Crystal and Molecular Structure of the Low-Spin Five-co-ordinate Complex Chloro[tris-(2-diphenylphosphinoethyl)amine]nickel(II) Hexafluorophosphate

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The structure of the low-spin five-co-ordinate title complex (I) has been determined by Patterson and Fourier methods, from photographic *X*-ray data and refined by least-squares techniques to R 0·093 for 2373 observations. Crystals are monoclinic, space group $P2_1/c$, and $Z = 4$ in a unit cell of dimensions: $a = 16{\cdot}741(26)$, $b = 14{\cdot}116(16)$, $c = 16{\cdot}945(17)$ Å, $\beta = 98{\cdot}55(8)°$. The co-ordination geometry is essentially trigonal bipyramidal with the phosphorus atoms of the ligand in the equatorial plane (Ni–P 2·194—2·298 Å), and the chlorine and nitrogen atoms in the apical positions [Ni–Cl 2·169(4), Ni–N 1·965(10) Å].

As part of a systematic investigation [1] on the effect of the nature of the donor-set on the spin-state of the metal in five-co-ordinate cobalt(II) and nickel(II) complexes, a series of complexes of general formula [MLX]Y has been prepared,[2] where L is the tripod-like ligand tris-(2-diphenylphosphinoethyl)amine $(Ph_2P{\cdot}CH_2{\cdot}CH_2)_3N$, containing the mixed NP_3 donor-set, X is Cl, Br, I, or NCS, and Y is X, BF_4, PF_6, or BPh_4.

The spectroscopic and magnetic properties vary remarkably through the series.[2] The variations are related to notable changes in co-ordination, as has been established by various structural investigations.[3-5] The high-spin state for Co^{II} complexes in the series is found when X = Cl or Br, irrespective of the nature of Y, and also when X = I and Y = BPh_4. These complexes are essentially isospectral [2] and may be assigned tetrahedrally distorted five-co-ordination, which has been detected for solid $[CoLCl]PF_6$,[3] and for other high-spin complexes of the series (preliminary data were reported in ref. 6). All NCS derivatives of cobalt and all the iodo-derivatives having Y different from BPh_4 are low spin. Determination [4] of the structure of [CoLI]I has shown its co-ordination to be distorted square pyramidal. All Ni^{II} complexes of the series are low spin and essentially isospectral.[2] The co-ordination geometry is trigonal bipyramidal, with crystallographic C_3 symmetry in the complex [NiLI]I.[5]

The study of the structure of the present complex $[NiLCl]PF_6$ (I) has been undertaken by *X*-ray diffraction methods, in order to establish whether the same type of co-ordination may be safely assigned to all nickel complexes of this series. We were also interested in drawing possible comparisons with the known structure of the cobalt analogue.[3] It was felt that additional structural information on complexes of this series might prove valuable to an understanding of the relative importance of the factors which govern the geometry of their co-ordination.

EXPERIMENTAL

Crystal Data.—$C_{42}H_{42}ClF_6NNiP_4$, $M = 892{\cdot}85$, Monoclinic, $a = 16{\cdot}741(26)$, $b = 14{\cdot}116(16)$, $c = 16{\cdot}945(17)$ Å, $\beta = 98{\cdot}55(8)°$, $U = 3959{\cdot}9$ Å^3, $Z = 4$, $D_c = 1{\cdot}497$ g cm^{-3}, $F(000) = 1840$. Space group $P2_1/c$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 34·0 cm^{-1}.

Data Collection.—Cell constants were obtained from $hk0$ and $h0l$ Weissenberg photographs with the sodium chloride rotation pattern superimposed for calibration ($a = 5{\cdot}6273$ Å). Least-squares refinement of twenty-nine 2θ values was used. The crystal used for data collection was a tablet with average dimensions 0·45 × 0·30 × 0·18 mm in the [100], [010], and [001] directions, and was mounted along [010]. From the aspect of the *X*-ray photographs it was clear that internal disorder in varying amounts affected most crystals in the batch. However, it did not affect the crystal used for data collection. The disorder may have been responsible for the fact that attempts to obtain D_m by the flotation method did not yield consistent values. The reciprocal lattice levels $h0$—$10l$ were collected on a Nonius integrating Weissenberg camera with nickel-filtered Cu-K_α radiation, by use of the multiple-film equi-inclination technique. The intensities of a total 2373 reflections were measured on a Nonius microdensitometer. A correction for absorption was applied. The various levels were initially put on a common scale by means of two Weissenberg photographs, containing 30° samples from each level. Nine reflections exhibiting large negative ΔF values were later considered to be affected by extinction and were omitted from the least-squares refinement. The atomic scattering factors for all atoms except hydrogen were taken from ref. 7, that of nickel being corrected for the real part of the anomalous dispersion according to ref. 8; and that of hydrogen being taken from ref. 9.

