X-Ray Investigations on Spin-state Equilibria. Crystal and Molecular Structure of Two Five-co-ordinate Cobalt(II) Complexes with an N_4P Donor Set

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The crystal and molecular structures of two complexes of cobalt(II) isothiocyanate with the ligand *N*[(diphenylphosphino)ethyl]-*N*′-diethylethylenediamine (nnp) and its methyl derivative (nnpMe), have been determined. Crystals of $Co(nnp)(NCS)_2$ (I) are triclinic, space group $P\bar{1}$, with a = 15·896(4), b = 8·786(2), c = 9·402(2) Å, α = 111·3(1), β = 94·6(1), γ = 90·5(1)°, Z = 2. Crystals of $Co(nnpMe)(NCS)_2$ (II) are monoclinic, space group *Cc*, with a = 13·485(4), b = 13·503(4), c = 16·034(6) Å, β = 116·22(2)°. Counter methods were used to collect 1437 (I) and 1815 (II) reflections and the structures solved by the heavy-atom method; least-squares refinement gave R 7·4 (I) and 6·2% (II).

In both complexes the cobalt atom is five-co-ordinated by the two nitrogen and the phosphorus atoms of the ligand and the two nitrogen atoms of the thiocyanate groups. The two co-ordination polyhedra can be described as distorted trigonal bipyramids, that of (I) tending towards an elongated square pyramid, that of (II) towards the tetrahedron. The magnetic moment of (I) varies reversibly with temperature whereas (II) is constantly high spin. These differences are ascribed to different distortions of the two co-ordination polyhedra.

AMONG factors governing the spin state of five-co-ordinate cobalt(II) complexes are: the nature of the donor atoms quantitatively expressed by their electronegativity, χ, and their nucleophilicity n^0 (ref. 1), and the distortions of the co-ordination geometry.

Recent experimental results [2,3] and ligand-field calculations [4] show that, in fact, for trigonal bipyramidal cobalt(II) complexes the tetrahedral distortion, with the lengthening of one of the apical bonds, favours the high-spin state, whereas the elongation of the apical bond in square pyramidal complexes favours the low-spin state.

The five-co-ordinate complexes formed by cobalt(II) isothiocyanate with the tridentate ligand nnp (nnp = *N*-[(diphenylphosphino)ethyl]-*N*′-diethylethylenediamine, $(Et_2N{\cdot}[CH_2]_2{\cdot}NH{\cdot}[CH_2]_2{\cdot}PPh_2)$, $Co(nnp)(NCS)_2$ (I) and its *N*-methyl derivative (nnpMe), $Co(nnpMe)(NCS)_2$ (II), both with the chromophore $Co(N_2P)(NCS)_2$, have Σn^0 and $\Sigma\chi$ values which fall in the cross-over range between high- and low-spin complexes. However the methyl derivative is high spin (μ_{eff} 4·5 B.M.), whereas the unsubstituted complex shows a magnetic moment varying reversibly with the temperature from 2·16 at 77 up to 4·32 B.M. at 418 K, the value at room temperature being 3·58 B.M.[5]

Anomalies in the magnetic behaviour could arise from [6] antiferromagnetic exchange between adjacent cobalt atoms, conformational equilibrium between two different stereochemical forms, one high- and the other low-spin (although such equilibria, which are well known in solution, are unlikely in the solid state) and spin-state

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[1] L. Sacconi, *J. Chem. Soc.* (*A*), 1970, 248.

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

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

[4] L. Sacconi, *Co-ordination Chem. Rev.*, 1972, **8**, 351.

[5] R. Morassi and L. Sacconi, *J. Amer. Chem. Soc.*, 1970, **92**, 5241.

