Trigonal-bipyramidal Cobalt(II) Complexes of Difluorophenylphosphine: Spectral, *X*-Ray, and Electron Spin Resonance Studies

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E.s.r. and u.v.–visible spectral studies of the complexes $[CoX_2(PPhF_2)_3]$ (X = Br or I) indicate a distorted trigonal-bipyramidal co-ordination geometry at cobalt with two axial and one equatorial phosphorus ligand. Cobalt-59 hyperfine and ^{31}P superhyperfine coupling constants have been obtained by analysis of the e.s.r. spectra of frozen solutions in dichloromethane–paraffin oil at 100 K and interpreted in terms of delocalisation of unpaired electron spin density. The *X*-ray structure of $[CoBr_2(PPhF_2)_3]$ has been determined in order to substantiate the results of the spectroscopic investigations. Crystals of $[CoBr_2(PPhF_2)_3]$ are monoclinic, $P2_1/n$, with $a = 8.428(4)$, $b = 16.304(8)$, $c = 17.206(9)$ Å, $\beta = 98.58(6)°$, $Z = 4$. The molecules display a trigonal-bipyramidal geometry with the two bromine atoms equatorially substituted. Principal bond lengths are: $Co-P_{ax.}$ 2.158(5) and 2.158(5), $Co-P_{eq.}$ 2.120(5), and $Co-Br_{eq.}$ 2.383(2) and 2.367(3) Å.

THERE has been considerable interest in structural and spectral data on low-spin cobalt(II) complexes,[1] due partly to the fact that some cobalt complexes show a tendency to exhibit reversible oxygen activation.[2] The nature of the ground state in these systems was discerned mainly from the e.s.r. parameters and, in favourable cases, also from the electronic-spectral data. E.s.r. studies have been made on a large number of cobalt(II) complexes in tetragonal and square-pyramidal ligand fields. On the other hand, little information is available on trigonal-bipyramidal cobalt(II) complexes. In the present work we discuss spectral and e.s.r. data on two cobalt(II) difluorophosphine complexes having trigonal-bipyramidal geometry.

While fluorodi(t-butyl)phosphine forms complexes with nickel and cobalt halides, $[MX_2(PBu^t_2F)_2]$ (M = Co or Ni; X = Cl, Br, or I),[3] difluorophenylphosphine gives five-co-ordinate complexes with cobalt(II) halides, $[CoX_2(PPhF_2)_3]$.[4] (Dimethylamino)difluorophosphine is known to form similar complexes which have been studied by means of e.s.r. spectroscopy.[5,6] The chemistry of these complexes is, however, completely different from that of the difluorophenylphosphine complexes. The redox disproportionation of Co^{II} in the presence of excess of $PPhF_2$ was not observed in the case of the cobalt(II) complexes of $PF_2(NMe_2)$. In order to show whether this different behaviour is a consequence of structural peculiarities, we have undertaken e.s.r. spectroscopic and *X*-ray structural investigations. For one of the systems, namely $[CoBr_2(PPhF_2)_3]$, both the *X*-ray structure analysis and the e.s.r. data obtained from frozen solutions are presented.

EXPERIMENTAL

Preparation of the Complexes $[CoBr_2(PPhF_2)_3]$ (1) *and* $[CoI_2(PPhF_2)_3]$ (2).—These complexes were prepared according to the literature.[4] The purity was checked by chemical analysis, i.r., and n.m.r. spectroscopy.

X-*Ray Diffraction*.—Intensity data, from a prismatic crystal sealed into a Lindemann glass capillary tube, were collected on a Syntex $P2_1$ four-circle diffractometer by use of graphite-monochromated Mo-K_α radiation. Measurements were made in the θ—2θ mode ($3.0 \leqslant 2\theta \leqslant 50.0°$) at scan speeds varying linearly between 2.93 ($\leqslant 150$) and 19.53° min^{-1} ($\geqslant 3\,500$ count s^{-1}). Scan and total-background times were equal. Three standard reflections, monitored at regular intervals, showed no significant variations due to crystal deterioration during data collection. Of the 3 734 reflections recorded (one quadrant of reciprocal space), 2 380 were considered to be observed, having $F \geqslant 3.0\sigma(F)$ (R 0.023). Lorentz and polarisation, but no absorption, corrections were applied to the raw intensity data. Accurate cell dimensions were obtained from measurements of 15 reflections ($\pm hkl$) by use of Mo-K_α radiation.

