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2,6-Bis(diphenylphosphinomethyl)pyridine Complexes of Nickel(II), Cobalt(II), Iron(II)

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Some new 2,6-bis(diphenylphosphinomethyl)pyridine (pnp) complexes of nickel(II), cobalt(II) and iron(II) were prepared and their physical properties were determined and compared with those of some previously described nickel(II) complexes. A penta-co-ordinate molecular structure (distorted trigonal bipyramidal), instead of the previous square-planar, is now suggested for $[Ni(pnp)_2]^{2+}$. *For* $Ni(pnp)(NCS)_2$, *previously described as a mixture of low-spin and high-spin forms of a five-co-ordinated molecule, the interallogon formulation* $[Ni(pnp)NCS][Ni(pnp)(NCS)_3]$, *which receives strong support from the experimental data, is suggested. The hexa-co-ordinated* $Ni(pnp)(NO_3)_2$, *the penta-co-ordinated high spin* $Co(pnp)(NO_3)_2$ *and* $Fe(pnp)(NO_3)_2$, *and the hexa-co-ordinated low-spin* $[Co(pnp)_2](ClO_4)_2$ *and* $[Fe(pnp)_2](ClO_4)_2$ *are also described. The equilibrium constant for the hydration reaction of* $Ni(pnp)Cl_2$ *in* n-$BuOH$–H_2O *solution is determined.*

Introduction

In the course of our studies on the reactivity of 2,6-bis(diphenylphosphinomethyl)pyridine (pnp; Hpnp = protonated form) complexes of nickel(II) [1], we have found that the properties of some of the complexes prepared by us did not correspond to those described in the literature [2]. This prompted us to undertake a detailed study both of some of the already described complexes of nickel(II), and of some new iron(II), cobalt(II) and nickel(II) complexes of the terdentate ligand pnp (Table I).

Results and Discussion

Among the 2,6-bis(diphenylphosphinomethyl)-pyridine complexes of nickel(II) described by Dahlhoff and Nelson [2], the compounds $[Ni(pnp)_2](ClO_4)_2$ and $Ni(pnp)(NCS)_2$ attracted our attention because of their intriguing properties. On the basis of its i.r. spectrum (which shows that at least one of the pyridyl groups is not coordinated)

TABLE I. Properties and Analytical Data for the New Complexes.

Compound	Colour	Found % (Calculated values in parentheses)
1 $[Ni(pnp)I]ClO_4$	Deep red	Ni 7.8(7.7); P 8.0(8.1); I 16.8(16.7); Cl 4.5(4.66)
2 $[Ni(pnp)(NCMe)](ClO_4)_2$	Red-brown	Ni 7.5(7.58); P 7.9(8.0); Cl 9.0(9.16)
3 $[Ni(pnp)Py](ClO_4)_2$	Yellow-brown	Ni 7.2(7.23); P 7.5(7.63); N 3.5(3.45); Cl 8.7(8.73)
4 $[Ni(pnp)Py](ClO_4)_2Me_2CO$	Orange	Ni 6.8(6.74); P 7.1(7.12); N 3.2(3.22); Cl 8.2(8.15)
5 $[Ni(pnp)PEtPh_2](ClO_4)_2$	Yellow-brown	Ni 6.2(6.20); P 9.8(9.81); Cl 7.5(7.48)
6 $[Ni(pnp)_2](NO_3)_2$	Light-brown	Ni 5.0(5.18); P 10.8(10.93); N 4.9(4.94)
7 $Ni(pnp)(NO_3)_2$	Blue	Ni 8.9(8.92); P 9.4(9.41); N 6.4(6.38)
8 $[Co(pnp)_2](ClO_4)_2$	Red-brown	Co 4.8(4.88); P 10.1(10.25); Cl 5.7(5.87)
9 $Co(pnp)(NO_3)_2$	Yellow-green	Co 8.9(8.95); P 9.2(9.41); N 6.3(6.38)
10 $[Fe(pnp)_2](ClO_4)_2$	Violet	Fe 4.6(4.63); P 10.1(10.3); Cl 5.85(5.88)
11 $Fe(pnp)(NO_3)_2$	Yellow	Fe 8.4(8.52); P 9.4(9.45); N 6.4(6.41)

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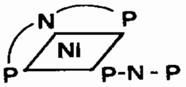
TABLE II. Conductivity, Magnetic Data and I.r. Spectra of the Complexes.

