X-Ray Structural Evidence for the Influence of Geometrical Distortion on the Spin-state of Five-co-ordinate Cobalt(II) and Nickel(II) Complexes

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The structures of the two isomorphous complexes [CoLI]I and [NiLI]I [L = the tripod-like quadridentate ligand *NN*-bis-(2-diphenylphosphinoethyl)-*N*-(2-diethylaminoethyl)amine] have been determined from *X*-ray diffractometer data, that of the Ni complex by Patterson and Fourier methods, and of the Co complex by symbolic addition methods. The nickel complex is low-, the cobalt complex high-spin.

Both complexes are monoclinic, space group $P2_1/c$, $Z = 4$. Cell dimensions are: Ni, $a = 19{\cdot}881(2)$, $b = 9{\cdot}468(1)$, $c = 19{\cdot}783(1)$ Å, $\beta = 113{\cdot}75(1)^\circ$; Co, $a = 20{\cdot}309(2)$, $b = 9{\cdot}432(1)$, $c = 20{\cdot}100(3)$ Å, $\beta = 115{\cdot}52(1)^\circ$. The structures were refined by full-matrix least-squares methods to R 6·9 (Co, 1875 independent reflections) and 5·2% (Ni, 3093 independent reflections).

The geometries of both complexes are trigonal-bipyramidal, but the nickel complex is distorted toward an elongated square-pyramid, whereas the cobalt complex is distorted toward a tetrahedron. This distortion can account for the different spin states of the two complexes.

It has been suggested that the electronegativity χ and the nucleophilicity n° of the donor atoms are important factors which govern the spin state in five-co-ordinate cobalt- and nickel-(II) complexes.[1a] As a general rule the cross-over point between high- and low-spin states occurs in the same range of $\Sigma\chi$ and Σn° values (the sum being taken over all donor atoms) for both cobalt- and nickel-(II), when the complexes have a regular or 'standard' geometry, *i.e.* when all five metal–ligand bond lengths are close to the values normally found in five-co-ordinate complexes.[1b] Departures from this rule may occur if one of the five donor atoms is significantly far from the metal atom.

The tripod-like ligand *NN*-bis-(2-diphenylphosphinoethyl)-*N*-(2-diethylaminoethyl)amine, $[\{PPh_2{\cdot}[CH_2]_2\}_2{\cdot}N{\cdot}[CH_2]_2{\cdot}NEt_2$, $n_2p_2]$, forms two isomorphous complexes of nickel- and cobalt-(II), of formula $[M(n_2p_2)I]I$, having different spin states: the nickel complex is low-, the cobalt high-spin.[2]

On the other hand, the compound [Co(pnnp)I]I, having the same set of donor atoms, N_2P_2I, has a low-spin square-pyramidal structure {where pnnp is the open-chain ligand *NN'*-bis-(2-diphenylphosphinoethyl)-*NN'*-dimethylethylenediamine, $PPh_2{\cdot}[CH_2]_2{\cdot}NMe{\cdot}[CH_2]_2{\cdot}NMe{\cdot}[CH_2]_2{\cdot}PPh_2$}.[3,4] It therefore seems that, at least with this set of donor atoms, some factors other than the nature of the donor atoms determine the spin state of these complexes.

In order to clarify this problem, an *X*-ray analysis of the two compounds $[M(n_2p_2)I]I$ (M = Co and Ni) has been undertaken.

EXPERIMENTAL

Crystal Data.—(*a*) $[Ni(n_2p_2)I]I$. $C_{34}H_{42}I_2N_2NiP_2$, $M = 853{\cdot}13$, Monoclinic, $a = 19{\cdot}881 \pm 0{\cdot}002$, $b = 9{\cdot}468 \pm 0{\cdot}001$, $c = 19{\cdot}783 \pm 0{\cdot}001$ Å, $\beta = 113{\cdot}75 \pm 0{\cdot}01^\circ$, $U = 3408{\cdot}45$ Å^3, $D_m = 1{\cdot}66$, $Z = 4$, $D_c = 1{\cdot}672$. Space group $P2_1/c$. $\lambda(\text{Mo-}K_\alpha) = 0{\cdot}70926$ Å, $\mu(\text{Mo-}K_\alpha) = 25{\cdot}28$ cm^{-1}.

(*b*) $[Co(n_2p_2)I]I$. $C_{34}H_{42}CoI_2N_2P_2$, $M = 853{\cdot}41$, Monoclinic, $a = 20{\cdot}309 \pm 0{\cdot}002$, $b = 9{\cdot}432 \pm 0{\cdot}001$, $c = 20{\cdot}100 \pm 0{\cdot}003$ Å, $\beta = 115{\cdot}52 \pm 0{\cdot}01^\circ$, $U = 3474{\cdot}69$ Å^3, $D_m = 1{\cdot}63$, $Z = 4$, $D_c = 1{\cdot}641$. Space group $P2_1/c$. $\mu(\text{Mo-}K_\alpha) = 24{\cdot}42$ cm^{-1}.

