THE SYNTHESIS, CHARACTERIZATION AND ELECTRONIC PROPERTIES OF SOME ALKYLAMINOFLUOROPHOSPHINE COMPLEXES OF COBALT (II) HALIDES

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ABSTRACT

THE SYNTHESIS, CHARACTERIZATION AND ELECTRONIC PROPERTIES OF SOME ALKYLAMINOFLUOROPHOSPHINE COMPLEXES OF COBALT(II) HALIDES

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Pentacoordinate complexes of the type CoL_3X_2 (where L is an alkylaminofluorophosphine and X is Cl, Br, I) were obtained from the interaction of anhydrous cobalt(II) halides with dimethylaminodifluorophosphine, $(CH_3)_2NPF_2(apf_2)$, or bis(dimethylamino)fluorophosphine, $[(CH_3)_2N)_2PF(a_2pf)]$. The pentacoordinate complexes $Co(apf_2)_3I_2$, $Co(apf_2)_3Br_2$, and $Co(a_2pf)_3I_2$ have been characterized both by analytical and magnetic moment data and by visible and electron-spin resonance spectral data. Although the complexes $Co(a_2pf)_3Cl_2$ and $Co(a_2pf)_3Br_2$ were not isolated, magntic moment and spectroscopic data strongly suggest their existence in solution. When the complex $Co(a_2pf)_3I_2$ is dissolved in either methylene chloride or benzene, an equilibrium is established between the pentacoordinate low-spin complex and a four-coordinate high-spin complex of the type $Co(a_2pf)_2I_2$. Formation constants K_f, ΔH^0, and ΔS^0 values were obtained for the equilibrium. Similar results were obtained for the analogous $CoCl_2$ and $CoBr_2$ complexes. The electronic properties of these complexes are discussed and correlated with the thermodynamic stability constants (K_f).

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INTRODUCTION

There have been several recent investigations on the factors which influence the ability of transition metals such as cobalt(II) and nickel(II) to form pentacoordinate complexes.[1-9] Steric and electronic effects, in addition to the nature of the coordinated anions, have been examined.

Some investigators have suggested that electronic factors[1,2] may be more important than steric factors in stabilizing pentacooridnate cobalt(II) and nickel(II) complexes. Specifically, steric interactions[3] have been invoked to rationalize the fact that bulky tertiary phosphines such as $(C_6H_5)_3P$ do not form stable pentacoordinate cobalt(II) complexes. However, Coskran et al.[4] concluded from results obtained on spectral studies with phosphite ligands that the importance of steric factors has been overemphasized.

Turco and coworkers[5-9] have considered the role of the anion in stabilizing pentacoordinate cobalt(II) complexes. They proposed that a "strong field" anion was required for the formation of complexes of the type CoL_3X_2, where L is a neutral donor atom and X is a coordinated anion. For example, the "strong field" pseudohalogen anions CN^- and SCN^- have been used to prepare $Co[PC_2H_5(C_6H_5)_2]_3(CN)_2$,

$Co[P(C_2H_5)_2C_6H_5]_3(CN)_2$,[5,6] and $Co[P(C_2H_5)_3]_2(SCN)_2$.[7-9] They also reported that similar low-spin pentacoordinate complexes do not form when the anion is Cl^-, Br^-, I^-, or NCO^-.

No quantitative information has been reported on the role the halogens play in stabilizing the pentacoordinate complex.

The present investigation was undertaken to obtain information on how the electronic effects of the anions (Cl^-, Br^-, I^-) and of the ligands influence the formation of pentacoordinate cobalt(II) complexes. I evaluated these effects with monodentate ligands in order to eliminate any possibility that the geometry of the resulting complex was controlled by steric requirements imposed by multidentate ligands. Numerous pentacoordinate complexes of cobalt(II) with polydentate ligands have been examined.

The relative thermodynamic stability of four and five coordinate complexes of the type $Co(a_2pf)_2X_2$ and $Co(a_2pf)_3X_2$ (where X is Cl, Br or I) have been determined. These data are discussed and correlated with the electronic properties as indicated from the electron spin resonance spectral data obtained for these complexes.

HISTORICAL INTRODUCTION

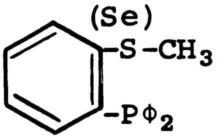
A survey of the previous work reported for pentacoordinate low-spin cobalt(II) complexes will be discussed in three parts. First, synthesis of pentacoordinate low-spin complexes will be reviewed. Second, a summary of the equilibria investigations that have been reported for cobalt(II) complexes is given. Finally, the electron spin resonance studies that have involved pentacoordinate cobalt(II) complexes will be presented.

Synthesis of Pentacoordinate Cobalt(II) Complexes

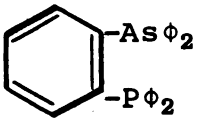
Pentacoordinate complexes of cobalt(II) which contain coordinated anions and neutral ligands attached to the metal have been reported for various types of chelating ligands.

The first pentacoordinate complex of this type was reported in 1960 by Issleib and Wenschush.[10] When excess diphenylphosphine (dpp) was allowed to interact with anhydrous cobalt(II) bromide in either dichloromethane or benzene a brown crystalline solid, $Co(dpp)_3Br_2$, (U_{eff} 2.01 B.M.) was isolated. Recently, it has been shown by a single crystal X-ray diffraction study[11] that the structure of this pentacoordinate complex is intermediate between a trigonal bipyramidal and square pyramidal configuration, the two possible idealized pentacoordinate structure types. The axial site is occupied by one of the three phosphorus donor atoms. Until this present investigation, no other pentacoordinate complex of the type CoL_3X_2 where L is a monodentate ligand and X a halogen had been reported, although Rigo and coworkers had reported a series of complexes of the type $CoL_3(CN)_2$ where L is diethylphenylphosphine $P(C_2H_5)_2C_6H_5$, and ethyldiphenylphosphine $PC_2H_5(C_6H_5)_2$.[5,6]

Other pentacoordinate ionic complexes of the type $(CoL_2X)Y$ where L is a bidentate ligand, X a coordinated anion and Y a non-coordinating anion such as perchlorate or another halogen atom have been reported. These include ditertiary phosphine complexes of the type $Co[\Phi_2P(CH_2)_2P\Phi_2]_2X_2$ in which X is Cl, Br, and I.[12] Dyer and Meek reported the preparation of similar complexes which incorporated the ligands diphenyl(o-methylthiophenyl)phosphine



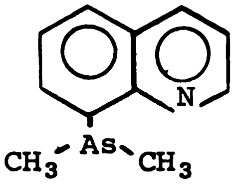
and diphenyl(o-diphenylarsinophenyl)phosphine



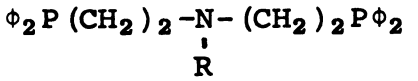
.[13]

Other pentacoordinate complexes of cobalt(II) which contained

8-dimethylarsinoquinoline



as the ligand have been prepared.[14]

Pentacoordinate complexes of the type $CoLX_2$ where L are tridentate ligands have been prepared as part of a systematic investigation that was undertaken to determine the effect various sets of donor atoms have on determining the spin-multiplicity of the ground state of cobalt(II). For example, the ligands bis-(2-diphenylphosphinoethyl) R-amine,  $\Phi_2P(CH_2)_2\text{-}\underset{\displaystyle R}{N}\text{-}(CH_2)_2P\Phi_2$ (R = H or CH_3)[15] and 2,6-di(β-diphenylphosphinoethyl)pyridine (a PNP donor atom set) yield low-spin complexes.[16]

Finally, quadridentate ligands[17,19] such as P(o-$\Phi_2PC_6H_4)_3$ (QP) have been employed in the preparation of low-spin complexes of the type (CoLX) where L is a quadridentate ligand and X and Y are coordinated and non-coordinated anions, respectively.

There is a complete review of tri- and quadridentate ligands which have been used to prepare pentacoordinate complexes.[20]

Solution Equilibrium Studies Involving Cobalt(II) Complexes

There are various types of equilibria involving high- and low-spin cobalt(II) complexes in non-coordinating solvents. A series of investigations by Everett and Holm[21-23] has suggested a structural equilibrium which involves strictly four coordinate cobalt(II) complexes in which the two forms are interconnected by a torsional deformation. This equilibrium may be represented as:

$$\text{Planar (low spin)} \rightleftharpoons \text{tetrahedral (high spin)}.$$

A similar equilibrium in which the high and low-spin species are both pentacoordinate has been suggested recently. Nelson and Kelly suggested the following interconversion [24]

$$\underset{\text{(low spin)}}{\text{square pyramidal}} \rightleftharpoons \underset{\text{(high spin)}}{\text{trigonal bipyramidal}} .$$

The existence of high-spin, low-spin solution equilibrium in which a configurational change is involved has been reported for $Co[P(C_2H_5)_3]_2(SCN)_2$.[8] The high spin form has been identified as a monomeric species with a tetrahedral configuration about the cobalt(II). The low-spin species is dimeric in solution, and it has been suggested that the cobalt atoms are linked by SCN bridges to give a pentacoordinate species. This type of equilibrium can be expressed as:

$$\underset{\text{tetrahedral high-spin}}{2[Co[P(C_2H_5)_3]_2(NCS)_2]} \rightleftharpoons \underset{\text{low-spin dimer}}{[Co[P(C_2H_5)_3]_2(NCS)_2]_2}.$$

A similar type of equilibrium which involved only monomeric species has also been reported, and may be expressed as:

$$\underset{\text{tetrahedral high-spin}}{CoL_2(NCS)_2} + L \rightleftharpoons \underset{\text{low-spin-monomer}}{CoL_3(NCS)_2}$$

The ligands employed in this study were $P(C_2H_5)_2C_6H_5$ and $PC_2H_5(C_6H_5)_2$. This latter equilibrium is analogous to the one I investigated in the present study, however, I was able to study the role of the halogen in stabilizing the pentacoordinate species. In all previous work it was noted that halocomplexes of the type $Co(PR_3)_2X_2$ (R is ethyl or phenyl) did not show any tendency to coordinate a third phosphine molecule.

Electron Spin Resonance Studies (esr) of Cobalt(II) Complexes

There have been relatively few reports of esr studies on five coordinate low-spin cobalt(II) complexes and, consequently, the electronic properties of this type of complex are not well known.

Horrocks and coworkers[12] reported that the esr spectra of the polycrystalline complexes, $Co[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2X_2$ (where X is a coordinated and a non-coordinating halogen, Cl, Br or I), showed three distinct $\underline{g}$ values. This observation indicates that the symmetry has been reduced from idealized C_{4v} to C_{2v}. The electronic ground state suggested was $|(\overset{+}{xy})(\overset{-}{xy})(x^2 \overset{+}{-} y^2)\rangle$ (vacancy configuration) and the energies of the one-electron d-orbitals were estimated using the observed optical data and the interelectronic interaction energies calculated for the low-spin d^7 system. No cobalt or ligand hyperfine interaction was observed in the esr spectra of these complexes.

There has been only one other esr investigation of pentacoordinate cobalt complexes. Genser reported[25] esr results obtained from a bis-dithiodiketone complex. The fifth coordination site was occupied by a neutral phosphite ligand. It should be pointed out that it is not clear if this complex should be considered as a cobalt(II) $3d^7$ derivative with two monovalent bidentate ligands. It may be thought of as a cobalt(IV) derivative with two divalent ligands. Hence, the conclusions about the electronic properties of this complex may not be useful in comparisons with other cobalt(II) low-spin complexes.

No esr results have been reported for complexes of the type CoL_3X_2 (where L is a monodentate neutral ligand and X is a coordinated anion). Most of the known complexes of this type are dissociated in solution (in contrast to the numerous dissociatively stable pentacoordinate complexes prepared with polydentate ligands).

EXPERIMENTAL

General Procedure

The cobalt(II) complexes of dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$(apf$_2$), and bis(dimethylamino)fluorophosphine, $[(CH_3)_2N]_2PF$(a$_2$pf), are sensitive to air. However, solutions of these complexes could be stored in methylene chloride or benzene for serveral hours in a glove bag filled with dry nitrogen without any observable changes in their spectral and magnetic properties. Therefore, these solutions were prepared under an atmosphere of dry nitrogen in a glove bag just prior to use. Solid materials which contained apf$_2$ were handled in an atmosphere of dry nitrogen in a dry box. The complexes Co(apf$_2$)$_3$X$_2$ (X = Br, I) were prepared by use of standard vacuum techniques. A complete description of these techniques and a diagram of a suitable vacuum line can be found in "The Synthesis and Characterization of Inorganic Compounds," William L. Jolly, Prentice-Hall (1970), pages 139-181.

The complex Co(a$_2$pf)$_3$I$_2$ was prepared under a nitrogen atmosphere and was handled in a glove bag that contained phosphorus pentoxide as a desiccant.

Elemental analyses were carried out by Galbraith Laboratories, Inc. (Knoxville, Tennessee) or Spang Laboratories (Ann Arbor, Michigan).

Materials

Anhydrous cobalt(II) fluoride, chloride, and iodide were used as obtained from Alfa Inorganics (Beverly, Massachusetts). Anhydrous cobalt(II) bromide was used as obtained from Research Inorganic Chemical (Sun Valley, California).

The solvents employed in this research (methylene chloride, benzene and pentane) were dried by refluxing over calcium hydride for at least twenty-four hours and were then distilled just prior to use.

The ligand apf$_2$ was prepared from dimethylaminodichlorophosphine.[26] The identity of the ligand was established by comparison of its infrared spectrum with a previously reported spectrum;[27] by its vapor pressure of 93.7 mm at 0^0, and by its nmr spectral data ($\delta_1$ppm(TMS) -2.69, J_{PH} 9.6, J_{FH} 3.8).

Bis(dimethylamino)fluorophosphine, a$_2$pf, was prepared by the reaction:

$$(CH_3)_2NPF_2 + [(CH_3)_2N]_3P \longrightarrow 2[(CH_3)_2N]_2PF$$

In a typical experiment a 58.5 g sample (0.52 mol) of dimethylaminodifluorophosphine and an 89.2 g sample (0.55 mol) of tris(dimethylamino)phosphine were combined. This mixture (approximately 140 ml) was added to a 200 cc "monel" bomb. The bomb was sealed and maintained for three days at 155^0 in an oil bath. The bomb was opened after it had cooled to 23^0. The contents (nmr spectral data indicated that approximately 75% of this mixture was a_2pf) was transferred to a glass vessel equipped with a stopcock.

Impurities were removed by (a) fractional distillation. The product distilled at 50°/50 mm (b) trap to trap distillation in vacuo from -22° to -49° to -78°. The product remained in the -45° trap, (c) gas chromatography. The details of the gas chromatography experiment have been previously described.[28] The identity of the ligand was established from nmr spectral data (δ,ppm(TMS)-2.5, J_{PH} 8.8, J_{FH} 3.0).[29] The ligand purified by gas chromatography exhibited an nmr spectrum in which no absorptions attributable to either $(CH_3)_2NPF_2$ or $[(CH_3)_2N]_3P$ were observed, and was used for the final preparative work and the equilibrium studies. The nmr of the ligand purified by both of the other methods indicated slight traces (less than 5%) of $[(CH_3)_2N]_3P$ in the product and was used in preliminary investigations.

Tris(dimethylamino)phosphine $[(CH_3)_2N]_3P$ was prepared by a modification of a previously reported method[30] as follows: Six moles of dimethylamine was added dropwise to an ether solution which contained one mole of phosphorus trichloride. The reaction was carried out at -78°. Ether was removed by distillation, 35°/760 mm. Tris(dimethylamino)-phosphine was distilled, 47°/10 mm. The identity of the product was established by nmr spectral data (δ,ppm(TMS) -2.43; J_{PH} 8.9).[31]

Magnetic Moment Measurements

Magnetic susceptibilities of solids were measured by the Guoy method by use of an apparatus described by Vander Vennen.[32] In this work the low temperature dewar apparatus was modified to allow a constant stream of helium to pass over the sample tube. This gas flow prevented water from condensing on the sample tube at low temperatures and also protected the sample from hydrolysis. The magnetic moment was measured at room temperature and at -196^0. In those cases where a large change occurred, the moment at -78^0 was also determined.

The nmr method of Evans[33] was used to obtain the solution magnetic susceptibilities over a range of temperatures. The magnetic resonance spectra were obtained by the use of a Varian A-60 analytical spectrometer equipped with a Model V-6040 Varian variable temperature controller. Temperatures were determined by measuring the chemical shift[34] difference for methanol (low temperatures) or ethylene glycol (elevated temperatures). The nmr tubes which were used have been described.[35] These were sealed to avoid air oxidation of the solution.

The separation of the "paramagnetic" and "diamagnetic" signals ($\Delta\nu$) was measured by using both TMS and methylene chloride as the internal standards.

Identical results were obtained within experimental error 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.

The frequency separations ($\Delta\nu$) are related to the molar susceptibility of the complex by:

$$\chi_m = \frac{3\Delta\nu \ mw}{2\pi(60 \times 20^6)c}$$

where mw is the molecular weight of the paramagnetic complex, 60×10^6 is the frequency of the proton resonance, and c is the concentration of complex (paramagentic solute) in gml^{-1}.

Figure 1 shows a typical nmr spectra recorded from a solution that contained $Co(apf_2)_3I_2$. As the temperature was lowered two effects were observed. First, the increased broadening of the resonance line which arises from protons in the paramagnetic environment and, secondly, an increase in frequency separation. Concentrated solutions were not used because the broadening of the paramagnetic resonance line reduced the precision. It was found that with the concentration used in this work (approximately 10^{-2} M or c = 0.02 gml^{-1}) the broadening of resonance lines was not severe and the peak separation was measured easily.

Measurement of Equilibrium Constants

These measurements were carried out by a modification of a method described by Everett and Holm.[21] The solutions used contained a large excess of ligand. For example, a

Figure 1. Nmr spectra of $Co(apf_2)_3I_2$ dissolved in methylene chloride and excess ligand.

