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Transition Metal Complexes Of Some Fluorinated Diols

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TRANSITION METAL COMPLEXES OF
SOME FLUORINATED DIOLS

by

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of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
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ABSTRACT

This thesis describes a study of the application of some fluorinated diols as ligands to transition metal ions, and it may conveniently be divided into three parts.

In the first section, we consider the use of the dianion of perfluoropinacol, $(CF_3)_2C(OH)C(OH)(CF_3)_2$, ($H_2PFP$), as a chelating, dinegative, ligand. A series of neutral complexes has been prepared of general formula $L_2M(PFP)$, where M = Ni^{2+}, Cu^{2+}, Pd^{2+}, or Pt^{2+}, and L = phosphine; L_2 = diphosphine or diamine. Exclusively square-planar geometry is observed for the Ni^{2+} derivatives; this is explained on electronic, rather than steric, grounds. Certain of the Ni^{2+} complexes, on dissolving in donor solvents, become mono-solvated, and an equilibrium exists between 4- and 5-coordinate species. This unusual behaviour is attributed to the steric requirements of the PFP^{2-} ligand. A comparison is made between the ligand properties of PFP^{2-} and those of a pair of halide ions, and with the oxalate ion.

In the second section, the diol of interest is perfluoro(2,3-diphenylbutane-2,3-diol), which is first separated into meso- and rac- forms, then the latter resolved into the optical enantiomers. Like perfluoropinacol, this diol ionizes and forms a number of neutral complexes with Ni^{2+} or Cu^{2+} as metal, and a variety of phosphines or diamines as co-ligand. The use of optically active forms of the diol leads to complexes containing a chiral chelate ring, and a study of their circular dichroism enables an assignment of absolute configuration to be made.

In the final section of this work, a brief examination is made of the use of some partially fluorinated diols as ligands. Compounds included are $[(CF_3)(C_6H_5)C(OH)-]_2$, $[(CF_3)(CH_3)C(OH)-]_2$, and $[(CH_3)(C_6F_5)C(OH)-]_2$. Only limited success in the preparation of metal complexes of these diols is obtained, and this may be explained by the reduced acidity associated with the replacement of fluorine by hydrogen.

Our general conclusion from this work is that perfluoropinacol remains unexcelled among fluorinated diols in its utility as a chelating ligand, since it combines high acidity with chemical stability and ease of preparation. The fluorinated diols offer many opportunities for the preparation of metal complexes showing novel structures or properties, and much work remains to be done in this field.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. C. J. Willis for his help, supervision and patience throughout this work. The author also wishes to thank his co-workers, Mr. I. S. Chang, Mr. W. H. Dawson, Dr. Celia A. MacDonald, Dr. J. T. Price and Dr. A. J. Tomlinson for many enlightening discussions.

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INTRODUCTION

The work described in this thesis forms part of a study extending over several years in this laboratory, in which we have been investigating the behaviour of highly fluorinated molecules. Of special interest to the inorganic chemist are those which may act as ligands to transition metal ions, since the presence of fluorine in the molecule often leads to profound alteration in the properties of the ligand and of the complexes which it forms. This introduction will therefore briefly outline the properties of highly fluorinated molecules, with particular emphasis on those related to the problems currently under investigation.

Although fluorine was first isolated as early as 1886 by the French chemist Moissan,[1] the only fluorocarbon compounds definitely characterized and reported in the literature before 1937 were carbon tetrafluoride,[2] hexafluoroethane,[3] and tetrafluoroethylene.[4]

The Second World War was a great moving force into extensive research in fluorocarbon chemistry and during the last twenty-five years, interest in fluorocarbon chemistry has blossomed. This has resulted in a vast number of fluorinated and partially fluorinated analogues of hydrocarbons and a variety of synthetic methods of their preparation.

Since the work presented in this thesis concerns partially and totally fluorinated diols, it is important to appreciate the difference between perfluoro-alcohols and their hydrocarbon analogues, and the reason for this difference. Fluorine is the most electronegative element, and as such, when bonded to other elements, fluorine polarizes the bond, drawing electrons to it. With this in mind, a carbon-fluorine bond can be represented and physically visualized as a mixture of ionic and covalent bonding, e.g.

$$C:F \longleftrightarrow C^{+}:F^{-}$$

Pauling[5] has calculated the percent ionic character of various single bonds and listed below are his derived values for carbon-halogen bonds.

TABLE 1

IONIC CHARACTER OF CARBON-HALOGEN BONDS

Bond	% Ionic Character
CF	43
CCl	12
CBr	2
CI	0

As is apparent from these values, fluorine is a better electron withdrawing agent than chlorine, bromine or iodine.

The concept that fluorine exerts a large inductive effect through its σ bond to carbon is illustrated by comparing the K_a's of a series of fluoro- and chloro-substituted acetic acids.[6]

TABLE 2

DISSOCIATION CONSTANTS OF HALO-SUBSTITUTED ACETIC ACIDS

Compound	K_a	Compound	K_a
CH_3CO_2H	1.77×10^{-5}		
FCH_2CO_2H	2.20×10^{-3}	$ClCH_2CO_2H$	1.4×10^{-3}
F_2CHCO_2H	5.7×10^{-2}	Cl_2CHCO_2H	3.3×10^{-2}
F_3CCO_2H	5.9×10^{-1}	Cl_3CO_2H	0.2×10^{-1}

Both the consequences of the progressive fluorination of acetic acid and the greater inductive effect of fluorine over chlorine are obvious from the above.

Similarly, the K_b's of bases are also affected by fluorine substitution as shown below.[7]

TABLE 3

DISSOCIATION CONSTANTS OF FLUORINATED AMINES

Amine	K_b	Fluorinated Amine	K_b
$CH_3CH_2NH_2$	4.5×10^{-4}	$CF_3CH_2NH_2$	5.0×10^{-9}
$CH_3CH_2CH_2NH_2$	4.5×10^{-4}	$CF_3CH_2CH_2NH_2$	5.0×10^{-6}
$n-C_4H_9NH_2$	4.1×10^{-4}	$n-C_3F_7CH_2NH_2$	1.8×10^{-6}

Another pertinent example of this powerful inductive effect relates to the reactions of olefins. When a hydrogen on an sp^2 carbon is replaced by fluorine, the strong electron withdrawing power of the fluorine atom removes electron density from the π framework of the molecule. As a consequence of this effect, fluorinated olefins are more susceptible to nucleophilic attack and resistant to electrophilic substitution, while the reverse is true for hydrocarbon olefins.[8] Although there are other examples which illustrate fluorine's powerful inductive effect, only those relevant to perfluoro-alcohols will be discussed henceforth.

Before discussing the increased acidities of fluorinated alcohols relative to their hydrocarbon analogues, we should discuss what classes of perfluoro-alcohols can be prepared. Perfluoro-alcohols of the type R_fCF_2OH are unstable because of the ready elimination of hydrogen fluoride, and thus primary perfluoro-alcohols are not known. Secondary perfluoro-alcohols are likewise unstable and although reactions of perfluoro-ketones with anhydrous hydrogen fluoride are claimed to yield unstable secondary perfluoro-alcohols,[9] only perfluoro-cyclobutanol appears to have been isolated and fully characterized.[10] However, perfluoro-alkoxides of analogous primary and secondary alcohols have been prepared,[11,12,13,14] i.e.

$$MF + R_fCOF \rightleftharpoons {}^+M^-OCF_2R_f$$

$$MF + (CF_3)_2CO \rightleftharpoons {}^+M^-OCF(CF_3)_2$$

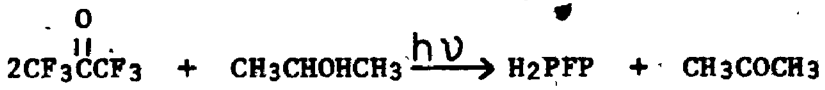
(M = Rb or Cs, R_f = CF_3, C_2F_5, or C_3F_7.)

Thus, the main classes of known fluorinated alcohols are of the types R_fCH_2OH, R_fCHOHR_f and $(R_f)_3COH$. In summary, perfluoro-alcohols do not exist when the ready elimination of HF is possible and tertiary perfluoro-alcohols form the main class of totally fluorinated alcohols.

As mentioned previously, fluoro-alcohols are much more acidic than their hydrocarbon analogues. The most striking example of this is t-butanol. The unfluorinated compound has a pK_a of 20.0 while that of perfluoro-t-butanol is 5.4,[15] which is very close to that of acetic acid (4.76).

Since the work in this thesis concerns fluorinated diols, the remainder of this introduction will mainly deal with perfluoro-2,3-dimethylbutane-2,3-diol (perfluoropinacol, H_2PFP). This diol has been prepared by a variety of methods which are outlined below.

(i) Photoinitiated bimolecular reduction of hexafluoroacetone with isopropyl alcohol.[16]

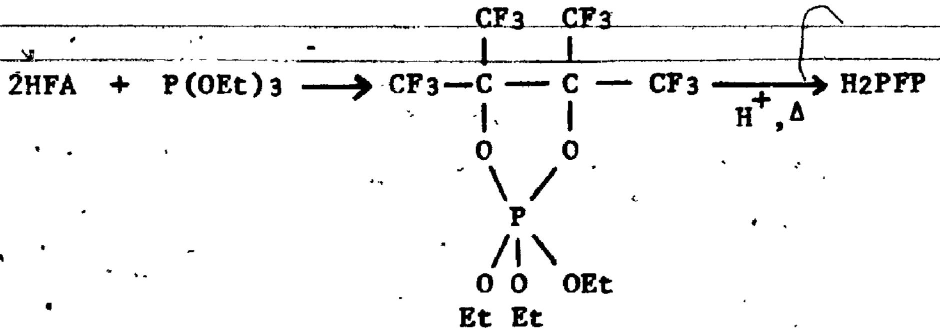


$$2CF_3\overset{O}{\overset{\|}{C}}CF_3 + CH_3CHOHCH_3 \xrightarrow{h\nu} H_2PFP + CH_3COCH_3$$

(ii) Reduction of hexafluoroacetone with magnesium amalgam.[16]

$$2CF_3COCF_3 \xrightarrow[THF]{Mg/Hg} H_2PFP$$

(iii) Reaction of hexafluoroacetone (HFA) with triethyl phosphite $[P(OEt)_3]$.[17,18] The use of triphenylphosphine in lieu of $P(OEt)_3$ also produces perfluoropinacol.[19] Ramirez et al.[20] have shown that the type of cyclic intermediate phospholane shown above is formed from the reaction of HFA with a variety



of organo-phosphines.

(iv) Reductive dimerization of HFA with sodium or lithium. Erye et al.[21] initially postulated that the dilithium alkoxide of perfluoropinacol was an intermediate in the reaction of HFA with trimethylchlorosilane and lithium as outlined below.

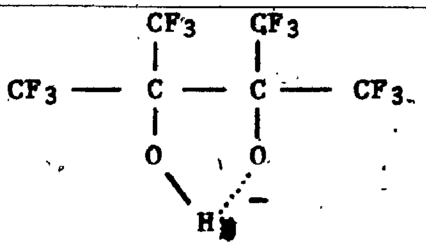
$$2HFA + 2Li + 2Me_3SiCl \longrightarrow 2LiCl + Me_3SiOC(CF_3)_2\cdot C(CF_3)_2OSiMe_3$$

Although they did not isolate the alkoxide of lithium, further investigators succeeded in preparing the disodium alkoxide of perfluoropinacol which was stable in THF.[22,23,24]

$$2(CF_3)_2CO + 2Na \xrightarrow{THF} Na_2PFP \xrightarrow{H^+} H_2PFP$$

A similar method was recently used to prepare and isolate the dilithium salt of perfluoropinacol.[25] This briefly summarizes the various methods used to date to prepare perfluoropinacol and its disodium or dilithium alkoxide.

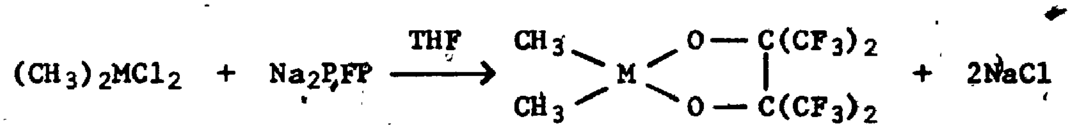
Perfluoropinacol has a pK_a in water of 5.95.[16] Middleton and Lindsey[16] proposed that this abnormally low pK_a was due not only to the cumulative inductive effect of the CF_3 groups present but also to strong intramolecular hydrogen bonding which could stabilize the anion, as shown below.



Although their basis for suggesting that perfluoropinacol's acidity was abnormally high was erroneous (through comparison with the pK_a of perfluoro-t-butanol which was incorrectly reported in the literature at that time to be 9.52[26]), their proposed structure does inevitably stabilize the anion to some extent. The readily isolated solid monosubstituted potassium salt of perfluoropinacol[24] probably contains the anion as shown above.

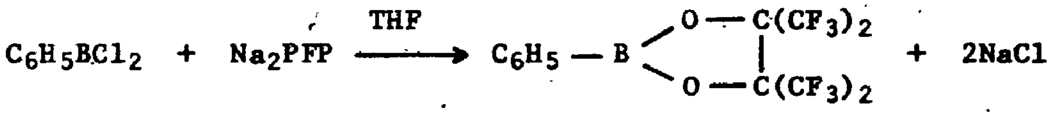
Results reported to date indicate that perfluoropinacol is capable of behaving as a dinegative, bidentate, ligand with both non-transition elements and transition metals. The majority of the work with the non-transition elements involved the use of the disodium[23,24] or the dilithium alkoxide[25] as the reactive reagent for the preparation of cyclic fluorinated alkoxides by reaction with the appropriate dihalide. A few examples of this preparative work to date are illustrated below.[23,24]

(i)

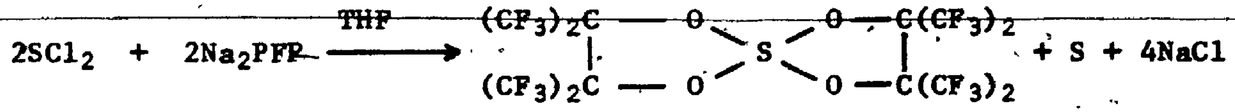


M = Si, Ge or Sn.

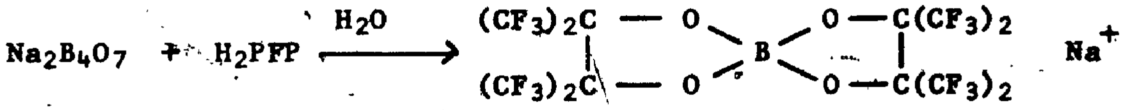
(ii)



(iii)



(iv)



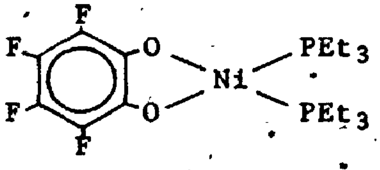
Dresdner and Conroy[25] later did similar reactions with the dilithium alkoxide reagent and compounds such as $SOCl_2$, SO_2Cl_2, $COCl_2$, $C_6H_5BCl_2$ and $C_6H_5PCl_2$ resulting in analogous reactions to those listed above.

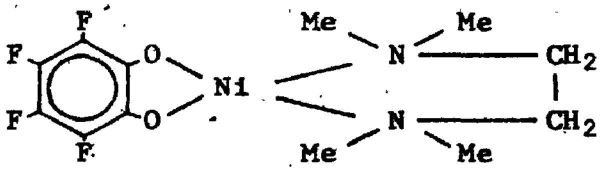
Transition metal complexes of perfluoropinacol have also been prepared.[27] Complex ions of the type $[M(PFP)_3]^{3-}$ were prepared $[M = Fe^{3+}$ or $Al^{3+}]$ while those of the type $[M(PFP)_2]^{2-}$ were also reported $[M = Ni^{2+}, Cu^{2+}$ and $Zn^{2+}]$. The general method of preparation involved adding aqueous KOH to 1:1 water/methanol mixtures of H_2PFP and the appropriate metal salt in the desired stoichiometry. It has been

$$nH_2PFP + M^{n+} + 2nOH^- \longrightarrow M(PFP)_n^{n-} + 2nH_2O$$

reported[28] that the reduction of chromate ion in the presence of perfluoropinacol leads to the formation of a stable chelated alkoxide containing chromium(V) in the ion $CrO(PFP)_2^-$. The isoelectronic vanadium(IV) complex was also reported.

The fluorinated diol, tetrafluoro-1,2-dihydroxybenzene (tetrafluorocatechol, TFC) has exhibited very limited ability to act as a dinegative bidentate ligand.[29] Amongst the few complexes M^{ac}Donald et al. were able to prepare were neutral mixed ligand complexes of nickel with nitrogen or phosphorus donors and tetrafluorocatechol, as shown below.





Several other papers[30,31] have recently appeared in which fluorinated alkoxides have been used as ligands. The chelating reagents utilized in these studies were monoalcohols containing another functional group capable of co-ordination.

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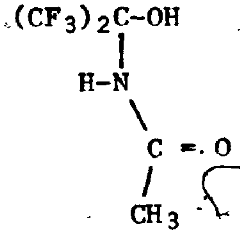

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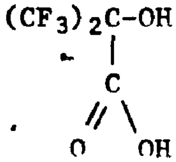


With both ligands, the alcoholic protons were found to be acidic and the compounds behaved generally in a bidentate fashion. A variety of metal complexes were prepared with both ligands.

This thesis will continue the work on fluorinated diols and will be presented in three parts:

(i) Metal complexes of perfluoropinacol;

(ii) Perfluoro(2,3-diphenylbutane-2,3-diol), its resolution and application in the preparation of optically active metal complexes;

(iii) A brief investigation of partially fluorinated diols.

PART I

METAL COMPLEXES OF PERFLUOROPINACOL

RESULTS AND DISCUSSION

Perfluoropinacol, the simplest totally fluorinated ditertiary alcohol, is stable, since there is no possibility of eliminating an α-fluorine, and is acidic, due to the inductive effect of the CF_3 groups. As a consequence of these properties, bis-perfluoropinacolato transition metal complexes have been prepared[27] with, among others, nickel(II) and copper(II). The nickel complex was reported to be diamagnetic, suggesting a square planar structure, while the copper complex had a magnetic moment of 2.0 B.M., typical of a d^9 system.

With this background, we decided to investigate the versatility of perfluoropinacol as a bidentate ligand, to determine whether the reported metal complexes of perfluoropinacol are unique or whether a whole range of metal complexes of perfluoropinacol can be prepared. Although the work involves mainly nickel(II) and copper(II), attempts have been made to extend it to palladium(II) and platinum(II).

When it was initially decided to investigate the versatility of perfluoropinacol as a bidentate ligand, it was considered important to examine in more detail the only previously reported nickel compound with this ligand, namely, $Ni(PFP)_2^{2-}$. This complex was reported as being diamagnetic, suggesting a square planar structure, which was subsequently confirmed by an X-ray structure determination.[32] However, its behaviour in methanol solution was somewhat anomalous, since it changed from a deep blue to a pale yellow colour as the temperature was lowered.[33]

Although the ^{19}F nmr spectrum of the complex is a sharp singlet at room temperature, it becomes quite broad at -40°C and flattens out completely by -80°C, indicative of the presence of a paramagnetic species at this temperature. Whereas the solid exhibited one absorption band in the visible region of the spectrum (Figure 1), typical of square planar Ni^{2+} complexes, the solution spectra were considerably more complex. While the spectrum recorded in diethyl ether (anhydrous) differed only slightly (Figure 2) from that of the solid, the spectrum recorded in a lower grade of the same solvent was quite different (Figure 3). The anomalous behaviour of nickel(II) compounds in solution is well documented,[34] but solubility problems, apparent decomposition in aqueous mixtures and extreme sensitivity to solvent purity rendered a satisfactory explanation of this solution behaviour difficult at this time. It was initially thought that a solute-solvent interaction, of the type,

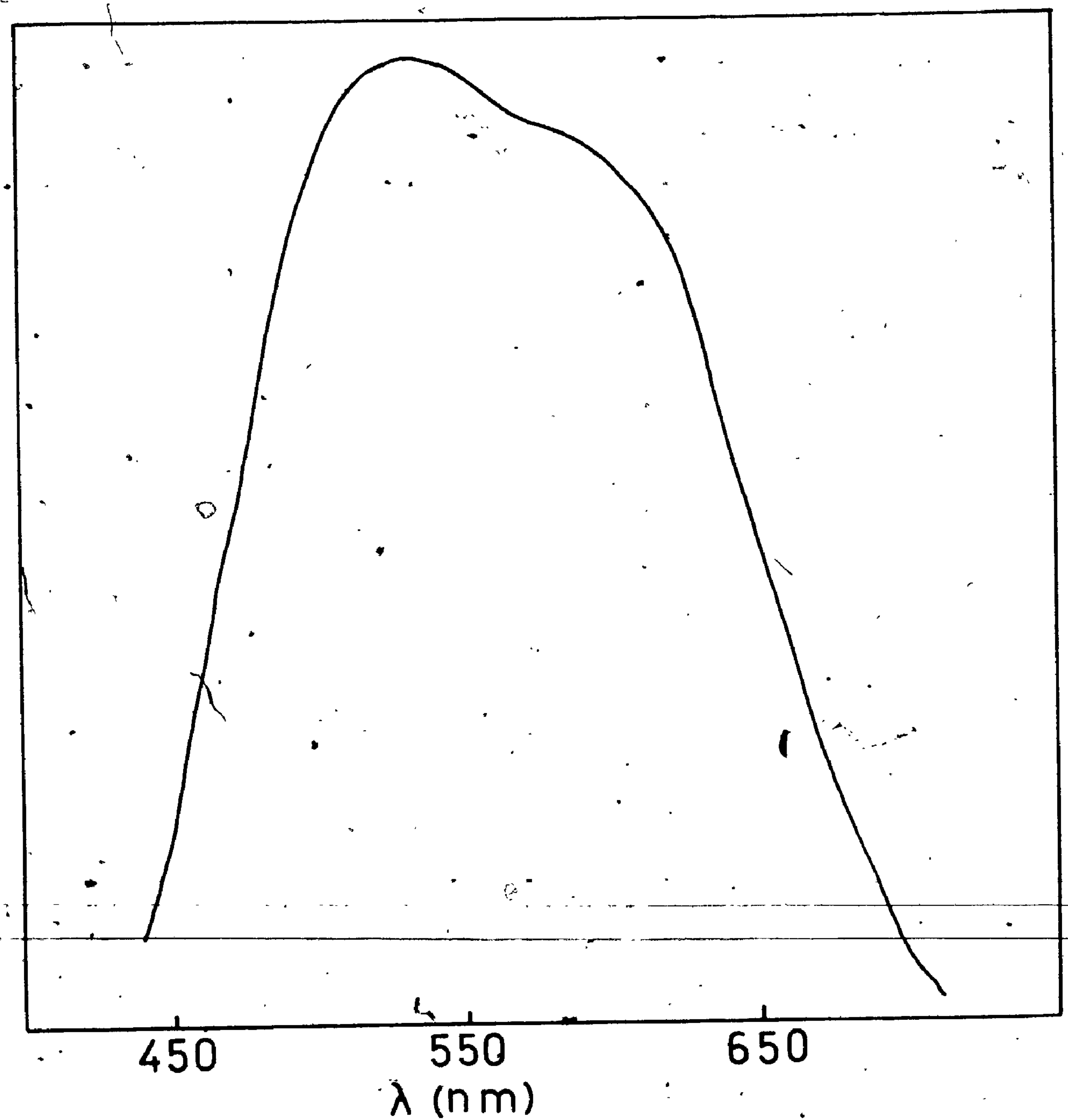
$$\underset{\text{square planar}}{\mathrm{Ni(PFP)_2^{2-}}} + 2S \rightleftharpoons \underset{\text{octahedral}}{\mathrm{Ni(PFP)_2S_2^{2-}}}$$

was responsible for the solution behaviour. The thermochroic behaviour and the sensitivity to solvent purity of the visible spectra are consistent with the above process whereas the positions and intensities of the new bands in the visible spectra are not indicative of the presence of an octahedral species. Nevertheless, attempts were made to isolate phosphine adducts; however, instead of increasing the coordination number of the bis-complex, a displacement of one PFP^{2-} ligand occurred, which led to a new class of perfluoropinacol complexes. The

