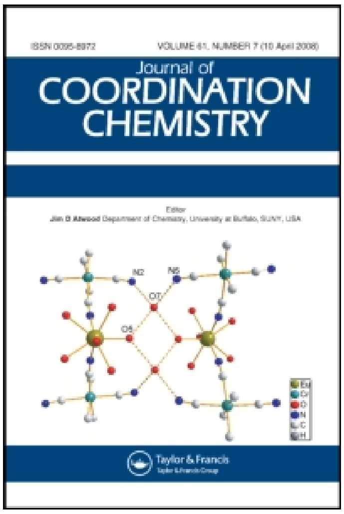

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FIVE-COORDINATION WITH "HYBRID" LIGANDS. PART VIII.[1]

Cobalt(II) and Nickel(II) Complexes with an Open-Chain Tetradentate Nitrogen-Phosphorus Ligand

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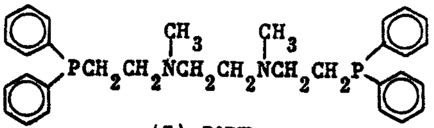
The *open-chain* tetradentate ligand *N,N'*–bis(2-diphenylphosphinoethyl)–*N,N'*-dimethylethylenediamine, (PNNP), forms square planar, five-coordinate and octahedral cobalt(II) and nickel(II) complexes. The five-coordinate complexes, having the general formula [M(PNNP)X]Y (X = halogen, pseudohalogen; Y = Br, I, ClO_4, BPh_4, PF_6) are low-spin and square pyramidal in structure, whereas the corresponding cobalt(II) complexes with the tripod ligand having the same N_2P_2 donor set are high-spin and have a distorted trigonal bipyramidal structure.[5b] It is suggested that square pyramidal symmetry favours the cobalt(II) low-spin ground state.

INTRODUCTION

A large number of five-coordinate cobalt(II) and nickel(II) complexes are formed by tripod-like tetradentate ligands, whose steric requirements impart a high degree of stability to such compounds.[2] These complexes are either low- or high-spin.

In previous work the spin ground state of these complexes has been correlated with some peculiar parameters of the donor atoms, like electronegativity or nucleophilic reactivity constant.[3] As a result, the magnetic cross-over point between high- and low-spin complexes has been identified for each of the metals. Some results, however, suggest that also the stereochemistry greatly influences the spin multiplicity of five-coordinate complexes.[4]

In order to investigate the effects of the geometry of the ligands on the stereochemistry and spin state of the complexes, we have now considered some open-chain tetradentate ligands having steric requirements that differ from the other tripod ligands previously studied.[1, 5] In particular, the tripod ligand *N,N*-bis(2-diphenylphosphinoethyl)-*N',N'*-diethylethylenediamine, having N_2P_2 as donor set, was found to give high-spin cobalt(II) and low-spin nickel(II) complexes.[5b] We have now prepared a ligand containing the same N_2P_2 donor set, but as an open-chain, namely *N,N'*-bis(2-diphenylphosphinoethyl)-*N,N'*-dimethylethylene-diamine (PNNP) (I)



(I) PNNP

This ligand forms four-, five- and six-coordinated complexes with nickel(II) and cobalt(II), which have been characterized.

EXPERIMENTAL SECTION

Synthesis of the Ligand

The ligand was prepared by the reaction

$$2\ KP(C_6H_5)_2\cdot 2\ \text{dioxan} + [ClCH_2CH_2N(CH_3)CH_2-]_2 \rightarrow$$
$$\rightarrow 2\ KCl + [(C_6H_5)_2PCH_2CH_2N(CH_3)CH_2-]_2$$

A 35 g (0.085 moles) sample of $KP(C_6H_5)_2\cdot 2$ dioxan[6] was dissolved under dry nitrogen in 70 ml of anhydrous tetrahydrofuran (THF). About 0.10 moles of $[ClCH_2CH_2N(CH_3)CH_2-]_2\cdot 2\ HCl$, obtained by treatment of the corresponding alcohol with thionyl chloride (m.p. > 300° C; calcd. for $C_8H_{20}N_2Cl_4$: C, 33.59; H, 7.05; N, 9.79; Cl, 49.56; found: C, 33.3; H, 7.3; N, 9.6; Cl, 49.6) were treated with 40% KOH, the amine being freed as an insoluble oil. It was separated and dissolved in a small amount of anhydrous THF. The solution was dried over BaO, and then it was quickly added dropwise with stirring to the orange red solution of

