

Iron(II), Cobalt(II) and Nickel(II) Complexes with the Tripod Ligand Tris(2-dicyclohexylphosphinoethyl)amine

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Received March 4, 1981

The tripod ligand tris(2-dicyclohexylphosphinoethyl)amine (Cynp₃), sterically hindered on the three phosphorus atoms, forms iron(II), cobalt(II) and nickel(II) complexes of general formula [MX(Cynp₃)]Y, (M = Co, Ni; X = Cl, Br, I, NCS; Y = BPh₄. M = Fe; X = Cl, Br, I; Y = BPh₄. M = Co; X = Y = Cl, Br, I, NCS and M = Fe; X = Y = NCS).

The iron complexes are five-coordinate with a trigonal bipyramidal structure. The nickel complexes are four-coordinate (donor set NP₂X) with a square planar geometry and a non-bonded phosphine group. The cobalt complexes [CoX(Cynp₃)]-BPh₄ are high-spin five-coordinate with a distorted trigonal bipyramidal geometry both in the solid state and in solution. In the [CoX(Cynp₃)]X complexes the ligand acts as tetradentate in the solid state, whereas in solution tetrahedral species in which the ligand acts as bidentate (donor set P₂X₂) are also formed. Two isomeric bis-thiocyanate derivatives have been obtained, one blue and one brown. The former is high-spin with a pseudotetrahedral geometry, whereas the latter is low-spin with a trigonal bipyramidal geometry and donor set NP₂(NCS)₂. In solution, both complexes give rise to the same trigonal bipyramidal species.

Introduction

The tripod ligand tris(2-diphenylphosphinoethyl)amine, np₃, has shown interesting properties in forming stable transition metal complexes with a wide range of features [1]. Such complexes are generally mononuclear, the metal ion being four- or five-coordinated. Their coordination polyhedra approach the idealized geometries of the trigonal pyramid [2], trigonal bipyramid [3] and square pyramid [4].

Recently a series of ligands tris(2-dialkylphosphinoethyl)amine (alkyl = methyl [5], ethyl [6]) having the same inner skeleton of np₃ has been synthesized. In their complexes, reduction of the

steric hindrance on the terminal donor atoms has the effect of allowing further donors to bond the metal ion, with an increase of the coordination number up to six, or of stabilizing polynuclear species in which the ligands share their donor atoms among two or three metal ions.

To investigate further the changes of coordinating properties of such tripod ligands on modifying the steric hindrance on the faces of the donor atoms, we have synthesized and characterized iron(II), cobalt(II) and nickel(II) complexes with the ligand tris(2-dicyclohexylphosphinoethyl)amine, Cynp₃, in which each phosphorus atom has a large cone angle [7] due to the two cyclohexyl groups.

Experimental

All the solvents were reagent grade and were used without further purification. Iron(II) and cobalt(II) complexes were synthesized and manipulated under dry nitrogen.

The synthesis of the Cynp₃ ligand has been reported [8].

Physical Measurements

Infrared and electronic spectra, conductivities and magnetic susceptibilities were measured as reported previously [9]. ³¹P n.m.r. spectra were collected on a Varian CFT 20 spectrometer operating at 32.19 MHz with proton noise decoupling and deuterium lock. Positive chemical shifts are downfield relative to H₃PO₄ 0.0 ppm. The chemical shifts are reproducible to 0.1 ppm. Coordination chemical shifts are reported in ppm relative to the corresponding phosphorus in the free ligand (-7.18 ppm).

Analytical, conductometric and magnetic data of the complexes are reported in Table I. Table II lists maxima and extinction coefficients of the electronic spectra. ³¹P{¹H} n.m.r. spectra of the nickel derivatives are reported in Table III.

TABLE I. Analytical and Physical Data for the Complexes.

