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Electron Spin Resonance and Electronic Absorption Studies of Low-Spin, Five-Coordinate Complexes of Cobalt(II)

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Electron spin resonance studies of a series of five-coordinate, low-spin cobalt(II) complexes of the type CoL_3X_2, where L is $(CH_3)_2NPF_2$ and $[(CH_3)_2N]_2PF$ and X is Cl, Br, and I, have been shown to be consistent with a configuration intermediate between a square-pyramidal geometry, with the basal plane defined by two phosphorus and two halogen atoms with the apex being occupied by the third phosphorus atom, and a trigonal-bipyramidal geometry. The esr spectra of all the complexes exhibit ^{59}Co hyperfine and some complexes also exhibited ^{31}P superhyperfine splittings. The isotropic contact terms and hyperfine constants were correlated with the charge distribution. There is a correlation between the ionic character of the Co–P bond and the stability of the five-coordinate complex. The one-electron orbital energies were determined for the complexes which contain $(CH_3)_2NPF_2$ as a ligand.

The preparation and properties of five-coordinate complexes have been topics of current discussion. We recently reported the synthesis and properties of five-coordinate low-spin cobalt(II) complexes of the type CoL_3X_2 where L is $(CH_3)_2NPF_2$[1] and $[(CH_3)_2N]_2PF$[2] and X is Cl, Br, and I. When the ligand $[(CH_3)_2N]_2PF$ was employed we suggested that in solution an equilibrium existed between a five-coordinate low-spin complex, CoL_3X_2, and a four-coordinate high-spin complex, CoL_2X_2.[2] We wished to examine the electronic spectral, magnetic, and esr data for these compounds to see if these properties could be correlated satisfactorily. Several esr studies of low-spin cobalt(II) ions have suggested that the single unpaired electron is in the d_{z^2} orbital of cobalt.[3] In other studies[4,5] it was suggested that although the low-spin cobalt(II) complex had a square-pyramidal geometry, the unpaired electron resided in the $d_{x^2-y^2}$ or the d_{xy} orbital.

In this paper we report the results of our esr studies of the low-spin complexes $Co[(CH_3)_2NPF_2]_3X_2$, $Co\{[(CH_3)_2N]_2PF\}_3X_2$, and $Co(Ph_2PH)_3Br_2$. The last complex, whose preparation was reported by Issleib and Wenschul,[6] is included in this study because it has been shown by a single-crystal X-ray diffraction study to be a five-coordinate complex, the structure of which lies intermediate between a square pyramid and trigonal bipyramid.[7]

We suggest that the unpaired electron orbital of the complexes consists of predominantly $3d_{z^2}$ character plus a small amount of s character. However, the s orbital gives a significant positive contribution to the metal hyperfine interaction. The direct mixing and the consequent positive isotropic coupling constant is symmetry allowed with both the 4s and $3d_{z^2}$ orbitals belonging to A′ representation under the C_s point group, the assumed symmetry for these complexes. The covalency of these complexes will be discussed in terms of spin delocalization and the isotropic contribution to the metal hyperfine interaction. The electronic ground state suggested is

$$|\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(z^2)}\rangle \text{ (vacancy configuration)}$$

The energies of the one-electron d orbitals were estimated for the pentacoordinate complexes which contain dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$, by using the observed optical spectra and the interelectronic interaction energies calculated for the low-spin d^7 system. We were unable to quantitatively handle the optical spectra of the complexes of bis(dimethylamino)-fluorophosphine, $[(CH_3)_2N]_2PF$, because of the presence of a substantial concentration of tetrahedral high-spin complex, but the strikingly similar esr and optical spectra of the $[(CH_3)_2N]_2PF$- and the $(CH_3)_2NPF_2$-containing complexes suggest that the pentacoordinate low-spin complexes formed with both ligands are similar. We were also unable, for reasons which will be presented, to obtain a satisfactory agreement between the calculated and observed *g*-tensor components.

Experimental Section

Because the compounds employed in the reactions are sensitive to traces of moisture or oxygen, the preparative work and handling of solutions were carried out in an atmosphere of dry nitrogen using a drybag.

The preparation of the $Co[(CH_3)_2NPF_2]_3X_2$[1] and $Co\{[(CH_3)_2N]_2PF\}_3X_2$[2] complexes, as well as that for $Co(Ph_2PH_3)Br_2$,[8] has been described previously.

The esr spectra at room temperature and the frozen solution spectra (77°K) were obtained in methylene chloride solution at a concentration of approximately 10^{-2} *M*. The solutions were prepared by allowing an excess of ligand to interact with the appropriate cobalt(II) halide. All esr spectra were recorded as first derivative using a Varian E-4 spectrometer with the magnet regulated by fieldial.

The optical spectra at room temperature were observed in solutions using a Unicam Model SP 820 Series 2 double-beam spectrophotometer. Solutions were prepared as described[1,2] with the reference solution containing an equivalent amount of ligand.