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*To whom correspondence and proofs are to be sent the phosphine salt until a sharp decoloration occurred. The solution was heated under reflux for ten minutes, then concentrated to a small volume on a steam bath. Ether was added to precipitate KCl. The precipitate was filtered off, and after removing the solvent under vacuum, a dense yellow oil was obtained. The pure ligand was crystallized from ligroin as white crystalline powder. (M.p. 64° C; calcd. for $C_{32}H_{38}N_2P_2$: C, 75.03; H, 7.48; N, 5.32; found: C, 75.0; H, 7.5; N, 5.4).

Preparation of the Complexes

The metal complexes were collected on a sintered glass funnel, recrystallized, and dried *in vacuo* at 70°C.

Nickel Complexes

To a solution containing 1 mmole of the appropriate metal salt in 10 ml of hot butan-1-ol, 1 mmole of ligand in 10 ml of the same solvent was added. The solution was filtered and concentrated until crystallization occurred. Cyclohexane was eventually added to induce the precipitation of the complexes. The addition of $NaBPh_4$ or $[(n\text{-}C_4H_9)_4N]PF_6$ to any of the above solutions led to precipitation of $[Ni(PNNP)](BPh_4)_2$ or $[Ni(PNNP)](PF_6)_2$. The compound $[Ni(PNNP)][NiCl_4]$ was prepared from acetone using a metal ligand ratio 2 : 1. The complexes were recrystallyzed from butan-1-ol or acetone. The complex $[Ni(PNNP)]Br_2 \cdot 1.25CHCl_3$ was obtained by recrystallization of [Ni(PNNP]Br]Br from chloroform.

Cobalt Complexes

The preparation of the complexes [Co(PNNP)Br]Br, [Co(PNNP)I]I and $[Co(PNNP)](ClO_4)_2$ was similar to that of the nickel complexes. The $[Co(PNNP)X]BPh_4$ or $[Co(PNNP)Br]PF_6$ complexes were prepared by addition of a stoichiometric amount of ligand in 10 ml of acetone and $NaBPh_4$ or $[(n\text{-}C_4H_9)_4N]PF_6$ in 15 ml of ethanol or butan-1-ol, to a solution of 1 mmole of appropriate metal salt in 20 ml of ethanol or butan-1-ol. The complex $[Co(PNNP)Br]ClO_4$ was prepared by addition of a stoichiometric amount of ligand to a solution containing equimolar amounts of $CoBr_2$ and $Co(ClO_4)_2 \cdot 6\,H_2O$ in butan-1-ol. Recrystallization of these complexes was carried out in acetone-ethanol or acetone-butan-1-ol mixtures.

The complex $[Cosalen \cdot CHCl_3]$ was prepared according to the literature method.[7]

Materials and Physical Measurements

All solvents were reagent grade. All physical measurements were carried out as described previously.[5b, 8]

RESULTS

The complexes, which are reasonably soluble in polar organic solvents (nitro- and chloro-derivatives) are listed in Table I with their elemental analyses. Table II shows the results of magnetic, conductometric and spectrophotometric measurements. Two complexes, [M(PNNP)Br]Br (M=Co, Ni), were found to be isomorphous from X-ray powder photographs.

COBALT(II) COMPLEXES

$[Co(PNNP)](ClO_4)_2$. This low-spin, uni-divalent electrolyte compound (Table II) has band maxima at 1100 and 625 cm^{-1} in the infrared spectrum which are not split, indicating probably uncoordinated ClO_4^-.[9] The reflectance and absorption spectra are very similar, with a broad band at

