Crystal Structure of the Low-spin Five-co-ordinate Complex Bromo[tris-(2-diphenylphosphinoethyl)phosphine]cobalt(II) Hexafluorophosphate

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Crystals of the title compound are triclinic, space group $P\bar{1}$, with a = 12.267(1), b = 12.903(1), c = 16.532(1) Å, α = 106.30(1), β = 91.59(1), γ = 121.08(1)°, Z = 2. The structure was solved by Patterson and Fourier methods from diffractometer data and refined by least-squares techniques to R 0.064 for 3 831 independent reflections. The geometry of co-ordination is distorted square-pyramidal, with a phosphorus in the apical position [Co–P 2.281(3) Å], the other three phosphorus atoms [Co–P 2.285, 2.254, and 2.156(3) Å] and the halogen atom [Co–Br 2.380(2) Å] lying approximately in the base of the pyramid. Comparison with the structures of analogous complexes suggests the role played by ligand molecules in determining the co-ordination geometry. Further evidence for the effects of a Jahn–Teller distortion in Co^{II} low-spin complexes of this class is provided. The reflectance spectra of a set of related complexes are compared.

Of the two idealized geometries of five-co-ordination, the trigonal bipyramidal is attained or closely approached in some high-spin Co^{II} complexes,[1,2] but has not so far been verified for low-spin Co^{II} complexes. In the complex [Co(qp)Cl]BPh$_4$, where a rigid tripod ligand is employed [qp = tris(*o*-diphenylphosphinophenyl)phosphine], a large distortion from three-fold symmetry is found[3] and in the complex [Co(np$_3$)I]I, formed with a more flexible tripod ligand [np$_3$ = tris(2-diphenylphosphinoethyl)amine], essentially square-pyramidal geometry is attained.[4] In contrast, crystallographic C_3 symmetry exists in the [Ni(np$_3$)I]I complex[5] and approximate three-fold symmetry is found in other Ni^{II} complexes with similar ligands.[6] A static Jahn–Teller effect has been invoked to rationalize the geometry of the cobalt complexes.[3,4] The flexible tripod ligand pp$_3$ [tris(2-diphenylphosphinoethyl)phosphine, P(CH$_2$·CH$_2$·PPh$_2$)$_3$] containing the same nucleophilic (P$_4$) donor set as the ligand qp, which is suitable for stabilizing the low-spin state,[7] has been used to prepare the complex [Co(pp$_3$)Br]PF$_6$, as described in ref. 8. *X*-Ray analysis of its structure was undertaken in order to understand better the nature of the factors determining the co-ordination geometry in this class of complexes.

EXPERIMENTAL

Crystal Data.—C$_{42}$H$_{42}$BrCoF$_6$P$_5$, M = 954.5, Triclinic, a = 12.267(1), b = 12.903(1), c = 16.532(1) Å, α = 106.30(1), β = 91.59(1), γ = 121.08(1)°, U = 2 102.92 Å^3, D_c = 1.507, Z = 2, D_m = 1.50, $F(000)$ = 970. Mo-K_α radiation, λ = 0.70 926 Å, μ (Mo-K_α) = 16.6 cm^{-1}. Space group $P\bar{1}$.

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TABLE 1

Positional parameters (× 10^4) and anisotropic * temperature factors (× 10^3), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	2 158(1)	2 163(1)	−1 224(1)	68(1)	45(1)	46(1)	26(1)	19(1)	8(1)
Co	2 268(1)	1 080(1)	−2 614(1)	36(1)	33(1)	34(1)	20(1)	8(1)	11(1)
P(1)	4 126(2)	1 149(2)	−2 277(1)	36(1)	39(1)	44(1)	21(1)	5(1)	12(1)
P(2)	652(2)	−953(2)	−2 709(1)	32(1)	35(1)	43(1)	16(1)	5(1)	10(1)
P(3)	2 894(2)	2 811(2)	−3 009(1)	45(1)	40(1)	47(1)	24(1)	13(1)	20(1)
P(4)	2 187(2)	168(2)	−3 945(1)	48(1)	48(1)	34(1)	28(1)	8(1)	10(1)
P(5)	6 964(3)	3 711(3)	−4 851(2)	59(2)	63(2)	57(2)	36(1)	15(1)	10(1)
F(1)	6 641(10)	3 421(11)	−5 822(5)	164(9)	190(10)	82(6)	69(8)	21(6)	27(6)
F(2)	7 246(15)	4 010(18)	−3 898(6)	337(17)	537(27)	76(6)	375(20)	58(8)	102(10)
F(3)	8 106(11)	5 006(9)	−4 734(10)	133(9)	79(6)	335(17)	−20(6)	87(10)	−42(8)
F(4)	7 783(10)	3 125(11)	−5 019(7)	162(9)	193(10)	183(9)	152(9)	−13(7)	−18(8)
F(5)	5 677(10)	2 341(10)	−5 077(10)	134(8)	113(7)	349(18)	51(7)	110(10)	116(10)
F(6)	6 075(9)	4 232(10)	−4 693(6)	131(7)	164(8)	134(7)	112(7)	13(6)	29(6)