Data Collection.—(*a*) $[Ni(n_2p_2)I]I$. The olive-green crystals are monoclinic prisms $\{1\bar{1}\bar{1}\}$ delimited by pinacoids {100}. The space group was determined from *h0l* and *hk0* Weissenberg photographs. The crystal used for data collection (0·41 × 0·20 × 0·10 mm) was mounted along the longest dimension so that the *c* axis coincided with the ϕ axis of the goniostat. Cell dimensions and their estimated standard deviations were obtained from least-squares refinement of twenty 2θ values (means $+2\theta$ and -2θ), collected with a Hilger and Watts four-circle automatic diffractometer. Intensity data were collected by the ω—2θ scan technique with zirconium-filtered Mo-K_α radiation. The take-off angle was 3·0°. 3093 reflections having $I \geqslant 3\sigma(I)$ were measured in the range $0 < 2\theta \leqslant 50^\circ$. Scans of 80 s, with steps of 0·01° and a count of 1 s for each step were taken across the peaks; background was counted for 20 s on each side of the peak. Two standard Reflections were monitored every 60 measurements. The intensities were calculated according to the expression: $I = P - 0{\cdot}5(T_p/T_b)(B_1 + B_2)$, where P is the peak count, B_1 and B_2 are the background counts, and T_p and T_b are the count times on the peak and background respectively. The standard deviations on the intensities were calculated by use of the expression: $\sigma = [P + 0{\cdot}25(B_1 + B_2)(T_p/T_b)^2 + (0{\cdot}02I)^2]^{1/2}$.[5] The observed intensities were corrected for Lorentz and polarization effects. An absorption correction was applied by numerical methods:[6] transmission factors varied between 0·72 and 0·82. Atomic scattering factors were used without correction for anomalous dispersion and were taken from ref. 7 for iodine, nickel, phosphorus, nitrogen, and carbon and from ref. 8 for hydrogen. The effects of the extinction were neglected.

(*b*) $[Co(n_2p_2)I]I$. Cell parameters were determined as

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[1] (*a*) L. Sacconi, *J. Chem. Soc.* (*A*), 1970, 248; (*b*) *Co-ordination Chem. Rev.*, 1972, **8**, 351.

[2] L. Sacconi and R. Morassi, *J. Chem. Soc.* (*A*), 1969, 2904.

[3] L. Sacconi and A. Dei, *J. Co-ordination Chem.*, 1971, **1**, 229.

[4] A. Bianchi, C. A. Ghilardi, C. Mealli, and L. Sacconi, J.C.S. *Chem. Comm.*, 1972, 651.

[5] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[6] Hamilton's GONO9 programme for absorption correction, with local modification for the IBM 1130 computer.

[7] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

before. The crystal used for the collection was a rhombic *plate* (0·50 × 0·25 × 0·08 mm). Data were collected as before with scans of 70 s, with steps of 0·01° and a count of 1 s for each step, across the peaks; background was counted for 35 s on each side of the peak. Three check reflections were monitored every 50 measurements. 1875 Reflections having $I \geqslant 3\sigma(I)$ were obtained in the range $0 < 2\theta \leqslant 40°$. Lorentz-polarization corrections were applied together with an absorption correction: transmission factors varied between 0·83 and 0·45. No corrections were made for anomalous dispersion nor for extinction. Scattering factors for non-hydrogen atoms were taken from ref. 7 and for hydrogen atoms from 9.

TABLE 1

$[Ni(n_2p_2)I]I$: Positional parameters and anisotropic temperature factors [a] with estimated standard deviations in parentheses

Atom	$10^5x/a$	$10^5y/b$	$10^5z/c$	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
I(1)	33736(4)	58811(10)	18183(5)	224(3)	1229(13)	264(3)	−201(5)	126(2)	−59(5)
I(2)	4678(5)	52737(11)	34917(5)	262(3)	1183(13)	279(3)	104(5)	109(2)	8(5)
Ni	22687(8)	44004(16)	17272(8)	157(4)	687(18)	163(5)	−76(7)	80(4)	−37(7)
	$10^4x/a$	$10^4y/b$	$10^4z/c$	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
P(1)	2330(2)	3298(3)	769(2)	15(1)	81(4)	18(1)	−2(2)	8(1)	−6(2)
P(2)	2714(2)	3913(4)	2946(2)	15(1)	91(4)	18(1)	−4(2)	8(1)	−1(2)
N(1)	1405(5)	3136(10)	1614(5)	23(3)	66(12)	22(3)	−10(5)	10(3)	−7(5)
N(2)	1422(5)	6194(11)	1451(6)	22(3)	97(14)	25(4)	0(5)	12(3)	−6(6)