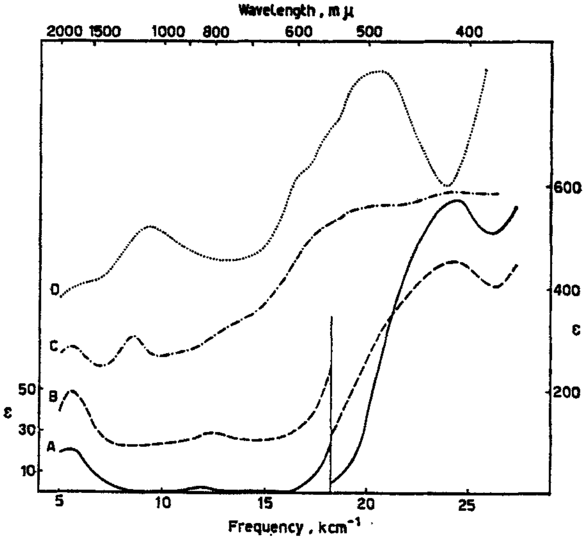


FIGURE 1. Absorption spectrum of 1,2-dichloroethane solution of: A, $[Co(PNNP)](ClO_4)_2$. Reflectance spectrum (arbitrary scale) of: B, $[Co(PNNP)](ClO_4)_2$; C, [Cosalen] · $CHCl_3$; D, $[Co(PNNP)CH_3COO]BPh_4$ ·

TABLE I

Analytical data for the complexes

Compound	Colour	M.p.[a]	% C		% H		% N		% Metal	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
(1) $[Co(PNNP)](ClO_4)_2$	Yellow	172–180	50.01	50.3	4.98	5.3	3.64	3.3	7.64	7.3
(2) $[Co(PNNP)]ClO_4)_2 \cdot CHCl_3$	Yellow	168–172	44.54	44.9	4.42	4.4	3.15	3.4	6.63	6.7
(3) $[Co(PNNP)Cl]BPh_4$	Violet	208–214	72.60	72.7	6.32	6.3	3.02	2.8	6.29	6.6
(4) $[Co(PNNP)Br]Br$	Garnet violet	133–136	52.56	52.2	5.23	5.8	3.83	3.6	8.04	7.4
(5) $[Co(PNNP)Br]BPh_4$	Garnet violet	208–214	69.30	69.5	6.03	6.0	2.89	2.6	6.08	6.3
(6) $[Co(PNNP)Br]PF_6$	Garnet violet	187d	48.38	48.6	4.81	5.4	3.51	3.6	7.40	6.9
(7) $[Co(PNNP)Br]ClO_4$	Garnet violet	212–214	51.25	50.6	5.12	5.0	3.74	3.8	7.85	7.7
(8) $[Co(PNNP)I]I$	Brown	170–175	46.52	46.9	4.64	5.1	3.40	3.5	7.15	7.1
(9) $[Co(PNNP)NCS]BPh_4$	Brown	188–192	72.15	70.7	6.16	6.1	4.43	4.4	6.19	6.3
(10) $[Co(PNNP)CH_3COO]BPh_4$	Cherry-red	177–182	73.50	72.2	6.27	6.4	2.96	2.9	6.20	5.9
(11) $[Ni(PNNP)](ClO_4)_2$	Yellow	>300	50.03	49.3	4.99	5.0	3.64	3.8	7.63	7.6
(12) $[Ni(PNNP)](BPh_4)_2$	Yellow	219–222	79.42	79.3	7.28	7.0	2.32	2.2	4.85	4.9
(13) $[Ni(PNNP)](PF_6)_2$	Yellow	285d	44.62	44.6	4.45	4.7	3.25	3.2	6.84	6.8
(14) $[Ni(PNNP)]I_2$	Yellow	235–242	46.52	46.7	4.64	4.7	3.40	3.2	7.12	7.0
(15) $[Ni(PNNP)Br]Br \cdot 0.5\ C_4HgOH$	Violet	168–172	53.29	53.2	5.39	6.0	3.66	3.5	7.66	7.8
(16) $[Ni(PNNP)]Br_2 \cdot 1.25\ CHCl_3$	Yellowish green	161–164	45.35	45.2	4.49	4.7	3.18	3.1	6.67	6.7
(17) $[Ni(PNNP)][NiCl_4]$	Green	210d	49.80	49.6	4.96	5.2	3.63	3.6	15.20	14.9
(18) $[Ni(PNNP)(NCS)_2]$	Violet	203–207	59.57	59.3	5.58	5.9	8.14	8.2	8.56	8.4

[a] *d* — decomposes.

5.5 kcm^{-1}, one of low intensity at 12.5 kcm^{-1}, and a very intense band at 24 kcm^{-1} (Figure 1, Table II). A similar spectrum is found in square planar bis(salicylaldehyde)ethylenediiminecobalt(II) monochloroformate (Cosalen·$CHCl_3$) (Figure 1), whose structure has been determined by X-ray analysis.[7] On this assumption, a planar structure is assigned to $[Co(PNNP)](ClO_4)_2$.