[6] E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev.*, 1968, **22**, 457.

equilibrium between a doublet ground-state and a thermally accessible quartet state ($^2A_1 \rightleftarrows {}^4A_2$ in C_{4v} symmetry, $^2E' \rightleftarrows {}^4A_2$ in D_{3h} symmetry). Although molecular weight, spectral, and magnetic properties supported the last hypothesis, we undertook an *X*-ray analysis since there are few studies concerning the structural aspects of spin-state equilibria.[7,8]

In order to discuss in detail bond distances and angles in the co-ordination polyhedron, the structure of the *N*-methylated high-spin derivative was also determined. Since the donor set $N_2P(NCS)_2$ is the same in both complexes, the difference in spin state was expected to be mainly due to geometrical factors affecting the co-ordination polyhedron.

EXPERIMENTAL

Crystal Data.—(*a*) Co(nnp)(NCS)$_2$ (I). $C_{22}H_{28}CoN_4PS_2$, M = 503·55, Triclinic, a = 15·896(4), b = 8·786(2), c = 9·402(2) Å, α = 111·3(1), β = 94·6(1), γ = 90·5(1)°, U = 1218·58 Å^3, D_m = 1·33, Z = 2, D_c = 1·38. λ(Mo-K_α) = 0·70926 Å, μ(Mo-K_α) = 9·56 cm^{-1}. Space group $P\bar{1}$.

(*b*) Co(nnpMe)(NCS)$_2$ (II). $C_{23}H_{31}CoN_4PS_2$, M = 517·58, Monoclinic, a = 13·485(4), b = 13·503(4), c = 16·034(6) Å, β = 116·22(2)°, U = 2619·07 Å^3, D_m 1·35, Z = 4, D_c = 1·32. μ(Mo-K_α) = 9·18 cm^{-1}. Space group *Cc* or *C*2/*c* from systematic absences, the former confirmed by the successful refinement of the structure.

Data Collection.—(*a*) (I). Crystals of (I) were prepared as described elsewhere.[5] A crystal, with dimensions *ca.* 0·08 × 0·06 × 0·5 mm was approximately mounted along *c* on a Hilger four-circle computer-controlled diffractometer and the θ, χ, and ϕ values of 12 reflections were accurately centred and used for the refinement of cell parameters and orientation matrix.

Intensity data were collected with a ω—2θ scan technique at a take-off angle of 3°. All possible independent reflections within 2θ 40° were measured, zirconium filtered Mo-K_α radiation being used. After correction for background, the standard deviation $\sigma(I)$ of the corrected intensity I was estimated according to the following expression:[9]

$$\sigma(I) = [P + 0{\cdot}25(B_1 + B_2)(T_p/T_b)^2 + (0{\cdot}02I)^2]^{1/2}$$

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. 1437 Reflections having $I > 2\sigma(I)$ were considered observed, and were corrected for Lorentz-polarization effects. Absorption corrections were neglected, since with a calculated linear absorption coefficient μ of 9·56 cm^{-1}, transmission factors varied between 0·93 and 0·95.

(*b*) (II). This was also prepared as described in ref. 5. The crystal used for data collection, of dimensions *ca.* 0·60 × 0·20 × 0·15 mm, was mounted along the longest dimension and the *c* axis was aligned so as to coincide with the ϕ axis of the goniostat. Cell dimensions were refined as already described for (I). Intensity data were collected as before and corrected for Lorentz-polarization effects, but no corrections were applied for absorption. 1815 Reflections having $I > 2\sigma(I)$ were obtained in the range $0 < 2\theta \leqslant 50°$