Crystal data. $C_{18}H_{15}Br_2CoF_6P_3$, $M = 657.0$, Monoclinic, $a = 8.428(4)$, $b = 16.304(8)$, $c = 17.026(9)$ Å, $\beta = 98.58(6)°$, $U = 2\,313.3(20)$ Å^3, $Z = 4$, $D_c = 1.89$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 43.2 cm^{-1}. Systematic absences $h0l$ ($h + l = 2n$) and $0k0$ ($k = 2n$) indicate the centrosymmetric space group $P2_1/n$.

Structure solution and refinement. The structure was solved by a multisolution technique in which 2^{14} sign permutations were expanded by the Σ_2 formula (SHELX, G. M. Sheldrick). A permutation is rejected in this method if its internal consistency falls at any stage below a preset value. Additionally, a similarity test is applied to avoid the calculation of too many closely similar E maps. In this case two E maps were computed, of which the best (in terms of Σ_2 consistency) revealed the positions of the Co, Br, and P atoms. The remaining atoms, except for hydrogen, were located from subsequent difference-Fourier syntheses. Refinement of these positional parameters, together with their associated anisotropic temperature factors, was by full-matrix least squares with the function $\Sigma w\Delta^2$ being minimised. Satisfactory positions for the benzene-ring hydrogens could not be located by a final difference-Fourier synthesis, which however revealed large peaks of electron density in the neighbourhood of the Co and Br atoms, as a result of the failure to apply absorption corrections. This is reflected in the relatively high terminal values of the generalised index R_G [$= \Sigma w\Delta^2/\Sigma wF_o^2]^{\frac{1}{2}}$ of 0.125, the weighted residual R' [$= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o$] of 0.104, and the corresponding unweighted R of 0.101. The weights applied were given by

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TABLE 1

Atom positional parameters (× 10^4)

	x	y	z
Co	6 767(2)	5 292(1)	2 612(1)
Br(1)	4 775(2)	5 214(1)	1 464(1)
Br(2)	8 354(2)	4 191(1)	3 195(1)
P(1)	8 540(5)	5 471(3)	1 834(3)
P(2)	4 987(6)	4 949(3)	3 341(3)
P(3)	7 032(6)	6 506(3)	3 061(3)
F(11)	8 209(15)	6 206(6)	1 245(6)
F(12)	10 220(12)	5 723(7)	2 283(7)
C(11)	9 037(18)	4 678(9)	1 193(8)
C(12)	10 313(19)	4 153(11)	1 461(9)
C(13)	10 714(22)	3 550(12)	940(11)
C(14)	9 854(21)	3 430(12)	197(10)
C(15)	8 588(21)	3 984(11)	−56(9)
C(16)	8 169(19)	4 602(10)	448(10)
F(21)	3 501(13)	5 525(8)	3 293(8)
F(22)	5 607(15)	5 052(9)	4 251(6)
C(21)	4 066(19)	3 937(12)	3 288(10)
C(22)	4 322(21)	3 409(11)	2 682(11)
C(23)	3 491(22)	2 629(10)	3 632(12)
C(24)	2 448(25)	2 440(17)	3 188(16)
C(25)	2 221(29)	3 018(20)	3 744(19)
C(26)	2 935(27)	3 786(16)	3 813(12)
F(31)	5 582(13)	6 835(8)	3 438(9)
F(32)	7 003(18)	7 187(6)	2 446(7)
C(31)	8 664(20)	6 848(12)	3 790(9)
C(32)	9 758(23)	6 264(11)	4 122(9)
C(33)	11 071(27)	6 485(13)	4 695(10)
C(34)	11 198(26)	7 322(17)	4 923(11)
C(35)	10 116(26)	7 902(13)	4 579(12)
C(36)	8 801(21)	7 673(12)	3 993(10)

TABLE 2

Bond lengths (Å)