FIGURE 1

DIFFUSE REFLECTANCE SPECTRUM

OF $K_2Ni(PFP)_2 \cdot 4H_2O$



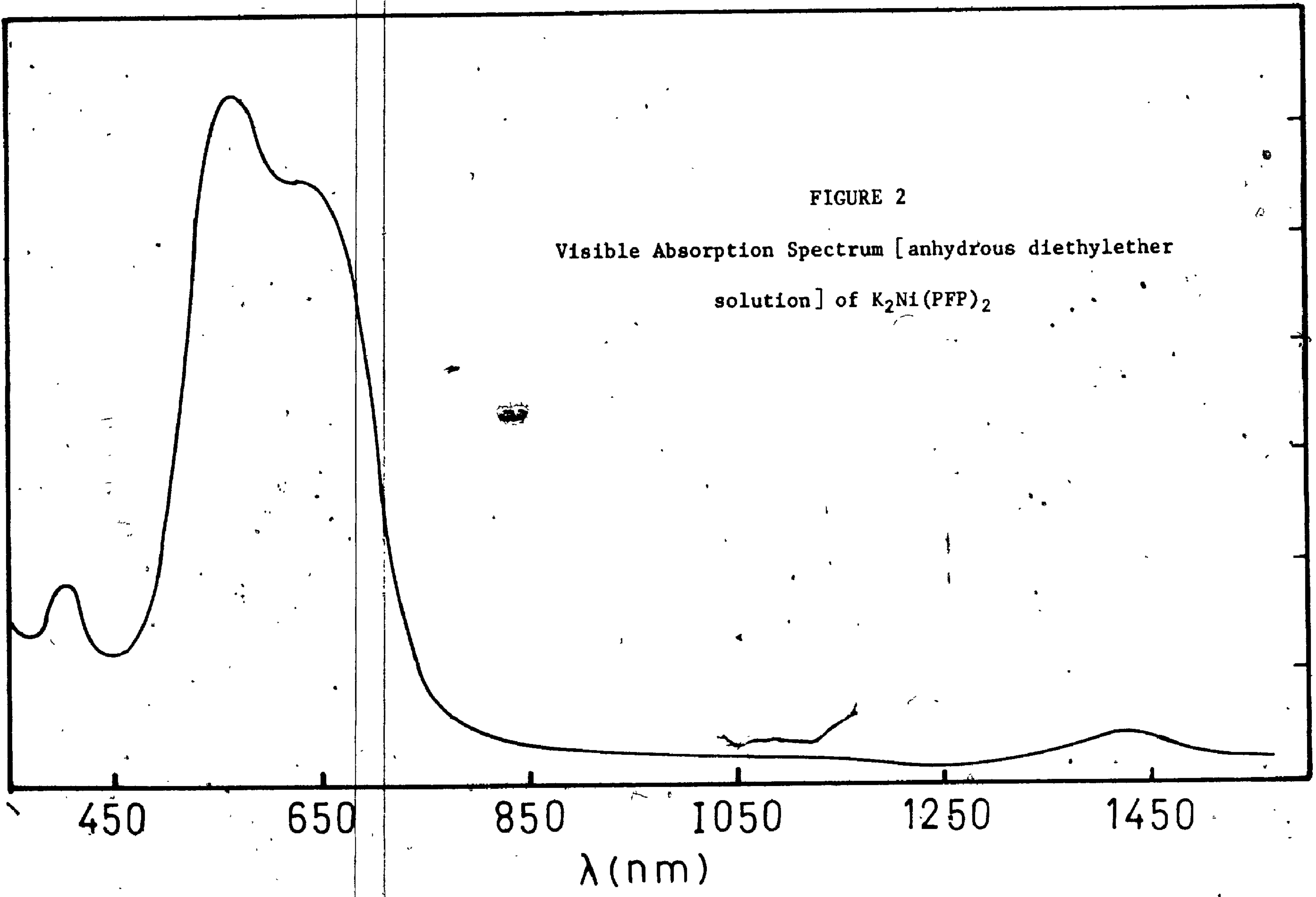


FIGURE 2

Visible Absorption Spectrum [anhydrous diethylether solution] of $K_2Ni(PFP)_2$

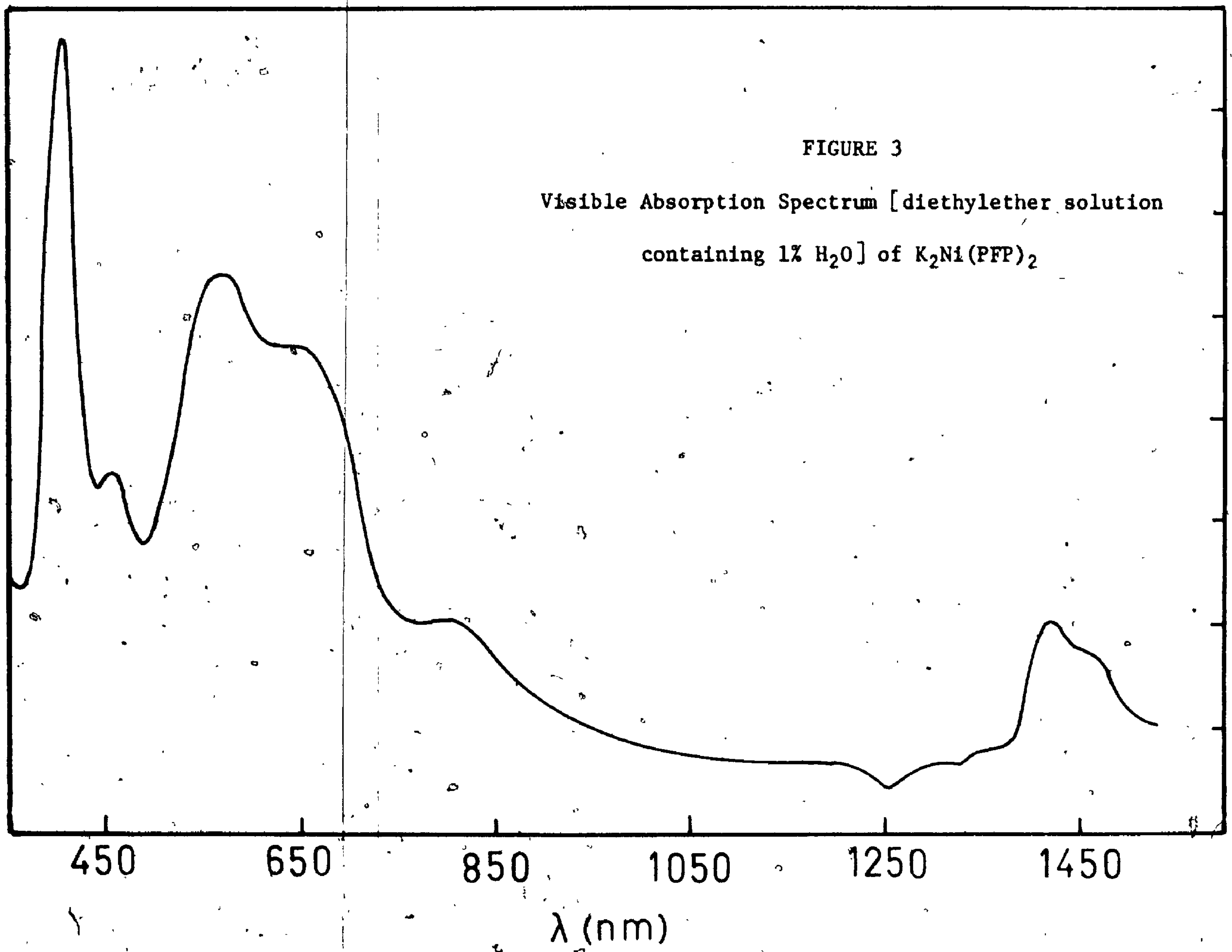


FIGURE 3

Visible Absorption Spectrum [diethylether solution containing 1% H_2O] of $K_2Ni(PFP)_2$

remainder of this chapter will describe these complexes and offer an explanation for the previously described solution phenomenon which also occurs with some of the new mixed ligand perfluoropinacol complexes.

A. Characterization of the Metal Complexes

The compounds studied in this work were generally of the type $M(L)_2(PFP)$, where $L \equiv$ phosphine or $L_2 \equiv$ diamine and were characterized by microanalysis, ^{19}F nmr and infrared spectroscopy. The nickel(II) compounds were generally diamagnetic, while the copper(II) complexes had magnetic moments characteristic of a d^9 system. The compounds were monomers in benzene solution and non-electrolytes in methanol. A detailed discussion of the properties of these mixed ligand complexes of PFP^{2-} follows.

B. Preparation of Metal Complexes

The transition metal complexes described herein were prepared either by displacement of perfluoropinacol from a bis-perfluoropinacolato metal complex or by displacement of two chloride ions from the appropriate transition metal complex, as shown below. Although

$$M(PFP)_2^{2-} + 2L \longrightarrow M(PFP)L_2 + PFP^{2-}$$

$$ML_2X_2 + H_2PFP + 2KOH \longrightarrow M(PFP)L_2 + 2KX + 2H_2O$$

in practice, most complexes could be prepared directly by the addition of L to a 1:1 mixture of the appropriate metal salt, MX_2 and H_2PFP, no doubt the intermediate ML_2X_2 was formed prior to the coordination of perfluoropinacol. This was especially evident in the preparation of nickel-phosphine complexes where the initial addition of phosphine resulted in a deep, wine coloured solution, typical of $Ni(PR_3)_2X_2$, which turned orange upon coordination of perfluoropinacol.

These metal complexes are air stable but often do decompose over a period of several months due to hydrolysis, although they were initially prepared in an aqueous medium. This is a reflection of their kinetic, rather than thermodynamic stability. The main obstacle encountered in the preparations involves coordination of the diol at a low enough pH to preclude either metal hydroxide formation, or in the case of platinum(II) or palladium(II), reduction of the metal. Although this difficulty can be overcome to some extent with Ni^{2+} and Cu^{2+} due to the ready availability of $Ni(PFP)_2^{2-}$ and $Cu(PFP)_2^{2-}$, such is not the case with Pd^{2+} and Pt^{2+}, since the analogous bis-chelates have not yet been prepared.

C. Infrared Spectra

The absence of OH stretches and the presence of strong CF_3 stretches at ~1200 cm^{-1} readily confirms the presence of ionized perfluoropinacol in the transition metal complexes studied to date. However, the infrared spectra can also distinguish between a cyclic and a linear bridging perfluoropinacol chelate.

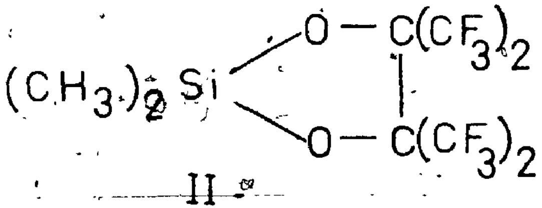
Previous workers[24,35] have prepared derivatives of H_2PFP containing linear (Figure 4, Structure I) and cyclic (Figure 4, Structures II and III) PFP^{2-} and have reported that the infrared spectra of the latter two compounds were different from and more complex than that of the former compound in the 1150-650 cm^{-1} region. It was noted that five bands for compounds II and III, similar in intensity and position, were absent from the infrared spectrum of compound I and it was suggested that

FIGURE 4

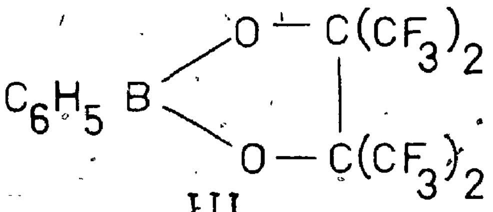
STRUCTURES OF SOME PFP^{2-} COMPOUNDS

$$(CH_3)_3Si-OC(CF_3)_2C(CF_3)_2O-Si(CH_3)_3$$

I



II



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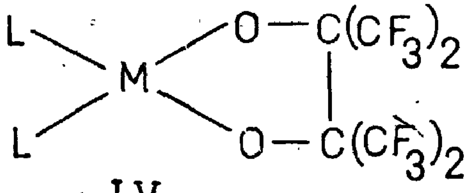

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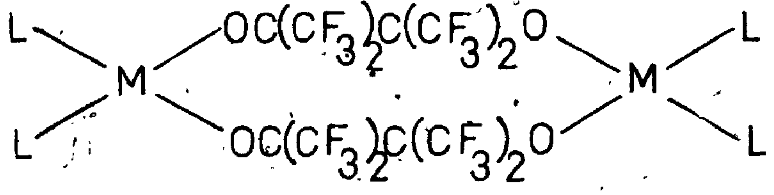


V

these bands arise from the presence of a five-membered cyclic ring. Listed in Table 4 are the infrared data for compounds II and III, mixed ligand complexes of the type $ML_2(PFP)$ and for the previously reported bis-chelate complexes $Cu(PFP)_2^{2-}$ and $Ni(PFP)_2^{2-}$, the last of which are known to contain five-membered cyclic rings. Although the infrared spectra of the mixed ligand transition metal complexes are very complicated in the 1150-650 cm^{-1} region, the five previously mentioned bands appear to be common to the infrared spectra of all the complexes prepared in this work, as shown in Table 4. Thus, they can be assigned the monomeric structure IV rather than the dimeric structure V, which is consistent with molecular weight measurements. Thus, H_2PFP prefers to coordinate as a cyclic ring unless this possibility is prevented, as is obviously the case with compound I.

A final point of interest concerns the possible presence of water, either in the coordination sphere or in the crystalline lattice. Both the copper(II) and nickel(II) bis-chelates were reported as being hydrates and the X-ray structure of the latter[32] indicates that it is a tetrahydrate with the water molecules not coordinated, the nearest water oxygen lying beyond four Å from the central metal atom. This lattice water manifests itself in the infrared spectrum as two sharp peaks at 3690 cm^{-1} and 3610 cm^{-1} due to symmetric and asymmetric OH stretches as well as a broader peak centred at $\sim$3480 cm^{-1}, presumably due to some of the water molecules in the lattice being hydrogen bonded.

D. Phosphine-Perfluoropinacol Complexes of Nickel(II), Palladium(II) and Platinum(II)

A series of nickel(II) compounds have been prepared with L ≡ phosphorus donor ligand and they all have the same general

TABLE 4

INFRARED DATA FOR PFP^{2-} DERIVATIVES (cm^{-1})

$(CH_3)_2Si(PFP)$	1120(s), 1003(w), 952(m), 887(m), 742(m)
$C_6H_5B(PFP)$	1110(s), 1007(m), 954(s), 889(m), 747(m)
$K_2Ni(PFP)_2 \cdot 4H_2O$	1110(s), 985(m), 950(s), 885(s), 750(s)
$Ni(PEt_3)_2(PFP)$	1120(s), 1010(w), 945(m), 870(m), 745(m)
Ni(TMED)(PFP)	1115(s), 1015(m), 840(s), 871(m), 742(m)
Ni(DETA)(PFP)	1110(s), 1000(m), 940(s), 870(s), 740(m)
$K_2Cu(PFP)_2$	1110(m), 980(w), 945(s), 870(s), 744(m)
Cu(TMED)(PFP)	1115(s), 1000(w), 940(s), 872(s), 740(m)
$Pt(PMe_2Ph)_2(PFP)$	1110(s), 990(w), 945(s), 870(m), 745(m)

formula, namely, $Ni(L)_2(PFP)$. At no time could a compound of formula $Ni(L)_3(PFP)$ be isolated, even when a threefold excess of phosphine was used. The compounds and their salient physical properties are listed in Table 5. Also, the compounds have a singlet in their ^{19}F nmr spectra in the region expected for CF_3 groups. The molecular weights indicate that the complexes are monomers exhibiting some degree of association except when L ≡ PPh_3, where the considerably low experimental molecular weight is indicative of dissociation.

TABLE 5

Compound	Colour	M.P. (°C)	Mol. Wt. (calc.)	Mag. Mom.
$Ni(PEt_3)_2(PFP)$	orange	181°	651 (627)	diam.
$Ni(PMe_2Ph)_2(PFP)$	orange	132-133°	740 (667)	diam.
$Ni(PMePh_2)_2(PFP)$	orange	172-173°	856 (791)	diam.
$Ni(PPh_3)_2(PFP)$	brick orange	208°	727 (915)	diam.
$Ni(P[OEt]_3)_2(PFP)$	yellow	85-87°	751 (723)	diam.
Ni(diphos)(PFP)	gold	228°	843 (789)	diam.

All the complexes listed are diamagnetic and as such have a square planar structure. For nickel(II) compounds possessing a coordination number of four, either a square planar or a tetrahedral structure is possible, the structure found in practice apparently depending mainly on the strength of the ligand field. In general, a strong field favours a square planar arrangement of the ligands whereas a weak field results in a tetrahedral arrangement (i.e. $NiCl_4^{2-}$), which, considering only ligand-ligand repulsions, is the most stable.

Before discussing the perfluoropinacol complexes further, it is necessary to appreciate the considerable work done in the past on compounds of the type $Ni(PR_3)_2X_2$ where X ≡ Cl^-, Br^-, I^-, NO_3^- and NCS^-, and the phosphine is varied from trialkyl to triaryl. With these tertiary phosphines, octahedral compounds of the type $Ni(PR_3)_4X_2$ are not encountered, no doubt attributable to the bulkiness of the phosphine ligand, although $Ni(PR_3)_3(CN)_2$[36] complexes have been reported. When the phosphorus ligand is a trialkyl- or a dialkyarylphosphine,[37] the resulting metal complex is diamagnetic, usually with a trans square planar structure, whereas with triphenylphosphine, the complexes formed are paramagnetic and tetrahedral in structure.[37,38] With alkyldiarylphosphines,[39,40] however, an intermediate situation is encountered where the square planar and the tetrahedral isomers are of nearly equal energy, and both structures occur. For example,[40] in the series of compounds $Ni(PEtPh_2)_2X_2$ (X ≡ Cl^-, Br^-, I^-), the iodo compound is tetrahedral, the chloro compound is planar and the bromo compound has been isolated with both structural forms. Since all the phosphine complexes with perfluoropinacol are planar in structure, one might initially suppose that perfluoropinacol exhibits a relatively strong ligand field strength. If this is not the case, the alternative explanation would be based on the structural requirements of the bidentate ligand.

With respect to the latter, it is known that perfluoropinacol forms a planar compound of the type $Ni(PFP)_2^{2-}$ and that compounds of the type $Ni(PFP)_3^{4-}$ have not been prepared. Sterically, perfluoropinacol is similar to the substituted diamine C,C,C',C'-tetramethylethylenediamine, which has been found[41] to yield exclusively planar complexes of the type $Ni(diamine)_2^{2+}$. It seems that the bulkiness of the perfluoropinacol can readily explain the preference of the four coordinate planar structure over an octahedral structure but not that of a planar structure over a tetrahedral.

The rationale of the visible absorption spectra of planar Ni^{2+} is even yet not well understood but it is generally agreed that the $d_{x^2-y^2}$ orbital is much higher in energy than the other four orbitals which lie in the order $xy > z^2 > xz,yz$,[42,43] the position of the z^2 orbital being in some doubt. Although some authors attribute the[44,45] single band in the visible spectrum of planar Ni^{2+} complexes to one electronic transition, it is likely that more than one d-d transition lies under this band, a situation which would arise if the xy, z^2, xz and/or yz orbitals were very close in energy. The appearance of a shoulder on the main band in the visible spectra of $Ni(PFP)_2^{2-}$ (Figure 1) supports this premise. As a consequence of the above, the discussion of these spectra will be qualitative in nature.

If we assume that the observed peaks in compounds of the type $Ni(PR_3)_2X_2$ are due to the same transitions, we can place perfluoropinacol in the spectrochemical series, relative to other anionic ligands. Listed in Table 6 are the data from the visible absorption spectra for the various phosphine-perfluoropinacol complexes. All these compounds exhibit one peak in the visible region of the spectrum, with little change on going from solid to solution. Also, there is no change in the spectra of $Ni(PEt_3)_2(PFP)$ or $Ni(PMe_2Ph)_2(PFP)$ in the presence of a five-fold excess of the appropriate phosphine, precluding the possibility of a five-coordinate species being present in solution. The instability of the triphenylphosphine complex in certain solvents has been noted previously[38] for the analogous halide compounds, and is probably due to complete dissociation in polar solvents.

TABLE 6

Compound	Solid	Methanol	Benzene	Acetone
$Ni(PEt_3)_2(PFP)$	460*	461 (254)	460 (230)	461 (242)
$Ni(PMe_2Ph)_2(PFP)$	454	460 (263)	452 (302)	459 (320)
$Ni(PMePh_2)_2(PFP)$	463	466 (270)	464 (316)	467 (348)
$Ni(PPh_3)_2(PFP)$	475	decomp.	477 (274)	decomp.
Ni(Diphos)(PFP)	448	445 (298)	439 (314)	445 (274)
$Ni[P(OEt)_3]_2(PFP)$	417	415 (315)	415 (272)	414 (325)

*nm

For a given series of compounds in which the anionic ligand is varied, it is possible to prepare compounds having a square planar structure and hence to place them in the spectrochemical series. For example, for the complexes of the type $Ni(PEt_3)_2X_2$,[46] where X = I^-, Br^-, Cl^-, SCN^-, the positions of the d-d bands are as follows:

X	I^-	Br^-	Cl^-	SCN^-
λ(nm)	610	542	490	450-525 (sh)

This gives the same series which has been reported exhaustively in the past. The analogous perfluoropinacol complex has a peak at 460 nm (benzene) which gives the following sequence:

$$I^- < Br^- < Cl^- < SCN^- \sim PFP^{2-}$$

Unfortunately, the band for SCN^- appears as a shoulder and thus it is not possible to tell with certainty whether PFP^{2-} is above or below SCN^- in the spectrochemical series.

Of all the anionic ligands listed above, only SCN^- gives exclusively square planar complexes, irrespective of the nature of the phosphine. This is attributed to the increased crystal field splitting of SCN^- relative to Cl^-, Br^- and I^-. Perfluoropinacol fits into this scheme of thought since it also gives exclusively square planar complexes and has a crystal field splitting energy comparable to SCN^-. It is noteworthy that, whereas all the planar compounds with monodentate anionic ligands have a trans geometry, thereby minimizing steric interaction between the bulky phosphine groups, this is not so with the perfluoropinacol complexes. Evidently, the energy gained through the increased crystal field splitting energy of the perfluoropinacol offsets that which would have been gained by the minimization of steric interaction in a tetrahedral structure.

Just as the relative ordering of the anionic ligands in the spectrochemical series can be determined, the same can be done with the neutral phosphine ligands, as shown below.

$$PPh_3 < PMePh_2 \sim PMe_2Ph \sim PEt_3 < \text{diphos} < P(OEt)_3$$

Surprisingly, there is very little difference on going from PEt_3 to $PMePh_2$ in spite of the decreased basicity and increased steric requirements of the latter ligand.

Attempts to prepare the complexes $Pt(PFP)_2^{2-}$ and $Pd(PFP)_2^{2-}$ were unsuccessful, which is not surprising considering that PFP^{2-} is a "hard" ligand and Pd^{2+} and Pt^{2+} are "soft" metals. However, we were able to prepare $Pd(PMe_2Ph)_2(PFP)$ and $Pt(PMe_2Ph)_2(PFP)$ from the corresponding dichloro complexes. Although hydrocarbon alkoxides are unusual with Pd^{2+} and Pt^{2+},[47] numerous examples of fluorinated alkoxides are known. Stone et al.[48] have prepared $Pd(PEt_3)_2(PFP)$ by the reaction of $Pd(PEt_3)_2Me$ with H_2PFP while Hayward and Nyman[49] have prepared $\overline{PtOC(CF_3)_2O}(PPh_3)_2$, a Pt^{2+} derivative of hexafluoropropane-2,3-diol. Since our method of preparation involves a one step synthesis from the readily available dihalide compounds, no doubt a variety of phosphine-PFP^{2-} and diamine-PFP^{2-} complexes of Pt^{2+} and Pd^{2+} are easily accessible.