Compound	Λ cm^2 Ω^{-1} mol^{-1}			μ_{eff}/B.M. at 239 K	I.r. absorption bands/cm^{-1}
	Me_2CO	$MeNO_2$	$C_2H_4Cl_2$		
1 $[Ni(pnp)I]ClO_4$	112			diam.	1606(m), 1575(w), 1561(w), 1095(vs), 626(vs)
2 $[Ni(pnp)(NCMe)](ClO_4)_2$		112		diam.	1608(m), 1575(w), 1567(w), 1095(vs), 626(vs)
3 $[Ni(pnp)Py](ClO_4)_2$		120		diam.	1608(m), 1575(w), 1565(w), 1095(vs), 624(vs)
4 $[Ni(pnp)Py](ClO_4)_2Me_2CO$		120		diam.	1608(m), 1576(w), 1567(w), 1707(m), 1095(vs) 626(vs)
5 $[Ni(pnp)PEtPh_2](ClO_4)_2$		128		diam.	1609(m), 1578(w), 1568(w), 1095(vs), 625(vs)
6 $[Ni(pnp)_2](NO_3)_2$		163		0.9	1609(m), 1593(m), 1569(m), 1375(s), 830(s)
7 $Ni(pnp)(NO_3)_2$			0.6	3.10	1604(m), 1570(m), 1485(vs), 1430(vs), 1297(vs), 1268(vs), 1200(vs)
8 $[Co(pnp)_2](ClO_4)_2$		120		2.36	1605(m), 1570(w), 1095(vs), 628(vs)
9 $Co(pnp)(NO_3)_2$		12		4.28	1604(m), 1570(w), 1300(vs), 1278(sh), 1031(s)
10 $[Fe(pnp)_2](ClO_4)_2$		133		1.8–2.1	1605(m), 1570(w), 1095(vs), 628(vs)
11 $Fe(pnp)(NO_3)_2$			0.6	5.39	1600(m), 1569(m), 1440(vs), 1300(vs), 1031(s)

the square-planar structure I has been suggested for the diamagnetic $[Ni(pnp)_2](ClO_4)_2$. For Ni(pnp)-$(NCS)_2$, which shows an anomalously low magnetic moment of 2.2–2.5 B.M., a temperature-dependent equilibrium between low-spin and high-spin forms of a five co-ordinated molecule has been suggested.



I

In a preliminary study, we have found that Job's diagram for the nickel perchlorate/pnp system in acetone (Fig. 1) does not show any evidence of polynuclear species formation as expected, on the basis of the suggested structure I, in presence of an excess of Ni^{2+} ions. However, since in some cases this method can fail to give such evidence, we prepared some new complexes of the type $[Ni(pnp)X]^+$ and $[Ni(pnp)L]^{2+}$ (where X is an anionic and L a neutral ligand) in order to investigate the influence of the fourth ligand on the electronic spectra of the square-planar pnp complexes of nickel(II). The compounds containing the neutral ligands acetonitrile, pyridine or ethyldiphenylphosphine show a strong tendency to crystallize with solvent molecules, which however can be easily removed by heating the compounds at about 100 °C under vacuum. The electronic spectra of the solvated species did not show any difference from those of the corresponding desolvated species. The square-planar structure of these latter compounds is proved by their conductivity and magnetic properties, and by their i.r. spectra (Table II), which show for the pyridine ring vibrations in the 1570–1610 cm^{-1}

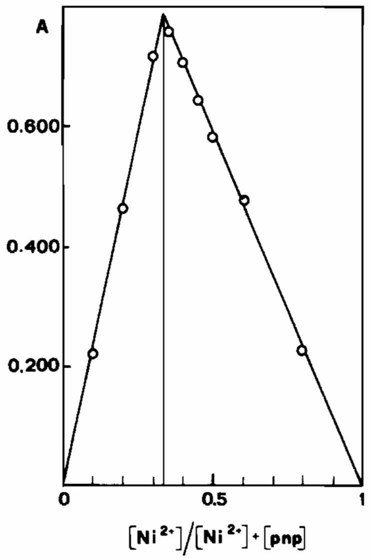


Fig. 1. Job's diagram for the system $Ni(H_2O)_6(ClO_4)_2$ + pnp in Me_2CO. A = absorbance at 454 nm.