Compound	Λ_M^a (cm ² /ohm mol)	% Calcd				% Found				μ_{eff} (293 K) μ_B
		C	H	N	M	C	H	N	M	
[FeCl(Cynp ₃)] BPh ₄ ^b	44	72.03	8.98	1.27	5.07	72.01	9.01	1.31		5.22
[FeBr(Cynp ₃)] BPh ₄	44	69.23	8.63	1.22	4.88	69.37	8.80	1.25	4.76	5.16
[FeI(Cynp ₃)] BPh ₄ ^c	45	66.50	8.29	1.18	4.68	66.31	8.19	1.28		5.18
[Fe(NCS) ₂ (Cynp ₃)]	9	61.31	9.12	4.87	6.48	61.32	9.22	4.90		5.20
[CoCl(Cynp ₃)] BPh ₄ ^d	43	71.83	8.95	1.27	5.34	71.64	8.99	1.34	5.19	4.32
[CoBr(Cynp ₃)] BPh ₄	46	69.04	8.60	1.22	4.86	68.94	8.63	1.18		4.49
[CoI(Cynp ₃)] BPh ₄	45	66.33	8.27	1.17	4.93	66.39	8.43	1.12	4.85	4.43
[Co(NCS)(Cynp ₃)] BPh ₄	42	71.45	8.77	2.49	5.23	71.32	8.81	2.40	5.04	4.12
[CoCl(Cynp ₃)] Cl ^e	40	61.53	9.59	1.71	7.19	61.41	9.78	1.73	7.06	4.18
[CoBr(Cynp ₃)] Br	68	55.51	8.65	1.54	6.49	55.56	8.80	1.62	6.35	4.15
[CoI(Cynp ₃)] I	73	50.31	7.84	1.40	5.88	50.19	7.99	1.52	5.64	4.27
[Co(NCS) ₂ (Cynp ₃)] ^f	9	61.09	9.09	4.86	6.81	61.13	9.24	5.03	6.67	2.07
brown isomer										
[Co(NCS) ₂ (Cynp ₃)]	11	61.09	9.09	4.86	6.81	61.19	8.97	5.03	6.73	4.34
blue isomer										
[NiCl(Cynp ₃)] BPh ₄	46	71.84	8.95	1.27	5.32	71.76	8.90	1.31	5.30	diam.
[NiBr(Cynp ₃)] BPh ₄	45	69.06	8.61	1.22	5.12	69.02	8.70	1.24	5.01	diam.
[NiI(Cynp ₃)] BPh ₄ ^g	44	66.34	8.27	1.17	4.91	66.40	8.31	1.16	4.79	diam.
[Ni(NCS)(Cynp ₃)] BPh ₄	45	71.46	8.77	2.49	5.21	71.31	8.79	2.40	5.17	diam.

^aMolar conductance of ca. 10⁻³ solution in nitroethane at 20 °C. ^bCalcd: Cl, 3.22. Found: Cl, 3.15. ^cCalcd: P, 7.80. Found: P, 7.64. ^dCalcd: Cl, 3.21. Found: Cl, 3.15. ^eCalcd: Cl, 8.65. Found: Cl, 8.46. ^fCalcd: S, 7.41; P, 10.74. Found: S, 7.41; P, 10.53. ^gCalcd: I, 10.62. Found: I, 10.47.

TABLE II. Electronic Spectra of the Complexes.