Co–Br(1)	2.383(2)	Co–Br(2)	2.367(3)
Co–P(1)	2.158(5)	Co–P(2)	2.158(5)
Co–P(3)	2.120(5)	P(1)–F(11)	1.561(10)
P(1)–F(12)	1.560(11)	P(1)–C(11)	1.783(16)
P(2)–F(21)	1.558(12)	P(2)–F(22)	1.569(11)
P(2)–C(21)	1.821(21)	P(3)–F(31)	1.558(12)
P(3)–F(32)	1.524(12)	P(3)–C(31)	1.799(18)
C(11)–C(12)	1.40(2)	C(12)–C(13)	1.40(2)
C(13)–C(14)	1.38(2)	C(14)–C(15)	1.42(2)
C(15)–C(16)	1.40(2)	C(16)–C(11)	1.37(2)
C(21)–C(22)	1.39(2)	C(22)–C(23)	1.45(2)
C(23)–C(24)	1.42(3)	C(24)–C(25)	1.37(3)
C(25)–C(26)	1.39(3)	C(26)–C(21)	1.42(2)
C(31)–C(32)	1.39(2)	C(32)–C(33)	1.41(3)
C(33)–C(34)	1.42(3)	C(34)–C(35)	1.38(3)
C(35)–C(36)	1.43(3)	C(36)–C(31)	1.39(2)

TABLE 3

Selected bond angles (°)

P(1)–Co–P(2)	172.5(2)	P(1)–Co–Br(1)	88.4(1)
P(1)–Co–Br(2)	87.7(1)	P(1)–Co–P(3)	92.9(2)
P(2)–Co–Br(1)	89.6(1)	P(2)–Co–Br(2)	87.7(2)
P(2)–Co–P(3)	94.5(2)	P(3)–Co–Br(1)	111.7(2)
P(3)–Co–Br(2)	122.3(2)	Br(1)–Co–Br(2)	126.0(1)
Co–P(1)–F(11)	115.1(5)	Co–P(1)–F(12)	113.3(5)
Co–P(1)–C(11)	121.8(5)	F(11)–P(1)–F(12)	100.0(7)
F(11)–P(1)–C(11)	101.4(6)	F(12)–P(1)–C(11)	102.2(7)
Co–P(2)–F(21)	115.9(6)	Co–P(2)–F(22)	112.5(6)
Co–P(2)–C(21)	122.3(6)	F(21)–P(2)–F(22)	97.7(7)
F(21)–P(2)–C(21)	102.1(5)	F(22)–P(2)–C(21)	102.8(7)
Co–P(3)–F(31)	115.0(5)	Co–P(3)–F(32)	116.3(5)
Co–P(3)–C(31)	124.5(7)	F(31)–P(3)–F(32)	95.6(9)
F(31)–P(3)–C(31)	100.1(8)	F(32)–P(3)–C(31)	100.3(8)

the expression $w = k[\sigma^2(F_o) + gF_o^2]$, where k and g refined to 1.808 3 and 0.004 832 respectively. Complex neutral-atom scattering factors [7,8] were employed for all the atoms. The results from the final least-squares cycle, summarised in Table 1, were used, together with the full covariance matrix, to calculate the bond lengths and angles and their estimated standard deviations (Tables 2 and 3). Observed and calculated structure factors, and anisotropic temperature factors, are in Supplementary Publication No. SUP 21998 (17 pp.).* Figure 1 depicts the molecule in perspective with the numbering system used. The contents of the unit cell projected perpendicular to x are shown in Figure 2.