TABLE III. Electronic Spectra of the Square-planar Nickel(II) Complexes and of $[Ni(pnp)_2](ClO_4)_2$.

Compound	State	Absorption maxima/kK		Donor set
		This work	from ref. 2	
$[Ni(pnp)I](ClO_4)$	solid	19.5		P_2NI
	CH_2Cl_2	19.1		
	Me_2CO	19.2		
$[Ni(pnp)Br](ClO_4)$	solid	20.5	20.4	P_2NBr
	CH_2Cl_2	20.5		
	Me_2CO	20.6		
	$MeNO_2$		20.7	
$[Ni(pnp)Cl](ClO_4)$	solid	21.3	20.4	P_2NCl
	CH_2Cl_2	21.2		
	Me_2CO	21.2		
	$MeNO_2$		20.8	
$[Ni(pnp)(NCS)](ClO_4)$	solid		21.6	P_2N_2
	$MeNO_2$		21.7	
$[Ni(pnp)NCMe](ClO_4)_2$	solid	23.0		P_2N_2
	CH_2Cl_2	23.0		
$[Ni(pnp)Py](ClO_4)_2$	solid	23.4		P_2N_2
	Me_2CO	24		
$[Ni(pnp)PEtPh_2](ClO_4)_2$	solid	24.4		P_3N
	Me_2CO	24.8		
$[Ni(pnp)_2](ClO_4)_2$	solid	22.4	22	
	CH_2Cl_2	22.4		
	Me_2CO	22.3		
	$MeNO_2$		21.9	

TABLE IV. Electronic Spectra of the Complexes.

Compound	State	Absorption maxima/kK (ϵ_M for solutions)
$[Ni(pnp)_2](NO_3)_2$	solid	22.7
	MeCN	22.5 (1500)
$Ni(pnp)(NO_3)_2$	solid	10.2(sh), 12.1(br), 17.4
	Me_2CO	10.2(sh), 11.6(84), 17.2(77)
$[Co(pnp)_2](ClO_4)_2$	solid	7.1(br), 10.5(sh), 14.2(sh), 18.2(sh), 22.2(sh), 25.3(sh)
	Me_2CO	5.6(sh), 6.2(br, 59), 14.3(sh), 18.2(sh), 22.2(sh)
$Co(pnp)(NO_3)_2$	solid	5.9(sh), 8.3(br), 18.2, 19.8
	$EtNO_2$	8(24), 18.2(136), 19.8(164)
$[Fe(pnp)_2](ClO_4)_2$	solid	18.2
	$EtNO_2$	18.2(510), 24.7(4406)
$Fe(pnp)(NO_3)_2$	solid	5.9(sh), 11.1(br), 16.5(sh)
	$C_2H_4Cl_2$	10.5(46), 16.6(sh)

range the features already recognised to be characteristic of the co-ordinate pyridyl group [2], and a single strong absorption at 1085 cm^{-1} for the not coordinated ClO_4^- ions.

The frequency of the absorption band shown by the electronic spectra of all the square-planar pnp-complexes of nickel(II) so far known (Table III) steadily increases as predicted from the spectro-

TABLE V. Properties of $Ni(pnp)(NCS)_2$ (value in square brackets from ref. 2).

