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Synthesis, Properties and X-Ray Characterization of Aquo and Hydroxo Complexes of Cobalt(II) and Nickel(II) with Poly(tertiary phosphines)

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Received August 5, 1975 AIC50587K

Cobalt(II) and nickel(II) aquo cations deriving from $[M(H_2O)_6](BF_4)_2$ (M = Co, Ni) reacting with poly(tertiary phosphines) (L_4) such as tris(2-diphenylphosphinoethyl)amine ($N(CH_2CH_2PPh_2)_3$; np_3), tris(2-diphenylphosphinoethyl)phosphine ($P(CH_2CH_2PPh_2)_3$; pp_3), and tris(*o*-diphenylphosphinophenyl)phosphine ($P(C_6H_4PPh_2)_3$; QP), according to the nature of the solvent form a series of hydroxo complexes $[M(OH)L_4]Y$ (Y = BF_4, BPh_4) and a series of aquo complexes $[M(H_2O)L_4](BF_4)_2$. All the nickel complexes are low spin and trigonal bipyramidal. The cobalt complexes with np_3 are high spin and are assigned a tetrahedrally distorted TBP geometry. The other cobalt complexes are low spin with distorted square-pyramidal geometry. This assignment comes from the results of x-ray structure determinations, performed on the complexes $[Co(OH)(pp_3)]BF_4\cdot C_2H_5OH$ and $[Co(H_2O)(pp_3)](BF_4)_2\cdot CH_3COCH_3$. Both the crystals are triclinic, space group $P\bar{1}$, with the following cell constants for the $[Co(OH)(pp_3)]BF_4\cdot C_2H_5OH$ and $[Co(H_2O)(pp_3)](BF_4)_2\cdot CH_3COCH_3$ respectively: $a = 11.826$ (2) Å, $b = 12.293$ (2) Å, $c = 16.690$ (4) Å, $\alpha = 92.72$ (3)°, $\beta = 90.88$ (3)°, $\gamma = 117.27$ (4)°; $a = 17.897$ (3) Å, $b = 12.237$ (2) Å, $c = 12.116$ (2) Å, $\alpha = 63.19$ (3), $\beta = 78.05$ (3), $\gamma = 83.57$ (3)°. Counter methods were used and least-squares refinements gave final R factors of 0.089 and 0.081, respectively.

Introduction

In a large number of papers published by Venanzi[1] and by Meek,[2] various series of 3d metal complexes, mostly five coordinated, containing polyfunctional ligands (L_n) with group 5 donor atoms, have been described. These complexes of general formula $[MX_mL_n]Y$ contain in the coordination sphere one or more rarely two anions (halides, pseudohalides, nitrate, perchlorate) besides the polyfunctional ligands.

No hydroxo complexes, however, have resulted, even from preparations starting from hydrated metal salts. Thus the only examples known to date of hydroxo–phosphino metal complexes remain those of Fe(I), Rh(I), and Ir(I).[3-5]

In very few cases, with ligands containing arsenic as the donor atoms, have nickel(II) complexes with a molecule of water as the fifth ligand been formed.[6-8]

In a previous paper we described the formation of a dimeric hydroxo complex of cobalt(II), $[(p_3)Co(OH)_2Co(p_3)](BPh_4)_2$, where p_3 is the poly(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$, which was obtained starting from $[Co(H_2O)_6](BF_4)_2$ in acetone solution. The fact that such a hydroxo species was formed under these circumstances was attributed to the basic nature of the phosphine, which is capable of taking protons from water molecules of the aquo cation to form phosphonium cations.[9]

This novel observation induced us to undertake a systematic study of the behavior of the tripod poly(tertiary phosphine) ligands toward the salts $[Ni(H_2O)_6](BF_4)_2$ and $[Co(H_2O)_6](BF_4)_2$ under conditions in which the only anion present in the reaction mixture could be the ion BF_4^-, which is believed to have very low coordinating power. The poly(tertiary phosphines) used were the following: tris(2-diphenylphosphinoethyl)amine ($N(CH_2CH_2PPh_2)_3$; np_3), tris(2-diphenylphosphinoethyl)phosphine ($P(CH_2CH_2PPh_2)_3$; pp_3), and the tris(*o*-diphenylphosphinophenyl)phosphine named by Venanzi (QP, $P(C_6H_4PPh_2)_3$).

Under such conditions two types of complexes have been isolated, both for nickel and for cobalt, the hydroxo complexes $[M(OH)L_4]Y$ (Y = BF_4, BPh_4) and the aquo complexes $[M(H_2O)L_4](BF_4)_2$.

All these complexes were characterized by means of magnetic, spectrophotometric, and conductivity measurements.

The structures of two of these complexes, $[Co(OH)(pp_3)]BF_4\cdot C_2H_5OH$ and $[Co(H_2O)(pp_3)](BF_4)_2\cdot CH_3COCH_3$, have been determined by means of x-ray diffraction.

Experimental Section

Reagents and Physical Measurements. The syntheses of the ligands np_3 and QP appear elsewhere.[10,11] The ligand pp_3 was acquired from the Pressure Chemical Co., Pittsburgh, Pa. Ethanol, acetone, and petroleum ether solvents were used without further purification, but the tetrahydrofuran was purified by distillation over $LiAlH_4$. The $NaBPh_4$ was A.R. grade. Both the perchlorates and tetrafluoroborates of cobalt and nickel were released from the metal carbonate by addition of the corresponding acid and then recrystallized from aqueous solutions.

The physical measurements were executed by the previously described method.[12] See Table I for analytical, magnetic, and conductivity data.

Preparation of the Complexes. All preparative operations were carried out in an atmosphere of dry nitrogen and complexes were dried off by standing in dry nitrogen current. Almost invariably the experimental quantities of ligand or aquo complex dissolved in the appropriate solvent were 1 mmol of solid in 20 ml of solvent. To avoid unnecessary repetition these ratios will be assumed throughout unless stated otherwise.

$[Co(OH)(np_3)]ClO_4\cdot C_2H_5OH$. Room-temperature solutions of the ligand in acetone and aquo complex $[Co(H_2O)_6](ClO_4)_2$ in ethanol (40 ml) were mixed and concentrated by means of a stream of dry nitrogen. On standing overnight red-brown crystals separated which were filtered off and washed with alcohol and petroleum ether.

$[Co(OH)(np_3)]BF_4\cdot C_2H_5OH$. The orange colored crystalline product was prepared by an analogous procedure to the perchlorate above, starting from $[Co(H_2O)_6](BF_4)_2$ and concentrating the mixture by heating to ca. 10 ml.