TABLE 1

(I): Positional parameters (×10^4), and isotropic thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B/Å^2
Co	2614(1)	1131(3)	1228(2)	*
S(1)	4463(2)	−3189(5)	−1006(5)	*
S(2)	1168(3)	−3043(6)	2101(6)	*
P	3056(2)	2385(4)	3806(4)	*
N(1)	3546(8)	−409(16)	322(15)	*
N(2)	1889(8)	−519(19)	1435(15)	*
N(3)	1951(6)	1284(12)	−700(11)	*
N(4)	3332(6)	3088(13)	1088(12)	*
C(1)	3934(8)	−1597(20)	−269(17)	*
C(2)	1594(9)	−1594(22)	1682(17)	*
C(3)	2551(9)	2091(18)	−1370(17)	5·6(3)
C(4)	2968(9)	3586(17)	−183(16)	5·1(3)
C(5)	3521(8)	4509(16)	2530(16)	4·5(3)
C(6)	3810(9)	3934(17)	3785(17)	5·0(3)
C(7)	3590(8)	1333(15)	4932(15)	4·1(3)
C(8)	3324(10)	−231(19)	4672(18)	5·9(4)
C(9)	3738(11)	−1068(20)	5612(20)	6·9(4)
C(10)	4370(10)	−244(19)	6702(18)	5·6(3)
C(11)	4620(10)	1246(20)	6891(18)	6·2(4)
C(12)	4243(10)	2104(19)	6025(18)	6·1(4)
C(13)	2266(8)	3476(15)	5039(14)	3·9(3)
C(14)	1452(10)	2949(19)	4705(19)	6·4(4)
C(15)	821(12)	3622(24)	5712(23)	8·4(5)
C(16)	1077(12)	4906(22)	7036(21)	7·4(4)
C(17)	1863(11)	5455(21)	7388(20)	7·3(4)
C(18)	2488(9)	4746(18)	6391(17)	5·3(3)
C(19)	1202(12)	2374(22)	−309(21)	7·5(4)
C(20)	578(15)	1902(28)	493(28)	10·5(6)
C(21)	1700(1)	−360(21)	−1815(20)	6·9(4)
C(22)	1249(13)	−480(25)	−3334(25)	9·4(5)

* Anisotropic parameters; see Table 2.

TABLE 2

(I): Anisotropic thermal parameters * (×10^4), with estimated standard deviations in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	36(1)	268(5)	149(4)	0(2)	9(1)	117(3)
S(1)	50(2)	165(8)	242(8)	6(3)	15(3)	45(6)
S(2)	81(3)	242(10)	296(11)	−21(4)	37(5)	77(8)
P	43(18)	135(7)	106(6)	−2(3)	2(3)	36(5)
N(1)	52(7)	218(27)	217(25)	8(12)	1(11)	115(22)
N(2)	53(7)	361(37)	189(25)	−22(13)	3(10)	127(26)
N(3)	43(5)	118(19)	123(18)	−5(8)	14(8)	1(15)
N(4)	41(5)	180(21)	153(19)	−2(8)	15(8)	77(18)
C(1)	24(6)	230(34)	180(26)	−23(13)	−17(11)	116(26)
C(2)	33(7)	270(38)	143(27)	6(13)	19(11)	19(26)

* Anisotropic thermal factors are of the form:

$$\exp\left(-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\right).$$

Structure Determination.—(*a*) (I). A three-dimensional Patterson synthesis gave the positions of cobalt, phosphorus, and two sulphur atoms. A series of four electron-density syntheses showed all the non hydrogen atoms positions.

Refinement was continued by means of full-matrix least-squares, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. Weights used followed Hughes scheme, with $w = 1$ for reflections with $F_o \leqslant 19$ and $\sqrt{w} = 19/F_o$ for reflections with $F_o > 19$. A series of cycles of least-squares reduced R to 8·6%. At this point a difference-Fourier synthesis was calculated and 20 out of 29 hydrogen atoms were located. These were included in the calculations with the temperature factors of the atoms to which they are attached

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[7] E. König and K. J. Watson, *Chem. Phys. Letters*, 1970, **6**, 457.

[8] P. C. Healy and A. H. White, *Chem. Comm.*, 1971, 1446.

[9] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 204.

and their positions were not refined. Two more cycles of refinement on positional and thermal parameters of the non-hydrogen atoms gave a final R of 7·4%. R' was 10·9% $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o{}^2|]^{1/2}\}$ and the standard deviation of an observation of unit weight 1·19. Final values of the atomic parameters with their estimated standard deviations are reported in Tables 1—3.

