Low- and High-Spin Five-Coordinate Cobalt(II) and Nickel(II) Complexes with Tris(2-diphenylphosphinoethyl)amine (NP$_3$)

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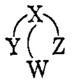
Abstract: The tetradentate "tripod-like" ligand tris(2-diphenylphosphinoethyl)amine (NP$_3$), which has donor atoms that tend to give both low- and high-spin five-coordinate complexes, forms complexes with nickel(II) and cobalt(II) salts of the general formula [M(NP$_3$)X]Y (where X = Cl, Br, I, NCS; Y = X or BPh$_4$). All of the complexes are five-coordinate, probably with a trigonal-bipyramidal structure. The nickel complexes are diamagnetic. The cobalt ones are high spin when X is Cl or Br and low spin when X is NCS. When the set of donor atoms is NP$_3$I, a high-spin complex is obtained when Y is BPh$_4$ and a low-spin complex is formed when Y is I. The set NP$_3$I appears to represent the crossover point between high- and low-spin species. In fact, both these high- and low-spin species are present together in solution in inert solvents.

Until 1965 the problem of the spin multiplicity of the ground state of pentacoordinate nickel(II) and cobalt(II) complexes had not been posed since all the pentacoordinate complexes known at that time were low spin.[1-4] After the first high-spin pentacoordinate complexes had been described,[5,6] it became necessary to study the influence of the nature of the ligand on the magnetic and spectroscopic properties of the complexes. Up to the present time it has been shown that low-spin complexes are formed by ligands with donor atoms of low electronegativity, such as P, As, and C;[1-4,7] while high-spin complexes are formed by ligands having donor atoms of high electronegativity, in particular O and N.[5,6,8] Sulfur participates to both types of complexes.[4,8c] For this reason we have undertaken a systematic study of pentacoordinate complexes with ligands having mixed donor atoms which give complexes of high and low spin. We call these ligands "hybrid" ligands. Among the tetrafunctional ligands of tripod form (I), those with X = P, Y = W = Z = P or As, and X = Y = W = Z = As give low-spin nickel(II)[2,3,9] and cobalt(II)[10] complexes, while those with X = Y = W = Z = N give high-spin complexes.[11] The three equatorial atoms are linked to the central atom X through either *o*-phenylene or alkyl groups. The bonding properties of ligands containing donor atoms of both high- and low-spin character, using sets of donor atoms NP$_3$, NAs$_3$, N$_2$P$_2$, N$_3$P, N$_3$As, etc., have been studied. Preliminary results for nickel complexes with NP$_3$ and NAs$_3$ have already been published.[12] In the present paper we report on the compounds formed between the ligand tris(2-diphenylphosphinoethyl)amine (II) and salts of nickel(II) and cobalt(II).



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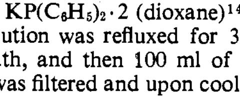

II

Experimental Section

Preparation of the Ligand. In a dry nitrogen atmosphere and at room temperature, 6.10 g of N(CH$_2$CH$_2$Cl)$_3$[13] (0.03 mole) in 30 ml of tetrahydrofuran was dropped slowly into a solution of 40 g (0.1 mole) of KP(C$_6$H$_5$)$_2$·2 (dioxane)[14] in 200 ml of tetrahydrofuran. The solution was refluxed for 30 min and concentrated on a steam bath, and then 100 ml of ethanol was added. The boiling solution was filtered and upon cooling colorless needles separated.

Anal. Calcd for C$_{42}$H$_{42}$NP$_3$: C, 77.15; H, 6.47; P, 14.15. Found: C, 77.39; H, 6.45; P, 14.18.

Preparation of the Complexes [M(NP$_3$)X]BPh$_4$. Stoichiometric amounts of NP$_3$ in 15 ml of acetone and NaBPh$_4$ in 20 ml of ethanol were added to a solution of 1 mmole of the appropriate salt in 20 ml of ethanol (anhydrous salts were used except for NiCl$_2$·6H$_2$O). The complex and the sodium halide precipitated immediately. The complex was recrystallized from a solvent solution which was either CHCl$_3$–ethanol or dimethylformamide–ethanol. The yield was about 80–90%.