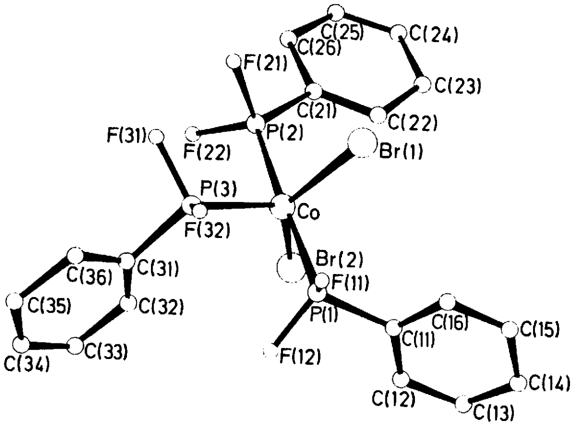

FIGURE 1 The molecule in perspective showing the numbering scheme

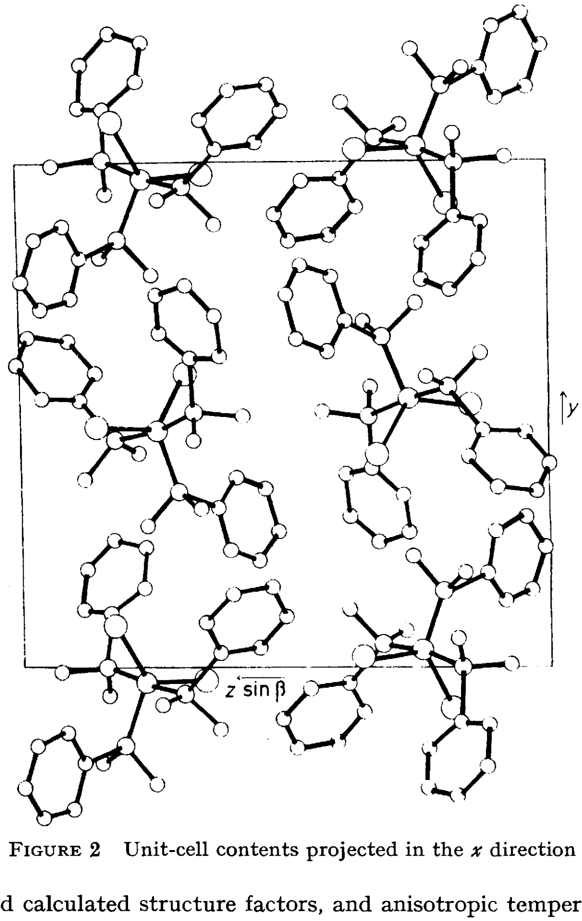

FIGURE 2 Unit-cell contents projected in the x direction

Electronic Spectra.—The electronic spectra were recorded

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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on a Beckman Acta III or Zeiss-DMR spectrophotometer using 0.1-cm quartz cells and dichloromethane distilled twice over P_4O_{10} as solvent. Solid-state spectra were obtained *for* Nujol mulls between quartz plates.

E.S.R. Measurements.—E.s.r. spectra were recorded on a Bruker BER 414S spectrometer operating at *X*-band with 100-kHz field modulation. The magnetic field was calibrated with an ALPHA-AL 675 n.m.r. gaussmeter. Solid diphenylpicrylhydrazyl (dpph) was used as the *g* marker. Solutions of the cobalt complex (*ca.* 10^{-4} mol dm^{-3}) in dichloromethane–liquid paraffin were used for the measurements. All the spectra of the frozen solutions were recorded at 100 K. Powder e.s.r. spectra in axial and rhombic environments were simulated with a PDP 10 computer using a program developed by one of the authors (J. S.).

RESULTS AND DISCUSSION

X-*Ray Crystal Structure.*—Although the quality of the overall refinement is limited by the failure to apply a suitable absorption correction, the resulting precision of the bond lengths and angles at cobalt is high enough to justify a detailed discussion. Trigonal-bipyramidal geometry is observed at cobalt with the two bromine atoms equatorially substituted at distances of 2.383(5) and 2.367(3) Å. The two axial Co–P bonds [2.158(5) and 2.158(5) Å] are significantly longer than the equatorial Co–P bond [2.120 Å] and are bent markedly away from this bond and into the Br–Co–Br angle [P–Co–P 92.9(2) and 94.5(2)°]. The two equatorial P–Co–Br angles [111.7(2) and 122.3(2)°] are remarkably different.

Co–P distances of 2.054(5) and 2.049(4) Å were found for the analogous trigonal-bipyramidal fluorophosphine complex $[CoH(PF_3)_4]$ which possesses a crystallographically imposed C_2 symmetry.[9] In other phosphine complexes, Co–P bond lengths in the range 2.16—2.28 Å have been observed [*e.g.* 2.16(1) in $[\{Co(C_5H_5)(PPh_2)\}_2]$ [10] and 2.28(1) Å in $[CoCl(Ph_2PCH_2CH_2PPh_2)_2]^+$ (ref. 11)]. Thus the Co–P distance of 2.05 Å in $[CoH(PF_3)_4]$ is at least 0.11(2) Å shorter than in the analogous phosphine complexes, which suggests that π back donation from the zerovalent metal atom is considerably enhanced in this case, because of the presence of the highly electronegative fluorine atoms which will lower the energy of the phosphorus 3*d* orbitals. The effect of such π bonding between the metal and phosphorus is most likely to be of significance when the metal is in a low or zero oxidation state. In $[CoBr_2(PPhF_2)_3]$, the Co–P distances are also short in comparison with the above phosphine complexes, but 0.07—0.11 Å longer than in $[CoH(PF_3)_4]$, from which it may be concluded that π back donation may play a much less significant role in this cobalt(II) complex. The mean P–F distances [1.562(3) and 1.541(17) Å] for the axial and equatorial phosphorus atoms are somewhat shorter than that [1.570(1) Å] in PF_3.[12]