TABLE 3

(I): Positional parameters ($\times 10^3$) of hydrogen atoms, numbered according to the atom to which they are attached

Atom	x/a	y/b	z/c
H *	380	270	100
H(3,1)	298	131	−155
H(3,2)	220	230	−216
H(5,1)	293	500	255
H(5,2)	400	529	233
H(6,1)	400	480	480
H(6,2)	439	335	375
H(19)	146	330	37
H(21,1)	144	−79	−125
H(21,2)	223	−78	−208
H(22)	158	−3	−403
H(8)	283	−87	414
H(9)	340	−200	530
H(10)	467	−86	770
H(11)	500	196	768
H(12)	436	332	615
H(14)	133	169	406
H(16)	61	580	785
H(17)	220	632	800
H(18)	310	520	666

* Attached to N(4).

(*b*) (II). A three-dimensional Patterson function gave the positions of the cobalt and one sulphur atom. The x and z co-ordinates of the cobalt atom were set at 1/2 to fix the origin of the unit cell and their values were kept constant during the refinement. The other non-hydrogen atoms were located from successive three-dimensional Fourier maps. Refinement was then undertaken by means of full-matrix least-squares techniques. In the first two isotropic cycles the parameters oscillated largely, the temperature factor of one carbon atom became negative, and R increased. This fact was attributed to ill-conditioning of the normal-equation matrix, due probably to the polarity of the space group and a 'damping' factor of 1/3 was applied. In this way two isotropic cycles followed by two mixed cycles, isotropic on the carbon atoms and anisotropic on the heavier atoms, reduced R to 6·8%. The F_o values were weighted according to the Hughes expression: $w = 1$ for $F_o \leqslant 17$ and $\sqrt{w} = 17/F_o$ for reflections with $F_o > 17$. At this point a difference-Fourier synthesis showed the positions of 24 out of the 31 hydrogen atoms which were introduced in the following calculations as fixed contributions with the temperature factor of the carbon atom to which they are attached.

The effects of anomalous dispersion were then included in the calculation of F_c. In fact, due to the polar nature of the space group *Cc*, two possible orientations of the structure must be considered: the structure x,y,z so far considered and the inverted structure $\bar{x},y,\bar{z}$. Two mixed cycles on the two structures gave R and R' values of 6·2 and 8·4% ($\bar{x},y,\bar{z}$) and 6·4 and 8·6% (x,y,z) respectively. On the basis of Hamilton's test,[10] the hypothesis that the x,y,z structure is correct can be rejected at the 99·5% significance level. The standard deviation of an observation of unit weight for the correct structure is 1·07. Bond distances and angles in the two structures do not differ by $>4\sigma$.

The final values of the parameters of the correct structure and their estimated standard deviations are reported in Tables 4—6.

Atomic scattering factors for both structure determinations were taken from ref. 11 for cobalt, phosphorus, nitrogen, and carbon and from ref. 12 for hydrogen. Scattering factors for cobalt, sulphur, and phosphorus were corrected for both the real and imaginary parts of the