* In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Crystals were grown under nitrogen from acetone–ethanol. A crystal of dimensions *ca.* 0.35 × 0.36 × 0.18 mm (along the [100], [010], and [001] directions, respectively) was mounted with the b axis approximately coincident with the ϕ axis of the goniostat of a Hilger and Watts automated diffractometer. Cell constants were obtained by least-squares refinement of the 2θ values of 30 high-angle reflections. Of 5 210 independent reflections in the range $2\theta < 44°$ collected by a ω—2θ scan, 3 831 reflections, having $I > 3\sigma(I)$, were used in the subsequent structure solution and refinement, after correction for Lorentz and polarization effects. [$\sigma(I)$ is defined as in ref. 9, with the constant $p = 0.02$.] No correction for absorption was applied. No systematic variations were observed in the intensities of the three standard reflections, (503), ($32\bar{8}$), and ($\bar{6}5\bar{5}$), measured after every 50 reflections.

TABLE 2

Positional parameters (× 10^4) and isotropic temperature factors (× 10^3) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U/Å^2
C(1)	3 619(9)	63(9)	−4 067(6)	57(2)
C(2)	4 735(9)	965(9)	−3 268(6)	56(2)
C(3)	807(9)	−1 499(9)	−4 394(6)	56(2)
C(4)	633(9)	−2 083(9)	−3 686(6)	55(2)
C(5)	2 156(9)	1 053(9)	−4 614(6)	57(2)
C(6)	3 157(9)	2 467(9)	−4 122(6)	58(2)
C(7)	5 592(9)	2 477(9)	−1 485(6)	52(2)
C(8)	5 677(9)	3 563(9)	−1 001(6)	62(2)
C(9)	6 832(12)	4 555(11)	−339(8)	84(3)
C(10)	7 773(13)	4 378(13)	−230(9)	97(4)
C(11)	7 755(14)	3 338(14)	−692(10)	108(4)
C(12)	6 617(12)	2 350(12)	−1 346(8)	88(4)
C(13)	3 869(8)	−149(8)	−1 907(5)	42(2)
C(14)	3 706(9)	−32(9)	−1 063(6)	57(2)
C(15)	3 503(10)	−984(10)	−738(7)	64(3)
C(16)	3 460(11)	−2 039(11)	−1 252(7)	74(3)
C(17)	3 606(11)	−2 188(11)	−2 081(8)	79(3)
C(18)	3 800(9)	−1 240(9)	−2 416(6)	56(2)
C(19)	506(8)	−1 648(8)	−1 861(6)	46(2)
C(20)	554(10)	−990(10)	−1 047(7)	67(3)
C(21)	340(11)	−1 524(11)	−394(7)	76(3)
C(22)	31(12)	−2 750(12)	−598(8)	86(4)
C(23)	−5(12)	−3 424(12)	−1 393(8)	87(4)
C(24)	211(10)	−2 895(10)	−2 055(7)	68(3)
C(25)	−980(8)	−1 240(8)	−2 890(6)	49(2)
C(26)	−1 985(9)	−2 300(9)	−3 570(6)	60(2)
C(27)	−3 225(11)	−2 510(11)	−3 655(7)	75(3)
C(28)	−3 450(12)	−1 703(12)	−3 095(8)	88(4)
C(29)	−2 508(12)	−691(12)	−2 402(8)	87(4)
C(30)	−1 231(10)	−448(10)	−2 310(7)	67(3)
C(31)	1 573(9)	3 069(8)	−3 115(6)	50(2)
C(32)	356(11)	2 186(11)	−3 004(7)	74(3)
C(33)	−656(13)	2 392(13)	−3 082(8)	94(4)
C(34)	−414(12)	3 455(12)	−3 290(8)	87(4)
C(35)	698(12)	4 221(11)	−3 453(8)	80(3)
C(36)	1 722(10)	4 049(10)	−3 377(7)	66(3)
C(37)	4 307(9)	4 410(8)	−2 380(6)	50(2)
C(38)	4 174(10)	5 172(10)	−1 696(7)	65(3)
C(39)	5 278(11)	6 359(11)	−1 156(7)	78(3)
C(40)	6 487(12)	6 727(12)	−1 372(8)	82(3)
C(41)	6 608(11)	5 973(11)	−2 051(8)	82(3)
C(42)	5 522(10)	4 786(10)	−2 585(7)	65(3)