State	I.r. bands/cm^{-1}	absorption max./kK (ϵ_M for solution)	μ_{eff}/B.M. at 293 K
Solid	2105(s), 2090(vs), 2080(s)	6.9, 11.1, 20.8	2.27 ± 0.05
	[2080]	[6.8, 11.0, 20.2, 26.0(sh)]	[2.50]
$EtNO_2$		11.0(22), 12.0(27), 21.5(2380)	
$MeNO_2$		[21.6(2000)]	
Me_2CO/H_2O (6:1)		11.0(18), 12.0(22), 21.1(2260)	2.20
Me_2CO/H_2O (6:1) + KCNS		11.0(30), 12.0(35), 17.2(sh), 21.1(400)	3.28

chemical series of the ligands. In particular, the absorption band shown by $[Ni(pnp)PEtPh_2](ClO_4)_2$ occurs at a frequency higher than that shown by $[Ni(pnp)_2](ClO_4)_2$, suggesting that the proposed square-planar structure I, with a donor set P_3N, should be ruled out for this latter compound.

For comparison with the nickel compound, we prepared the analogous complexes $[Co(pnp)_2](ClO_4)_2$ and $[Fe(pnp)_2](ClO_4)_2$. Although the magnetic susceptibility of the iron complex varied strongly from sample to sample (due to high-spin impurities that we were not able to remove completely) the magnetic and electronic properties (Tables II and IV) of these complexes are typical of low-spin six-co-ordinated cobalt(II) and iron(II) [3]. This molecular structure is confirmed by the i.r. spectra, which show that both the pyridyl groups are co-ordinated to the metal and that the ClO_4^- ions are not co-ordinated.

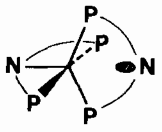
More interesting results were obtained on studying the reactions between the ligand and the nickel nitrate in various solvents. According to the ligand/nickel ratio and the donor strength of the solvent, we obtained the mononuclear species $[Ni(pnp)_2](NO_3)_2$ and $Ni(pnp)(NO_3)_2$. The first compound presents the same features of the corresponding perchlorate, *viz.*, it is diamagnetic, both the nitrato groups are not co-ordinated, and at least one of the pyridyl groups is not co-ordinated.

The room temperature magnetic and electronic properties of $Ni(pnp)(NO_3)_2$ are typical of six-co-ordinated nickel(II). The structure is confirmed by the i.r. spectrum, which shows that the pyridyl group is co-ordinated and that both the nitrato groups are co-ordinated, one as monodentate and the other as bidentate group [4]. In solution this compound is in equilibrium with the $[Ni(pnp)_2](NO_3)_2$ (eqn. 1):

$$2Ni(pnp)(NO_3)_2 + nD = [Ni(pnp)_2]^{2+} + NiD_n^{2+} + 4NO_3^- \quad (1)$$

The equilibrium, which can be easily followed spectroscopically, proceeds to the right with increasing donor strength of the solvent D. In this case we did not observe any evidence of formation of polynuclear species.

It has been suggested [2] that, because of the planarity of the pyridine ring and the α-methylene carbon atoms, the pnp ligand can only co-ordinate in a planar (or approximately planar) fashion; however, the electronic repulsion between the filled d orbitals of the metal and the pyridyl lone pair can force the pyridyl groups to lie well out of the plane defined by the metal and the two binding phosphorus atoms. This occurs in $Ni(pnp)(CO)_2$, which shows in its i.r. spectrum the same features [1] shown in the i.r. spectrum of the $Ni(pnp)_2^{2+}$ moiety and characteristic of a not co-ordinated pyridyl group. The same kind of interaction could occur for a d^8 ion in a very strong ligand field, making a hexa-co-ordinate structure (donor set P_4N_2) unstable in comparison with a low-spin penta-co-ordinate (donor set P_4N) or tetra-co-ordinate (donor set P_3N) molecular structure. Since the electronic spectrum of the $[Ni(pnp)_2]^{2+}$ moiety does not agree with a planar tetra-co-ordinate structure, and since for steric reasons the pnp ligand can only make a P–Ni–P angle not too different from 180° when it co-ordinates through the phosphorus atoms, we suggest for this compound the distorted trigonal bipyramidal structure II, which agrees with the experimental data.



II

In the case of the pnp reaction with cobalt and iron nitrates, only the high-spin compounds $Co(pnp)(NO_3)_2$ and $Fe(pnp)(NO_3)_2$ were prepared by us. Both the electronic [6] and i.r. spectra [4] seem to indicate a penta-co-ordinate molecular structure, with two monodentate co-ordinated nitrato groups, rather than a six-co-ordinate one as in the case of the corresponding nickel compound.