TABLE 4

State and transition energies for the three vacancy configurations for the $|(x^2-y^2)^+(x^2-y^2)^-z^{2+}\rangle$ ground state

	$[CoBr_2(PPhF_2)_3]$			$[CoI_2(PPhF_2)_3]$			
		Transition energy			Transition energy		
Vacancy configuration	State energy	obs.	calc.	State energy	obs.	calc.	Interelectronic repulsion terms
$\|z^{2+}(x^2-y^2)^-(x^2-y^2)^+\rangle$	5 420			5 047			R_1
$\|z^{2+}(x^2-y^2)^-xy^+\rangle$	11 769	6 349	6 349	11 144	6 097	6 097	R_2
$\|z^{2+}z^{2-}(x^2-y^2)^+\rangle$	17 115	11 695	11 695	15 916	10 869	10 869	R_1
$\|z^{2+}(x^2-y^2)^-xz^+\rangle$	21 723	16 420	16 303	20 414	15 384	15 366	R_2
$\|z^{2+}(x^2-y^2)^-yz^+\rangle$	24 139		18 719	25 730	20 833 [b]	20 682	R_2
$\|(x^2-y^2)^+(x^2-y^2)^-xz^+\rangle$	30 247	24 827	24 827	28 302	23 255	23 255	R_3
$\|(x^2-y^2)^+(x^2-y^2)^-xy^+\rangle$	30 751		25 330	28 735		23 687	R_4
$\|(x^2-y^2)^+(x^2-y^2)^-yz^+\rangle$	32 663	27 243	27 243	33 618	28 571	28 571	R_3

[a] Energies are in cm^{-1}. The Condon–Shortley parameters are: (for the bromide complex) $F_2 = 1\,195$ and $F_4 = 99.6$ cm^{-1}; (for the iodide complex) $F_2 = 1\,094.4$ and $F_4 = 91.2$ cm^{-1}. The repulsion terms are $R_1 = -8F_2 + 33F_4$, $R_2 = -12F_2 - 87F_4$, $R_3 = -3F_2 + 8F_4$, and $R_4 = 12F_2 - 67F_4$. [b] Observed only as a shoulder in the observed spectrum.

Electronic Spectra of $[CoBr_2(PPhF_2)_3]$.—The electronic spectra of low-spin trigonal-bipyramidal cobalt(II) complexes with three-fold symmetry axes have been interpreted quantitatively in some cases.[13-18] Under C_{3v} symmetry the *d* orbitals split into three groups, namely $a(d_{z^2})$, e_1 $(d_{xy}, d_{x^2-y^2})$, and e_2 (d_{xz}, d_{yz}). In cases in which the symmetry is lower than C_{3v}, e_1 and e_2 are further split depending on the nature of the distortion from C_{3v}. The energy levels for a distorted trigonal-bipyramidal system have been computed by Venanzi and Norgatt [19] using the angular-overlap model. Using this model as a guideline, assignments of the electronic transitions were made for $[CoBr_2(PPhF_2)_3]$ and for the corresponding iodo-complex.

The following co-ordinate system was used to interpret the electronic and e.s.r. spectral data. The C_2 axis along the shortest Co–P bond was chosen as the *z* axis. The

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axial P–Co–P direction was taken as the y axis. The electronic-spectral transitions were assigned conventionally [6,20] by calculating the energies of various excited states, using the three-electron hole formalism. The state energy (E_i) is the sum of the one-electron orbital energies (ε_i) and the interelectronic interaction energy. The latter was estimated using the Condon–Shortley parameters F_2 and F_4. Of the five observed transitions, four were used to calculate the one-electron orbital energies. The fifth was computed using these orbital energies and the Condon–Shortley parameters. Good agreement was obtained between the experimental and calculated transition energies only when the F_2 and F_4 terms were reduced by 20% (see Tables 4 and 5). Unfortunately this method did not lead to a unique ordering of energy levels. Good agreement between the observed and calculated transitions was obtained for both the ground states, $|(z^{2+}z^{2-}(x^2-y^2)^+\rangle$ and $|(x^2-y^2)^+(x^2-y^2)^-z^{2+}\rangle$, in the hole formalism. However, the latter ground state was chosen for the following reasons. It is expected that F_2 and F_4 are smaller for the iodo- than the bromo-complex. This is observed with the $|(x^2-y^2)(x^2-y^2)z^2\rangle$ ground state. Also, better agreement was obtained between the experimental and calculated transition energies for the iodo-complex with the latter ground state than with $|z^2z^2(x^2-y^2)\rangle$.