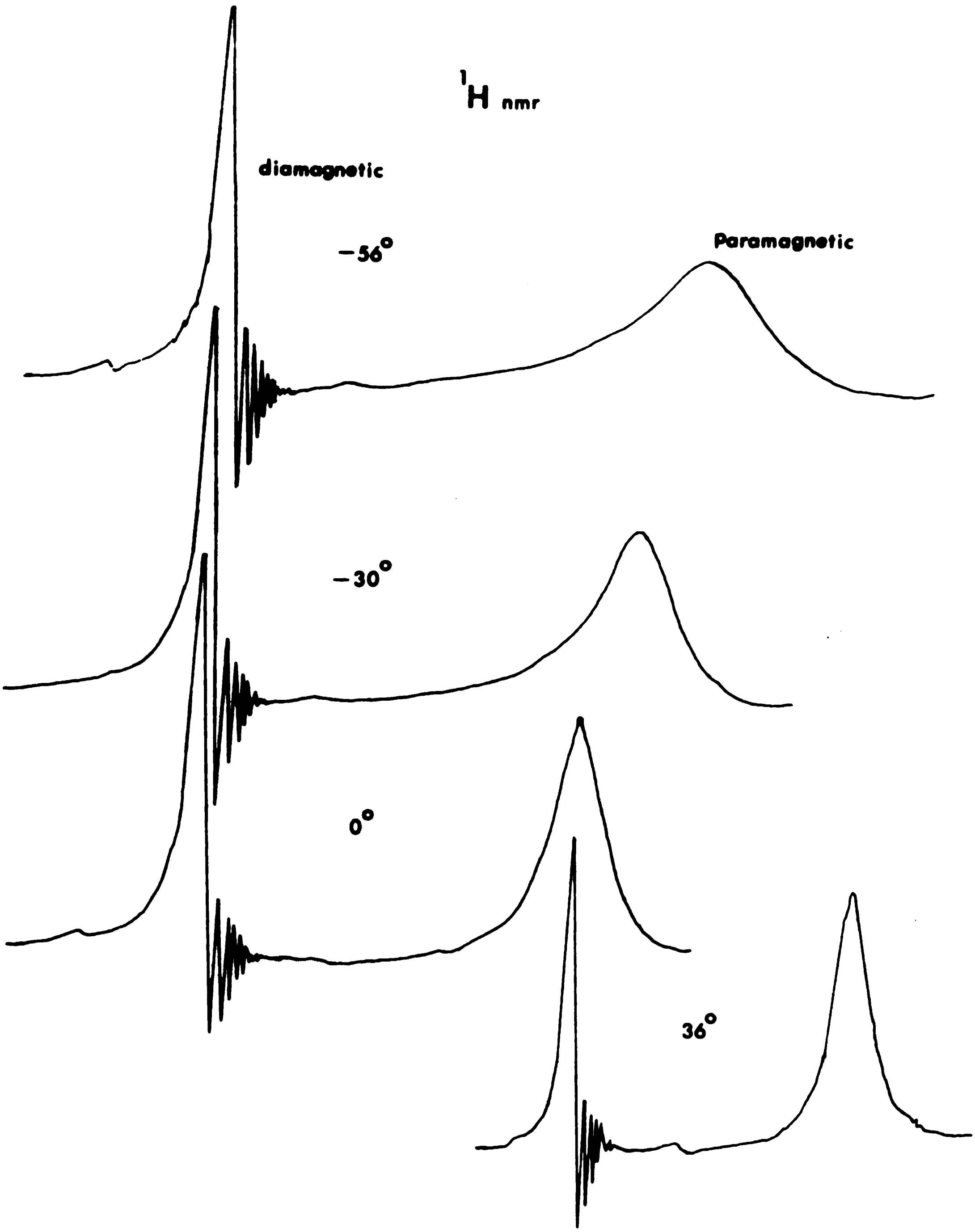


Figure 1.

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 a_2pf contained in a 2.00 ml volumetric flask. The solution of $CoCl_2$ and a_2pf was then diluted with methylene chloride so that the total volume was 2.00 ml.

To obtain the formation constant, K_f, for the equilibrium

$$\begin{array}{llcl} CoL_2X_2 \quad + & L & \rightleftharpoons & CoL_3X_2 \\ \text{high spin-} & & & \text{low spin-} \\ \text{tetrahedral} & & & \text{pentacoordinate} \end{array}$$

the magnetic moment of the solution was measured, and K_f was calculated by a modification of the basic equation

$$K_f = \frac{N_f}{N_t(L)}$$

where N_t and N_f are the mole fractions of the tetrahedral and five-coordinate species, respectively ($N_t + N_f = 1$), and L is the concentration of the free ligand. The expression for the equilibrium constant is given by

$$K_f = \frac{u_t^2 - u_{obs}{}^2}{u_{obs} - u_f^2} \; \frac{1}{(L)}$$

where u_t and u_f are the limiting moments of the tetrahedral and five coordinate complexes, respectively. The value of u_t was estimated from known moments of similar phosphine cobalt(II) complexes (X = Cl, 4.40 B.M.; X = Br, 4.45 B.M.; X = I, 4.50 B.M.).[8]

The limiting value of u_f was estimated to be 2.0 B.M. for the bromide and chloride complexes and determined as 2.10 B.M. 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 magneitude less than the standard error in K_f. The uncertainity in the solution susceptibility measurements allowed us to estimate the standard error of K_f to be ±20%.

The ΔH^0 values were obtained from plots of $\ln K_f$ vs $1/T$ by measuring the equilibrium constants at four or five different temperatures selected in the range 2 to 40^0 at approximately 6^0 intervals. Equilibrium results could be obtained only in methylene chloride or benzene. Either poor solubility of the complexes in other weakly coordinating solvents or reactivity of the ligand with the solvents precluded the use of other solvents.

Measurement of the esr Spectra

Both the room temperature (23^0) and the frozen solution (-196^0) esr spectra were obtained in methylene chloride solutions made approximately 10^{-2}M in complex. These 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 curves by use of a Varian E-4 spectrometer with the magnet regulated by a fieldial. The spectra were determined at frequencies which ranged from 9.2 to 9.5 KHz and were recorded on an x-y recorder with the x-axis proportional to the magnetic field strength. A three millimeter diameter quartz tube approximately twelve inches in length was used as a sample container.

Values of g were determined from the measured klyston frequency (ν^k) and the field strength H_0 by the expression

$$g = \frac{h\nu^k}{BH_0} \;;\text{ where } \frac{h}{B} = 0.714489 \text{ sec}\cdot\text{Gauss}$$

h is Planck's constant and B is the Bohr magneton.

Infrared and Optical Spectra

Either a Perkin-Elmer 237B or 457 spectrophotometer was employed to obtain ir spectra. The solid materials were examined as Nujol and Fluorolube mulls between cesium iodide plates. For volatile materials a gas cell with a 7.5 cm path length and KBr windows was used. Solution and mull electronic spectra were obtained by use of either a Cary 14 or a Unicam model SP 820- series 2 double beam spectrophotometer. Solutions which were examined contained the complex plus excess ligand in methylene chloride while the reference solution contained an equivalent amount of ligand, but no metal salt. Mull spectra were obtained by using Nujol mulls between quartz plates.[36] Solution temperatures were controlled to ±0.2° by the use of a thermostated cell compartment.

Preparation of the Complexes

Dibromotris(dimethylaminodifluorophosphine)cobalt(II) $Co(apf_2)_3Br_2$

In a typical reaction a 1.8 g (8.3 mmol) sample of anhydrous cobalt(II) bromide was transferred to a 50 ml flask which was equipped with a standard taper joint and a magnetic stirrer. The flask was evacuated and a 6.90 g (61.1 mmol) sample of apf_2 was condensed into the flask at -196°. The mixture was warmed to room temperature and the resulting dark green solution was stirred with a magnetic stirrer for twelve hours. At the end of this time the reaction mixture was opened to the vacuum pumping system (while the stirring was continued) for about one-half hour, and the unreacted apf_2 (3.90 g; 34.5 mmol) was collected in a -196° trap. In a number of separate experiments the mole ratio ($apf_2/CoBr_2$) of the dark green solid which remained in the reaction flask varied from 2.98 to 3.18. Shorter reaction times (three to four hours) did not seem to affect the composition of the reaction product. Since the complex has a small apf_2 dissociation pressure at room temperature, it was stored in a closed container under a nitrogen atmosphere.

Anal. calculated for $C_6H_{18}CoF_6Br_2N_3P_3$: C, 12.93; H, 3.23; N, 7.54; Br, 28.70. Found: C, 12.65; H, 3.13; N, 7.59; Br, 28.59.

Because of the limited solubility of the $CoBr_2$ complex in organic solvents, the value of the molecular weight was obtained by determining the vapor pressure lowering of apf_2 when $CoBr_2$ is dissolved in it. A mercury differential manometer of a type previously described was employed.[37]

Molecular weight determinations were made on solutions which contained 10.9% and 10.7% $CoBr_2$ by weight in excess apf_2. If the two sets of data are averaged and the complex is assumed to be only $Co(apf_2)_3Br_2$, the calculated molecular weight is 630 ± 100 g/mol (theory: 558 g/mol).

Diiodotris(dimethylaminodifluorophosphine)cobalt(II)-$Co(apf_2)_3I_2$

In a typical experiment, a 2.50 g (7.98 mmol) sample of anhydrous cobalt(II) iodide was transferred in a dry box to a 50 ml flask which was equipped with a stopcock, standard taper joints and a magnetic stirrer. The flask was evacuated and a 5.10 g (45.1 mmol) sample of apf_2 was condensed into the bulb at -196^0. The mixture was warmed to room temperature, approximately 30 ml of methylene chloride was added, and the solution was stirred for two hours. The reaction mixture was then transferred to a glove bag which had been purged with dry nitrogen several times, and was filtered through a sintered glass filter to remove unreacted CoI_2. The filtrate, which contained excess ligand, methylene chloride and complex was distilled in vacuo to remove the excess ligand and methylene chloride. The dark brown solid residue was then dried in vacuo for about one-half hour.

Anal. calculated for $C_6H_{18}CoF_6I_2N_3P_3$: C, 11.04; H, 2.76; I, 38.93; N, 6.44. Found: C, 11.03; H, 2.76; I, 39.88; N, 5.88.

Formation of a small variable amount of PF_3 from reaction of CoI_2 with apf_2 prevented molecular weight determinations of the CoI_2 complex by the method cited previously. Dissociation of the complex, similar to that observed for $Co(apf_2)_3Br_2$, prevented molecular weight determinations in other solvents. However, the hyperfine interaction of one unpaired electron with a single ^{59}Co ($I = 7/2$) nucleus observed in the esr frozen solution spectrum of this complex strongly suggests that it is monomeric. This esr spectrum and that of related complexes will be discussed later.

The green solution of $CoBr_2$ in excess apf_2 turned blue when a small amount of 1,2-dimethoxyethane, tetrahydrofuran, acetone, triethylamine, trimethylamine, or dioxane was added. This color change suggests that any of these neutral molecules is a better ligand toward $CoBr_2$ than apf_2, or alternatively, that they allow formation of CoX_4^{2-} ions. The addition of dimethylsulfoxide to the green solution of $CoBr_2$ in apf_2 yielded an almost colorless solution, again indicative that some sort of reaction, presumably displacement, occurs. The green solution turned pink when absolute ethanol was added. A brown solution of CoI_2 in apf_2

underwent similar ligand displacement reactions. No attempt was made to isolate any of the species formed. However, when the weakly coordinating solvent methylene chloride was employed, the solution optical and magnetic properties were identical to those observed when excess apf_2 was used as the solvent. Hence, these complexes could be studied in solution by making use of either methylene chloride in excess ligand or neat ligand as solvent. I found that these complexes can be kept in a solution of methylene chloride and apf_2 if the mole ratio of ligand to cobaltous halide is greater than approximately four to one. Other workers[5,10,38] have observed that dissociative processes occur with five-coordinate cobalt(II) complexes which contain phosphine ligands and have made use of excess phosphine ligand to stabilize the complexes in solution.

The Systems $CoCl_2$ and CoF_2 in $(CH_3)_2NPF_2$

A reaction identical to the one described for the $CoBr_2$-apf_2 system was employed. No absorption of apf_2 or any observable color change was found for interactions of the ligand with $CoCl_2$ or CoF_2.

Diiodotris[bis(dimethylamino)fluorophosphine]cobalt(II)-$Co(a_2pf)_3I_2$

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 one-half hour, and then 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 again added. A dark brown solid slowly precipitated when the solution was cooled.

Anal. calculated 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. U_{eff} 2.10 B.M. Molecular weight found 610, theory 727 (Galbraith Laboratories, Knoxville, Tennessee). The molecular weight supports the contention that the complex dissociates in solution. The solid complex shows no spectral or color changes when stored under nitrogen.

Dibromotris(diphenylphosphine)cobalt(II)

The complex $Co[(C_6H_5)_2PH]_3Br_2$ was prepared by the method reported by Issleib and Wenschul.[10] This complex was characterized by infrared and visible spectral data. It was included in the esr study because it has been shown by a single crystal X-ray diffraction study to be a pentacoordinate species. The structure lies intermediate between a square pyramid and trigonal bipyramid.[11]

Attempts to Prepare Complexes with the Ligand Tris(dimethylamino)phosphine, $[(CH_3)_2N]_3P$

Attempts to prepare complexes of the type CoL_3X_2 (where L is $[(CH_3)_2N]_3P$ and X is Br, I) were unsuccessful. The reactions were attempted by allowing an anhydrous cobalt(II) halide in a mixture of methylene chloride and ligand to reflux three hours. The ligand to cobalt ratio was slightly greater than three to one. The reaction mixture was allowed to cool to 23^0 and anhydrous ether was added to the blue-green solutions to promote precipitation. After the mixture has been maintained at -78^0 for four hours blue crystals can be recovered by filtration.

Analytical data are reported in Table 1. These data indicate that the N-P bond was cleaved in the reaction and that a decomposition product in which nitrogen acts as the donor atom was isolated. The elemental analyses of these decomposition products indicate that four coordinate dimethylamine adducts of the cobalt(II) halides were isolated. In addition, the visible spectra of the complexes mulled in Nujol or dissolved in acetone are similar to the spectra of four coordinate tetrahedral cobalt(II) complexes.[39] The infrared spectrum of the complex isolated with $CoBr_2$ is given in Figure 2.

Examination of the visible and esr spectra and solution magnetic moments of freshly prepared solutions of anhydrous cobalt(II) halides (Cl, Br, I) dissolved in $[(CH_3)_2N]_3P$ and

Table 1. Analytical data for complexes isolated with tris-(dimethylamino)phosphine, $[(CH_3)_2N]_3P$

$CoBr_2$[a]	1	2	3	Calculated for $Co[(CH_3)_2NH]_2X_2$
C	15.71(2.00)	16.09(1.97)	15.64(2.07)	15.55(2.00)
H	4.52(6.96)	4.68(6.88)	4.93(7.80)	4.53(7.00)
N	9.09(1.00)	9.55(1.00)	8.81(1.00)	9.07(1.00)
P	None	None	----	----
CoI_2[b]				
C	12.14(2.03)	12.32(2.04)	----	11.92(2.00)
H	3.58(7.16)	3.48(6.96)	----	3.48(7.00)
N	6.98(1.00)	7.02(1.00)	----	6.95(1.00)
P	None	None	----	----

[a] Results were obtained on three different samples. Atom ratios in parentheses.

[b] Results were obtained on two different samples.

Figure 2. Infrared spectrum of the complex isolated when $CoBr_2$ was allowed to interact with $[(CH_3)_2N]_3P$.

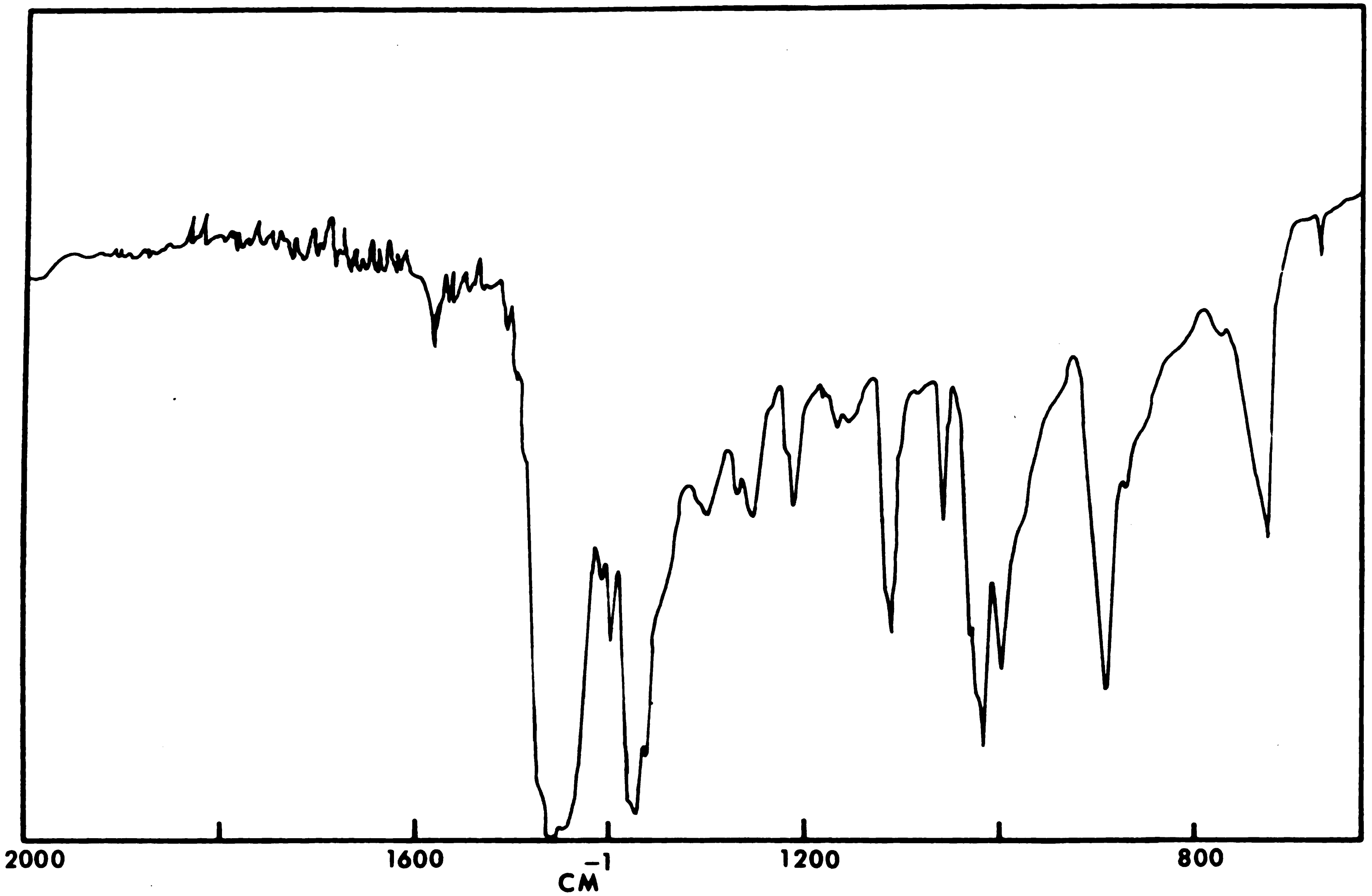


Figure 2.

methylene chloride indicated that some low spin cobalt(II) species was present. Unfortunately, the rapid decomposition of these solutions as demonstrated by the changes in the visible spectra and solution magnetic moments prevented any systematic investigation of the phosphine complexes I had hoped to isolate from this system.