Structure Determination.—The structure was solved by Patterson and heavy-atom Fourier methods. The halogen, metal, and two phosphorus atoms were located from the Patterson map. A series of Fourier syntheses revealed the positions of all non-hydrogen atoms. Least-squares refinement with individual isotropic temperature factors reduced R to 0.10. After a few cycles in the mixed mode, with anisotropic temperature factors for all atoms in the co-ordination polyhedron and in the anion, R was 0.072. Hydrogen atoms were introduced in calculated positions (C–H 1.07 Å) with individual temperature factors, close to those of the respective carbon atoms, and were not refined. Refinement was considered terminated at R 0.064, when the mean shift-to-error ratio was <0.15. A final ΔF Fourier showed no significant features. The function minimized in the least-squares was $\Sigma w(|F_o| - |F_c|)^2$. A Hughes-type weighting scheme was adopted, with $w = 1$ for reflections with $F_o \leqslant 30$ and $\sqrt{w} = 30/F_o$ for reflections with $F_o > 30$. Scattering factors for non-hydrogen atoms, uncorrected for anomalous dispersion, were taken from ref. 10, and for hydrogen from ref. 11. Final values of positional and thermal parameters are listed in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21439 (8 pp., 1 microfiche).* Calculations were made on a CII 10 070 computer with programs described in ref. 12.

RESULTS AND DISCUSSION

The structure consists of $[Co(pp_3)Br]^+$ cations and PF_6^- anions. Figure 1 shows a perspective view of the cation, with the labelling of the atoms. Selected bond

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full size copies).

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distances and angles are reported in Tables 3 and 4. The co-ordination geometry deviates considerably from that of a trigonal bipyramid, in spite of the shape of the ligand: it approaches rather closely that of a square pyramid having a phosphorus atom [P(1)] in the apical position. The most significant deviation from trigonal bipyramidal geometry is due to the large [148.0(01)°] P(2)–Co–P(3) angle, whose value is intermediate between those (137.2 and 159.8°) found in the structures of the related compounds (I) [Co(qp)Cl]BPh$_4$ (ref. 3) and (II) [Co(np$_3$)I]I.[4] The metal atom lies 0.37 Å above the best plane through the four donor atoms in the base of the square pyramid. Values of the three Co–P distances formed by the peripheral donor atoms of the ligand molecule are close to their mean value [*] (2.27 Å), which is in the range found in (I) and (II). The Co–P(4) bond, formed with the central phosphorus atom in the ligand, is quite short [2.156(3) Å], but it is definitely longer than that [2.057(4) Å] in (I). The Co–Br distance [2.380(2) Å] differs from the Co–I distance in (II) [2.578(4) Å] by an amount corresponding to the difference between the covalent radii of the halogens. On the other hand, it is much closer than would be expected, by the same criterion, to the Co–Cl distance [2.309(6) Å] in (I). This may be attributed to the intramolecular crowding observed in (I)[3] which may cause elongation of the metal–halogen bond. Distances and angles in the ligand of [Co(pp$_3$)Br]PF$_6$ agree essentially with expected values,[13] with possible exceptions concerning bond angles in the ethyl chains (discussed later). The anion shows the effects of large thermal motion, but not of disorder. There are several short non-bonded distances between atoms of the ligand molecule (Table 5), but there are few close intermolecular contacts.