The complex $[Co(PNNP)](ClO_4)_2 \cdot CHCl_3$, obtained recrystallizing $[Co(PNNP)](ClO_4)_2$ from chloroform, has spectral, conductometric and magnetic properties similar to the unsolvated complex.

[Co(PNNP)X]Y complexes (X=Cl, Br, I, NCS; Y=Br, I, ClO$_4$, BPh$_4$, PF$_6$). These low-spin complexes are uni-univalent electrolytes in nitroethane and have similar reflectance and absorption spectra with two bands in the regions 6.2–7.6 and 20.8–21.5 kcm^{-1}, and a shoulder at 17.5 kcm^{-1} (Figure 2, Table II). These complexes exhibit the usual spectral sequence NCS > Cl > Br > I, which is indicative of metal halogen coordination. The general features of these absorption bands are similar to those reported for low-spin five-coordinated square pyramidal cobalt(II) complexes,[8, 10] e.g. $[Co(PNP)I_2]$, where PNP=Bis(2-diphenyl-phosphinoethyl)amine. The infrared band at 2075 cm^{-1} of $[Co(PNNP)NCS]BPh_4$ is indicative of *N*-bonded non-bridging thiocyanate groups.[11]

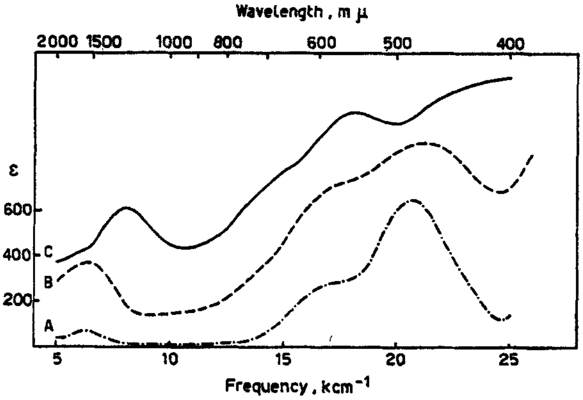


FIGURE 2. Absorption spectrum of 1,2-dichlorethane solution of: A, $[Co(PNNP)Br]BPh_4$. Reflectance spectra (arbitrary scale) of: B, $[Co(PNNP)Br]BPh_4$; C, $[Co(PNP)I_2]$.

An X-ray diffraction study on $[Co(PNNP)Br]PF_6$ has confirmed this hypothesis. The four donor atoms of the ligand are situated in the basal positions of a square pyramid and the halogen in the apex at 2.5 Å from the metal.[12]

The absorption spectra are identical to those obtained by adding a stoichiometric amount of the appropriate tetrabutyl-ammonium halide to a solution of the planar $[Co(PNNP)](ClO_4)_2$ complex.

$[Co(PNNP)CH_3COO]BPh_4$. Conductometric dilution studies on nitroethane solutions of this high-spin complex have shown that this compound follows the Onsager law,[13] the slope of Λ_0–Λ_e *vs.* $\sqrt{c}$ plot being in the range for typical 1 : 1 electrolytes, so excluding the presence of polymeric cations.[14] The reflectance and absorption spectra contains two bands at 9.3 and 20.2 kcm^{-1}, with two shoulders at 17 and 18 kcm^{-1} (Figure 1, Table II). This indicates a six-coordinated distorted chromophore as confirmed by the splitting of the