Compound		Absorption Max., KK (ε for soln., 1 mol ⁻¹ cm ⁻¹)
[FeCl(Cynp ₃)] BPh ₄	a	<5.0; 9.2
	b	<5.0; 9.3(60)
[FeBr(Cynp ₃)] BPh ₄	a	<5.0; 9.0
	b	<5.0; 9.1(67)
[FeI(Cynp ₃)] BPh ₄	a	<5.0; 8.7
	b	<5.0; 8.5(49); 16.9(10)
[Fe(NCS) ₂ (Cynp ₃)]	a	<5.0; 8.0
	b	<5.0; 8.1(64)
[NiCl(Cynp ₃)] BPh ₄	a	21.3
	b	21.1(1450)
[NiBr(Cynp ₃)] BPh ₄	a	20.8
	b	20.4(1218)
[NiI(Cynp ₃)] BPh ₄	a	19.4
	b	19.4(1005)
[Ni(NCS)(Cynp ₃)] BPh ₄	a	22.2
	b	22.2(2050)
[CoCl(Cynp ₃)] BPh ₄	a	5.9; 10.3; 13.3; 19.5
	b	5.7(106); 10.4(184); 12.6(320); 14.9(145); 18.5(650)
[CoBr(Cynp ₃)] BPh ₄	a	5.8; 10.1; 13.2; 17.9
	b	5.8(69); 8.3(84); 10.1(94); 13.2(187); 14.7(174); 16.4sh; 17.7(475)
[CoI(Cynp ₃)] BPh ₄	a	5.7; 10.0; 12.9; 17.3; 24.1sh
	b	5.8(75); 8.1(85); 9.4(88); 12.9(204); 15.4sh; 12.2(509)

(continued on facing page)

TABLE II. (continued)

Compound		Absorption Max., KK (ϵ for soln., $l \text{ mol}^{-1} \text{ cm}^{-1}$)
[Co(NCS)(Cynp ₃)]BPh ₄	a	6.0; 10.9sh; 14.0; 19.0
	b	6.2(85); 13.4(151); 16.1(303); 17.2(246); 18.9(313)
[CoCl(Cynp ₃)]Cl	a	5.8; 10.6; 13.3; 14.5sh; 18.7
	b	5.9(93); 10.3(134); 13.4(238); 14.3(197); 15.9sh; 16.7(238) 18.5(466)
[CoBr(Cynp ₃)]Br	a	5.7; 10.8; 13.0; 18.3;
	b	5.2(89); 10.3(142); 13.3(320); 18.0(605)
[CoI(Cynp ₃)]I	a	5.6; 10.5sh; 12.8; 18.2
	b	5.7(85); 10.1(123); 13.1(312); 14.9(132); 17.2(549)
[Co(NCS) ₂ (Cynp ₃)] brown isomer	a	5.9; 9.3; 20.8
	b	5.8(124); 9.0(65); 13.3(44); 16.1sh; 20.0sh
[Co(NCS) ₂ (Cynp ₃)] blue isomer	a	6.3; 7.4; 10.0; 14.5; 17.5
	b	5.8(120); 9.0(65); 13.3(42); 16.1sh; 20.0sh

^a Reflectance spectra. ^b Nitroethane solution.

TABLE III. ³¹P{¹H} NMR Spectral Data for the Nickel Complexes.

Compound	Chemical shifts, ppm ^a			Coord. Chem. Shift, ΔP^b	
[NiCl(Cynp ₃)]BPh ₄	51.80(2)	40.29(10)	-6.49(5)	58.96	47.45
[NiBr(Cynp ₃)]BPh ₄	52.90(1.8)	43.37(10)	-6.50(5)	60.06	50.33
[NiI(Cynp ₃)]BPh ₄	53.33(1.5)	49.56(10)	-6.50(5)	60.50	56.72

^a Chemical shifts are relative to 85% H₃PO₄; positive chemical shifts are downfield; values in parentheses are the relative intensities of the three resonances. ^b $\Delta P = \delta P_{\text{coord.}} - \delta P_{\text{free ligand}}$. Samples were dissolved in CDCl₃.

Synthesis of the Complexes

[MX(Cynp₃)]BPh₄. (*M* = Co, Ni; *X* = Cl, Br, I, NCS; *M* = Fe; *X* = Cl, Br, I)

The ligand (1 mmol) dissolved in acetone (30 ml) was added to a solution of the appropriate hydrated metal halide or pseudohalide (1 mmol) in ethanol (20 ml); sodium tetraphenylborate (1 mmol) dissolved in ethanol (10 ml) was then added and the resulting solution was concentrated until crystallization occurred. All the complexes were recrystallized from acetone-ethanol.