[a] In the form: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

TABLE 2

$[Ni(n_2p_2)I]I$: Positional parameters ($\times 10^3$) and isotropic temperature factors, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/Å^2$
C(1)	116(1)	227(1)	92(1)	3·2(0·2)
C(2)	180(1)	172(1)	77(1)	3·1(0·2)
C(3)	157(1)	214(1)	224(1)	2·9(0·2)
C(4)	197(1)	289(1)	298(1)	3·4(0·2)
C(5)	79(1)	407(1)	156(1)	3·2(0·2)
C(6)	74(1)	536(1)	112(1)	3·3(0·2)
C(7)	145(1)	722(1)	87(1)	3·0(0·2)
C(8)	84(1)	827(2)	58(1)	5·2(0·3)
C(9)	143(1)	700(1)	209(1)	3·5(0·3)
C(10)	207(1)	799(2)	242(1)	4·0(0·3)
C(11)	185(1)	408(1)	−15(1)	2·2(0·2)
C(12)	206(1)	542(1)	−27(1)	3·2(0·2)
C(13)	169(1)	606(2)	−94(1)	3·7(0·3)
C(14)	109(1)	542(2)	−148(1)	4·2(0·3)
C(15)	92(1)	408(1)	−137(1)	3·5(0·2)
C(16)	128(1)	342(1)	−70(1)	3·0(0·2)
C(17)	318(1)	263(1)	80(1)	2·6(0·2)
C(18)	362(1)	184(2)	140(1)	4·3(0·3)
C(19)	430(1)	124(2)	144(1)	6·0(0·4)
C(20)	452(1)	152(2)	87(1)	5·4(0·4)
C(21)	409(1)	235(2)	29(1)	5·3(0·3)
C(22)	344(1)	293(2)	26(1)	3·7(0·3)
C(23)	349(1)	265(1)	321(1)	3·0(0·2)
C(24)	338(1)	127(2)	329(1)	4·3(0·3)
C(25)	396(1)	33(2)	343(1)	7·2(0·5)
C(26)	464(1)	78(2)	351(1)	6·5(0·4)
C(27)	474(1)	220(2)	343(1)	5·2(0·3)
C(28)	416(1)	314(2)	327(1)	4·1(0·3)
C(29)	299(1)	509(1)	374(1)	3·2(0·2)
C(30)	355(1)	609(2)	388(1)	4·0(0·3)
C(31)	378(1)	700(2)	447(1)	5·1(0·3)
C(32)	344(1)	686(2)	496(1)	4·3(0·3)
C(33)	288(1)	593(2)	485(1)	4·7(0·3)
C(34)	264(1)	501(2)	421(1)	3·8(0·3)

Structure Determinations.—(*a*) $[Ni(n_2p_2)I]I$. A three-dimensional Patterson function yielded the positional parameters of the nickel and the iodine atoms. The other non-hydrogen atoms were located from successive three-dimensional Fourier maps. These calculations were performed on an IBM 1130.[10] Refinement was then undertaken by use of the full-matrix least-squares programs

TABLE 3

$[Ni(n_2p_2)I]I$: Positional parameters ($\times 10^3$) of the hydrogen atoms *

Atom	x/a	y/b	z/c
H(1,1)	95	163	102
H(1,2)	77	290	42
H(2,1)	217	124	128
H(2,2)	165	128	30
H(3,1)	112	150	216
H(3,2)	183	142	217
H(4,1)	191	213	330
H(4,2)	164	360	300
H(5,1)	84	434	209
H(5,2)	25	339	120
H(6,1)	25	625	107
H(6,2)	75	506	54
H(7,1)	190	751	99
H(7,2)	140	658	51
H(8,1)	104	899	28
H(8,2)	87	890	90
H(8,3)	50	770	40
H(9,1)	146	620	242
H(9,2)	96	750	195
H(10,1)	199	810	286
H(10,2)	266	735	253
H(10,3)	209	885	198
H(12)	247	590	17
H(13)	180	690	−83
H(14)	83	590	−196
H(15)	55	352	−152
H(16)	107	260	−65
H(18)	360	153	196
H(19)	435	31	175
H(20)	494	88	86
H(21)	439	209	−10
H(22)	316	348	−10
H(24)	295	76	318
H(25)	390	−80	330
H(26)	515	0	362
H(27)	520	260	334
H(28)	416	428	320
H(30)	378	630	350
H(32)	324	749	530
H(34)	215	435	410

* Numbered according to the carbon atom to which they are attached.

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.

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

of Busing and Levy, adapted for the IBM 360/67 by Stewart.[11] Two cycles of refinement with isotropic temperature factors for all non-hydrogen atoms reduced R to 8·7%. Then two cycles with isotropic temperature factors for carbon atoms and anisotropic parameters for the heavier atoms, brought R to 5·7%. At this point a difference-Fourier synthesis showed the positions of 40 hydrogen atoms, which were introduced in the subsequent calculations in fixed positions with a temperature factor B 5·5 Å^2. Two more cycles gave a final R of 5·2%. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The F values were weighted according to the Hughes expression: $w = 1$ for reflections with $F_o \leqslant 45$ and $\sqrt{w} = 45/F_o$ for reflections with $F_o > 45$.

