrangement in $Co(4PAP)Cl_2$. With respect to this transformation $ML_2Cl_2 \rightarrow MLCl_2 + L$, the complex $Co(4PAP)_2Cl_2$ is less stable than its nickel analog.

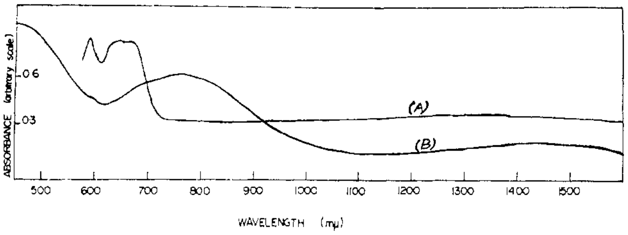

Figure 4.—Electronic transmittance spectra of Nujol mulls of (A) $Co(4PAP)Cl_2\cdot 1.5H_2O$ and (B) $Co(4PAP)_2Cl_2$.

The green complex $Co(4PAP)Cl_2\cdot 1.5H_2O$ may be dehydrated without change in color; magnetic susceptibility data and the electronic reflectance spectrum of the solid (see Figure 4) and of its solutions are characteristic of pseudotetrahedral compounds;[21] the visible (ν_3, ${}^4A_2 \rightarrow {}^4T_1(P)$) and the near-infrared (ν_2, ${}^4A_2 \rightarrow {}^4T_1(F)$) bands were clearly observed. From solution molecular weight data, $Co(4PAP)Cl_2$ is largely dimeric; and in nitrobenzene it is a nonelectrolyte; since the spectrum remains characteristic of pseudotetrahedral species, one possible implication is a neutral, chloro-bridged dimeric structure, with 4PAP functioning as a monodentate ligand.

Complexes of Ni(II) and Co(II) with 6PAP.—With the ligand 6PAP we obtained the complexes $Ni(6PAP)_2(ClO_4)_2$, $Ni(6PAP)Cl_2$, $Co(6PAP)_2(ClO_4)_2\cdot 5H_2O$, and $Co(6PAP)Cl_2$, but we were unable to prepare species containing 3 mol of ligand, *i.e.*, $M(6PAP)_3{}^{2+}$. By means of models, it can be shown that the methyl groups in the 6 positions of the pyridine ring experience steric crowding in planar $M(6PAP)_2$ and in octahedral $M(6PAP)_3$ structures. In fact, it appears that a perfectly planar structure cannot be attained for $Ni(6PAP)_2{}^{2+}$, but the distortion (if any) is insufficient to destroy the diamagnetism, implying an essentially square-planar complex. In addition, the ${}^1A_1 \rightarrow {}^1B_2$ transition for $Ni(6PAP)_2{}^{2+}$ is at a lower energy than that of its 4PAP analog (21,700 *vs.* 25,000 cm^{-1}), consistent with a steric weakening of ligand field strength in square-planar complexes of 6PAP. While similar stereochemical interactions are found for the methyl groups within complexes of the structurally similar ligand 6-methyl-2-aminomethylpyridine[44] (mepic, Figure 3, VII), these steric effects are insufficient

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[41] M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).

[42] G. A. Barclay, M. A. Collard, C. M. Harris, and J. V. Kingston, *J. Chem. Soc. A*, 830, 1684 (1969).

[43] A. Sacco and F. Gorieri, *Gazz. Chim. Ital.*, **93**, 687 (1963).

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to preclude the formation of $[Ni(mepic)_3](ClO_4)_2$.[45] Thus the phenyl substituents of 6PAP must contribute significantly to steric interactions within its complexes, even precluding the formation of $M(6PAP)_3{}^{2+}$. The formation of $[Ni(6PAP)_2](ClO_4)_2$ (square planar), rather than the octahedral analog of $[Ni(mepic)_2(H_2O)_2](ClO_4)_2$,[45] also appears to be due to steric crowding at the axial positions by the phenyl groups.

