An Equilibrium Involving Bis- and Tris-Fluorophosphine Complexes of Cobalt(II) Halides

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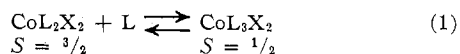A five-coordinate complex $Co\{[(CH_3)_2N]_2PF\}_3I_2$ can be obtained from the interaction of CoI_2 and $[(CH_3)_2N]_2PF$. This complex was characterized by analytical, magnetic moment, and uv–visible spectral data. When the complex is dissolved in either methylene chloride or benzene, an equilibrium is established between the low-spin, five-coordinate complex and a high-spin, pseudotetrahedral, four-coordinate complex of the type $Co\{[(CH_3)_2N]_2PF\}_2I_2$. Formation constants, ΔH, and ΔS values were obtained for the equilibrium. Similar results were obtained for analogous $CoCl_2$ and $CoBr_2$ complexes.

Introduction

Alkylaminofluorophosphines will displace carbon monoxide from metal carbonyls to form a variety of coordination compounds.[1] In these complexes the metal atoms are generally in zero oxidation states. It also has been reported that ligands of this type will interact with copper(I) chloride[2] and cobalt(II) halides[3] to form the complexes $(CuClL)_4$ and CoL_3X_2, where L is $(CH_3)_2NPF_2$ and X is bromine or iodine. In order to examine what effect increasing the number of electron-donating groups attached to phosphorus has on the coordinating ability of these ligands, we examined the complexes formed when cobalt(II) halides (Cl, Br, I) are allowed to interact with bis(dimethylamino)fluorophosphine, $[(CH_3)_2N]_2PF$.

We report here the preparation, spectral properties, and magnetic moments of the low-spin, five-coordinate complex $Co\{[(CH_3)_2N]_2PF\}_3I_2$, and we suggest that in solution an equilibrium exists between this complex and a high-spin, four-coordinate, pseudotetrahedral complex, $Co\{[(CH_3)_2N]_2PF\}_2I_2$. We were unable to isolate any complexes of other halogens, but we also suggest, on the basis of extensive magnetic and spectral data, that similar equilibria which involve chloride and bromide ligands also exist. These equilibria may be represented by

$$CoL_2X_2 + L \rightleftharpoons CoL_3X_2 \qquad (1)$$
$$S = {}^3/_2 \qquad\qquad S = {}^1/_2$$

where X is Cl, Br, or I and L is $[(CH_3)_2N]_2PF$. We also examined the thermodynamic parameters for these equilibria to investigate the role of the halogen ligands in determining the relative stability of the four- and five-coordinate complexes.

Although other five-coordinate compounds are stabilized in the presence of excess phosphine ligand,[3–5] suggesting that an associative process similar to that represented by eq 1 occurs in solution, evidence supporting such an equilibrium has been reported only for cobalt(II) thiocyanate complexes.[6,7]

(1) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964); C. G. Barlow, R. Jefferson, and J. F. Nixon, *J. Chem. Soc. A*, 2692 (1968); C. G. Barlow, J. F. Nixon, and J. R. Swain, *ibid.*, 1082 (1969); T. Kruck, M. Höfler, H. Jung, and H. Blume, *Angew. Chem.*, **81**, 533 (1969); R. B. King, M. I. Shag, and W. C. Zipperer, Fluorine Symposium, Milwaukee, Wis., June 1970.
(2) K. Cohn and R. W. Parry, *Inorg. Chem.*, **7**, 46 (1968).
(3) T. Nowlin and K. Cohn, *Inorg. Chem.*, **10**, 2801 (1971).
(4) P. Rigo, M. Bressan, and A. Turco, *Inorg. Chem.*, **7**, 1460 (1968).
(5) K. Issleib and E. Wenschuh, *Z. Anorg. Allg. Chem.*, **305**, 15 (1960).
(6) T. Boschi, P. Rigo, C. Pecile, and A. Turco, *Gazz. Chim. Ital.*, **97**, 1391 (1967).
(7) M. Nicolini, C. Pecile, and A. Turco, *J. Amer. Chem. Soc.*, **87**, 2379 (1965).