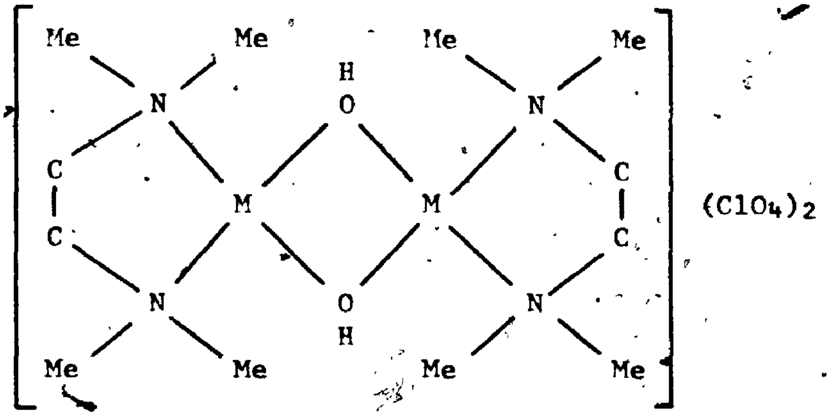
E. Square Planar Nickel(II) and Copper(II) Complexes with Nitrogen Donor Atoms

It was expected that mixed ligand complexes of perfluoropinacol with nitrogen donor atoms in the secondary ligand could also be prepared but attempts to prepare nickel complexes with ligands of the type NR_3 (where R ≡ H, Et, or n-butyl) resulted merely in the salts of the planar bis-perfluoropinacol nickel complexes of the type $(NR_3H)_2^{+2}-Ni(PFP)_2^{2-}$. The potential ligand here acts solely as a base. The fact that tertiary aliphatic amines are almost devoid of an ability to coordinate has been noted elsewhere[50] and rationalized on steric grounds. It also became known at this time that ethylenediamine formed a mixture of complexes whose separation and identification proved to be problematic.[33]

The use of N-substituted ethylenediamines was then considered. Two opposing effects can be expected on N-alkyl substitution of ethylenediamine, namely an increased basicity of the donor nitrogen due to the inductive effect of the substituent plus an increased steric effect. The first effect could produce the problem that occurred with the trialkyl amines, and indeed this problem was observed with tetrafluorocatechol[29] and hydroxyhexafluoroisobutyric[31] acid where the compounds $[H_2TMED]^{2+}[Cu(TFC)_2]^{2-}$ and $[H_2TMED]^{2+}[Cu(HHIB)_2]^{2-}$ respectively were prepared. However, the steric restrictions imposed by nitrogen substitution should reduce the possibility of complex mixtures, and simplify the type of compounds prepared. Indeed, it has been found that although ethylenediamine and N-methylethylenediamine form tris complexes with $RhCl_3$, further substitution results in trans-dichloro bis chelates, even in the presence of excess ligand.[51]

With perfluoropinacol, we find that complexes of the type Ni(diamine)(PFP) readily form with various N,N,N',N'-substituted diamines. Only one molecule of diamine chelates, even when an excess is used, and no tendency to form amine salts was detected, no doubt reflecting the higher acidity of perfluoropinacol versus tetrafluorocatechol or hydroxyhexafluoroisobutyric acid. Mixed ligand complexes have been prepared with the substituted diamines tetramethylethylenediamine, tetraethylethylenediamine and N,N'-dimethyl-N,N'-dibenzylethylenediamine as well as with dipyridyl. These complexes are diamagnetic, exhibit a single peak in their visible spectra and have been assigned a square planar structure. Although the ^{19}F nmr spectra exhibited a singlet for the symmetrical diamines, the dimethyldibenzyl-pinacol complex exhibited a complex multiplet. Two isomers are possible with this ligand, but attempts to detect their presence by fractional recrystallization and TLC were unsuccessful. Also, the complex had a sharp melting point. It was concluded that only one isomer was present and that the complex multiplet in the ^{19}F nmr spectrum was due to the presence of magnetically different CF_3 groups.

With respect to the Ni(TMED)(PFP) complex, previous workers have spent considerable time trying to prepare the bis complex of the type $Ni(TMED)_2^{2+}$. Meek[52,53] and co-workers have easily prepared $Pd(TMED)_2Cl_2$ but were unable to synthesize the analogous Ni^{2+} and Cu^{2+} complexes, getting instead the dinuclear species shown below. They



suggest that the central metal ion must be of a certain critical size before bis complexes can be prepared.

Contrary to the above results, Baldwin and Leigh[45] have been successful in preparing bis complexes and they attribute their success to the use of weakly co-ordinating solvents and anion, i.e. perchlorate. Compounds of the type $Ni(TMED)X_2$ have been prepared when a non-co-ordinating solvent is used but a co-ordinating anion is present. We have found that Ni(TMED)(PFP) can readily be prepared in aqueous solution in the presence of either Cl^- or NO_3^-, which is indicative of the greater co-ordinating ability of PFP^{2-} over OH^-, Cl^- or NO_3^-. The inability to prepare $Ni(TMED)_2(PFP)$, even in the presence of an excess of diamine, is obviously due to interligand interactions.

The halide analogues of these diamines, of the type $Ni(TMED)X_2$ have been known for some time.[54] Whereas the phosphine-halide compounds generally have tetrahedral and/or square planar structures, the diamine-halide complexes, of empirical formula Ni(TMED)X_2, are either tetrahedral or octahedral, the latter being achieved via halide bridges. The preference of Ni(TMED)(PFP) for a planar rather than a tetrahedral structure is consistent with PFP^{2-}'s greater ligand field strength over two halide ligands, whereas the occurrence of an octahedral structure via bridging PFP^{2-}'s is not likely. The persistence of the planar geometry even with bulkier substituents on the nitrogen atoms rules out steric factors as being of importance. Similarly Ni(bipy)(PFP) is square planar while the analogous chloride compound is octahedral through halide bridging.[55a] Also, while Ni(bipy)$_2$Cl$_2$,[55b] an octahedral monomer, is readily prepared, Ni(bipy)(PFP) does not take up an additional ligand to give Ni(bipy)$_2$(PFP), due to the bulkiness of PFP^{2-}. While a planar structure for Ni(bipy)(PFP) is consistent with the greater ligand field strength of PFP^{2-}, the steric requirements of the diamine ligand, bipy, could also be a factor.

A rather interesting series of compounds, of the type $Ni(TMED)(L)^{+1}$ where L ≡ acetylacetonate (acac) or benzoylacetonate (bzacac), have been reported by Fukuda and Sone.[56] With an anion of poor coordinating ability as the counter ion, the compounds are red, diamagnetic and square planar. However, the compounds change from red (inert solvent and/or high temperature) to blue (coordinating solvent and/ or low temperature) and this behaviour has been attributed to an equilibrium of the type:

$$\underset{\text{Red}}{Ni(TMED)(acac)} + 2(S) \rightleftharpoons \underset{\text{Blue}}{Ni(TMED)(acac)S_2}$$

Such behaviour has not been observed for the tetra-alkyl diamine complexes we have studied and we conclude that this is a direct consequence of the greater steric requirements of PFP^{2-} over acac.

As with the Ni^{2+} complexes of TMED, Meek and Ehrhardt[53] have prepared the dimeric hydroxy compound (TMED)Cu$(OH)_2$Cu(TMED) but were unable to prepare a bis-chelate compound. Bertini and Mani[57] have prepared Cu(TMED)Cl_2 and Cu(TMED)Br_2 to which they have assigned a planar structure based on their visible spectra. We have prepared the complexes Cu(TMED)(PFP) and Cu(TEED)(PFP), which have magnetic moments of 1.85 and 1.87 B.M. respectively and infrared spectra consistent with the presence of cyclic PFP^{2-}. The visible spectra of both compounds have a broad band at ∿ 550 nm which does not shift on changing solvents from CH_2Cl_2 to CH_3OH, eliminating the possibility of axial coordination with the latter solvent. The ability to prepare complexes of this nature while M$(TMED)_2^{2+}$ cannot be prepared is no doubt due in part to the absence of bulky substituents on the oxygen donor atoms. In fact, a series of such mixed ligand complexes have been prepared by Fukuda and Sone,[58] with ethylenediamine (en), oxalate (ox), glycinate (gly), and acetylacetonate (acac) as the secondary ligands and they attribute the formation of these to the lack of bulky groups around the donor atoms of the secondary ligand. Data from the visible spectra (solid) of the above compounds are listed in Table 7, confirming PFP^{2-}'s position in the spectrochemical series.

F. Five-Coordinate Nickel(II) Complexes

The visible absorption spectra of Ni(TMED)(PFP) did not show any particular solvent effects, nor did those of the phosphine complexes. However, the colour of solutions of Ni$(PFP)_2^{2-}$ was very solvent-dependent,

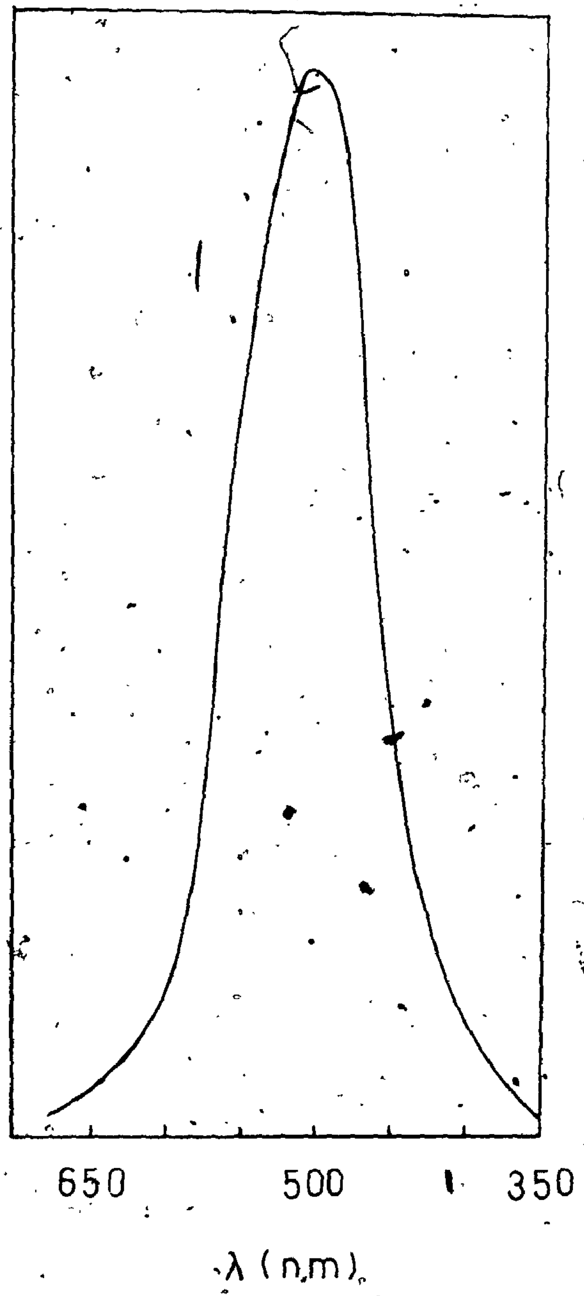
TABLE 7

Compound	λ max (cm^{-1})
$[Cu(TMED)en]^{2+}$	18,180
$[Cu(TMED)acac]^{+1}$	17,640
Cu(TMED)(PFP)	16,700
$[Cu(TMED)(gly)]^{+1}$	16,210
$Cu(TMED)Cl_2$	15,000
$Cu(TMED)Br_2$	14,500
$(Cu(TMED)(OX)]\cdot 4H_2O$	14,030

being yellow in water and purple in anhydrous methanol; the latter solution went yellow on cooling, showing thermochroic behaviour similar to that reported by Fukada and Sone[56] for compounds of the type $Ni(TMED)(acac)^{+1}$. This behaviour suggested that coordination of solvent molecules was occurring with some PFP^{2-} complexes of nickel, but was prevented in others by steric hindrance, e.g. with tetra-N-substituted diamines. In order to investigate this further, we prepared complexes of the less hindered N,N'-diethylethylenediamine (N,N'-diethen) and N,N'-dibenzylethylenediamine (N,N'-dibenzen).

These compounds are red crystalline solids whose visible spectra in CH_2Cl_2 (Figure 5) have a single peak at ∿ 500 nm, similar to those of the previously discussed square planar Ni^{2+} compounds. However, in coordinating solvents, the spectra are entirely different, as illustrated in Figures 6 and 7. Solutions of the complexes in DMF are reddish brown at room temperature but turn bright green on cooling,

FIGURE 5



Visible Absorption Spectrum [CH_2Cl_2 solution] of Ni(N,N'-diethen)(PFP)

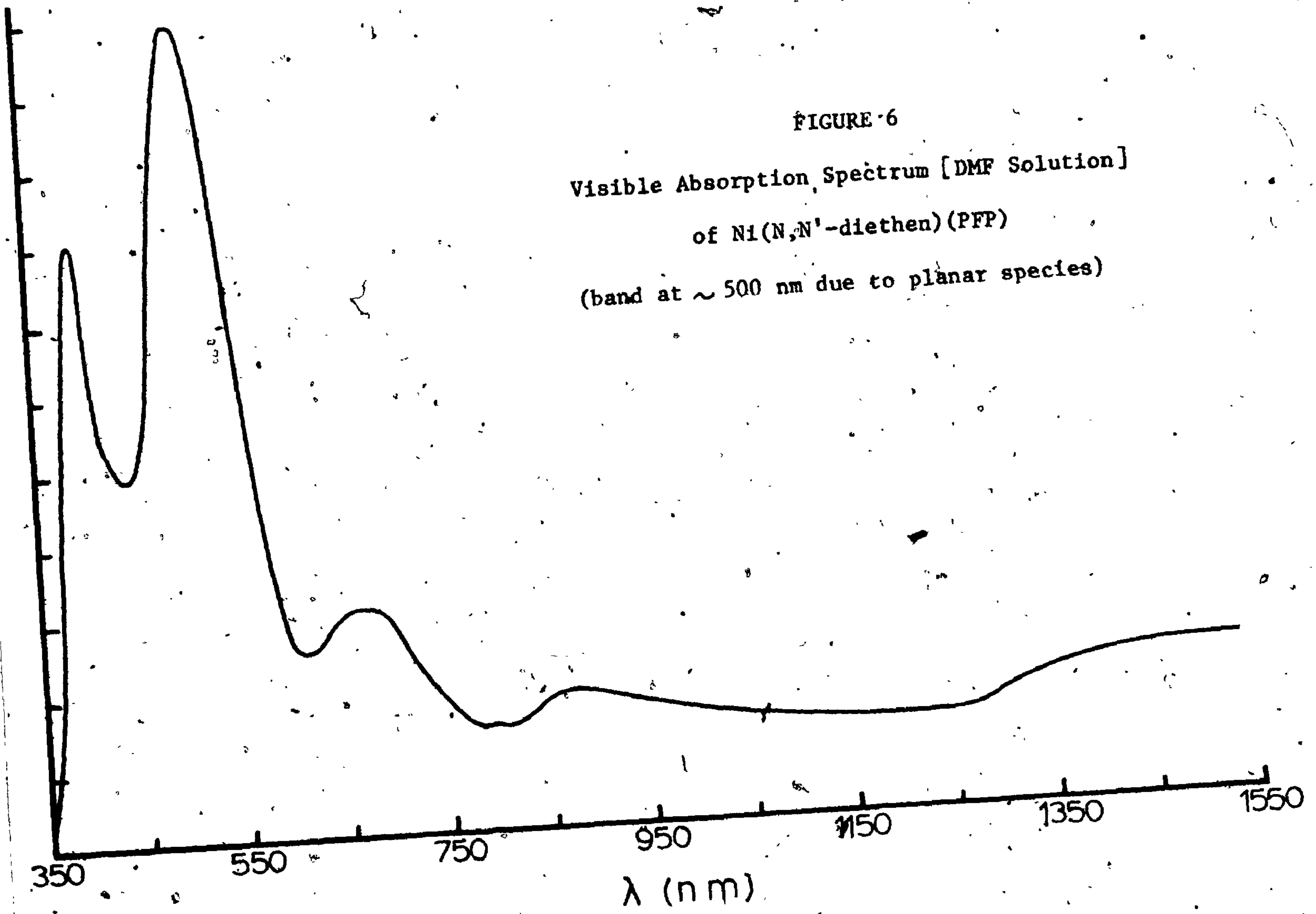


FIGURE 6

Visible Absorption Spectrum [DMF Solution]

of Ni(N,N'-diethen)(PFP)

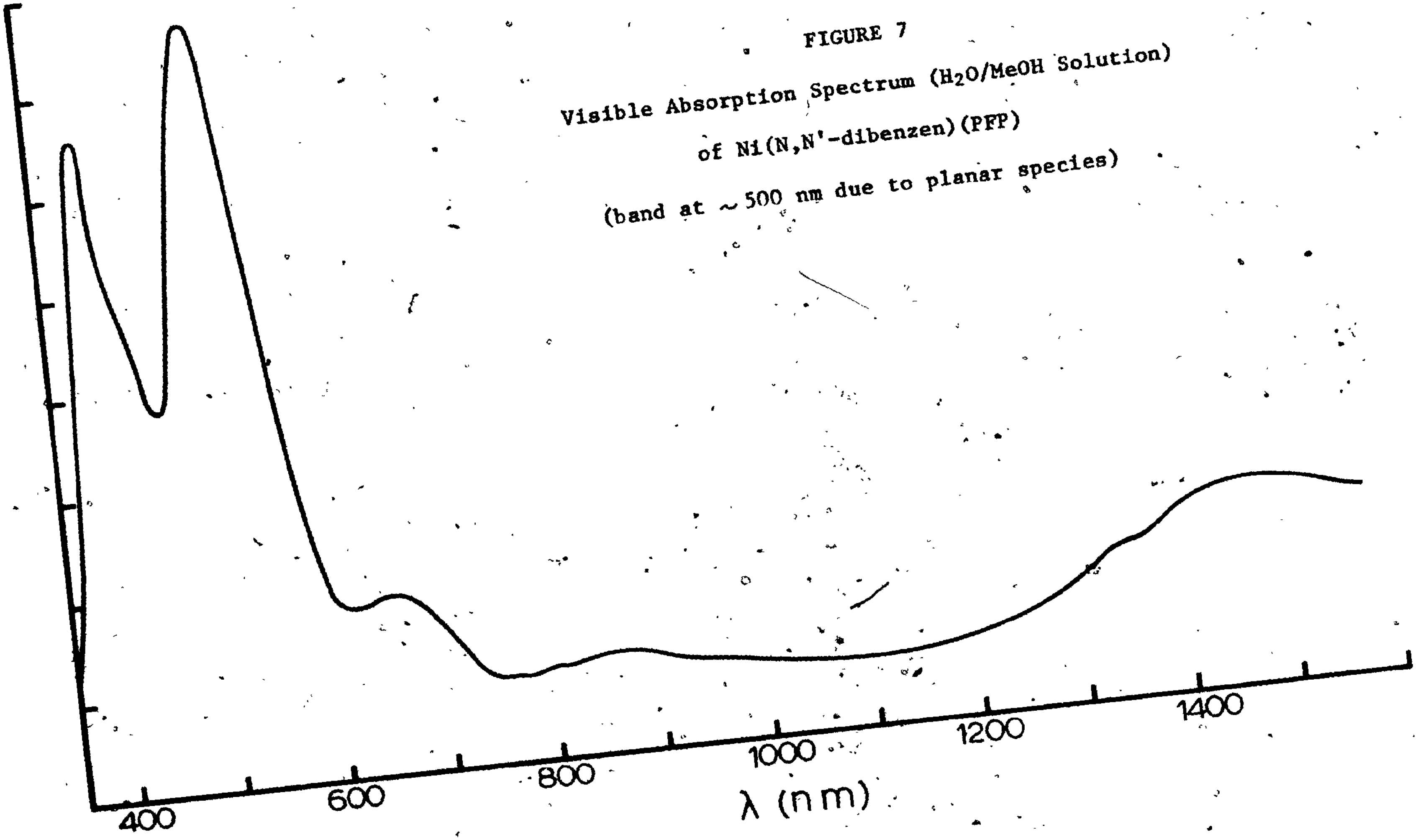
(band at ~ 500 nm due to planar species)

FIGURE 7

Visible Absorption Spectrum (H_2O/MeOH Solution)

of Ni(N,N'-dibenzen)(PFP)

(band at ~ 500 nm due to planar species)



whereas water/methanol solutions, which are green at room temperature, turn bright red on heating. The complexes are bright green on recrystallization from water/methanol solutions but are readily converted to the red modification under vacuum or on heating.

A comparison of the spectra of $K_2Ni(PFP)_2$ with those of the disubstituted diamine complexes, coupled with their similar thermochroic behaviour in solution, suggests that the same process in solution is responsible for the observed anomalies. With the latter compounds, their better solubility characteristics plus their stability in coordinating solvents enabled a detailed study to be made of these systems.

In order to ascertain whether more than two species were present in solution, visible spectra of Ni(N,N'-dibenzen)(PFP) were recorded in a series of methanol/water mixtures. The results, illustrated in Figure 8, show the presence of two isosbestic points, indicative of the presence of only two species in solution, one of which is the planar compound whose relative abundance decreases as water concentration increases. Similar spectra have been obtained with CH_2Cl_2/pyridine mixtures (Figure 9).

