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X-Ray Structures of two Five-coordinated Nickel(I) Complexes with the Tripod Ligands Tris(2-diphenylphosphinoethyl)amine and Tris(2-diphenylarsinoethyl)amine

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The tripod ligands tris(2-diphenylphosphinoethyl)amine, np_3, and tris(2-diphenylarsinoethyl)amine, nas_3, form nickel(I) complexes having formulas Ni(np_3)I and Ni(nas_3)I. These complexes have been studied by X-ray analysis, using diffractometric data. The two compounds are isomorphous, monoclinic, space group Cc, *with the following cell constants: Ni(np_3)I,* a *= 10.474(4),* b *= 21.167(7),* c *= 16.986(6) Å, β = 99.11(4)°; Ni(nas_3)I,* a *= 10.699(4),* b *= 21.445(7),* c *= 16.846(6) Å, β = 98.19(4)°. The structures were refined by least-squares techniques to final R factors of 0.069 and 0.041 for the np_3 and nas_3 derivatives, respectively. The structures consist of discrete trigonal-bipyramidal molecules. Some peculiar structural features are discussed on the basis of the crystal field theory.*

Introduction

Although in the last few years some structures of nickel(I) complexes have been determined [1–3],

TABLE I. Crystal Data and Data Collection Details.

	Ni(np_3)I	Ni(nas_3)I
Molecular formula	$C_{42}H_{42}NP_3INi$	$C_{42}H_{42}NAs_3INi$
Mol wt	839.34	971.18
a, Å	10.474(4)	10.699(4)
b, Å	21.167(7)	21.445(7)
c, Å	16.986(6)	16.846(6)
β, deg	99.11(4)	98.19(4)
d_{obsd} (by flot), gcm^{-3}	1.51	1.70
d_{calcd}, gcm^{-3}	1.508	1.696
U, Å^3	3718.3	3825.7
Z	4	4
Space group	*Cc*	*Cc*
Abs coeff. (MoKα), cm^{-1}	14.69	38.83
Color	yellow-green	yellow
λ(MoKα), Å	0.7093	0.7093
Monochromator	Flat graphite crystal	Flat graphite crystal
Take-off angle, deg	2.0	2.0
Method	ω–2θ	ω–2θ
Scan speed	0.08°/s for 0.8° in ω	0.08°/s for 0.8° in ω
Background time	5s on each side	5s on each side
2θ limit	5° ≤ 2θ ≤ 50°	5° ≤ 2θ ≤ 50°
Standards	3 every 120 min	3 every 120 min
No. of total data	3484	3593
No. of data used ($I \geq 3\sigma_I$)	2116	2591

TABLE II. Positional Parameters (× 10^4) and Anisotropic Temperature Factors[a] (×10^3) for Ni(np_3)I.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0	−596(1)	0	25(1)	35(2)	47(2)	0(1)	1(1)	−7(1)
I	−587(3)	−1344(1)	1413(2)	44(1)	61(1)	62(1)	5(1)	1(1)	−6(1)
P(1)	−44(5)	−1465(2)	−773(4)	35(3)	32(3)	36(3)	−1(3)	3(3)	−1(3)
P(2)	1911(5)	−178(2)	629(4)	25(3)	36(3)	41(3)	−3(2)	8(2)	−4(3)
P(3)	−1800(5)	5(3)	−204(4)	27(3)	27(3)	42(3)	1(2)	6(2)	2(3)
N	507(13)	−92(7)	−1081(10)	24(8)	20(9)	58(11)	−18(7)	9(8)	−7(8)

[a] The temperature factor is defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots)]$.

until now no five-coordinated mononuclear complexes of nickel(I) have been reported. For this reason we have undertaken the structural determination of two complexes synthesized and characterized some years ago in our Laboratory, namely the two nickel(I) complexes with the tripod ligands tris(2-diphenylphosphinoethyl)amine, np_3, and tris(2-diphenylarsinoethyl)amine, nas_3, having formulas Ni(np_3)I [4, 5] and Ni(nas_3)I [6], which appeared to be five-coordinated. These determinations may be important also in order to make some comparisons with several five-coordinated nickel(II) complexes with the same ligands, which have also been studied by X-rays, *e.g.* the complex cations $[Ni(np_3)I]^+$, $[Ni(np_3)COCH_3]^+$, $[Ni(np_3)CH_3]^+$, $[Ni(np_3)SO_2OC_2H_5]^+$ [7–10], $[Ni(nas_3)Ph]^+$ [6], and the dinuclear $[(nas_3)Ni\text{-}I\text{-}Ni(nas_3)]^+$ cation [3].