RESULTS AND DISCUSSION

(A) Characterization of Dimethylaminodifluorophosphine Cobalt(II) Complexes

Preparation of Complexes

Two pentacoordinate low-spin cobalt(II) complexes were prepared. These complexes are the second and third examples of species of the general form CoL_3X_2 where L is a monodentate ligand and X a coordinated halogen anion. The complex $Co(apf_2)_3I_2$ was prepared by a method similar to that used to prepare $Co(dpp)_3Br_2$, where (dpp) is diphenylphosphine, while $Co(apf_2)_3Br_2$ was prepared by allowing anhydrous $CoBr_2$ to interact with a large excess of ligand. No solvent was employed in this preparation.

Infrared Spectra

The ligand, $(CH_3)_2NPF_2$, possesses both a nitrogen and phosphorus atom that could potentially act as the donor site in forming a coordination compound. The C-H (3000-2700 cm^{-1}) and the P-F (900-700 cm^{-1}) stretching region of the infrared spectra of these complexes provides evidence which suggests that the phosphorus atom was the donor site.

The infrared spectrum of $Co(apf_2)_3I_2$ and $Co(apf_2)_3Br_2$ mulled in Fluorolube and Nujol have been obtained in the region 4000-625 cm^{-1}. Figure 3 shows the carbon hydrogen region (Fluorolube mull) and Figures 4 and 5 show the 2000-625 cm^{-1} region (Nujol mull). Table 2 summarizes the phosphorus fluorine and carbon hydrogen regions of these and related compounds.

As can be seen from Figure 3, the absorption in the 3000-2700 cm^{-1} region is virtually identical in the complex and in the uncomplexed ligand. Previous work[27,40,41,42] strongly suggests that the retention of the absorption band at about 2800 cm^{-1} is indicative of an uncoordinated nitrogen. The ir spectrum of a complex that contains a coordinated nitrogen does not exhibit this band. If this is the case, phosphorus rather than nitrogen may act as the bonding site. Shifts in infrared absorptions upon complexation, which are attributed to phosphorus fluorine stretching modes, add additional support for bonding through phosphorus rather than nitrogen. Specifically, the P-F symmetric stretch (ν_1) in uncomplexed $(CH_3)_2NPF_2$ has been assigned to bands at 770 cm^{-1}.[43] In solid $Co(apf_2)_3I_2$ the P-F symmetric stretch appears at 812 cm^{-1}, and $Co(apf_2)_3Br_2$ at 805 cm^{-1}. The shift of the P-F stretching mode to higher wave numbers has also been observed in the B_4H_8 adduct of $(CH_3)_2NPF_2$, which has been shown by single crystal X-ray diffraction study[44] to contain a B-P rather than a B-N bond, and has been attributed to a significant shortening of the P-F bond.

Figure 3. Infrared spectra (3100-2700 cm^{-1}) of (A) $(CH_3)_2NPF_2$, neat, gas phase (10 mm pressure); (B) $Co(apf_2)_3Br_2$, fluorolube mull.

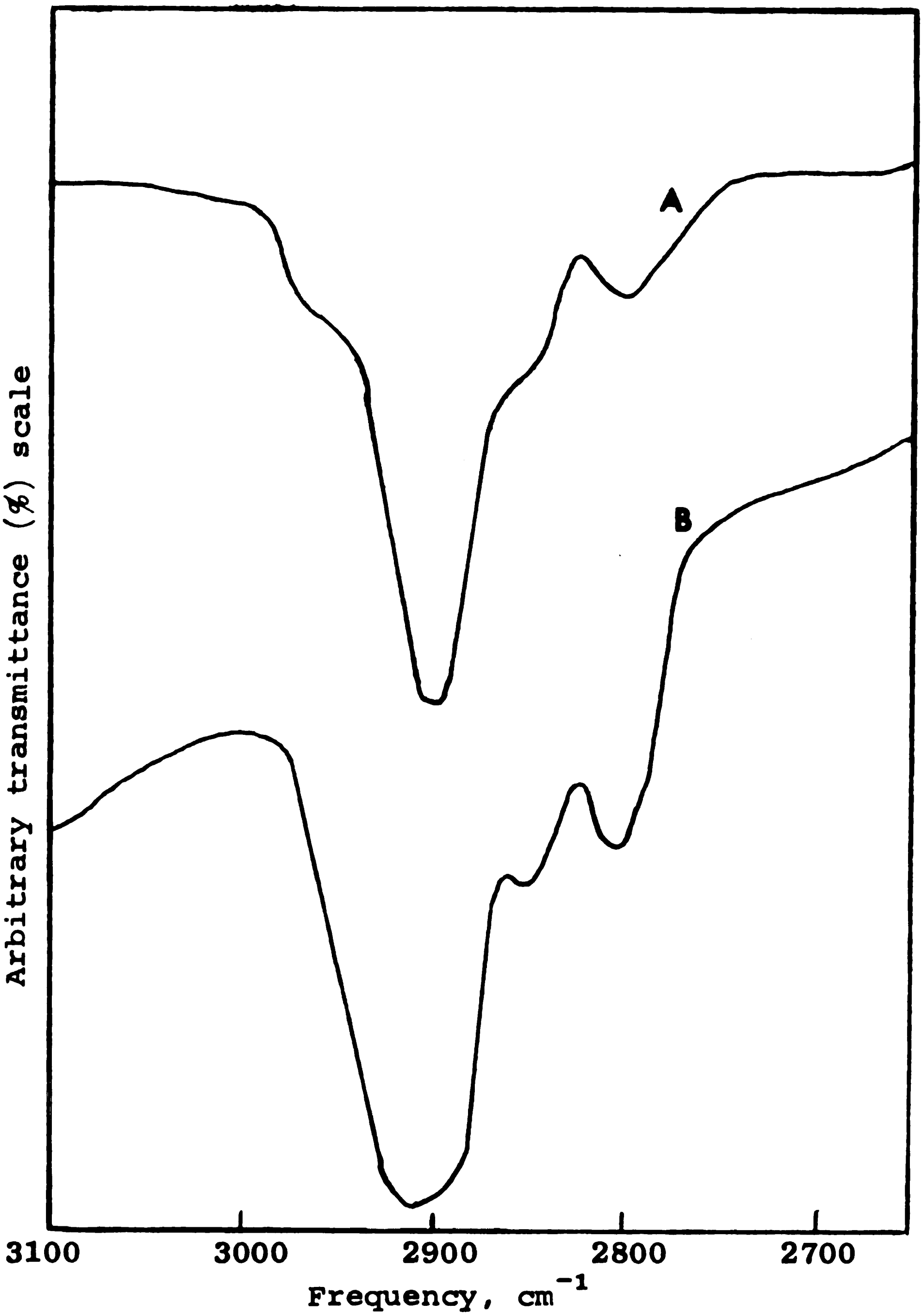

A
B
Arbitrary transmittance (%) scale
3100
3000
2900
2800
2700
Frequency, cm^{-1}

Figure 3.

Figure 4. Infrared spectrum (2000-625 cm^{-1}) of $Co(apf_2)_3I_2$, Nujol mull.

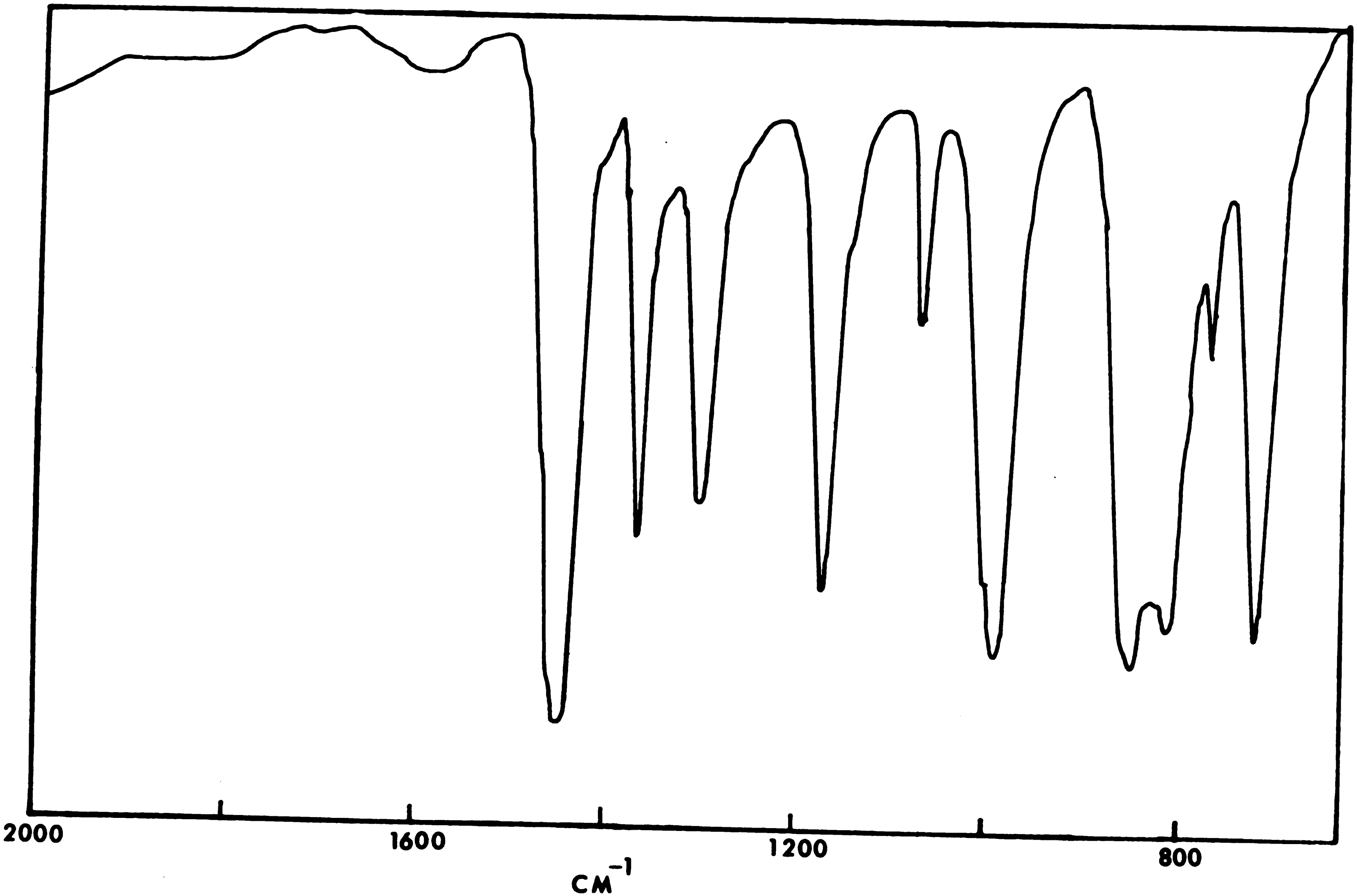


Figure 4.

Figure 5. Infrared spectrum (2000-625 cm^{-1}) of $Co(apf_2)_3Br_2$, Nujol mull.

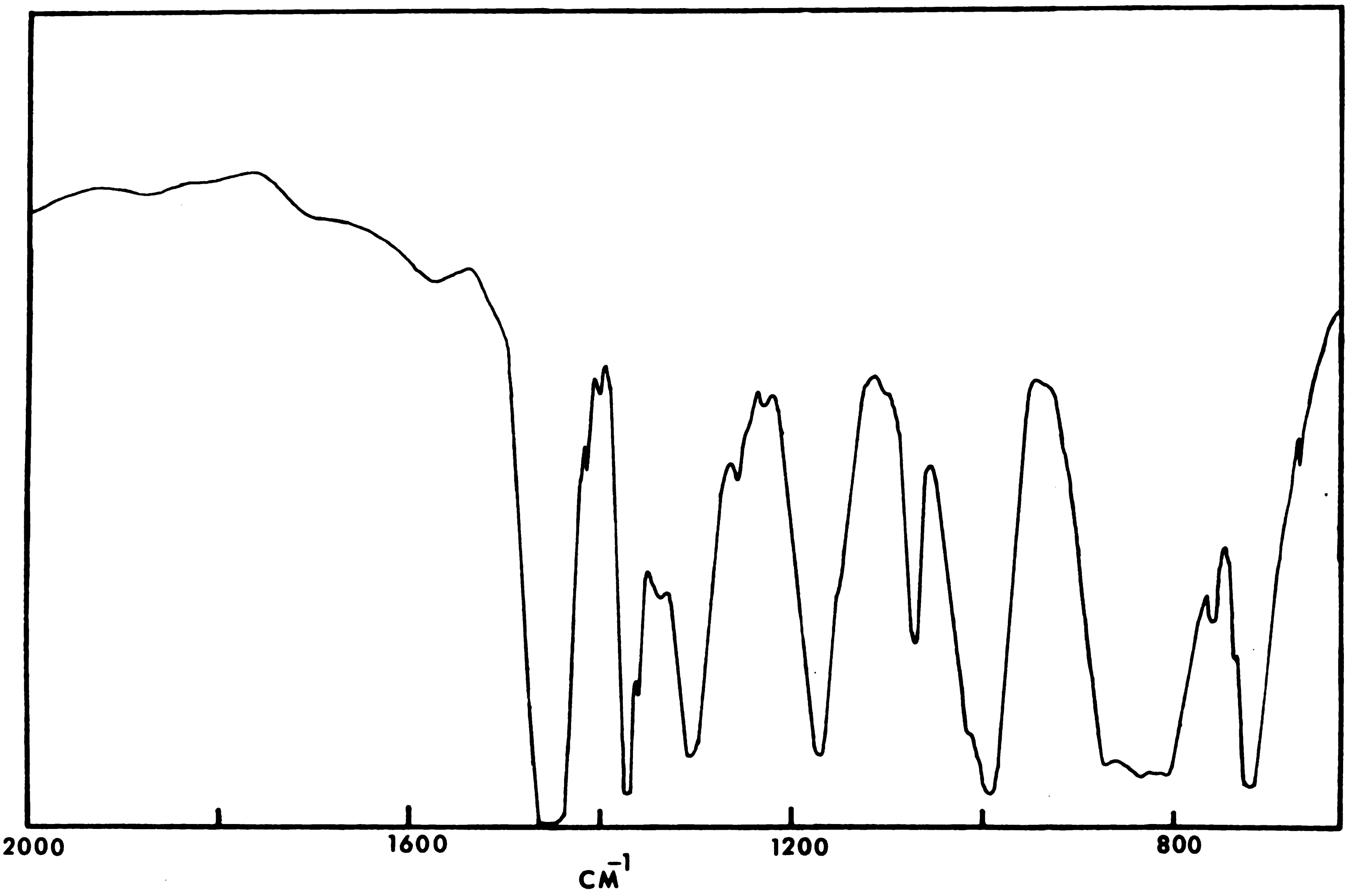


Figure 5.

Table 2. Summary of the infrared spectra of $Co(apf_2)_3I_2$ and $Co(apf_2)_3Br_2$ (C-H and P-F regions).

Compound	apf_2	$CoBr_2(apf_2)_3$	$CoI_2(apf_2)_3$	$B_4H_8apf_2$	BH_3apf_2
v_1 P-F	770	805	812	786	851
v_3 P-F	714	760	760	729	765

all frequencies in cm^{-1}

C-H infrared data

$(CH_3)_2NPF_2$	$CoI_2(apf_2)_3$	$apf_2:B_4H_8$	$apf_2:BH_3$
solid	solid	solid	liquid
3003	3001	----	----
2935	2935	2948	2937
2868	2860	2866	----
2911	----	2910	2917
2822	2825	2824	2810

Magnetic Susceptibility

Magnetic susceptibility measurements obtained from the solid complexes and from the complexes in solution are presented in Table 3. The magnetic moments of these cobalt(II) pentacoordinate complexes fall in the range 2.0 to 2.5 B.M. These values should be compared with a range of 1.8 to 2.9 B.M. for low-spin, planar cobalt(II) complexes. The results reported in Table 3 are consistent with an $S = 1/2$ ground state. The small discrepancy between the magnetic moments determined by different methods lies within experimental error.

The moments observed for these complexes can be compared to those reported for similar pentacoordinate low-spin cobalt(II) complexes.[10,12,13,45] The values of the effective moments of both the solid complex and the complex dissolved in methylene chloride and excess ligand were constant over the temperature change investigated. These results indicate that no appreciable spin state isomerization occurs either in solution or in the solid state. However, the fact that these complexes are stable in solution in the presence of excess ligand suggests that a dissociative process of the type

$$Co(apf_2)_3 \rightleftharpoons Co(apf_2)_2 + apf_2$$

occurs in solution.[5] However, this equilibrium probably favors the pentacoordinate low-spin species with the

Table 3. Magnetic moments of the complexes $Co(apf_2)_3I_2$ and $Co(apf_2)_3Br_2$, solutions contain excess ligand.

Complex	Phase	Method	Temp (°K)	μ_{eff}(B.M.)
$Co(apf_2)_3Br_2$	solid	Guoy	293	2.27(±0.10)
			195	2.29
	solution in CH_2Cl_2	Evans	308	2.00(±0.06)
			265	1.98
			238	2.00
			217	1.99
$Co(apf_2)_3I_2$	solid	Guoy	297	2.42(±0.10)
			195	2.30
	solution in CH_2Cl_2	Evans	309	2.46(±0.06)
			263	2.49
			233	2.47
			206	2.45

concentration of the four coordinate high-spin species relatively small and undetectable by the methods used in this work.

Optical Spectra

Visible results are presented in Table 4 and Figure 6. The fact that the visible spectra of both solid $Co(apf_2)_3I_2$ and $Co(apf_2)_3Br_2$ are almost identical with the solution spectra suggests that the structures of the solids dissolved in excess ligand are unchanged. All solution spectra were independent of temperature. All observed transitions and intensities of the $Co(apf_2)_3X_2$ complexes (where X is I or Br) are consistent with a low-spin pentacoordinate structure. Other pentacoordinate low-spin cobalt(II) complexes exhibit absorptions similar to those which are observed for $Co(apf_2)_3I_2$ and $Co(apf_2)_3Br_2$.[5,12,13,20,45] The true geometry of these pentacoordinate complexes probably is intermediate between a trigonal-bipyramidal and a square-pyramidal configuration.