[CoX(Cynp₃)]X (*X* = Cl, Br, I)

The ligand (1 mmol) dissolved in ethanol (30 ml) was added to a solution of hydrated cobalt(II) halide (1 mmol) in ethanol (20 ml). The complexes, obtained by concentrating the resulting solution, were recrystallized from ethanol.

[Fe(NCS)₂(Cynp₃)]

A solution containing the ligand (1 mmol) in acetone (20 ml) was added to a filtered solution of iron(II) bromide (1 mmol) and potassium thiocyanate (2 mmol) in ethanol (30 ml).

The crystalline product, obtained by evaporation of the solvent, was recrystallized from acetone and ethanol.

[Co(NCS)₂(Cynp₃)], brown isomer

This derivative was prepared as the previously described bis-halide cobalt(II) complexes.

[Co(NCS)₂(Cynp₃)], light blue isomer

The compound was prepared by adding the solid ligand (1 mmol) to a solution of hydrated Co(NCS)₂ (1 mmol) in acetone (30 ml). Blue needles were obtained by addition of methanol (10 ml) and concentration.

Results and Discussion

Nickel(II) Complexes

All the complexes are diamagnetic in the solid state and soluble in the common organic solvents. In nitroethane solution they behave as 1:1 electrolytes [10], Table I. In the thiocyanate derivative the pseudohalide is N-bonded to the metal ($\nu(\text{CN}) = 2080 \text{ cm}^{-1}$) [11]. Spectral data of the complexes