Experimental

Crystal Data and Data Collection

The crystals of Ni(np_3)I (I) and Ni(nas_3)I (II) used for data collection were parallelepipeds having dimensions 0.03 × 0.20 × 0.70 and 0.10 × 0.25 × 0.70 mm, respectively.

Unit cell parameters for each complex were determined by carefully measuring the setting angles of 25 reflections at room-temperature (about 22 °C) on a Philips PW 1100 diffractometer. Details of crystal data and data collection for the two complexes are given in Table I. The cell constants clearly show that the two compounds are isomorphous. After correction for background, the standard deviations $\sigma(I)$ of the intensity, I, of a reflection was calculated as described elsewhere [11], using values of the instability factor, k, of 0.03 for both complexes. The observed intensities were corrected for Lorentz and polarization effects. An absorption correction based upon a numerical method was applied using SHELX program [12].

Atomic scattering factors were taken from ref. 13 (all the atoms were considered in the neutral state). Corrections for anomalous dispersion effects were applied [14]. The application of the $\Delta f''$ corrections

TABLE III. Positional Parameters (×10^4), Isotropic Temperature Factors (×10^2) for 'Non-Group' and 'Group' Atoms of Ni(np_3)I.

Atom	x/a	y/b	z/c	U (A^2)
C(1)	885(18)	−553(9)	−1673(11)	3.6(5)
C(2)	−21(19)	−1097(10)	−1742(12)	4.0(5)
C(3)	1610(19)	356(10)	−840(13)	4.5(6)
C(4)	2626(19)	71(10)	−224(12)	4.2(5)
C(5)	−591(19)	284(10)	−1482(12)	4.2(6)
C(6)	−1339(18)	580(10)	−895(12)	3.8(5)
C(7)	1418(13)	−1955(6)	−622(7)	3.3(5)
C(8)	2202(13)	−1930(6)	122(7)	5.8(7)
C(9)	3354(13)	−2273(6)	258(7)	6.0(7)
C(10)	3721(13)	−2640(6)	−351(7)	4.6(6)
C(11)	2937(13)	−2664(6)	−1095(7)	5.6(7)
C(12)	1786(13)	−2321(6)	−1231(7)	5.3(6)
C(13)	−1308(13)	−2072(6)	−1004(7)	3.7(5)
C(14)	−2001(13)	−2139(6)	−1771(7)	4.7(6)
C(15)	−2973(13)	−2594(6)	−1924(7)	4.9(6)
C(16)	−3254(13)	−2981(6)	−1309(7)	5.2(6)
C(17)	−2561(13)	−2914(6)	−541(7)	6.4(7)
C(18)	−1588(13)	−2459(6)	−389(7)	4.5(6)
C(19)	1883(10)	599(6)	1115(8)	4.3(6)
C(20)	3029(10)	937(6)	1333(8)	4.6(6)
C(21)	2985(10)	1568(6)	1563(8)	4.8(6)
C(22)	1796(10)	1862(6)	1574(8)	5.0(6)
C(23)	651(10)	1525(6)	1355(8)	4.9(6)
C(24)	694(10)	894(6)	1126(8)	4.2(6)
C(25)	3241(11)	−581(7)	1261(9)	4.2(5)
C(26)	2963(11)	−828(7)	1976(9)	5.0(6)
C(27)	3910(11)	−1160(7)	2483(9)	6.6(7)
C(28)	5134(11)	−1244(7)	2274(9)	6.8(7)
C(29)	5412(11)	−997(7)	1559(9)	6.3(7)
C(30)	4465(11)	−666(7)	1052(9)	5.1(6)
C(31)	−3246(12)	−375(6)	−727(7)	3.4(5)
C(32)	−3414(12)	−1003(6)	−516(7)	4.3(6)
C(33)	−4488(12)	−1341(6)	−883(7)	6.0(6)
C(34)	−5394(12)	−1051(6)	−1462(7)	5.9(7)
C(35)	−5226(12)	−424(6)	−1673(7)	5.9(6)
C(36)	−4152(12)	−85(6)	−1305(7)	5.2(6)
C(37)	−2540(14)	486(7)	512(7)	3.8(5)
C(38)	−3067(14)	1080(7)	306(7)	5.5(6)
C(39)	−3605(14)	1434(7)	863(7)	7.4(8)
C(40)	−3617(14)	1195(7)	1627(7)	6.0(7)
C(41)	−3090(14)	601(7)	1834(7)	5.6(7)
C(42)	−2552(14)	247(7)	1276(7)	5.0(6)