TABLE 3

Interatomic distances (Å) and angles (°) in the cation, with standard deviations in parentheses

(*a*) Bond lengths

Co–Br	2.380(2)	P(2)–C(25)	1.84(1)
Co–P(1)	2.281(3)	P(3)–C(6)	1.85(1)
Co–P(2)	2.285(3)	P(3)–C(31)	1.83(1)
Co–P(3)	2.254(3)	P(3)–C(37)	1.83(1)
Co–P(4)	2.156(3)	P(4)–C(1)	1.84(1)
		P(4)–C(3)	1.82(1)
P(1)–C(2)	1.83(1)	P(4)–C(5)	1.81(1)
P(1)–C(7)	1.82(1)	C(1)–C(2)	1.54(1)
P(1)–C(13)	1.82(1)	C(3)–C(4)	1.53(2)
P(2)–C(4)	1.84(1)	C(5)–C(6)	1.52(1)
P(2)–C(19)	1.83(1)		

(*b*) Bond angles

Br–Co–P(1)	100.2(0.1)	C(4)–P(2)–C(25)	104.1(0.4)
Br–Co–P(2)	96.7(0.1)	C(19)–P(2)–C(25)	99.3(0.5)
Br–Co–P(3)	91.2(0.1)	Co–P(3)–C(6)	109.3(0.4)
Br–Co–P(4)	171.7(0.1)	Co–P(3)–C(31)	111.3(0.3)
P(1)–Co–P(2)	103.4(0.1)	Co–P(3)–C(37)	121.8(0.4)
P(1)–Co–P(3)	105.6(0.1)	C(6)–P(3)–C(31)	102.1(0.5)
P(2)–Co–P(3)	148.0(0.1)	C(6)–P(3)–C(37)	106.3(0.4)
P(1)–Co–P(4)	87.6(0.1)	C(31)–P(3)–C(37)	104.1(0.5)
P(2)–Co–P(4)	84.2(0.1)	Co–P(4)–C(1)	111.3(0.3)
P(3)–Co–P(4)	83.8(0.1)	Co–P(4)–C(3)	112.7(0.4)
		Co–P(4)–C(5)	112.0(0.4)
Co–P(1)–C(2)	106.5(0.4)	C(1)–P(4)–C(3)	104.2(0.5)
Co–P(1)–C(7)	126.5(0.4)	C(1)–P(4)–C(5)	106.7(0.5)
Co–P(1)–C(13)	113.7(0.3)	C(3)–P(4)–C(5)	109.4(0.5)
C(2)–P(1)–C(7)	102.5(0.4)	P(4)–C(1)–C(2)	112.4(0.8)
C(2)–P(1)–C(13)	107.3(0.5)	P(1)–C(2)–C(1)	111.8(0.7)
C(7)–P(1)–C(13)	98.7(0.5)	P(4)–C(3)–C(4)	107.1(0.6)
Co–P(2)–C(4)	107.4(0.3)	P(2)–C(4)–C(3)	107.2(0.8)
Co–P(2)–C(19)	124.9(0.3)	P(4)–C(5)–C(6)	106.8(0.7)
Co–P(2)–C(25)	112.9(0.4)	P(3)–C(6)–C(5)	107.3(0.7)
C(4)–P(2)–C(19)	106.2(0.5)		

(*c*) Phenyl rings

	Mean	Mean devn.	Max. devn.
(i) Bond lengths Ring			
A	1.37	0.04	0.07
B	1.38	0.01	0.02
C	1.37	0.02	0.03
D	1.38	0.03	0.05
E	1.38	0.03	0.08
F	1.38	0.03	0.05
(ii) Bond angles Ring			
A	120.0	1.8	4.5
B	120.0	0.8	1.5
C	120.0	1.3	1.8
D	120.0	0.7	2.0
E	119.9	0.9	1.6
F	120.0	1.3	2.1