[Ni(NP$_3$)Br]Br and [Ni(NP$_3$)I]I. A solution of NP$_3$ (1 mmole) in 20 ml butanol was added to a hot solution of NiX$_2$ (1 mmole) in 20 ml of butanol. Crystals were obtained upon boiling.

[Ni(NP$_3$)Cl]Cl. Solid NP$_3$ (1 mmole) was dissolved in a solution of NiCl$_2$·6H$_2$O (1 mmole) in 20 ml of ethanol. The complex was isolated and recrystallized from a solution of CHCl$_3$ and petroleum ether.

[Ni(NP$_3$)NCS]NCS. A solution of 1 mmole of Ni(NCS)$_2$ in 20 ml of ethanol was mixed with 1 mmole of NP$_3$ in 10 ml of acetone. Crystals were obtained upon the addition of ligroin.

[Co(NP$_3$)Br]Br and [Co(NP$_3$)I]I. These complexes were obtained by concentrating an acetone solution of NP$_3$ and the cobalt salt.

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Table I. Physical and Analytical Data for the Nickel(II) and Cobalt(II) Complexes

Compound	Color	Molar conductance, cm^2/ohm M^a Dichloroethane	Nitroethane	C, % Calcd	Found	H, % Calcd	Found	Metal, % Calcd	Found
$[Ni(NP_3)Cl]Cl^b$	Dark blue	15	55	64.37	64.30	5.41	5.70	7.49	7.46
$[Ni(NP_3)Cl]BPh_4$	Dark blue	21	42	74.29	73.63	5.85	6.04	5.50	5.30
$[Ni(NP_3)Br]Br$	Dark blue	14	60	57.70	57.22	4.85	4.70	6.75	6.69
$[Ni(NP_3)Br]BPh_4$	Dark violet	18	42	71.30	70.96	5.62	5.68	5.28	5.22
$[Ni(NP_3)I]I^c$	Dark violet	16	69	52.15	51.89	4.38	4.76	5.98	5.93
$[Ni(NP_3)I]BPh_4$	Brown violet	18	44	68.40	67.70	5.39	5.66	5.07	5.00
$[Ni(NP_3)NCS]NCS$	Dark blue	13	67	63.80	63.60	5.11	5.39	7.08	7.08
$[Ni(NP_3)NCS]BPh_4$	Dark blue	10	44	73.83	73.80	5.73	5.91	5.39	5.45
$[Co(NP_3)Cl]BPh_4$	Magenta	22	39	74.20	74.04	5.85	5.94	5.52	5.12
$[Co(NP_3)Br]Br^d$	Magenta	18	65	57.70	57.50	4.85	4.90	6.76	6.65
$[Co(NP_3)Br]BPh_4$	Crimson	20	42	71.30	71.44	5.62	5.75	5.30	5.36
$[Co(NP_3)I]I^e$	Brown	19	66	52.15	52.30	4.38	4.50	6.10	5.97
$[Co(NP_3)I]BPh_4$	Dark brown	21	43	68.40	68.67	5.39	5.43	5.09	5.00
$[Co(NP_3)NCS]BPh_4$	Light brown	18	40	73.83	73.90	5.73	5.98	5.41	5.27

[a] For *ca.* 10^{-3} M solutions at 20°. Reference values in 1,2-dichloroethane and nitroethane, respectively, are $[(n\text{-}C_4H_9)_4N]Br$, 19 and 70. [b] Calcd: P, 11.86. Found: P, 12.08. [c] Calcd: P, 9.64. Found: P, 9.93. [d] Calcd: P, 10.64. Found: P, 10.45. [e] Calcd: P, 9.64. Found: P, 9.84.

After a sufficient amount of time (usually overnight), the complexes were obtained directly by filtration from the solution.

Physical Measurements. The apparatus and experimental technique used for the magnetic measurements are described in a previous paper.[15] The Gouy tube was calibrated with freshly distilled water and $Hg[Co(NCS)_4]$.[16] Absorption spectra were recorded in the range 5000–30,000 cm^{-1} with a Beckman DK-2 spectrophotometer using 1-cm silica cells. The diffuse reflectance spectra were measured using the standard Beckmann reflectance attachment and magnesium oxide as the reference. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer employing mulls in Nujol supported on CsBr plates. The molar conductivity values were measured on a WTW Model LBR/B conductance bridge. Concentrations of the solutions were approximately 10^{-3} M.