Experimental Section

The cobalt(II) complexes of $[(CH_3)_2N]_2PF$ are sensitive to air; however solutions of these complexes in methylene chloride could be stored for several hours in a glove bag filled with dry nitrogen without any observable changes in their spectral and magnetic properties. Therefore, preparative work was carried out under an atmosphere of dry nitrogen in a glove bag. Methylene chloride was dried over calcium hydride and distilled just prior to use. Anhydrous cobalt(II) halides were used as obtained from Alfa Inorganics. The ligand bis(dimethylamino)fluorophosphine was prepared as previously described[8] and purified just prior to use by means of gas chromatography.[9] The ligand, purified by this procedure, exhibits an nmr spectrum in which no absorptions attributable to either $(CH_3)_2NPF_2$ or $[(CH_3)_2N]_3P$ can be observed.

The electronic spectra were obtained using a Unicam Model SP820 Series 2 double-beam spectrophotometer. Solution temperatures were controlled to $\pm0.5°$ by the use of a thermostated cell compartment.

Magnetic Susceptibility Measurements.—The nmr method of Evans was used to obtain the solution magnetic susceptibilities over a range of temperatures.[10] The magnetic resonance spectra were obtained using a Varian A-60 analytical spectrometer. The instrument was equipped with a Varian variable-temperature controller, Model V-6040. Temperatures were determined by measuring the chemical shift difference for methanol (low temperatures) or ethylene glycol (elevated temperatures).[11] The nmr sample tubes used have been described.[10]

Solutions were prepared under nitrogen and transferred to the sample tubes by means of a syringe. The sample tubes contained a capillary of pure solvent consisting of 10% v/v of TMS in methylene chloride. Solutions were prepared using this same solvent. The separation of the solution–solvent signals was measured using both TMS and methylene chloride as the internal standards. Identical results, within experimental error, were obtained in both cases which indicates that the frequency separations used to calculate the magnetic moments are due solely to bulk susceptibility differences and contain no contribution from isotropic contact shifts.

Measurement of Equilibrium Constants.—These were carried out by a modification of a method described by Everett and Holm.[12] The solutions which were prepared contained a large excess of ligand. For example, a typical solution was prepared by adding a 0.0097-g (0.075-mmol) sample of anhydrous $CoCl_2$ to a 0.3121-g (2.259-mmol) sample of $[(CH_3)_2N]_2PF$ contained in a 2.00-ml volumetric flask. The solution of $CoCl_2$ and $[(CH_3)_2N]_2PF$ was then diluted with methylene chloride so that the total volume was 2.00 ml.

To obtain the formation constant, K_f, for equilibrium 1, the magnetic moment of the solution was measured, and K_f was calculated by the equation $K_f = N_f/N_tL$, where N_t and N_f are the mole fractions of the tetrahedral and five-coordinate species,

(8) G. S. Reddy and R. Schmutzler, *Z. Naturforsch. B*, **20**, 104 (1965).
(9) For a description of the chromatography techniques employed see J. E. Clune and K. Cohn, *Inorg. Chem.*, **7**, 2067 (1968).
(10) D. F. Evans, *J. Chem. Soc.*, 2003 (1959); D. W. Herlocker and R. S. Drago, *Inorg. Chem.*, **7**, 1479 (1968).
(11) A. L. VanGeet, *Anal. Chem.*, **40**, 2227 (1968).
(12) G. W. Everett, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 2442 (1966).

respectively ($N_t + N_f = 1$), and L is the concentration of the free ligand. The expression for the equilibrium constant is given by $K_f = [(\mu_t{}^2 - \mu_{obsd}{}^2)/(\mu_{obsd}{}^2 - \mu_f{}^2)](1/L)$ where μ_t and μ_f are the limiting moments of the tetrahedral and five-coordinate complexes, respectively. The values of μ_t were estimated from known moments of similar phosphine–cobalt(II) complexes (X = Cl, 4.40 BM; X = Br, 4.45 BM; X = I, 4.50 BM).[13]