Results

At room temperature the esr spectra of all solutions showed only a broad structureless feature from which $\langle g \rangle$ values were calculated. These are reported in

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(1) T. Nowlin and K. Cohn, *Inorg. Chem.*, **10**, 2801 (1971).

(2) T. Nowlin and K. Cohn, *ibid.*, **11**, 560 (1972).

(3) (a) Y. Nishida and S. Kida, *Inorg. Nucl. Chem. Lett.*, **7**, 325 (1971); (b) J. M. Assour, *J. Chem. Phys.*, **43**, 2477 (1965); (c) J. M. Assour, *J. Amer. Chem. Soc.*, **87**, 4701 (1965); (d) J. M. Assour and W. K. Khan, *ibid.*, **87**, 207 (1965); (e) F. A. Walker, *ibid.*, **92**, 4235 (1970); (f) M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc.*, 2069 (1971).

(4) W. D. Horrocks, Jr., G. R. Van Hecke, and D. D. Hall, *Inorg. Chem.*, **6**, 694 (1967).

(5) E. E. Genser, *ibid.*, **7**, 13 (1968).

(6) K. Issleib and E. Wenschul, *Z. Anorg. Allg. Chem.*, **305**, 15 (1960).

(7) J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, **5**, 879 (1966).

(8) R. O. Hayter, *ibid.*, **2**, 932 (1963).

TABLE I

ESR PARAMETERS OF $Co\{[(CH_3)_2N]_2PF\}_3X_2$ and $Co[(CH_3)_2NPF_2]_3X_2$ COMPLEXES IN METHYLENE CHLORIDE SOLUTION

Halide	Ligand	$g_{\|\|}$ [a]	$g_{\perp}$ [a]	$\langle g \rangle$ [b]	$\langle g \rangle$ [c]	f_d	f_s	$A_{\|\|}(Co)$ [d]	$A_{\perp}(Co)$ [e]	$a_{\|\|}(P)$	A_{iso}	A_{dip}
I	$(CH_3)_2NPF_2$	2.288	2.117	2.171	2.141	0.730	0.049	102	45.0		64	38
Br	$(CH_3)_2NPF_2$	2.328	2.076	2.160	2.124	0.710	0.039	88	33.0	39.5	51	37
I	$[(CH_3)_2N]_2PF$	2.321	2.096	2.171	2.140	0.615	0.037	81	33.0	39.5	49	32
Br	$[(CH_3)_2N]_2PF$	2.381	2.079	2.179	2.136	0.540	0.033	71	29.5	35.5	43	28
Cl	$[(CH_3)_2N]_2PF$	2.401	2.072	2.181	2.140	0.520	0.031	68	27.5	33.0	41	27

[a] Error estimated in value determined from frozen solutions ±0.009. [b] $\langle g \rangle = \frac{1}{3}(g_{||} + 2g_{\perp})$. [c] $\langle g \rangle$ read directly from solution esr spectra at room temperature. [d] Error estimated ±0.5 G. [e] Perpendicular value of iodide complexes obtained from partially observable perpendicular regions; other values estimated from $\frac{1}{5}$ the width of the perpendicular region.

Table I. The room temperature esr spectra of polycrystalline samples of $Co\{[(CH_3)_2N]_2PF\}_3I_2$ and $Co(Ph_2PH)_3Br_2$ are shown in Figure 1. The g values obtained for these and related compounds are presented in Table II. The observation of three distinct g values for the compounds in Table II indicates that the symmetry is C_s or C_{2v} and we will assume, for the basis of further discussion, that the symmetry is C_s.

TABLE II

OBSERVED[a] g-TENSOR COMPONENTS FOR SOME POLYCRYSTALLINE PENTACOORDINATE LOW-SPIN COBALT(II) COMPLEXES

Complex	g_1	g_2	g_3	$\langle g \rangle$ [c]
$Co(Ph_2PH)_3Br_2$	2.339	2.092	2.045	2.159[d]
$Co\{[(CH_3)_2N]_2PF\}_3I_2$	2.249	2.147	2.080	2.159
$Co(dpe)_2Br_2$ [b]	2.258	2.075	2.037	2.123
$Co(dpe)_2Cl_2$ [b]	2.257	2.056	2.041	2.128

[a] Precision to ±0.005. [b] Bis(diphenylphosphine)ethane, ref 4. [c] $\langle g \rangle = \frac{1}{3}(g_1 + g_2 + g_3)$. [d] The room temperature spectrum of $Co(Ph_2PH)_3Br_2$ in CH_2Cl_2 yields a $\langle g \rangle$ value of 2.152.