Results

The compounds are all crystalline, stable in air, and soluble in polar organic solvents such as nitro and chloro derivatives. Table I shows analytical and conductometric data; the latter were obtained using solutions in 1,2-dichloroethane and nitroethane. The results of magnetic measurements on the cobalt complexes are shown in Table II; some are low spin (μ_{eff} = 2.0 BM) while others are high spin (μ_{eff} = 4.25–4.35 BM). The nickel complexes are all diamagnetic. Table III shows the absorption maxima of the electronic spectra in the range 5000–30,000 cm^{-1} for the complexes in the solid state and in solution. The infrared spectra of the complexes $[M(NP_3)NCS]BPh_4$ show a broad band at *ca.* 2090 cm^{-1} indicative of a NCS group linked through nitrogen.[17] In the complex $[Ni(NP_3)NCS]NCS$ there is also a band at 2060 cm^{-1}, characteristic of the free NCS ion.[17]

Table II. Magnetic Susceptibility Data for the Cobalt(II) Complexes

Compound	Temp, °C	$10^6\chi_g$	$10^6\chi_M$	μ_{eff}, BM
$[Co(NP_3)Cl]BPh_4$	20	6.59	7695	4.26
$[Co(NP_3)Br]BPh_4$	20	6.60	8006	4.35
$[Co(NP_3)Br]Br$	20	8.29	7815	4.30
$[Co(NP_3)I]BPh_4$	20	6.37	8064	4.36
$[Co(NP_3)I]I$	18	1.17	1737	2.02
$[Co(NP_3)NCS]BPh_4$	20	0.93	1683	2.00

Discussion

Nickel Complexes. The conductivity data for these complexes in nitroethane and 1,2-dichloroethane indicate that the compounds are essentially 1:1 electrolytes. Some of the complexes in 1,2-dichloroethane solution are partially associated; this is true particularly for the nickel thiocyanates (see Table I). The spectra of the compounds in the solid state and in a 10^{-4} M solution are practically identical, with bands at 13,000 cm^{-1} (ϵ 2000–3000) and 19,000 cm^{-1} (ϵ ~1000) as well as a more intense band with more than one maximum between 25,000 and 30,000 cm^{-1} (Figure 1). Only the diiodo derivative in nitroethane solution shows any diminution in intensity of the first two bands with time, and this is probably due to decomposition. These spectra are typical of low-spin pentacoordinate nickel(II) complexes.[2,3,9,18] Upon assigning the most intense and highest energy band to a charge transfer or to a ligand–ligand transition, the other two bands can be assigned to the three levels arising from the ^1D free ion term in a field of trigonal-bipyramidal symmetry.[19] Using the strong-field formalism, the first two bands correspond to the transitions $(a_1')^2 \rightarrow a_1'e'$ and $(a_1')^2 \rightarrow a_1'e''$ in D_{3h} symmetry.[20] The second band is weaker, in agreement with the fact that this transition is dipole forbidden in this symmetry.

It is interesting to note that the two d–d bands of these NP_3 complexes occur at lower frequencies than do the corresponding bands for complexes with donor atom sets P_4[2] (17,000, 26,600 cm^{-1}), PS_3[3] (15,400, 21,000 cm^{-1}), and PSe_3[18] (15,150, 20,300 cm^{-1}).[21] The mean field of the donor atom set NP_3X is stronger than that of PS_3X since S and Se are lower in the spectrochemical series than N.[22] The pattern of the observed frequen-

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Table III. Spectroscopic Data for the Nickel(II) and Cobalt(II) Complexes