TABLE IV. Positional Parameters (×10^4) and Anisotropic Temperature Factors (×10^3) for Ni(nas$_3$)I.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0	–640(1)	0	31(1)	36(1)	47(1)	1(1)	1(1)	–4(1)
I	–579(2)	–1330(1)	1355(1)	49(1)	56(1)	46(1)	0(1)	4(1)	7(1)
As(1)	–19(3)	–1516(1)	–846(2)	39(1)	30(1)	40(1)	0(1)	2(1)	–1(1)
As(2)	1926(3)	–182(1)	570(2)	29(1)	42(1)	43(1)	–5(1)	3(1)	–1(1)
As(3)	–1799(3)	–4(1)	–261(2)	33(1)	33(1)	42(1)	2(1)	4(1)	3(1)
N	525(12)	–119(6)	–1217(8)	28(7)	35(8)	38(7)	1(6)	8(6)	–2(6)

allowed the determination of the absolute structures for both complexes.

Solution and Refinement of the Structures

The structure of complex (I) was solved by the heavy-atom method, which showed the positions of nickel, iodine, and phosphorus atoms. Successive F_o Fourier syntheses showed the positions of all non-hydrogen atoms. The structure of complex (II) was solved by using the positions obtained for complex (I). Refinements were performed by use of the full-matrix least-squares of the SHELX program [12] The minimized function was $\Sigma w(|F_o|-|F_c|)^2$, in which w is the weight assigned to the F_o values, according to the expression $w = 1/\sigma^2(F_o)$. The hydrogen atoms were introduced in calculated positions (C–H distance of 0.95 Å), with an overall temperature factor B of 4 Å^2, and were not refined. The carbon atoms of the phenyl groups were refined as a rigid body, assuming a D_{6h} geometry for the rings. Anisotropic temperature factors were used for nickel, phosphorus, arsenic, and nitrogen atoms, and isotropic for the carbon atoms. The absolute structures were determined performing mixed cycles on the two possible configurations for both structures. The configurations which gave lower R and standard deviations values were considered the correct ones.

The final conventional R factors are 0.069 and 0.041 for structure (I) and (II), respectively. The R_w factors, defined as $[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, are 0.065 and 0.039. Final ΔF Fourier syntheses did not show remarkable features. The final values of the parameters and their standard deviations are reported in Tables II–V. Tables of structure factors for both complexes are available from the Editor on request.

Results and Discussion

The structures of the two complexes consist of Ni(np$_3$)I and Ni(nas$_3$)I molecules, respectively. The nickel atom, in both complexes, is five-coordinated, linked to the four donor atoms of the tripod ligand and to the iodine in a distorted trigonal-bipyramidal arrangement. In both cases the nitrogen

TABLE V. Positional Parameters (×10^4), Isotropic Temperature Factors (×10^2) for 'Non-Group' and 'Group' Atoms of Ni(nas$_3$)I.