The limiting value of μ_f was estimated to be 2.0 BM for the bromide and chloride complexes and determined as 2.10 BM for the iodide complex. The value of L was assumed to remain constant and equal to the initial ligand concentration. Because the ratio of ligand to metal ion was greater than 30:1 in every measurement and because the amount of ligand involved in establishing the equilibrium is small, the error associated with this assumption is about an order of magnitude less than the standard error in K_f. The standard error of K_f is estimated to be ±20%.

The ΔH values were obtained from plots of $\ln K$ *vs.* $1/T$ by measuring the equilibrium constant at four or five different temperatures at intervals of approximately 6°. The temperatures were selected in the range +2 to +40°. Results were obtained only in methylene chloride and benzene due either to poor solubility of these complexes in other weakly coordinating solvents or to the reactivity of the ligand with the solvent.
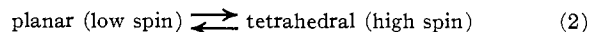
Preparation of Iodotris[bis(dimethylamino)fluorophosphine]-cobalt(II).—A 0.32-g sample of anhydrous cobalt(II) iodide (1.0 mmol) was added to approximately 20 ml of thiophene-free benzene containing 0.75 g (5.4 mmol) of bis(dimethylamino)-fluorophosphine. The brown solution which resulted was refluxed in a nitrogen atmosphere for approximately 0.5 hr. The solution was cooled, pentane (10 ml) was added to promote precipitation, and the solution was filtered. The filtrate was concentrated to one-fourth the original volume by distillation *in vacuo* and pentane (10 ml) was added again. On cooling, a dark brown solid slowly precipitated over a period of 12 hr. *Anal.* Calcd for $C_{12}H_{36}CoF_3I_2N_6P_3$: C, 19.83; H, 4.95; P, 12.82; N, 11.56; I, 34.91. Found: C, 19.82; H, 4.87; P, 12.63; N, 11.31; I, 34.62. The μ_{eff} is 2.10 BM. Ir spectrum of Nujol mull (Fluorolube between 2600 and 3200 cm⁻¹): 2920 (sh, m), 2880 (m), 2840 (m), 2800 (m), 1292 (m), 1190 (sh, w), 1175 (m), 1065 (w), 985 (s), 975 (sh, s), 775 (sh, m), 768 (s), 725 (sh, w), 712 (m), 675 (m), 498 (m), 448 (w), 413 (w), 355 (m), 330 (m) cm⁻¹. The solid compounds show no spectral changes when stored under nitrogen. The molar conductances of approximately 10^{-2} M solutions of CoX₂ (X is I, Br, Cl) dissolved in CH₂Cl₂ and excess ligand were 0.9, 1.0, and 0.8 cm²/ohm mol, respectively. The low conductivity values indicate that the complexes are nonelectrolytes in CH₂Cl₂. A solution of a 1:1 electrolyte in the same conductivity cell exhibits a molar conductance of about 20.0 cm²/ohm mol.
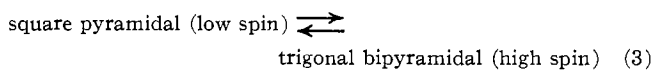
Results and Discussion

The Equilibrium Involving the Cobalt(II) Iodide Complex.

—A brown crystalline five-coordinate low-spin complex of the type Co{[(CH₃)₂N]₂PF}₃I₂ can be obtained when CoI₂ and [(CH₃)₂N]₂PF are allowed to interact in benzene. The uv–visible spectra and magnetic moment of this complex are almost identical with those of similar monomeric five-coordinate cobalt(II) complexes.[3–5,14] When this complex is dissolved in methylene chloride or benzene, the magnetic moment increases and the visible spectrum changes which suggests the formation of a new species.