TABLE 4

$[Co(n_2p_2)I]I$: Positional parameters ($\times 10^4$) and anisotropic temperature factors [a] ($\times 10^4$), 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}
I(1)	3430(1)	6540(2)	1908(1)	38(1)	198(3)	48(1)	−27(1)	22(1)	−4(1)
I(2)	475(1)	5339(2)	3485(1)	37(1)	108(2)	49(1)	8(1)	21(1)	1(1)
Co	2317(1)	4933(3)	1793(1)	26(1)	91(4)	35(1)	−3(2)	16(1)	−1(2)
P(1)	2368(3)	3320(6)	863(3)	27(2)	91(8)	39(2)	−5(3)	15(2)	−10(3)
P(2)	2726(3)	3996(6)	3026(3)	29(2)	110(8)	36(2)	−2(3)	16(2)	1(3)
N(1)	1388(8)	3170(15)	1657(8)	33(6)	58(21)	21(6)	−3(9)	7(4)	−12(8)
N(2)	1362(9)	6306(18)	1446(9)	34(6)	134(26)	33(6)	−13(11)	15(5)	−3(11)

[a] See footnote to Table 1.

Final values of the atomic parameters with their estimated standard deviations are reported in Tables 1—3. Standard deviations were calculated by use of the expression: $\sigma_j = [\Sigma w \Delta F^2 a^{jj}/(m - n)]^{1/2}$, where m is the number of the reflections, n the number of the parameters refined and a^{jj} the jjth element of the inverse least-squares matrix.

(b) $[Co(n_2p_2)I]I$. The structure was solved by obtaining signs for the normalized structure factors by the symbolic addition procedure for centrosymmetric crystals,[12] using Ahmed's programme SAP.[13] The origin was specified by assigning positive signs to the reflections $6,3,\bar{5}$, $13,3,\bar{5}$, and 5,5,0, all with $E > 2·9$. Three other strong reflections, 10,0,0, 12,2,3, and $12,1,\bar{3}$ were assigned symbols to represent the signs. These six reflections were used in the search of the signs (or symbols) of other reflections having $E \geqslant 1·60$, using the Σ_2 relationship.[12] In the course of this determination, the sign of each symbol became apparent. The signs of 274 reflections, on a total of 285 having $E \geqslant 1·60$, were so determined and used in the E-map calculation. This map revealed the positions of cobalt, iodine, and phosphorus atoms. Two subsequent Fourier syntheses showed all non-hydrogen atoms. At this point R was 23%. These calculations were made with an IBM 1130 computer with the programmes of ref. 10. The refinement was carried out as for the nickel with the Hughes weighting scheme. Three cycles of refinement of positional and isotropic thermal parameters and the scale factor lowered R to 11%. A difference-Fourier synthesis calculated at this point, showed the positions of 37 of the 42 hydrogen atoms. These hydrogen atoms were also introduced in the calculations in fixed positions, with an isotropic thermal parameter of 6 Å^2 for each atom. Three more cycles of refinement of atomic parameters and scale factor were performed with anisotropic temperature factors for iodine, cobalt, phosphorus, and nitrogen atoms and isotropic for carbon atoms. The final R was 6·9%. A final difference-Fourier synthesis showed no remarkable features. The final values of the parameters and their standard deviations are reported in Tables 4—6.†

DISCUSSION

Description of the Structures.—The molecular structures of the two compounds consist of discrete $[M(n_2p_2)I]^+$ and I^- anions. Both metal atoms are co-ordinated to the four donor atoms of the tripod ligand and to an

TABLE 5

$[Co(n_2p_2)I]I$: Positional parameters ($\times 10^3$) and isotropic temperature factors, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B/Å^2
C(1)	120(1)	233(3)	101(1)	5·5(0·5)
C(2)	187(1)	177(2)	91(1)	4·7(0·5)
C(3)	158(1)	228(2)	229(1)	4·8(0·5)
C(4)	195(1)	301(2)	300(1)	5·0(0·5)
C(5)	74(1)	406(2)	153(1)	4·7(0·5)
C(6)	69(1)	536(2)	109(1)	4·2(0·4)
C(7)	143(1)	731(2)	92(1)	4·7(0·5)
C(8)	74(1)	833(3)	60(1)	7·0(0·6)
C(9)	136(1)	705(2)	210(1)	4·4(0·5)
C(10)	196(1)	808(3)	248(1)	5·5(0·5)
C(11)	186(1)	402(2)	−4(1)	3·5(0·4)
C(12)	204(1)	536(3)	−17(1)	5·6(0·5)
C(13)	163(1)	609(3)	−86(1)	5·7(0·5)
C(14)	107(1)	529(2)	−142(1)	4·6(0·5)
C(15)	95(1)	389(2)	−129(1)	4·5(0·5)
C(16)	133(1)	327(2)	−60(1)	4·8(0·5)
C(17)	319(1)	265(3)	88(1)	5·3(0·5)
C(18)	361(1)	170(3)	141(1)	7·2(0·7)
C(19)	430(2)	109(4)	147(2)	9·6(0·9)
C(20)	450(2)	152(4)	94(2)	10·1(0·9)
C(21)	413(2)	244(4)	41(2)	8·6(0·8)
C(22)	346(1)	308(3)	37(1)	7·1(0·6)
C(23)	344(1)	270(2)	324(1)	4·6(0·5)
C(24)	335(2)	128(3)	337(2)	8·4(0·8)
C(25)	398(2)	30(3)	352(2)	8·4(0·8)
C(26)	459(2)	72(3)	353(1)	7·8(0·7)
C(27)	466(2)	215(3)	333(2)	8·5(0·8)
C(28)	406(1)	309(3)	320(1)	6·1(0·6)
C(29)	301(1)	516(3)	382(1)	5·3(0·5)
C(30)	360(1)	604(3)	395(1)	7·1(0·6)
C(31)	387(1)	696(3)	458(1)	7·0(0·6)
C(32)	353(1)	695(3)	505(1)	5·7(0·5)
C(33)	291(1)	605(3)	488(1)	6·5(0·6)
C(34)	268(1)	514(3)	428(1)	5·8(0·5)