TABLE 5

Single-electron d-orbital energies for $[CoBr_2(PPhF_2)_3]$ and $[CoI_2(PPhF_2)_3]$ *

Orbital	Br	I
x^2-y^2	35 494	36 248
z^2	23 799	25 379
xy	12 614	14 830
xz	2 416	5 316
yz	0	0

* Energies are in cm^{-1}, calculated using the interelectronic-interaction terms listed in Table 4. The assignment for yz is arbitrary.

E.S.R. Studies.—$[CoBr_2(PPhF_2)_3]$. The e.s.r. spectra of this system indicate axial symmetry both in polycrystalline and in frozen solutions. The general features of the e.s.r. spectra were $g_\parallel > g_\perp > 2.00$ and $A_\parallel^{Co} \gg A_\perp^{Co}$. Superhyperfine couplings were also observed in the parallel region from three nuclei each with spin $I = \frac{1}{2}$. A large coupling of 64.6×10^{-4} cm^{-1} was observed from a single nucleus and this is assigned to the ^{31}P in the $PPhF_2$ ligand in the z direction. A smaller coupling of 32.3×10^{-4} cm^{-1} was observed from two equivalent ($I = \frac{1}{2}$) nuclei. These couplings can be assigned either to other two ^{31}P nuclei in the x direction or to the two ^{19}F nuclei in the axial ligand.

The e.s.r. spectrum of a frozen solution of $[CoBr_2(PPhF_2)_3]$ in CH_2Cl_2–Nujol and that simulated using the coupling constants in Table 6 are presented in Figure 3. The spin-Hamiltonian parameters for this system are similar to those reported for $[CoBr_2\{PF_2(NMe_2)\}_3]$, except that only a single ^{31}P coupling was reported for the latter system.[6] In accordance with the co-ordinate system chosen, we assign $g_\parallel$ to g_{zz}. This assignment explains the large single ^{31}P coupling in the parallel region. Assuming the ground state $|(x^2-y^2)^+(x^2-y^2)^-z^{2+}\rangle$ deduced from the electronic-spectral data, one expects $g_{zz} \simeq 2.0 < g_{xx}, g_{yy}$. However, we found $g_{zz} > g_\perp$. A similar situation was envisaged by Nowlin *et al.*[6] who considered an admixture of $d_{x^2-y^2}$ and d_{z^2} in the ground-state wavefunction. In C_{2v} and lower symmetries the orbital $d_{x^2-y^2}$ can mix with d_{z^2} and hence the wavefunction can be represented as $|(d_{xz})^2(d_{yz})^2(d_{xy})^2(bd_{x^2-y^2}+ad_{z^2})^\pm\rangle$ with $a^2+b^2=1$. In the vacancy configuration, the ground state is $|(ad_{x^2-y^2}-bd_{z^2})^-(ad_{x^2-y^2}-bd_{z^2})^-(bd_{x^2-y^2}+ad_{z^2})^+\rangle$. The g values to second order in the spin–orbit coupling are as in equations (1)—(3),[21] where λ is the spin–orbit coupling constant for Co^{2+};

TABLE 6

Spin–Hamiltonian parameters for the low-spin difluorophenylphosphinecobalt(II) complexes [a]

System	$g_\parallel$	$g_\perp$	$10^4 A$/cm^{-1} $A_\parallel^{Co}$	$A_\perp^{Co}$	a^{P} [b]
$[CoBr_2(PPhF_2)_3]$	2.252	2.069	102	12	$a_\parallel^{P1}$ 64.6 $a_\parallel$ 32.3 [c]
$[CoI_2(PPhF_2)_3]$	2.202	g_{xx} 2.050	102	A_{yy}^{Co} 10	$a_\parallel^{P1}$ 64.6
		g_{yy} 2.150		A_{xx}^{Co} 10	$a_\parallel$ 32.3 [c]

[a] Measurements were made on frozen solutions of the complex in CH_2Cl_2–Nujol at 100 K. The estimated errors are g ±0.003 and A ±3 × 10^{-4} cm^{-1}. [b] The axial phosphorus ligand is assigned as P^1. [c] May be due to either the equatorial ^{31}P nuclei or the ^{19}F nuclei in the axial ligand.