There are various types of equilibria involving high- and low-spin cobalt(II) complexes in solutions of noncoordinating solvents which may occur. A series of investigations by Everett and Holm[12,15] has established a structural equilibrium involving strictly four-coordinate Co(II) complexes in which the two forms are interconnected by a torsional deformation proceed-

ing in ∼90° stages (eq 2). It recently has been suggested[16,17] that a similar equilibrium occurs in which the high- and low-spin species are both five-coordinate. Sacconi[11] suggested the interconversion

$$\text{planar (low spin)} \rightleftarrows \text{tetrahedral (high spin)} \qquad (2)$$

$$\text{square pyramidal (low spin)} \rightleftarrows$$
$$\text{trigonal bipyramidal (high spin)} \qquad (3)$$

We were able to rule out equilibria 2 and 3, which are not concentration dependent, and establish equilibrium 1 by measuring the concentration dependence of the solution magnetic moments when Co{[(CH₃)₂N]₂PF}₃I₂ is dissolved in methylene chloride or benzene. These results (Table I) are easily rationalized

TABLE I

MAGNETIC MOMENTS OF SOLUTIONS OF Co{[(CH₃)₂N]₂PF}₃I₂

Initial concn of Co{[(CH₃)₂N]₂PF}₃I₂, $M \times 10^2$	μ_{eff} (312°K), BM	Solvent	Initial concn of Co{[(CH₃)₂N]₂PF}₃I₂, $M \times 10^2$	μ_{eff} (312°K), BM	Solvent
2.16	3.42	CH₂Cl₂	1.93	3.41	C₆H₆
1.77	3.53	CH₂Cl₂	1.38	3.49	C₆H₆
1.49	3.68	CH₂Cl₂	1.29	3.62	C₆H₆
1.08	3.78	CH₂Cl₂			
0.75	3.98	CH₂Cl₂			
0.30	4.36	CH₂Cl₂			

by the equilibrium shown in eq 1. As the initial concentration of Co{[(CH₃)₂N]₂PF}₃I₂ is decreased from 2.16×10^{-2} to 0.30×10^{-2} M, the effective moment of species in solution increases from 3.42 to 4.36 BM, which shows that the ratio of the four-coordinate high-spin complex to the five-coordinate low-spin complex is increasing, as expected.

It was also observed that the addition of a 0.51-mmol sample of [(CH₃)₂N]₂PF to 2.00 ml of a 1.49 × 10^{-2} M solution of Co{[(CH₃)₂N]₂PF}₃I₂ in CH₂Cl₂[18] lowered the magnetic moment at 312°K from 3.68 to 3.24 BM.
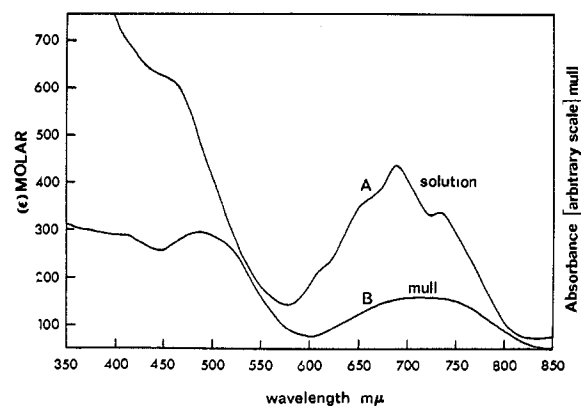
Figure 1.—Visible spectra of (A) solid Co{[(CH₃)₂N]₂PF}₃I² (Nujol mull between quartz plates) and (B) a 2.98×10^{-3} M solution of Co{[(CH₃)₂N]₂PF}₃I₂ in methylene chloride.