Although the solution behaviour is suggestive of a solute-solvent interaction similar to the well known square planar-octahedral equilibrium of the type:[34,56]

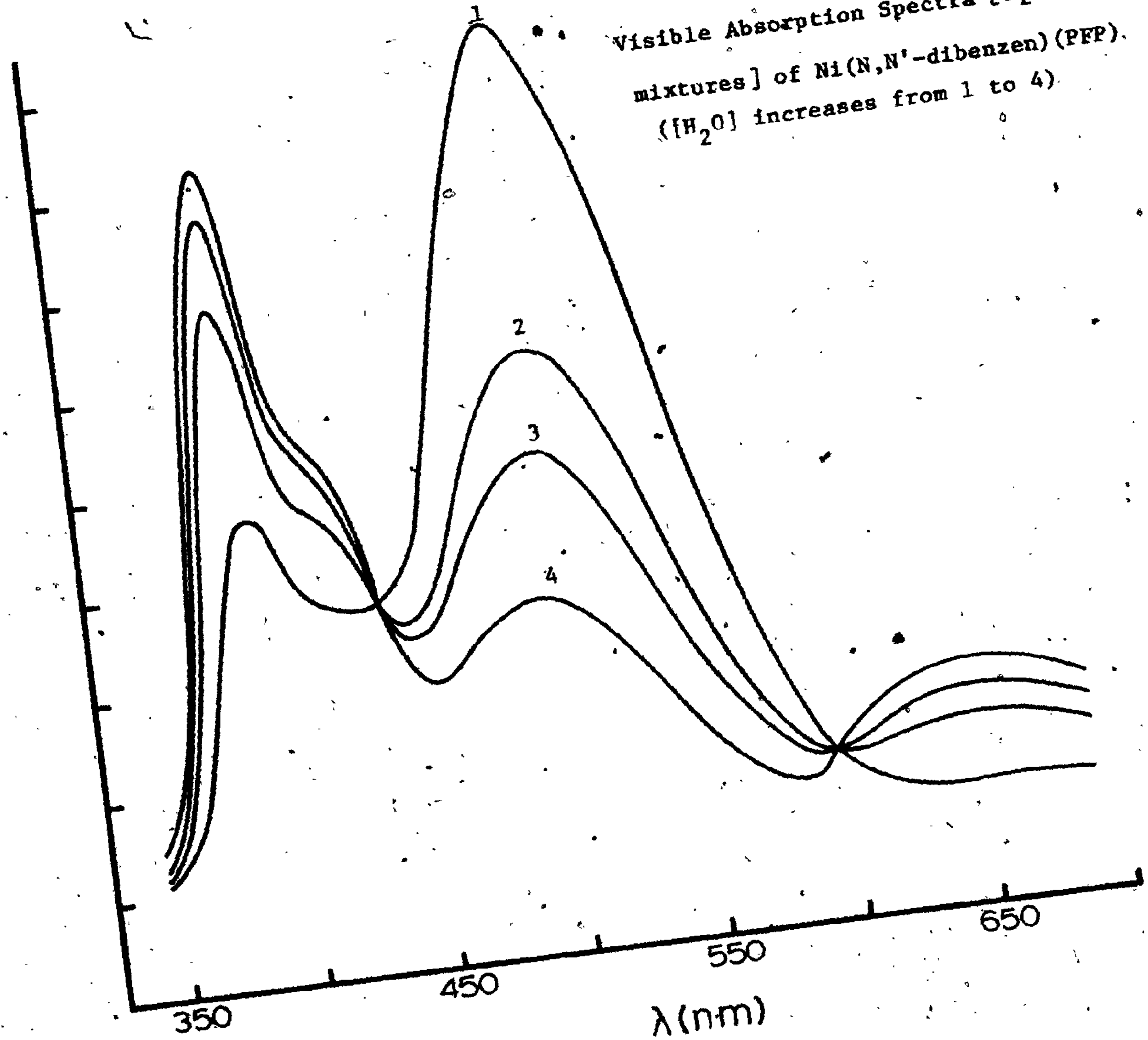
$$\underset{\text{square planar}}{NiL_4 + 2L'} \rightleftharpoons \underset{\text{octahedral}}{NiL_4L'_2}$$

the visible spectra bear no resemblance to those expected for octahedral Ni^{2+} complexes. It appears that the process occurring in solution is similar to the above but with only one additional ligand coordinating to

FIGURE 8

Visible Absorption Spectra [H_2O/MeOH mixtures] of Ni(N,N'-dibenzen)(PFP)

([H_2O] increases from 1 to 4)



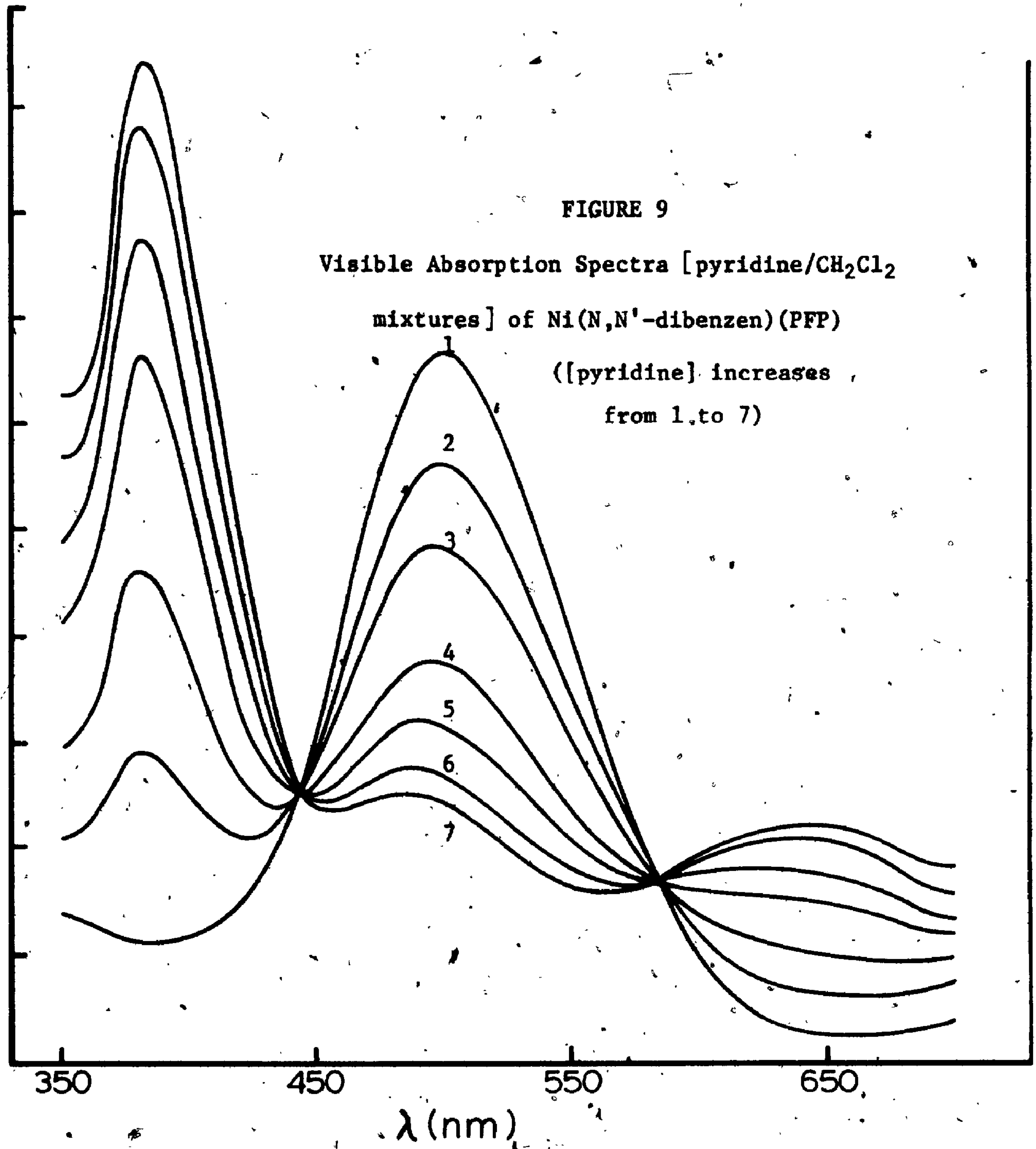


FIGURE 9

Visible Absorption Spectra [pyridine/CH_2Cl_2 mixtures] of Ni(N,N'-dibenzen)(PFP)

([pyridine] increases from 1 to 7)

give a five-coordinate species.

$$\underset{\text{square planar}}{\text{Ni(N,N'-dibenzen)}} + \text{L'} \rightleftharpoons \underset{\text{5-coordinate}}{\text{Ni(N,N'-dibenzen)(PFP)L'}}$$

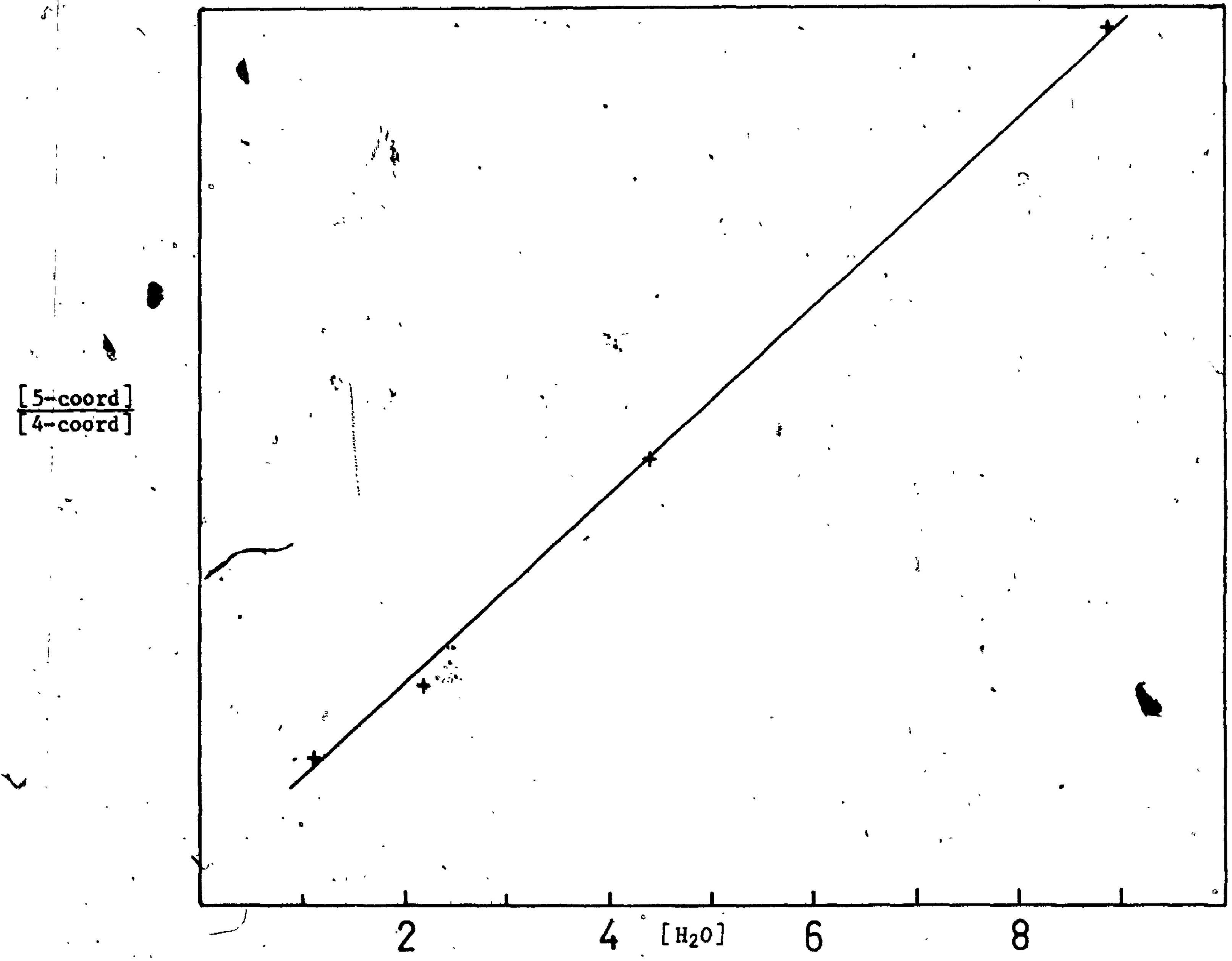
The equilibrium constant for the above is:

$$k = \frac{[\text{5-coord}]}{[\text{4-coord}][\text{L'}]} \quad \text{or} \quad k[\text{L'}] = \frac{[\text{5-coord}]}{[\text{4-coord}]}$$

and if this is indeed the process occurring, a plot of [L'] versus the ratio of 5-coordinate/4-coordinate species should produce a straight line, the ratios being easily calculated from the absorbance of each species at a suitable wavelength, where overlap of the absorption curves of the two species does not occur to any appreciable extent. Such a plot does produce such a straight line (Figure 10), in agreement with the process depicted above. Unfortunately, except when H_2O is the adduct, these postulated five-coordinate species have not yet been isolated. With benzylamine, the visible spectrum (Figure 11) clearly indicates that the suggested five-coordinate species is present in solution, but only a dark green intractable oil has been obtained to date by evaporation. Phenethylamine, pyridine (Figure.9) and n-butylamine exhibit a similar behaviour to the above, triethylamine shows no evidence of interaction while triethylphosphine does not give a stable 5-coordinate species, but merely displaces the diamine to yield $Ni(PEt_3)_2(PFP)$. Preliminary experiments indicate that anionic complexes of the type $[Ni(diamine)(PFP)X]^{-1}$ (where $X = SCN^-$) form in solution which may be isolable but further research is required in this area.

Although the previous results clearly suggest an

FIGURE 10: Plot of [H_2O] versus ratio of [5-coordinate]/[4-coordinate] species for Ni(N,N'-dibenzen)(PFP) MeOH



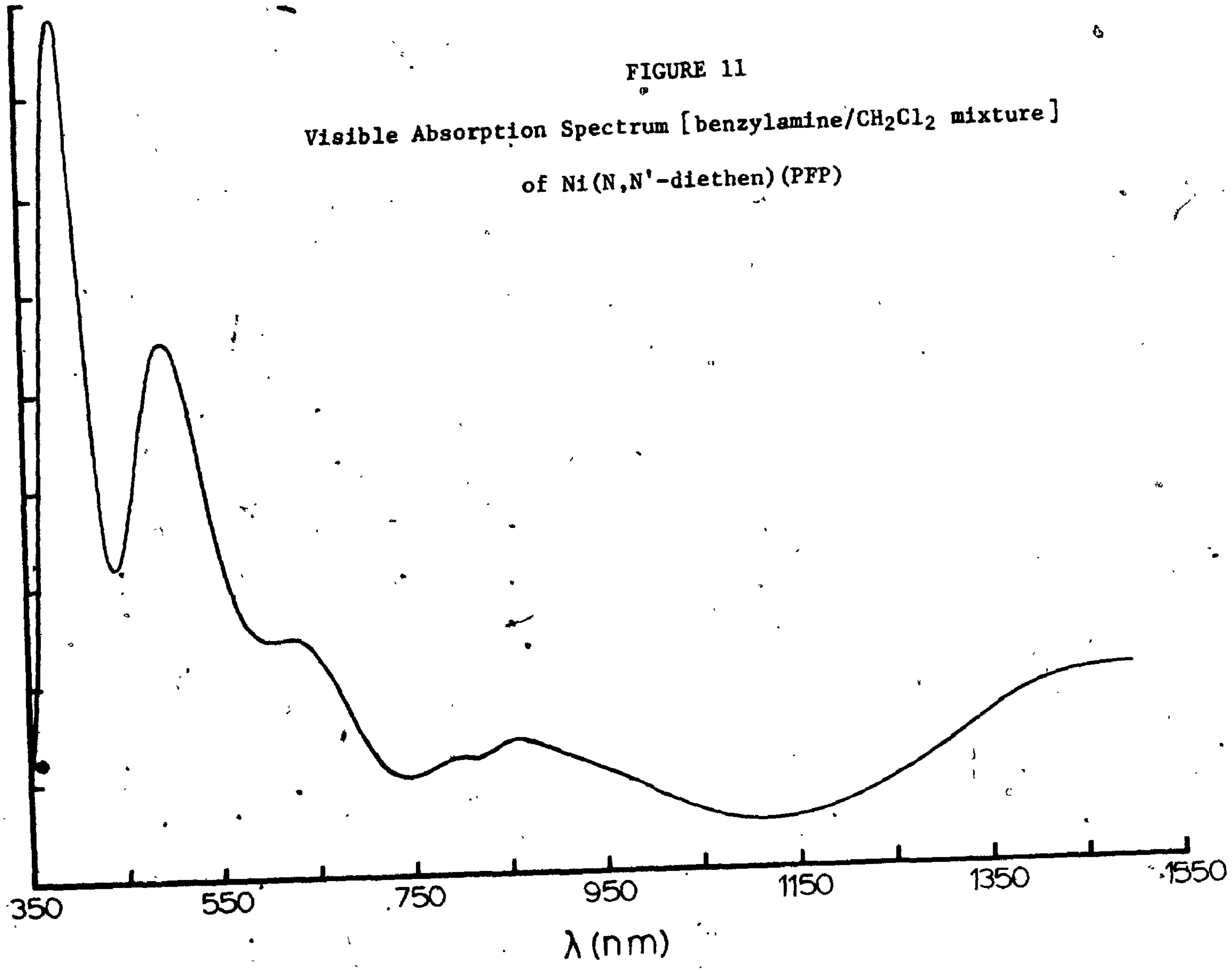


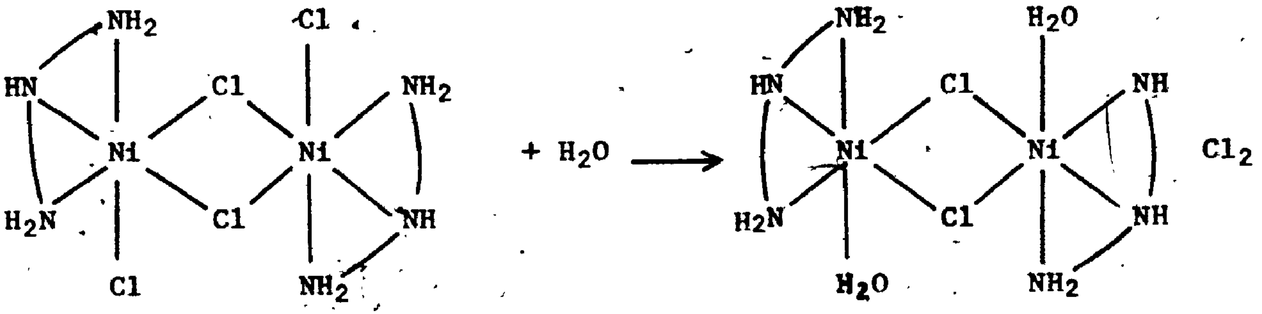
FIGURE 11

Visible Absorption Spectrum [benzylamine/CH_2Cl_2 mixture]

of Ni(N,N'-diethen)(PFP)

equilibrium between four- and five-coordinate species, we considered it important to attempt to isolate such a compound, since such solution behaviour is unusual, and five-coordinate species are usually unstable with respect to disproportionation to four- and six-coordinate species. Five-coordinate Ni^{2+} compounds are generally the result of steric requirements of the ligand which prevent occupation of the sixth coordination site. It was therefore decided to prepare a five-coordinate compound with PFP^{2-} and a potentially terdentate ligand which normally does not form five-coordinate Ni^{2+} complexes.

The ligand choosen was diethylenetriamine (DETA). This triamine readily forms octahedral compounds of the type $Ni(DETA)_2^{2+}$.[59,60] For the dichloro complex with the stoichiometry $Ni(DETA)Cl_2$, a dimer is formed via bridging chloride atoms,[61] which readily absorbs a mole of water that is incorporated into the coordination sphere, as shown below.



It is only the increased steric requirements introduced with N-methylated[62] triamines that produce five-coordinate complexes and it was anticipated that the bulky PFP^{2-} would preclude the necessity of methylating DETA.

It was indeed possible to prepare a complex of empirical formula Ni(DETA)(PFP) which has a magnetic moment of 3.14 B.M., normal for high spin five-coordinate Ni^{2+} compounds with oxygen and/or nitrogen donor atoms. The complex was a non-electrolyte in methanol eliminating the possibility of the complex salt $[Ni(PFP)_2]^{2-}$ $[Ni(DETA)_2]^{2+}$, and had no peaks in the infrared spectrum attributable to H_2O, eliminating the possibility that the sixth coordination site was thus occupied. The visible spectrum was the same in the solid state and in solution (Figure 12) and was almost identical to those of the postulated five-coordinate species.

A comparison of the visible spectrum of Ni(DETA)(PFP) with those reported for a series of five-coordinate complexes with the quadridentate ligand tris(2-dimethylaminoethyl)amine, [trenMe],[63,64] of the type [M(trenMe)X]X (where X ≡ Cl^-, Br^-, I^-, NO^-, ClO_4^-) shows that these spectra are virtually superimposable. This confirms that Ni(DETA)(PFP), as well as the adducts formed with $Ni(PFP)_2^{2-}$, Ni(N,N'-dibenzen)(PFP) and Ni(N,N'-diethen)(PFP) are 5-coordinate compounds. The salient features of the visible spectra of Ni(DETA)(PFP) and [Ni(TrenMe)Cl]Cl are listed in Table 8.

The Ni^{2+} complexes of trenMe have been shown to be trigonal bypyramidal by X-ray crystallography[65] and although Ni(DETA)(PFP) could conceivably have a distorted trigonal bypyramid structure, it is most likely that the adducts, at least, have a square pyramidal structure. On the basis of charge repulsions, it has been calculated that a square pyramidal structure, with the central metal ion above the basal plane, is only slightly less stable than a trigonal bypyramid structure and in fact, displacement of the Ni^{2+} atom above the basal plane is a common feature with this structure.[66] Molecular models indicate that a folding down of a PFP^{2-} ligand would allow a fifth ligand into the coordination sphere, effectively block the sixth coordination site, and lead to a distorted square pyramidal structure

FIGURE 12

Visible Absorption Spectrum (MeOH Solution) of Ni(DETA)(PFP)

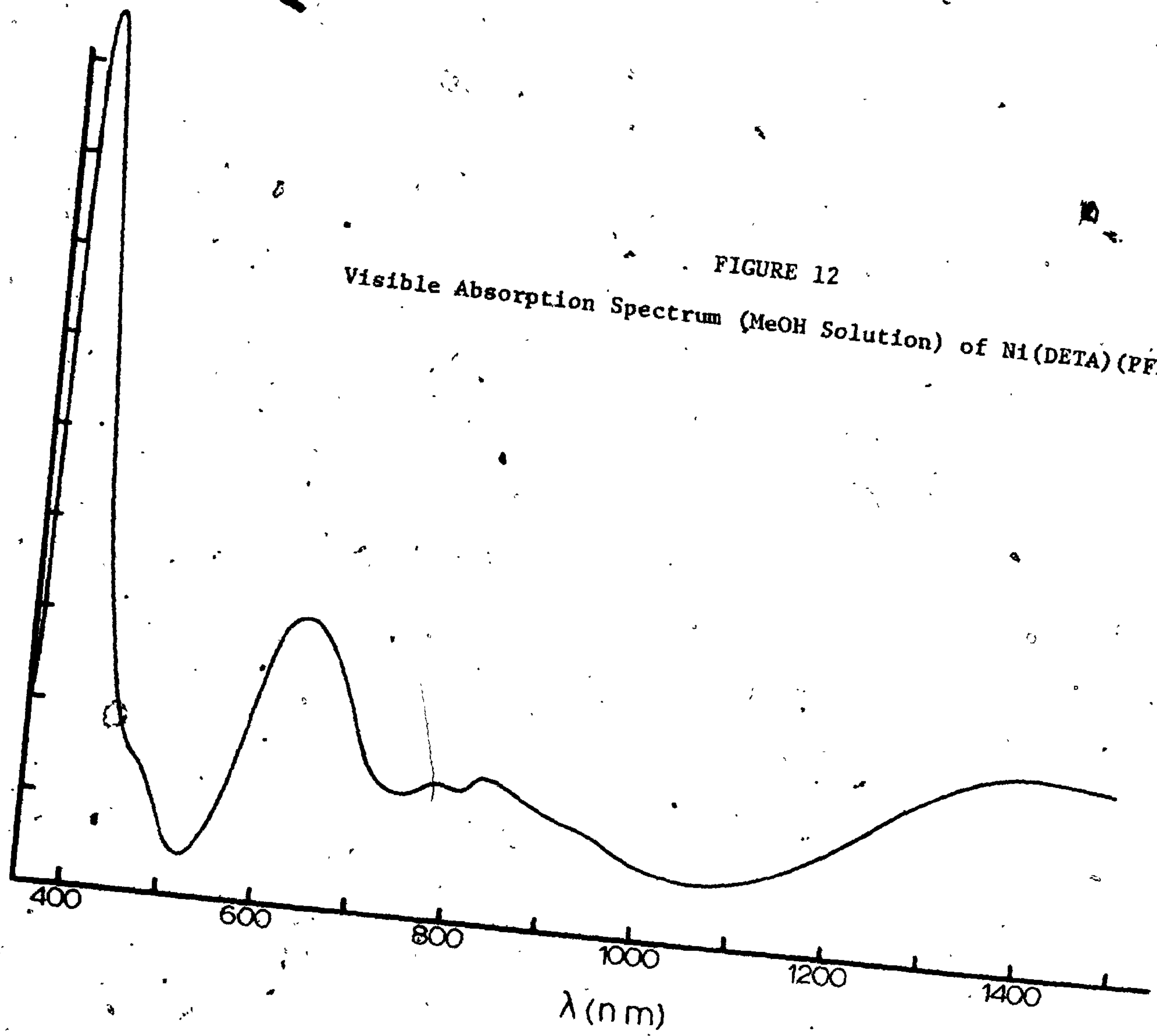
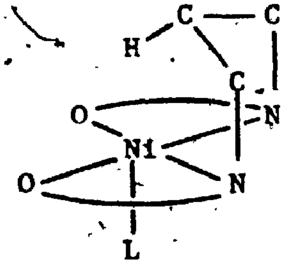


TABLE 8

Visible Spectra of Ni(DETA)PFP and [Ni(trenMe)Cl]Cl

Ni(DETA)(PFP)		[Ni(trenMe)Cl]Cl	
λ(cm^{-1})	λ(cm^{-1})	λ(cm^{-1})	λ(cm^{-1})
(MeOH solution)	(Solid)	($CHCl_3$ solution)	(Solid)
6,900 (15)	< 10,000	7,100 (26)	7,100
11,900 (12)	11,900	10,900 (22)	10,700
12,800 (10)	12,800	11,600 (19)	11,500 (sh)
15,700 (20)	15,700	14,900 (30)	14,600
21,200 (sh)	21,500	20,600 (sh)	20,000 (sh)
26,200 (65)	26,300	23,500 (172)	23,300

with the central metal above the basal plane. This is somewhat similar to a situation encountered by Legg and co-workers[67,68] with the tetradentate ligand, 1,5-diazacyclooctane-N,N'-diacetate [dacoda] in which an alkyl proton blocks the sixth coordination site, resulting in a five-coordinate square pyramidal complex with H_2O occupying the fifth coordination site, i.e.



[Ni(dacoda)H_2O]

The visible spectrum of [Ni(dacoda)H_2O] is similar to those we have observed, the main features being an intense band at $\sim$ 400 nm coupled with a multiple of less intense bands at lower energy (650-900 nm). Thus, it is certain that the unusual behaviour exhibited by these compounds in solution is due to a rather uncommon equilibrium between four- and five-coordinate species, which results from the steric requirements of the ligands involved.