$[Ni(NP_3)Cl]BPh_4$		13,900, 19,000, 26,700 sh
	$C_2H_4Cl_2$	13,900 (2930), 19,050 (820), 27,000 sh, 30,300 (6100)
	$C_2H_5NO_2$	13,900 (2900), 19,350 (780)
$[Ni(NP_3)Cl]Cl$		14,100 19,300, 26,800 sh
	$C_2H_4Cl_2$	13,900 (2930), 19,400 (750), 27,800 sh, 30,300 (6900)
$[Ni(NP_3)Br]BPh_4$		13,400, 18,870, 27,000 sh
	$C_2H_4Cl_2$	13,800 (3052), 18,800 (855), 27,800 sh, 30,300 (6970)
$[Ni(NP_3)Br]Br$		13,300, 18,900, 26,650 sh
	$C_2H_4Cl_2$	13,750, (2780), 18,700 (770), 27,000 sh, 30,300 (7390)
$[Ni(NP_3)I]BPh_4$		13,200 18,150, 23,200 sh
	$C_2H_4Cl_2$	13,150 (2370), 17,850 (1380), 23,000 sh, 27,400 sh
$[Ni(NP_3)I]I$		13,800, 18,850, 22,300 sh, 28,600 sh
	$C_2H_4Cl_2$	13,300 (2300), 18,000 (1380), 22,500 (1180), 27,000 sh, 30,300 (8030)
$[Ni(NP_3)NCS]BPh_4$		15,400, 20,000, 27,500 sh
	$C_2H_4Cl_2$	15,250 (4700), 19,600 (1780), 28,200 sh, 29,400 (6760)
$[Ni(NP_3)NCS]NCS$		15,400, 20,000, 28,500 sh
	$C_2H_4Cl_2$	15,150 (4600), 19,600 (1600), 27,800 sh, 30,300 (6500)
	$C_2H_5NO_2$	15,100 (4800), 19,600 (1450)
$[Co(NP_3)Cl]BPh_4$		5950, 10,000, 13,300, 18,200, 27,400
	$C_2H_4Cl_2$	6000 (89), 10,520 (190), 13,350 (280), 18,500 (860), 27,800 (3840), 29,850 (3910)
$[Co(NP_3)Br]Br$		5900, 10,900, 13,750, 18,170, 26,700
	$C_2H_4Cl_2$	5800 (77), 10,520 (171), 13,500 (250), 17,800 (560), 22,300 sh
$[Co(NP_3)Br]BPh_4$		6100, 10,000, 13,300, 17,850
	$C_2H_4Cl_2$	5960 (84), 10,360 (180), 13,250 (260), 17,800 (660), 22,220 sh
$[Co(NP_3)I]BPh_4$		5590, 10,000, 13,150, 18,200, 27,000
	$C_2H_4Cl_2$	6320 (88), 10,800 (220), 13,400 (246), 18,900 (800), 22,400 sh
	$C_2H_5NO_2$	6300 (87), 10,850 (210), 13,200 (215), 18,900 (750)
$[Co(NP_3)I]I$		6700, 10,600, 16,600 sh, 19,200 sh, 28,600
	$C_2H_4Cl_2$	6700 (100), 11,100 (220), 12,800 sh, 15,900 sh, 22,400 sh
	$C_2H_5NO_2$	6700 (71), 11,350 (165), 12,800 sh, 17,200 sh
$[Co(NP_3)NCS]BPh_4$		8000, 13,000, 19,000, 25,000 sh
	$C_2H_4Cl_2$	7550 (215), 13,340 (380), 19,000 (960), 25,000 sh, 29,200 (9540)
	$C_2H_5NO_2$	7600 (220), 13,300 (390), 19,200 (940)

cies may be attributed to the fact that substitution of the apical donor atom causes the highest perturbation on the ground-state $^1A_1'$ corresponding to two electrons in the d_{z^2} orbital in D_{3h} symmetry.