Further support for the suggestion that the equilibrium described by eq 1 is established when solid Co{[(CH₃)₂N]₂PF}₃I₂ is dissolved in either methylene chloride or benzene is obtained by comparison of the visible spectrum of the solid with that of the solution (Figure 1). In fact, the position, intensity, and band

(13) M. Nicolini, C. Pecile, and A. Turco, *J. Amer. Chem. Soc.*, **87**, 2379 (1965).

(14) G. Dyer and D. W. Meek, *J. Amer. Chem. Soc.*, **89**, 3983 (1967); W. D. Horrocks, Jr., G. R. VanHecke, and D. D. Hall, *Inorg. Chem.*, **6**, 694 (1967).

(15) G. W. Everett, Jr., and R. H. Holm, *ibid.*, **7**, 776 (1968).

(16) S. M. Nelson and W. S. J. Kelly, *Chem. Commun.*, 94 (1969).

(17) L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

(18) In other words, the solution was about 0.36 M with respect to ligand.

shape of the 500–800-mμ region in the spectrum of a 2.98 × 10^{-3} M solution of the solid complex in CH$_2$Cl$_2$ are typical of the ν_3[^{4}A$_2 \rightarrow$ ^{4}T$_1$(p)] transition found in high-spin, four-coordinate, pseudotetrahedral Co(II) complexes.[19]

In addition to these data, the uv–visible spectra of a solution which was 1.49 × 10^{-2} M with respect to Co{[(CH$_3$)$_2$N]$_2$PF}$_3$I$_2$ and 0.36 M with respect to [(CH$_3$)$_2$N]$_2$PF was obtained at a number of different temperatures to establish the existence of the equilibrium. Because all Co(II) species absorb in the uv–visible region, the presence of isosbestic points at 600 and 550 mμ indicates that there are only two species in solution. The temperature dependences of the magnetic moments, equilibrium constants, ΔH, and ΔS for this solution are presented in Table II. Table II also presents data for the complex dissolved in benzene.

TABLE II
TEMPERATURE DEPENDENCE OF MAGNETIC MOMENTS
AND STABILITY CONSTANTS FOR SOLUTIONS
Co{[(CH$_3$)$_2$N]$_2$PF}$_3$I$_2$ IN CH$_2$Cl$_2$ AND C$_6$H$_6$[a]

Solvent	Temp, °K	μ_{eff}, BM	K	$-\Delta H$, kcal/mol	$-\Delta S$, cal/mol deg
CH$_2$Cl$_2$	315	3.24	4.17		
CH$_2$Cl$_2$	308	3.14	4.92	3.6	8.5
CH$_2$Cl$_2$	301	3.05	5.74		
CH$_2$Cl$_2$	293	2.99	6.36		
C$_6$H$_6$	320	3.54	4.53		
C$_6$H$_6$	313	3.35	6.25	6.8	18.2
C$_6$H$_6$	309	3.24	7.50		
C$_6$H$_6$	301	3.12	9.17		

[a] Solutions in both solvents were 1.49 × 10^{-2} M with respect to Co{[(CH$_3$)$_2$N]$_2$PF}$_3$I$_2$ and 0.36 M with respect to [(CH$_3$)$_2$N]$_2$PF.

Equilibria Involving CoBr₂ and CoI₂ Complexes.—

Although we were unable to isolate the five-coordinate complexes of CoCl$_2$ and CoBr$_2$ with [(CH$_3$)$_2$N]$_2$PF, the analogous temperature dependence and concentration dependence of the visible spectra and solution moments of solutions of CoBr$_2$ and CoCl$_2$ dissolved in excess [(CH$_3$)$_2$N]$_2$PF indicate an equilibrium identical with that observed for the CoI$_2$ complex occurs in these solutions (Table III).

Specifically, when the concentration of CoCl$_2$ is held constant and the concentration of the ligand varied from about 0.05 to 0.15 M, Beer's law does not hold.