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† Observed and calculated structure factors for both structures are published in Supplementary Publication No. SUP 20612 (6 pp., 1 microfiche). Details of Supplementary Publications are in Notice to Authors, No. 7, *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[11] J. M. Stewart, '*X*-Ray '63,' 1967 version, Technical Report TR 67 58, University of Maryland, Computer Science Centre, 1967.

[12] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[13] F. S. Ahmed, SAP programme, with local modifications.

iodine atom. Figures 1 and 2 show perspective views of the cations. Bond distances and angles in the two cations are reported in Tables 7 and 8. Both cations have a distorted trigonal bipyramidal structure, with the central nitrogen atom of the ligand and the iodine atom in the axial positions, the N(1)–M–I(1) angles being 176·4 and 171·7° respectively for the nickel and the cobalt complex. However, the type of distortion from the idealized geometry is different in the two cases (Figure 3).

TABLE 6

$[\mathrm{Co(n_2p_2)I}]\mathrm{I}$: Positional parameters ($\times 10^3$) of the hydrogen atoms *

Atom	*x*/*a*	*y*/*b*	*z*/*c*
H(1,1)	85	144	95
H(1,2)	87	296	51
H(2,1)	219	120	147
H(2,2)	172	88	38
H(3,1)	120	226	246
H(3,2)	193	160	232
H(4,1)	211	248	333
H(4,2)	175	368	293
H(5,1)	87	420	195
H(5,2)	39	370	115
H(6,1)	27	620	115
H(6,2)	62	514	58
H(7,1)	190	770	111
H(7,2)	135	662	57
H(8,1)	77	890	9
H(8,3)	25	790	25
H(9,1)	127	628	247
H(9,2)	80	732	193
H(10,1)	181	870	293
H(10,2)	235	780	271
H(10,3)	189	900	212
H(12)	255	590	28
H(14)	95	440	−187
H(15)	55	340	−180
H(16)	109	246	−73
H(18)	360	170	189
H(19)	445	50	190
H(20)	508	80	86
H(21)	424	228	−6
H(22)	313	374	−2
H(24)	275	28	320
H(27)	488	166	278
H(28)	417	376	302
H(30)	395	616	367
H(31)	447	750	477
H(32)	367	740	570
H(33)	265	570	545

* Numbered according to the carbon atom to which they are attached.

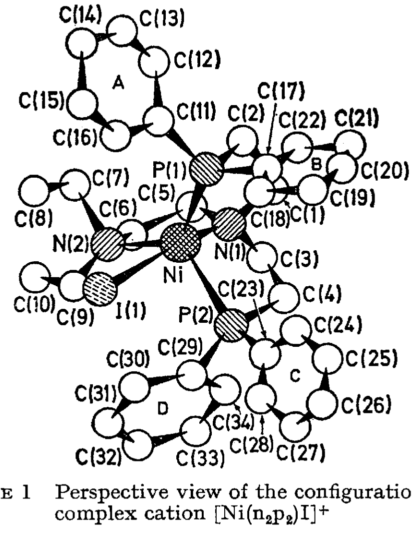

FIGURE 1 Perspective view of the configuration of the complex cation $[\mathrm{Ni(n_2p_2)I}]^+$

TABLE 7

$[\mathrm{Ni(n_2p_2)I}]\mathrm{I}$: Interatomic distances (Å) and angles (°), with their standard deviations

(*a*) Bond lengths

Ni–I(1)	2·550(2)	N(1)–C(1)	1·50(2)
Ni–P(1)	2·209(3)	N(1)–C(3)	1·49(2)
Ni–P(2)	2·256(3)	N(1)–C(5)	1·48(2)
Ni–N(1)	2·030(10)	N(2)–C(6)	1·47(2)
Ni–N(2)	2·296(10)	N(2)–C(7)	1·53(2)
		N(2)–C(9)	1·47(2)
P(1)–C(2)	1·83(1)	C(1)–C(2)	1·51(2)
P(1)–C(11)	1·84(1)	C(3)–C(4)	1·53(2)
P(1)–C(17)	1·79(1)	C(5)–C(6)	1·48(2)
P(2)–C(4)	1·79(1)	C(7)–C(8)	1·48(2)
P(2)–C(23)	1·85(1)	C(9)–C(10)	1·50(2)
P(2)–C(29)	1·82(1)		