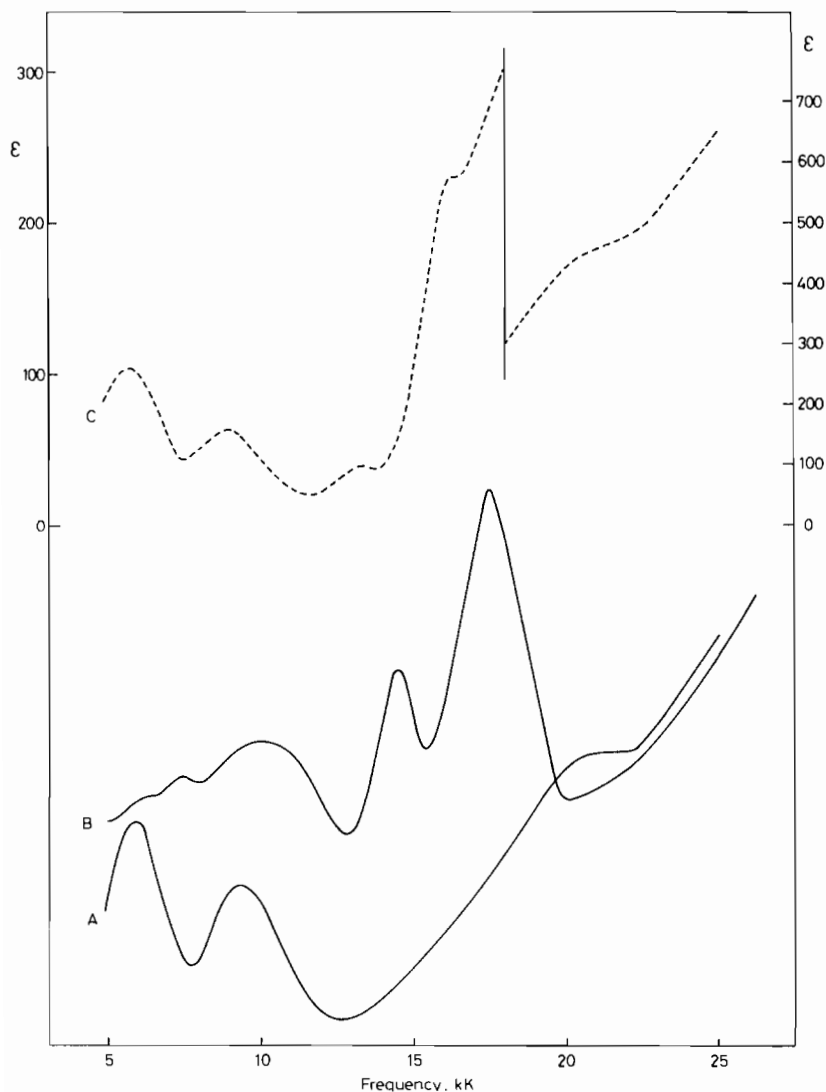


Fig. 1. Absorption spectra of nitroethane solutions of $[\text{CoCl}_2(\text{NOP}_2)]$ (curve A) and of $[\text{CoCl}(\text{Cynp}_3)]\text{Cl}$ (curve B). Reflectance spectra (arbitrary scale) of $[\text{CoCl}(\text{np}_3)]\text{Cl}$ (curve C) and of $[\text{CoCl}(\text{Cynp}_3)]\text{Cl}$ (curve D).

are consistent with a square planar geometry both in the solid state and in solution (Table II). It is reasonable to assume that one of the phosphorus atoms is not bound to the metal, the ligand acting as tridentate with a NP_2 donor set. This is supported by the similarity of these spectra to that exhibited by the $[\text{NiBr}(\text{Pr-PNP})]\text{BPh}_4$ complex [12] (square planar chromophore NiNP_2X ; Pr-PNP = N,N-bis(2-diphenylphosphinoethyl)-n-propylamine).

$^{31}\text{P}\{^1\text{H}\}$ spectra of the complexes (Table III) show a resonance at -6.50 ppm, close to the value of the chemical shift of the free ligand (-7.18 ppm), and two single sharp resonances with positive chemical shifts in the expected region for coordinated phosphorus atoms. The relative intensities of the three resonances for the chloro-derivative are 2:10:5 (Table III). On going from the chloro- to the iodo-derivative

the intensity of the resonance at lowest field decreases, whereas the relative intensities of the other two resonances do not change (Table III). This resonance pattern shows that two species are present in solution. The constant ratio (2:1) between the strongest resonance and that corresponding to the dangling phosphorus atom indicate that they are mutually related and originate from a square planar species having two bound and one free phosphorus atom. The other resonance should be assigned to a trigonal bipyramidal cation whose concentration, relative to that of the square planar species, decreased with increasing halogen size. The intensity ratio of the resonances corresponding to the coordinated phosphorus atoms, taking into account the different number of phosphorus atoms involved, indicates that the ratio between the concentration