The compound $Ni(6PAP)Cl_2$ is insoluble, with a reflectance spectrum (Table IV) and a magnetic moment (3.12 BM) indicative of an octahedral configuration, presumably achieved in a chloro-bridged polymeric structure, with 6PAP as a bidentate ligand. Corresponding five-membered chelate complexes $NiLX_2$ are paramagnetic for L = *o*-(dimethylamino)phenylenediphenylphosphine[11a] (mixed PN donor sites, Figure 3, VIII) and for L = 2,2′-bipyridine[40b] (two equivalent N donor sites), but for L = *cis*-1,2-bis(diphenylphosphino)ethylene[3a] or 1,2-bis(diphenylphosphino)ethane[3c] (two equivalent P donor sites in both cases) the complexes are diamagnetic and planar. Thus the P–N donor set is akin to an N–N rather than a P–P combination in these five-membered chelate systems.

The blue compound $[Co(6PAP)_2](ClO_4)_2 \cdot 5H_2O$ has a magnetic moment and a reflectance spectrum characteristic of tetrahedral Co(II),[21] the preferred structure for four-coordinate cobalt and one in which the interaction of the two 6-methyl groups of the chelating ligands is minimized. The complex $Co(6PAP)Cl_2$ (deep green), a nonelectrolyte in nitromethane, has similar magnetic and electronic absorption properties and hence a structure very similar to that of $[Co(6PAP)_2](ClO_4)_2$. In the spectrum, however, corresponding transitions appear at slightly lower energies, in keeping with a lowering of the field strength on replacing the chelating donor set P–N (*i.e.*, 6PAP) by two chloro groups. Unlike $Co(4PAP)Cl_2$, the 6PAP analog is monomeric in solution, implying chelation by 6PAP across two apices of the tetrahedron.

Other Complexes.—The complexes obtained with 4PAP or 6PAP and Pd(II), Hg(II), and Ag(I), indicate the affinity of the phosphinoaminopyridine type of ligand for "soft," as well as "hard," metal ion acceptors. An interesting comparison with *N,N*-dimethyl-*N′*-diphenylphosphinohydrazine (DPH) shows that, where $Pd(DPH)_2Cl_2$ is readily formed,[23c] the corresponding analogs with 4PAP and 6PAP are not obtained. It appears likely that the complexes Pd(4- or 6-PAP)Cl_2 contain relatively stable five-membered ring systems, whereas the strained, four-membered chelate ring system of $Pd(DPH)Cl_2$ is readily converted to $Pd(DPH)_2Cl_2$, containing monodentate ligands, by reaction with a second mole of DPH. Structural studies on these systems are in progress.

Acknowledgment.—The financial support of the National Research Council of Canada is gratefully acknowledged. We thank Dr. D. L. Goodgame for assistance with spectral measurements.

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Transition Metal Complexes of 1,10-Phenanthroline and 2,2′-Bipyridine

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Four unique groups of powder pattern have been obtained corresponding to $[M(bipy)_2X_2]Y \cdot nH_2O$, $[M(phen)_2(H_2O)_2]Y_3 \cdot nH_2O$, and $[M(phen)_2X_2]Y \cdot nH_2O$ (two sets), with phen = 1,10-phenanthroline; bipy = 2,2′-bipyridine; M = Co, Cr, Rh, and Ir; X = Cl and Br; Y = Cl, Br, and NO_3; and *n* variable. The cations of all these compounds are formulated as the cis isomers, with the latter two groups corresponding to two crystal forms. *cis*-$[Ir(phen)_2Cl_2]Cl \cdot 3H_2O$, crystal form A, and *cis*-$[Ir(phen)_2Cl_2]Cl \cdot 2H_2O$, crystal form B, have been prepared in this work and the facile conversion of the A to the B form by rapid recrystallization has been demonstrated. Previous evidence for the nonexistence of trans cations and existence of polymorphism in these systems is augmented and confirmed.

Introduction

The cis–trans isomeric configurations of complexes of the type $[M(NN)_2X_2]Yy$, where NN = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy), have been assigned by various methods, including, color,[2,3] solubility,[3] acid adduct formation,[4] and infrared,[5,6] visible–ultraviolet,[7] and nuclear magnetic resonance[8,9] spec-

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