(*b*) Bond angles

I(1)–Ni–P(1)	88·7(0·1)	Ni–P(2)–C(4)	100·4(0·4)
I(1)–Ni–P(2)	94·6(0·1)	Ni–P(2)–C(23)	110·8(0·4)
I(1)–Ni–N(1)	176·4(0·3)	Ni–P(2)–C(29)	130·3(0·5)
I(1)–Ni–N(2)	97·9(0·3)	C(4)–P(2)–C(23)	104·0(0·6)
P(1)–Ni–P(2)	133·4(0·1)	C(4)–P(2)–C(29)	105·5(0·6)
P(1)–Ni–N(1)	87·9(0·3)	C(23)–P(2)–C(29)	103·1(0·6)
P(1)–Ni–N(2)	115·7(0·3)	Ni–N(1)–C(1)	112·0(0·7)
P(2)–Ni–N(1)	87·0(0·3)	Ni–N(1)–C(3)	113·1(0·7)
P(2)–Ni–N(2)	109·9(0·3)	Ni–N(1)–C(5)	107·2(0·7)
N(1)–Ni–N(2)	84·4(0·4)	C(1)–N(1)–C(3)	107·1(0·9)
		C(1)–N(1)–C(5)	107·6(0·9)
P(1)–C(11)–C(12)	118·1(0·9)	C(3)–N(1)–C(5)	109·7(0·9
P(1)–C(11)–C(16)	122·3(0·9)	Ni–N(2)–C(6)	99·2(0·7)
P(1)–C(17)–C(18)	119·3(1·0)	Ni–N(2)–C(7)	114·1(0·7)
P(1)–C(17)–C(22)	123·0(1·0)	Ni–N(2)–C(9)	115·4(0·8)
P(2)–C(23)–C(24)	120·6(1·0)	C(6)–N(2)–C(7)	107·9(0·9)
P(2)–C(23)–C(28)	118·3(1·0)	C(6)–N(2)–C(9)	110·7(1·0)
P(2)–C(29)–C(30)	122·3(1·0)	C(7)–N(2)–C(9)	109·0(1·0)
P(2)–C(29)–C(34)	119·2(1·0)	N(1)–C(1)–C(2)	112·0(1·0)
Ni–P(1)–C(2)	98·8(0·4)	P(1)–C(2)–C(1)	104·5(0·9)
Ni–P(1)–C(11)	118·4(0·4)	N(1)–C(3)–C(4)	111·0(1·0)
Ni–P(1)–C(17)	121·1(0·4)	P(2)–C(4)–C(3)	109·4(0·9)
C(2)–P(1)–C(11)	105·4(0·5)	N(1)–C(5)–C(6)	112·5(1·0)
C(2)–P(1)–C(17)	104·5(0·6)	N(2)–C(6)–C(5)	111·0(1·0)
C(11)–P(1)–C(17)	106·2(0·5)	N(2)–C(7)–C(8)	115·9(1·0)
		N(2)–C(9)–C(10)	114·1(1·1)

(*c*) Phenyl rings

	Mean	Mean devn.	Max. devn.
(i) Bond lengths			
Ring			
A	1·37	0·01	0·02
B	1·39	0·02	0·05
C	1·37	0·02	0·03
D	1·39	0·02	0·05
(ii) Bond angles			
Ring			
A	119·9	0·7	1·4
B	120·0	1·3	2·3
C	120·0	0·8	1·2
D	120·0	2·5	3·9

In the cobalt complex the metal atom lies 0·48 Å below the equatorial plane (equation $2{\cdot}92x + 1{\cdot}15y - 0{\cdot}84z = 1$; monoclinic co-ordinates), toward the iodine atom. Also, the Co–N(1) distance [2·44(1) Å] is markedly longer than Co–N distances normally found in high-spin five-co-ordinate complexes, so that the structure tends towards being tetrahedral with a mean I–Co–L(eq) angle of 102°.

This type of co-ordination which is intermediate between a trigonal bipyramid and a tetrahedron, where an apical donor atom can be considered to be 'semi-co-ordinated,'[14] is also found in other high-spin cobalt complexes with tripod ligands.[15-17]

In contrast, the nickel atom, in the $[Ni(n_2p_2)I]^+$ chromophore, is only 0·12 Å out of the equatorial plane (equation $2{\cdot}97x + 1{\cdot}13y - 0{\cdot}84z = 1$), toward the iodine atom. The Ni–N(1) distance is 2·03(1) Å. On the other hand, the Ni–N(2) distance [2·30(1) Å], is significantly greater than either the Co–N(2) distance or the Ni–N bond distances normally found in five-co-ordinate low-spin Ni^{II} complexes. Finally, the angle opposite to this bond is expanded to 133·4° from the idealized 120°.