TABLE 4

(II): Positional parameters ($\times 10^4$) and isotropic thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
Co	−5000	4691(1)	5000	*
S(1)	−1445(4)	4754(4)	5132(5)	*
S(2)	−7052(3)	3182(4)	2047(3)	*
P	−5626(2)	6364(2)	4588(2)	*
N(1)	−3510(8)	4533(8)	5085(8)	*
N(2)	−5851(8)	3994(7)	3774(7)	*
N(3)	−5838(8)	3990(7)	5702(6)	*
N(4)	−4117(7)	5463(7)	6468(6)	*
C(1)	−2646(12)	4602(10)	5108(10)	5·6(3)
C(2)	−6347(9)	3653(8)	3057(8)	3·9(2)
C(3)	−5222(11)	4154(10)	6727(9)	5·5(3)
C(4)	−4824(10)	5205(9)	6930(9)	5·0(2)
C(5)	−4078(11)	6541(10)	6376(9)	5·3(2)
C(6)	−5177(10)	6985(10)	5697(9)	4·9(2)
C(7)	−5082(8)	7115(7)	3958(7)	3·5(2)
C(8)	−5550(11)	8001(10)	3574(9)	5·4(3)
C(9)	−5056(12)	8589(10)	3143(10)	6·1(3)
C(10)	−4098(11)	8291(10)	3099(9)	5·5(3)
C(11)	−3636(10)	7428(9)	3485(8)	4·6(2)
C(12)	−4088(9)	6819(8)	3925(7)	4·0(2)
C(13)	−7101(9)	6533(7)	3943(7)	3·7(2)
C(14)	−7636(10)	5976(9)	3140(8)	4·7(2)
C(15)	−8762(11)	6014(10)	2633(9)	5·4(2)
C(16)	−9375(12)	6588(11)	2911(10)	6·3(3)
C(17)	−8871(14)	7161(12)	3697(12)	7·0(3)
C(18)	−7727(11)	7136(10)	4219(9)	5·4(2)
C(19)	−5945(11)	2913(10)	5492(9)	5·4(2)
C(20)	−4909(13)	2437(12)	5609(11)	6·5(3)
C(21)	−6956(10)	4480(8)	5321(8)	4·4(2)
C(22)	−7758(13)	4027(12)	5657(11)	6·7(3)
C(23)	−2986(12)	5078(10)	7040(10)	6·1(3)

* Anisotropic thermal parameters: see Table 5.

TABLE 5

(II): Anisotropic thermal parameters * ($\times 10^4$), with estimated standard deviations in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	56(1)	52(1)	46(1)	2(1)	23(1)	1(1)
S(1)	87(3)	108(4)	188(5)	−3(3)	81(3)	4(3)
S(2)	77(2)	149(4)	59(2)	−32(2)	34(2)	−34(2)
P	63(2)	52(2)	45(1)	2(1)	29(1)	−1(1)
N(1)	83(8)	80(7)	74(6)	5(6)	44(6)	−4(5)
N(2)	84(8)	62(6)	51(5)	−1(6)	27(5)	−9(5)
N(3)	83(7)	66(6)	45(5)	−9(5)	31(5)	7(4)
N(4)	60(6)	71(6)	45(4)	−5(5)	17(4)	−6(4)

* Anisotropic thermal factors are of the form:

$$\exp\left(-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\right).$$

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[10] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

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

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

anomalous dispersion terms.[13] Programs used in the calculations were: data reduction, Fourier synthesis, and *structure factors*, from the series written for the IBM 1130 computer by the A.R.C. unit of Structural Chemistry, University College, London; full-matrix least-squares from '*X*-Ray '70,' written or adapted by J. M. Stewart and co-workers for the CDC 6600, UNIVAC 1108, and IBM 360 computers; a modification of Martin, Busing, and Levy's ORFLS to include both the real and imaginary parts of the anomalous dispersion by E. Cannillo of the University of Pavia, was also used.*

TABLE 6

(II): Positional parameters ($\times 10^3$) of hydrogen atoms (numbered according to the atom to which they are attached)

Atom	x/a	y/b	z/c
H(3)	−470	376	684
H(4,1)	−544	550	688
H(4,2)	−440	535	762
H(5,1)	−350	678	617
H(5,2)	−350	682	700
H(6,1)	−500	770	567
H(6,2)	−562	706	619
H(19,1)	−670	294	475
H(19,2)	−630	268	592
H(21,1)	−744	445	452
H(21,2)	−690	520	550
H(20,1)	−448	236	625
H(20,2)	−490	160	550
H(20,3)	−456	246	529
H(22)	−720	390	644
H(23)	−289	540	759
H(8)	−634	844	357
H(9)	−558	930	294
H(10)	−374	882	280
H(11)	−304	702	340
H(14)	−720	540	317
H(15)	−930	562	204
H(16)	−30	644	234
H(18)	−720	754	492

DISCUSSION

Both structures consist of discrete molecules of the complexes, in which the cobalt(II) atoms are five-co-ordinated by the three donor atoms of the ligand and the two nitrogen atoms of the isothiocyanate group (Figure 1). Bond lengths and angles in the co-ordination polyhedra of the two complexes are reported in Table 7.