PART II

PERFLUORO-2,3-DIPHENYLBUTANE-2,3-DIOL AND ITS METAL COMPLEXES

INTRODUCTION

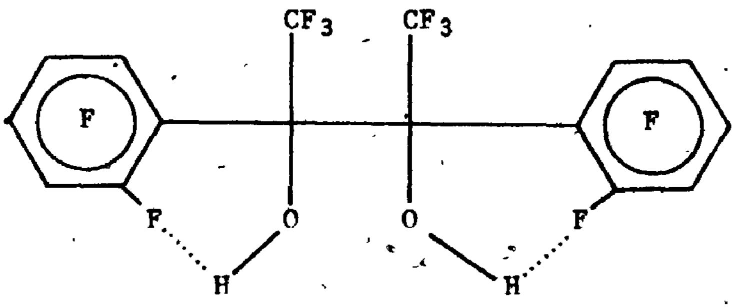
The compound perfluoro-2,3-diphenylbutane-2,3-diol was first prepared by Price et al.[69] This diol was of interest primarily because it was a perfluoro tertiary diol which could potentially act as a di-negative chelating ligand. However, attempted preparations of metal complexes with this ligand at that time were unsuccessful. Also, its ^{19}F nmr was unusual because the aryl fluorines were apparently magnetically non-equivalent.[70]

It was decided to reinvestigate this ligand for the following reasons:

i) Theoretically, racemic (rac) and/or meso isomers could be produced in the reaction, introducing the problem of isomer identification and resolution, if indeed the active form were produced.

ii) Previous attempts at the formation of transition metal complexes with this ligand were oriented towards preparing bis- and tris-chelate compounds similar to those reported for perfluoropinacol.[27] Because, as has been discussed in Part I, H_2PFP readily forms mixed ligand complexes, it was believed that the complexation of this ligand could be achieved in a similar manner. It was hoped that this approach would provide some indication of whether other fluorinated diols are capable of behaving as bidentate di-negative ligands or whether H_2PFP is unusual in this respect.

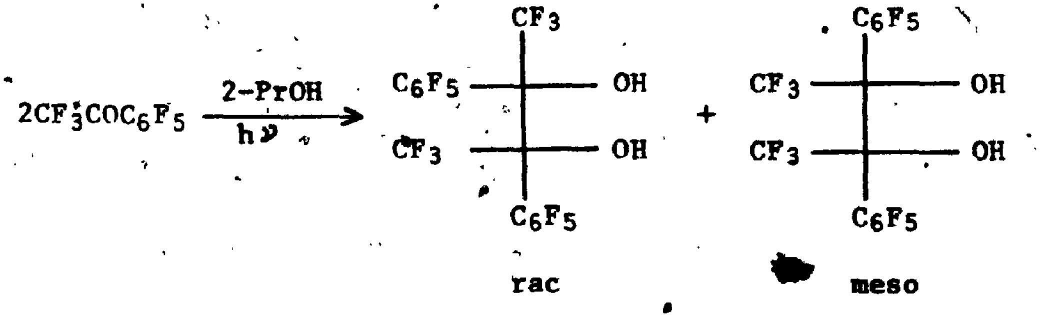
iii) The explanation of the ^{19}F nmr spectra was based on the following model in which hydrogen bonding was invoked to explain the non-equivalence of the aryl fluorines. Since alternative explanations for the observed spectra are possible, a further investigation of this aspect was undertaken.



RESULTS AND DISCUSSION

A. Investigation of the Ligand System

The C_6F_5-diol was prepared by the photolytic reduction of octafluoroacetophenone in the presence of isopropanol. Attempts to prepare the diol via the triethyl phosphorane intermediate failed to give any product, contrary to previous work.[70] Fractional recrystallization of the reaction products indicated that two isomers were present, one with a melting point of 119-120°C (meso) and another with a melting point



of 129-130°C (rac)*. Although two isomers are present, this is not the reason for the complex nature of the ^{19}F nmr spectra, as previously suggested.[69] This point will be discussed in detail further on.

~~Elemental analysis~~ indicated that both compounds had the same empirical formula, $C_{16}H_2F_{16}O_2$. Molecular weights in benzene of 535 (meso) and 543 (rac) agree quite well with the theoretical value for the diol of 530. Although the molecular ion peak did not appear in the virtually identical mass spectra of the two isomers, the major peaks observed are consistent with the assigned structures. There are apparently two major routes in the fragmentation of these compounds, namely, the loss of HF, CF_3, etc. from the parent ion and the cleavage of the dimer, which manifests itself in a very intense peak at m/e of 265. This latter route is quite characteristic of fluorinated and partially fluorinated diols, having been observed in perfluoropinacol[71] as well as the other diols studied in this project.

The pK_a's of the two diols were measured in a 50:50 water/ethanol mixture and although these values cannot be directly compared to pK_a's determined in aqueous solution, they do enable a comparison of the relative acid strengths of various diols determined in the same solvent system. As expected, based on purely inductive effects, the pK_a of perfluoropinacol ($pK_a = 6.5$) is greater than those of the isomeric C_6F_5-diols [pK_a(rac) = 9.1; pK_a(meso) = 8.7] which differed from each other. If we were to invoke the argument used by Middleton and Lindsey[16] to explain the "abnormal" acidity of perfluoropinacol, namely stabilization of the anion through hydrogen bonding, to rationalize the observed

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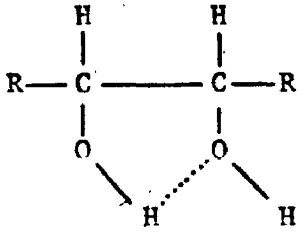
*The two forms are so designated for convenience, their identification being described subsequently.

difference, we would erroneously conclude that the racemic should be more acidic than the meso diol. This is based on the fact that the steric interaction for the meso isomer in this conformation would be greater than for the racemic which should therefore have the lower pK_a. The only other apparent reason for this difference is a greater stabilization of the meso anion over the racemic anion through hydrogen bonding with the solvent.

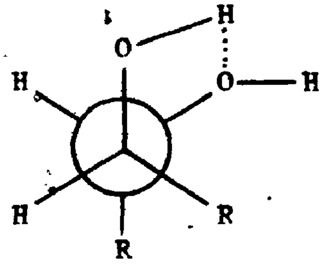
The infrared spectra (nujol mulls) of the two isomers were almost identical. Both compounds exhibited strong peaks above 3600 cm^{-1} [3640 cm^{-1} (meso) and 3627 cm^{-1} (rac)] in their infrared spectra indicative of free OH stretching modes. For a series of unfluorinated 1:2 diols, the free OH band occurs at 3630 ± 5 cm^{-1}.[72] Ring skeletal modes characteristic of the C_6F_5 group were present at 1651 cm^{-1} and 1534 cm^{-1} for the meso compound and at 1654 cm^{-1} and 1535 cm^{-1} for the rac compound. The infrared spectra of the two diastereoisomers contained strong bands in the 1100-1300 cm^{-1} region, characteristic of CF_3 symmetric and asymmetric stretching modes. The major distinguishing feature in their infrared spectra occurs in the 1000 cm^{-1} region. The meso isomer has two sharp bands at 995 and 945 cm^{-1}, while the racemic isomer has a strong, broad, poorly resolved doublet at ∿ 1010 and ∿ 990 cm^{-1}. While these bands are possibly due to an aryl-F or a C-O stretch and the differences a reflection of the two alternative configurations of the isomers, the complexity of the system prevents an identification of the isomers. These differences do, however, give a good indication of the purity of the individual isomers.

The infrared spectra of the two isomers, recorded in a non-polar solvent (CCl_4), exhibit an intense peak above 3600 cm^{-1} (3610 cm^{-1}

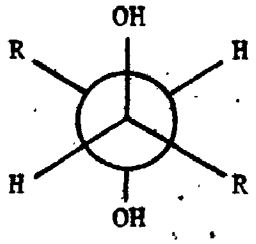
[rac] and 3625 cm^{-1} [meso]) due to free hydroxyl and a broad band at ∿ 3200 cm^{-1} due to intermolecular hydrogen bonding. Kuhn[73] has studied a series of 1,2-diols, some of which possess two OH bands, one due to a free hydroxyl and the other to intramolecular hydrogen bonding, and he suggests that the following structure exists in solution.



For those compounds where two configurations are possible, he finds that the difference between free and intramolecularly bonded hydroxyl peaks is a reflection of the configuration, rac-diols being capable of forming stronger hydrogen bonds and thus exhibit a larger difference in stretching frequencies between the bonded and unbonded species. For the rac-diol, he observes two peaks even with R = t-butyl ($\Delta\upsilon$ = 94 cm^{-1}) but the meso-diol has only one peak due to the free OH when R = t-butyl, due to the fact that the hydroxyl groups are in an anti position.



gauche (meso)



anti (meso)

However, neither isomers of the C_6F_5-diol show evidence of intramolecular hydrogen bonding and we must conclude that fluorine substitution reduces the tendency towards hydrogen bonding, as has been noted elsewhere.[74]

B. Identification and Résolution of rac-C_6F_5-diol.

The photolytic dimerization of octafluoroacetophenone yielded two isomers, a racemic and a meso form, whose identification was uncertain at that time. Although enantiomers have identical properties in a symmetric environment, this is not true of a dissymmetric medium. For example Pirkle[75] reports that the ^{19}F nmr spectrum of racemic 2,2,2-trifluoro-1-phenylethanol exhibits a doublet in CCl_4 but two sets of doublets in optically active α-phenethylamine. However, this technique was inconclusive for identifying the C_6F_5-isomers and the results will be presented in the next section.

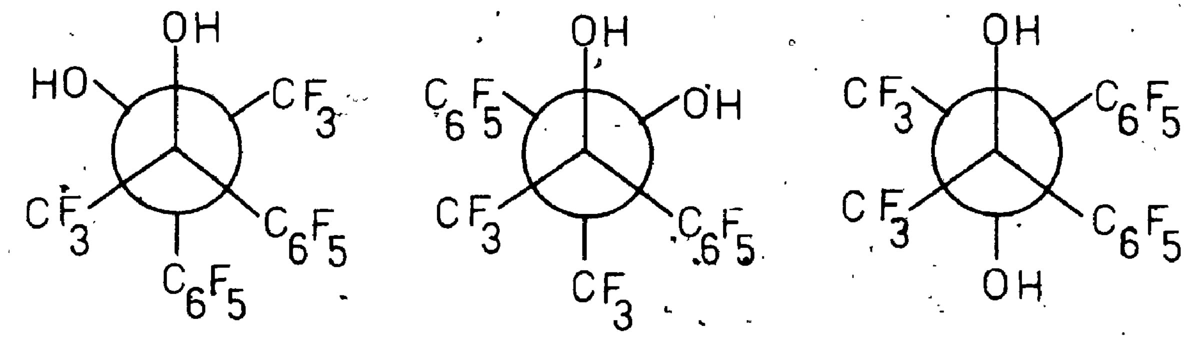
Another approach to the identification of isomers involves the relative ability of the two ligands to form metal complexes. With the ligand 1,2-diphenylethylenediamine (stien), $Ni(stien)_3^{2+}$ forms more readily with the racemic rather than with the meso ligand,[76] for steric reasons. Similarly, we expect the rac-diol to preferrentially coordinate over the meso since chelation can occur with the bulky C_6F_5-groups anti to each other only with the racemic isomer (Figure 13: II versus IV and V). It was found that the metal complex, $Ni(TMED)(C_6F_5\text{-diol})$, resulting from the addition of TMED to a solution of a 1:1:1 mixture of the two isomers and nickel nitrate, contains only the higher melting isomer. Although this certainly suggests that the higher melting compound is the racemic diol, it was considered important to resolve the racemic diol to confirm this tentative assignment.

Most primary and secondary alcohols can be converted to their corresponding hydrogen phthalates or hydrogen succinates which, containing a free carboxyl-group, can be resolved as typical acids. Although it was once believed that tertiary alcohols and glycols could

FIGURE 13

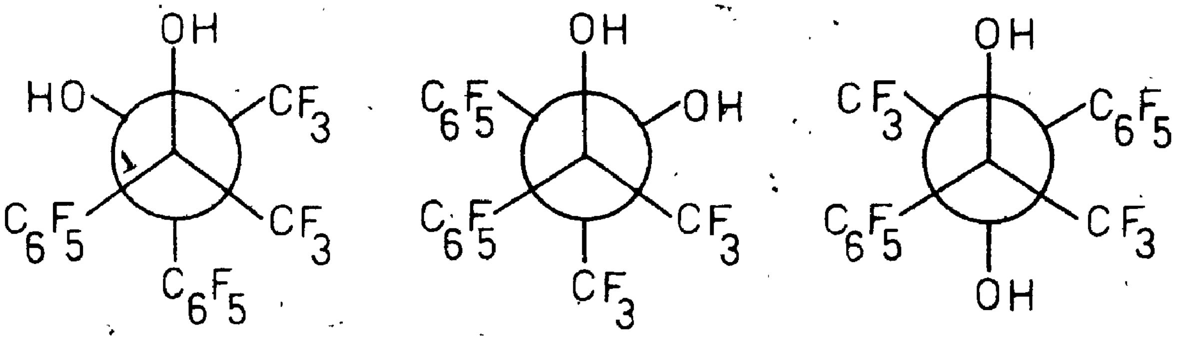
CONFORMATIONS OF RAC- AND MESO-C_6F_5-DIOLS

RAC



I II III

MESO



IV V VI

not satisfactorily be resolved by this method, a number of tertiary alcohols and several glycols have been resolved by this method.[77] Unfortunately the reaction of the C_6F_5-diol with phthalic anhydride did not give the desired product. An alternative approach was to prepare diastereoisomeric square planar metal complexes of the type Ni(diol)(L), where L ≡ optically active diamine, which could theoretically be separated. However, attempts to isolate stable compounds with 1,2-diaminopropane were unsuccessful.

The next attempt to solve this problem focused on the inherent difference between fluorinated and non-fluorinated alcohols, namely, the higher acidity of the former. It was well known[24] that H_2PFP formed a monosubstituted potassium salt in aqueous solution which could be readily isolated. Furthermore, the infrared spectra of the reaction products of H_2PFP with ammonium hydroxide and strychnine in both instances indicated that salts had been formed. Although the two isomeric diols are weaker acids than H_2PFP, having pK_a's of 8.7 (m.p. 120) and 9.1 (m.p. 129-130°C) in a 1:1 water/ethanol solution versus 6.50 for H_2PFP under similar conditions, it was expected that they would behave in an analogous fashion, simplifying the resolution to that of a typical acid.

Attempts to prepare crystalline diastereoisomeric salts with the two isomeric diols and the alkaloids brucine, strychnine and quinine and the synthetic bases (+)-α-phenethylamine, l-α-(1-naphthyl)-ethylamine and dehydroabiethylamine were unsuccessful. With these reagents, either the starting materials were recovered or persistent oils were produced. With l-cinchonidine, a microcrystalline product was obtained whose infrared spectrum (nujol mull) lacked the characteristic strong OH stretch of the free diol while retaining peaks due to the CF_3 and C_6F_5 groups.

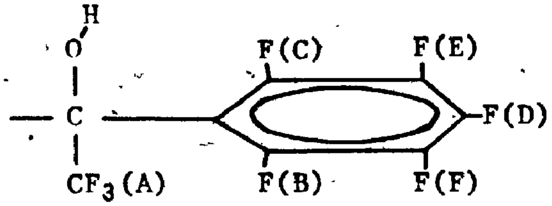
Elemental analysis was consistent with the formation of a 1:1 complex. Molecular weight studies of the complex yielded a value of 405 on extrapolation to infinite dilution, which is indicative of complete dissociation. Conductance measurements show that the complex is an electrolyte in solution (methanol; 40 mhos/cm^2). On the basis of the above, we conclude that the complex is a salt rather than a strongly hydrogen-bonded adduct.

Regardless of the true nature of the complex, it afforded a potential method to determine the stereochemistry of the two isomers through resolution of the active form. Fractional recrystallization of the salt formed from the higher melting isomer, followed by regeneration of the free diol, yielded (+)-C_6F_5-diol (mp 89-90°, $[\alpha]_{589}^{20} = 96.6°$). This shows unambiguously that the higher melting isomer is the racemic compound, which is in agreement with the observed preferential coordination of this isomer.

C. Fluorine NMR Spectra

The ^{19}F nmr spectrum of either isomer has five peaks, of approximately equal intensity, in the area expected for aromatic fluorine atoms. Usually, the ^{19}F nmr spectrum of a pentafluorophenyl compound has three peaks, in the ratio of 2:2:1, corresponding to the two ortho, the two meta and the single para fluorine, with their magnetic shifts increasing in the order, ortho < para < meta. The five peaks we observed are presumably due to the magnetic non-equivalence of the five aromatic fluorine atoms.

The observed peaks have been labelled A through to F in order of their increasing chemical shifts and have been assigned, based on their chemical shifts and on decoupling experiments, according to the following scheme.



The important features of the ^{19}F nmr spectra of both isomers are described below.

Rac-C_6F_5-diol

A: 73.25 ppm from CCl_3F, CF_3. The peak is a second order doublet of triplets (J = 24.3, 1.4), which collapses to a broad singlet upon irradiation of B but retains its doublet character with the loss of the small triplets on irradiation of C.

B: 129.9 ppm, ortho-F. Unresolved broad peak, 125 hz. in width.

C: 143.2 ppm, ortho-F. Unresolved broad peak, 70 hz. in width.

D: 148.7 ppm, para-F. The peak is a triplet of triplets ($J_{ED} = J_{FD} =$ 21.5 hz, $J_{DB} = J_{DC} = 5.9$ hz.). Irradiation of B or C produces a triplet of doublets.

E: 159.3 ppm, meta F. The multiplet is a triplet of doublets of doublets ($J_{ED} = J_{EC} = 21.5$ hz., $J_{EF} = 1.0$ hz, $J_{EB} = 6.0$ hz.). Irradiation of B removes the 6.0 hz. coupling, producing a triplet while irradiation of F removes the small doublets.

F: 160.2 ppm, meta F. The multiplet is an overlapping doublet of doublets, further split into a doublet of doublets (J_{FB} = 23.2, J_{FD} = 21.5, J_{FC} = 7.3 and J_{FE} = 1.0 hz.). Irradiation of E removes the small doublets while irradiation of C produces a triplet.

meso-C_6F_5-diol

A: 71.58 ppm from CCl_3F, CF_3. The peak is a complicated second order multiplet, which collapses to a broad singlet on irradiation of B and to a doublet with some fine structure on irradiation of C.

B: 129.2 ppm, ortho F. Broad multiplet, 170 hz. in width.

C: 140.5 ppm, ortho F. Broad multiplet, 75 hz. in width.

D: 149.6 ppm, para F. The peak is a triplet of triplets (J_{ED} = J_{FD} = 22.0 hz., J_{DB} = J_{DC} = 6.1 hz.). Irradiation of B or C produces a triplet of doublets.

E: 160.3 ppm, meta F. Overlapping doublet of doublets, further split into a doublet of doublets (J_{EF} = 1.3, J_{EB} = 5.6, J_{EC} = 20.8, J_{ED} = 22.0 hz.). Irradiation of B removes the 5.6 hz. coupling.

F: 160.6 ppm, meta F. Triplet of doublets of doublets (J_{FE} = 1.3, J_{FC} = 6.7, J_{FB} = J_{FD} = 22.0 hz.). Irradiation of C removes the 6.7 hz.

coupling.

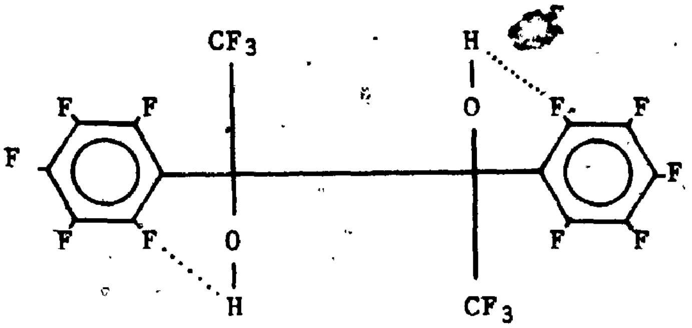
In addition to the two isomers of the C_6F_5-diol, the ^{19}F nmr spectrum of the metal complex $Ni(PMe_2Ph)_2$([+]-C_6F_5-diol) was also obtained. Attempts to get a suitable ^{19}F nmr spectrum of the co-ordinated meso ligand were not successful because of limited solubility and decomposition of these complexes. The chemical shift data for these three compounds are listed in Table 9.

TABLE 9

	rac-C_6F_5-diol	meso-C_6F_5-diol	$Ni(PMe_2Ph)_2$([+]-C_6F_5-diol)
CF_3 (A)	73.25*	71.58	67.43
ortho-F (B)	129.9	129.3	132.6
ortho-F (C)	143.2	140.5	133.4
para-F (D)	148.7	149.6	157.4
Meta F (E)	159.3	160.3	164.2
Meta F (F)	160.2	160.6	166.9

* In p.p.m. from $CFCl_3$.

It has previously been suggested[70] that the observed non-equivalence arises from hydrogen bonding of the type O-H----F, as shown below.



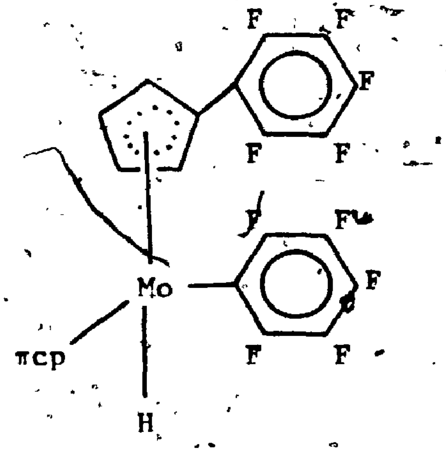
This explanation is reasonable and has been postulated for fluoro-alcohols by previous workers.[78] However, it is possible that the hindered rotation present is strictly the result of steric interactions of the bulky C_6F_5-groups with the rest of the molecule. To resolve this problem, the possibility of hydrogen-bonding was eliminated through coordination of the (+)-C_6F_5-diol to a transition metal. If the former model is the correct one, the ^{19}F nmr spectrum of the complex should have only three peaks due to the pentafluorophenyl groups while if the latter is correct, five peaks should persist. In fact, the ^{19}F nmr spectrum of Ni(PMe_2Ph)([+]-C_6F_5-diol) had five peaks rather than three, proving that the hindered rotation is steric rather than chemical in nature.

The peak due to the CF_3 groups is a complicated 2nd order doublet, yet some information regarding the structure can be obtained through decoupling experiments. Irradiation of B causes the CF_3 peak to collapse to a broad singlet but the doublet is retained on irradiation of C, although some fine structure is removed. The enhanced coupling of one ortho fluorine over the other is strongly suggestive of a through space mechanism which could result from a C_6F_5 group being oriented with F_B closer to the CF_3 group than F_C.

The ^{19}F nmr spectra[69] of the mono-alcohols perfluoro(2-

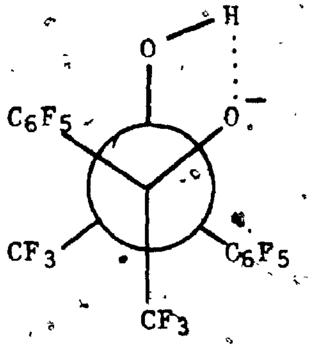
phenylpropan-2-ol), perfluoro(1,1-diphenylethanol), and perfluoro(triphenylcarbinol) have three peaks attributable to the C_6F_5 groups, indicating that no hindered rotation is present in these alcohols. We conclude that the steric hindrance arises from the interaction of the C_6F_5 group principally with a vicinal rather than a gem CF_3-group.

Although this is the only example to date where all five fluorine atoms of a C_6F_5 group have different chemical shifts, several compounds of the type shown below[79] also exhibit anomalous ^{19}F nmr spectra. With the above compound, the ortho fluorine atoms of the Mo-C_6F_5 ring have different chemical shifts and there is coupling between Mo-H and one of the ortho-fluorines. The authors suggest that the Mo-C_6F_5 ring may not rotate freely about the Mo-C axis due to interaction with the two π-cp rings. This is analogous to the C_6F_5-diols except that in the above, the meta-fluorines are accidentally coincident.