Structure Determination.—The structure was solved by the heavy-atom technique. When the positions of the non-hydrogen atoms had been determined diagonal least-squares refinement with unit weights was undertaken, with individual isotropic temperature factors for all atoms, and was continued until R was 0·13. All calculations were performed on an IBM 1130 with programs written by Ahmed,[10] except for the correction for absorption, for which the BURNAM program was used [ref. 11(*a*)].

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[10] Series of programmes for the A.R.C., Unit of Structural Chemistry, University College London, for the I.B.M. 1130 computer.

[11] (*a*) '*X*-Ray '63,' J. M. Stewart, Technical Report TR 64 6, University of Maryland, 1964; (*b*) 'X-Ray '72,' J. M. Stewart, Technical Report, TR 192, University of Maryland, 1972,

TABLE 1

Positional parameters ($\times 10^4$) and anisotropic temperature factors * ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	7431(1)	4937(2)	2163(1)	31(1)	74(2)	27(1)	−6(1)	−3(1)	−2(1)
Cl	6503(2)	3953(3)	1646(2)	37(1)	83(3)	44(1)	−13(2)	−7(1)	−3(2)
P(1)	8138(2)	4854(3)	1101(2)	36(1)	72(3)	28(1)	−3(2)	2(1)	−1(2)
P(2)	6524(2)	6070(3)	2062(2)	37(1)	77(3)	30(1)	2(2)	−3(1)	−4(2)
P(3)	7816(2)	4028(3)	3223(2)	33(1)	80(3)	27(1)	−2(2)	0(1)	0(2)
P(4)	1240(3)	3936(4)	3862(2)	51(2)	88(5)	44(2)	5(2)	2(1)	−7(2)
F(1)	653(8)	4357(13)	3182(8)	124(9)	260(19)	86(6)	39(11)	−31(6)	33(9)
F(2)	1883(7)	3823(10)	3291(7)	100(7)	190(13)	95(6)	−1(8)	55(6)	2(8)
F(3)	970(12)	2989(11)	3679(11)	214(14)	121(13)	182(13)	−83(12)	96(12)	−80(11)
F(4)	1831(8)	3594(15)	4572(8)	104(8)	316(22)	105(8)	60(11)	14(6)	92(11)
F(5)	616(7)	4045(10)	4454(7)	81(6)	183(13)	102(7)	18(7)	30(5)	−7(7)
F(6)	1579(10)	4883(11)	4087(9)	158(11)	134(13)	142(10)	−40(10)	30(9)	−37(9)
N	8250(5)	5840(8)	2656(5)	33(4)	74(9)	36(4)	−11(5)	4(3)	−9(5)

* Anisotropic temperature factors are of the form: $\exp(-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij})$.

Least-squares refinement was then continued in the full-matrix mode with anisotropic temperature factors for atoms heavier than carbon. Each cycle of anisotropic refinement was followed by one cycle of isotropic refinement on carbon atoms. Scale factors were not allowed to change during the anisotropic cycles. The refinement was considered to be complete when the average shift-to-error ratio was $<0{\cdot}10$. The final R was 0·093 for observed reflections only. The function minimized in the least-squares was $\Sigma w(|F_o| - |F_c|)^2$ and the weighting scheme was: $w = 1$ for reflections with $F_o \leqslant 30$ and $\sqrt{w} = 30/F_o$ for reflections with $F_o > 30$. Hydrogen atoms were introduced in calculated position during the last set of cycles and were not refined. Each was assigned a temperature factor quite close to that of its own carbon atom. A short 1·00 Å C–H distance was assigned in view of the choice made for the scattering factor of hydrogen [9] and in order partially to account for the apparent contraction of C–H bond lengths from X-ray diffraction data. A difference-Fourier calculated with the final parameters showed two peaks of height 0·6 eÅ^{-3} close to the heavy-atom position and failed to reveal major features. Final calculations were performed on an IBM 360/67 of CNUCE in Pisa, with programs written by Stewart.[11b]