TABLE II

Physical data for the complexes

Compound	$\mu_{eff.}$ (B.M.)[a]	Λ_M* (cm.^{2} ohm^{-1}) D[b]	N[b]	State[b]	Absorption max. (kcm^{-1}) with ϵ_{molar} for soln. in parentheses[c].
(1) $[Co(PNNP)](ClO_4)_2$	2.18 (18)	8	131	*R*	5.5 vbr, 12.5, 24.1
				D	5.5 vbr (20), 12.5 (4), 24.7 (610)
(2) $[Co(PNNP)](ClO_4)_2 \cdot CHCl_3$	2.22 (24)	—	133	*R*	5.5 vbr, 12.5, 24.1
				D	5.4 vbr (20), 12.5 (4), 24.7 (610)
(3) $[Co(PNNP)Cl]BPh_4$	2.10 (26)	23	49	*R*	6.5, 17.5sh, 21.5
				D	6.7 (69), 17.2sh, 21.0 (695)
(4) $[Co(PNNP)Br]Br$	2.11 (20)	8	66	*R*	6.4, 17.3sh, 21.3
				D	6.5(50), 17.6sh, 20.9(430)
(5) $[Co(PNNP)Br]BPh_4$	2.09 (20)	23	51	*R*	6.4, 17.3sh, 21.3
				D	6.5(65), 17.1sh, 20.8(650)
(6) $[Co(PNNP)Br]PF_6$	2.08 (23)	22	75	*R*	6.4, 17.3sh, 21.2
				D	6.5(60), 17.1sh, 20.9(620)
(7) $Co(PNNP)Br]ClO_4$	2.11 (23)	17	71	*R*	6.4, 17.3sh, 21.2
				D	6.4 (65), 17.1sh, 20.9 (650)
(8) $[Co(PNNP)I]I$	2.00 (23)	12	68	*R*	6.2, 16.1sh, 21sh, 24.4
				D	6.2 (65), 12.8sh, 16.3 (274), 20.8sh, 23.8(1466)
(9) $[Co(PNNP)NCS]BPh_4$	2.16 (21)	21	47	*R*	7.6, 17.4sh, 21.5sh
				D	7.6 (50), 17.5sh, 21.5sh.
(10) $[Co(PNNP)CH_3CO_2]BPh_4$	4.62 (23)	26	50	*R*	9.3, 16.8sh, 18.2sh, 20.5
				D	9.4 (33), 16.5sh, 18.0sh, 20.0 (131)
(11) $[Ni(PNNP)](ClO_4)_2$	diam. (21)	*d*	134[e]	*R*	24.7
				N	23.4 (750)
				W	23.7 (805)
(12) $[Ni(PNNP)](BPh_4)_2$	diam. (21)	*d*	110	*R*	24.0
				N	23.7 (805)
(13) $[Ni(PNNP)](PF_6)_2$	diam. (20)	*d*	156	*R*	24.7
				N	23.5 (750)
(14) $[Ni\ (PNNP)]I_2$	diam. (23)	4.5	119[e]	*R*	26.0
				N	23.5 (760)
(15) $[Ni(PNNP)Br]Br \cdot 0.5\ C_4H_9OH$	diam. (20)	—	61	*R*	16sh, 20.6
				N	15.4sh, 20.2 (390)
(16) $[Ni(PNNP)]Br_2 \cdot 1.25\ CHCl_3$	diam. (21)	—	67	*R*	24.6
				N	15.4sh, 20.2 (390)
(17) $[Ni(PNNP)][NiCl_4]$	3.74 (23)	*d*	39	*R*	7.4, 11.5sh, 15.2, 25.0
				N	6.4 (16) br, 9.2 (30), 10.4 (20), 15.6sh, 20.0 (505)
(18) $[Ni(PNNP)(NCS)_2]$	3.12 (23)	0.4	21	*R*	10sh, 11.6, 18.9
				D	10sh, 11.6 (60), 18.7 (60)

* For ca. 10^{-3} *M* soln. at 20°. Ref. Values: $[Bu^n{}_4N]BPh_4$, 22(*D*), 58(*N*); $[Bu^n{}_4N]_2[NiBr_4]$, 14(*D*), 125(*N*)

[a] Temp. (°C) in parentheses.

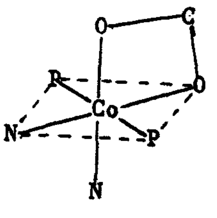
[b] *R* = Diffuse reflectance, *N* = nitroethane, *D* = 1,2-dichloroethane, W = Water

[c] sh = shoulder, v = very, br = broad

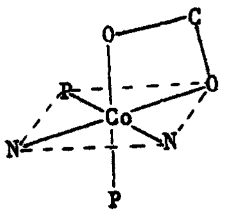
[d] Not soluble.

[e] Molar conductivity in water at 20°: compound (11), 190; (14), 200.

$F \rightarrow P$ transitions (presumably 18 and 20.2 kcm^{-1}) bands. As the acetate ion behaves as a bidentate ligand, the complex must possess one of the two *cis*-α or *cis*-β geometries. Using similar arguments



cis-α



cis-β

advanced for octahedral complexes with tetradentate open-chain ligand triethylenetetramine,[15] which contains three ethylene bridges between the four donor atoms like PNNP, the *cis*-α appears most likely.