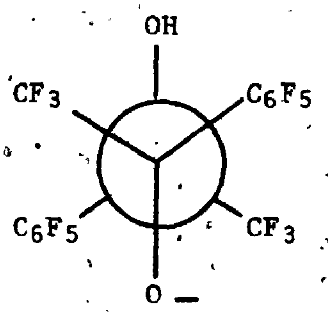


Finally, the ^{19}F nmr spectrum of the rac-C_6F_5 diol, recorded in (+)-α-phenethylamine, did not show the anticipated further splitting in the CF_3 region, probably due to the extensive coupling present and the broadness of the CF_3 peak. However, the ^{19}F nmr spectrum of the meso compound, recorded in the same solvent, changed radically in the CF_3

region. Instead of a broad, second-order doublet at 71.6 ppm, there were two peaks, a doublet of doublets at 73.9 ppm and a doublet of quartets at 79.1 ppm, in the ratio of 1:1. The non-equivalence of the CF_3 groups in the meso compound can be related to the conformation of this diol in solution. Of the possible conformations of the two diols (Figure 13) we expect II and VI to be the dominant conforms for the racemic and the meso diols respectively. In the presence of a base, these diols should exist as monoanions, stabilized through hydrogen bonding as shown below, either with an adjacent OH (rac) or with the solvent (meso). Although this would explain the non-equivalence of the CF_3-groups of the meso isomer, the situation may be more complex than this.



rac



meso

D. Transition Metal Complexes

Repeated attempts to prepare the bis-complex, $Ni(C_6F_5\text{-diol})_2^{2-}$, were unsuccessful with both isomers, as a previous study had indicated,[70] even in the presence of a large cation. A mixture of the (+)-C_6F_5-diol and Ni^{2+} (2:1) was titrated with potassium hydroxide and monitored by ORD, but no indication of a Cotton effect was detected in the visible region of the spectrum and $Ni(OH)_2$ was precipitated throughout the titration. Continued addition of KOH after complete conversion of Ni^{2+} to the hydroxide resulted in decomposition of the ligand, probably due to nucleophilic attack by the base. This inability to prepare a bis-complex results from conversion of the Ni^{2+} to $Ni(OH)_2$ before a pH can be attained that would lead to anion formation and chelation. To confirm the absence of an interaction of Ni^{2+} with the (+)-C_6F_5-diol, ORD spectra were recorded of mixtures in which the ligand to metal ratio was varied from 1.0:0.5 to 1.0:5.0 and these spectra consistently showed that there was no interaction between Ni^{2+} and the optically active ligand.

Although nickel complexes containing the C_6F_5-diol as the sole ligand could not be prepared, mixed ligand complexes of the type $Ni(L)_2(C_6F_5$-diol) could be prepared with both isomers. For L ≡ phosphine, the complexes $Ni(PEt_3)_2(C_6F_5$-diol) and $Ni(PMe_2Ph)_2(C_6F_5$-diol) were prepared and characterized. For L ≡ $PMePh_2$, a complex was formed in solution which rapidly decomposed before it could be isolated while with L ≡ PPh_3, there was no evidence of complex formation with either isomer. With L_2 ≡ TMED or TEED, the complexes Ni(TMED)(C_6F_5-diol) and Ni(TEED)(C_6F_5-diol) were readily prepared and isolated. These complexes had visible spectra similar to the analogous PFP^{2-} complexes and they are assigned a square planar structure. As well, a copper(II) complex, Cu(TMED)(C_6F_5-diol), was prepared and although Co(TMED)(C_6F_5-diol) could not be isolated, CD and ORD spectra indicated that it was present in solution.

In order to ascertain the relative chelating ability of rac-C_6F_5-diol, meso-C_6F_5-diol, H_2PFP and meso-C_6H_5-diol (part III), a series of competitive reactions were undertaken between Ni^{2+}, TMED, and various 1:1 mixtures of the above ligands, producing metal complexes of the type Ni(TMED)(DIOL). The products of these reactions contained in all cases a specific diol, rather than a mixture, and these were identified by their infrared spectra. The results of these reactions are summarized in Table 10.

TABLE 10

Ligands Present in Reactions	Diol Selectively Chelated
H_2PFP/rac-C_6F_5-diol	H_2PFP
H_2PFP/meso-C_6F_5-diol	H_2PFP
H_2PFP/meso-C_6H_5-diol	H_2PFP
rac-C_6F_5-diol/meso-C_6F_5-diol	rac-C_6F_5-diol
rac-C_6F_5-diol/meso-C_6H_5-diol	rac-C_6F_5-diol
meso-C_6F_5-diol/meso-C_6H_5-diol	meso-C_6F_5-diol

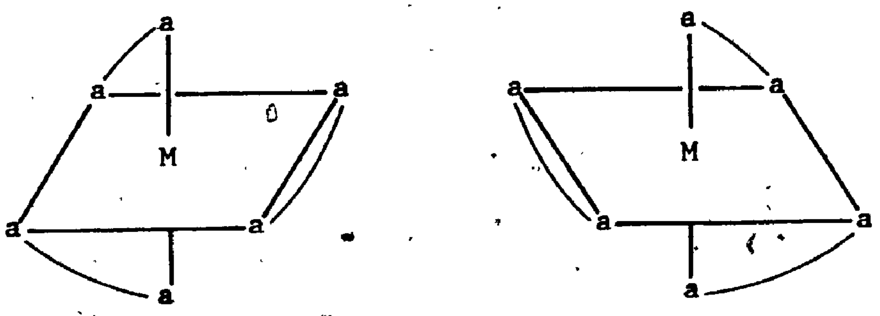
Therefore, the order of chelating ability is: H_2PFP > rac-C_6F_5-diol > meso-C_6F_5-diol > meso-C_6H_5-diol. This parallels the relative pK_a's of the diols except for the isomeric C_6F_5-diols where steric factors determine their relative chelating ability.

E. Determination of Absolute Configuration

Before discussing the assignment of an absolute configuration, it is necessary to consider briefly the various sources of dissymmetry which give rise to the optical activity and the resulting Cotton effects observed in transition metal complexes. Optical activity arises when a molecule is nonsuperimposable on its mirror image. In order to satisfy this requirement, a compound must not possess a centre of symmetry, a plane of symmetry or an improper axis of symmetry although a proper axis of rotation may be present. Optical isomers possessing a proper axis are classified as dissymmetric while those possessing no symmetry element other than the identity are classified as asymmetric.

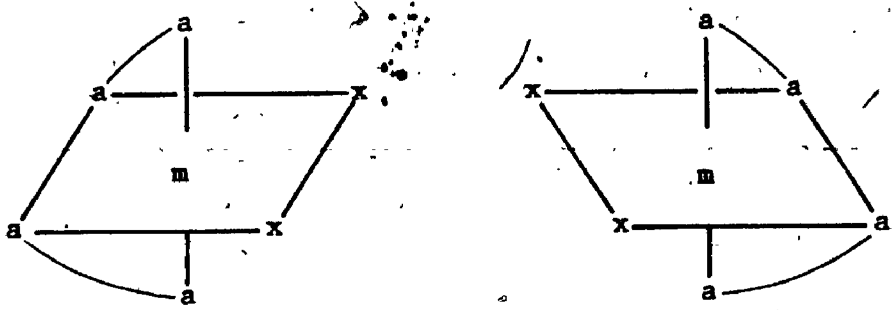
The most intensively studied class of potentially optically active metal complexes are those containing two or three bidentate ligands. The major contribution to optical activity in these types of compounds arises from the distribution of the ligands around the central metal, as shown below. The $M(aa)_3$ and cis-$M(aa)_2X_2$ types of compounds

$M(aa)_3$

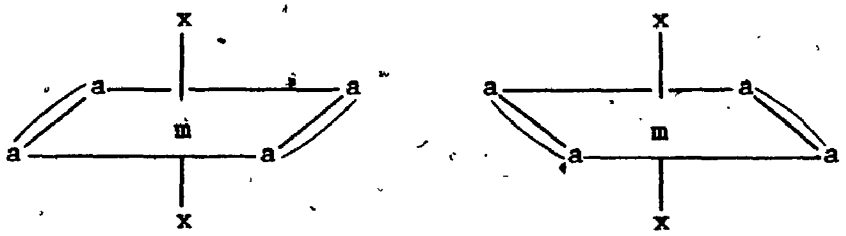


$M(aa)_2X_2$

cis



trans



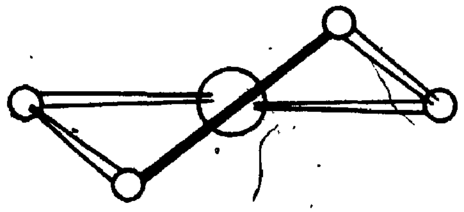
are non-superimposable on their mirror images while trans-$M(aa)_2X_2$ complexes are superimposable and therefore not optically active. Although perfluoropinacol forms complexes of the type $M(PFP)_3^{3-}$, which should theoretically be capable of resolution, the C_6F_5-diols have shown no evidence to date of being able to form bis-chelate metal complexes, let alone tris-chelate complexes. Therefore, optical activity arising from the distribution of chelate rings about a central metal is not relevant to this discussion.

Another source of optical activity, which is relevant to this work, arises from the coordination of an optically active ligand containing an asymmetric carbon atom. This is commonly referred to as the vicinal effect.

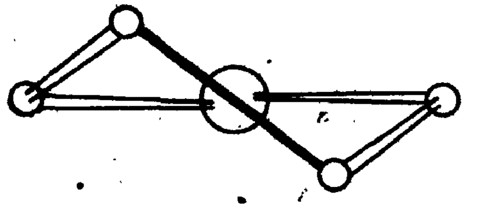
Organic chemists have realized for many years that an asymmetric centre in an organic compound will induce rotational power in a chromophore removed by several bonds from the asymmetric centre. Much of the work in this area has been done on carbonyl compounds, principally because the carbonyl chromophore absorbs in a readily accessible region of the ultraviolet spectrum. Similarly, an optically active ligand induces rotational power into the central metal ion chromophore, presumably through the coordination bonds or by a through space mechanism. The size of the rotational strengths observed depends on the nature of the coordinated ligand while the sign of the Cotton effect will be a reflection of the absolute configuration of the ligand. This in theory should allow one to assign an absolute configuration to a coordinated optically active ligand by an empirical approach, assuming one can make comparisons with very similar systems of known absolute configuration and can be sure that the CD and ORD effects being compared arise from identical d-d transitions. Therefore, it was expected that, through coordination of the resolved C_6F_5-diol to a metal, the Cotton effects observed would perhaps enable an assignment of the absolute configuration of the diol as well as elucidating the origins of the transitions observed. It is very important to realize that in the study of planar complexes, the classical approach to the introduction of optical activity through the distribution of chelate rings is inoperative since the situation for a bis-chelate compound is analogous to the trans-$M(aa)_2X_2$ situation, assuming that the X groups are not in the coordination sphere. Therefore to study these systems, one must resort to the use of optically active ligands or optically active solvents.

The conformations of the chelate rings give rise to another source of dissymmetry. Because chelate rings are puckered, rather than planar, they can exist in conformations that are enantiomeric. This effect complements the optical activity which arises from both the configurational and the vicinal effects.

For a symmetric skew five-membered chelate ring, two conformations are possible as shown below. In octahedral systems of the type $M(aa)X_4$, when the chelating ligand is a C-substituted ethylenediamine, such as propylenediamine, the methyl group can be situated in an equatorial or an axial position, depending on which conformation is



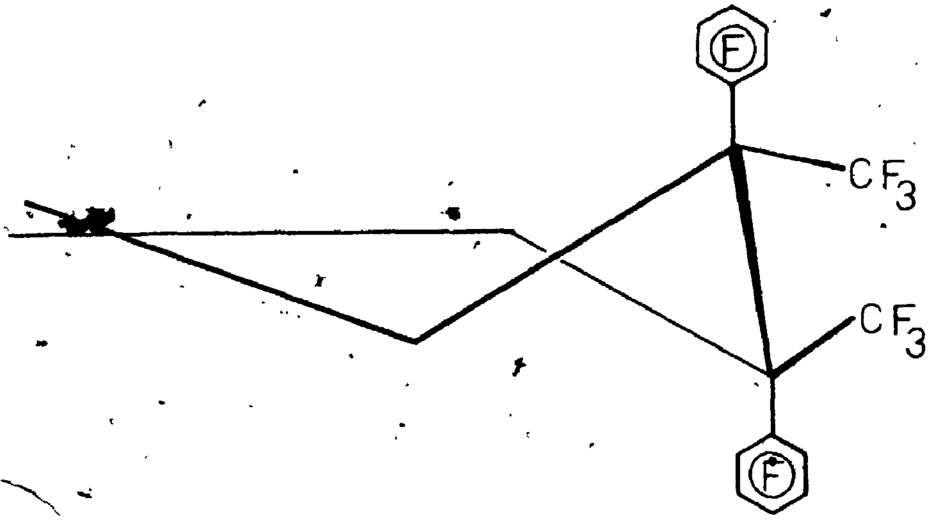
λ (left-handed helix)



δ (right-handed helix)

favoured. Calculations indicate that the conformation with the methyl group in the equatorial position will be more stable because an axial methyl would have significant interaction with the X group in the axial position on the metal.[80] In square planar metal complexes, this would not be a relevant factor, unless solvent molecules were oriented in the axial positions, and the two conformations should be of approximately the same energy.

The situation for the rac-C_6F_5-diol differs from the above because intra-ligand, rather than inter-ligand, interactions should determine the preferred conformation. For a specific absolute configuration of the diol, either the two CF_3-groups or the two C_6F_5-groups can be axial. Molecular models indicate that there would be a steric advantage for the C_6F_5-groups to be in the axial positions, thereby eliminating interaction with themselves and minimizing their interaction with the CF_3-groups, the latter depending on the degree of puckering of the ring. The presence of steric hindrance in the ligand system is supported by ^{19}F nmr spectra. Therefore, we expect the 2R,3R configuration to exist predominantly in the δ conformation, as shown below, while the 2S,3S configuration should prefer the λ conformation.

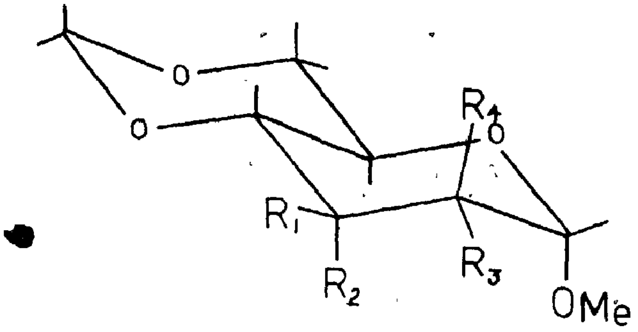


2R,3R-configuration
δ-conformation

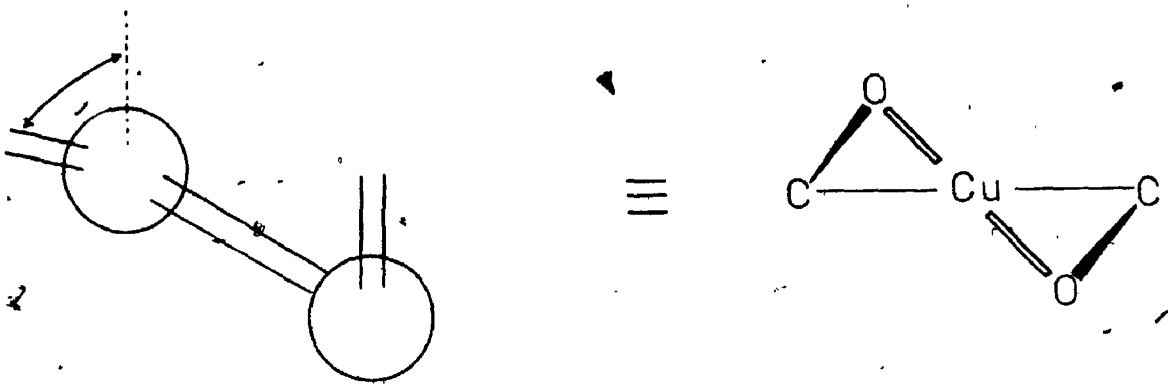
Although a vicinal and a conformational contribution to the rotational strength is expected in this system, it is probable that the latter effect will dominate. This is supported by various studies with C-substituted diamines containing one and two asymmetric carbon atoms. It was found[81] that the rotational strength for the bis(propylenediamine) Co(III) complex was only slightly less than for the bis(trans-1,2-diaminocyclohexane) Co(III) system although propylenediamine has only one asymmetric carbon compared with two in the latter ligand. Similar studies[81] with Rh(III) and the ligands R-propylenediamine and R,R,-2,3-diaminobutane led to almost identical rotations for analogous compounds. This approach assumes that the chelate rings in these systems are puckered to the same extent since the rotational strength due to the conformational effect should be a function of the degree of puckering in the chelate ring, the greater the puckering, the greater the rotational strength. With the rac-C_6F_5-diol, a strongly puckered ring should decrease the steric interaction within the ligand and a strong conformational contribution to the rotational strength is therefore expected. One must remember, however, that it is difficult to separate these effects, even when a series of related ligands are being studied.

An assignment of an absolute configuration to the optically active diol has been made using an empirical approach first developed by R. E. Reeves.[82] This method involves the formation of a five-membered ring between an optically active diol and copper(II) in a cuprammonium solution[83] and was initially investigated by measuring the difference in rotational strength between the complexed diol and the free diol at a specific wavelength, 436 nm. It was found that this rotational shift was negative when the projected angle was negative and vice-versa. The correlations between Reeve's nomenclature and those in vogue at this time are illustrated below.

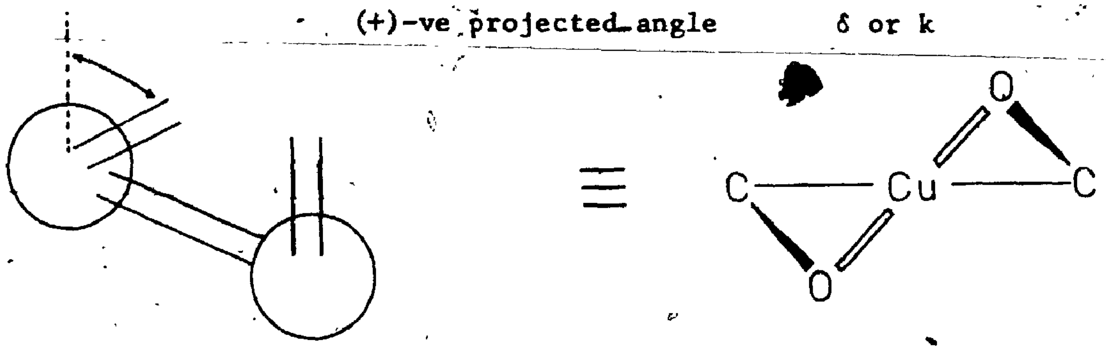
This approach has been extended to relate the signs of the observed CD bands to the conformation of the ligand.[84] It has been found that the rotational shift previously used as the criterion for assignment of a conformation manifests itself as a low intensity band at about 580-600 nm and a band of opposite sign and increased intensity at ∿ 280 nm. A relationship between conformation and sign of the observed CD bands has been established through the use of a conformationally rigid ligand, shown below.



Conformationally Rigid Ligand System



(+)-ve projected angle δ or k



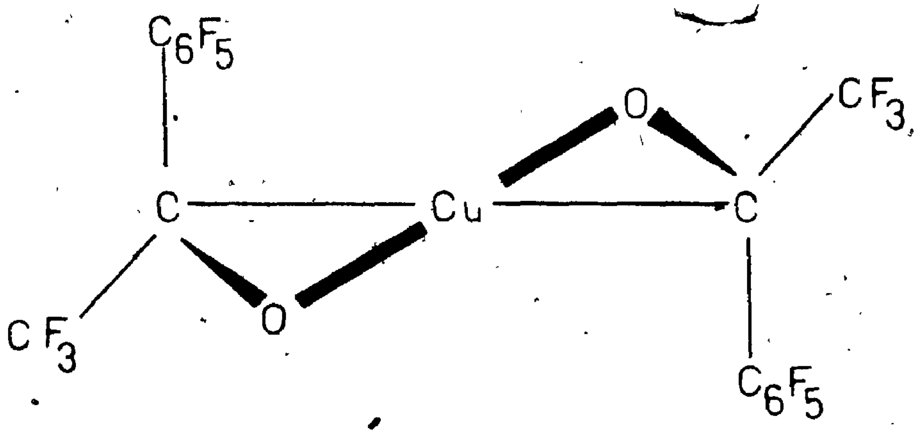
(-)-ve projected angle λ or k'

Correlation of Nomenclature

It was found that with $R_1 = R_3 = OH$, the band in the visible region of the spectrum was positive while with $R_1 = R_4 = OH$ or $R_2 = R_3 = OH$, a negative CD band was observed in the 600 nm region. No CD bands were present when $R_2 = R_4 = OH$. Therefore, the δ or k conformation is associated with a positive CD in the 600 nm region and the λ or k' conformation with a negative band.

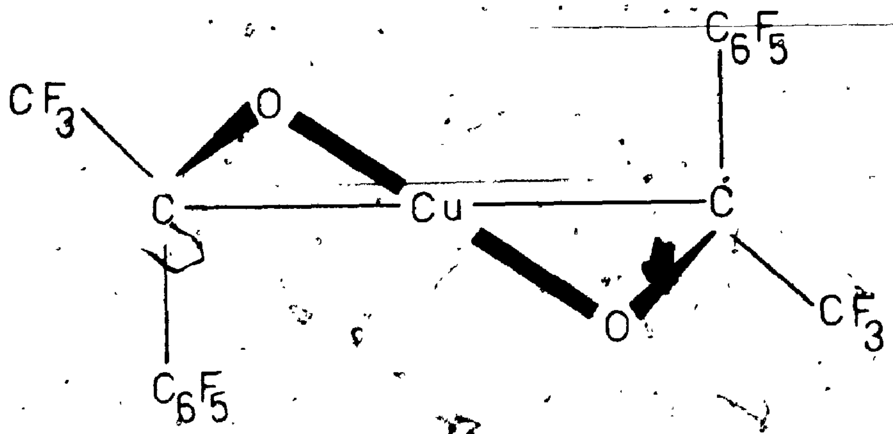
In order to extend this method to assign an absolute configuration to the C_6F_5-diol, we must assume that the same type of species gives rise to the CD effect here as in the previously studied systems with unfluorinated diols. This is not an unreasonable assumption since previous studies have indicated that the copper to diol combining ratio is one to one,[85] the same ratio as has been found for all transition metal complexes of the C_6F_5-diol isolated to date. The only difference anticipated between fluorinated and unfluorinated diols is the extent of complex formation, the equilibrium lying further to the right for the more acidic fluorinated ligand.

If one knows the conformation of the diol, the configuration can be deduced by this method, and vice-versa. With the C_6F_5-diol, as was previously discussed, the bulky C_6F_5-group must be in the axial positions upon coordination, and hence the conformation of a specific configuration is fixed. The CD spectrum of the (+)-C_6F_5-diol in a cuprammonium solution exhibits a positive peak at ∿ 610 nm and a negative peak of enhanced intensity below 300 nm while the (-) isomer exhibits peaks of opposite signs in the same positions. Hence, the (+) isomer has a δ conformation and the (-) isomer a λ conformation. The assigned conformations and absolute configurations are illustrated below.



(-)-C_6F_5-Diol

*λ-conformation; S,S-configuration



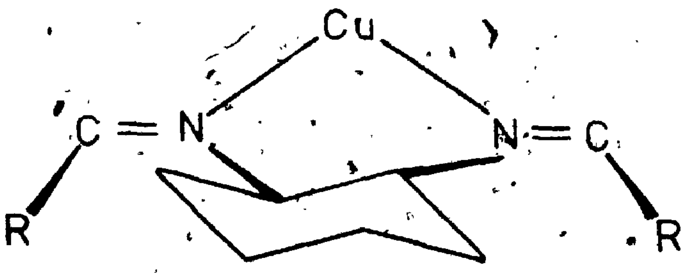
(+)-C_6F_5-Diol

δ-conformation; R,R-configuration

Another method of assigning an absolute configuration involves comparing the CD spectra of Ni[(+)-C_6F_5-diol]L_2 and Cu[(+)-C_6F_5-diol]L_2 [Figures 14, 15 and 16] with those of analogous systems. The prerequisite for an analogous system is the presence of NiO_2P_2, NiO_2N_2 or CuO_2N_2 chromopore, with the central metal in a planar environment, whose optical activity arises predominantly from the conformation of a chelate ring. In the absence of strictly analogous complexes, tetradentate Schiff base chelates of Ni^{2+} and Cu^{2+} meet the criteria outlined above, and should prove useful in determining the configuration of the diol.