TABLE 2

Positional parameters ($\times 10^4$) and isotropic temperature factors, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
C(1)	9055(8)	5749(11)	2345(9)	5·5(0·3)
C(2)	8927(8)	5725(11)	1412(8)	4·5(0·3)
C(3)	7983(10)	6828(12)	2478(9)	6·4(0·4)
C(4)	7124(9)	7003(12)	2614(8)	5·6(0·3)
C(5)	8459(8)	5727(11)	3552(8)	5·2(0·3)
C(6)	8599(8)	4737(10)	3789(8)	4·6(0·3)
C(7)	7758(8)	5131(11)	84(8)	4·8(0·3)
C(8)	8217(11)	5666(13)	−397(11)	7·5(0·4)
C(9)	7938(12)	5803(14)	−1226(12)	8·5(0·5)
C(10)	7219(12)	5496(15)	−1517(11)	7·6(0·4)
C(11)	6734(10)	4990(13)	−1078(10)	7·0(0·4)
C(12)	7034(9)	4842(12)	−267(9)	5·8(0·3)
C(13)	8660(8)	3812(11)	994(7)	4·4(0·3)
C(14)	9431(11)	3652(15)	1346(11)	7·8(0·4)
C(15)	9752(14)	2753(19)	1253(13)	10·4(0·6)
C(16)	9304(12)	2051(16)	926(12)	8·5(0·5)
C(17)	8528(11)	2188(14)	631(10)	7·4(0·4)
C(18)	8206(9)	3044(13)	681(9)	5·9(0·4)
C(19)	5585(8)	6009(12)	2489(8)	4·9(0·3)
C(20)	5381(9)	5238(13)	2812(9)	6·0(0·4)
C(21)	4641(12)	5187(15)	3151(11)	8·0(0·5)
C(22)	4173(10)	5974(14)	3116(10)	6·7(0·4)
C(23)	4385(10)	6681(14)	2805(10)	6·7(0·4)
C(24)	5109(9)	6791(12)	2447(9)	6·1(0·4)
C(25)	6204(8)	6515(11)	1074(8)	4·8(0·3)
C(26)	6577(10)	7212(14)	751(10)	7·3(0·4)
C(27)	6337(12)	7515(15)	−59(12)	8·7(0·5)
C(28)	5701(11)	7072(15)	−466(10)	7·5(0·4)
C(29)	5322(10)	6396(13)	−206(10)	6·5(0·4)
C(30)	5560(9)	6113(12)	596(9)	5·9(0·3)
C(31)	8239(8)	2901(11)	3138(8)	4·6(0·3)
C(32)	8867(10)	2600(14)	3724(10)	6·7(0·4)
C(33)	9156(11)	1748(15)	3682(10)	7·5(0·5)
C(34)	8825(11)	1170(14)	3109(11)	7·5(0·4)
C(35)	8229(10)	1437(14)	2516(10)	7·0(0·4)
C(36)	7936(9)	2322(13)	2557(9)	6·1(0·4)
C(37)	7074(7)	3840(11)	3863(7)	4·0(0·3)
C(38)	6701(10)	3052(13)	3894(10)	6·9(0·4)
C(39)	6079(11)	2883(15)	4386(11)	8·1(0·5)
C(40)	5875(10)	3650(14)	4823(10)	6·7(0·4)
C(41)	6297(12)	4414(16)	4855(12)	8·6(0·5)
C(42)	6869(10)	4561(14)	4344(10)	7·1(0·4)

Final values of the parameters for atoms other than hydrogen and their estimated standard deviations are reported in Tables 1 and 2. Standard deviations of the parameters were calculated by the least-squares program according to the expression: $\sigma_j = [\Sigma w \Delta F^2 a^{jj}/(m - n)]^{1/2}$, where m is the number of reflections, n the number of parameters and a^{jj} is the JJ^{th} element of the inverse least-squares matrix. The values reported have been multiplied by a suitable correction factor,* accounting for the factorization of the least-squares matrix, that was imposed through the separate isotropic and anisotropic refinements. Observed and calculated structure factors are published in Supplementary Publication No. SUP 21184 (6 pp., 1 microfiche).†

DISCUSSION

The structure of the compound (I) consists of $[\mathrm{NiLCl}]^+$ cations and of $\mathrm{PF_6}^-$ anions. The Figure shows a perspective view of the cation with the labelling of the atoms. Selected values of bond distances and angles in the cation are reported in Tables 3 and 4 respectively. Values for the anion are reported in Table 5.