TABLE 4

Bond distances (Å) and angles (°) in the anion

P(5)–F(1)	1.53(1)	P(5)–F(4)	1.53(2)
P(5)–F(2)	1.50(1)	P(5)–F(5)	1.57(1)
P(5)–F(3)	1.48(1)	P(5)–F(6)	1.56(1)
F(1)–P(5)–F(2)	177.9(1.3)	F(2)–P(5)–F(6)	87.3(1.1)
F(1)–P(5)–F(3)	91.0(0.8)	F(3)–P(5)–F(4)	91.4)0.8)
F(1)–P(5)–F(4)	89.0(0.8)	F(3)–P(5)–F(5)	172.9(1.0)
F(1)–P(5)–F(5)	82.6(0.8)	F(3)–P(5)–F(6)	91.8(0.8)
F(1)–P(5)–F(6)	90.5(0.8)	F(4)–P(5)–F(5)	91.6(0.7)
F(2)–P(5)–F(3)	89.2(0.9)	F(4)–P(5)–F(6)	176.8(0.6)
F(2)–P(5)–F(4)	93.1(1.1)	F(5)–P(5)–F(6)	85.2(0.7)
F(2)–P(5)–F(5)	97.1(0.9)		

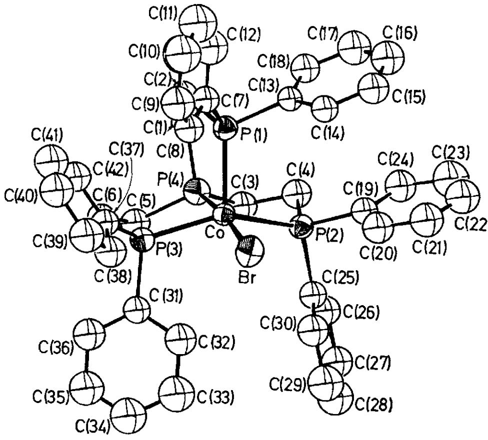

FIGURE 1 A perspective view of the cation [Co(pp$_3$)Br]$^+$ with the labelling of the atoms. 50% Probability contours for the ellipsoids are shown

The present results substantiate the hypothesis which has been advanced[3,4] of a Jahn–Teller mechanism operating for trigonal low-spin d^7 complexes. As the e' $D_{(3h)}$ orbitals in the equatorial plane of the trigonal bipyramid

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[*] As a referee has pointed out, taking the mean of the three Co–P values is not strictly correct, since the Co–P(3) distance differs significantly from the other two (Table 3). However, in view of the small difference involved, it should be possible to use the mean value for crude comparisons.

[13] *Chem. Soc. Special Publ.*, No. 18, 1965.

are involved, a large stereochemical effect is expected. In addition, CFSE may contribute[14] to stabilize the square-pyramidal arrangement, for low-spin Co^{II} complexes, if sufficiently flexible ligands are employed. No significant elongation of the Co–P bond opposite the large P–Co–P angle is observed in the present complex nor in complexes (I) and (II). In contrast, significant elongation of the apical bond is observed in other low-spin Co^{II} complexes having square-pyramidal or intermediate stereochemistry,[15a–c] although chemical inequivalence between the donor atoms may prevent us from drawing clear conclusions, in some of the last-mentioned cases. It seems that the effect of elongation of the apical bond, in the distortion toward square-pyramidal geometry, which is quite evident in the low-spin d^8 complexes,[16] is not so large in the low-spin d^7 complexes. This may be ascribed, by simplified considerations,[2] to the fact that the d_{z^2} antibonding orbital is (essentially) doubly occupied in the d^8 case, whereas it is only singly occupied in the d^7 case. There is e.s.r. evidence[17] for approximate d_{z^2} character of the unpaired electron in Co^{II} complexes of this type.

TABLE 5

Shortest contact distances *

C(4) · · · C(26^{I})	3.09	F(3) · · · C(4^{II})	3.28
C(4) · · · C(24^{I})	3.12	F(1) · · · C(18^{III})	3.23
C(6) · · · C(42^{I})	3.19	C(10) · · · C(22^{II})	3.54
C(7) · · · C(14^{I})	3.15	C(15) · · · C(15^{IV})	3.50
C(31) · · · C(38^{I})	3.18		

* Intramolecular contacts <3.20 Å, contacts <3.30 Å involving fluorine atoms and other intermolecular contacts <3.60 Å are listed. Superscripts refer to the following equivalent positions, relative to the reference molecule at x, y, z: I x, y, z; II $x+1, y+1, z$; III $1-x, -y, -1-z$; IV $1-x, -y, -z$.