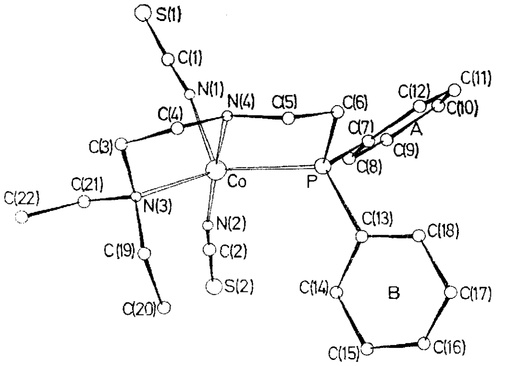

FIGURE 1 A perspective view of complex (I). The labelling is the same as in (II)

TABLE 7

Bond lengths (Å) and angles (°), with estimated standard deviations, in the co-ordination polyhedra

	(I)	(II)
Co–P	2·32(1)	2·40(1)
Co–N(1)	2·04(1)	1·97(1)
Co–N(2)	1·92(2)	2·02(1)
Co–N(3)	2·07(1)	2·14(1)
Co–N(4)	2·10(1)	2·36(1)
P–Co–N(1)	105·1(4)	110·3(3)
P–Co–N(2)	96·5(4)	101·1(3)
P–Co–N(3)	148·0(3)	111·0(3)
P–Co–N(4)	82·0(3)	79·6(3)
N(1)–Co–N(2)	95·3(6)	98·1(5)
N(1)–Co–N(3)	102·6(5)	132·7(4)
N(1)–Co–N(4)	89·6(5)	86·0(4)
N(2)–Co–N(3)	96·6(5)	95·8(4)
N(2)–Co–N(4)	175·1(5)	175·3(5)
N(3)–Co–N(4)	82·4(4)	79·7(4)

Although both polyhedra can be described as distorted trigonal bipyramids the high-spin complex is distorted towards a tetrahedron, while the intermediate spin complex appears to be distorted towards a square pyramid. Figure 2 shows a schematic view of the co-ordination polyhedra of the two complexes together with a sketch of the limit geometries, to which the two structures tend.

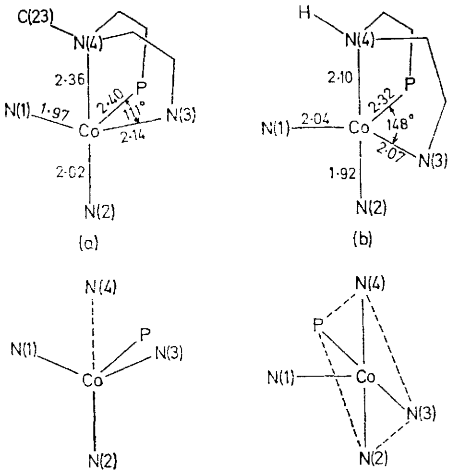

FIGURE 2 Sketch of the co-ordination polyhedra of the two complexes together with the limit geometries, to which the two structures tend. (a) high-spin complex (II), (b) intermediate-spin complex (I)

In fact, in complex (II), the apical Co–N(4) bond (2·36 Å) appears rather elongated, the metal atom lies

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* A list of observed and calculated structure factors for both structures is published in Supplementary Publication No. SUP 20691 (7 pp., 1 microfiche). Details of Supplementary Publications are in Notice to Authors, No. 7, *J.C.S. Dalton*, 1972, Index issue.

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

0·30 Å below the equatorial plane and the mean N(2)–Co–eq donor angle is 98·3°.