Downing and Urbach[86] have investigated a series of Cu^{2+} complexes with the tetradentate Schiff base chelates derived from (R)-(-)-propane-1,2-diamine [(-)pn] and (R,R)-(-)-cyclohexane-1,2-diamine [(-)chxn] and report that the CD of the (-) pn series is the mirror image of the (-)chxn system, even though the optically active diamines used to prepare the tetradentate chelates have the same absolute configuration.

To explain this, they assume that the observed CD is a reflection of the conformation of the central chelate ring. For the (-)chxn system, the chelate ring is stereospecifically locked into the λ conformation, as shown below.



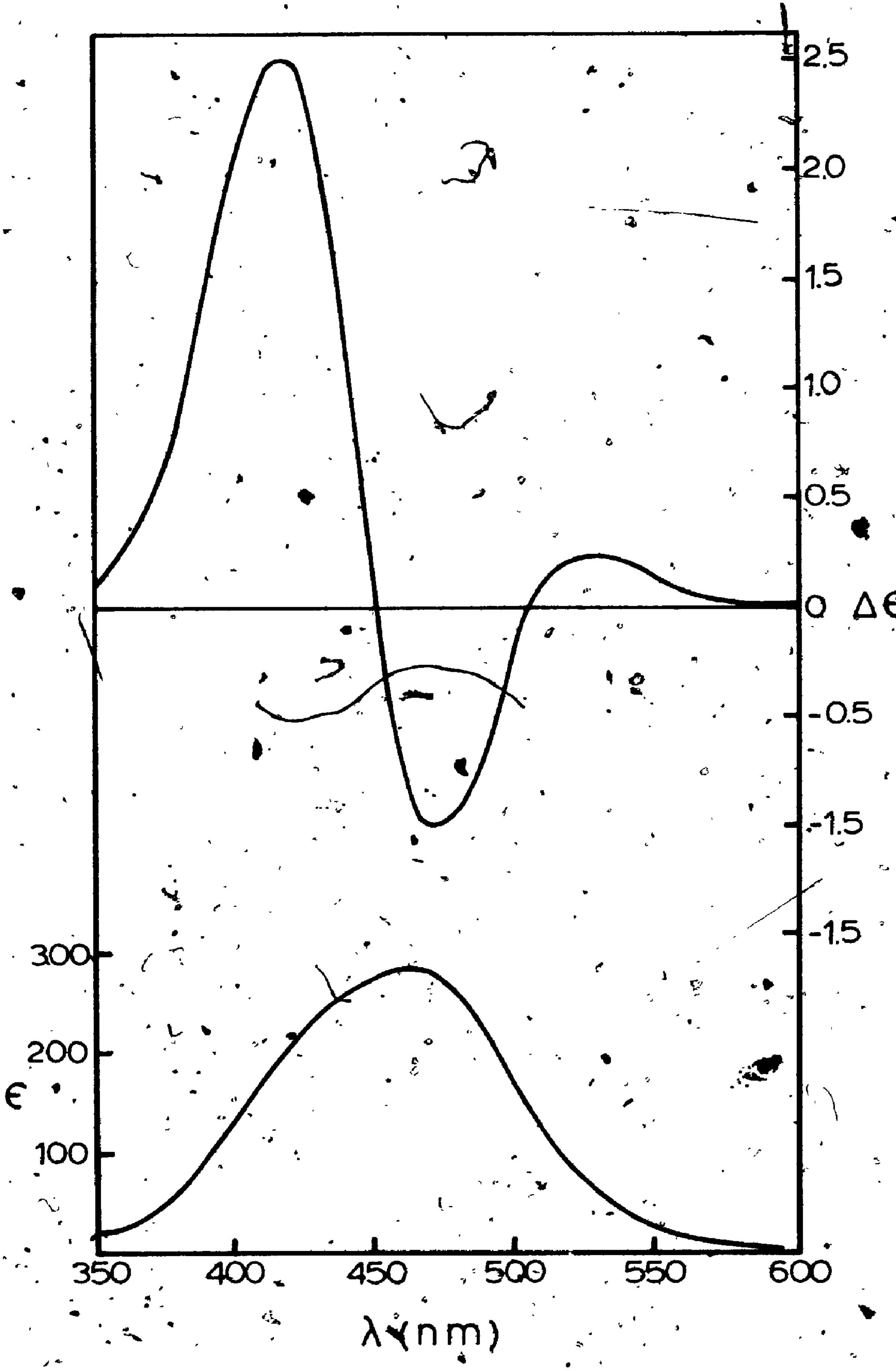


FIGURE 14

CD and Visible Spectra [MeOH Solution] of Ni[(+)-C_6F_5-diol][PMe_2Ph]$_2$

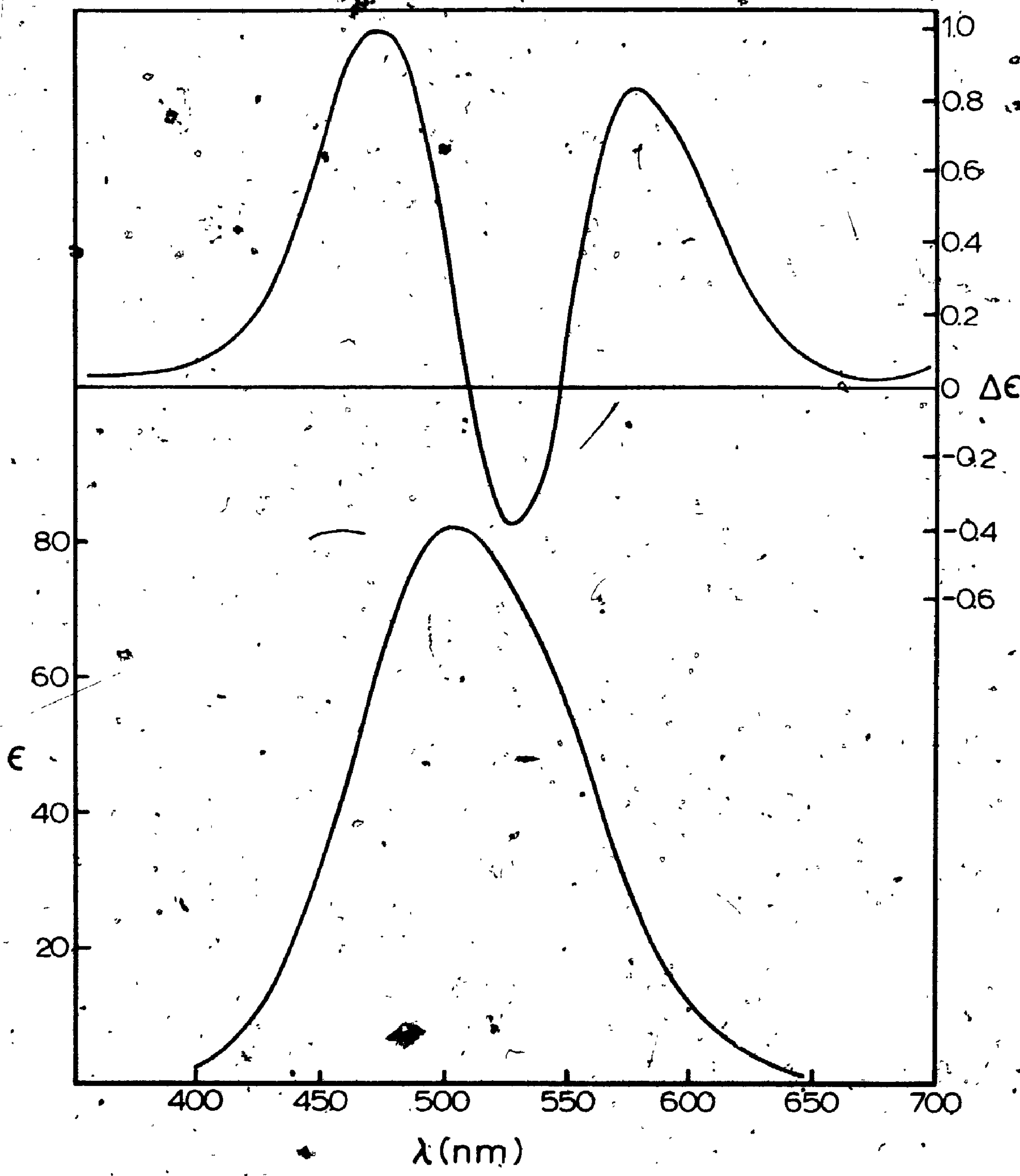


FIGURE 15

CD and Visible Spectra (MeOH Solution) of Ni[(+)-C_6F_5-diol][TMED]

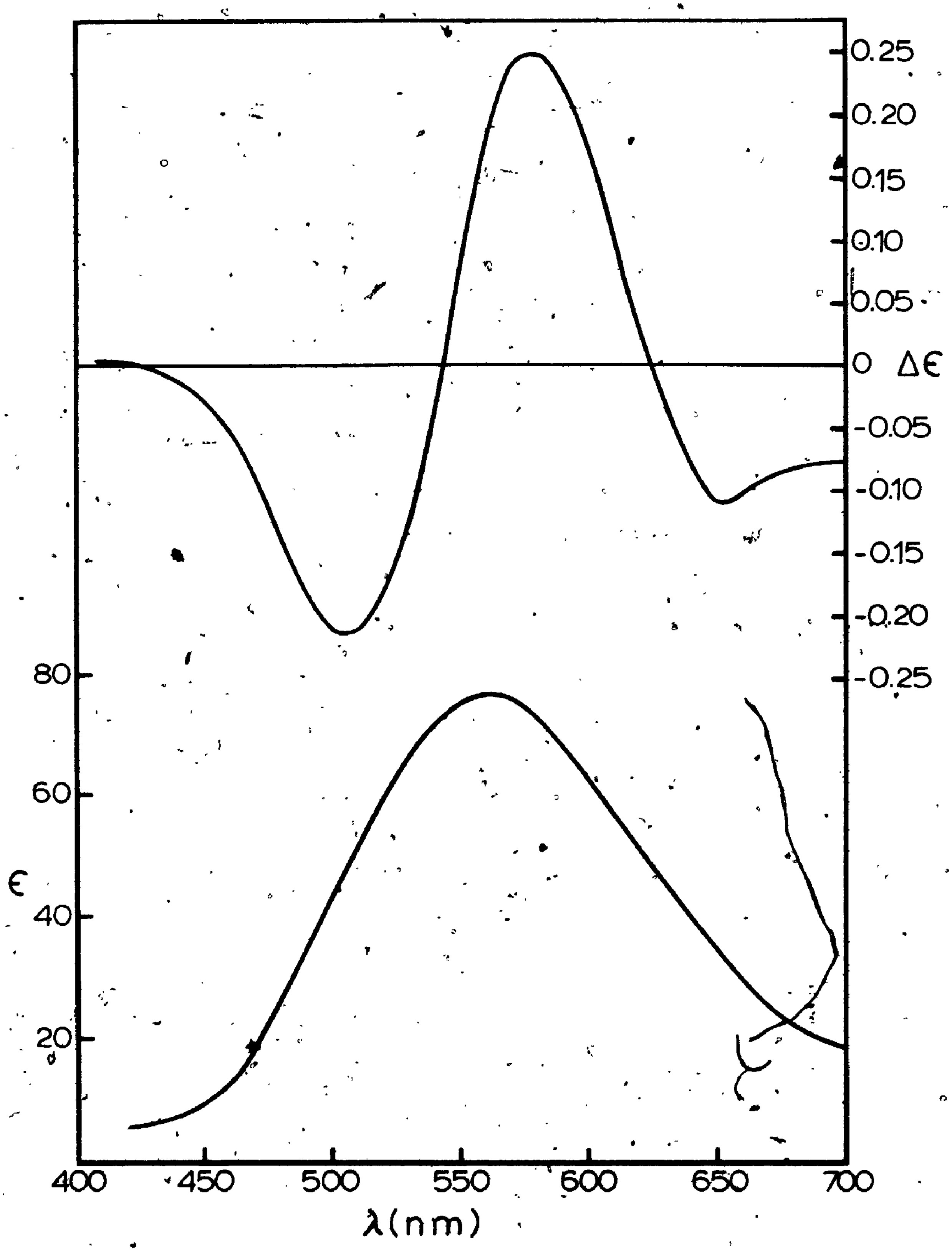
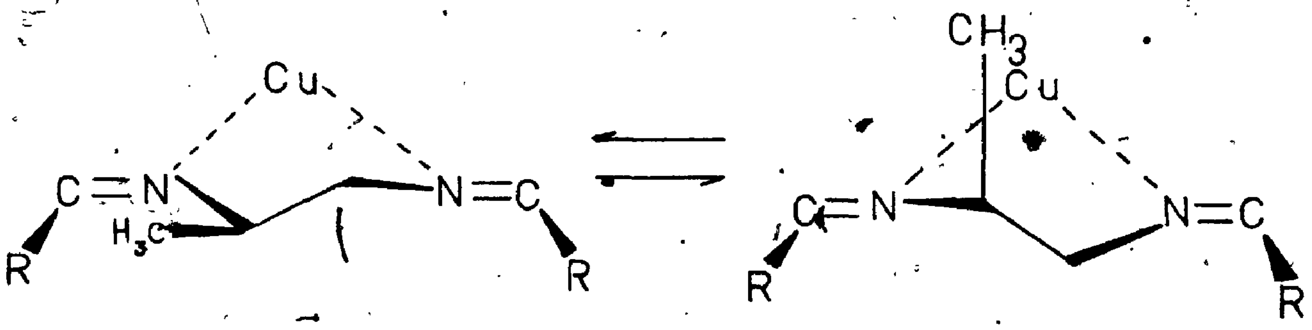


FIGURE 16

CD and Visible Spectra (MeOH Solution) of Cu[(+)-C_6F_5-diol][TMED]

For the (-)pn system, either the λ conformation (methyl equatorial) or the δ conformation (methyl axial) is possible, as illustrated below.



λ δ

The authors predict that the δ conformation will predominate because of the steric interaction that would exist in the λ conformation between the methyl and R groups. Therefore, the main source of optical activity is due to the conformation of the central chelate ring and the mirror image relationship between the (-)pn and (-)chxn systems arises from the presence of the δ and λ conformations respectively.

The CD spectra of these Cu^{2+} complexes exhibit three peaks that are attributed to d-d transitions although for several of the complexes investigated, the low energy band was absent. The pertinent CD data for Cu(Sal)$_2$(-)pn, Cu(Sal)$_2$(-)chxn, Cu(7-Mesal)$_2$(-)pn, Cu(7-Mesal)$_2$(-)chxn as well as for Cu(+)-diol(TMED) are summarized in Table 11. These data illustrate that the CD spectrum of Cu[(+)-C_6F_5-diol]TMED is similar to that of the (-)pn series and is of the opposite sense to the (-)chxn series. This leads to the assignment of a δ conformation and a R,R configuration for the (+)-diol, in agreement

TABLE 11

CD Spectra of Cu^{2+} Complexes

Compound	Band I λ(cm^{-1})[ΔΣ]	Band II λ (cm^{-1})[ΔΣ]	Band III λ (cm^{-1})[ΔΣ]
$Cu(Sal)_2(-)pn$	Absent	16,900 (0.95)	20,700 (-0.57)
$Cu(Sal)_2(-)chxn$	13,890 (0.11)	17,360 (-1.49)	20,920 (1.07)
$Cu(7\text{-}MeSal)_2(-)pn$	16,030 (-1.47)	18,350 (0.18)	20,580 (-0.14)
$Cu(7\text{-}MeSal)_2(-)chxn$	14,490 (2.93)	18,180 (-1.16)	21.410 (2.54)
Cu(+)diol(TMED)	15,300 (-0.12)	17,350 (0.24)	19,900 (-0.22)

with the assignment previously made using the 'Cupra A' method of Reeves.

Downing and Urbach[87] have also investigated the circular dichroism of the square planar Ni^{2+} analogues of the Cu^{2+} Schiff base complexes. However, these spectra are considerably more complicated than those for the Cu^{2+} system and the mirror image relationship between the (-)pn and the (-)chxn systems is not obvious. Independent Gaussian analysis of the CD spectrum of $Ni(Sal)_2$(-)pn[87,88] led to different signs for the low energy band and therefore attempts to assign an absolute configuration based on these Ni^{2+} complexes would be meaningless.

With respect to the assignment of the d-d transitions, it is generally accepted that all four possible d-d transitions for Cu^{2+} come under the main absorption envelope. The three peaks observed in the CD spectrum of Cu[(+)-C_6F_5-diol]TMED (Figure 16) are tentatively assigned to originate from the following d-orbit ordering: $dx^2-y^2 > dxy > dz^2 > dxz \approx dyz$, in line with Downing and Urbach's findings.[86] Similarly, with the Ni^{2+} complexes, three CD peaks (Figures 14 and 15) are observed under the main absorption band. These bands are tentatively assigned to originate from the following ordering of d-orbitals: $x^2-y^2 > xy > z^2 > xz, yz$, but the exact ordering of the xy and z^2 orbitals is questionable.[87]

PART III

PARTIALLY FLUORINATED DIOLS: PREPARATION AND METAL COMPLEXES

INTRODUCTION

It was decided that, owing to the successful preparation of metal complexes of totally fluorinated diols, an attempt should be made to extend this work to partially fluorinated diols and to perfluorotertiary alcohols. The diols investigated were $(CF_3CH_3COH)_2$, $(CF_3C_6H_5COH)_2$ and $(CH_3C_6F_5COH)_2$. Also, attempts were made to prepare Ni^{2+} complexes of the tertiary alcohols $(C_6F_5)_3COH$, $CF_3(C_6F_5)_2COH$, $(CF_3)_2C_6F_5COH$ and $(CF_3)_3COH$.

RESULTS AND DISCUSSION

The diols studied in this chapter were only partially fluorinated and it was anticipated that they would be less likely to form metal complexes due to their decreased acidity. Also, although the perfluoro monoalcohols, which were briefly investigated, have pK_a values comparable to those of H_2PFP and the CF_3-C_6F_5-diol,[69] the inability to form chelate rings suggests that complexes of these ligands will be difficult to prepare. The above considerations did prove to be applicable but before discussing those few complexes which were prepared a brief account of the ligands will be presented.

A. Properties of Partially Fluorinated Diols

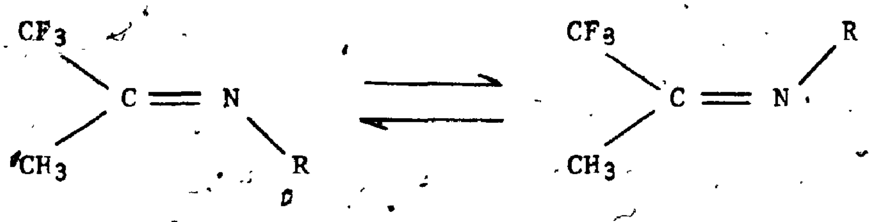
The CF_3-C_6H_5-diol was previously prepared by Mosher and Heindel[89] by the photolytic reduction of trifluoroacetophenone. The authors report only one compound as the product of the reaction but fail to identify which, of the two isomers possible, they had prepared. They do report that the diol does not undergo a pinacol rearrangement as is the case with F_2PFP and the CF_3-C_6F_5-diols. We found also that only one isomer was produced in the reaction and attempted to identify it.

The ^{19}F nmr spectrum of the diol exhibited a single peak in both chloroform and an optically active solvent. The equivalence of the CF_3 groups in the latter solvent is indicative of the meso isomer rather than the racemic one.[75] We also attempted to resolve the compound by a similar method to that successfully employed for the rac-CF_3-C_6F_5-diol. Although a salt-like compound was obtained with strychnine, no resolution was achieved. The above evidence is somewhat negative in substance but does indicate that the meso isomer has been obtained. Unfortunately, attempts to prepare this diol by alternative methods to get the racemic isomer were unsuccessful. While this work was in progress, an alternative method of preparation of the same isomer appeared in the literature[90] and its configuration, as determined by X-ray crystallographic analysis of the dimethyl derivative, was found to be meso, in agreement with our results.

The CH_3-C_6F_5-diol was prepared by the photolytic reduction of methyl pentafluorophenyl ketone. Only one isomer, whose configuration was not determined, was obtained from the reaction. Its elemental analysis, infrared spectrum, mass spectrum, and nmr spectra were consistent with the assigned structure. The infrared spectrum (nujol) had peaks due to the

C_6F_5 group as well as a peak at 3575 cm^{-1} due to the O-H stretching mode. The proton nmr spectrum had two peaks in a 3:1 ratio due to the methyl and hydroxyl protons respectively.

The ^{19}F nmr spectrum of this diol is "normal" insofar as only three peaks were present at 138.0, 154.7 and 162.3 ppm (from $CFCl_3$), due to the ortho, para and meta fluorines respectively. The C_6F_5 groups in this diol are free to rotate and therefore the ortho fluorines and the meta fluorines respectively are magnetically equivalent. The explanation for the difference between this diol and the two isomers CF_3-C_6F_5-diols is the greater steric requirements of the trifluoromethyl groups versus the methyl groups. Steric substituent constants, E_s, derived from ester hydrolysis experiments,[91] indicate that CF_3 groups (E_s = -1.16) are closer in bulkiness to $(CH_3)_3C$ groups (E_s = -1.54) than to CH_3 groups (E_s = 0). Also, ^{19}F nmr studies on various imines have shown[92] that the anticipated inversion shown below does not occur, but that only species I is present in solution at room temperature. This has been attributed to the bulkiness of the CF_3 group.



I II

The mass spectrum of both diols has its most intense peak at one-half the theoretical molecular weight, which indicates that the major fragmentation process involves the symmetrical cleavage of the diol. This process is characteristic of the other diols studied and provides an easy method of identification of this class of compounds. Titration of the

CH_3-C_6F_5-diol with 0.10 M NaOH did not give a discernible end-point while titration of the CF_3-C_6H_5-diol gave an end-point, yielding a pK_a of ∿ 11.4. Therefore, the relative acidities of the diols studied is:

$$H_2PFP > meso\text{-}CF_3\text{-}C_6F_5 > rac\text{-}CF_3\text{-}C_6F_5 > CF_3\text{-}C_6H_5 > CH_3\text{-}C_6F_5$$

This is the order one expects, based on purely inductive effects, with the exception of the ordering of the meso- and rac-CF_3-C_6F_5-diols as was discussed in Part II. As with the other fluorinated diols studied, neither the CF_3-C_6H_5-diol[89] nor the CH_3-C_6F_5-diol underwent a pinacol rearrangement.

The CF_3-CH_3-diol, produced photolytically, was not isolated as the free diol and thus its properties were not investigated. The properties of the perfluoro tertiary alcohols have been reported elsewhere[31] and will not be discussed here.

B. Transition Metal Complexes

All attempts to prepare Ni^{2+} complexes with perfluoro tertiary alcohols of the type $K_2Ni(L)_4$ and $Ni(TMED)L_2$ where L ≡ anion of tertiary alcohol, were unsuccessful. One might expect difficulty with the alcohols containing C_6F_5 groups due to their instability in the basic medium necessary for complexation to occur, but this does not explain the inability to prepare complexes with perfluoro-t-butanol since it is known that it is both soluble and stable in a basic aqueous medium.[93] Although the inability to prepare complexes with this alcohol could be attributable to steric reasons, more detailed studies would have to be undertaken to categorically rule out the existence of such complexes. As well, no metal complexes could be prepared with the CH_3-C_6F_5-diol, which is a direct consequence of its low acidity and instability in concentrated basic solutions. The CH_3-CF_3-diol was prepared in extremely low yields and was not isolated. However, a red crystalline product was readily obtained on addition of $Ni(NO_3)_2$ and TMED to the product of the photolysis of CF_3COCH_3, and its infrared and visible spectra suggest that it is the square planar Ni^{2+} complex, Ni(TMED)(CF_3-CH_3-diol). The low yields of the diol obtained by photolysis plus the inability to prepare the diol by an alternative method precluded a further investigation of this ligand system.

The CF_3-C_6H_5-diol exhibited a greater tendency towards chelation than the other partially fluorinated diols investigated; however, isolation of the metal complexes, which were readily formed in solution, was generally problematic. A Ni^{2+} complex of the diol was formed in a concentrated ethanolic KOH solution which has tentatively been assigned as the bis diol complex, $[Ni(CF_3\text{-}C_6H_5\text{-diol})_2]^{2-}$, based on the visible spectrum of the solution which is virtually superimposable upon the spectrum of $[Ni(PFP)_2]^{2-}$ (solid). Unfortunately, the complex could not be isolated. The existence of this complex, at least in solution, despite the fact that bis-complexes could not be detected with the more acidic CF_3-C_6F_5-diols, is a result of the CF_3-C_6H_5-diol's greater stability in a basic medium.