$[Co(OH)(np_3)]BPh_4$. An ethanolic solution of $[Co(H_2O)_6](BF_4)_2$

Table I. Analytical Data and Physical Constants

		Calcd %					Found %					μ_{eff}, μ_B (293 K)	Λ_M,[a] cm^2 ohm^{-1} mol^{-1}
Compd	Color	C	H	N	M	P	C	H	N	M	P		
$[Co(OH)(np_3)]ClO_4 \cdot C_2H_5OH$	Red-brown	60.38	5.64	1.60	6.73		59.95	6.02	1.49	6.26		4.25	75
$[Co(OH)(np_3)]BF_4 \cdot C_2H_5OH$	Orange	61.27	5.73	1.62	6.83		61.16	5.53	1.56	6.58		4.21	76
$[Co(OH)(np_3)]BPh_4$	Orange-brown	75.57	6.05	1.33	5.62	8.86	74.65	6.10	1.22	5.63	8.90	4.47	37
$[Co(H_2O)(np_3)](BF_4)_2 \cdot THF$	Purple-magenta	56.58	5.37	1.43	6.04		57.19	5.26	1.42	6.42		4.56	19[b]
$[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$	Brown	60.08	5.62		6.70	14.09	59.99	5.70		6.75	14.38	1.98	80
$[Co(OH)(pp_3)]BPh_4$	Brown	74.37	5.96		5.53	11.63	74.58	5.95		5.45	11.30	2.00	42
$[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$	Brown	55.18	5.15		6.02	12.65	55.58	5.41		5.93	12.47	2.07	159
$[Co(H_2O)(pp_3)](BF_4)_2 \cdot THF$	Brown	55.61	5.28		5.93	12.47	55.82	5.35		5.98	12.20	2.15	150
$[Co(OH)(QP)]BF_4 \cdot C_2H_5OH$	Brown	65.70	4.82		5.76		64.83	4.24		5.93		2.10	87
$[Co(OH)(QP)]BPh_4$	Brown	77.42	5.25		4.87		76.67	5.86		4.70		2.10	44
$[Co(H_2O)(QP)](BF_4)_2 \cdot THF$	Maroon-brown	61.24	4.61		5.18		60.01	5.02		5.09		2.1	140
$[Ni(OH)(pp_3)]BF_4 \cdot C_2H_5OH$	Deep-blue	60.09	5.62		6.67		58.94	5.08		6.75		diam	75
$[Ni(OH)(pp_3)]BPh_4$	Violet-blue	74.40	5.96		5.51	11.63	74.90	6.05		5.25	11.29	diam	46
$[Ni(pp_3)_2](BF_4)_2$	Light-yellow	64.10	5.38		3.73	15.75	64.71	5.20		3.75	15.53	diam	
$[Ni(OH)(QP)]BF_4 \cdot C_2H_5OH$	Blue	65.72	4.83		5.74		66.42	4.55		5.52		diam	78
$[Ni(OH)(QP)]BPh_4$	Blue	77.43	5.24		4.85		76.80	5.49		4.87		diam	47
$[Ni(H_2O)(QP)](BF_4)_2 \cdot THF$	Deep-blue	61.25	4.61		5.16	10.93	60.64	4.98		4.92	10.70	diam	153

[a] Molar conductance of ca. 10^{-3} *M* solution in nitroethane at 20°C. [b] In 1,2-dichloroethane.

was carefully added to a hot solution of free ligand in acetone (15 ml), followed by a 2.0-mmol quantity of $NaBPh_4$ dissolved in ethanol (10 ml). Orange-brown crystals, formed from the concentrated solution, were recrystallized twice from an ethanol–acetone mixture, filtered off, and then finally washed in petroleum ether.

$[Co(H_2O)(np_3)](BF_4)_2 \cdot THF$. To a solution of the ligand (1 mmol in 15 ml of THF) was added a solution of $[Co(H_2O)_6](BF_4)_2$ in THF (10 ml). After bringing it to a boil the cloudy solution was filtered. Well formed magenta-purple crystals precipitated from the concentrate, which were separated off and washed with THF.

$[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$. A suspension of the ligand in ethanol (15 ml) was mixed with a stoichiometric amount of $[Co(H_2O)_6](BF_4)_2$ in ethanol (15 ml). The solution was concentrated by heating to ca. 15 ml and left overnight. Brown colored crystals that formed were recrystallized from ethanol. The solid product after filtration was washed with ethanol and petroleum ether in turn.

$[Co(OH)(pp_3)]BPh_4$. Ethanolic solutions of $[Co(H_2O)_6](BF_4)_2$ and $NaBPh_4$ (2.2 mmol in 10 ml ethanol) were mixed into a solution of the ligand in acetone. Brown crystals separated from the concentrate were washed by decantation and then ultimately recrystallized from an ethanolic acetone solution.

$[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$. A brown crystalline product was released from the concentrated solution of ligand and aquo complex $[Co(H_2O)_6](BF_4)_2$ in acetone, to which 15 ml of cyclohexane had been added prior to concentration. Washing was accomplished using a 1:1 acetone–cyclohexane mixture.

$[Co(H_2O)(pp_3)](BF_4)_2 \cdot THF$. To 1 mmol of the ligand in 15 ml of THF a solution of $[Co(H_2O)_6](BF_4)_2$ in the same solvent (15 ml) was slowly added. After bubbling nitrogen gas through the reaction mixture, brown crystals separated, which were washed by decantation in THF, filtered, and finally washed with petroleum ether.

$[Co(OH)(QP)BF_4 \cdot C_2H_5OH$. The blue colored reaction mixture composed of ethanolic ligand and $[Co(H_2O)_6](BF_4)_2$ solutions was refluxed for ca. 3 hr. Following filtration the solution was heated to small bulk (10 ml), from which on cooling light-brown crystals were obtained. The solid product was recrystallized from ethanol and washed with a small quantity of the same solvent.

$[Co(OH)(QP)]BPh_4$. A boiling solution of the latter product $[Co(OH)(QP)]BF_4 \cdot C_2H_5OH$ in ethanol (0.5 mmol in 30 ml) was added to 0.5 mmol of $NaBPh_4$ in 10 ml of ethanol. The resulting brown crystals were recrystallized from an acetone–ethanol mixture.

$[Co(H_2O)(QP)](BF_4)_2 \cdot THF$. A mixture of the boiling THF solutions of ligand (1 mmol in 40 ml) and $[Co(H_2O)_6](BF_4)_2$ (1 mmol in 30 ml) was refluxed for ca. 10 min sufficient to cause precipitation on cooling of brown colored crystals, which were filtered off and washed in THF.

$[Ni(OH)(pp_3)]BF_4 \cdot C_2H_5OH$. To an ethanolic solution of the nickel aquo complex $[Ni(H_2O)_6](BF_4)_2$ a solution of the corresponding stoichiometric amount of ligand in acetone was added and the mixture was concentrated to small bulk (ca. 15 ml). Making up the concentrate with a further batch of ethanol (30 ml) was followed by evaporation to small volume again. Finally water was added and the whole mixture was heated. Gently scratching the side of the reaction vessel induced precipitation of tiny blue crystals, which were filtered off and washed in aqueous ethanol (one-fourth part C_2H_5OH). The recrystallization from aqueous ethanol was repeated twice and the crystals were then dried over P_4O_{10} for a period of 2 days.

$[Ni(OH)(pp_3)]BPh_4$. A boiling methanolic suspension of the ligand (1 mmol in 40 ml of methanol) was slowly added to the complex $[Ni(H_2O)_6](BF_4)_2$ dissolved in methanol. The mixture was filtered and concentrated (ca. 20 ml) in the usual manner before pouring in an ethanolic $NaBPh_4$ solution (2.2 mmol in 10 ml of ethanol). Resultant blue colored crystals were filtered off and recrystallized from methanol and THF.

$[Ni(pp_3)_2](BF_4)_2$. Light-yellow crystals of the product precipitated from a concentrated mixture of the ligand and $[Ni(H_2O)_6](BF_4)_2$ in THF. Petroleum ether and THF were employed as washing agents.

$[Ni(OH)(QP)]BF_4 \cdot C_2H_5OH$, $[Ni(OH)(QP)]BPh_4$, and $[Ni(H_2O)(QP)](BF_4)_2 \cdot THF$. The above complexes were generated by analogous procedures to the cobalt(II) counterparts.

Collection and Reduction of the X-Ray Intensity Data. The crystals of both complexes, $[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$ (complex I) and $[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$ (complex II), suitable for X-ray work, were sealed in glass capillaries, to prevent crystal air decomposition.

Cell constants were determined from a least-squares refinement of the setting angles of 25 reflections, which had been carefully centered on a Philips PW 1100 diffractometer. Details of crystal data and data collection for the two compounds are given in Table II. All data processing was carried out as previously described.[13] After correction for background the intensities were assigned standard deviations according to the formula: $\sigma(I) = [P + 0.25(t_c/t_b)^2(B_1 + B_2) + (0.05I)^2]^{1/2}$, where P is the total integrated peak count obtained in scan time t_c and B_1 and B_2 are the background counts in time t_b.[14] The observed intensities were corrected for Lorentz and polarization effects. No absorption correction was applied, owing to the small linear absorption coefficients of the two compounds ($\mu(\text{Mo } K\alpha) = 6.20 \text{ cm}^{-1}$ for complex I and $\mu(\text{Mo } K\alpha) = 5.71 \text{ cm}^{-1}$ for complex II). The neglect of absorption effects in the two complexes was estimated to introduce a maximum error of ±4 and ±3% in intensity, respectively.