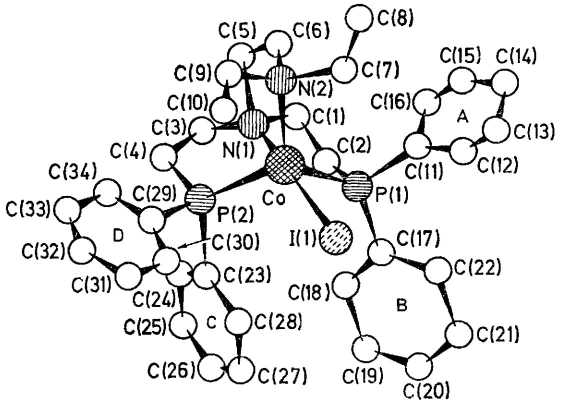

FIGURE 2 Perspective view of the configuration of the complex cation $[Co(n_2p_2)I]^+$

This geometry then can be considered as a trigonal bipyramid distorted towards a square pyramid, where the N(2) atom represents the apex. The lengthening of the Ni–N(2) bond corresponds to the apical elongation which is peculiar to most low-spin square pyramidal d^8 complexes.[18-23]

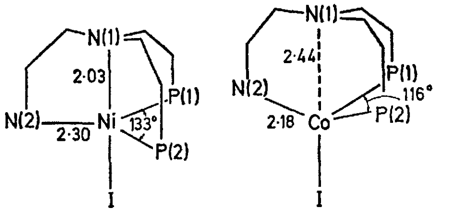

FIGURE 3 Schematic drawing showing the distortions of the co-ordination polyhedra of the two complexes

TABLE 8

$[Co(n_2p_2)I]I$: Interatomic distances (Å) and angles (°), with their standard deviations

(*a*) Bond lengths

Co–I(1)	2·647(3)	N(1)–C(1)	1·43(3)
Co–P(1)	2·446(6)	N(1)–C(3)	1·44(3)
Co–P(2)	2·416(6)	N(1)–C(5)	1·48(3)
Co–N(1)	2·440(15)	N(2)–C(6)	1·52(3)
Co–N(2)	2·181(17)	N(2)–C(7)	1·46(3)
		N(2)–C(9)	1·50(3)
P(1)–C(2)	1·80(2)	C(1)–C(2)	1·56(3)
P(1)–C(11)	1·79(2)	C(3)–C(4)	1·46(3)
P(1)–C(17)	1·78(2)	C(5)–C(6)	1·49(3)
P(2)–C(4)	1·82(2)	C(7)–C(8)	1·58(3)
P(2)–C(23)	1·81(2)	C(9)–C(10)	1·48(3)
P(2)–C(29)	1·81(2)		

(*b*) Bond angles

I(1)–Co–P(1)	96·1(0·1)	Co–P(2)–C(4)	104·6(0·7)
I(1)–Co–P(2)	102·5(0·1)	Co–P(2)–C(23)	112·2(0·7)
I(1)–Co–N(1)	171·7(0·3)	Co–P(2)–C(29)	121·4(0·8)
I(1)–Co–N(2)	107·2(0·4)	C(4)–P(2)–C(23)	105·3(1·0)
P(1)–Co–P(2)	116·5(0·2)	C(4)–P(2)–C(29)	105·6(1·0)
P(1)–Co–N(1)	77·0(0·4)	C(23)–P(2)–C(29)	106·4(1·0)
P(1)–Co–N(2)	116·7(0·4)	Co–N(1)–C(1)	111·7(1·2)
P(2)–Co–N(1)	76·9(0·4)	Co–N(1)–C(3)	113·5(1·2)
P(2)–Co–N(2)	114·2(0·4)	Co–N(1)–C(5)	102·5(1·1)
N(1)–Co–N(2)	80·2(0·5)	C(1)–N(1)–C(3)	110·8(1·6)
		C(1)–N(1)–C(5)	107·0(1·6)
P(1)–C(11)–C(12)	116·4(1·5)	C(3)–N(1)–C(5)	110·7(1·5)
P(1)–C(11)–C(16)	123·0(1·6)	Co–N(2)–C(6)	107·1(1·2)
P(1)–C(17)–C(18)	120·6(1·9)	Co–N(2)–C(7)	105·6(1·2)
P(1)–C(17)–C(22)	122·5(1·9)	Co–N(2)–C(9)	109·4(1·2)
P(2)–C(23)–C(24)	121·9(1·9)	C(6)–N(2)–C(7)	112·5(1·5)
P(2)–C(23)–C(28)	118·6(1·9)	C(6)–N(2)–C(9)	110·6(1·5)
P(2)–C(29)–C(20)	116·3(1·8)	C(7)–N(2)–C(9)	111·4(1·6)
P(2)–C(29)–C(34)	122·5(1·9)	N(1)–C(1)–C(2)	113·3(1·8)
Co–P(1)–C(2)	104·8(0·7)	P(1)–C(2)–C(1)	105·8(1·5)
Co–P(1)–C(11)	110·8(0·7)	N(1)–C(3)–C(4)	115·3(1·9)
Co–P(1)–C(17)	123·6(0·8)	P(2)–C(4)–C(3)	109·7(1·5)
C(2)–P(1)–C(11)	105·4(1·0)	N(1)–C(5)–C(6)	113·4(1·7)
C(2)–P(1)–C(17)	104·6(1·1)	N(2)–C(6)–C(5)	112·3(1·6)
C(11)–P(1)–C(17)	106·0(1·0)	N(2)–C(7)–C(8)	110·6(1·8)
		N(2)–C(9)–C(10)	116·9(1·7)