(B) Characterization of the bis(dimethylamino)fluorophosphine Complexes

The complex $Co(a_2pf)_3I_2$ was characterized by analytical and magnetic moment data and by visible, infrared, and esr spectral data.

The infrared spectra of this complex and the ligand, a_2pf, are shown in Figure 7. Examination of this figure

Table 4. Summary of the visible spectra of Co$(apf_2)_3I_2$ and Co$(apf_2)_3Br_2$.

X	Solvent	$\lambda(\epsilon)^a$			
I	CH_2Cl_2[b]	26,109(1100)	23,697(1000)	20,408(750	14,881(400)
I	mull	25,773	23,202	19,960	14,706
Br	CH_2Cl_2[b]	25,510(sh)(1170)	21,692(1370)	d	15,625(760)
Br	mull	25,000(sh)	21,739(sh)	d	15,385

---

[a] Wavelength in cm^{-1}.

[b] Excess $(CH_3)_2NPF_2$ added.

[c] sh = shoulder.

[d] This transition not observed.

Figure 6. Visible spectra of $Co(apf_2)_3X_2$ complexes: $Co(apf_2)_3Br_2$ (A) solid, (B) solution, and $Co(apf_2)_3I_2$, (C) solution, (D) solid.

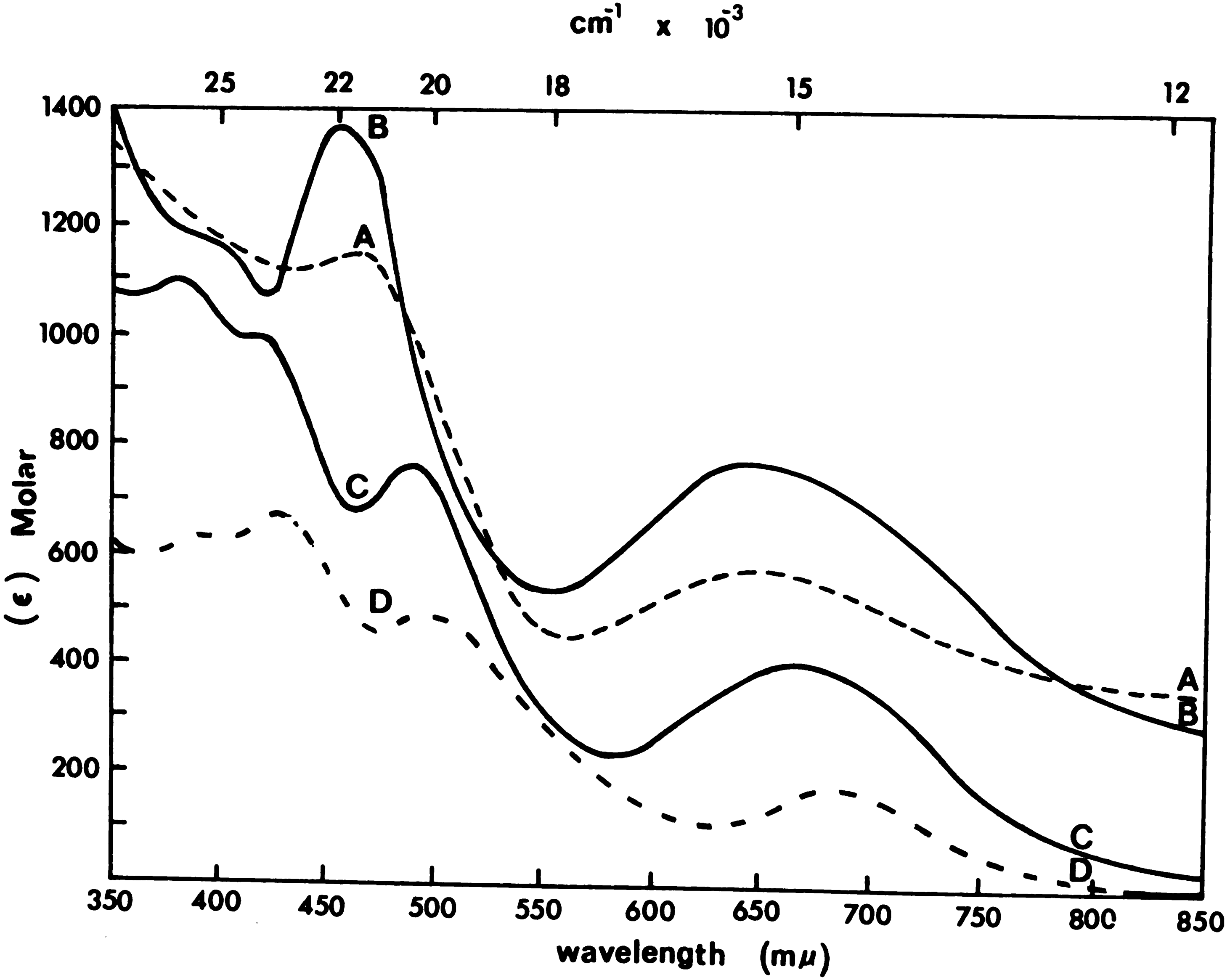

cm^{-1} x 10^{-3}
25
22
20
18
15
12
1400
1200
1000
800
600
400
200
(ε) Molar
350
400
450
500
550
600
650
700
750
800
850
wavelength (mμ)
A
B
C
D
A
B
C
D

Figure 6.

Figure 7. Infrared spectra of (A) neat a_2pf and (B) $Co(a_2pf)_3I_2$ (fluorolube mull 3100-2700 cm^{-1}, Nujol mull 1600-250 cm^{-1}).

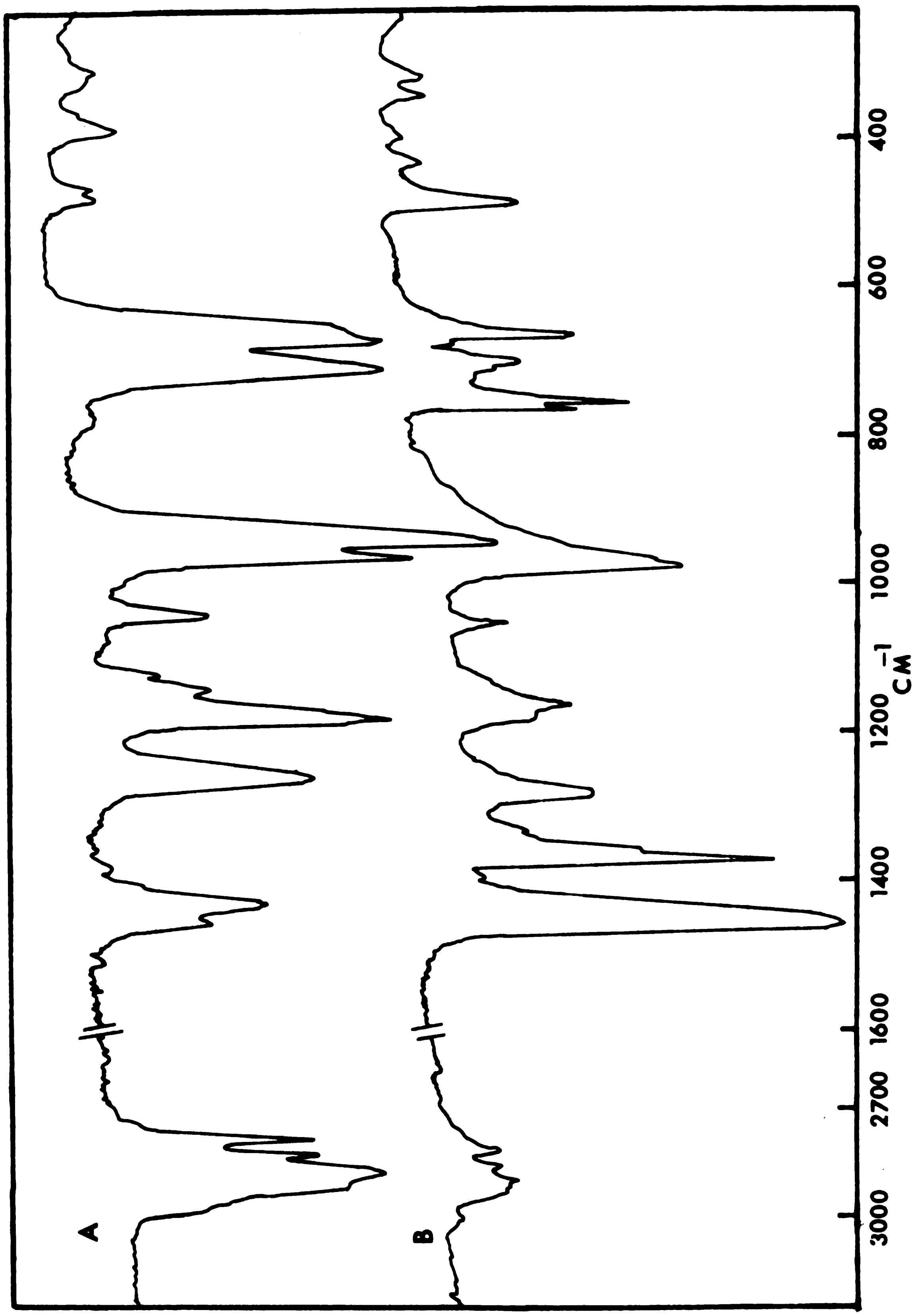


Figure 7.

strongly suggests that the structure of the ligand is essentially unchanged in the complex. When the complex is dissolved in either methylene chloride or benzene an equilibrium is established between the low-spin, pentacoordinate complex and a high-spin, pseudotetrahedral, four-coordinate complex of the type $Co(a_2pf)_2I_2$. Similar results were obtained for analogous $CoCl_2$ and $CoBr_2$ complexes, even though I was unable to isolate the species that contained the chloride or bromide anions. On the basis of extensive magnetic and spectral data I suggest that similar equilibria involve these anions. These equilibria may be represented by

$$Co(a_2pf)_2X_2 + a_2pf \rightleftharpoons Co(a_2pf)_3X_2 \qquad (1)$$

The Equilibrium Involving the Cobalt(II) Iodide Complex

A brown crystalline pentacoordinate, low-spin complex of the type $Co(a_2pf)_3I_2$ can be obtained when CoI_2 and a_2pf are allowed to interact in benzene. The visible spectrum and magnetic moment of this complex are almost identical to those of similar monomeric pentacoordinate cobalt(II) complexes.[5,12,13,20,45] When this complex is dissolved in methylene chloride or benzene, the magnetic moment increases and the visible spectrum undergoes a change which is suggestive of the formation of a new species.

I was able to establish equilibrium (1) by measuring the concentration dependence of the solution magnetic moments when $Co(a_2pf)_3I_2$ is dissolved in methylene chloride or benzene. These results (Table 5) are easily rationalized by the equilibrium shown in (1). As the initial concentration of $Co(a_2pf)_3I_2$ is decreased from 2.16 x 10^{-2}M to 0.30 x 10^{-2}M the effective moment of species in solution increases from 3.42 B.M. to 4.36 B.M., a change which is consistent with an increase in the ratio of the four-coordinate, high spin complex to the pentacoordinate, low-spin complex.

Further support for equation (1) is obtained by (A) examining the effect of the addition of excess a_2pf on the solution magnetic moment and (B) a comparison of the visible spectra of $Co(a_2pf)_3I_2$ dissolved in methylene chloride and mulled in Nujol.

The magnetic moment of a solution that was 1.49 x 10^{-2}M in $Co(a_2pf)_3I_2$ was 3.68 B.M. (Table 5). The addition of a 0.51 mmol sample of a_2pf to a solution that was also made 1.49 x 10^{-2}M in $Co(a_2pf)_3I_2$ lowered the magnetic moment to 3.24 B.M. These results are consistent with a shift in (1) as the concentration of free ligand is increased.

Figure 8 shows the visible spectra obtained from a sample of $Co(a_2pf)_3I_2$ mulled in Nujol and dissolved in methylene chloride. Examination of this figure clearly shows that the visible spectrum undergoes a change which is suggestive of the formation of a new species. In fact, the position, intensity and band shape in the 500-800 mμ region in the spectrum of a 2.98 x 10^{-3}M solution of the complex in CH_2Cl_2 is typical of the $\nu_3[{}^4A_2 \longrightarrow {}^4T_1(P)]$ transition

Table 5. Concentration dependence of solution magnetic moments when $Co(a_2pf)_3I_2$ was dissolved in either CH_2Cl_2 or C_6H_6.

Initial Concentration of $Co(a_2pf)_3I_2$ ($M \times 10^2$)	μ_{eff} at 312 K (B.M.) ± 0.06	Solvent
2.16	3.42	CH_2Cl_2
1.77	3.53	CH_2Cl_2
1.49	3.68	CH_2Cl_2
1.08	3.78	CH_2Cl_2
0.75	3.98	CH_2Cl_2
0.30	4.36	CH_2Cl_2
1.93	3.41	C_6H_6
1.38	3.49	C_6H_6
1.29	3.62	C_6H_6

Figure 8. Visible spectra of (A) 2.98 x 10^{-3} $\underline{M}$ solution of $Co(a_2pf)_3I_2$ dissolved in CH_2Cl_2 (path length 2 cm) and (B) solid $Co(a_2pf)_3I_2$.

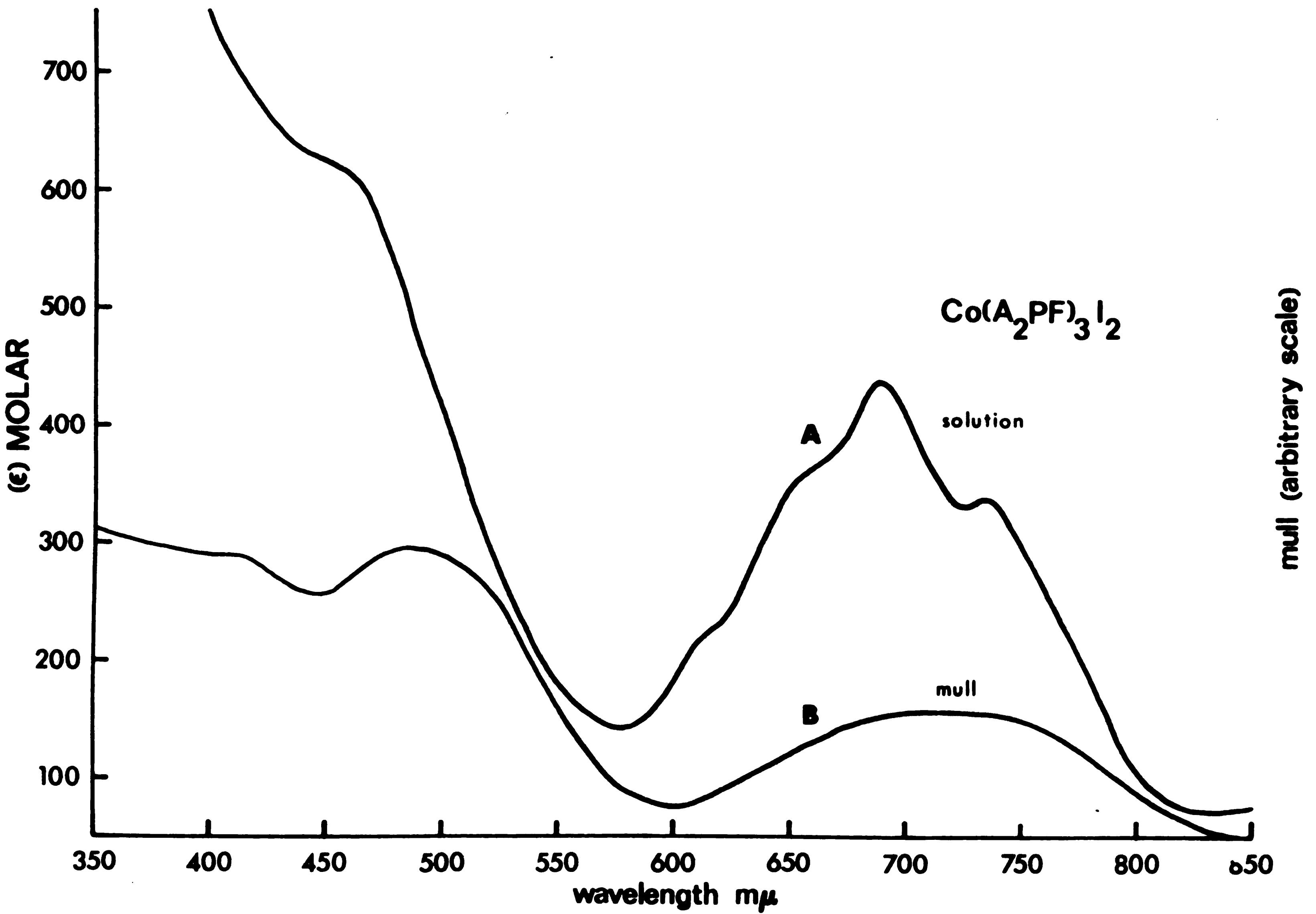

Co(A$_2$PF)$_3$ I$_2$
(ε) MOLAR
700
600
500
400
300
200
100
mull (arbitrary scale)
A
solution
B
mull
350
400
450
500
550
600
650
700
750
800
850
wavelength mμ

Figure 8.

found in high-spin four-coordinate pseudotetrahedral cobalt(II) complexes.[39] The magnetic moment of the solution (approximately 4.36, Table 5) supports the contention that the high-spin species predominates in this solution.

In addition to the above data, the visible spectra of the solution which was 1.49×10^{-2} M in $Co(a_2pf)_3I_2$ and 0.36 M in free ligand (a_2pf) were obtained at a number of different temperatures. The spectra are presented in Figures 9 and 10. Because all cobalt(II) species absorb in the visible region, the presence of isobestic points at 600 and 550 mμ indicate only two species are in solution. These spectra underwent reversible changes. The temperature dependence of the magnetic moments and the equilibrium constant (K_f), ΔH^0, and ΔS^0 values for this solution are presented in Table 6. Table 6 also presents data for the complex dissolved in benzene.

Equilibria Involving the $CoBr_2$ and $CoCl_2$ Complexes

Although we were unable to isolate the pentacoordinate complexes of $CoCl_2$ and $CoBr_2$ with a_2pf, analogous temperature and concentration dependence of the visible spectra and the solution magnetic moments indicates an equilibrium identical to that observed for $Co(a_2pf)_3I_2$ occurs in these solutions (Table 7).