The neutral scattering factors for Co, P, F, O, C, and B were taken from ref 15, while those for H were taken from ref 16. Corrections for anomalous dispersion effects for cobalt and phosphorus atom were taken from the compilation of Cromer and applied to the calculated structure factor amplitudes.[17]

Solution and Refinement of the Structures. The $[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$ Complex. The structure was solved by the standard heavy-atom techniques. The positional parameters of the cobalt and

Table II. Crystal Data and Data Collection Details

	$[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$	$[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$
Molecular formula	$C_{44}H_{49}O_2P_4CoBF_4$	$C_{45}H_{50}O_2P_4CoB_2F_8$
Mol wt	879.51	979.34
a, Å	11.826 (2)	17.897 (3)
b, Å	12.293 (2)	12.237 (2)
c, Å	16.690 (4)	12.116 (2)
α, deg	92.72 (3)	63.19 (3)
β, deg	90.88 (3)	78.05 (3)
γ, deg	117.27 (4)	83.57 (3)
d_{obsd}(by flot), g cm^{-3}	1.37	1.40
d_{calcd}, g cm^{-3}	1.36	1.40
U, Å^3	2152.46	2316.46
Z	2	2
Space group	$P\bar{1}$	$P\bar{1}$
Absorpt coeff (Mo Kα), cm^{-1}	6.20	5.71
Color	Brown	Brown
Habit	Very irregular parallelepiped	Irregular romboedrum
Dimensions, mm	0.3 × 0.2 × 0.1	0.33 × 0.3 × 0.3
Diffractometer	Philips PW 1100	Philips PW 1100
λ(Mo Kα), Å	0.7093	0.7093
Monochromator	Flat graphite crystal	Flat graphite crystal
Take-off angle, deg	1.5	1.7
Method	ω–2θ	ω–2θ
Scan speed	0.07°/sec in a range of 1° (a total of 14 sec across the peak)	0.08°/sec in a range of 0.8° (a total of 10 sec across the peak)
Background time	7 sec on each side of the peak	5 sec on each side of the peak
Standards	3 every 180 readings	3 every 180 readings
Max dev of standards	3%	2%
2θ limit	$2° \leqslant 2\theta \leqslant 50°$	$2° \leqslant 2\theta \leqslant 50°$
No. of data	7525	7987
No. of data with $I \geqslant 3\sigma(I)$	3595	5105

Table III. Positional Parameters (× 10^4) and Isotropic Temperature Factors with Estimated Standard Deviations in Parentheses for $[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$

Atom	x/a	y/b	z/c	B, Å^2
Co[b]	48453 (14)	35070 (14)	22186 (9)	[a]
P(1)	6897 (3)	4610 (3)	1881 (2)	[a]
P(2)	2768 (3)	2988 (3)	2038 (2)	[a]
P(3)	4813 (3)	1791 (3)	2721 (2)	[a]
P(4)	4630 (3)	2620 (3)	1056 (2)	[a]
F(1)	9105 (12)	2753 (10)	15 (9)	[a]
F(2)	8977 (15)	1040 (15)	291 (15)	[a]
F(3)	7768 (26)	1430 (23)	717 (16)	[a]
F(4)	7791 (27)	1231 (17)	−403 (13)	[a]
O(1)	5075 (6)	4559 (6)	3123 (4)	[a]
C(1)	7117 (13)	4012 (13)	909 (8)	6.6 (3)
C(2)	5980 (13)	3624 (13)	391 (8)	7.4 (3)
C(3)	2114 (12)	1870 (11)	1200 (7)	5.4 (3)
C(4)	3113 (12)	2228 (12)	555 (8)	6.0 (3)
C(5)	5341 (13)	1117 (12)	1904 (8)	6.5 (3)
C(6)	4749 (12)	1178 (12)	1115 (8)	6.0 (3)
C(7)	8189 (10)	4771 (10)	2547 (7)	4.6 (2)
C(8)	8881 (13)	4146 (13)	2416 (8)	6.5 (3)
C(9)	9777 (14)	4264 (14)	2990 (9)	7.1 (4)
C(10)	10031 (13)	4949 (13)	3622 (8)	6.6 (3)
C(11)	9378 (15)	5621 (14)	3801 (9)	7.5 (4)
C(12)	8462 (13)	5507 (12)	3228 (8)	6.6 (3)
C(13)	7245 (12)	6173 (11)	1709 (7)	5.5 (3)
C(14)	6397 (14)	6579 (14)	1819 (9)	7.7 (4)
C(15)	6636 (18)	7791 (17)	1693 (11)	9.7 (5)
C(16)	7845 (17)	8594 (15)	1464 (10)	8.7 (4)
C(17)	8695 (15)	8236 (15)	1331 (9)	8.2 (4)
C(18)	8449 (14)	7007 (14)	1427 (9)	7.7 (4)
C(19)	1662 (11)	2434 (10)	2857 (7)	4.8 (2)
C(20)	2077 (12)	2988 (11)	3599 (8)	5.5 (3)
C(21)	1238 (16)	2695 (15)	4236 (10)	8.3 (4)
C(22)	56 (16)	1851 (15)	4093 (10)	8.6 (4)
C(23)	−325 (16)	1287 (15)	3385 (10)	8.8 (4)
C(24)	421 (14)	1555 (13)	2702 (9)	7.0 (4)
C(25)	2528 (10)	4292 (10)	1756 (6)	4.3 (2)
C(26)	3122 (12)	5358 (12)	2252 (8)	6.2 (3)
C(27)	2887 (14)	6370 (14)	2102 (9)	7.9 (4)
C(28)	2112 (16)	6241 (15)	1449 (10)	8.3 (4)
C(29)	1564 (13)	5278 (13)	1002 (8)	6.6 (3)
C(30)	1754 (12)	4232 (11)	1132 (7)	5.4 (3)
C(31)	3259 (11)	576 (11)	3013 (7)	5.1 (3)
C(32)	2797 (12)	749 (12)	3701 (8)	5.6 (3)
C(33)	1586 (13)	−104 (13)	3957 (8)	6.7 (3)
C(34)	936 (15)	−1105 (14)	3468 (10)	7.7 (4)
C(35)	1341 (15)	−1364 (14)	2810 (10)	7.9 (4)
C(36)	2565 (14)	−482 (13)	2524 (8)	6.9 (3)
C(37)	5796 (12)	1939 (11)	3601 (7)	5.5 (3)
C(38)	5989 (15)	970 (15)	3854 (9)	8.1 (4)
C(39)	6625 (16)	1071 (16)	4554 (10)	9.5 (5)
C(40)	7094 (16)	2127 (16)	5052 (10)	9.1 (4)
C(41)	6928 (16)	3085 (16)	4834 (10)	9.2 (4)
C(42)	6265 (14)	2969 (13)	4079 (9)	7.5 (3)
B(1)	8415 (18)	1638 (17)	175 (11)	7.9 (5)
		Ethanol Molecule		
O(2)	6194 (14)	6073 (14)	4369 (9)	14.9 (4)
C(43)	6058 (25)	7254 (25)	4316 (15)	18.8 (7)
C(43)	7037 (24)	7937 (23)	3962 (15)	16.5 (7)

[a] These atoms were refined anisotropically. [b] The cobalt positional parameters are multiplied by 10^5.

the four phosphorus atoms were obtained from a three-dimensional Patterson synthesis. Subsequent Fourier maps revealed all nonhydrogen atoms, including the solvent atoms. The trial structure was refined by a full-matrix least-squares procedure, using the XRY72 crystallographic system kindly supplied by J. M. Stewart, adapted for the University of Florence C.I.I. 10070 computer. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is taken as $1/\sigma(F_o)$. The refinement was undertaken with two isotropic cycles on all nonhydrogen atoms; then further refinement was carried out with the assignment of anisotropic temperature factors to the fluorine atoms and to the coordination polyhedron atoms. At this point the hydrogen atoms were introduced in their calculated positions with B = 6 Å^2, but were not refined. Two final least-squares cycles led to convergence at the discrepancy indices R_1 = 8.9 and R_2 = 9.1%, where R_1 is $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. A final difference synthesis showed no peak higher than 0.7 e/Å^3. Most of the residual electronic density was close to the tetrafluoroborate ion and to the ethanol molecule. The maximum electronic density of a carbon atom on a regular electronic density map was 5.4 e/Å^3.

The estimated standard deviation of an observation of unit weight was 1.85. The positional and thermal parameters along with their estimated standard deviations are in Tables III and IV.