(*c*) Phenyl rings

	Mean	Mean devn.	Max. devn.
(i) Bond lengths			
Ring			
A	1·40	0·02	0·04
B	1·40	0·05	0·10
C	1·40	0·06	0·11
D	1·39	0·02	0·04
(ii) Bond angles			
Ring			
A	119·9	1·3	3·9
B	120·0	3·3	6·1
C	119·9	2·2	4·0
D	120·0	0·7	1·2

The Co–P (mean 2·43 Å) and Ni–P (mean 2·23 Å) bond distances are well within the range of values reported respectively for high-spin cobalt(II)[15-17] and low-spin nickel(II) complexes,[21,24-26] having trigonal bipyramidal

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[14] D. S. Brown, J. D. Lee, B. G. A. Melson, B. J. Hathaway, I. M. Procter, and A. A. G. Tomlinson, *Chem. Comm.*, 1967, **369**.

[15] L. Sacconi, M. Di Vaira, and A. Bianchi, *J. Amer. Chem. Soc.*, 1970, **92**, 4465.

[16] P. Dapporto, G. Fallani, and L. Sacconi, *J. Co-ordination Chem.*, 1971, **1**, 269.

[17] P. Dapporto and Giovanna Fallani, *J.C.S. Dalton*, 1972, 1498.

[18] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 1960, 415.

[19] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1362.

[20] E. B. Fleischer and S. W. Hawkinson, *Inorg. Chem.*, 1968, **7**, 2312.

[21] D. W. Allen, F. G. Mann, I. T. Millar, H. M. Powell, and D. Watkin, *Chem. Comm.*, 1969, 1004.

[22] P. Dapporto, R. Morassi, and L. Sacconi, *J. Chem. Soc.* (*A*), 1970, 1298.

[23] P. L. Orioli and C. A. Ghilardi, *J. Chem. Soc.* (*A*), 1970, 1511.

[24] J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, pp. 1084, 1090.

[25] H. M. Powell, D. J. Watkin, and J. B. Wilford, *J. Chem. Soc.* (*A*), 1971, 1803.

[26] E. F. Riedel and R. A. Jacobson, *Inorg. Chim. Acta*, 1970, 407.

geometry. The Co–I distance [2·647(3) Å] is as expected, but the Ni–I distance [2·550(2) Å] is rather short, compared with the values [2·609(3) and 2·624(3) Å] reported for equatorial Ni–I bonds in a low-spin trigonal bipyramidal complex.[27] This fact, together with the rather short Ni–N(1) bond, suggests an axial contraction, which is hardly surprising for a low-spin d^8 complex with C_{3v} symmetry, the d_{z^2} orbital being empty.[28] A closer approach of the iodine to the nickel atom seems to be hindered by the presence of short contacts [I(1) ⋯ P(1) 3·33 and I(1) ⋯ P(2) 3·54 Å]. All the other distances and angles in the two complexes are normal. There are no unusual intermolecular contacts.

Since the two $[M(n_2p_2)I]I$ compounds are isomorphous, the two different distortions from the trigonal bipyramid cannot be attributed to packing effects, but must be ascribed to the intrinsic electronic requirements of the two metal ions.[29]

A ligand-field treatment on five-co-ordinate cobalt(II) and nickel(II) has shown that, provided the five donor atoms are equivalent, the spin state is independent of the chromophore geometry.[1b] When, however, one of the donor atoms is ' semi-co-ordinated,' *i.e.*, at a longer distance from the metal than the ' standard ' one, the spin state may be affected by distortions towards four-co-ordination.

The axial elongation seems to be an important factor in stabilizing the low-spin state in square pyramidal nickel(II) complexes.[1b] On the other hand a trigonal bipyramidal cobalt(II) complex may be low-spin with an ^2E ground state, or high-spin with an $^4A_2$ ground state.[30] As the structure is distorted towards tetrahedral, the ^2E level is destabilized and the $^4A_2$ state, which is characteristic of the tetrahedral cobalt(II) complexes, is favoured as the ground state.[1b]

The tetrahedral distortion of the cobalt and the distortion toward the square pyramid of the nickel complex can therefore account for the different spin states of the two complexes $[M(n_2p_2)I]I$.

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[27] C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 1972, **11**, 828.

[28] K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1111.

[29] M. Ciampolini, M. Di Vaira, and P. L. Orioli, Proc. XI Internat. Conf. Co-ordination Chem., Israel, 1968, p. 217; P. L. Orioli, *Co-ordination Chem. Rev.*, 1971, **6**, 285.

[30] M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 540.