NICKEL(II) COMPLEXES

[Ni(PNNP)]Y_2 complexes (Y=ClO_4, PF_6, BPh_4, I). These complexes are all diamagnetic and soluble in nitroethane; the perchlorate and iodide are also soluble in water. In these solvents they are all 1 : 2 electrolytes (Table II). The spectra are similar both in solid state and solution, with a single intense band in the range 23.5–25.0 kcm^{-1} (Table II). These results indicate that the cation $[Ni(PNNP)]^{2+}$ is square planar.

No change occurs in the solution spectra on the addition of pyridine.

[Ni(PNNP)Br]Br·0.5 C_4H_9OH and [Ni(PNNP)]Br_2·1.25 $CHCl_3$. These two diamagnetic complexes have different reflectance spectra. The first compound has a band at 20.6 kcm^{-1} with a shoulder at 16 kcm^{-1} (Figure 3, Table II), which can attributed to a low-spin square pyramidal chromophore.[8, 16] An X-ray structural analysis shows that the chromophore is square pyramidal. The apical halogen is at an unusually large distance (2.8 Å) from the metal.[17]

The reflectance spectra of the chloroformate has only a single band at 24.6 kcm^{-1} diagnostic of the $[Ni(PNNP)]^{2+}$ square planar ion. However, in nitroethane solution, both the complexes are 1 : 1 electrolytes and show identical spectra (Figure 3, Table II), corresponding to the reflectance spectra of five-coordinate [Ni(PNNP)Br]Br compound. This suggests that in solution both the complexes mainly exist as five-coordinate $[Ni(PNN)Br]^+$ species. This spectrum is also identical to that obtained by adding a stoichiometric amount of $[(n\text{-}C_4H_9)_4N]Br$ to a solution of a planar [Ni(PNNP)]Y_2 complex.

Evidently the presence of chloroform in the crystal lattice stabilizes the square planar form.

[Ni(PNNP)][NiCl_4]. The value of $\chi_{Ni(II)}$ is equal to 2925·10^{-6} c.g.s. units at 294° K, which is about half the expected high-spin value for nickel(II). Three bands (7.4, 15.2 and 25.0 kcm^{-1}) are observed in the reflectance spectrum (Figure 3, Table II). The first two bands can be attributed to the tetrahedral $[NiCl_4]^{2-}$ ion,[18] while the third band is due to the planar $[Ni(PNNP)]^{2+}$ cation. Therefore the formula [Ni(PNNP)][NiCl_4] can be assigned to this compound. The results of magnetic measurements are consistent with this hypothesis. Allowing for one nickel in two to be diamagnetic, the value for paramagnetic species is 3.74 BM, compared to 3.8–3.9 BM for compounds of the type $B_2[NiCl_4]$ (B=R_4N^+, Ph_3MeAs^+).[19]

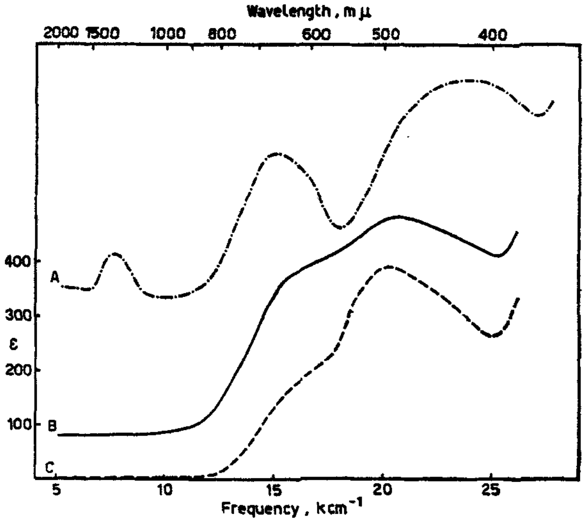


FIGURE 3. Reflectance spectra (arbitrary scale) of: A, [Ni(PNNP)][NiCl_4]; B, [Ni(PNNP)Br]Br. Absorption spectrum of nitroethane solution of: C, [Ni(PNNP)Br]Br.

The absorption spectrum in nitroethane is different from the reflectance spectrum, indicating that the particular species present in the solid state disappears, at least partially, in solution (Table II). Nevertheless, the identification of the species present in solution is not easy.