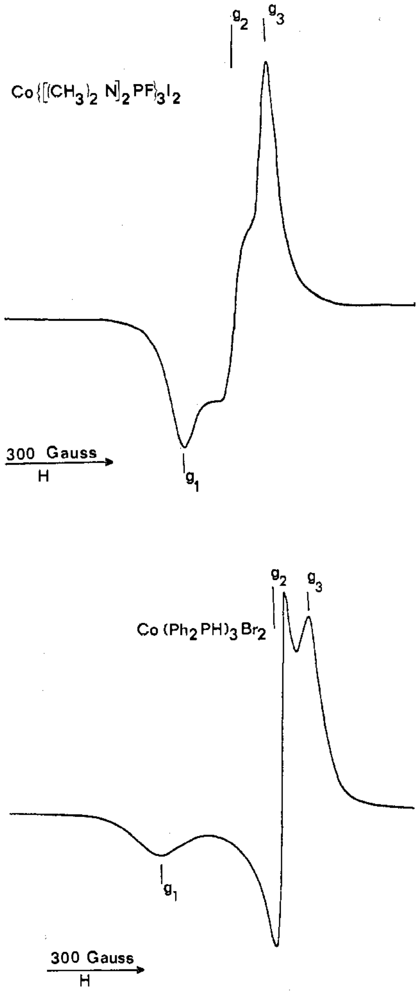

Figure 1.—Room temperature esr spectra of polycrystalline samples of (a) $Co\{[(CH_3)_2N]_2PF\}_3I_2$ and (b) $Co(Ph_2PH)_3Br_2$.

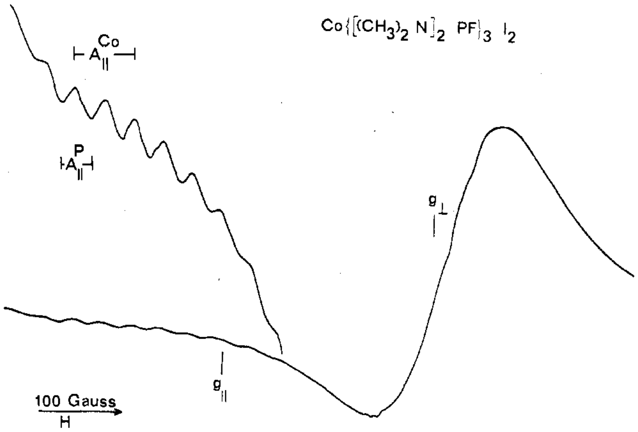

Figure 2.—Frozen solution spectrum (77°K) of $Co\{[(CH_3)_2N]_2PF\}_3I_2$ in excess $[(CH_3)_2N]_2PF$ and methylene chloride.

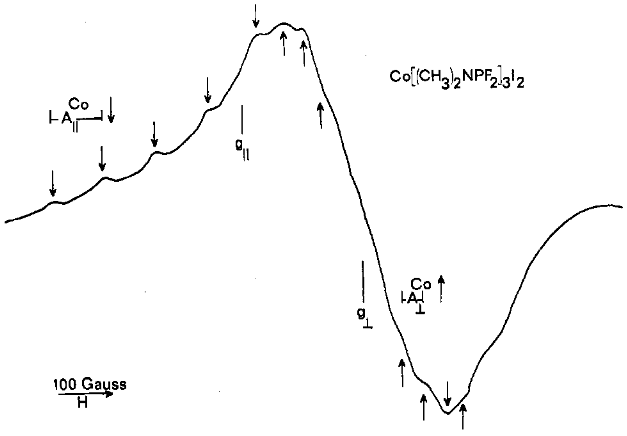

Figure 3.—Frozen solution spectrum (77°K) of $Co[(CH_3)_2NPF_2]_3I_2$ in excess $(CH_3)_2NPF_2$ and methylene chloride.

The esr spectra of polycrystalline samples of $Co[(CH_3)_2NPF_2]_3Br_2$ and $Co[(CH_3)_2NPF_2]_3I_2$ were poorly resolved and precise g values could not be obtained. On freezing solutions containing these complexes to 77°K ^{59}Co ($I = \frac{7}{2}$) hyperfine structure was resolved in the "parallel" band of all samples with the solutions containing $Co[(CH_3)_2NPF_2]_3I_2$ or $Co\{[(CH_3)_2N]_2PF\}_3I_2$ giving partially resolved "perpendicular" bands. Phosphorus hyperfine ^{31}P ($I = \frac{1}{2}$) lines were resolved in the "parallel" region of all solutions except for the solution containing $Co[(CH_3)_2NPF_2]_3I_2$ in which only the cobalt hyperfine structure was resolved. Typical frozen solution spectra (77°K) are shown in Figures 2 and 3.

Of the 16 lines expected in the "parallel" band due

TABLE III

SPECTROSCOPIC DATA FOR $Co[(CH_3)_2NPF_2]_3X_2$ AND $Co\{[(CH_3)_2N]_2PF\}_3X_2$ COMPLEXES

X	Solvent	Ligand	$\bar{\nu}(\epsilon)^a$					
I	CH_2Cl_2	$(CH_3)_2NPF_2$	26,100 (1100)	23,700 (1000)	20,500 (750)	14,800 (400)	13,150 (350) sh	5700 (50)
I	Mull		25,750	23,200	19,950	14,700		6000
Br	CH_2Cl_2			25,400 (1170) sh	21,650 (1370)	15,700 (760)	14,100 (700) sh	6000 (50)
Br	Mull			25,000 sh	21,750 sh	15,400		6000
I[c]	CH_2Cl_2	$[(CH_3)_2N]_2PF$	22,100 (620)	21,600 (210) sh	15,350 (360) sh	14,600 (44)	13,600 (340)	
I	Mull			24,400 sh	20,800	14,000		
Br[d]	CH_2Cl_2[b]		24,200 (900)	21,050 (600) sh	16,300 (580) sh	15,500 (640)	14,700 (580) sh	
Cl[e]	CH_2Cl_2[b]		25,400 (1600)	21,700 (450) sh	17,200 (300) sh	15,800 (480)	14,900 (450) sh	