As far as the $Ni(pnp)(NCS)_2$ is concerned, we have investigated its magnetic, electronic and vibrational properties (Table V) on several samples, obtained by different methods or recrystallized from various solvents. The unique nature of the compound was proved by the constancy of the measured values. We have found that the NCS stretching frequencies occur in all the samples as a triplet, the very strong band at 2090 cm^{-1} being accompanied by two less strong bands at 2105 and 2080 cm^{-1}. The weak bands shown by the electronic spectrum of the solid (ascribable to a high-spin component) were still present in the spectra of the nitroethane and acetone solutions. The magnetic susceptibility values of all the samples at room temperature gave a magnetic moment of 2.27 ± 0.05 B.M., not very different from that already reported.

A careful comparison of the electronic spectra of this compound with those of the square-planar diamagnetic $[Ni(pnp)(NCS)]ClO_4$ [2] and the six-co-ordinated paramagnetic $Ni(pnp)(NO_3)_2$ suggests for this compound the interallogon complex structure $[Ni(pnp)NCS][Ni(pnp)(NCS)_3]$. This structure agrees with: a) the strong electronic band at about 21 kK and the weak bands at 11.0 and 12.0 kK, observed both in the solid and in solution; b) the observed magnetic moment, assuming a well reasonable value of about 3.2 B.M. for the paramagnetic component; c) the three NCS stretching frequencies shown by the i.r. spectrum; d) the conductivity in nitromethane, similar to that shown by $[Ni(pnp)NCS](ClO_4)$ in the same solvent [2].

Moreover, we have found that the compound is also paramagnetic in acetone solution, where it shows a magnetic moment per nickel atom, determined by the N.M.R. method [5], of 2.2 B.M., very similar to that of the solid. On adding a slight excess of KCNS to the solution, the magnetic moment per nickel atom increases to 3.28 B.M., a value typical of six-co-ordinate nickel(II), due to the coordination of the NCS^- groups to the square-planar nickel moiety. The transformation of this square-planar moiety into the six-coordinate one is also indicated by the increased absorbance at 11.0 and 12.0 kK, and the strongly decreased absorbance at 21.1 kK.

However, although the interallogon formulation accounts for the experimental findings, other structures (probably easily interconvertible) cannot be completely ruled out for the above compound (such as, for instance, polynuclear species with NCS bridges), due to the great sensitivity shown by all the pnp–nickel(II) complexes to relatively small lattice or solvation effects.

TABLE VI. Absorbance (A) of n-BuOH–H_2O–HCl Solutions of $Ni(pnp)Cl_2$ at 470 nm (ϵ_M in pure n-BuOH = 2110) and 20 °C.

$[Ni] \times 10^4$	$[H_2O]$	$[HCl] \times 10^2$	A	A/A_o
4.275	2.22	0.844	0.753	0.835
4.275	2.22	1.69	0.700	0.776
4.275	2.22	2.53	0.657	0.728
4.275	2.22	3.38	0.634	0.703
4.275	2.22	4.22	0.613	0.680
3.61	2.61	2.53	0.511	0.671
3.61	2.61	3.38	0.479	0.629
3.61	2.61	4.22	0.452	0.594
3.61	2.61	5.06	0.437	0.574
2.706	3.11	1.69	0.341	0.597
2.706	3.11	2.53	0.322	0.564
2.706	3.11	3.38	0.293	0.513
2.706	3.11	4.22	0.275	0.482
2.706	3.11	5.06	0.249	0.436