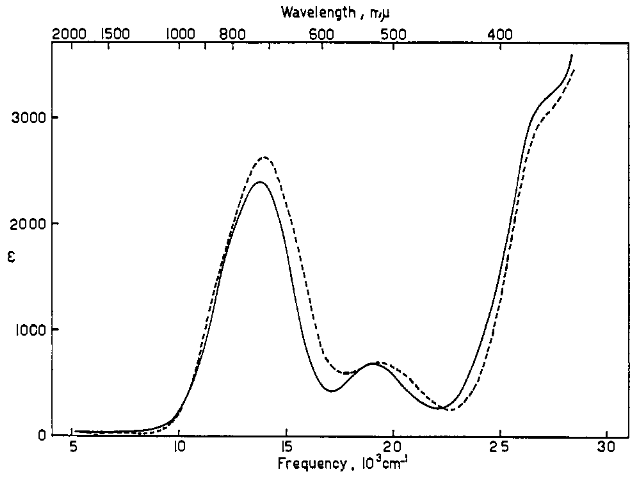

Figure 1. Absorption spectra in nitroethane of $[Ni(NP_3)Cl]BPh_4$ (- - - - -) and $[Ni(NP_3)Br]Br$ (——).

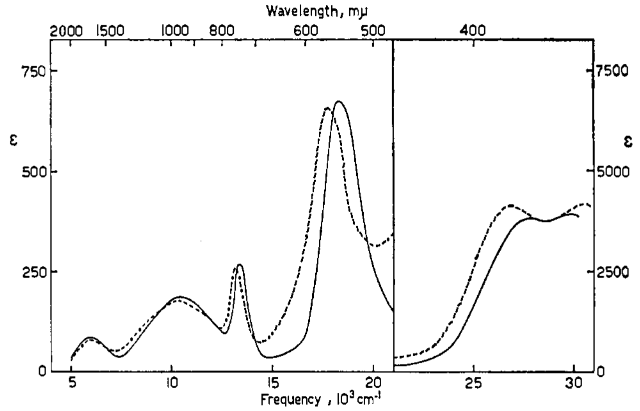

Figure 2. Absorption spectra in 1,2-dichloroethane of $[Co(NP_3)Cl]BPh_4$ (——) and $[Co(NP_3)Br]BPh_4$ (- - - - -).

High-Spin Cobalt Complexes. The complexes $[Co(NP_3)X]BPh_4$, where X = Cl, Br, or I, and the complex $[Co(NP_3)Br]Br$ are all high spin. In solution they behave practically as 1:1 electrolytes. The spectra of all the compounds are almost identical both in the solid state and in solution. The spectra have four well-defined bands at 6000, 10,500, 13,500, and 18,000 cm^{-1} (Figure 2). The features of the spectra as well as the frequencies are very similar to those found in other pentacoordinate cobalt complexes such as bis(N-methylsalicylaldiminato)cobalt (II)[6b] and $[Co(Me_6tren)Br]Br$[11] (Me_6tren = tris(2-dimethylaminoethyl)amine). The spectrum of the latter compound consists of four bands at 5700, 12,300, 16,000, and 19,500 cm^{-1}. Also the magnetic moment values lie in the range usually found for pentacoordinate complexes.

Low-Spin Cobalt Complexes. The two complexes $[Co(NP_3)NCS]BPh_4$ and $[Co(NP_3)I]I$ are low spin with μ_{eff} = 2.0 BM. In solution they are 1:1 electrolytes. The spectrum of the thiocyanate complex has two bands at 8000 and 12,900 cm^{-1}, respectively, and two shoulders at 19,000 and 24,000 cm^{-1} on a more intense band for both solid state and solution (Figure 3). The infrared spectrum shows that the thiocyanate is linked to the metal through nitrogen. The shape of the electronic spectrum is similar to that of the pentacoordinate complex $[Co(QP)Cl]ClO_4$[23] and the band frequencies can be correlated with those of the latter complex at 9700, 16,500, 19,600 and 25,000 (sh) cm^{-1}. The value of the magnetic moment also is lower than the values usually associated with square-planar complexes (2.3–2.9 BM) and falls in the range for low-spin pentacoordinate complexes (2.0–2.5 BM).[24] The fact that the ground state

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(23) QP is tris(*o*-diphenylphosphinophenyl)phosphine.[10]

(24) G. Dyer and D. W. Meek, *J. Am. Chem. Soc.*, **89**, 3983 (1967).