Comparison with complex (I) may help us to draw some conclusions about the short Co–P distances formed with the central phosphorus atom of the ligand, in both complexes. Surprisingly, the 2.156(3) Å value in [Co(pp$_3$)Br]PF$_6$ is attained without evident strains in the chains of the flexible pp$_3$ ligand {examination of bond angles reveals a possibly significant trend, consisting of a small extension of the chain of the 'apical' [P(1)] phosphorus donor and of a small compression of the other two chains; this may be easily understood in view of the geometry of chelation}. Compared with this value, the 2.057(4) Å Co–P(4) distance in (I) is definitely short and requires explanation. It has been ascribed[3] to the particular shape of the d-electron distribution. Contraction of the axial bonds in the trigonal bipyramidal co-ordination geometry, due to this sort of factor, is predicted[18] for low-spin d^7, d^8, and d^9 complexes. This is indeed observed in some cases,[19] where monodentate or flexible ligands are involved, but not in other cases.[5,15b] It is questionable whether this factor should still be operative, with the distortion from three-fold symmetry present in (I). Also, it is unlikely to produce appreciable effects when a rigid ligand is involved, unless it acts with other factors (*e.g.* geometric requirements of the ligand). The situation in (I) is probably too complicated to allow unambiguous conclusions. However, if the small bridging span and the deformations observed in the chelate rings of qp are dictated by intramolecular crowding as the authors imply,[3] then shortening of the Co–P(4) bond may be required, solely to allow better co-ordination to the metal by the other phosphorus atoms, in the 'equatorial' plane.

Figure 2 shows the reflectance spectra of the three complexes compared above. The spectra of five-co-ordinate Co^{II} complexes are not very sensitive to the details of the geometry of co-ordination, for either high-[20] or low-spin[15b] electronic configurations of the metal. However, it should be possible to rationalize some features appearing from Figure 2, in the light of the known structures. The assignmment proposed for complex (I)[21] in D_{3h} symmetry may be used, in the strong-field limit.[20,22] Since all ligand-field levels involved in the spin-allowed transitions originate from the same free-ion term, the effects of electron repulsions on the metal atom should be negligible, to a first approximation: this should make the interpretation of the effects due to the field of the ligands easier.

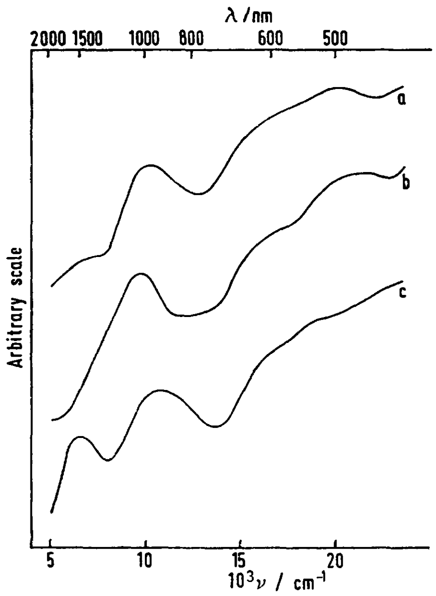

FIGURE 2 Reflectance spectra of: (a) [Co(qp)Cl]BPh$_4$, (b) [Co(pp$_3$)Br]PF$_6$, (c) [Co(np$_3$)I]I

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The band at *ca.* 10 × 10^3 cm^{-1} was assigned as $(e'')^4(e')^3 \rightarrow (e'')^3(e')^4$ in (I).[21] The bathochromic shift of the band in the present complex may be due to the decreased donor strength of the equatorial phosphorus atoms in pp_3 compared to qp and the broadening of the band on the low-energy side may be attributed to the greater distortion of the chromophore from C_{3v} symmetry in the present complex. Increase of the distortion may cause splitting of this band in (II). The bands at 15—20 × 10^3 cm^{-1} in (I) have been assigned to the $(e'')^4(e')^3 \rightarrow (e'')^4(e')^2 a_1'$ transition. They exhibit a low-energy shift in the spectrum of (II), compared to the other two cases. This indicates an overall decrease in the energy separation between the $\sim a_1'$ level and the underlying manifold in complex (II) and may be attributed to the combined effects of distortion from C_{3v} symmetry and decrease of the ' axial ' field strength.

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