In the course of our study on the reactivity of the pnp–Ni(II) complexes [1], we noted that the molar absorbance of n-BuOH–H_2O solutions of $Ni(pnp)Cl_2$ varied in an irreproducible manner with the water concentration. In order to obtain stable solutions, showing well reproducible absorbance values, we had to add small amounts of hydrochloric acid to the n-BuOH–H_2O solutions. As shown in Table VI, where [Ni], $[H_2O]$ and [HCl] are the molar concentrations of the total nickel, water and hydrochloric acid, the ratio between the measured absorbance A and the absorbance A_o, calculated from the total concentration of nickel and the molar absorbance of $Ni(pnp)Cl_2$ in pure n-BuOH, decreases with increasing concentrations of both the water and the acid. This suggests that the $[Ni(pnp)Cl]^+$ ion present in solution undergoes hydration and hydrolysis reactions according to the eqns. 2, 3 and 4:

$$[Ni(pnp)Cl]^+ + nH_2O \rightleftharpoons Ni(H_2O)_nCl^+ + pnp \qquad (2)$$

$$Ni(H_2O)_nCl^- + H_2O \rightleftharpoons Ni(H_2O)_nOH^+ + H^+ + Cl^- \qquad (3)$$

$$pnp + H^+ \rightleftharpoons Hpnp^+ \qquad (4)$$

In the presence of an excess of hydrochloric acid we can consider the hydrolysis indicated by eqn. 3 to be practically suppressed. In such a case, eqn. 5, in which K_1 and K_2 are the equilibrium constants of reactions 2 and 4 respectively, can be easily obtained.

$$[Ni]\,\frac{(1 - A/A_o)^2}{A/A_o} = K_1[H_2O]^n + K_1K_2[H_2O]^n[H^+] \qquad (5)$$

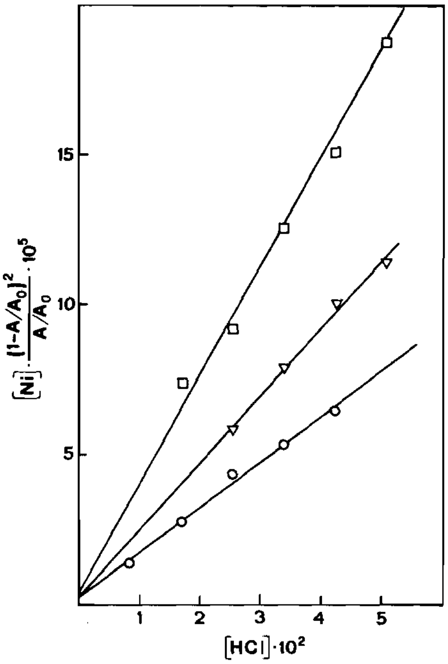


Fig. 2. Plot of $[Ni]A_0(1 - A/A_0)^2/A$ *vs.* [HCl] for the system $Ni(pnp)Cl_2 + H_2O + HCl$ in n-BuOH. $[H_2O]$: ○ 2.22 *M*; △ 2.61 *M*; □ 3.11 *M*.

Indeed, plotting the values of the first member of equation 5 *versus* the total hydrochloric acid concentration*, at constant water concentration, very good linear plots (Fig. 2) were obtained. From the slopes and the intercepts of these plots, calculated from a linear regression analysis, the equilibrium constants and the average number n of water molecules bound (together with n-BuOH) to the nickel ion were evaluated. Within the range of water concentrations used (4–6% v/v), we have found, at 20 °C: $K_1 = 2.3 \times 10^{-7}$; $K_2 = 8 \times 10^2$; $n = 2.63$.

Experimental

All preparations were carried out in deoxygenated solvents and all operations were routinely performed in an atmosphere of purified nitrogen using standard Schlenk techniques. Infrared spectra of nujol mulls were recorded on a Perkin-Elmer 577 instrument and the electronic spectra were recorded on a Varian Cary 219 spectrophotometer, solids as transmittance spectra of Nujol mulls mounted on filter paper, solutions in matched quartz cells. Magnetic susceptibilities were measured by the Faraday method as previously described [7]. The n.m.r. spectrometer was a Varian Associates HA 100 instrument. Electrical conductances were measured in a Pyrex cell with Pt electrodes, which formed one arm of a conventaionl A.C. RC bridge.

[Ni(pnp)I]ClO$_4$

a) A suspension of 0.500 g (0.634 mmol) of $Ni(pnp)I_2$ and of 0.240 g (1.96 mmol) of $NaClO_4$ in acetone (30 ml) was stirred at 50 °C until a deep red solution was obtained (about 2 h). From the filtered solution, concentrated *in vacuo* to about 10 ml, violet crystals were obtained on adding ethanol. The compound was recrystallized from acetone by adding ethanol. b) A suspension of 0.200 g (0.17 mmol) of $[Ni(pnp)_2](ClO_4)_2$ and of 0.054 g (0.17 mmol) of NiI_2 in warm acetone was stirred until a deep red solution was obtained (about 1 h). From the filtered solution violet crystals were obtained and recrystallized as above.