Atom	x/a	y/b	z/c	U (Å^2)
C(1)	968(18)	–578(10)	–1769(12)	4.7(5)
C(2)	33(19)	–1159(9)	–1907(12)	4.9(5)
C(3)	1578(19)	326(9)	–981(12)	4.6(5)
C(4)	2626(18)	58(10)	–407(12)	4.7(5)
C(5)	–593(18)	224(9)	–1639(11)	5.1(5)
C(6)	–1311(18)	575(9)	–1069(11)	4.8(5)
C(7)	1512(12)	–2019(6)	–723(7)	4.2(5)
C(8)	2351(12)	–1951(6)	–15(7)	5.6(5)
C(9)	3509(12)	–2261(6)	79(7)	7.6(6)
C(10)	3827(12)	–2639(6)	–536(7)	7.3(6)
C(11)	2988(12)	–2707(6)	–1244(7)	7.4(6)
C(12)	1830(12)	–2397(6)	–1338(7)	5.7(5)
C(13)	–1278(12)	–2544(6)	–541(7)	5.4(6)
C(14)	–1884(12)	–2225(6)	–1930(7)	4.9(6)
C(15)	–2857(12)	–2657(6)	–2114(7)	5.9(5)
C(16)	–3225(12)	–3032(6)	–1512(7)	5.3(5)
C(17)	–2619(12)	–2976(6)	–725(7)	5.7(5)
C(18)	–1646(12)	–2544(6)	–541(7)	5.4(6)
C(19)	1923(9)	658(5)	1032(8)	3.9(5)
C(20)	3028(9)	1001(5)	1238(8)	5.2(5)
C(21)	2961(9)	1631(5)	1434(8)	5.8(6)
C(22)	1788(9)	1918(5)	1423(8)	6.2(6)
C(23)	682(9)	1574(5)	1216(8)	6.3(6)
C(24)	750(9)	944(5)	1021(8)	4.7(5)
C(25)	3374(10)	-583(6)	1193(8)	4.5(5)
C(26)	3175(10)	–882(6)	1900(8)	6.0(5)
C(27)	4164(10)	–1200(6)	2357(8)	7.3(6)
C(28)	5352(10)	–1219(6)	2107(8)	7.1(6)
C(29)	5551(10)	–920(6)	1401(8)	7.2(6)
C(30)	4562(10)	–602(6)	944(8)	6.6(6)
C(31)	–3292(10)	–397(5)	–832(7)	4.0(4)
C(32)	–3416(10)	–1037(5)	–712(7)	4.7(5)
C(33)	–4453(10)	–1358(5)	–1113(7)	6.3(6)
C(34)	–5366(10)	–1039(5)	–1634(7)	6.5(6)
C(35)	–5242(10)	–399(5)	–1753(7)	6.3(6)
C(36)	–4205(10)	–79(5)	–1352(7)	5.2(5)
C(37)	–2566(12)	542(6)	444(6)	3.7(4)
C(38)	–3127(12)	1107(6)	181(6)	5.7(5)
C(39)	–3661(12)	1487(6)	715(6)	7.7(6)
C(40)	–3635(12)	1302(6)	1511(6)	6.4(6)
C(41)	–3074(12)	737(6)	1774(6)	6.1(6)
C(42)	–2540(12)	357(6)	1240(6)	4.7(5)

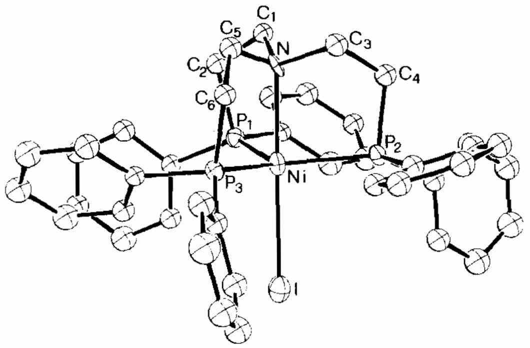

Fig. 1. Perspective view of the Ni(np$_3$)I molecule.

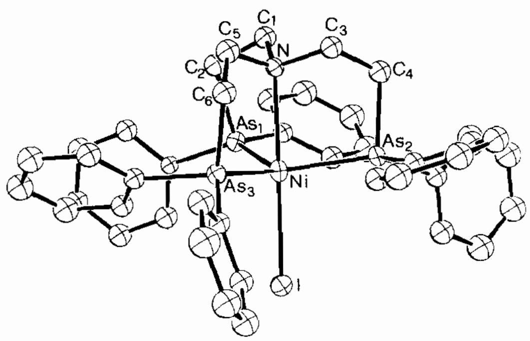

Fig. 2. Perspective view of the Ni(nas$_3$)I molecule.

TABLE VI. Ni(np$_3$)I. Selected Bond Distances (Å), and Angles (deg), with Their Estimated Standard Deviations.

	Bond Distances		
Ni–I	3.018(3)	C(5)–C(6)	1.50(3)
Ni–N	2.258(15)	P(1)–C(2)	1.82(2)
Ni–P(1)	2.256(6)	P(1)–C(7)	1.83(1)
Ni–P(2)	2.292(5)	P(1)–C(13)	1.84(1)
Ni–P(3)	2.256(5)	P(2)–C(4)	1.81(2)
N–C(1)	1.50(2)	P(2)–C(19)	1.84(1)
N–C(3)	1.50(2)	P(2)–C(25)	1.83(1)
N–C(5)	1.47(2)	P(3)–C(6)	1.81(2)
C(1)–C(2)	1.49(3)	P(3)–C(31)	1.82(1)
C(3)–C(4)	1.50(3)	P(3)–C(37)	1.85(1)
	Bond Angles		
I–Ni–N	176.3(4)	Ni–N–C(3)	110.3(11)
I–Ni–P(1)	92.7(2)	Ni–N–C(5)	111.4(10)
I–Ni–P(2)	96.0(2)	C(1)–N–C(3)	108.7(13)
I–Ni–P(3)	98.5(2)	C(1)–N–C(5)	108.1(14)
N–Ni–P(1)	84.1(4)	C(3)–N–C(5)	107.2(14)
N–Ni–P(2)	84.0(4)	N–C(1)–C(2)	108.9(14)
N–Ni–P(3)	84.6(4)	N–C(3)–C(4)	111.5(16)
P(1)–Ni–P(2)	121.5(2)	N–C(5)–C(6)	111.7(16)
P(1)–Ni–P(3)	115.5(2)	P(1)–C(2)–C(1)	111.1(14)
P(2)–Ni–P(3)	120.0(2)	P(2)–C(4)–C(3)	109.8(13)
Ni–N–C(1)	111.1(10)	P(3)–C(6)–C(5)	111.8(14)