The temperature dependence of the electronic absorption spectra of solutions of CoX$_2$ (X = Cl, Br) in excess [(CH$_3$)$_2$PF and methylene chloride establishes that only two species are involved in the equilibrium. The spectra for the CoCl$_2$ solutions are presented in Figures 2 and 3. As in the case of the CoI$_2$ complexes, the spectra underwent reversible changes over the temperature range investigated. Isosbestic points were observed for the solutions which contained CoCl$_2$ (at 610 and 560 mμ). This indicates the presence of only two species. It should be noted that isosbestic points identical with those in the temperature-dependent studies were obtained in the Beer's law studies, which also points to the conclusion that there are two species. We did not observe isosbestic points in the spectrum of solutions which contained CoBr$_2$. We were able

(19) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, **83**, 4690 (1961).

TABLE III
TEMPERATURE DEPENDENCE OF MAGNETIC MOMENTS
AND STABILITY CONSTANTS FOR
CoCl$_2$ AND CoBr$_2$ SOLUTIONS

Cobalt halide	Temp, °K	μ_{eff}, BM	K_f	$-\Delta H$, kcal/mol	$-\Delta S$, cal/mol deg
CoCl$_2$[a]	319	4.11	0.19		
	312	4.04	0.25		
	305	3.96	0.31		
	300	3.89	0.38	6.0	22
	291	3.77	0.50		
	282	3.68	0.61		
CoCl$_2$[b]	319	3.98	0.33		
	309	3.87	0.44	6.0	21
	303	3.77	0.56		
	297	3.68	0.67		
CoCl$_2$[c]	316	3.93	0.27		
	310	3.87	0.32	5.4	20
	303	3.78	0.39		
	296	3.69	0.48		
CoBr$_2$[a]	314	3.21	1.51		
	307	3.11	1.78		
	301	3.04	2.01		
	295	2.96	2.31	4.3	13
	287	2.85	2.83		
	281	2.75	3.43		

[a] Solutions were 0.37 M in CoX$_2$ and the concentration of free ligand was adjusted to 1.0 M in CH$_2$Cl$_2$. [b] Free ligand concentration adjusted to 0.9 M. [c] Free ligand concentration adjusted to 1.25 M.
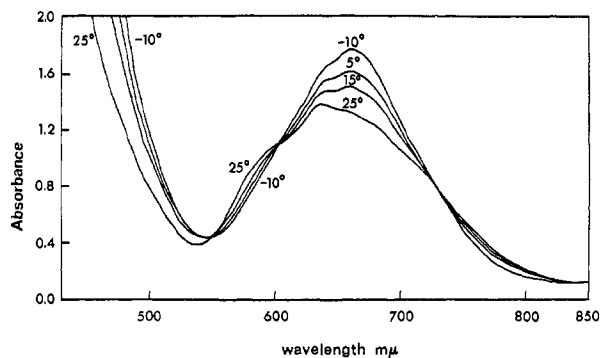

Figure 2.—Visible spectra temperature dependence of a 3.52 × 10^{-2} M solution of CoCl$_2$ in excess ligand.
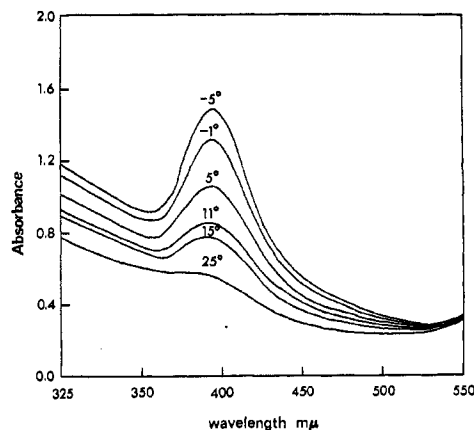

Figure 3.—Visible spectra temperature dependence of an approximately 1.0 × 10^{-2} M solution of CoCl$_2$ in excess ligand.

to establish the presence of only two absorbing species by the use of a recently described procedure.[20] A plot of absorbance ratios of the general form (A_{2j}/A_{1j}; $A_{3j}/$

(20) J. S. Coleman, L. P. Varga, and S. H. Mastin, *Inorg. Chem.*, **9**, 1015 (1970).