The $[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$ Complex. The structure solution of the complex II proceeded in a similar manner to complex I. A three-dimensional Patterson synthesis revealed the cobalt and phosphorus sites; then all the nonhydrogen atoms were located from a series of Fourier and difference Fourier maps, which were phased by the atoms already located. Isotropic cycles were followed by several mixed cycles, anisotropic for cobalt, phosphorus, fluorine, and oxygen atoms and isotropic for carbon atoms and acetone molecule atoms. The hydrogen atoms were introduced in their calculated positions (B = 6 Å^2), but not refined. The structure converged to a conventional R_1 index = 8.1 and R_2 index = 8.2%. Examination of a final difference Fourier map showed a number of small peaks (all ≤0.8 e/Å^3), generally close to the fluorine atom locations.

The positional and thermal parameters derived from the last cycle of least-squares refinement with their estimated standard deviations are given in Tables V and VI. The tables of the observed and calculated structure factors of both complexes are available.[18]

The Tetrafluoroborate Ions. In the complex I as well in the complex II the tetrafluoroborate ions show a very large vibrational motion and highly disordered fluorine positions. This is responsible for some poor quality in the tetrafluoroborate ion parameters; we notice bond distances considerably shorter than the expected value and angles either too large or too small. Deviations from tetrahedral symmetry in groups

Table IV. Anisotropic Thermal[a] Parameters (× 10 Å^2) with Estimated Standard Deviations in Parentheses for $[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	32 (1)	36 (1)	44 (1)	11 (1)	−2 (1)	1 (1)
P(1)	35 (1)	49 (2)	50 (2)	14 (1)	3 (1)	4 (1)
P(2)	34 (1)	40 (2)	45 (2)	16 (1)	−3 (1)	2 (1)
P(3)	33 (1)	36 (2)	63 (2)	13 (1)	−3 (1)	2 (1)
P(4)	42 (2)	57 (2)	45 (2)	19 (1)	1 (1)	−5 (1)
F(1)	118 (8)	81 (7)	223 (13)	18 (6)	−60 (8)	32 (7)
F(2)	152 (12)	177 (13)	462 (25)	115 (12)	153 (16)	227 (16)
F(3)	413 (28)	392 (26)	317 (26)	312 (24)	277 (24)	168 (21)
F(4)	406 (27)	153 (13)	253 (19)	−86 (15)	−244 (20)	32 (13)
O(1)	31 (3)	37 (3)	35 (4)	11 (3)	−2 (3)	−4 (3)

[a] The temperature factor is defined as: $\exp(-{}^1/_4 \Sigma_{i=1} \Sigma_{j=1} B_{ij} \cdot h_i h_j a_i^* a_j^*)$.

such as tetrafluoroborate or perchlorate ions are not unusual.[19-22] Often some type of orientational disorder is found. On the other hand, since the disorder and the thermal motion of the fluorine atoms are two closely linked phenomena, the temperature factors were not accurate and no vibrational corrections to the B–F bonds have been applied. Some attempts were carried out in order to obtain more information about the statistical disorder of the tetrafluoroborate ions. For instance, in the complex I a difference Fourier map was calculated with F_c values, from which the contribution of the fluorine atoms was omitted. We noticed that one fluorine atom showed an electron density nearly spherical, while the other three fluorine atoms had electron densities lying approximately on the circle passing through the idealized positions of the three fluorine atoms, but in an almost continuum of density. Many attempts were made to find a model which could be well refined, but all were unsuccessful, because the parameters tended to oscillate rather than converge. In addition the very expensive use of the computer induced us to give up a further study on the disorder of the tetrafluoroborate ions in view of the fact that the chemical purpose of our x-ray investigation was satisfactorily reached.

Results and Discussion

In the reactions of the aquo cations of cobalt(II) and nickel(II) with the ligands pp3, np3, and QP the medium used is extremely important in determining the course of the reaction. In fact two different series of products, hydroxo complexes and aquo complexes, are obtained according to whether ethanol or tetrahydrofuran (or acetone) is used as solvent.

For M = cobalt and L = np3, pp3, or QP the schemes suggested for the reactions are the following:

$$[Co(H_2O)_6]^{2+} + 2X^- + L(excess) \xrightarrow{EtOH} [Co(OH)L]X + (HL)^+ + X^- + 5H_2O$$

where X = ClO_4^- and BF_4^-;

$$[Co(H_2O)_6]^{2+} + 2BF_4^- + L \xrightarrow{\text{THF or acetone}} [Co(H_2O)L](BF_4)_2 + 5H_2O$$

When M = nickel the reactions which take place are more complicated but can be classified as follows: L = QP, products analogous to the cobalt case above, both in ethanol and THF; L = np3, in ethanol a series of nonstoichiometric hydrido–metal complexes are produced[23] having the general formula $[NiH_x(np_3)]Y$, where Y = BF_4^-, ClO_4^-, NO_3^- and $0 < x < 1$, no definitive formulas can be given for the products formed in THF; L = pp3, in ethanol analogous hydroxo complexes of formula $[Ni(OH)(pp_3)]X$ are formed, where X = BF_4^- and BPh_4^-. In THF (or acetone) compounds with the composition $[Ni(pp_3)_2](BF_4)_2$ are produced.

Table V. Positional Parameters (× 10^4) and Isotropic Temperature Factors with Estimated Standard Deviations in Parentheses for $[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$

Atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
Co[b]	20393 (6)	32638 (9)	46265 (9)	*a*
P(1)	1929 (1)	2741 (2)	6725 (2)	*a*
P(2)	1676 (1)	4383 (2)	2713 (2)	*a*
P(3)	2449 (1)	1452 (2)	4518 (2)	*a*
P(4)	895 (1)	2610 (2)	5167 (2)	*a*
F(1)	−19 (5)	2782 (7)	830 (8)	*a*
F(2)	−441 (6)	916 (9)	1739 (8)	*a*
F(3)	301 (9)	1386 (10)	2529 (11)	*a*
F(4)	564 (8)	1320 (11)	736 (11)	*a*
F(5)	3466 (5)	6270 (9)	2367 (9)	*a*
F(6)	4191 (8)	7892 (9)	1428 (13)	*a*
F(7)	4102 (15)	6738 (17)	2980 (17)	*a*
F(8)	4501 (10)	6139 (19)	1514 (19)	*a*
O(1)	3031 (3)	4130 (5)	4145 (5)	*a*
C(1)	1094 (5)	1782 (8)	7537 (8)	4.4 (2)
C(2)	467 (5)	2339 (8)	6749 (9)	5.3 (2)
C(3)	717 (5)	3952 (8)	2771 (8)	4.9 (2)
C(4)	261 (5)	3643 (8)	4106 (8)	5.0 (2)
C(5)	1608 (5)	865 (8)	4351 (8)	5.0 (2)
C(6)	885 (5)	1124 (8)	5144 (8)	5.0 (2)
C(7)	2676 (5)	1980 (7)	7620 (7)	3.9 (2)
C(8)	2547 (5)	865 (9)	8701 (9)	5.4 (2)
C(9)	3150 (6)	309 (10)	9390 (10)	6.8 (3)
C(10)	3846 (6)	866 (10)	8982 (10)	6.2 (2)
C(11)	3965 (6)	1957 (9)	7937 (9)	5.8 (2)
C(12)	3383 (5)	2527 (8)	7242 (8)	4.7 (2)
C(13)	1713 (5)	4101 (7)	7018 (7)	3.9 (2)
C(14)	1171 (5)	4075 (8)	8005 (8)	4.8 (2)
C(15)	1070 (6)	5135 (10)	8231 (10)	6.2 (2)
C(16)	1472 (6)	6126 (10)	7486 (10)	6.6 (2)
C(17)	2017 (6)	6176 (10)	6502 (10)	6.3 (2)
C(18)	2140 (5)	5137 (9)	6268 (9)	5.5 (2)
C(19)	1552 (5)	6004 (7)	2342 (8)	4.1 (2)
C(20)	1686 (5)	6414 (8)	3159 (8)	4.9 (2)
C(21)	1610 (6)	7667 (9)	2870 (10)	6.1 (2)
C(22)	1389 (6)	8468 (9)	1735 (10)	6.3 (2)
C(23)	1252 (6)	8077 (10)	953 (10)	6.3 (2)
C(24)	1335 (5)	6832 (9)	1228 (9)	5.4 (2)
C(25)	2254 (5)	4354 (7)	1314 (7)	3.9 (2)
C(26)	2127 (5)	3484 (8)	926 (9)	5.0 (2)
C(27)	2612 (6)	3398 (10)	−69 (10)	6.3 (2)
C(28)	3244 (7)	4126 (11)	−66 (11)	7.3 (3)
C(29)	3357 (6)	5007 (10)	−29 (10)	6.5 (2)
C(30)	2852 (5)	5112 (8)	697 (8)	5.0 (2)
C(31)	2796 (5)	216 (7)	5896 (7)	4.1 (2)
C(32)	2337 (5)	−766 (9)	6802 (9)	5.4 (2)
C(33)	2619 (6)	−1627 (10)	7817 (10)	6.9 (3)
C(34)	3385 (6)	−1554 (10)	7920 (10)	6.6 (2)
C(35)	3812 (6)	−600 (10)	7079 (10)	6.3 (2)
C(36)	3504 (5)	311 (8)	6039 (9)	5.2 (2)
C(37)	3202 (5)	1434 (8)	3246 (8)	4.5 (2)
C(38)	3304 (7)	413 (10)	3016 (11)	7.0 (3)
C(39)	3912 (7)	412 (11)	2036 (12)	7.7 (3)
C(40)	4393 (7)	1345 (11)	1438 (11)	7.9 (3)
C(41)	4286 (6)	2354 (10)	1673 (11)	7.1 (3)
C(42)	3686 (5)	2378 (8)	2590 (9)	5.2 (2)
B(1)	83 (7)	1620 (12)	1580 (12)	6.3 (3)
B(2)	4041 (8)	6847 (13)	1866 (13)	9.1 (3)
		Acetone Molecule		
O(2)	4412 (4)	3058 (7)	4560 (7)	7.7 (2)
C(43)	5568 (13)	2023 (22)	5150 (22)	13.0 (6)
C(44)	5115 (11)	3166 (17)	4461 (17)	8.8 (4)
C(45)	5498 (18)	4238 (29)	4032 (28)	18.9 (1.0)