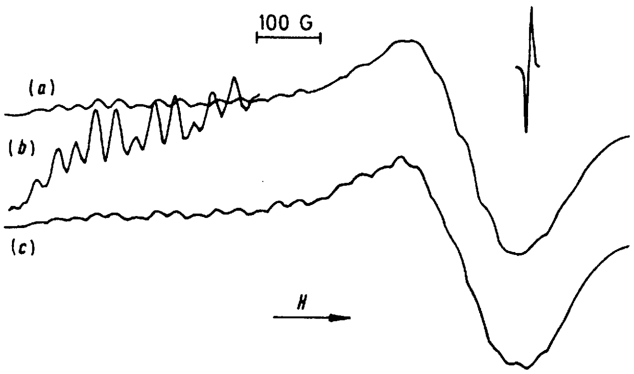

FIGURE 3 E.s.r. spectra of $[CoBr_2(PPhF_2)_3]$: (a) observed spectrum in CH_2Cl_2–Nujol at 100 K (Mod. amplitude = 10 G, ν = 9.4 GHz. The sharp single line signal at the right is that of dpph); (b) the low-field portion recorded at a higher sensitivity; (c) computer-simulated spectrum obtained using the parameters in Table 6

$$g_{zz} = 2.0023 - (8\lambda b^2/\Delta_1) \qquad (1)$$

$$g_{xx} = 2.0023 - [2\lambda(3^{\frac{1}{2}}a + b)^2/\Delta_2] \qquad (2)$$

$$g_{yy} = 2.0023 - [2\lambda(3^{\frac{1}{2}}a - b)^2/\Delta_3] \qquad (3)$$

λ is negative since the transition involves promotion of an electron from a filled to a partly filled orbital in all the three cases. If we designate the ground state as ϕ_g then $\Delta_1 = E(\phi_g \longleftrightarrow |xy\rangle)$, $\Delta_2 = E(\phi_g \longleftrightarrow |yz\rangle)$, and $\Delta_3 =$

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[20] W. D. Horrocks, G. R. Van Hecke, and D. D. Hall, *Inorg. Chem.*, 1967, **6**, 694.

$E(\phi_g \longleftrightarrow |xz\rangle)$. Similarly the hyperfine tensor components of ^{59}Co are given by equations (4)—(6) where

$$A_{zz} = K + P[\tfrac{4}{7}(a^2 - b^2) + \tfrac{1}{7}(3a^2 - 3b^2 + 2\cdot3^{\frac{1}{2}}ab)(\lambda/\Delta_3) + \tfrac{1}{7}(3a^2 - 3b^2 - 2\cdot3^{\frac{1}{2}}ab)(\lambda/\Delta_2) - 8b^2(\lambda/\Delta_1)] \quad (4)$$

$$A_{xx} = K + P[-\tfrac{2}{7}(a^2 - b^2) - 2(-3^{\frac{1}{2}}a + b)^2(\lambda/\Delta_3) - \tfrac{1}{7}(3a^2 - 3b^2 + 2.3^{\frac{1}{2}}ab)(\lambda/\Delta_2)] \quad (5)$$

$$A_{yy} = K + P[-\tfrac{2}{7}(a^2 - b^2) - 2(3^{\frac{1}{2}}a - b)^2(\lambda/\Delta_3) - \tfrac{1}{7}(3a^2 - 3b^2 - 2\cdot3^{\frac{1}{2}}ab)(\lambda/\Delta_2)] \quad (6)$$

$P = 2.0023g_N\beta_e\beta_N\langle r^{-3}\rangle_{av.}$ and K is the isotropic Fermi-contact interaction. The above expressions were taken from ref. 21, neglecting the contributions from quartet excited states and taking into account the negative sign of λ. It has been pointed out that the neglect of excited quartet states may lead to a considerable error in the calculation of spin-Hamiltonian parameters for low-spin cobalt(II) systems. Hence an estimate of b^2 from equations (1)—(3) may not be reliable. Nevertheless, one can estimate qualitatively the relative magnitudes of a^2 and b^2. Since there is axial symmetry, *i.e.* $g_{xx} \simeq g_{yy}$, b must be smaller than a. If a^2 and b^2 were of comparable magnitude, one expects from equations (4)—(6) that the anisotropic terms containing $(a^2 - b^2)$ will be very small and consequently lead to comparable magnitudes of $A_{\|}$ and $A_{\perp}$. Since $A_{\|}^{Co} \gg A_{\perp}^{Co}$, the magnitude of b^2 should be definitely smaller than that of a^2. This places the unpaired electron predominantly in the d_{z^2} orbital.