In complex (I), the P–Co–N(3) angle (148°) is largely expanded from the idealized value of 120°, and the Co–N(1) bond opposite to it is clearly elongated [Co–N(1) 2·04, Co–N(2) 1·92 Å]. The geometry (Figure 2b) of the complex (I) is then intermediate between a trigonal bipyramid and a square pyramid, where the N(1) atom represents the apex. The elongation of the Co–N(1) bond is a common feature of low-spin square pyramidal cobalt(II) and nickel(II) complexes and can be simply attributed to the stereochemical activity of the *d* electrons.[14] More sophisticated ligand-field arguments lead to the same conclusions.[4]

Comparison of the metal–ligand distances in the two complexes is interesting. With the exception of the Co–N(1) bond, whose elongation has been discussed, all the distances in the intermediate-spin complex are shorter than the analogous distances in the high-spin complex. On the other hand, these distances appear to be longer than similar distances in five-co-ordinate low-spin cobalt(II) complexes, such as the mean Co–P bond length (2·26 Å) in [Co(np$_3$)I]I [15] or mean Co–N (2·03) and Co–P (2·22 Å) distances in [Co(pnnp)Br]PF$_6$.[3] Unfortunately in these cases a rigorous comparison is not possible, owing to the different nature of the ligand and to the different stereochemistry of the complexes. Variations of the metal–ligand distances with the spin-state of the complex have been reported, but only for Fe$^{\text{II}}$ and Fe$^{\text{III}}$ six-co-ordinate complexes.[7,8,16]

The possibility of a statistical distribution in the lattice of two slightly different molecules, one low- and one high-spin in Co(nnp)(NCS)$_2$ can be ruled out because the difference Fourier showed no peak higher than those attributed to the hydrogen atoms, the standard deviations on bond lengths and angles are of the same magnitude as those in Co(nnpMe)(NCS)$_2$, and the values of the thermal ellipsoid parameters of the atoms refined

TABLE 8

Selected inter- and intra-molecular contacts (Å)

Co(nnp)(NCS)$_2$		Co(nnpMe)(NCS)$_2$	
C(17) ··· C(21$^{\text{I}}$)	3·49	C(23) ··· N(1)	2·99
C(10) ··· C(1$^{\text{II}}$)	3·57	C(23) ··· C(1)	3·39
C(21) ··· C(17$^{\text{III}}$)	3·49	C(23) ··· C(3)	3·09
C(12) ··· C(10$^{\text{IV}}$)	3·47	C(3) ··· C(11$^{\text{VII}}$)	3·43
N(4) ··· S(1$^{\text{V}}$)	3·51	C(3) ··· C(12$^{\text{VII}}$)	3·42
C(20) ··· C(20$^{\text{VI}}$)	3·57		

Superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z

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

TABLE 9

Bond lengths (Å) and angles (°) with estimated standard deviations in the remainder of the molecule