[a] These atoms were refined anisotropically. [b] The cobalt positional parameters are multiplied by 10^5.

Cobalt Complexes with np3. $[Co(OH)(np_3)]Y$, $[Co(H_2O)(np_3)](BF_4)_2$. From observed magnetic moments in the range 4.2 to 4.5 μ_B a high-spin electronic configuration can be postulated for the cobalt[7] ions. Some clue as to the extent of the distortion in the chromophores is afforded by the electronic reflectance spectra which are composed of four transitions at ca. 6.1–6.7, 10.5–11.1, 13.3–14.1, and 18.9–20.4 kK (see Table VII). The positions of the bands closely resemble the spectrum of the related complex $[CoCl(np_3)]PF_6$,[24] (see Figure 1), known through an x-ray analysis to have a TBP geometry strongly bent toward tetrahedral, and this argues that distortions of comparable magnitudes are operating here.

Table VI. Anisotropic Thermal Parameters ($\times 10$ Å^2) with Estimated Standard Deviations in Parentheses for $[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	29 (1)	30 (1)	30 (1)	−2 (1)	−5 (1)	−12 (1)
P(1)	33 (1)	35 (1)	30 (1)	−4 (1)	−4 (1)	−14 (1)
P(2)	37 (1)	36 (1)	34 (1)	−1 (1)	−11 (1)	−13 (1)
P(3)	47 (1)	31 (1)	35 (1)	1 (1)	−11 (1)	−15 (1)
P(4)	31 (1)	44 (1)	39 (1)	−7 (1)	−6 (1)	−14 (1)
F(1)	159 (7)	71 (4)	108 (5)	18 (4)	2 (5)	−24 (4)
F(2)	191 (9)	193 (8)	96 (5)	−142 (7)	−41 (6)	−5 (5)
F(3)	410 (17)	145 (8)	149 (8)	−110 (10)	−185 (10)	4 (6)
F(4)	244 (12)	154 (9)	159 (9)	82 (9)	37 (8)	−42 (7)
F(5)	109 (6)	148 (7)	143 (7)	−75 (5)	5 (5)	−35 (6)
F(6)	227 (11)	76 (6)	212 (11)	−38 (6)	58 (9)	−24 (6)
F(7)	460 (32)	290 (18)	233 (17)	−196 (20)	−144 (19)	−121 (15)
F(8)	288 (17)	438 (25)	472 (24)	18 (17)	70 (17)	−355 (22)
O(1)	34 (2)	44 (3)	47 (3)	−5 (2)	−4 (2)	−17 (2)

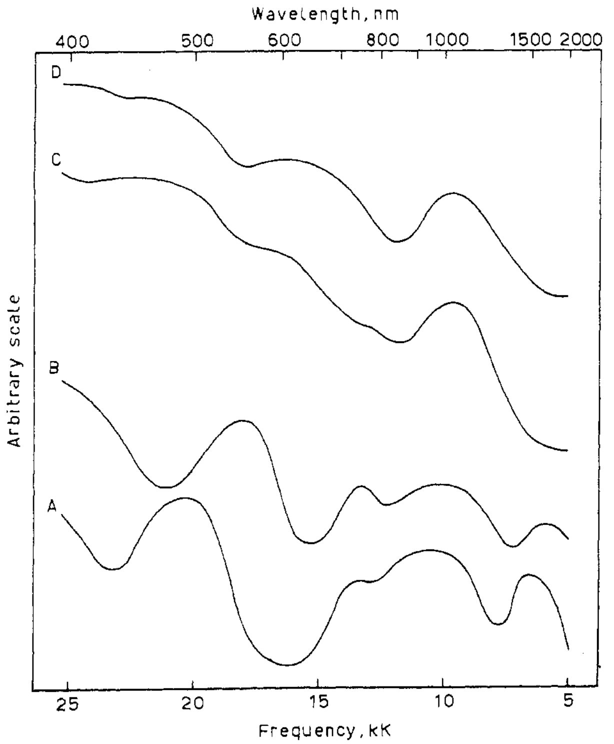

Figure 1. Reflectance spectra of (A) $[Co(OH)(np_3)]BF_4 \cdot C_2H_5OH$, (B) $[CoCl(np_3)]PF_6$, (C) $[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$, and (D) $[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$.

In addition the spectra in nitroethane suggest the solid state geometry is substantially retained in solution.

Spectral transitions are assigned in terms of excitations from an $^2A_2(F)$ ground state to the $^4E(F)$, $^4E(F)$, $^4A_2(P)$, and $^4E(P)$ levels, respectively.[25]

The hydroxo–phosphino and aquo–phosphino complexes behave as 1:1 and 1:2 electrolytes, respectively, in nitroethane in accord with the formulas above.

Cobalt Complexes with pp3. $[Co(OH)(pp_3)]Y$, $[Co(H_2O)(pp_3)](BF_4)_2$. The sudden drop in magnetic moments to the region 1.98 to 2.15 μ_B appropriate for low-spin cobalt(II) is the first sign that contrasting stereochemical factors are important for these complexes. This view is corroborated by the electronic spectra which are composed of four absorptions between 9.5 and 25 kK. The pattern of the bands is in line with similar previously characterized cobalt chromophores having a square-pyramidal geometry.[26] A complete absence of excitations below 9 kK frequencies is typical of these low-spin cobalt(II) complexes.