The co-ordination about the metal is essentially trigonal bipyramidal. The chlorine and the nitrogen atoms are at the apices of the bipyramid and the three phosphorus atoms in the equatorial plane, the equation of which is: $10{\cdot}303x + 9{\cdot}519y + 5{\cdot}288z = 13{\cdot}567$, in

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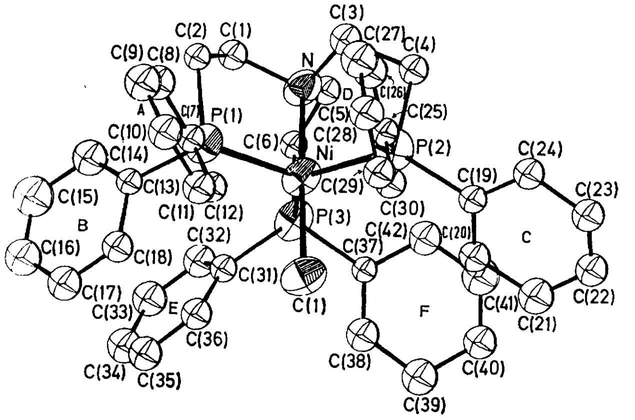
* $[(m - n_i)/(m - n_t)]^{\frac{1}{2}}$, where n_t is the total number of parameters and n_i is the number of parameters refined in the i-th block.

† See Notice to Authors in *J.C.S. Dalton*, 1973, Index issue.

monoclinic fractional co-ordinates. The metal atom deviates by 0·09 Å from this plane, towards chlorine; the best line through Cl, Ni, and N forms an angle of 2·44° with the normal to the equatorial plane. The geometry of co-ordination in the present complex is therefore closely similar to that found in (II), [NiLI]I,[5] where, however, crystallographic C_3 symmetry exists.



Perspective view of the cation, showing 50% probability ellipsoids for metal and ligand atoms, and 25% for carbon atoms

TABLE 3

Selected distances in the cation (Å), with standard deviations in parentheses

Ni–Cl	2·169(4)	P(2)–C(19)	1·83(1)
Ni–P(1)	2·298(4)	P(2)–C(25)	1·79(1)
Ni–P(2)	2·194(5)	P(3)–C(6)	1·81(2)
Ni–P(3)	2·223(4)	P(3)–C(31)	1·76(2)
Ni–N	1·965(10)	P(3)–C(37)	1·79(1)
		N–C(1)	1·52(2)
		N–C(3)	1·48(2)
P(1)–C(2)	1·82(2)	N–C(5)	1·51(2)
P(1)–C(7)	1·79(1)	C(1)–C(2)	1·56(2)
P(1)–C(13)	1·73(2)	C(3)–C(4)	1·51(2)
P(2)–C(4)	1·83(2)	C(5)–C(6)	1·46(2)

TABLE 4

Selected bond angles (°) in the cation, with standard deviations in parentheses

Cl–Ni–N	178·2(0·3)	C(4)–P(2)–C(19)	105·7(0·7)
Cl–Ni–P(1)	94·2(0·2)	C(4)–P(2)–C(25)	106·9(0·7)
Cl–Ni–P(2)	89·4(0·2)	C(19)–P(2)–C(25)	103·3(0·6)
Cl–Ni–P(3)	93·4(0·2)	Ni–P(3)–C(6)	102·1(0·5)
P(1)–Ni–P(2)	114·0(0·2)	Ni–P(3)–C(31)	121·9(0·5)
P(1)–Ni–P(3)	118·8(0·2)	Ni–P(3)–C(37)	115·6(0·5)
P(2)–Ni–P(3)	126·7(0·2)	C(6)–P(3)–C(31)	106·0(0·7)
P(1)–Ni–N	87·6(0·3)	C(6)–P(3)–C(37)	106·0(0·6)
P(2)–Ni–N	89·5(0·3)	C(31)–P(3)–C(37)	103·9(0·7)
P(3)–Ni–N	86·0(0·3)	Ni–N–C(1)	113·3(0·8)
		Ni–N–C(3)	110·7(0·8)
		Ni–N–C(5)	113·6(0·8)
Ni–P(1)–C(2)	100·1(0·4)	C(1)–N–C(3)	105·4(1·1)
Ni–P(1)–C(7)	126·3(0·5)	C(1)–N–C(5)	104·7(1·0)
Ni–P(1)–C(13)	116·8(0·5)	C(3)–N–C(5)	108·7(1·1)
C(2)–P(1)–C(7)	105·6(0·7)	P(1)–C(2)–C(1)	106·9(0·9)
C(2)–P(1)–C(13)	104·2(0·6)	N–C(1)–C(2)	110·9(1·1)
C(7)–P(1)–C(13)	101·4(0·7)	P(2)–C(4)–C(3)	105·5(1·1)
Ni–P(2)–C(4)	99·5(0·5)	N–C(3)–C(4)	112·9(1·3)
Ni–P(2)–C(19)	124·1(0·6)	P(3)–C(6)–C(5)	108·0(1·0)
Ni–P(2)–C(25)	115·8(0·5)	N–C(5)–C(6)	112·3(1·2)