[a] Frequencies in cm^{-1}. [b] Solutions prepared by dissolving anhydrous CoX_2 in an excess of ligand and CH_2Cl_2. [c] Concentration of $Co\{[(CH_3)_2N]_2PF]\}_3I_2$ 3.0×10^{-2} *M*. [d] Concentration of $CoBr_2$ approximately 10^{-3} *M*. [e] Concentration of $CoCl_2$ approximately 10^{-3} *M*.

to metal and ligand coupling, typically 10–13 lines were resolved, the rest being obscured by the overlapping "perpendicular" band. In the frozen solution spectrum of $Co[(CH_3)_2NPF_2]_3I_2$ in excess ligand and methylene chloride, in which phosphorus hyperfine lines were not resolved, 12 of the 16 combined "parallel" and "perpendicular" features were observed. No cobalt or ligand hyperfine was observed in the solid spectra of any of the polycrystalline complexes either at room temperature or at 77°K.

The visible spectra of the complexes CoL_3X_2 (when L is $[(CH_3)_2N]_2PF$ and X is Cl, Br, and I; and when L is $(CH_3)_2NPF_2$ and X is Br and I) in both solution and mull have been previously reported.[1,2] The band positions and molar extinction coefficients are presented in detail in Table III.

Discussion

^{59}Co Hyperfine Interaction.—For the complexes studied in the frozen state, the epr spectra were characterized by axially symmetric *g* and *A* tensors, and the hyperfine structure attributable to an interacting ^{59}Co nucleus was best resolved in the "parallel" component of the spectra. In contrast to the observation that three distinct *g*-tensor components were resolved in the polycrystalline solids (Table II), only two *g*-tensor components could be resolved in the frozen solution spectra. We suggest that these observations can be rationalized by suggesting that the broadening of the perpendicular region, which arises from the closeness of the magnitude of the g_2- and g_3-tensor components together with the additional ^{59}Co hyperfine broadening, prevents resolution of the g_2- and g_3-tensor components in the "perpendicular" band. A comparison of the $\langle g \rangle$ values calculated from the spectra of the polycrystalline solids and frozen solutions supports this contention (Table I).

The experimental hyperfine coupling constants consist of dipolar hyperfine coupling between the unpaired electron in the cobalt d orbital and the nucleus and isotropic coupling due to the presence of the unpaired electron in cobalt s orbitals. These have the tensor form $(a_{\|}, -B_{\perp}, -B_{\perp}) + (A_{iso}, A_{iso}, A_{iso})$ in the parallel (*z*) and the perpendicular (*x*, *y*) directions. The absence of well resolved cobalt hyperfine lines in the "perpendicular" region indicates that the magnitudes of *dipolar* and isotropic coupling are nearly equal and that the sign of A_{iso} and $A_{\|}$ are the same.

Spin Densities of the Cobalt d_{3z^2} and 4s Orbitals.—The values of the spin density on cobalt $3d_{z^2}$ (f_d) were calculated by setting an upper limit for the direct dipolar anistropic contribution to the hyperfine coupling value $|A'|_{max}$ of approximately 52 G.[9] The spin densities of the cobalt 4s orbital (f_s) were calculated by using a hyperfine interaction for unit occupancy of a cobalt 4s orbital as 1308 G.[10] Values of f_s and f_d are given in Table I.

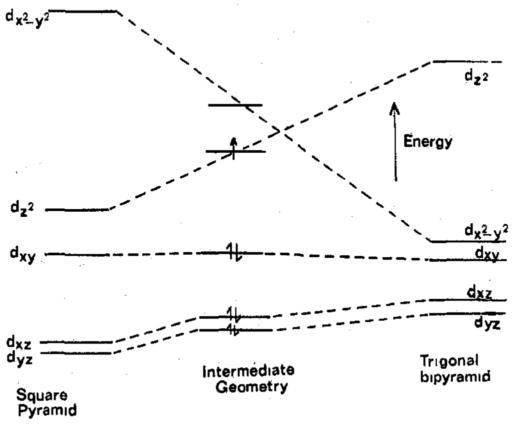

Figure 4.—One-electron energy level of the d orbitals in square-pyramidal and trigonal-bipyramidal geometry. The geometry of the complexes under consideration is intermediate between these two.