Table VII. Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

Compd	Absorption max,[a] kK (ϵ_M for soln)
$[Co(OH)(np_3)]ClO_4 \cdot C_2H_5OH$	(a) 6.7, 11.1 sh, 13.3, 19.8 (b) 7.1 (70), 11.1 (128), 13.7 (145) 14.6 sh, 20.0 (410)
$[Co(OH)(np_3)]BF_4 \cdot C_2H_5OH$	(a) 6.5, 10.7, 13.4, 20.4 (b) 6.5 (117), 11.0 (182), 13.3 sh, 13.8 (165), 20.8 (660)
$[Co(OH)(np_3)]BPh_4$	(a) 6.5, 10.7, 13.3 sh, 20.4 (b) 6.5 (115), 10.9 (173), 13.3 sh, 13.8 (155), 20.8 (650)
$[Co(H_2O)(np_3)](BF_4)_2 \cdot THF$	(a) 6.1, 10.5, 14.1, 18.9
$[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$	(a) 9.7, 12.7 sh, 16.9, 22.2 (b) 9.7 (204), 12.5 (133), 16.9 (678), 21.7 (2340)
$[Co(OH)(pp_3)]BPh_4$	(a) 10.0, 15.9 sh, 21.3 (b) 9.7 (215), 12.5 (146), 16.9 (678), 21.3 (2890)
$[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$	(a) 9.5, 16.3, 22.2 sh, 25.0 (b) 10.0 (245), 13.3 sh, 18.2 (850), 25.0 (6400)
$[Co(H_2O)(pp_3)](BF_4)_2 \cdot THF$	(a) 9.7, 13.3 sh, 15.9, 20.8, 25.0 (b) 9.9 (197), 13.3 sh, 18.2 (710), 25.0 (5820)
$[Co(OH)(QP)]BF_4 \cdot C_2H_5OH$	(a) 10.3, 15.9, 20.0, 25.0 (b) 9.9 (306), 16.7 sh, 20.8 (3400)
$[Co(OH)(QP)]BPh_4$	(a) 10.0, 16.7 sh, 20.8, 26.7 sh (b) 10.0 (255), 16.7 sh, 20.8 (3230)
$[Co(H_2O)(QP)](BF_4)_2 \cdot THF$	(a) 9.6, 15.4 sh, 20.0, 25.0 (b) 10.5 (290), 17.4 (1195), 23.0 (5200)
$[Ni(OH)(pp_3)]BF_4 \cdot C_2H_5OH$	(a) 17.8, 25.0 sh (b) 18.5 (3180)
$[Ni(OH)(pp_3)]BPh_4$	(a) 18.5, 24.4 sh (b) 19.6 (4080)
$[Ni(OH)(QP)]BF_4 \cdot C_2H_5OH$	(a) 18.2 (b) 18.5 (4430)
$[Ni(OH)(QP)]BPh_4$	(a) 18.2 (b) 18.3 (5310)
$[Ni(H_2O)(QP)](BF_4)_2 \cdot THF$	(a) 17.4 (b) 19.4 (5700)

[a] Key: a, solid; b, nitroethane solution.

Interpretation of the spectra is made on the basis of transitions from the $(e'')^4(e_a')^2(e_b')^1$ ground state to the $(e'')^4(e_a')^1(e_b')^2$, $(e'')^4(e_a')^2(a_1')^1$, and $(e'')^3(e_a')^2(e_b')^2$ excited states.[27]

The reasoning that chromophores involving pp3 ligand adopt a pentacoordinated square-pyramidal stereochemistry was confirmed by full x-ray determinations performed on two members of the series.

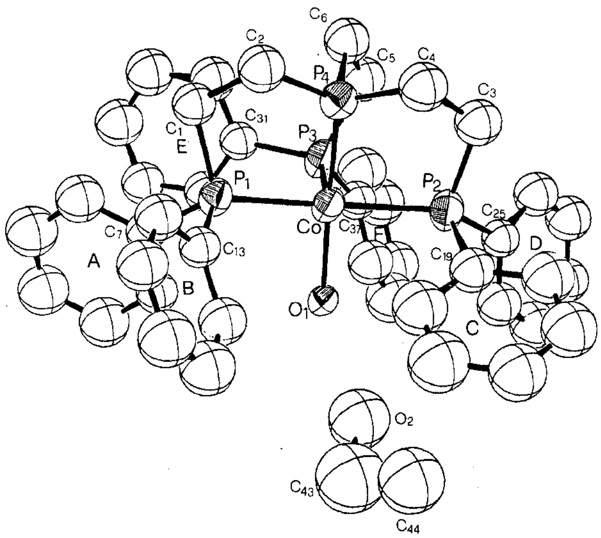

Figure 2. A perspective view of the $[Co(OH)(pp_3)]^+$ cation (ORTEP diagram).

Table VIII. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in the Coordination Polyhedra

	$[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$	$[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$
Co-P(1)	2.268 (3)	2.294 (3)
Co-P(2)	2.249 (4)	2.287 (2)
Co-P(3)	2.291 (4)	2.308 (3)
Co-P(4)	2.133 (4)	2.145 (3)
Co-O(1)	1.873 (7)	2.102 (6)
P(1)-Co-P(2)	150.3 (1)	151.9 (1)
P(1)-Co-P(3)	103.3 (2)	102.8 (1)
P(1)-Co-P(4)	83.7 (1)	83.7 (1)
P(1)-Co-O(1)	92.2 (2)	94.0 (2)
P(2)-Co-P(3)	103.1 (1)	101.3 (1)
P(2)-Co-P(4)	84.5 (1)	83.0 (1)
P(2)-Co-O(1)	93.9 (2)	94.9 (2)
P(3)-Co-P(4)	86.9 (1)	87.9 (1)
P(3)-Co-O(1)	104.7 (3)	101.7 (2)
P(4)-Co-O(1)	168.3 (3)	170.3 (2)

Completely analogous behavior of the hydroxo–phosphino and aquo–phosphino complexes to the high spin counterparts is observed in nitroethane, namely they act as 1:1 and 1:2 electrolytes, respectively.

Description of the Structures of the $[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$ (I) and $[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$ (II) Complexes. The structure of the complex I consists of $[Co(OH)(pp_3)]^+$ cations and BF_4^- anions, while the structure of the complex II consists of $[Co(H_2O)(pp_3)]^{2+}$ cations and BF_4^- anions. Figures 2 and 3 show perspective views of the two cations. Bond distances and bond angles with their estimated standard deviations are given in Tables VIII and IX.

In both the cations the cobalt atom is five coordinated by the four phosphorus atoms of the tripod ligand and one oxygen atom, which pertain to a hydroxide and to a water molecule, respectively. The geometries of the two polyhedra are very similar and can be described as distorted square pyramids, with one of the three peripheral phosphorus atoms of the pp_3 ligand at the apex of the square pyramid and the other phosphorus atoms and the oxygen lying in the basal plane. The coplanarity of the four basal atoms is within 0.18 Å in both the complexes, with the metal atom lying above the plane by 0.37 and 0.34 Å in complexes I and II, respectively. The weighted least-squares planes through the four basal atoms in the same order have equations: $-4.52x + 10.66y - 8.98z = -0.07$ and $-5.46x + 11.13y + 4.90z = 5.13$.

The distortion of the square pyrimid from the limit geometry

Table IX. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in the Remainder of the Molecule