TABLE VII. Ni(nas$_3$)I. Selected Bond Distances (Å), and Angles (deg), with Their Estimated Standard Deviations.

	Bond Distances		
Ni–I	2.860(2)	C(5)–C(6)	1.51(2)
Ni–N	2.469(9)	As(1)–C(2)	1.95(1)
Ni–As(1)	2.357(2)	As(1)–C(7)	1.95(1)
Ni–As(2)	2.360(2)	As(1)–C(13)	1.96(1)
NI–As(3)	2.349(2)	As(2)–C(4)	1.97(1)
N–C(1)	1.48(2)	As(2)–C(19)	1.96(1)
N–C(3)	1.49(2)	As(2)–C(25)	1.94(1)
N–C(5)	1.49(1)	As(3)–C(6)	1.97(1)
C(1)–C(2)	1.59(2)	As(3)–C(31)	1.94(1)
C(3)–C(4)	1.49(2)	As(3)–C(37)	1.93(1)
	Bond Angles		
I–Ni–N	175.8(2)	Ni–N–C(3)	108.8(7)
I–Ni–As(1)	94.9(1)	Ni–N–C(5)	110.9(6)
I–Ni–As(2)	99.6(1)	C(1)–N–C(3)	107.3(9)
I–Ni–As(3)	100.7(1)	C(1)–N–C(5)	109.6(9)
N–Ni–As(1)	80.9(2)	C(3)–N–C(5)	109.6(9)
N–Ni–As(2)	82.0(2)	N–C(1)–C(2)	111.2(10)
N–Ni–As(3)	81.9(2)	N–C(3)–C(4)	113.4(11)
As(1)–Ni–As(2)	120.6(1)	N–C(5)–C(6)	112.8(10)
As(1)–Ni–As(3)	114.5(1)	As(1)–C(2)–C(1)	105.8(8)
As(2)–Ni–As(3)	118.6(1)	As(2)–C(4)–C(3)	107.6(9)
Ni–N–C(1)	110.7(7)	As(3)–C(6)–C(5)	109.5(9)

and iodine atoms lie in the axial positions of the bipyramid. Figs. 1 and 2 show perspective views of the two molecules. Tables VI and VII report the most significant distances and angles for the two complexes. The nickel atom is displaced from the equatorial plane, toward the iodine atom, by 0.23 Å in the np$_3$ derivative and by 0.34 Å in the nas$_3$ derivative. This displacement is evidenced also by the I–Ni–P and I–Ni–As angles, which are 95.7° (av) and 98.4° (av), respectively.

The Ni–P and Ni–As equatorial distances, 2.268 Å (av) and 2.355 Å (av), respectively, are in good agreement with the sum of the covalent radii reported for these atoms [15], and with the values of the Ni–P and Ni–As distances found in the already mentioned five-coordinated nickel(II) complexes. The axial distances, on the contrary, exhibit significant differences. In particular, if we consider the Ni(np$_3$)I complex, the Ni–N, 2.258(15) Å, and Ni–I, 3.018(3) Å, distances are remarkably longer than the sums of the values of the covalent radii, 1.90 and 2.48 Å, respectively. These distances are also very much longer than the analogous distances found in the trigonal-bipyramidal nickel(II) complexes with the np$_3$ ligand [7–10]. For instance, in the [Ni(np$_3$)I]I complex [7], the Ni–N and the Ni–I distances have been found to be 2.13 and 2.71 Å, respectively. The latter distance, in spite of being 0.3 Å shorter than the analogous Ni–I distance in the nickel(I) complex, is still rather long, such lengthening being accounted for by short contacts between the iodine and some np_3 ligand atoms. The lengthening of the Ni–I distance in the $Ni(np_3)I$ complex is much more evident if this distance is compared, for instance, with the Ni–I distance found in the nickel(II) complex $[Ni(n_2p_2)I]I$ [16], 2.55 Å, where the n_2p_2 ligand is NN-bis(2-diphenylphosphinoethyl)-N-(2-diethylaminoethyl)amine, $(C_2H_5)_2NC_2H_4N(C_2H_4PPh_2)_2$.