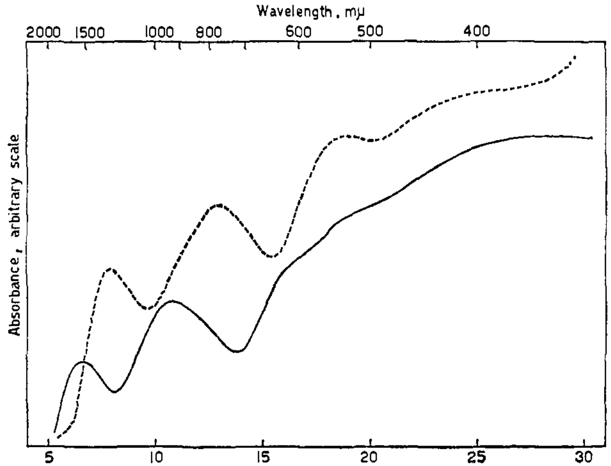

Figure 3. Reflectance spectra of $[Co(NP_3)I]I$ (——) and $[Co(NP_3)NCS]BPh_4$ (- - - - -).

of this NP_3 complex is a doublet can be ascribed to the high-field strength of the NCS group.

The complex $[Co(NP_3)I]I$ has a similar spectrum, with respect to the shape and frequencies of the bands, to that of the thiocyanate complex. The absorption maxima at 6500, 10,700, 16,000, and 20,000 cm^{-1} show the displacement, with respect to the thiocyanate, to be expected from the relative positions of iodide and thiocyanate in the spectrochemical series. Thus it may be concluded that this complex contains the low-spin pentacoordinate ion $[Co(NP_3)I]^+$. On the other hand, the cation $[Co(NP_3)I]^+$ in the compound $[Co(NP_3)I]BPh_4$ is high-spin five-coordinate. This leads to the conclusion that the set of donor atoms NP_3I represents the crossover point between ligands giving high-spin cobalt(II) complexes and those giving low-spin complexes. The difference in the environment caused by the difference in the counteranions is enough to change the spin multiplicity of the complexes.[25]

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[25] The spectrum of the complex $[Co(NP_3)I]I$ in nitroethane solution shows the coexistence of both high- and low-spin species. The relative proportion changes with temperature.

Reactions of Tetracyanoethylene with Hydridoplatinum(II) Complexes[1]

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Abstract: Reactions of tetracyanoethylene (TCNE) with the complexes *trans*-$PtHX(PR_3)_2$ (R = Et, X = Cl, Br, I, NO_2, CN, NCO; R = Ph, X = Cl, Br, I, CN) have been studied under preparative and kinetic conditions. The square-planar complex $Pt(PR_3)_2TCNE$ is obtained in good yield for X = Cl and Br, but only in trace amounts, or not at all, for the other X groups, where the reactions are complicated because of formation of side products. Kinetic data are reported for reactions of the substrates where R = Et, X = Cl and R = Ph, X = Cl, Br, and are interpreted mechanistically in terms of the formation of a 1:1 adduct of TCNE and the platinum substrate *via* a fast preequilibrium step. The subsequent steps are believed to involve either (a) the reductive elimination of HX as the intermediate decomposes or (b) a hydrogen transfer to C_6N_4, followed by an acid-base equilibrium and an internal nucleophilic substitution reaction. For the reaction of *trans*-$PtHCN(PEt_3)_2$ with TCNE, a 1:1 adduct has been isolated and characterized as a hydridoolefinic complex, $PtHCN(PEt_3)_2TCNE$, which is believed to be the type of intermediate formed in homogeneous hydrogenation processes. The stereochemistry of the $PtHCN(PEt_3)_2TCNE$ has been deduced from a comparison of the infrared spectra of the hydrido complex and the analogous deuterated compound, in which a resonance interaction between the C≡N and Pt—H stretching vibrations has been observed.

The role of transitional metal complexes in homogeneous catalytic processes is currently a topic of great interest, from both a fundamental and practical point of view. One of the more prominent catalytic reactions is that whereby olefins may be hydrogenated in the presence of certain transitional metal substrates under very mild conditions. Successful attempts have been made by several workers[3-6] to understand the mechanisms of these reactions in which hydrido complexes are either starting materials or reactive intermediates. Pertinent to this general theme is an understanding of the fundamental principles involved in the reactions of olefins and metal hydrides, and at the present time these principles are by no means clarified.

One general feature which has emerged from studies

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