When the concentration of $CoCl_2$ is held constant and that of the ligand is increased from approximately 0.05M to 0.15M, Beer's law does not hold (Figure 11). Isobestic

Figure 9. Temperature dependence of the visible spectra exhibited by a solution which was $1.49 \times 10^{-2}\underline{M}$ in $Co(a_2pf)_3I_2$ and $0.36\underline{M}$ in a_2pf, 500-800 mμ (path length 1.0 mm).

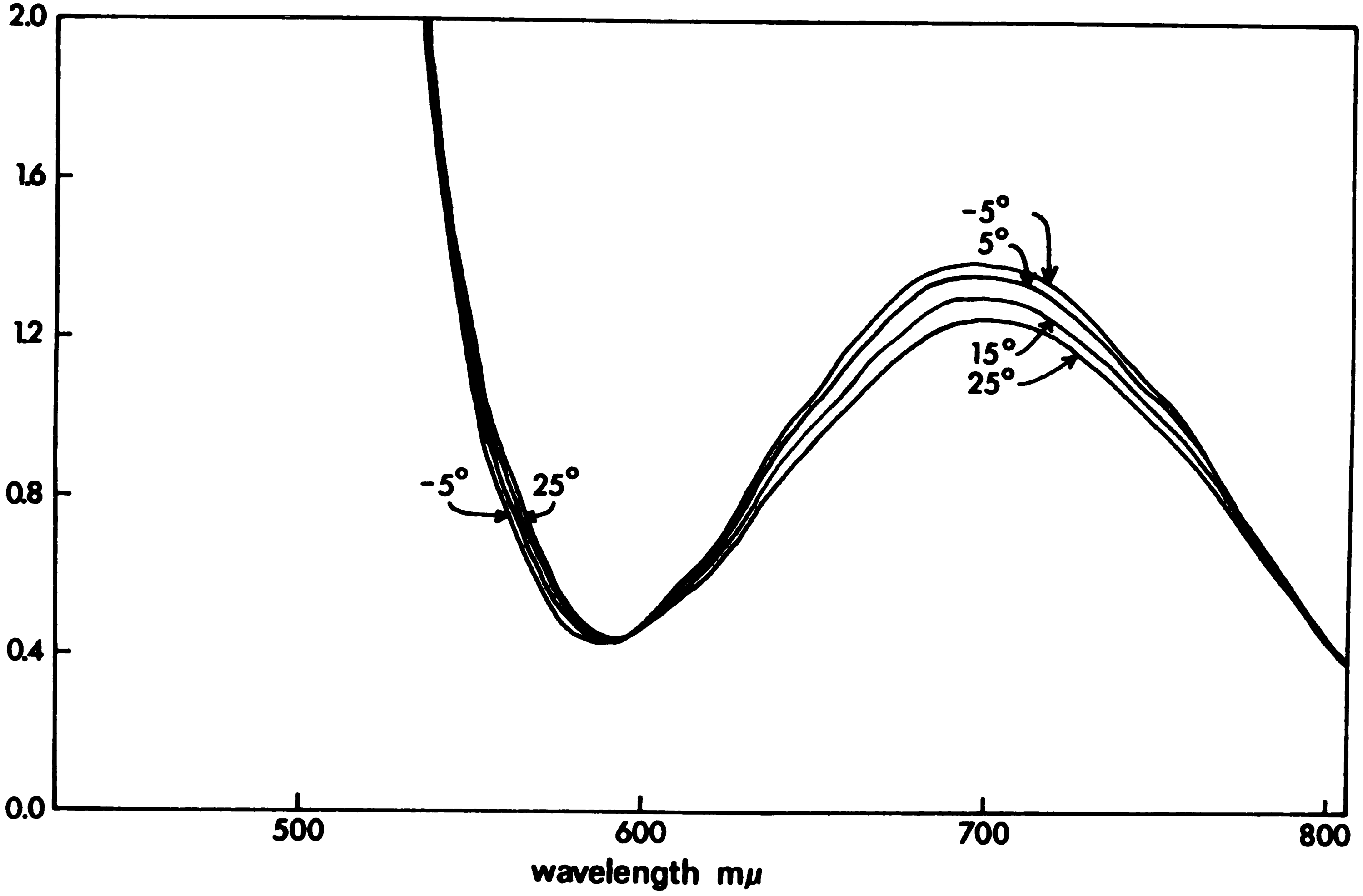


Figure 9.

Figure 10. Temperature dependence of the visible spectra of a $5.0 \times 10^{-3}\underline{M}$ solution of $Co(a_2pf)_3I_2$ and $0.12\underline{M}$ in a_2pf, 550–350 mμ (path length 1.0 mm).

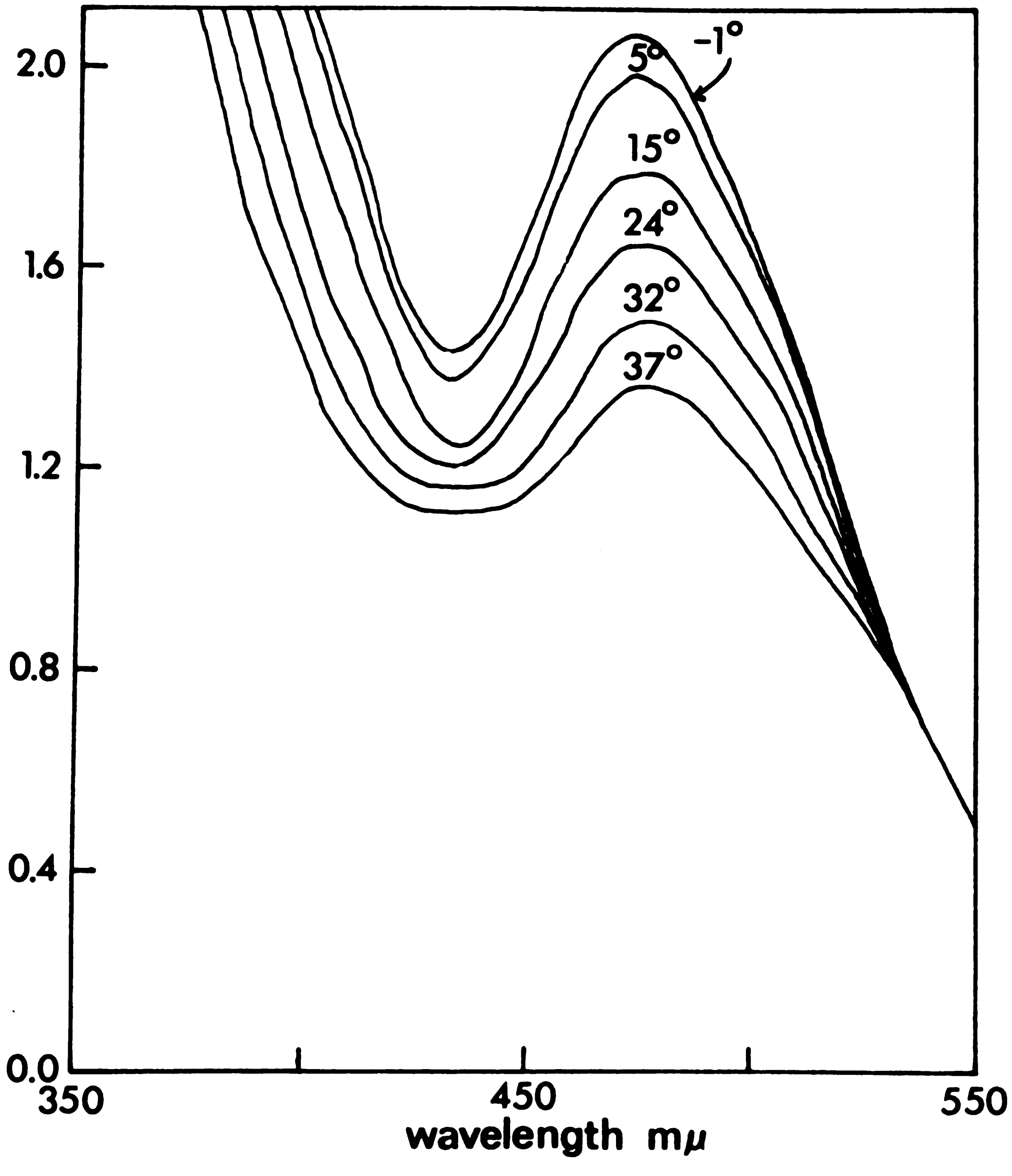


Figure 10.

Table 6. Equilibrium constants K_f, ΔH^0 and ΔS^0 values of a solution which was 1.49×10^{-2}<u>M</u> with respect to $Co(a_2pf)_3I_2$ and 0.36<u>M</u> with respect to a_2pf.

Solvent	T(K)	μ_{eff}(B.M.)[a]	K_f[b]	$-\Delta H^0$ (kcal/mol)	$-\Delta S^0$
CH_2Cl_2	315	3.24	4.17	3.6	8.5
CH_2Cl_2	308	3.14	4.92		
CH_2Cl_2	301	3.05	5.74		
CH_2Cl_2	293	2.99	6.36		
C_6H_6	320	3.54	4.53	6.8	18.2
C_6H_6	313	3.35	6.25		
C_6H_6	309	3.24	7.50		
C_6H_6	301	3.12	9.17		

[a] Solution moments ±0.08 B.M. ±0.06.

[b] Error in measurements estimated to be ±20%.

Table 7. Temperature dependence of the solution magnetic moments and the equilibrium constants calculated for the solutions obtained when $CoCl_2$ or $CoBr_2$ were allowed to interact with excess ligand in methylene chloride.

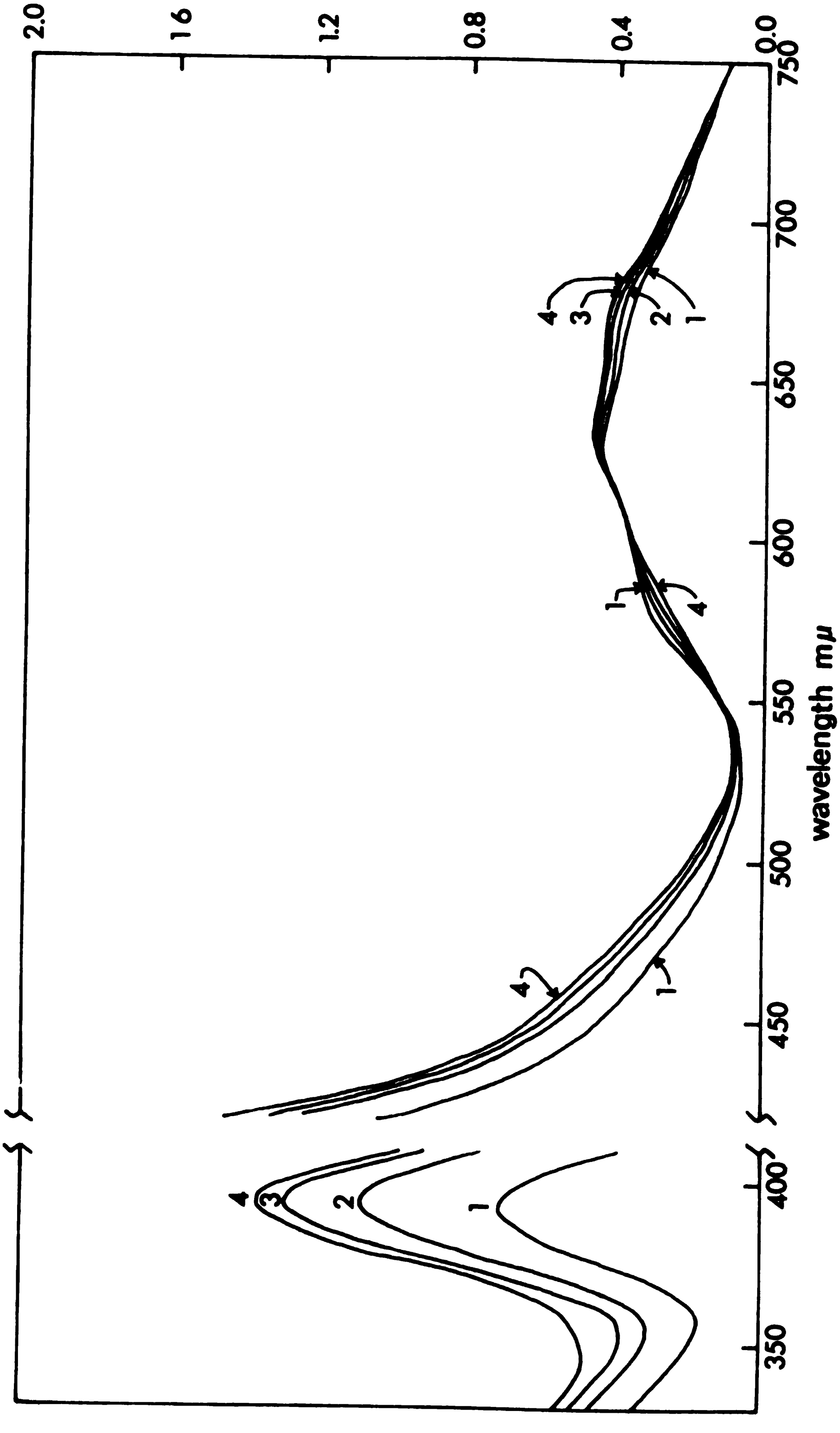
Cobalt Halide	T K	μ_{eff}(B.M.)	K_f	$-\Delta H$ kcal/mole	ΔS
$^{a}CoCl_2$	319	4.11	0.19	6.0	22
	312	4.04	0.25		
	305	3.96	0.31		
	300	3.89	0.38		
	291	3.77	0.50		
	282	3.68	0.61		
$^{b}CoCl_2$	319	3.98	0.33	6.0	21
	309	3.87	0.44		
	303	3.77	0.56		
	297	3.68	0.67		
$^{c}CoCl_2$	316	3.93	0.27	5.4	20
	310	3.87	0.32		
	303	3.78	0.39		
	296	3.69	0.48		
$^{a}CoBr_2$	314	3.21	1.51	4.3	13
	307	3.11	1.78		
	301	3.04	2.01		
	295	2.96	2.31		
	287	2.85	2.83		
	281	2.75	3.43		

[a] Solutions were 0.37$\underline{M}$ in CoX_2 and a concentration of free ligand adjusted to 1.0$\underline{M}$ in CH_2Cl_2.

[b] Free ligand concentration adjusted to 0.9$\underline{M}$.

[c] Free ligand concentration adjusted to 1.25$\underline{M}$.

Figure 11. Visible spectra at 25^0 of solutions containing a $CoCl_2$ concentration of $1.48 \times 10^{-2}\underline{M}$, with the concentration of $a_2$pf increasing from approximately 0.05 to $0.15\underline{M}$, 1-4, respectively (path length 1.0 mm).



2.0
1.6
1.2
0.8
0.4
0.0
350
400
450
500
550
600
650
700
750
wavelength mμ
1
2
3
4

Figure 11.

points were observed at 610 and 560 mμ. This indicates that two species are in solution.

The temperature dependence of the visible spectra exhibited by solutions of $CoCl_2$ and $CoBr_2$ in excess a_2pf and methylene chloride also establish that only two species are involved in the equilibrium. The spectra for the $CoCl_2$ solutions are presented in Figures 12 and 13. As in the case of $Co(a_2pf)_3I_2$, the spectra underwent reversible changes over the temperature range investigated. Isobestic points at 610 and 560 mμ were observed for the solution which contained $CoCl_2$. This observation indicates the presence of only two complexes. This is substantiated by comparing Figures 11 and 12. Identical isobestic points were obtained from both the Beer's law and temperature dependence studies.

I did not observe isobestic points in the spectrum of solutions which contained $CoBr_2$ in excess a_2pf (Figures 14 and 15). I was able to establish the presence of only two absorbing species by the use of a recently described procedure. Three arbitrary wavelengths are chosen from the visible spectrum shown in Figures 14 and 15. These wavelengths were chosen in regions that exhibit the greatest temperature dependence (i.e. 412, 480 and 690 mμ). A plot of absorbance ratios of the general form

$$\left(\frac{A_2T_1}{A_1T_1}, \frac{A_3T_1}{A_1T_1}\right)$$

where A_2T_1 represents the absorbance at one of the

Figure 12. Visible spectra temperature dependence of a 3.52 x 10^{-2}M solution of $CoCl_2$ in excess $a_2$pf, 450-890 mμ (path length 1.0 mm).

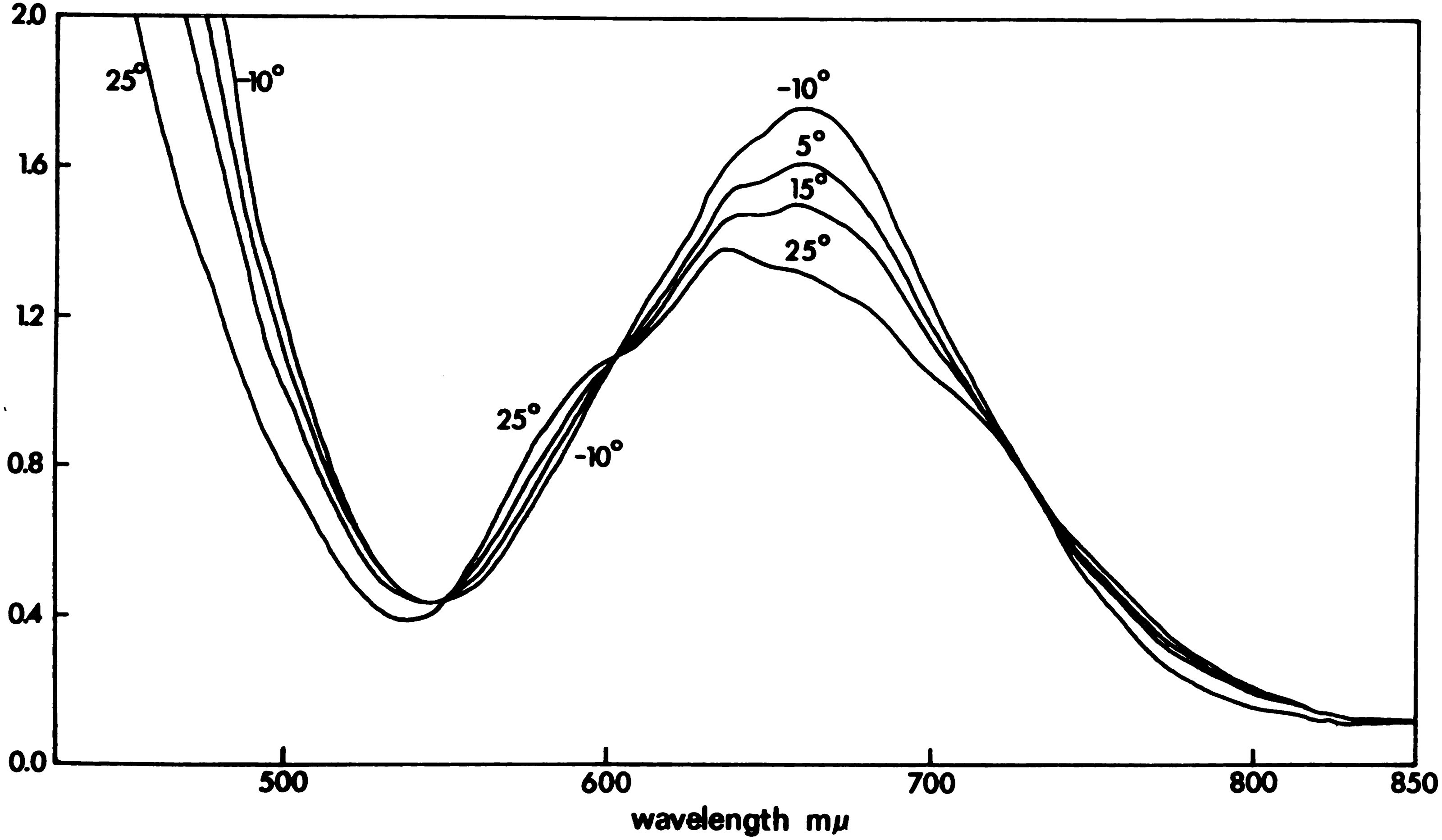

2.0
1.6
1.2
0.8
0.4
0.0
500
600
700
800
850
wavelength mμ
25°
-10°
-10°
5°
15°
25°
25°
-10°

Figure 12.