Phosphorus Hyperfine Structure and Probable Spin Density.—The resolution of phosphorus hyperfine structure only in the parallel band and not in the perpendicular band indicates a reasonably high anisotropic ^{31}P hyperfine tensor, that is ($a^{\|}_P \gg a^{\perp}_P$). Because $a^{\|}_P$ was found to be about 40 G, the phosphorus $\perp$ component could approach the line width of the absorption, about 10 G, and consequently could not be resolved. If we estimate a $\perp$ coupling of about 10 G the dipolar contribution to the phosphorus hyperfine is about 20 G. The $|A'|_{max}$ for phosphorus is 206 G or about 6–10% spin density in the phosphorus sp^3 hybrid orbital. There could be considerable backbonding between the ligand phosphorus outer d orbitals, which are lowered in energy by the presence of the electron-withdrawing fluorine atoms, and the cobalt d orbitals.

To help rationalize these data, the symmetry of these five-coordinate low-spin cobalt(II) complexes and the consequent ordering of the d orbitals will be considered. From a single-crystal X-ray diffraction study[7] of $Co(Ph_2PH)_3Br_2$ it has been shown that this complex has a basic trigonal-bipyramidal structure with two phosphorus atoms in axial positions and the third phosphorus and two bromide atoms in the basal

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(9) E. Strouse and L. F. Dahl, *Discuss. Faraday Soc.*, 93 (1969).

(10) E. Clementi, *J. Chem. Phys.*, **41**, 295 (1965).

plane. The basal plane, however, *does not* show trigonal geometry and the overall geometry is perhaps best described as intermediate between square pyramidal and trigonal bipyramidal. We believe that the geometry of the five-coordinate cobalt complexes examined in this study is best described as being close to square pyramidal and near the point where the $d_{x^2-y^2}$ and d_{z^2} levels cross (Figure 4). We base this belief on three experimental observations.

First, previous reports[3] of the g factors of a large number low-spin, four-, five-, and six-coordinate cobalt(II) complexes have the form $g_\perp > g_\| > 2.0023$ which corresponds well with a square-pyramidal arrangement and an unpaired electron in the d_{z^2} orbital. In these reports the mixing of the $d_{x^2-y^2}$ and the d_{z^2} states was generally not taken into account when the g values for d_{z^2} ground state were calculated. Although this mixing is not permitted in a zero-order approximation, spin–orbital coupling mixes the lower d_{xy}, d_{xz}, and d_{yz} with the $d_{x^2-y^2}$ and d_{z^2} levels (as allowed by the angular momentum operator $\hat{L}$). Because of mixing of the d_{z^2} and $d_{x^2-y^2}$ levels with the lower d_{xy}, d_{yz}, and d_{xy} levels, the angular momentum operator can now mix the $d_{x^2-y^2}$ and the d_{z^2} levels. The extent of this mixing, which depends on the separation between the two levels, is relatively negligible for a square-pyramidal geometry (Figure 4) but becomes considerably more important as the geometry changes from a square-pyramidal to a trigonal-bipyramidal arrangement. The d orbital wave functions can be described[11] as (in the order of decreasing energy)

$$\psi_1 = (\cos\alpha)d_{x^2-y^2} - (\sin\alpha)d_{z^2}$$

$$\psi_2 = (\sin\alpha)d_{x^2-y^2} - (\cos\alpha)d_{z^2}$$

where α is an angle which describes the size of the nonaxial component of the crystal field in such a way so that $\sin\alpha$ and $\cos\alpha$ are normalized mixing coefficients. The other orbitals are $\psi_3 = d_{xy}$, $\psi_4 = d_{xz}$, and, $\psi_5 = d_{yz}$. The principal g factors are described by constructing the matrix of ($\hat{L}$ and $2\hat{S}$) for the two Kramer's doublets derived from the state ψ_2 using standard expressions.[12] To a first order these are given by

$$g_{zz} = 2 - 8\lambda(\cos^2\alpha)/E(\psi_3\text{–}\psi_2) \qquad (1)$$

$$g_{xx} = 2 - 2\lambda(\cos\alpha + \sqrt{3}\sin\alpha)^2/E(\psi_5\text{–}\psi_2) \qquad (2)$$

$$g_{yy} = 2 - 2\lambda(\cos\alpha - \sqrt{3}\sin\alpha)^2/E(\psi_4\text{–}\psi_2) \qquad (3)$$

Because all these transitions, which correspond to the denominators in the above equations, involve promotion of an electron from a filled level (*i.e.*, they are hole transitions) λ is negative. Because the three denominators are also negative, the principal g factors should be above the free spin value (2.0023). For a square-pyramidal arrangement the separation between d_{z^2} and $d_{x^2-y^2}$ is large, the amount of mixing is small (*i.e.*, α is small) and eq 1 reduces to

$$g_{zz} \cong 2 - 8\lambda/E(\psi_3\text{–}\psi_2)$$

Thus, g_{zz} depends on the amount of mixing between d_{z^2} and d_{xy} orbital levels. In a similar manner eq 2 and 3 reduce to

$$g_{yy}, g_{xx} \cong 2 - 2\lambda/E(\psi_{4,5}\text{–}\psi_2)$$

This leads to the fact that g_{xx} and g_{yy} depend on the separation between the d_{z^2} and d_{xz}, d_{yz} levels. This, in turn, leads to the conclusion that $g_{zz} > g_{xx}$, $g_{yy} > 2.0023$. This conclusion is supported by a large body of experimental evidence.[3]