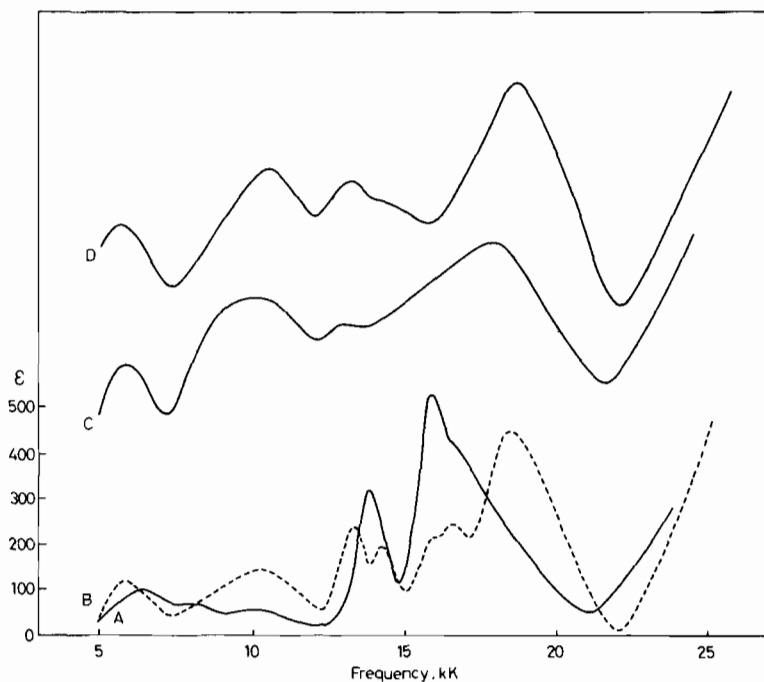


Fig. 2. Reflectance spectra (arbitrary scale) of $[\text{Co}(\text{NCS})_2(\text{Cynp}_3)]$, brown isomer (curve A) and of $[\text{Co}(\text{NCS})_2(\text{Cynp}_3)]$, blue isomer (curve B). Absorption spectrum of nitroethane solution of $[\text{Co}(\text{NCS})_2(\text{Cynp}_3)]$ (curve C).

of the trigonal bipyramidal and square planar cations is approximately 1:10.

Cobalt Complexes

$[\text{CoX}(\text{Cynp}_3)]\text{BPh}_4$ ($X = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$)

All these complexes are high-spin in the solid state, and 1:1 electrolytes in nitroethane. The infrared spectrum of the thiocyanate derivative shows that the NCS ion is N-bonded to the metal ($\nu(\text{CN}) = 2030 \text{ cm}^{-1}$). The shapes of the electronic spectra of these compounds are all similar and characteristic of five-coordinate high-spin cobalt(II) complexes with trigonal bipyramidal geometry [13]. It should be recalled that the analogous thiocyanate complex with the phenylated ligand np_3 is low-spin, and that the $[\text{CoI}(\text{np}_3)]^+$ cation is at the cross-over point between high- and low-spin states, being high-spin when the counterion is BPh_4 and low-spin with I^- as counterion [4]. The high-spin state of all the Cynp_3 derivatives can hardly be accounted for by the different overall nucleophilicity [14] of phosphorus atoms according to whether they bear aromatic (np_3) or aliphatic (Cynp_3) substituents. Rather, a higher distortion towards a tetrahedron, which stabilizes the high-spin state, can explain the spin state of the Cynp_3 complexes [1]. Such a distortion is in accordance with the larger cone angle of phosphorus donors in the Cynp_3 ligand with respect to the same donors in the np_3 ligand. This hypothesis is also supported by the formation of variable amounts of tetrahedral

species in solution (band at *ca.* 14.7 and shoulder at 16.9 kK, see Table II), which may originate from the detachment of the apical nitrogen donor atom (donor set P_3X); these species have not been observed in the np_3 cobalt complexes.

$[\text{CoX}(\text{Cynp}_3)]\text{X}$ ($X = \text{Cl}, \text{Br}, \text{I}$)

The reflectance spectra of these complexes are identical to those found for the analogous complexes with tetraphenylborate as counterion, and suggest an ionic structure containing the five-coordinate cation $[\text{CoX}(\text{Cynp}_3)]^+$, still distorted towards the tetrahedron as accounted for by the high-spin state. The bromide and iodide derivatives behave as 1:1 electrolytes in nitroethane solution, and their electronic spectra in this solvent are the same as in the solid state, thus indicating that the trigonal bipyramidal geometry is essentially retained. The chloro-derivative has a remarkably lower conductivity (Table I), and its absorption spectrum shows bands at 14.3 and at 16.7 kK, which are typical of pseudotetrahedral species (Fig. 1). The intensity of these bands rise at the expense of the five-coordinate bands upon addition of chloride ions. This behaviour suggests that the pseudotetrahedral species is formed through coordination of a further chloride ion and detachment of two donor atoms of the ligand (one phosphorus atom and, presumably, the nitrogen atom) leaving a donor set P_2X_2 . This hypothesis is supported by the correspondence of the bands attributed to the pseudotetrahedral species to those

exhibited by the $[\text{CoX}_2(\text{NOP}_2)]$ complexes ($\text{X} = \text{Cl}, \text{Br}$; $\text{NOP}_2 = \text{N,N-bis(2-diphenylphosphinoethyl)-2'-methoxyethylamine}$) having the same pseudotetrahedral geometry and donor set [12] (Fig. 1).