Figure 13. Visible spectra temperature dependence of a 1.0 x $10^{-2}\underline{M}$ solution of $CoCl_2$ in excess a_2pf, 325-550mμ (path length 1.0 mm).

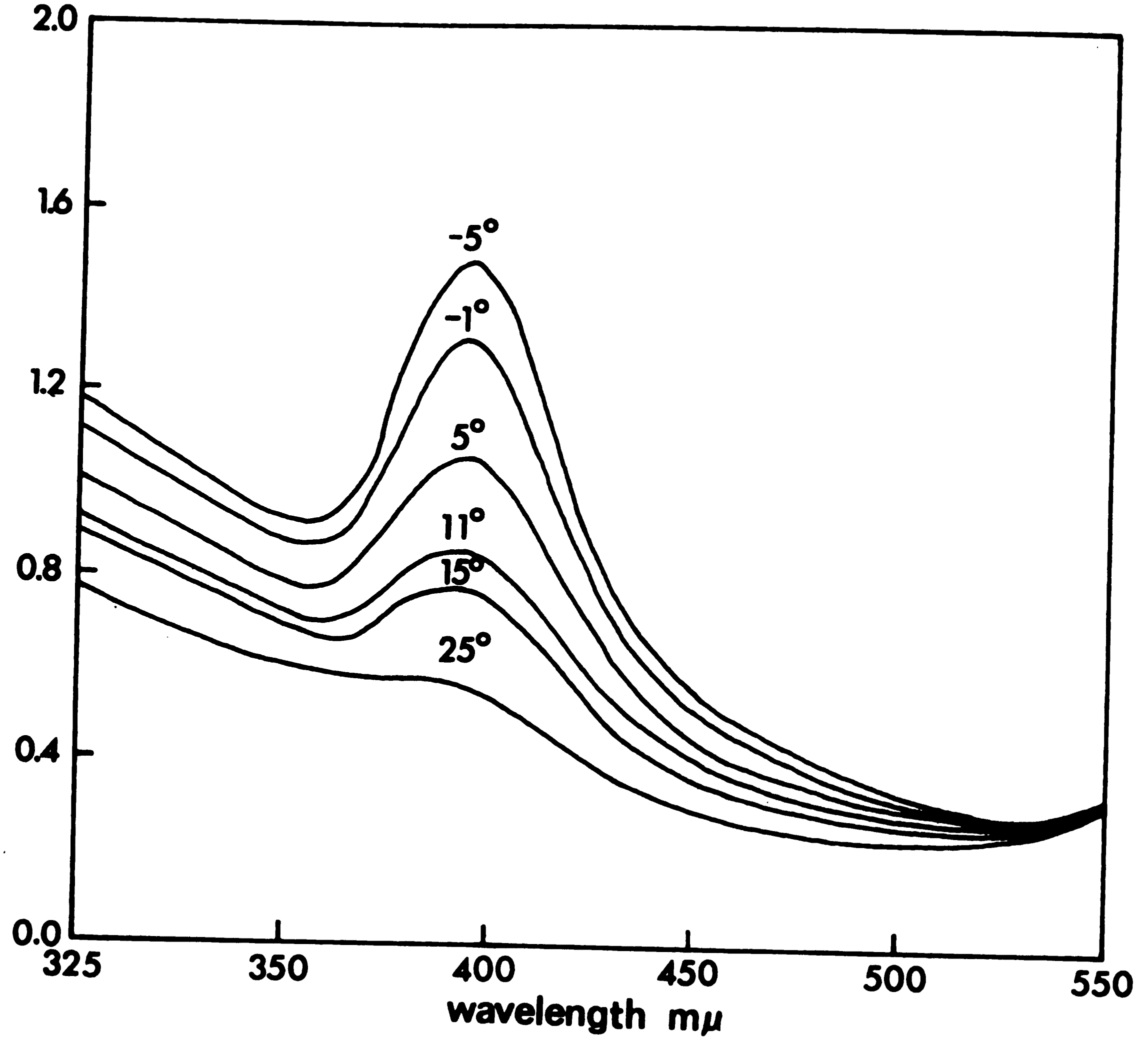

2.0
1.6
1.2
0.8
0.4
0.0
325
350
400
450
500
550
wavelength mμ
-5°
-1°
5°
11°
15°
25°

Figure 13.

Figure 14. Visible spectra temperature dependence of a 2.34 x 10^{-2} M solution of $CoBr_2$ in excess a_2pf, 500-850 mμ (path length 1.0 mm).

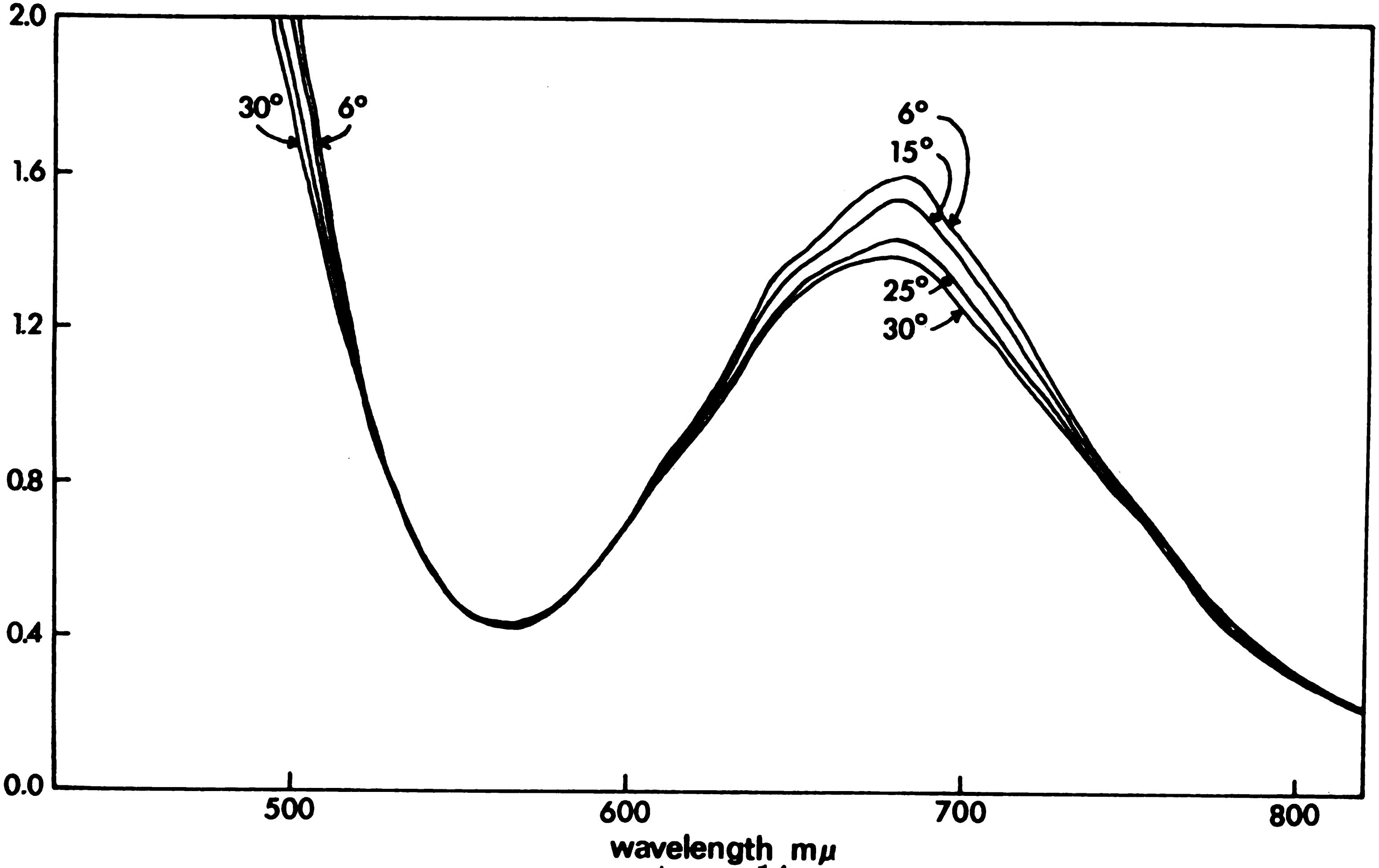


Figure 14.

Figure 15. Visible spectra temperature dependence of a 7.80 x 10^{-3} $\underline{M}$ solution of $CoBr_2$ in excess $a_2$pf, 300-550 mμ (path length 1.0 mm).

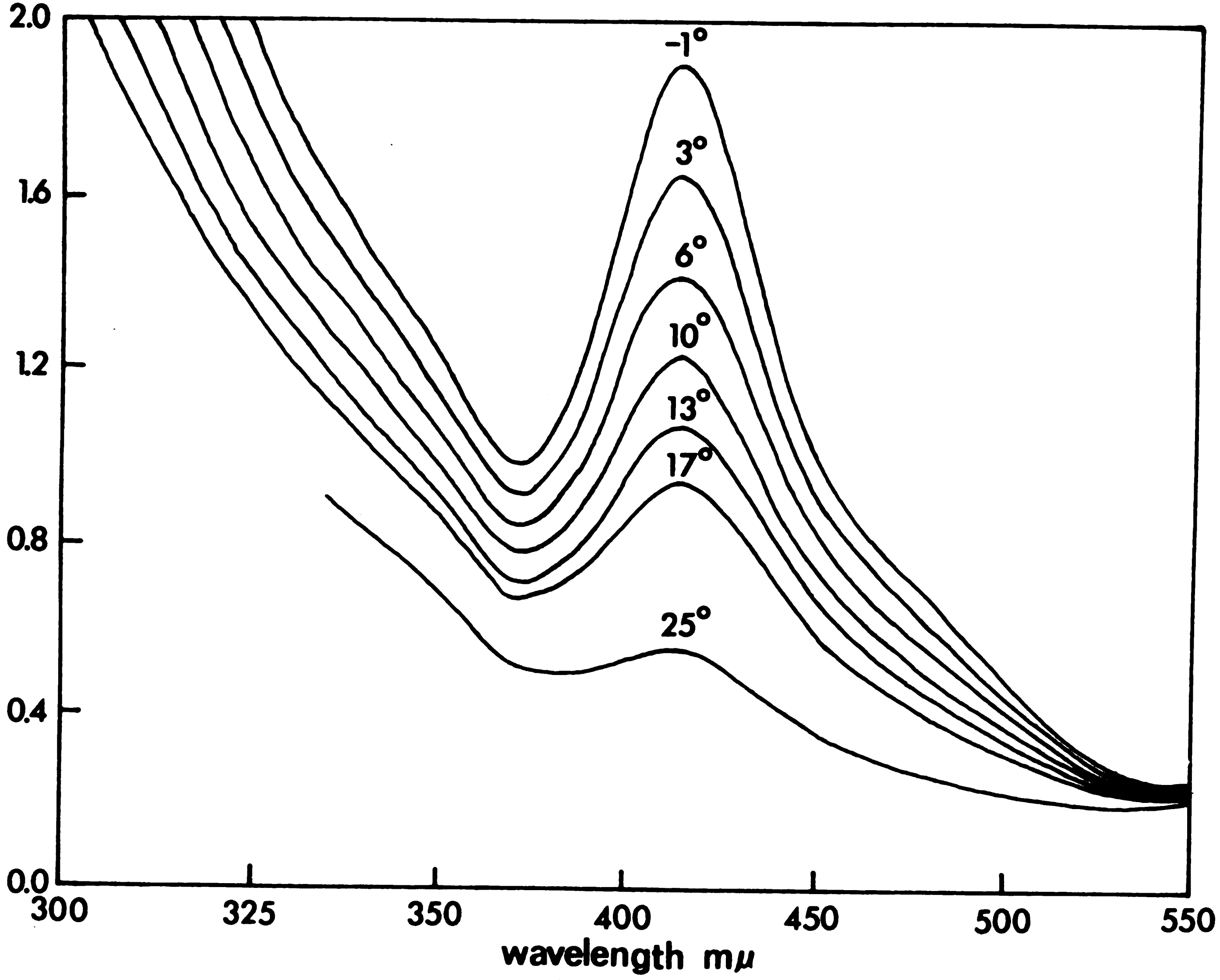

2.0
1.6
1.2
0.8
0.4
0.0
300
325
350
400
450
500
550
wavelength mμ
-1°
3°
6°
10°
13°
17°
25°

Figure 15.

wavelengths at temperature T_1 was made. In this manner one set of coordinates is calculated for each temperature and a plot of these absorbance ratios is constructed. The straight line that resulted indicated that only two species are in equilibrium. This method was also used to confirm the existence of two absorbing species in the case of the CoI_2 and $CoCl_2$ complexes.

An examination of the visible 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 cobalt(II) ion as the high-spin component involved in equilibrium (1). The visible spectrum of a $CoCl_2$ solution at 25° (Figure 12) exhibits a maximum at 636 mμ and shoulders at 590, 670 and 710 mμ. The position and intensity of those bands are characteristic of the $\nu_3[^4A_2 \longrightarrow {}^4T_1(p)]$ absorption of a tetrahedral, high-spin cobalt(II) complex.[39] The magnetic moment of this solution is 3.89 B.M., a value which supports the contention that the cobalt(II) solution species is predominantly high-spin (Table 7).

As the temperature is lowered, the changes in the visible spectra, as well as magnetic moment data, show that the concentration of the pentacoordinate low-spin cobalt(II) species increases. 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 at 660 mμ attributable to the low-spin species forms. 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 I assign to a transition involving the low-spin, pentacoordinate 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, pentacoordinate cobalt(II) complexes.[5,12,13,20,45,47] The changes in the spectra are almost identical to changes which occur in solutions of $Co(a_2pf)_3I_2$.

Further support for the existence of a low-spin, pentacoordinate cobalt(II) complex can be seen by comparison of the esr spectra of the frozen solutions (77 K) of these complexes with the spectra of the monomeric complexes of $Co(apf_2)_3X_2$ (X = Br, I) and $Co(dpp)_3Br_2$. The esr spectra of these complexes will be discussed in Part C of this thesis.

The equilibrium constant (K_f) as well as ΔH^0 and ΔS^0 values are presented in Table 7. If one assumes no error in the limiting moments estimated for the high and low-spin species involved in equilibrium (1), the thermodynamic stability of the pentacoordinate complexes relative to the four-coordinate complexes as measured by the equilibrium constant (K_f) 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[20] in terms of the "softness" or polarizability of the atoms as measured by the values of the overall nucleophilic reactivity constant n^0 [48] of the donor atoms in the complex. ΔS^0 values are all negative and notably large in some cases. This magnitude is to be expected since the equilibria involve a change in coordination number between neutral species in relatively weakly coordinating solvents.

(c) Electron Spin Resonance Spectra of the Complexes

There have been relatively few reports of esr studies on pentacoordinate, low-spin cobalt(II) complexes[12,25] and, consequently, the electronic properties of this type of complex are not well understood.

In this part of the manuscript, I report the results of esr studies on the low-spin complexes, $Co(apf_2)_3X_2$, $Co(a_2pf)_3X_2$ and $Co(dpp)_3Br_2$.

It will be shown 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 the totally symmetric a_1 representation under the C_{2v} 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. A satisfactory correlation between the measured electronic spectral, magnetic and esr data is found. The electronic ground state suggested is $|(x^2 \overset{2}{-} y^2)(x^2 \overset{-}{-} y^2)(\overset{+}{z^2})>$ (vacancy configuration). The energies of the one electron d-orbitals were estimated for the pentacoordinate complexes involving apf_2 by use of the observed optical spectra and the interelectronic interaction energies calculated for the low-spin d^7 system. Quantitative handling of the optical spectra of the complexes of a_2pf is prevented due to the presence of a substantial concentration of tetrahedral high-spin complex. However, the strikingly similar esr and optical spectra of the a_2pf complexes and the apf_2 complexes suggest that the pentacoordinate low-spin complexes formed with both ligands are quite similar.

At room temperature the esr spectra of all solutions showed only a broad structureless feature from which g_{av} values were calculated. These are reported in Table 8. A typical room temperature spectrum is shown in Figure 16. The room temperature esr spectra of polycrystalline samples of $Co(a_2pf)_3I_2$ and $Co(dpp)_3Br_2$ are shown in Figures 17 and 18, respectively. The $\underline{g}$ values obtained for these and related compounds are presented in Table 9. The observation

Table 8. ESR parameters of $Co(a_2pf)_3X_2$ and $Co(apf_2)_3X_2$ complexes in methylene chloride solution at room temperature and 77^0K.