[Ni(pnp)NCMe](ClO$_4$)$_2$

A solution of the ligand (0.235 g; 0.50 mmol) in benzene (10 ml) was added with stirring to a solution of 0.183 g (0.50 mmol) of $Ni(ClO_4)_2\cdot 6H_2O$ in 5 ml of MeCN. The red oil formed was separated, repeatedly washed with benzene and dried under vacuum. The brown microcrystalline product obtained was washed again with benzene and dried *in vacuo*.

[Ni(pnp)Py](ClO$_4$)$_2$·Me$_2$CO

0.476 g (1.0 mmol) of the pnp ligand were added with stirring to a solution of 0.366 g (1.0 mmol) of $Ni(ClO_4)_2\cdot 6H_2O$ and 0.160 g (2.02 mmol) of pyridine in acetone (10 ml). The light orange crystals formed on standing from the red brown solution were filtered off, washed with ethanol and dried at room temperature *in vacuo*. An absorption band at 1705 cm^{-1} shown by the i.r. spectrum of the solid suggested the presence of Me_2CO, which has been confirmed by gas chromatographic analysis of its pyrolysis (260 °C) products (molar ratio $Me_2CO/Ni = 1$).

[Ni(pnp)Py](ClO$_4$)$_2$

This compound has been obtained by heating at 110 °C under vacuum (3 h) the above-cited complex.

[Ni(pnp)PEtPh$_2$](ClO$_4$)$_2$

0.476 g (1.0 mmol) of pnp were added with stirring to a solution of 0.366 g (1.0 mmol) of $Ni(ClO_4)_2\cdot 6H_2O$ and 0.214 g (1 mmol) of $PEtPh_2$ in acetonitrile (15 ml). The brown microcrystalline product precipitated on standing from the brown solution was filtered off, washed with ethanol and dried *in vacuo*.

[Ni(pnp)$_2$](NO$_3$)$_2$

This was prepared by addition of pnp to $Ni(NO_3)_2\cdot 6H_2O$ in $EtOH-H_2O$ (5:1 v/v) in 2:1 ratio. Yellow-brown crystals separated on cooling.

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*Within the range of the used concentration, the hydrochloric acid is completely dissociated in the n-BuOH–H_2O solutions.

$Ni(pnp)(NO_3)_2$

A solution of the ligand (0.476 g; 1.0 mmol) in benzene (10 ml) was added with stirring to a solution of 0.291 g (1.0 mmol) of $Ni(NO_3)_2 \cdot 6H_2O$ in anhydrous ethanol (5 ml). The blue crystals formed on standing from the brown solution were filtered off, washed with C_6H_6 and EtOH, and dried *in vacuo.*

$Ni(pnp)(NCS)_2$

This was prepared both as previously described [2] and by addition of KNCS to $[Ni(pnp)_2](ClO_4)_2$ in acetone in 2:1 ratio.

$[Co(pnp)_2](ClO_4)_2$

This was prepared by addition of pnp to $Co(ClO_4)_2 \cdot 6H_2O$ in acetone in 2:1 ratio. Deep red crystals separated on standing (10 m).

$Co(pnp)(NO_3)_2$

This was prepared from pnp and $Co(NO_3)_2 \cdot 6H_2O$ in benzene–ethanol solution as for the corresponding nickel compound. Yellow-green crystals separated on standing.

$[Fe(pnp)_2](ClO_4)_2$

This was prepared by addition of a solution of the pnp ligand to a solution of $Fe(ClO_4)_2 \cdot 6H_2O$ in ethanol in 2:1 ratio. The violet microcrystalline product separated on standing.

$Fe(pnp)(NO_3)_2$

This was prepared from pnp and iron(II) nitrate in benzene–ethanol as for the corresponding nickel compound. Yellow crystals separated on standing.

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