There are two minor but significant differences between the two complexes. Some contraction of the apical bonds is found in (I) compared to (II). This is clearly indicated by the values of the Ni–N distances [1·96(1) in (I), *vs.* 2·13(4) Å in (II)] and by the large difference (0·54 Å) between the metal–halogen bond lengths, which far exceeds the difference in covalent radii[12] of the two halogens involved. The Ni–Cl distance in (I) [2·169(5) Å] is less than that [2·227(7) Å] in a low-spin five-co-ordinate Ni^{II} complex of similar geometry,[13] and is even lower than tetrahedral values (ref. 14 and refs. therein). Some contraction of the apical bonds in trigonal bipyramidal low-spin d^8 complexes would be expected from qualitative considerations[15] accounting for repulsions between the ligand atoms and the non-spherical *d*-shell distribution. Such a contraction has been observed in several cases.[16] The reason for the absence of apparent contraction in complex (II) is not completely clear. Short I · · · C contacts may affect the metal–halogen interactions,[5] whereas the accumulation of negative charge on the metal [relative to complex (I)] caused by iodine may not favour bonding to the metal by the electronegative nitrogen atom. Geometric factors due to the ligand may also be involved (see later).

TABLE 5

Bond distances (Å) and angles (°) in the anion, with standard deviations in parentheses

P(4)–F(1)	1·52(2)	F(1)–P(4)–F(6)	91·2(1·0)
P(4)–F(2)	1·56(1)	F(2)–P(4)–F(3)	89·7(1·0)
P(4)–F(3)	1·43(2)	F(2)–P(4)–F(4)	91·8(0·8)
P(4)–F(4)	1·52(2)	F(2)–P(4)–F(5)	178·4(0·7)
P(4)–F(5)	1·56(1)	F(2)–P(4)–F(6)	88·8(0·9)
P(4)–F(6)	1·48(2)	F(3)–P(4)–F(4)	91·3(1·1)
		F(3)–P(4)–F(5)	90·6(1·0)
F(1)–P(4)–F(2)	89·9(0·7)	F(3)–P(4)–F(6)	175·4(1·1)
F(1)–P(4)–F(3)	93·0(1·1)	F(4)–P(4)–F(5)	86·6(0·7)
F(1)–P(4)–F(4)	175·4(1·1)	F(4)–P(4)–F(6)	84·5(1·0)
F(1)–P(4)–F(5)	91·7(0·8)	F(5)–P(4)–F(6)	90·8(0·9)

The second difference between (I) and (II) is in the arrangement of the ligand atoms in the equatorial plane. In (I) the Ni–P(1) distance [2·298(4) Å] differs from the other two Ni–P distances, whose mean [2·21(2) Å *] compares favourably with the 2·22(1) Å for complex (II). The 'long' Ni–P(1) distance in complex (I) lies opposite the largest of the three angles in the equator [P(2)–Ni–P(3) 126·7°]. The deviation from C_3 symmetry which results is such that it matches the trend[16] exhibited by other low-spin five-co-ordinate complexes of Ni^{II}, whose geometry may be described as approximately distorted trigonal bipyramidal. In the limit of considerable elongation of one equatorial bond and increase of the opposite angle toward 180°, this trend correlates with a mode of distortion common to square-pyramidal Ni^{II} complexes.[6,16,18]

Packing forces in the solid may well contribute

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* Errors on mean values of bond distances or angles considered to be chemically equivalent are estimated using the formula: $\sigma = [\Sigma_i(X_i - \bar{X})^2/n(n - 1)]^{1/2}$ (ref. 17).