	$[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$	$[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$
	(a) Distances	
P(1)-C(1)	1.82 (2)	1.82 (1)
P(1)-C(7)	1.80 (1)	1.80 (1)
P(1)-C(13)	1.81 (1)	1.84 (1)
P(2)-C(3)	1.80 (1)	1.83 (1)
P(2)-C(19)	1.83 (1)	1.82 (1)
P(2)-C(25)	1.83 (1)	1.81 (1)
P(3)-C(5)	1.82 (2)	1.82 (1)
P(3)-C(31)	1.85 (1)	1.84 (1)
P(3)-C(37)	1.81 (1)	1.83 (2)
P(4)-C(2)	1.92 (1)	1.80 (1)
P(4)-C(4)	1.81 (1)	1.83 (1)
P(4)-C(6)	1.85 (2)	1.83 (1)
C(1)-C(2)	1.46 (2)	1.52 (1)
C(3)-C(4)	1.53 (2)	1.55 (1)
C(5)-C(6)	1.50 (2)	1.54 (1)
B(1)-F(1)	1.28 (2)	1.31 (1)
B(1)-F(2)	1.21 (3)	1.27 (2)
B(1)-F(3)	1.16 (3)	1.19 (2)
B(1)-F(4)	1.15 (3)	1.35 (2)
B(2)-F(5)		1.20 (2)
B(2)-F(6)		1.18 (2)
B(2)-F(7)		1.32 (3)
B(2)-F(8)		1.28 (3)
	(b) Angles	
Co-P(1)-C(1)	109.1 (4)	107.1 (3)
Co-P(1)-C(7)	120.6 (4)	123.7 (3)
Co-P(1)-C(13)	110.8 (5)	110.7 (3)
C(1)-P(1)-C(7)	107.2 (7)	106.1 (3)
C(1)-P(1)-C(13)	103.7 (7)	105.5 (4)
C(7)-P(1)-C(13)	104.0 (6)	102.5 (5)
Co-P(2)-C(3)	108.8 (5)	109.8 (3)
Co-P(2)-C(19)	121.7 (4)	111.7 (3)
Co-P(2)-C(25)	111.7 (3)	120.4 (3)
C(3)-P(2)-C(19)	107.5 (5)	102.8 (4)
C(3)-P(2)-C(25)	105.3 (6)	105.9 (5)
C(19)-P(2)-C(25)	100.5 (6)	104.7 (4)
Co-P(3)-C(5)	104.7 (5)	104.9 (3)
Co-P(3)-C(31)	117.5 (5)	117.5 (4)
Co-P(3)-C(37)	119.7 (4)	120.9 (3)
C(5)-P(3)-C(31)	106.6 (6)	106.1 (4)
C(5)-P(3)-C(37)	106.8 (7)	105.3 (5)
C(31)-P(3)-C(37)	100.5 (6)	100.7 (4)
Co-P(4)-C(2)	110.6 (4)	113.3 (4)
Co-P(4)-C(4)	113.0 (5)	112.6 (3)
Co-P(4)-C(6)	111.0 (4)	110.4 (3)
C(2)-P(4)-C(4)	109.4 (6)	108.4 (4)
C(2)-P(4)-C(6)	105.6 (7)	104.9 (4)
C(4)-P(4)-C(6)	106.8 (6)	106.7 (5)
P(1)-C(1)-C(2)	110.0 (1.2)	107.7 (5)
P(2)-C(3)-C(4)	108.0 (7)	107.4 (8)
P(3)-C(5)-C(6)	110.4 (1.2)	110.7 (8)
P(4)-C(2)-C(1)	103.3 (1.0)	106.3 (6)
P(4)-C(4)-C(3)	107.5 (9)	104.7 (6)
P(4)-C(6)-C(5)	112.0 (1.0)	113.1 (6)
F(1)-B(1)-F(2)	116.0 (1.8)	115.4 (1.2)
F(1)-B(1)-F(3)	118.9 (2.3)	117.3 (1.6)
F(1)-B(1)-F(4)	102.4 (1.9)	97.6 (1.0)
F(2)-B(1)-F(3)	102.2 (2.5)	112.7 (1.1)
F(2)-B(1)-F(4)	107.7 (2.4)	94.5 (1.4)
F(3)-B(1)-F(4)	109.1 (2.4)	116.3 (1.4)
F(5)-B(2)-F(6)		135.0 (1.5)
F(5)-B(2)-F(7)		87.5 (1.5)
F(5)-B(2)-F(8)		103.8 (1.6)
F(6)-B(2)-F(7)		89.0 (1.7)
F(6)-B(2)-F(8)		118.5 (1.5)
F(7)-B(2)-F(8)		113.5 (1.7)
	(c) Mean Distances and Angles in the Benzene Rings	
Ring A	1.36 (2) 120.0 (1.5)	1.39 (1) 120.0 (0.9)
Ring B	1.38 (3) 120.0 (1.7)	1.38 (2) 120.0 (1.0)
Ring C	1.36 (2) 120.0 (1.3)	1.38 (2) 120.0 (1.0)
Ring D	1.37 (2) 120.0 (1.4)	1.38 (2) 120.0 (0.9)
Ring E	1.37 (2) 120.0 (1.3)	1.38 (1) 120.0 (0.9)
Ring F	1.38 (2) 120.0 (1.6)	1.38 (2) 120.0 (1.1)

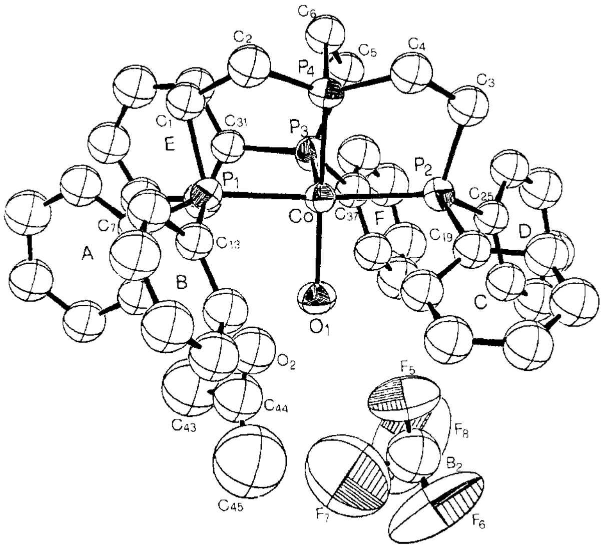

Figure 3. A perspective view of the $[Co(H_2O)(pp_3)]^{2+}$ cation (ORTEP diagram).

is evidenced by the basal P(1)–Co–P(2) angles of 150.3 (1) and 151.9 (1)° in both the complexes, respectively, instead of the idealized 180°. Such a distortion has been already noticed in other low-spin cobalt(II) square-pyramidal complexes, as the $[Co(np_3)I]I$ and $[Co(pp_3)Br]BPh_4$ compounds.[28] The Co–P distances as well as the Co–O(1)(hydro) and Co–O(1)(water) distances agree very well with other analogous bond distances reported in literature.[9,29]

In the $[Co(H_2O)(pp_3)](BF_4)_2\cdot CH_3COCH_3$ complex the oxygen atom of the water group lies at 2.70 Å from the oxygen atom of an acetone molecule and at 2.60 Å from one fluorine of a tetrafluoroborate. These two distances are clearly indicative of hydrogen-bonding interactions. In fact the separation O(1)···O(2) of 2.70 Å is considerably shorter than twice the van der Waals radius of oxygen, as reported by Pauling (2.84 Å) and as reported by Bondi (3.04 Å).[30,31] Also the value of 2.60 Å for the O(1)···F(5) distance is less than the sum of the van der Waals radii of oxygen and fluorine, as reported by Pauling (2.82 Å) and as reported by Bondi (2.99 Å). The existence of hydrogen-bonded water is confirmed by a broad band at 3600 cm^{-1} in the infrared spectrum of the complex.

In the $[Co(OH)(pp_3)]BF_4\cdot C_2H_5OH$ complex the oxygen atom of the hydroxide group lies at 2.61 Å from the oxygen atom of an ethanol molecule. Also in this case the value of the O(1)···O(2) distance suggests hydrogen-bonding interactions, supported by the infrared spectra, which show a broad band at ca. 3600 cm^{-1}.

The difference between the O(1)···O(2) separation (2.70 Å) in complex II and the O(1)···O(2) separation (2.61 Å) in complex I could be attributed to the lower electronegativity of the ketonic group with respect to the hydroxide group; nevertheless the packing forces should not be underestimated.

In complex I the Co–O(1)···O(2) angle is 159.6°. In complex II the two groups hydrogen bonded to the water molecule are arranged so that the Co–O(1)···F(5) and the Co–O(1)···O(2) angles are 130.8 and 126.2°, respectively. It is interesting to note that the value of the F(5)···O(1)···O(2) angle (99.3°) is very close to the angle reported for the water molecule (104°5′). This suggests some linearity in the hydrogen bonds.

The shortest inter- and intra-molecular contacts are given in Table X.

Cobalt Complexes with QP. [Co(OH)(QP)]Y, [Co(H₂O)(QP)](BF₄)₂. Magnetic measurements on these cobalt(II) d^7 complexes show the ions have a moment very close to the value expected for one unpaired electron. The close similarity between the electronic spectra taken in solid phase and nitroethane and those of the complexes containing pp_3 ligand suggests that here also a square-based pyramid stereochemistry exists. Conductivity properties are consistant with the formulations above, since the hydroxo–phosphine and aquo–phosphine derivatives act as 1:1 and 1:2 electrolytes in nitroethane solvent.