If we consider now the $Ni(nas_3)I$ complex, the Ni–N distance is found to be even longer, 2.469(9) Å, than in the np_3 derivative, whereas the Ni–I distance, 2.860(2) Å, is a little shorter.

This Ni–N distance is longer by 0.37 Å than the Ni–N distance found in the $[Ni(nas_3)Ph]BPh_4$ nickel(II) complex [6], whereas the Ni–As distances are about the same: 2.338 Å (av) in the nickel(II) complex against 2.355 Å (av) in the nickel(I) complex. Finally, if we compare the axial distances in the $Ni(nas_3)I$ complex with the analogous distances found in the dinuclear nickel(I) complex $[(nas_3)Ni–I–Ni(nas_3)]BPh_4$ [3], we observe that the Ni–N distance in the mononuclear complex is longer by 0.16 Å, whereas the Ni–I distance is shorter by 0.13 Å, as compared to the dinuclear complex. The Ni–As distances are very close in all these complexes (the average value for the dinuclear complex is 2.349 Å).

These geometrical features of the five-coordinated nickel(I) complexes can be schematically justified on the basis of a crystal field model. If an idealized C_{3v} geometry is assumed for these complexes, the d_{z^2} (a_1') orbital, which has the highest energy [17], in the nickel(I) d^9 ion possesses one electron, while it is empty in the nickel(II) d^8 ion. In the d^9 configuration, therefore, there is a larger axial repulsion between the ligands and the metal with a consequent increase of the axial distances in a trigonal-bipyramidal arrangement.

The differences in the axial distances in the two nickel(I) complexes, $Ni(nas_3)I$ and $[(nas_3)Ni–I–Ni(nas_3)]^+$, can be accounted for by considering the electron occupying the d_{z^2} orbital: since in the dinuclear complex this electron is engaged in antiferromagnetic exchange through the bridging iodine atom, it gives rise to less repulsion toward the nitrogen atom which lies in the opposite apex.

A useful comparison can be made also between the distances of the $Ni(np_3)I$ complex and those found in the analogous nickel(I) complex with the tridentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, p_3, having formula $Ni(p_3)I$, which is tetrahedral [1]. The Ni–P distances in the latter complex are close to those found in the $Ni(np_3)I$ complex (2.221 Å (av) against 2.268 Å (av) in the np_3 derivative), whereas the Ni–I distance (2.546 Å) is remarkably shorter than that found in the five-coordinated complex. This comparison confirms that the long Ni–N and Ni–I distances in the five-coordinated nickel(I) complexes depend exclusively on the coordination geometry, in accordance with the assumed crystal field model.

Finally it may be interesting to point out that the various nickel(0) complexes with the np_3 ligand, whose structures have been reported, are all tetracoordinated: the $Ni(np_3)$ complex has the unusual trigonal-pyramidal geometry [4], whereas the $Ni(np_3)CO$ [18] and $Ni(np_3)P_4$ [19] complexes have tetrahedral geometry, the nitrogen atom being in both cases not-coordinated. Nickel(0) complexes with the nas_3 ligand are not known.

Therefore we can conclude that the tripod ligands np_3 and nas_3 give rise to a trigonal-bipyramidal geometry in the nickel(II) complexes, to a trigonal-bipyramidal geometry having long axial distances in the nickel(I) complexes, and, limited to the np_3 derivatives, to a tetracoordination (trigonal-pyramidal or tetrahedral) in the nickel(0) complexes. The nickel(II) and nickel(0) complexes are therefore diamagnetic, the metal atom in every case achieving the very stable configuration of 18 electrons. An analogous computation of the total electrons around the metal would not be meaningful for the mononuclear five-coordinated nickel(I) complexes on account of the long distances, and therefore of the poor orbital overlap, between the axial ligands and the metal. However it is evident that only through a super-exchange mechanism, as found in the $[(nas_3)Ni-I-Ni(nas_3)]^+$ cation, could the nickel(I) d^9 complex become diamagnetic.

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