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towards stabilizing the symmetrical arrangement in complex (II) with respect to less symmetrical arrangements. However, the same factors should not be a determinant for the particular distortions found in (I). These in fact may be rationalized within the trends which characterize a whole class of Ni^{II} complexes (see earlier).

Individual values of distances and angles in the ligand molecule deviate from expected values[19] by $>3\sigma$, in a few cases. These may be caused, in part, by systematic errors in the data. However, deviations consistently affecting chemically equivalent distances and angles may be produced by the requirements of the present mode of ligand co-ordination (see later). The mean C–C bond length in the phenyl rings has a rather low value (1·36 Å), probably imposed by the choice of C–H distance. Mean bond angles in the phenyl rings deviate by 2·4° from 120°. The PF_6^- anion (Table 5) exhibits the usual effects of large thermal motion or partial disorder.

Table 6 lists the contacts in the structure <3·40 Å.

TABLE 6

Contact distances <3·4 Å

C(1) ··· C(6)	3·03	C(24) ··· C(25)	3·19
C(2) ··· C(3)	3·01	C(31) ··· C(38)	3·05
C(2) ··· C(8)	3·12	C(32) ··· C(17$^{\mathrm{I}}$)	3·38
C(2) ··· C(14)	3·05	F(6) ··· C(17$^{\mathrm{II}}$)	3·30
C(4) ··· C(5)	3·12	C(2) ··· F(3$^{\mathrm{II}}$)	3·21
C(4) ··· C(19)	2·91	C(3) ··· F(2$^{\mathrm{II}}$)	3·12
C(4) ··· C(24)	3·36	C(3) ··· F(3$^{\mathrm{II}}$)	3·26
C(4) ··· C(26)	3·17	F(2) ··· C(3$^{\mathrm{III}}$)	3·12
C(6) ··· C(32)	3·05	F(3) ··· C(2$^{\mathrm{III}}$)	3·21
C(6) ··· C(42)	3·18	F(3) ··· C(3$^{\mathrm{III}}$)	3·26
C(7) ··· C(18)	3·17	C(17) ··· F(6$^{\mathrm{III}}$)	3·30
C(19) ··· C(30)	3·20		

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $x, \frac{1}{2} - y, \frac{1}{2} + z$
II $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
III $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$

There are far more than for (II), or for (III), $[CoLCl]PF_6$. Intramolecular crowding should originate in the present complex from the apical contraction in the co-ordination, discussed earlier. The absence of crowding in (III) has been ascribed to the tetrahedral distortion in the co-ordination, which causes an expansion of the volume occupied by the ligand molecule in the high-spin cobalt complexes of the series.[3]

If the orientation of the phenyl groups about their P–C bond direction is ignored, the conformation of the ligand molecule appears to be sufficiently similar in the three complexes for comparisons to be drawn between them. Significant differences involve the M–P–C angles (M = metal) whose mean is 100·5 (I), 95·9 (II), and 109·1° (III). The mean M–N–C values for the three complexes [112·5(1·2), 105·2(1·8), and 110·0(0·6)°] may reveal the effect of the axial contraction present in (I) and possibly of the opposite tendency in (II). There is further evidence that the largest differences in the conformation of the ligand molecule exist between the two nickel complexes, whereas the situation for the cobalt complex, which presents no apparent strains,[3] is somewhat intermediate between those of the other two. Indeed, the mean values of the torsion angles about the C–C bonds in the chains of the ligand are: (I) 49·6, (II) 61·0, and (III) 55·4°. Moreover, the means of the angles formed by the P–C bonds in the chains with the normal to the equatorial plane of the bipyramid are: (I) 9·3, (II) 18·7, and (III) 13·1°. The arrangement of those P–C bonds is sensitive to any changes in the conformation of the ligand. The arrangement in complex (I) should be compatible with the close approach of nitrogen to the metal atom. Moreover, it should produce a rather uniform distribution of the P–C(aryl) bonds in the proximity of the equatorial plane of the bipyramid. Indeed, none of the P–C(aryl) bonds, which lie below the equatorial plane, deviates by more than 26·3° from the plane, in the present complex, whereas there are three in complex (II) which deviate by as much as 31·8°. The reduced hindrance by the phenyl groups should allow the halogen atom to approach to the metal more closely in the present complex, as is actually found. In conclusion, geometric and steric requirements due to the ligand molecule may establish a correlation in the mode of bonding to the metal by the two apical donors, in the nickel complexes of this series. In the present complex, this mechanism seems to be acting together with electronic factors due to the *d* charge distribution.

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