Conductometric titrations of the square planar

$[Ni(PNNP)](ClO_4)_2$ complex with $[(n\text{-}C_4H_9)_4N]Cl$ in nitroethane give a sharp break at 1 : 1 mole ratio.[14] The spectrum of the resulting solution shows a band at 20 kcm^{-1}, with a shoulder at 16 kcm^{-1}, which is analogous to that of [Ni(PNNP)Br]Br complex, suggesting the presence of the five-coordinate species $[Ni(PNNP)Cl]^+$.

[Ni(PNNP)(NCS)$_2$]. The complex is paramagnetic ($\mu_{eff.}$ = 3.12 BM) monomeric and a non-electrolyte in 1,2-dichloroethane, although it does conduct slightly in nitroethane (Table II). The reflectance and absorption spectra in the former solvent are similar, both showing two bands around 11.6 and 18.9 kcm^{-1} (Table II) and are clearly indicative of a pseudo-octahedral structure.

Three geometries, *trans-*, *cis-α* and *cis-β*, can be proposed. Significantly all attempts to obtain the acetate complex, analogous to the cobalt one, have failed. In every case the resulting products were the planar complexes $[Ni(PNNP)]Y_2$. Consequently, it is suggested that the *trans-* arrangement is the most probable for this complex. This assignment is corroborated by the existence of a non-split band at 2075 cm^{-1} in the region of the ν (C—N) stretching.

DISCUSSION

The ligand *N,N'*-bis(2-diphenylphosphinoethyl)-*N,N'*-dimethyl-ethylenediamine (PNNP) shows a strong tendency to arrange itself with its four donor atoms around the metal in a plane. As a result it is possible for it to form either square planar or five-coordinate square pyramidal complexes. This depend on: (i) the presence or absence of a fifth donor atom, halogen or pseudohalogen; (ii) the presence of a bulky anion as ClO_4^-, BPh_4^-, PF_6^-, I^-; (iii) the nature of the metal, nickel(II) or cobalt(II).

Nickel shows the maximum tendency to give planar complexes not only in the presence of bulky counterions, but also with small anions such as Cl^-. In this case the formation of the $[NiCl_4]^{2-}$ ion permits the stabilization of the planar cation $[Ni(PNNP)]^{2+}$. Cobalt gives square planar complexes only in the absence of halogen ions. If these ions are present, five-coordinated complexes are formed.

The conditions of solid complex formation is shown schematically:

Anions present in solution		Cl	*X* Br	I	*X* + *Y*	*Y*
Coordination number of the complexes in the solid state.	Co		5	5	5	4
	Ni	4	4, 5	4	4	4

Y = ClO_4, BPh_4, PF_6.

Molecular models indicate that the ligand PNNP cannot be arranged around the metal atom to form a trigonal bipyramid, without great strain. The trigonal bipyramid is favored if the four donor atoms of the open-chain ligand are connected through a trimethylene bridge. This is the case with 1,3-bis(3-diphenylphosphinopropylthio)propane, described by Meek and DuBois.[20]

It has been found[5b] that five-coordinated cobalt(II) complexes formed by a tripod ligand, with the same N_2P_2 donor set as the present ligand, are high-spin with a distorted trigonal-bipyramidal geometry. This high-spin state fits in with an empirical rule which relates the spin multiplicity of five-coordinate complexes of cobalt(II) and nickel(II) with tetradentate tripod ligands and the sum of the electronegativities (ΣX) or the overall nucleophilic reactivity constants (Σn^0) of the donor atoms.[3] As the electronegativity of the donor atoms diminishes and the value of the nucleophilic reactivity constants increases, low-spin state is favored. For tripod ligands containing N and P as donor atoms, CoN_3PX, CoN_2P_2X and most $CoNP_3X$ chromophores are high-spin. The magnetic cross-over point corresponds to the $CoNP_3I$ chromophore, which can exist in a high- or low-spin ground state. The five-coordinate square pyramidal complexes described in this paper are low-spin, although the set of donors is the same as for the tripod ligand N_2P_2. It appears from these results that the low-spin state for cobalt(II) is favored by a square pyramidal geometry. The dependence of the magnetic cross-over point on the geometry of the complex has already been pointed out.[3] Further study of the relationship between spin state and geometry of five-coordinated complexes will be reported in short time.

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