Halide	Ligand	$g_{\|\|}$[a]	$g_{\perp}$[a]	g_{av}[b]	g_{av}[c]	f_d	f_s	$A_{\|\|}^{Co}$[d]	$A_{\perp}^{Co}$[e]	$a_{\|\|}^{P}$	A_{iso}	$A_{dipolar}$
I	apf_2	2.288	2.117	2.171	2.141	0.730	0.049	102	45.0	--	64	38
Br	apf_2	2.328	2.076	2.160	2.124	0.710	0.039	88	33.0	39.5	51	37
I	a_2pf	2.321	2.096	2.171	2.140	0.615	0.037	81	33.0	39.5	49	32
Br	a_2pf	2.381	2.079	2.179	2.136	0.540	0.033	71	29.5	35.5	43	28
Cl	a_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] $g_{av} = \frac{1}{3}(g_{||} + 2g_{\perp})$. [c] g_{av} read directly from solution esr spectra at room temperature. [d] Error estimated ±0.5 gauss. [e] Perpendicular value of iodide complexes obtained from partially observable perpendicular regions, other values estimated from 1/5 the width of the perpendicular region.

Figure 16. Typical room temperature esr solution spectrum of CoL_3X_2 (L = a_2pf or apf_2, X = Cl, Br, or I) in methylene chloride and excess ligand.

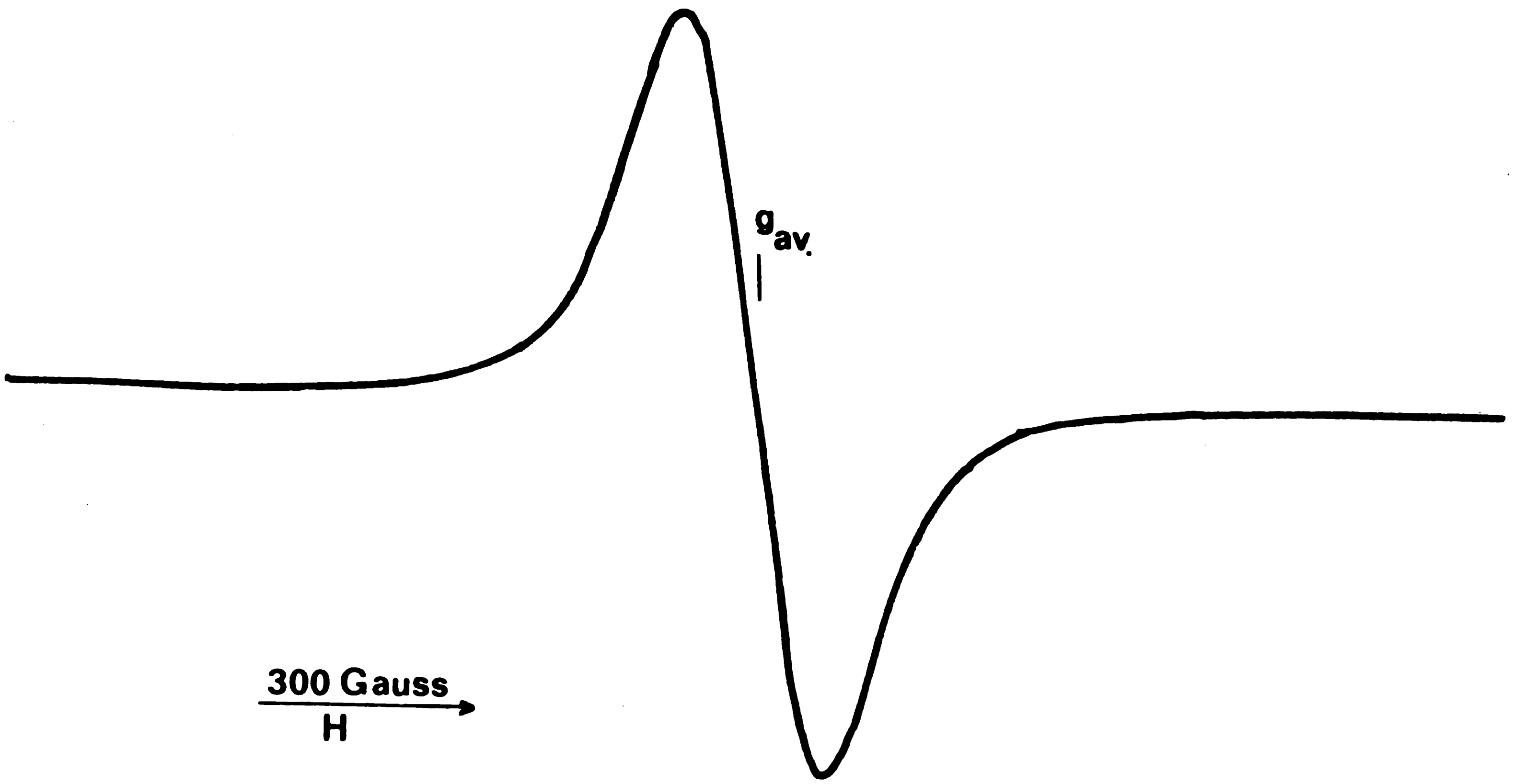


Figure 16

Figure 17, Room temperature esr spectrum of a polycrystalline sample of $Co(a_2pf)_3I_2$.

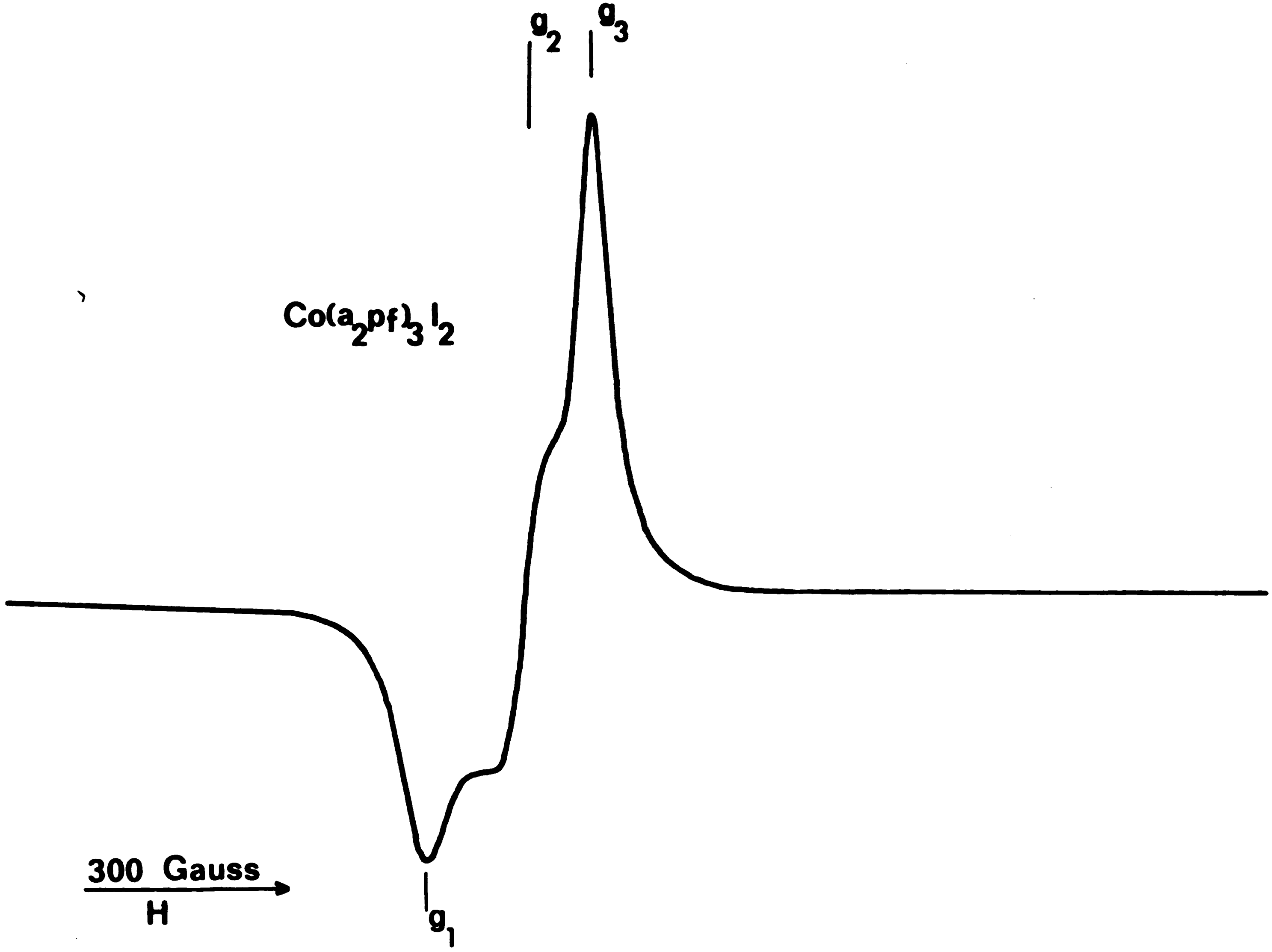


Figure 17.

Figure 18. Room temperature esr spectrum of a polycrystalline sample of $Co(dpp)_3Br_2$.

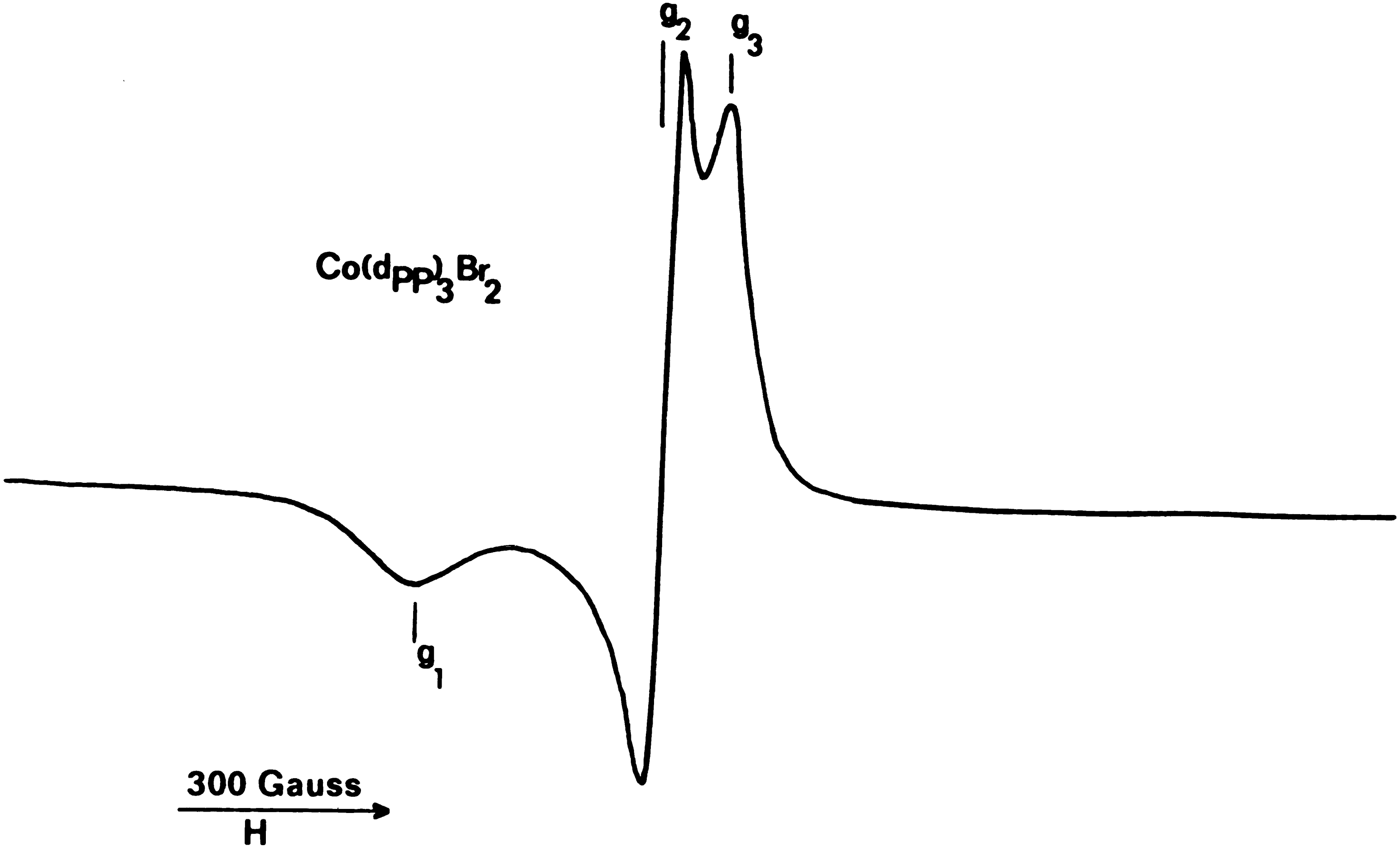


Figure 18.

Table 9. g values calculated from the room temperature esr spectra of polycrystalline samples of $Co(a_2pf)_3I_2$ and $Co(dpp)_3Br_2$ (this work) and related compounds.

Complex	g_1	g_2	g_3	$g_{(av)}$ [a]
$Co(dpp)_3Br_2$ [b]	2.339	2.092	2.045	2.159 [f]
$Co(a_2pf)_3I_2$ [c]	2.249	2.147	2.080	2.159
$Co(dpe)_2Br_2$ [d]	2.258	2.075	2.037	2.123
$Co(dpe)_2Cl_2$ [d]	2.257	2.056	2.041	2.128

[a] Accurate to ±0.005.

[b] Diphenylphosphine.

[c] bis(dimethylamino)fluorophosphine.

[d] bis(diphenylphosphine)ethane, reference 12.

[e] $g_{av} = \frac{1}{3}(g_1 + g_2 + g_3)$.

[f] The room temperature spectrum of $Co(dpp)_3Br_2$ in CH_2Cl_2 yields a g_{av} value of 2.152 -- Figure 16.

of three distinct g values for the compounds in Table 9 indicates that the symmetry is C_{2v}.[12]

The esr spectra of polycrystalline samples of $Co(apf_2)_3Br_2$ and $Co(apf_2)_3I_2$ were poorly resolved and accurate g values could not be obtained. When solutions of these complexes were frozen to 77K the ^{59}Co ($I = 7/2$) hyperfine structure was resolved in the parallel band of all samples with the solutions containing $Co(apf_2)_3I_2$ giving partially resolved perpendicular bands. Phosphorus hyperfine ^{31}P ($I = 1/2$) lines were resolved in the parallel region of all solutions except for the solution containing $Co(apf_2)_3I_2$ in which only the cobalt hyperfine structure was resolved. Typical frozen solution spectra (77K) are shown in Figures 19 and 20.

Of the 16 lines expected in the "parallel" band due to metal and ligand coupling, typically ten to thirteen lines were resolved, the rest being obscured by the overlapping "perpendicular" band. In the frozen solution spectrum of $Co(apf_2)_3I_2$ in excess ligand and methylene chloride, in which phosphorus hyperfine lines were not resolved, twelve of the sixteen combined "parallel" and "perpendicular" features were observed. No cobalt or ligand hyperfine structure was observed in the spectra of any of the polycrystalline solid complexes either at room temperature or 77K.

The visible spectra of the complexes CoL_3X_2 (when L is a_2pf, X is Cl, Br or I; and when L is apf_2, X is

Figure 19. Frozen solution spectrum (77K) of $Co(a_2pf)_3I_2$ in excess a_2pf and CH_2Cl_2.