A_{1j}), where 1, 2, and 3 are the wavelengths obtained from the visible spectrum of the jth solution, results in a straight line. This method was also used to confirm the existence of only two absorbing species in the case of the CoI_2 and $CoCl_2$ solutions.

An examination of the electronic absorption spectra and magnetic moment data obtained for solutions in which the high-spin species predominate again provides compelling evidence for the presence of a tetrahedral Co(II) ion as the high-spin component involved in equilibrium 1. For example, the visible spectrum of a $CoCl_2$ solution at 25° (Figure 2) exhibits a maximum at 636 mμ and shoulders at 590, 670, and 710 mμ. The positions and intensities of those bands are characteristic of the $\nu_3[^4A_2 \rightarrow {}^4T_1(p)]$ absorption of a tetrahedral, high-spin Co(II) complex.[18] The magnetic moment of this solution is 3.89 BM which supports the contention that the Co(II) solution species is predominantly high spin (Table III).

As the temperature is lowered, the changes in the visible spectra, as well as magnetic moment data, show that the concentration of the five-coordinate low-spin cobalt(II) species increases. If, for example, Figure 2 is examined, at 25° the maximum at 636 mμ and the shoulders at 590, 670, and 710 mμ are particularly evident. As mentioned, these are characteristic of the ν_3 absorption of the tetrahedral species. The intensity of the ν_3 band is markedly reduced as the temperature is lowered. At 15° the shoulders at 590, 670, and 710 mμ begin to collapse while the maximum at 636 mμ begins to lose intensity as a new maximum attributable to the low-spin species forms at 660 mμ. These changes progress as the temperature is lowered and at −10° the shoulders at 590, 670, and 710 mμ are no longer discernible while the original maximum at 636 mμ has lost intensity and is now distinguishable only as a shoulder. The new maximum at 660 mμ which we assign to a transition involving the low-spin five-coordinate species is now even more pronounced. It should also be noted that the absorbance in the 400–500-mμ region also gained intensity as the temperature is lowered. Absorbance in this region is particularly characteristic of low-spin five-coordinate cobalt(II) complexes.[3,4,14,21] The changes in the spectra are almost identical with changes which occur in solutions of Co$\{[(CH_3)_2N]_2PF\}_3I_2$.

Further support for the existence of a low-spin five-coordinate cobalt(II) complex can be seen by comparison of the epr spectra of the frozen solutions (77°K) of these complexes with the previously reported spectra of the monomeric complexes of Co$[(CH_3)_2NPF_2)]_3X_2$ (X = Br, I) and Co(Ph$_2$PH)$_3$Br$_2$.[22]

The equilibrium constants as well as ΔH and ΔS values were calculated as described in the Experimental Section and are presented in Table III. Assuming no error in the limiting moments estimated for the high- and low-spin species involved in equilibrium 1, the thermodynamic stability of the five-coordinate complexes relative to the four-coordinate complexes as measured by the equilibrium constants increases in the order I > Br > Cl. This ordering, which is opposite to what one would expect on the grounds of ligand field stabilization energies, has been discussed[17] in terms of the "softness" or polarizability of the atoms as measured by the value of the overall nucleophilic reactivity constant $n°$[23] of the donor atoms in the complex. ΔS values are all negative and notably large in some cases. This is to be expected since the equilibria involve a change in coordination number between neutral species in relatively weakly coordinating solvents.

(21) K. Issleib and E. Wenschuh, *Z. Anorg. Allg. Chem.*, **305**, 15 (1960); R. Davis and J. E. Fergusson, *Inorg. Chim. Acta*, **4**, 23 (1970).

(22) A complete report of the epr data is contained in T. Nowlin and K. Cohn, submitted for publication in *Inorg. Chem.*

(23) F. Basolo and R. G. Pearson "Mechanism of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 93.