Table X. The Shortest Contacts[a] (≤3.4 Å)

$[Co(OH)(pp_3)]BF_4\cdot C_2H_5OH$		$[Co(H_2O)(pp_3)](BF_4)_2\cdot CH_3COCH_3$	
$O(1)\cdots O(2^{I})$	2.61	$O(1)\cdots O(2^{I})$	2.70
$F(1)\cdots C(30^{II})$	3.30	$O(1)\cdots F(5^{I})$	2.60
$F(1)\cdots C(28^{III})$	3.37	$F(2)\cdots C(I^{V})$	3.30
$F(3)\cdots C(5^{I})$	3.40	$F(3)\cdots C(5^{I})$	3.36
$F(4)\cdots C(6^{IV})$	3.26	$F(5)\cdots C(20^{I})$	3.14
		$F(5)\cdots C(30^{I})$	3.34
		$O(2)\cdots C(12^{I})$	3.20
		$O(2)\cdots C(42^{I})$	3.37

[a] Superscripts refer to the following equivalent positions relative to the reference molecule at x,y,z: (I) x,y,z; (II) $\frac{1}{2}+x,y,z$; (III) $\frac{1}{2}-x,\frac{1}{2}-y,-z$; (IV) $\frac{1}{2}-x,-y,-z$; (V) $-x,-y,\frac{1}{2}-z$.

Nickel Complexes with pp₃. [Ni(OH)(pp₃)]Y, [Ni(pp₃)₂](BF₄)₂. Without exception members of the hydroxophosphine nickel series are blue, diamagnetic crystals. A TBP arrangement for the formula unit $[Ni(OH)(pp_3)]^+$ has been proposed on the grounds of characteristic electronic spectra which are principally composed of a single intense band at ca. 17.8–18.5 kK plus a weaker excitation in the vicinity of 25 kK. The molar conductivity values are indicative of 1:1 electrolytes.

Turning attention to the second spectral complex $[Ni(pp_3)_2](BF_4)_2$ according to the stoichiometry and diamagnetism, some sort of square-planar structure can be postulated. Experimentally it is found to be resistant to all solvents, which carries the implication of a polymeric arrangement. If this is true it means that perhaps only some fraction of the total phosphino ligands are actually coordinated to the nickel site.

Nickel Complexes with QP. [Ni(OH)(QP)]Y, [Ni(H₂O)(QP)](BF₄)₂. Very similar features of color and magnetism are observed for this series of phosphino complexes. Both the hydroxo and aquo compounds appear also to have a TBP conformation in common with the latter complexes. The hydroxo complexes behave as 1:1 electrolytes and the aquo derivatives as 1:2 electrolytes.

Conclusions

The extent to which tertiary phosphines behave as π acceptors toward metal ions has been disputed for some time. Arguments for strong π acidity were based principally on the behavior of phosphines in the formation of the metal complexes, in particular the well-known tendency to stabilize metal ions in unusually low oxidation states. Recent physical measurements on phosphine complexes (mainly NMR), however, have led to a decrease in the importance attributed to π contributions.[32]

Phosphines, in fact, bind very readily to metal complexes containing so called "soft" ligands which have a high π-bonding propensity, e.g., CO, NO, N_2, CN^-, isonitriles, etc., whereas the tendency to form metal complexes with strongly electronegative ligands such as F^-, OH^-, and H_2O is much less pronounced. Indeed it is exceptional to find hydroxo or aquo ligands in a metal phosphino chromophore.

The present work shows quite clearly that under suitable conditions it is possible to obtain hydroxo– and aquo–phosphino complexes of 3d metal ions.

The fact that such stable hydroxo and aquo complexes can be obtained comparatively easily suggests that the presence of "soft" ligands is not indispensable for the formation of stable

Table XI. Spin State and Geometry of Some Cobalt(II) Complexes with Tripod Ligands

Donor set	Σn^0	Spin state	Geometry	Ref
$(H_2O)NP_3$[a]	31.87	H	Dist TBP	
$(OH)NP_3$[a]	31.87	H	Dist TBP	
$ClNP_3$	32.51	H	Dist TBP	24
$BrNP_3$	33.65	H	Dist TBP	34
INP_3	34.89	H	Dist TBP	34
		L	Dist SP	28a
$(H_2O)PP_3$	37.56	L	Dist SP	
$(OH)PP_3$	37.56	L	Dist SP	
$ClPP_3$	38.20	L	Dist SP	35
$BrPP_3$	39.34	L	Dist SP	28b

[a] Structure assigned on the basis of spectrophotometric measurements.

phosphino complexes and seems to support the point that π acidity of tertiary phosphines is not a particularly marked characteristic.

Structural and spectromagnetic studies of many five-coordinate complexes of cobalt(II) with tetradentate tripod ligands containing phosphorus donor atoms have shown that these complexes can be either high or low spin.[33] Invariably the high-spin complexes contain a nitrogen as the central atom of the ligand and have a TBP geometry. This nitrogen atom is located far from the cobalt atom, so that the geometry of the complexes is strongly distorted toward the tetrahedron, a situation which favors the high-spin state. The low-spin complexes have a distorted square-pyramidal geometry, which can be accounted for remembering that the ground level of low-spin cobalt(II) complexes of D_{3h} symmetry is anticipated to be orbitally degenerate; subsequent distortion reorientates the molecule toward a square pyramid (symmetry C_{4v} via a C_{2v} intermediate state). A knowledge of the overall nucleophilicity Σn^0 for the five-donor atoms can be a useful guide to predicting stoichiometries, since values of Σn^0 for high- and low-spin species are found to fall on either side of the crossover value 34.89 (high spin < low spin). This critical value is that for the related donor set INP_3. Interestingly the complex cation $[CoI(np_3)]^+$ is known to exist in the solid state in both distorted conformations depending on the nature of the counterion; with I^-, BF_4^-, and PF_6^- the low-spin square pyramidal cation results, while BPh_4^- gives the high-spin distorted TBP form. Table XI shows a series of cobalt chromophores formed by tetradentate tripod ligands for which reliable structural data are available from either x-ray or spectrophotometric measurements. The validity of the above criterion can now be seen in the cases of the complexes $[Co(OH)(pp_3)]^+$ and $[Co(H_2O)(pp_3)]^{2+}$ which, as expected, are low-spin square-pyramidal species. Similarly the chromophores $[Co(OH)(np_3)]^+$ and $[Co(H_2O)(np_3)]^{2+}$, which are both assigned a distorted TBP geometry on the basis of their spectra, fall within the Σn^0 zone of high-spin TBP complexes.

Acknowledgment. Thanks are due to Mr. F. Zanobini for technical assistance and to Mr. F. Nuzzi and G. Vignozzi for microanalyses.

Registry No. $[Co(OH)(np_3)]ClO_4$, 57016-06-5; $[Co(OH)(np_3)]BF_4$, 57016-07-6; $[Co(OH)(np_3)]BPh_4$, 57016-08-7; $[Co(H_2O)(np_3)](BF_4)_2$, 57016-10-1; $[Co(OH)(pp_3)]BF_4\cdot C_2H_2OH$, 57016-13-4; $[Co(OH)(pp_3)]BPh_4$, 57049-21-5; $[Co(H_2O)(pp_3)](BF_4)_2\cdot CH_3COCH_3$, 57016-16-7; $[Co(H_2O)(pp_3)](BF_4)_2$, 57016-15-6; $[Co(OH)(QP)]BF_4$, 57016-18-9; $[Co(OH)(QP)]BPh_4$, 57016-19-0; $[Co(H_2O)(QP)](BF_4)_2$, 57016-21-4; $[Ni(OH)(pp_3)]BF_4$, 57016-23-6; $[Ni(OH)(pp_3)]BPh_4$, 57016-24-7; $[Ni(pp_3)_2](BF_4)_2$, 57016-26-9; $[Ni(OH)(QP)]BF_4$, 57016-28-1; $[Ni(OH)(QP)]BPh_4$, 57016-29-2; $[Ni(H_2O)(QP)](BF_4)_2$, 57016-31-6; $[Co(H_2O)_6](BF_4)_2$, 37041-75-1; $[Ni(H_2O)_6](BF_4)_2$, 14322-78-2.

Supplementary Material Available: Final values of structure factor amplitudes, 43 pages. Ordering information is given on any current masthead page.

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