In the case of the complexes which we examined, $Co[(CH_3)_2NPF_2]_3X_2$, $Co\{[(CH_3)_2N]_2PF\}_3X_2$, and $Co(Ph_2PH)_3Br$, the smaller separation of the $d_{x^2-y^2}$ and d_{z^2} levels leads to considerable mixing (*i.e.*, α is large). Also, the separation between the d_{z^2} and the d_{xy} orbitals is larger. These factors lower the difference between g_{zz} and the free-spin value (2.0023). When eq 2 and 3 are examined, the small increase in the numerator which contains terms in $3\sin^2\alpha$ and the difference between g_{xx}, g_{yy} and the free-spin value (2.0023) is increased. This argument leads to the conclusion g_{xx}, $g_{yy} > g_{zz} > 2.0023$ and can be used to rationalize the data presented in Table I.

Second, it has been pointed out[4] that if the g-tensor components expected for three-vacancy configurations are calculated, starting with the strong-field determinantal wave function correct to first order in the spin–orbit coupling perturbation, for four possible ground states, only two are in agreement with the epr data which we have obtained ($g_1 > g_2 \approx g_3 > 2.0023$)

$$|\overset{+}{(xy)}\overset{-}{(xy)}\overset{+}{(yz)}\rangle \text{ and } |\overset{+}{(xy)}\overset{-}{(xy)}\overset{-}{(x^2 - y^2)}\rangle$$

If we are compelled to put the unpaired electron in either the $d_{x^2-y^2}$ or the d_{yz} orbital in order to explain the epr data, it becomes difficult to rationalize that superhyperfine interactions are observed for only *one* phosphorus nucleus (Figures 3 and 4, Table I). The presence of a superhyperfine interaction with only one of the phosphorus nucleus clearly leads to the conclusion that the unpaired electron formally occupies a d_{z^2} orbital.

Third, if we place the unpaired electron in the d_{yz} orbital, which would lead to good agreement between the observed and calculated g factors, we are unable to account for the ^{59}Co hyperfine coupling constants. Under a square-pyramidal geometry the d_{yz} orbital can π overlap with three of the ligands: the two basal plane ligands and the apical ligand. Such a structure will not show the presence of a single ligand superhyperfine structure and large ^{59}Co hyperfine structure in the parallel direction. The only alternative is to place the unpaired electron in the d_{z^2} orbital. Then in the parallel direction we expect the largest coupling from both the ^{59}Co and the apical ligand hyperfine interaction, which was observed.

To summarize, in contrast to what would be expected and has been observed[3] with complexes which were square pyramidal and which belonged to the C_s or C_{2v} point group (*i.e.*, $g_\perp > g_\| > 2.0023$), we find for the complexes $Co[(CH_3)_2NPF_2]_3X_2$, $Co\{[(CH_3)_2N]_2PF\}_3X_2$, and $Co(Ph_2PH)_3Br_2$ our data show that $g_\| > g_\perp > 2.0023$. To help understand these data and to account for the fact that the interactions are observed for only one phosphorus nucleus rather than more than one phosphorus or halogen nucleus, we are forced to conclude that extensive mixing occurs between the d_{z^2} and $d_{x^2-y^2}$ and that the unpaired electron formally occupies the d_{z^2} orbital. If eq 1, 2, and 3 are used with the data in Table I, values of 0.8 for $\cos\alpha$ and 0.6 for $\sin\alpha$ are

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[11] B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

[12] A. Carrington and H. C. Lonquet-Higgins, *Quart. Rev., Chem. Soc.*, **14**, 427 (1960).

TABLE IV

STATE AND TRANSITION ENERGIES FOR THREE-VACANCY CONFIGURATIONS FOR $|\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(z^2)}\rangle$ GROUND STATE

State (vacancy configuration)	$CoBr_2[(CH_3)_2NPF_2]_3$			$CoI_2[(CH_3)_2NPF_2]_3$			Interelectronic interaction term
		Calcd	Obsd		Calcd	Obsd	
$|\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(z^2)}\rangle$	14,050	0	Gd state	13,150	0	Gd state	$3F_0 - 8F_2 + 33F_4$ (−5430)
$|\overset{+}{(x^2-y^2)}\overset{-}{(z^2)}\overset{+}{(xy)}\rangle$	35,050	6,000	6,000	33,850	5,700	5,700	$3F_0 - 12F_2 - 87F_4$ (−20, 430)
$|\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(xy)}\rangle$	21,000	5,050		20,700	4,450		$3F_0 + 12F_2 - 67F_4$ (+6970)
$|\overset{+}{(z^2)}\overset{-}{(z^2)}\overset{+}{(x^2-y^2)}\rangle$	28,200	14,050	14,050	26,300	13,150	13,150	$3F_0 - 8F_2 + 33F_4$ (−5430)
$|\overset{+}{(x^2-y^2)}\overset{-}{(z^2)}\overset{+}{(xz)}\rangle$	46,900	17,800		44,100	16,000		$3F_0 - 12F_2 - 87F_4$ (−20, 430)
$|\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(xz)}\rangle$	32,800	15,700	15,700	31,000	14,800	14,800	$3F_0 - 3F_2 + 8F_4$ (−2430)
$|\overset{+}{(x^2-y^2)}\overset{-}{(z^2)}\overset{+}{(yz)}\rangle$	50,750	21,650	21,650	48,650	20,500	20,500	$3F_0 - 12F_2 - 87F_4$ (−20, 430)
$|\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(yz)}\rangle$	42,450	25,400	25,400	39,850	23,700	23,700	$3F_0 - 3F_2 + 8F_4$ (−2430)