Neglecting the higher-order terms one can make a crude estimate of K and P; $K = \frac{1}{3}(2A_{\perp} + A_{\|})$ and $P = \frac{7}{6}(A_{\|} - A_{\perp})$. Assuming positive signs for $A_{\|}$ and $A_{\perp}$ ($b = 0$, $a = 1$), we obtain $K = 42 \times 10^{-4}$ cm^{-1} and $P = 100 \times 10^{-4}$ cm^{-1}. The value of P is somewhat too low, since for free Co^{2+} $P = 254 \times 10^{-4}$ cm^{-1}. This again is possibly due to neglect of the second- and higher-order terms. The ^{31}P couplings in the perpendicular direction are uncertain. In the computer simulation, $A_{\perp}^{Co}$ was taken to be 12×10^{-4} cm^{-1} and ^{31}P couplings were neglected. These latter couplings cannot be larger than 5×10^{-4} cm^{-1}. On this basis we conclude that the ^{31}P couplings are highly anisotropic.

[CoI$_2$(PPhF$_2$)$_3$]. The iodo-complex yielded a rhombic g tensor both in the polycrystalline state and in dilute frozen solutions. The g values are similar to these of the bromo-complex. The observed e.s.r. spectrum of a frozen solution of the iodo-complex in CH$_2$Cl$_2$–Nujol is presented in Figure 4. As with the bromo-complex, in the parallel region we observed a large ^{59}Co hyperfine coupling and one single ^{31}P (64×10^{-4} cm^{-1}) and two equivalent ^{19}F (32×10^{-4} cm^{-1}) couplings. The magnitudes of the hyperfine couplings are also identical to those observed for the bromo-complex. Here also no superhyperfine couplings were observed in the perpendicular region.

The assignment of the smaller superhyperfine couplings is not unambiguous. If these are due to the other two ^{31}P nuclei then our assignments of g_{zz}, g_{xx}, and g_{yy} are strengthened. In fact there is one argument which favours the choice of two equivalent ^{31}P nuclei. Since the ^{19}F coupling is expected to be highly isotropic, one expects the same couplings to appear in the perpendicular region. Inclusion of such couplings in the computer-simulated spectra did not produce good agreement with the observed e.s.r. spectra. Certainly, more e.s.r. data on similar systems are required to settle this point.

Phosphorus-3*s* and cobalt-4*s* spin densities were calculated using the theoretical nuclear hyperfine coupling constants for unit occupancy [*i.e.* 3 630 G (ref. 22) for P 3*s* and 1 308 G (refs. 23 and 24) for Co 4*s*].* If 5 G is assumed for $a_{\perp}^{P}$ (the linewidth), we obtain 25 G for a_{iso}^{P1}, the isotropic phosphorus hyperfine coupling constant. From this value a phosphorus-3*s* spin density of 0.7% was estimated. Using the data for $A_{\perp}^{Co}$ and $A_{\|}^{Co}$ given in Table 6, a cobalt-4*s* spin density of *ca.* 3% may be calculated. These values are similar to those obtained for the corresponding aminofluorophosphine complexes, *e.g.* [CoX$_2${PF(NMe$_2$)$_2$}$_3$] (X = Br or I) by Nowlin *et al.*[6]

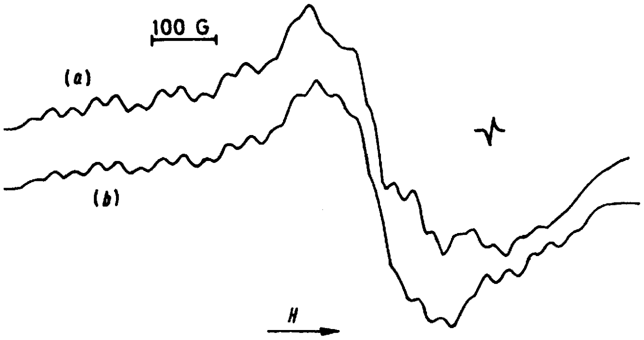

FIGURE 4 E.s.r. spectra of [CoI$_2$(PPhF$_2$)$_3$]: (*a*) observed spectrum in CH$_2$Cl$_2$–Nujol at 100 K (the sharp single line signal is that of dpph); (*b*) computer-simulated spectrum obtained using the parameters in Table 6

On the whole, it may be concluded that the e.s.r. data are consistent with the distorted trigonal-bipyramidal geometry as inferred from the X-ray studies, although the assignments of the superhyperfine couplings are uncertain.

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* Throughout this paper: 1 G = 10^{-4} T.

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