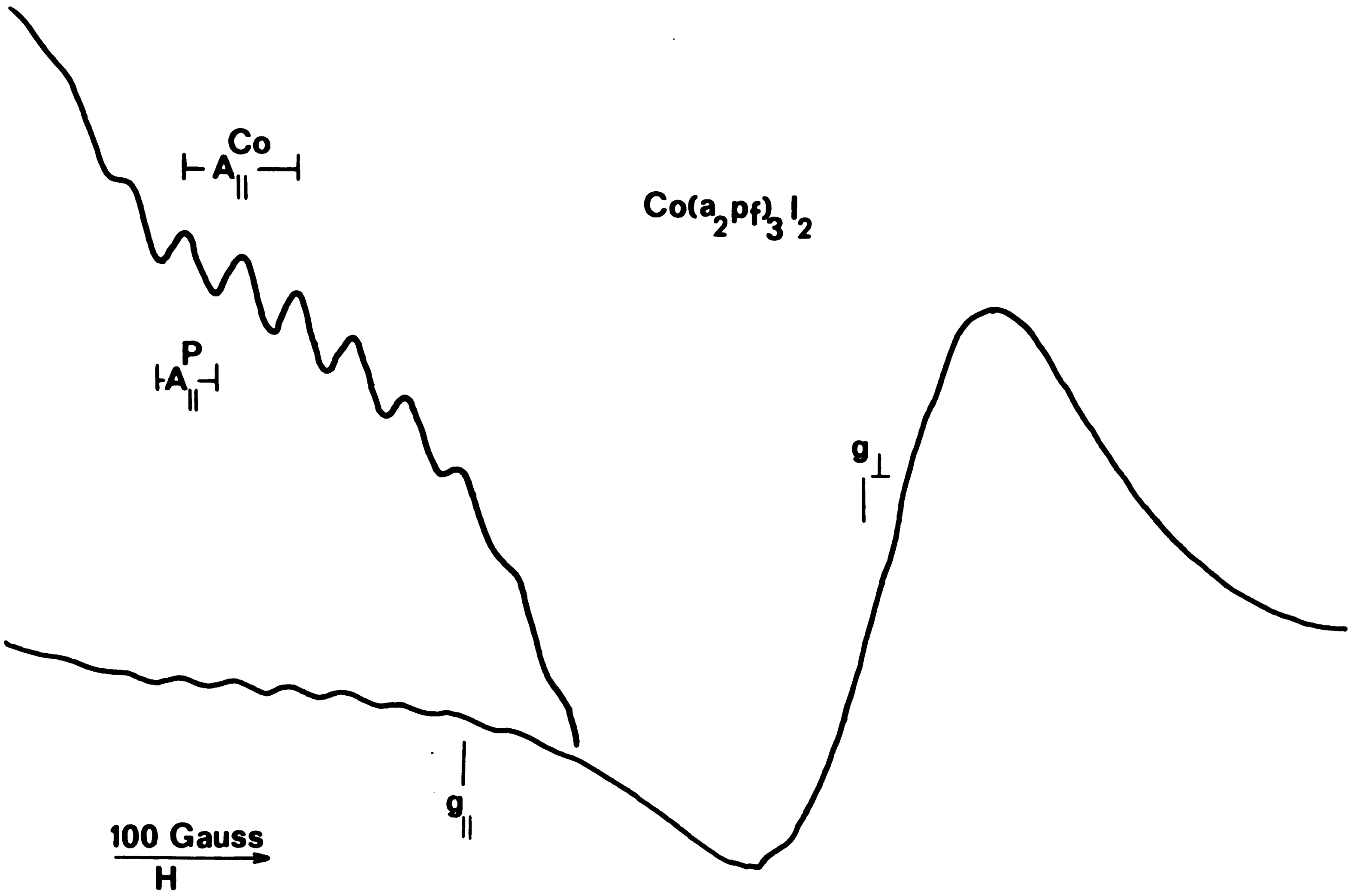
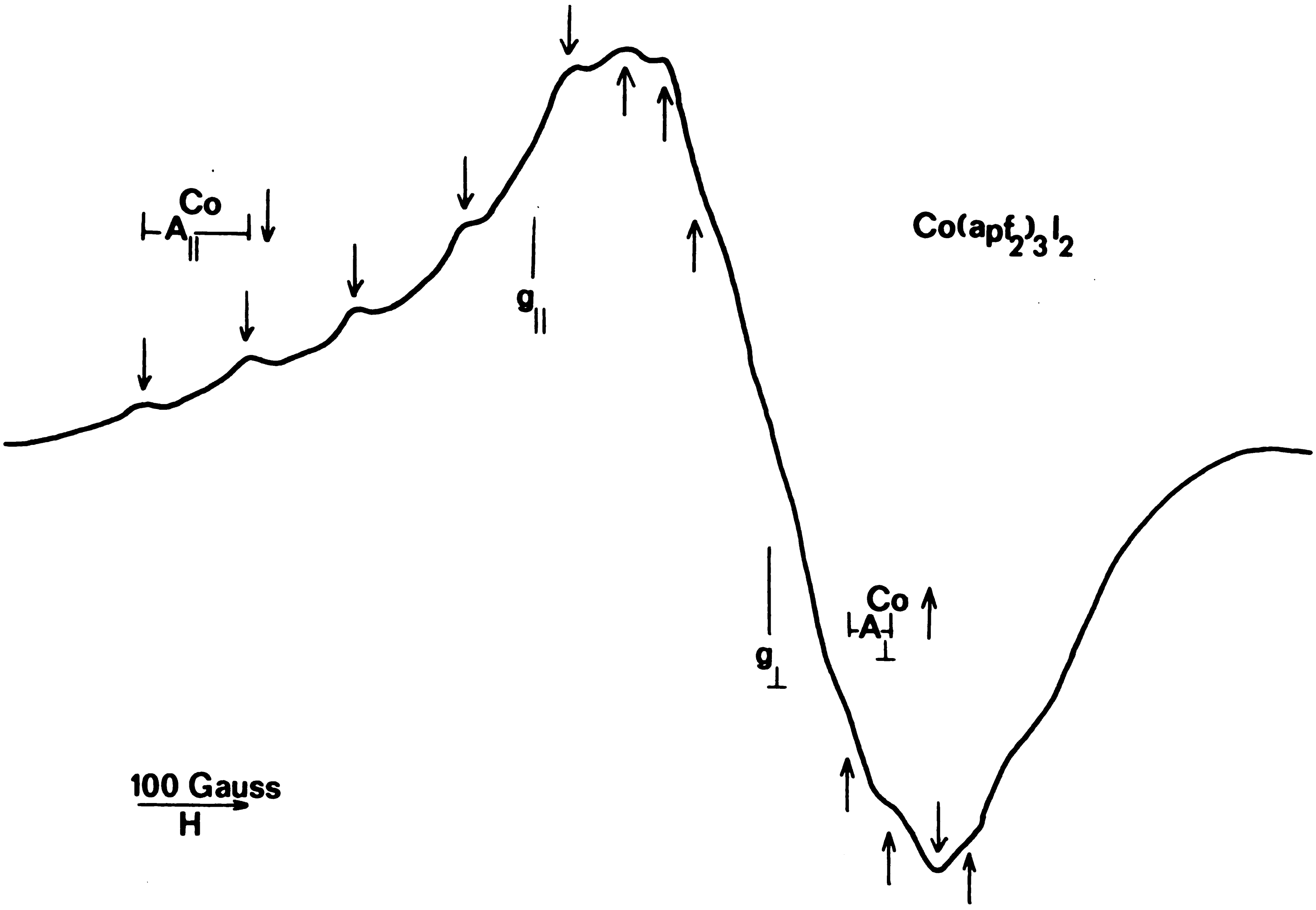

$A_{\parallel}^{Co}$
$A_{\parallel}^{P}$
$Co(a_2pf)_3I_2$
$g_{\perp}$
$g_{\parallel}$
100 Gauss
H

Figure 19.

Figure 20. Frozen solution spectrum (77K) of $Co(apf_2)_3I_2$ in excess apf_2 and CH_2Cl_2.



$A_{\parallel}^{Co}$
$g_{\parallel}$
$Co(apf_2)_3I_2$
$g_{\perp}$
$A_{\perp}^{Co}$
100 Gauss
H

Figure 20.

Br or I) in both solution and mull are shown in Figures 6 and 8-15. The band positions and molar extinction coefficients are presented in detail in Table 10.

^{59}Co Hyperfine Interaction

For the complexes studied in the frozen state, the esr spectra were characterized by axially symmetric $\underset{\sim}{g}$- and $\underset{\sim}{A}$-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 $\underset{\sim}{g}$-tensor components were resolved in the polycrystalline solids (Table 8), only two $\underset{\sim}{g}$-tensor components could be resolved in the frozen solution spectra. 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 g_{av} values calculated from the spectra of the polycrystalline solids and frozen solutions supports this contention (Table 8).

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 (A_{iso}) due to the presence of unpaired electron density in cobalt s- orbitals. These have the tensor form

Table 10. Summary of the visible spectra of the complexes $Co(apf_2)_3X_2$ (X = Br, I) and $Co(a_2pf)_3X_2$ (X = Cl, Br, I) for complexes mulled in Nujol and dissolved in CH_2Cl_2.

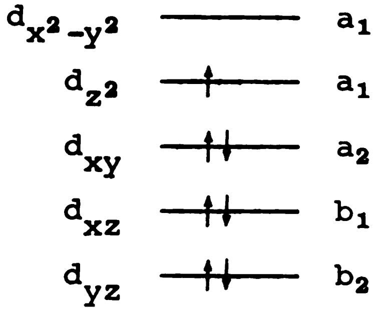
X	Solvent	Ligand	$\lambda(\epsilon)$[a]					
I	CH_2Cl_2	apf_2	26109(1100)	23696(1000)	20492(750)	14792(400)	13157(350)sh	5692(50)
I	mull	apf_2	25773	23202	19960	14706	----	6000
Br	CH_2Cl_2	apf_2	----	25380(1170)sh	21645(1370)	15725(760)	14085(700)sh	6000(50)
Br	mull	apf_2	----	25000 sh	21739 sh	15385	----	6000
I[c]	CH_2Cl_2	a_2pf	22100(620)	1633(210)sh	15350(360)sh	14590(44	1359(340)	----
I	mull	a_2pf	----	24400 sh	20820	14020	----	----
Br[d]	CH_2Cl_2[b]	a_2pf	24190(900)	21040(600)sh	16300(580)sh	1550(640)	14690(580)sh	----
Cl[e]	CH_2Cl_2[b]	a_2pf	25390(1600)	21710(450)sh	17220(300)sh	15790(480)	14890(450)sh	----

[a] Wavelength in cm^{-1}. [b] Solutions prepared by dissolving anhydrous CoX_2 in an excess of ligand and CH_2Cl_2. [c] Concentration of $Co(a_2pf)_3I_2$ 3.0×10^{-2} Molar. [d] Concentration of $CoBr_2$ approximately 10^{-3} Molar. [e] Concentration of $CoCl_2$ approximately 10^{-3} Molar.

$(A_{||}, -B_{\perp}, -B_{\perp}) + (A_{iso}, A_{iso}, A_{iso})$ in the parallel (z) and the perpendicular (x, y) directions. The values of A_{iso} and the dipolar contribution are indicated in Table 8. The large positive values of A_{iso} are consistent with a direct transfer of electron-density from the cobalt d-orbital which is occupied by the unpaired electron to the cobalt 4s-orbital. If we assume C_{2v} symmetry for all of the above pentacoordinate complexes, only the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals belong to the totally symmetric a_1 representation and can mix directly with cobalt s-orbitals leading to a transfer of spin-density into the cobalt 4s-orbital.

Examination of the esr spectra and the esr parameters calculated from the spectra, supports the $3d_{z^2}$ orbital as the orbital which is occupied by the unpaired electron. The fact that both cobalt hyperfine, and phosphorus hyperfine from a single phosphorus atom were resolved only in the parallel (z) direction and not the x, y direction suggests that the $3d_{x^2-y^2}$ orbital is not the orbital of the unpaired electron. This is supported by the relative magnitudes of the $\underline{g}$ tensor values $(g_{||} > g_{\perp})$ and the relative magnitudes between the observed "parallel" and "perpendicular" cobalt hyperfine $(A_{Co_{||}} > A_{Co_{\perp}})$. On the other hand, under the same symmetry the remaining cobalt d-orbitals belong to other representations (d_{yz}, b_2; d_{xz}, b_1; and d_{xy}, a_2) and as such direct participation of these orbitals with the 4s-orbital that form the molecular orbital of the unpaired electron is symmetry forbidden. The ordering of the cobalt d orbitals under C_{2v} symmetry can be qualitatively represented as:

C_{2v} - d^7 strong field case



The monomeric nature of these complexes is clearly shown by the hyperfine interaction of an unpaired electron with a single ^{59}Co nucleus. The fact that the cobalt hyperfine is split into a doublet by a single phosphorus atom suggests that the axial site of these square pyramidal complexes is occupied by only one of the three donor phosphorus atoms.

Spin Densities of the Cobalt $d_{3z^2-r^2}$ and 4s orbitals

The values of the spin density on cobalt d_{3z^2} (f_d) were calculated by setting an upper limit for the direct dipolar anisotropic contribution to the hyperfine coupling value $|A'|_{max}$ of approximately 52 gauss.[49] 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 gauss.[50] Values of f_s and f_d are given in Table 8.

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. Assuming a perpendicular coupling constant of about 10 gauss I estimate the unpaired electron has about 6-10% spin density in the phosphorus sp^3 hybrid orbital. There could be considerable back-bonding 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.

Covalency of the Metal-Ligand Bond

Consideration of the total cobalt hyperfine interaction for the complexes studied (Table 8) indicates that there is more delocalization in a_2pf complexes than in apf_2 complexes. This suggests that the former complexes are more covalent.[51] If one considers the cobalt hyperfine interaction of the complexes involving the same phosphine ligand, but different halides, then one would predict by use of the same arguments that the covalency of the complexes decreases in the order Cl > Br > I.

The same conclusions regarding covalency can be reached if one considers the trend in the metal isotropic coupling constant. Other workers have suggested that the fractional s character should in large part be determined by the relative energy separation between 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 energy 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.

Electronic Factors

On the basis of simplified force constant calculations, it has been suggested that apf_2 has more π-accepting ability (through a d_π-d_π interaction) than a_2pf[52] in molybdenum carbonyl complexes of the type $L_nMo(CO)_{6-n}$, where L is apf_2 and a_2pf and $n = 2$. On the other hand, it may be reasonably suggested that a_2pf is a better σ donor than apf_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. This donation makes the electrons on phosphorus more available.[53] From the data obtained in this study, together with the expectations which can be reasonably made on σ and π bond character in the Co-P bond, it appears that the degree of covalency in a bond in which both σ- and π-bonding may be important, is determined primarily by the σ-bond.

The observed trend showing the $Co(a_2pf)_3I_2$ complexes to possess a greater degree of covalency than the

$Co(apf_2)_3I_2$ complexes may be related further to the tendency of these two phosphines to form pentacoordinate complexes.

It has been previously shown that when $Co(a_2pf)_3I_2$ is dissolved in methylene chloride and excess a_2pf and equilibrium (1) is established with a significant amount of high-spin four-coordinate complex in solution ($K = 0.17$ at 27^0). On the other hand, when $Co(apf_2)_3I_2$ is dissolved in methylene chloride and excess apf_2 no significant concentration of high-spin four-coordinate $[(Co(apf_2)I_2]$ is detected. Hence, the tendency towards pentacoordination seems to be greater for the apf_2 complexes than for the a_2pf complexes. The identical results are obtained with the analogous bromide complexes CoL_3Br_2 ($L = apf_2$ and a_2pf).

The role the anion plays in determining the covalency of the complexes has been discussed above and is $Cl > Br > I$. The trend away from bond covalency towards increased stability of the pentacoordinate complexes, as found in the case of the phosphines, is found also for the anions. The stability of the $Co(a_2pf)_3X_2$ complexes has been determined to be $I > Br > Cl$ while in the present study the bond covalency for these $Co(a_2pf)_3X_2$ complexes is $Cl > Br > I$.

g Tensor Values and Optical Spectra

The observed relation between the magnitude of the *g* tensor components is in agreement with the criterion for the unpaired electron to be in the $3d_{z^2}$ orbital. The trend in $g_{||}$ and $g_{\perp}$ is consistent with the spectrochemical series. As the halogen becomes a better ligand $g_{||}$ values increase and $g_{\perp}$ values decrease. This suggests a decrease in the mixing of the $3d_{z^2}$ and $3d_{x^2-y^2}$ levels as their relative energy separation increases. The change in the optical absorption maxima as well as $g_{||}$ and $g_{\perp}$ and the electronegativity of the halogen are all measures of the relative energy separation of the higher lying a_1 orbitals. The large number of transitions in the higher energy region of the visible spectra and the observation of three distinct $\underline{g}$-values indicate that the geometry of the complexes can be best represented under a C_{2v} point group. The most reasonable geometry for these pentacoordinate complexes is a square pyramid with the basal plane defined by two phosphorus and two halogen atoms with the apex occupied by the third phosphorus atom. I 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. The best agreement between esr and electronic spectra is consistent with the ground state vacancy configuration of $|(x^2 \overset{+}{-} y^2)(x^2 \overset{-}{-} y^2)(\overset{+}{z^2})>$. In this case the expression for the principle $\underline{g}$-tensor components are:

$$g_{xx} = 2 - \{2\lambda / [E(|(x^2 \overset{+}{-} y^2)(x^2 \overset{-}{-} y^2)(\overset{+}{xz})>) - E(|(x^2 \overset{+}{-} y^2)(x^2 \overset{-}{-} y^2)(\overset{+}{z^2})>)]\} \tag{2}$$

$$g_{yy} = 2 - \{2\lambda/[E(|\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(yz)}>) - E(|\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(z^2)}>)]\} \qquad (3)$$

$$g_{zz} = 2 - \{2\lambda/[E(|\overset{+}{(z^2)}\overset{-}{(z^2)}\overset{+}{(x^2-y^2)}>) - E(|\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(z^2)}>)]\} \qquad (4)$$

Arbitrarily, we assign g_1 as g_{zz} and $g_2 = g_{yy}$ and $g_3 = g_{xx}$. g values were calculated (Table 11) according to equations 2-4 by using a spin orbit coupling constant (λ) of 500 cm^{-1}, 95% of the free ion value. Only three of the seven possible one electron transition excited states contribute to the g values. These excited states are given in the second term of equations 2-4, while the third term represents the proposed ground state. The remaining transition energies in the electronic spectra of the complexes involving dimethylaminodifluorophosphine were calculated as described previously.[12] 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.[54] The values of these interaction energies for the various states and the calculated transition energies are given in Table 12. 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

Table 11. Observed and calculated *g*-values for the complexes $Co(apf_2)_3X_2$ ($X = Br, I$).

	Observed[a]			Calculated			
X	g_1	g_2, g_3[b]	g_{av}[c]	g_1	g_2	g_3	g_{av}
Br	2.328	2.076	2.160	2.290	2.040	2.064	2.131
I	2.288	2.117	2.174	2.310	2.043	2.069	2.174

[a] Error estimated from values determined using the frozen solution spectra ± 0.009.

[b] Due to the broad structureless nature of the perpendicular band only one perpendicular value is observed (see text).

[c] The g_{av} values obtained from the room temperature solution spectra are given in Table 8.

Table 12. State and transition energies calculated for the $Co(apf_2)_3X_2$ (X = Br, I) complexes, the three-vacancy configurations.

State (vacancy Configuration)	$CoBr_2[(CH_3)_2NPF_2]_3$			$CoI_2[(CH_3)_2NPF_2]_3$			Interelectronic Interaction Terms
	$\Sigma\epsilon_\kappa$	Calcd.	obsd.	$\Sigma\epsilon_\kappa$	calcd.	obsd.	
$\lvert\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(z^2)}\rangle$	14,085	0	gd. state	13,157	0	gd. state	$3F_0-8F_2+33F_4$ (-5430)
$\lvert\overset{+}{(x^2-y^2)}\overset{-}{(z^2)}\overset{+}{(xy)}\rangle$	35,085	6,000	6,000	33,849	5,692	5,692	$3F_0-12F_2-87F_4$ (-20, 430)
$\lvert\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(xy)}\rangle$	21,000	5,085	---	20,692	4,463	---	$3F_0+12F_2-67F_4$ (+6970)
$\lvert\overset{+}{(z^2)}\overset{-}{(z^2)}\overset{+}{(x^2-y^2)}\rangle$	28,170	14,085	14,085	26,314	13,157	13,157	$3F_0-8F_2+33F_4$ (-5430)
$\lvert\overset{+}{(x^2-y^2)}\overset{-}{(z^2)}\overset{+}{(xz)}\rangle$	46,895	17,810	---	44,106	15,949	---	$3F_0-12F_2-87F_4$ (-20, 430)
$\lvert\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(xz)}\rangle$	32,810	15,725	15,725	30,949	14,792	14,792	$3F_0-3F_2+8F_4$ (-2430)
$\lvert\overset{+}{(x^2-y^2)}\overset{-}{(z^2)}\overset{+}{(yz)}\rangle$	50,730	21,645	21,645	48,649	20,492	20,492	$3F_0-12F_2-87F_4$ (-20, 430)
$\lvert\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(yz)}\rangle$	42,465	25,380	25,380	39,853	23,696	23,696	$3F_0-3F_2+8F_4$ (-2430)

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 13. As mentioned earlier, the quantitative handling of the optical spectra of the complexes of bis(dimethylamino)fluorophosphine is disabled by the complexity of the optical spectra arising presumably by the presence of a substantial concentration of tetrahedral high-spin complex.

Table **13.** Single-electron d-orbital energies for the $Co(apf_2)_3X_2$ (X = Br, I) complexes.[a]

Orbital	X = I	X = Br
x^2-y^2	39,853	42,465
3^2	26,696	28,380
xy	19,161	21,465
xz	8,904	9,655
yz[b]	0	0

[a] Energies in cm^{-1}.

[b] Assigned arbitrarily as the lowest lying orbital.

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