obtained which shows that considerable mixing of the $d_{x^2-y^2}$ and d_{z^2} orbitals has occurred.

Covalency of the Metal–Ligand Bond.—Consideration of the total cobalt hyperfine interaction for the complexes studied (Table I) indicates that delocalization decreases in the series $[(CH_3)_2N]_2N]_2PF > (CH_3)_2NPF_2$ and in the series Cl > Br > I, suggesting that the former complexes are more covalent.[13]

The same conclusions regarding covalency are reached when the trend in the metal isotropic coupling constant is considered. Other workers have suggested that the fractional s character should in large part be determined by the relative separation of the s and d orbitals and, consequently, may depend on the nature of the axial ligand. As the cobalt–phosphorus bond becomes more covalent one would expect the separation of the s and d orbitals to increase (larger effective nuclear charge on cobalt) and therefore would expect the isotropic contribution to the metal hyperfine coupling to decrease. These arguments lead to the same prediction in covalency as do the total cobalt hyperfine interaction considerations.

This observed trend showing the $Co\{[(CH_3)_2N]_2PF\}_3I_2$ complexes to possess a greater degree of covalency than the $Co[(CH_3)_2NPF_2]_3I_2$ complexes may be related further to the tendency of these two phosphines to form five-coordinate complexes.

It has been previously shown[2] that the tendency toward five-coordination seems to be greater for the $(CH_3)_2NPF_2$ complexes than for the $[(CH_3)_2N]_2PF$ complexes. Also, it has been shown[2] that the role of the anion in determining the stability of the complexes has been discussed and is I > Br > Cl. In these cases it appears that as the bond covalency decreases, the stability of the five-coordinate complexes increases. Of course several effects are reflected in the entropy and enthalpy data. We do not wish to imply that the stability of the five-coordinate complex is entirely a function of the covalency of the five-coordinate complexes, but there does appear to be a correlation, on the basis of these studies, between the stability of the five-coordinate complex CoL_3X_2 and the relative covalency of the complex.

In addition, on the basis of simplified force constant calculation, it has been suggested that $(CH_3)_2NPF_2$ has more π-accepting ability (through a N–P d_π–d_π interaction) than $[(CH_3)_2N]_2PF$[14] in molybdenum carbonyl complexes of the type $L_nMo(CO)_{6-n}$, where $n = 2$. On the other hand, it may be reasonably suggested that $[(CH_3)_2N]_2PF$ is a better σ donor than $(CH_3)_2NPF_2$. This argument is based on the observation that there appears to be a donation of the lone pair of electrons on nitrogen to the empty d orbitals of phosphorus which makes the electrons on phosphorus more available.[15]

To summarize these arguments, we again call attention to the fact that from the data obtained in this study, together with the expectations which can be reasonably made on the σ and π character in the Co–P bond, it appears that the degree of covalency in a bond in which σ and π bonding may be important is determined primarily by the σ bond and not by $(d\text{–}d)_\pi$ effects. It is also suggested that the stability of five-coordinate compounds is related to the ionic character of the Co–P bond. Specifically, as the ionic character of this bond increases, the stability of the five-coordinate complex increases.

Electronic Spectra.—If we define a coordinate system where the (*z*) direction consists of the axial Co–P bond and the *y* axis lies in a plane which bisects the "basal atoms," then we find that the best agreement between our epr and electronic spectra is consistent with the ground-state vacancy configuration which follows.

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$$|\overset{+}{(x^2 - y^2)}\overset{-}{(x^2 - y^2)}\overset{+}{(z^2)}\rangle$$

Only three of the seven possible one-electron transition excited states contribute to the g values. The remaining transition energies in the electronic spectra of the complexes involving dimethylaminodifluorophosphine were calculated as described previously.[4] Briefly, the coulomb and exchange integrals representing the interelectronic interaction energies involved in each of the eight (including ground state) electronic configurations are found tabulated for d orbitals in terms of Condon–Shortley parameters F_0, F_2 and F_4.[16] The values of these interaction energies for the various states and the calculated transition energies are given in Table IV. By reducing the Condon–Shortley and spin–orbit coupling constant from the free-ion values one accounts for the mixing of metal and ligand orbitals in a molecular orbital formulation. Good agreement between the observed and calculated transition energies is obtained for the states used in determining the one-electron orbital energies which are given in Table V.