$[\text{Co}(\text{NCS})_2(\text{Cynp}_3)]$

Two isomeric compounds with this formula have been obtained depending on the experimental conditions: one brown (low-spin) and one blue (high-spin) (Table I). The infrared spectra of both derivatives in the 2000 cm^{-1} region show intense bands at 2090, 2085 and at 2085, 2065, 2040 cm^{-1} for the brown and blue derivative, respectively; these bands are indicative of multiple N-bonded, non-equivalent, non-bridging thiocyanate groups. The reflectance spectra of the two compounds suggest a pseudotetrahedral geometry (C_{2v} symmetry) for the high-spin derivative and a trigonal bipyramidal geometry for the low-spin complex (Fig. 2). In solution, both complexes are practically non-electrolytes and give rise to the same spectrum, *i.e.* that of the low-spin species. This is similar to that of the pentacoordinate complex $[\text{Co}(\text{NCS})_2(\text{Pr-PNP})]$ [12], having a donor set $\text{NP}_2(\text{NCS})_2$ (Fig. 2). As it often happens, both NCS ions get in the coordination sphere of the metal ion [1, 12], but their reduced steric hindrance is not enough to induce the detachment of two donor atoms to give tetrahedral species unless solid-state factors are effective, as in the blue isomer.

Iron Complexes

$[\text{FeX}(\text{Cynp}_3)]\text{BPh}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)

These complexes are all high-spin, and 1:1 electrolytes in nitroethane solution. Their diffusion reflectance and adsorption spectra are practically identical, and typical of a five-coordinate chromophore with trigonal bipyramidal geometry [15].

$[\text{Fe}(\text{NCS})_2(\text{Cynp}_3)]$

Also this complex is five-coordinate, both in the solid state and in solution, as shown by its electronic spectra (Table II). It is, however, practically a non-electrolyte like its cobalt analogue: this again indicates that five-coordination can only be attained by detachment of a donor atom of the ligand, probably a phosphorus atom. This behaviour contrast with that of analogous phenylated ligands which invariably give six-coordinate octahedral complexes $[\text{Fe}(\text{NCS})_2\text{-L}]$, $\text{L} = \text{np}_3, \text{pp}_3, \text{QP}$ ($\text{pp}_3 = \text{tris(2-diphenylphosphinoethyl)phosphine}$, $\text{QP} = \text{tris}(o\text{-diphenylphosphinophenyl)phosphine}$) [1], and it should be correlated to the increased steric hindrance of the Cynp_3 ligand.

Conclusions

The ligand behaviour of the Cynp_3 ligand towards iron(II), nickel(II) and cobalt(II) salts, as compared

to that of the analogous np_3 ligand, clearly shows that substitution of cyclohexyl groups for phenyl groups on the phosphine donors is enough to induce a substantially higher strain in some complexes. This results either in *detachment* of a donor group with reduction of the coordination number from five to four (as in the $[\text{NiXL}]\text{BPh}_4$ complexes) and from six to five (as in the $[\text{Fe}(\text{NCS})_2\text{L}]$ complexes) or in a *higher distortion* towards the tetrahedron when five-coordination is still favoured (as in the $[\text{CoXL}]\text{Y}$ complexes). The latter feature has the remarkable effect of restoring the high-spin state in those complexes ($[\text{Co}(\text{NCS})\text{L}]\text{Y}$, $[\text{CoIL}]\text{Y}$) which were fully low-spin or at the magnetic cross-over point with the np_3 ligand.

Acknowledgements

Thanks are expressed to Prof. L. Sacconi for his continued interest in this work and to Mr. F. Cecconi for technical assistance.

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