	(I)	(II)
(*a*) Distances		
S(1)–C(1)	1·60(2)	1·62(2)
S(2)–C(2)	1·62(2)	1·60(1)
P–C(6)	1·81(2)	1·81(1)
P–C(7)	1·81(2)	1·80(1)
P–C(13)	1·81(1)	1·80(1)
N(1)–C(1)	1·19(2)	1·15(2)
N(2)–C(2)	1·16(3)	1·14(1)
N(3)–C(3)	1·49(2)	1·49(2)
N(3)–C(19)	1·52(2)	1·49(2)
N(3)–C(21)	1·47(2)	1·51(2)
N(4)–C(4)	1·49(2)	1·48(2)
N(4)–C(5)	1·48(2)	1·47(2)
N(4)–C(23)		1·48(2)
C(3)–C(4)	1·49(2)	1·50(2)
C(5)–C(6)	1·49(2)	1·52(2)
C(19)–C(20)	1·44(3)	1·47(2)
C(21)–C(22)	1·51(3)	1·53(3)
(*b*) Angles		
Co–P–C(6)	101·7(5)	104·0(4)
Co–P–C(7)	123·4(4)	120·2(4)
Co–P–C(13)	116·3(4)	116·2(4)
C(6)–P–C(7)	105·8(7)	104·3(6)
C(6)–P–C(13)	105·8(6)	108·1(6)
C(7)–P–C(13)	102·2(7)	103·1(5)
Co–N(1)–C(1)	163·6(12)	169·0(10)
Co–N(2)–C(2)	166·7(14)	175·9(10)
Co–N(3)–C(3)	105·4(8)	110·3(8)
Co–N(3)–C(19)	112·4(9)	109·6(10)
Co–N(3)–C(21)	110·5(10)	105·1(7)
C(3)–N(3)–C(19)	106·7(12)	110·2(9)
C(3)–N(3)–C(21)	109·5(11)	110·5(11)
C(19)–N(3)–C(21)	111·9(11)	111·0(9)
Co–N(4)–C(4)	111·0(7)	104·0(6)
Co–N(4)–C(5)	116·5(9)	111·3(8)
Co–N(4)–C(23)		113·0(9)
C(4)–N(4)–C(5)	112·0(11)	110·1(12)
C(4)–N(4)–C(23)		108·6(11)
C(5)–N(4)–C(23)		109·7(10)
S(1)–C(1)–N(1)	178·1(17)	177·2(12)
S(2)–C(2)–N(2)	177·4(13)	179·5(18)
N(3)–C(3)–C(4)	111·4(12)	110·6(11)
N(4)–C(4)–C(3)	106·5(13)	111·1(12)
N(4)–C(5)–C(6)	109·7(12)	113·3(10)
C(5)–C(6)–P	108·6(9)	108·6(10)
P–C(7)–C(8)	118·0(10)	121·7(11)
P–C(7)–C(12)	120·7(12)	119·2(8)
P–C(13)–C(14)	119·9(9)	117·0(9)
P–C(13)–C(18)	121·3(10)	124·5(8)
N(3)–C(19)–C(20)	116·0(18)	114·0(12)
N(3)–C(21)–C(22)	117·6(16)	114·7(10)

(*c*) Phenyl rings

	Mean	Mean devn.	Max. devn.
(i) (I)			
Bond lengths			
Ring A	1·38	0·04	0·08
Ring B	1·38	0·03	0·06
Bond angles			
Ring A	120·0	1·7	2·3
Ring B	120·0	1·9	3·8
(ii) (II)			
Bond lengths			
Ring A	1·38	0·02	0·04
Ring B	1·37	0·01	0·03
Bond angles			
Ring A	120·0	1·1	2·2
Ring B	120·0	0·6	1·6

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[14] P. L. Orioli, *Co-ordination Chem. Rev.*, 1971, **6**, 285, and references therein.

[15] C. Mealli, P. L. Orioli, and L. Sacconi, *J. Chem. Soc.* (*A*), 1971, 2691.

[16] B. F. Hoskins and B. P. Kelly, *Chem. Comm.*, 1968, 1517; 1970, 45.

anisotropically and the temperature factors of the isotropic ones, although somewhat large, are comparable with the analogous values of the methylated complex.

The results of the structural investigation of (I) appear then to be in agreement with the assumption of a spin-state equilibrium between two thermally accessible electronic states. The different magnetic behaviours of (I) and (II) can be attributed to the different geometries of their co-ordination polyhedra, which are respectively distorted towards the elongated square pyramid and the tetrahedron.

It seems obvious to assume that the substituent at the central nitrogen plays the main role in determining the distortions in the co-ordination geometry of the two complexes. It is less easy to establish whether it is a matter of steric or inductive effects or a combination of both, but the methyl group in (II) has some very short intramolecular contacts (Table 8). The short contact distance C(23) · · · N(1) could be responsible for the expansion of the N(1)–Co–N(3) angle from the idealized value of 120°. Bond lengths and angles in the ligand molecule in both complexes show no apparent anomalies (Table 9).

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