TABLE V

SINGLE-ELECTRON d ORBITAL ENERGIES FOR THE CoL_3X_2 COMPLEXES [$L = Me_2NPF_2$; $X = I, Br$][a]

Orbital	X = I	X = Br
$x^2 - y^2$	39,850	42,450
z^2	26,700	28,400
xy	19,150	21,450
xz	8,900	9,650
yz[b]	0	0

[a] Energies in cm^{-1}. [b] Assigned arbitrarily as the lowest lying orbital.

As mentioned earlier, the optical spectra of the complexes of bis(dimethylamino)fluorophosphine cannot be quantitatively handled because of the complexity of the optical spectra which arises from the presence of a substantial concentration of tetrahedral high-spin complex.

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Mercuric Halide Adducts of Ruthenocene and Ferrocene

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The reaction of ruthenocene and ferrocene with HgX_2 ($X = Cl, Br$) gives various adducts. A very recent X-ray crystal structure has shown these to be ruthenium–mercury bonded compounds. Raman and ir data are presented for these compounds and interpreted in terms of their known structures. An intense Raman band at 137 cm^{-1} (130 cm^{-1}) was assigned as the Ru–Hg stretch in the compound $Ru(C_5H_5)_2 \cdot HgX_2$ where $X = Cl(Br)$. Ferrocene reacts with HgX_2 to give $Fe(C_5H_5)_2 \cdot nHgX_2$ where $n \simeq 7$. In the case of the chloride, the initial product is a red diamagnetic material which converts ($\sim$1 day at 27°) to a blue paramagnetic ferricenium compound. Indications of an Fe–Hg interaction are seen in the infrared spectrum of the red compound.

Introduction

In a recent paper[1] we reported that the product of electrochemical oxidation of ruthenocene at a mercury anode is the mercury-bridged cation $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2]^{2+}$. It was found possible to prepare salts of the same cation by direct reaction of ruthenocene with $Hg(CN)_2$ in the presence of various acids. Formation of the mercury-bridged ruthenocene cation can be viewed as an acid–base interaction between mercuric ion and ruthenocene.

In the light of the above finding and the reported[2] basicity of ruthenocene and ferrocene toward the proton, we have initiated a program to investigate the basicity of ruthenocene and ferrocene. A reaction was found between HgX_2 ($X = Cl, Br$) and ferrocene and ruthenocene. An X-ray crystal structure report[3] appeared for two of the ruthenocene–mercuric halide adducts near the completion of our physical studies. In this paper we report the results of a Raman and infrared study of these ruthenium–mercury bonded compounds.

Experimental Section

Ruthenocene (ROC/RIC) was purified by sublimation under vacuum. All other chemicals used were reagent grade unless otherwise specified. Chemical analyses were performed by the University of Illinois microanalytical laboratory.

$Ru(C_5H_5)_2 \cdot HgCl_2$.—Ruthenocene (200 mg, 0.86 mmol) was dissolved in approximately 150 ml of absolute ethanol. To this solution was added 235 mg (0.87 mmol) of $HgCl_2$ dissolved in 150 ml of absolute ethanol. On standing for several minutes, a light yellow precipitate formed. The solution was then slowly evaporated to about half its original volume. The solid material was filtered and washed with ethanol and dried under vacuum. *Anal.* Calcd for $Ru(C_5H_5)_2 \cdot HgCl_2$: C, 23.89; H, 2.00; Ru, 20.10; Hg, 39.90; Cl, 14.10. Found: C, 23.82; H, 1.85; Ru, 19.07; Hg, 39.5; Cl, 13.6.

$Ru(C_5H_5)_2 \cdot 3HgCl_2$.—Ruthenocene (200 mg) was dissolved in 150 ml of absolute ethanol and this was added to an ethanol solution saturated with 2.0 g of $HgCl_2$. A light yellow solid precipitated, and this was filtered, washed with ethanol, and vacuum dried. *Anal.* Calcd for $Ru(C_5H_5)_2 \cdot 3HgCl_2$: C, 11.49; H, 0.96; Ru, 9.66; Hg, 57.54; Cl, 20.34. Found: C, 11.63; H, 1.15; Ru, 9.95; Hg, 57.25; Cl, 20.10. It was not possible to make the $Ru(cp)_2 \cdot nHgCl_2$ compound with n greater than 3; however, compounds with $3 > n > 1$ are possible.

$Ru(C_5H_5)_2 \cdot HgBr_2$.—Ruthenocene (143 mg, 0.62 mmol) was dissolved in 150 ml of absolute ethanol and added to 223 mg of $HgBr_2$ (0.62 mmol) dissolved in 50 ml of ethanol. The solution color turned light yellow. After standing for 1.5 hr, a light yellow crystalline precipitate started to form. The volume of the solution was reduced to less than half the original and the pre-

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