The mixed ligand compound, Ni(TMED)(CF_3-C_6H_5-diol) was prepared and characterized as a square planar complex, similar to those previously described for the other diols. Although phosphine complexes of the type $Ni(L)_2$(CF_3-C_6H_5-diol), (where L ≡ PEt_3, PMe_2Ph or $PMePh_2$), were observed in solution, attempts to isolate them were unsuccessful. Finally, a series of competitive reactions, similar to those described in Part II, led to the following overall sequence of chelating ability for the diols studied.

$$PFP^{2-} > rac\text{-}CF_3\text{-}C_6F_5\text{-diol} > meso\text{-}CF_3\text{-}C_6F_5\text{-diol} > CF_3\text{-}C_6H_5\text{-diol} >> CH_3\text{-}C_6F_5\text{-diol}$$

In general, the diols described in this section were inferior as ligands compared to H_2PFP and this is attributed to their lower acidities, instability in basic solutions, and/or their preparative difficulties.

CONCLUSIONS

The acidic nature of perfluoropinacol has enabled previous workers to prepare transition metal complexes with this ligand.[27,28] This work has been extended to include mixed ligand complexes of Ni^{2+}, Pd^{2+} and Cu^{2+}. The square planar structure which predominates in the series of Ni^{2+} complexes of the type $Ni(L)_2(PFP)$, when the co-ligand is a phosphine or a N,N,N',N'-tetrasubstituted diamine has been attributed mainly to electronic rather than steric effects. When the co-ligand is a N,N'-disubstituted diamine, an unusual equilibrium exists in coordinating solvents between 4- and 5-coordinate species. The failure of these complexes to attain 6-coordination is explained by the overall bulk of the PFP^{2-} ligand. The unusual solution properties of the previously prepared bis-complex, $[Ni(PFP)_2]^{2-}$, have been attributed to a similar equilibrium.

From a consideration of this and previous work,[27,28] it is concluded that PFP^{2-} and other fluorinated diols can be envisaged as a "pseudo" bidentate di-halide,[94] rather than as an oxalate ligand, as has been previously suggested.[31] In accordance with this concept, perfluoropinacol complexes can generally be prepared if the corresponding halide complexes are known, although the structures may differ, and it is anticipated that this approach to the synthesis of PFP^{2-} complexes will lead to an even greater variety of complexes of this ligand.

A re-investigation of the photo-pinacolization of perfluoroacetophenone proved that two isomers had been produced in the reaction, a meso and a racemic form. Attempts to identify the isomers were initially inconclusive, although the ability of one to preferentially coordinate over the other indicated that it was the racemic compound. Conclusive identification was obtained by resolving the racemic isomer. Whereas previous resolutions of alcohols generally involved converting them to their hydrogen phthalates, followed by resolution as typical acids, the acidity of the diols made possible a direct resolution. The alkaloid base l-cinchonidine formed a 1:1 salt with both diols and subsequent regeneration of the free diols produced one isomer which was optically active. This is apparently the first time a diol has been resolved by this method and its applicability to other fluorinated diols and alcohols is unknown.

Although transition metal complexes of the type $[M(CF_3-C_6F_5\text{-diol})_2]^{2-}$, ($M \equiv Cu^{2+}$ and Ni^{2+}) could not be prepared, the isomeric diols did form a limited number of transition metal complexes with Ni^{2+} and Cu^{2+} of the type $M(L)_2(CF_3-C_6F_5\text{-diol})$. The Cotton effect, which was observed in the ORD and CD spectra of the metal complexes with the resolved diol, has been attributed largely to the preferred conformation of the chelate ring, rather than to the vicinal effect. An assignment of absolute configuration has been made, based on an empirical method developed by Reeves[82] as well as on a comparison of the CD spectra of Cu(TMED)([+]-$CF_3-C_6F_5$-diol) with those obtained for somewhat similar tetradentate Schiff base complexes of Cu^{2+}.[86] Both approaches lead to the assignment of the R,R-configuration to the (+)-isomer.

The ^{19}F nmr spectra of both $CF_3-C_6F_5$-diols exhibit five peaks for the C_6F_5-groups rather than the expected three and this anomaly arises from the sterically hindered rotation of the C_6F_5-group rather than from hydrogen bonding, as previously suggested.[70] The fact that the

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CH_3-C_6F_5-diol does not exhibit a similar anomaly in its ^{19}F nmr spectrum is due to the smaller spatial requirements of the CH_3 groups compared to the CF_3 groups.

In the investigation of partially fluorinated diols and perfluoro tertiary alcohols, a very limited number of transition metal complexes could be prepared. No complex formation was detected with the perfluoro alcohols or the CH_3-C_6F_5-diol. Those compounds that were prepared and isolated, i.e. Ni(TMED)(CF_3-C_6H_5-diol) and Ni(TMED)(CF_3-CH_3-diol), were square planar complexes similar to Ni(TMED)(PFP). It is concluded that the lower acidities of these diols, their instability in basic solutions and/or difficulties in their preparation make them inferior to H_2PFP as ligands.

Based on a series of competitive reactions between the diols investigated, it is concluded that their complexing ability is as follows:

$$H_2PFP > \text{rac-}CF_3\text{-}C_6F_5\text{-diol} > \text{meso-}CF_3\text{-}C_6F_5\text{-diol} > CF_3\text{-}C_6H_5\text{-diol} \gg CH_3\text{-}C_6F_5\text{-diol}$$

Also, the relative acidities of the diols are of the order:

$$H_2PFP > \text{meso-}CF_3\text{-}C_6F_5 > \text{rac-}CF_3\text{-}C_6F_5\text{-diol} > CF_3\text{-}C_6H_5\text{-diol} \gg CH_3\text{-}C_6F_5\text{-diol}$$

As expected, the relative acidities parallel the complexing abilities except for the two isomeric diols, where for steric reasons, the rac preferentially coordinates over the meso isomer, in spite of their relative acidities.

EXPERIMENTAL SECTION

A. General Procedure

Reactions were carried out according to standard procedures, under an atmosphere of nitrogen where indicated. A 400 W G.E. mercury lamp was used for photolysis reactions, which were carried out in silica or Pyrex reaction vessels as noted. Standard vacuum techniques were used where necessary.

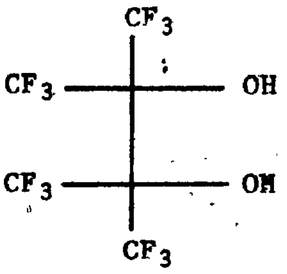
Infrared spectra were recorded on either Beckman model IR-10 or Perkin Elmer 620 instruments, visible spectra on either Beckman DK-I or Cary model 14 instruments and ORD-CD spectra on a Durrum-Jasco ORD-UV-5 spectropolarimeter. ^1H nmr spectra were recorded on a Varian T-60 or an HA-100 spectrometer with tetramethylsilane as an internal standard. ^{19}F nmr spectra were recorded on an HA-100 spectrometer at 94.1 MHz with "freon 11" ($CFCl_3$) as the internal standard. Mass spectra were recorded on a Varian M-66 instrument.

Conductivity measurements were made with an Industrial Industries RC18 conductivity bridge, magnetic moments were determined at room temperature by the Gouy method and molecular weights were determined with an Hitachi Perkin-Elmer molecular weight apparatus. A Corning model 12 pH meter was used for pKa determinations and a Thomas Hoover Uni-Melt Capillary Melting Point Apparatus for melting points. Microanalyses were performed by Alfred Bernhardt Laboratories.

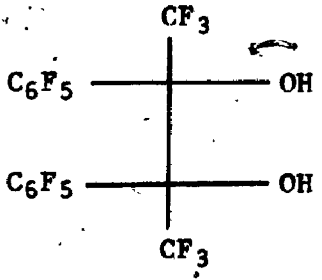
Hexafluoroacetone (Allied Chemical), pentafluorobromobenzene (Imperial Smelting and PCR), trifluoroacetic acid (Eastman), 1,1,1-trifluoroacetone (PCR), perfluoro-t-butanol (PCR) and triethylphosphite (Eastman) were used directly without purification. Triethylphosphine, methyldiphenylphosphine and dimethylphenylphosphine were prepared by standard Grignard reactions. Perfluoro(2-phenylpropan-2-ol), perfluoro(1,1-diphenylethanol) and perfluoro(triphenylcarbinol) were obtained from Dr. A. J. Tomlinson. Transition metal salts and other phosphine and diamine ligands were purchased and used without further purification.

B. Nomenclature

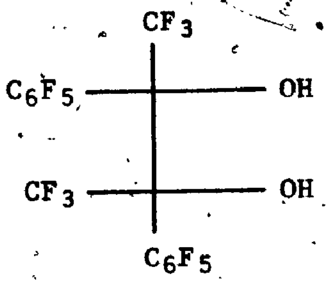
Due to the lengthy formal names of the ligands used throughout this work, a series of systematic abbreviations has been used. The structures of the ligands, their formal names and abbreviations [ ] are listed below.



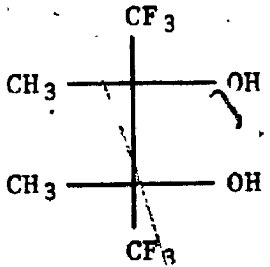
perfluoro-2,3-dimethyl-
butane-2,3-diol
[H_2PFP]
[perfluoropinacol]



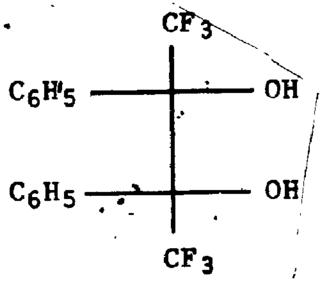
meso-perfluoro(2,3-
diphenylbutane-2,3-diol)
[meso-CF_3-C_6F_5-diol]



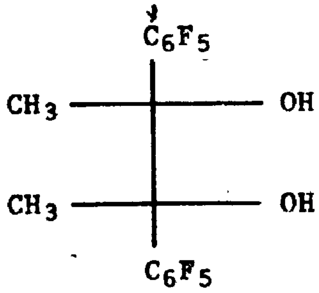
rac-perfluoro(2,3-diphenylbutane-2,3-diol)
[rac-CF_3-C_6F_5-diol]



1,1,1,4,4,4-hexafluoro-2,3-dimethylbutane-2,3-diol
[CH_3-CF_3-diol]



1,1,1,4,4,4-hexafluoro-2,3-diphenylbutane-2,3-diol
[C_6H_5-CF_3-diol]



bis(pentafluorophenyl)-butane-2,3-diol
[CH_3-C_6F_5-diol]

All the ligands have been named according to the different substituents on the diols, with the exception of perfluoropinacol which remains H_2PFP for historical reasons. The ionized form of H_2PFP is represented by PFP^{2-}. Also, abbreviations for other ligands, used throughout the text, include:

PEt_3: triethylphosphine

$PMePh_2$: methyldiphenylphosphine

PMe_2Ph: dimethylphenylphosphine

PPh_3: triphenylphosphine

Diphos: 1,2-bis(diphenylphosphino)ethane

TMED: N,N,N',N'-tetramethylethylenediamine

TEED: N,N,N',N'-tetraethylethylenediamine

N,N'-Diethen: N,N'-diethylethylenediamine

N,N'-Dibenzen: N,N'-dibenzylethylenediamine

Dipy: Dipyridyl

$P(OEt)_3$: triethylphosphite

DETA: diethylenetriamine

N,N'-dibenzen-N,N'-dimethen: N,N'-dibenzyl-N,N'-dimethylethylenediamine

C. Metal Complexes of Perfluoropinacol

Preparation of Perfluoropinacol[17]

Hexafluoroacetone (HFA) was bubbled into cooled (0°C) triethylphosphite (125 gm, 0.75 mole) until the reaction was complete, based on no further uptake of HFA and the final weight of the reaction mixture (348 gm, 0.70 mole). Concentrated sulphuric acid (90 ml) was added slowly to the stirring mixture, followed by H_2O (90 ml). The solution was refluxed for 2 hours, reacidified with sulphuric acid (50 ml) and on cooling, repeatedly extracted with methylene chloride and dried ($MgSO_4$). The solution was distilled to yield crude perfluoropinacol (241 gm, b.p. 110-131°C, liquid). The crude product was redistilled from concentrated sulphuric acid to give anhydrous H_2PFP. (215 gm, 0.64 mole, 85%: b.p. 129-130°C). The compound had a pKa of 6.5 in a 50/50 ethanol/water mixture.

Preparation of $K_2Ni(PFP)_2$

This complex was prepared by the reported method[27] of Allan and Willis, and was identified by comparing its infrared spectrum with that of an authentic sample.

The compound has a molar conductivity of 207 mhos at infinite dilution (MeOH). The diffuse reflectance spectrum of the complex exhibits peaks at 550 nm and 640 nm (sh). The solution visible spectra differed from the solid state spectrum as illustrated in Figures 1, 2 and 3.

Preparation of $Ni[P(OEt)_3]_2(PFP)$

Excess triethyl phosphite (0.75 gm) was slowly added to a solution of $K_2Ni(PFP)_2$ (1.50 gm) in a 3:1 ethanol/water mixture. The resulting solution was reduced in volume to yield a yellow waxy precipitate. The complex was recrystallized from a methylene chloride/pet. ether mixture (mp 85-87°, decomp.).

Anal. Calcd. for $NiC_{18}H_{30}F_{12}O_8P_2$: C, 29.91; H, 4.15; F, 31.55; Ni, 9.13. Found: C, 28.91; H, 4.21; F, 31.19; Ni, 9.21.

The complex was diamagnetic* and had an infrared spectrum consistent with the presence of both PFP^{2-} and $P(OEt)_3$. The visible spectra of the complex exhibited one peak at 417 nm (solid), 415 nm (ε = 272, benzene), 414 nm (ε = 325, acetone) and 415 nm (ε = 315, methanol).

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*Term consistently used to indicate complete lack of paramagnetism.

Preparation of $Ni(PEt_3)_2(PFP)$

(i) Triethylphosphine (PEt_3) (2.0 gm, 17 mmoles) was slowly added under nitrogen to a water/methanol solution containing nickel nitrate hexahydrate (2.60 gm, 8.9 mmoles) and perfluoropinacol (2.80 gm, 8.4 mmoles). Potassium hydroxide in methanol was slowly added until a pH of approximately 8 was attained. The resulting orange precipitate was filtered and recrystallized from a methanol/water mixture (mp 181°).

Anal. Calcd. for $NiC_{18}H_{30}F_{12}O_2P_2$: C, 34.14; H, 4.87; F, 39.45; Ni, 9.60; P, 9.73. Found: C, 34.54; H, 4.79; F, 36.42: Ni, 9.38; P, 9.89. Molecular Weight. Calcd: 627. Found: 651.

The compound was diamagnetic, had a singlet in the ^{19}F nmr spectrum at 71.3 ppm from freon 11 and had an infrared spectrum consistent with the presence of $R(Et)_3$ and PFP^{2-}. The visible spectrum showed one peak: 460 nm (solid), 460 nm (ϵ = 230, benzene), 461 nm (ϵ = 254, methanol), 461 nm (ϵ = 242, acetone).

(ii) Addition of an excess of $P(Et)_3$ to a solution (methanol) of potassium bis(perfluoropinacolato)nickelate(II) caused an immediate colour change from blue to orange. The orange precipitate was filtered, recrystallized from methanol and identified as $Ni(PEt_3)_2(PFP)$.

Preparation of $Ni(PMe_2Ph)_2(PFP)$

(i) A slight excess of dimethylphenylphosphine (PMe_2Ph) (2.20 gm, 16.0 mmoles) was added slowly under nitrogen to a water/methanol solution of nickel nitrate hexahydrate (2.00 gm, 6.90 mmoles) and perfluoropinacol (2.30 gm, 6.90 mmoles). Potassium hydroxide in methanol was added dropwise until the colour of the solution changed from a deep red to orange and an orange crystalline compound precipitated. The precipitate was filtered and recrystallized from water/methanol (mp 132-133°).

Anal. Calcd. for $NiC_{22}H_{22}F_{12}P_2O_2$: C, 39.64; H, 3.28; F, 34.19. Found: C, 39.45; H, 3.42; F, 34.42. Molecular Weight. Calcd: 667. Found: 740.

The compound was diamagnetic, had a singlet in the ^{19}F nmr spectrum at 71.2 ppm from freon 11 and had an infrared spectrum compatible with the presence of both PFP^{2-} and PMe_2Ph. The visible spectrum exhibited a single band: 454 nm (solid); 455 nm (ε = 302, benzene), 460 nm (ε = 263, MeOH), 459 nm (ε = 320, acetone).

(ii) This comple[illegible]ould also be prepared be adding an excess of PMe_2Ph to a solution (methanol) of $K_2Ni(PFP)_2$.

Preparation of $Ni(PMePh_2)_2(PFP)$

Methyldiphenylphosphine ($PMePh_2$) (1.50 gm, 7.5 mmoles) was added slowly under nitrogen to an ethanol/water solution of nickel nitrate hexahydrate (1.09 gm, 3.75 mmoles) and perfluoropinacol (1.25 gm, 3.75 mmoles). Ethanolic potassium hydroxide was added slowly until a pH of approximately 8 was reached. The resulting orange precipitate was filtered and recrystallized from ethanol (mp 172-173°).

Anal. Calcd. for $NiC_{32}H_{26}F_{12}P_2O_2$: C, 48.59; H, 3.31. Found: C, 48.41; H, 3.49. Molecular Weight. Calc: 791. Found: 856.

The compound was diamagnetic, exhibited a singlet in the ^{19}F nmr spectrum at 70.95 ppm from freon 11 and had an infrared spectrum consistent with the presence of PMe_2Ph and PFP^{2-}. One band was present in the visible spectrum of the compound: 463 nm (solid), 464 nm (ε = 316, benzene), 466 nm (ε = 270, methanol), 467 nm (ε = 348, acetone).

(ii) An excess of methyldiphenylphosphine was added to an ethanol solution of potassium bis(perfluoropinacolato)nickelate(II). The orange crystalline product that precipitated on concentrating the solution was filtered, recrystallized from ethanol and identified as $Ni(PMePh_2)_2(PFP)$.

Preparation of Ni(diphos)(PFP)

Bis(diphenylphosphino)ethane [diphos] (0.60 gm, 1.50 mmoles) was dissolved in methylene chloride and slowly added to an ethanol solution of nickel nitrate hexahydrate (0.44 gm, 1.50 mmoles) and H_2PFP (0.50 gm, 1.50 mmoles). Potassium hydroxide in ethanol was slowly added to the solution until a pH of approximately 8 was attained and the resulting gold solution was centrifuged to remove potassium nitrate. Concentration of the solution resulted in the precipitation of a golden crystalline product which was recrystallized from a water/methanol mixture (mp 228°).

Anal. Calcd. for $NiC_{32}H_{24}F_{12}O_2P_2$: C, 48.72; H, 3.04; F, 28.89; Ni, 7.44. Found: C, 47.85; H, 3.62; F, 30.71; Ni, 8.53. Molecular Weight. Calcd: 789. Found: 843.

The complex, which was found to be diamagnetic, had a singlet in its ^{19}F nmr spectrum at 70.95 ppm from freon 11 and an infrared spectrum consistent with the presence of both diphos and PFP^{2-}. The visible spectrum of the compound exhibited a single band: 448 nm (solid), 439 nm (ε = 314, benzene), 445 nm (ε = 298, methanol), 445 nm (ε = 274, acetone).

Preparation of $Ni(PPh_3)_2(PFP)$

(i) Triphenylphosphine (2.00 gm, 7.65 mmoles) and perfluoropinacol (1.30 gm, 3.90 mmoles) were dissolved in t-butyl alcohol with warming. Potassium hydroxide in butyl alcohol was added to the solution until the pH was approximately 8.5, An excess of nickel nitrate hexahydrate in t-butyl alcohol was slowly added to the solution resulting in initially a blue solution and finally an orange solution. The solution was reduced in volume, and an orange precipitate was collected and recrystallized from a chloroform/pet. ether (30:60) mixture (mp 208°). Attempts to prepare the compound in methanol or ethanol were unsuccessful.

Anal. Calcd. for $NiC_{42}H_{30}F_{12}O_2P_2$: C, 55.12; H, 3.30; F, 24.90. Found: C, 54.95; H, 3.43; F, 25.23.

The compound had an infrared spectrum consistent with the presence of PFP^{2-} and PPh_3. The compound was diamagnetic and had a singlet in its ^{19}F nmr spectrum ($CHCl_3$) at 70.63 ppm from freon 11. The complex had molecular weight of 727 (benzene) versus a calculated value of 915.

The diffuse reflectance spectrum of the complex exhibited one band at 475 nm and the solution visible spectrum also exhibited one peak at 477 nm (ε = 274, benzene). The complex decomposed in ethanol, methanol and acetone and hence solution spectra were not recorded in these solvents.

(ii) An alternative method of preparation involved the addition of base to a 1:1 mixture of perfluoropinacol and dichlorobis-(triphenylphosphine)nickel(II) in butyl alcohol. Work up as before yielded a brick orange crystalline complex which was identified by its infrared and visible spectra as being the desired compound. Similarly, the compound was prepared from potassium bis(perfluoropinacolato)-nickelate(II) and triphenylphosphine.

Preparation of Ni(TMED)(PFP)

(i) A slight excess of tetramethylethylenediamine (TMED) (1.41 gm, 0.83 mmoles) was added dropwise to a water/methanol (1:2) solution of perfluoropinacol (H_2PFP) (2.50 gm, 7.50 mmoles) and nickel nitrate hexahydrate (2.20 gm, 7.11 mmoles). Potassium hydroxide solution was added slowly with stirring until a pH of approximately 8 was attained. The resulting red precipitate was filtered and recrystallized from methanol/water to yield a red crystalline compound (mp 232°, decomp).

Anal. Calcd. for $NiC_{12}H_{16}F_{12}O_2N_2$: C, 28.9; H, 2.9; Ni, 11.5; N, 6.2. Found: C, 28.7; H, 3.2; Ni, 11.6; N, 5.5. Molecular Weight: Calcd. 504. Found: 622.

The infrared spectrum showed peaks characteristic of perfluoropinacol and tetramethylethylenediamine. The diffuse reflectance spectrum has one band at 491 nm and the solution spectrum (methanol) exhibits one band at 501 nm (ϵ = 75). The compound is diamagnetic and the ^{19}F nmr spectrum ($CHCl_3$) has one singlet at 71.3 ppm from freon 11.

(ii) Addition of an excess of tetramethylethylenediamine to a solution (ethanol) of potassium bis(perfluoropinacolato)-nickelate(II), produces an immediate colour change from blue to red. Concentration of the solution causes the precipitation of a red compound (mp 232°, decomp). The infrared, visible and ^{19}F nmr spectra confirm that the two compounds are identical.

Preparation of Ni(TEED)(PFP)

This compound was prepared by the analogous two procedures as used for Ni(TMED)(PFP). The two compounds (magenta) isolated were similar in all respects (mp 239-240° decomp.).

Anal. Calcd. for $NiC_{16}H_{24}F_{12}N_2O_2$: C, 34.14; H, 4.26; F, 40.51; Ni, 10.43; N, 4.98. Found: C, 34.84; H, 4.73; F, 41.67; Ni, 10.37; N, 4.99: Molecular Weight. Calcd: 563. Found: 622.

The compound was diamagnetic and had an infrared spectrum consistent with the presence of TEED and PFP^{2-}. The ^{19}F nmr spectrum showed a singlet at 71.1 ppm from freon 11. The visible spectrum showed one peak: 517 nm (solid), 508 nm (ε = 67, benzene), 518 nm (ε = 70, methanol), 515 nm (ε = 74; acetone).

Preparation of Ni(N,N'-dibenzen-N,N'-dimethen)(PFP)

N,N'-dibenzyl-N,N'-dimethylethylenediamine (1.50 gm, 5.60 mmoles) in ethanol was added dropwise to an ethanol solution of perfluoropinacol (1.87 gm, 5.60 mmoles) and nickel nitrate hexahydrate (1.65 gm. 5.71 mmoles). Ethanolic potassium hydroxide was added until a pH of approximately 8 was reached. The resulting red solution was centrifuged to remove potassium nitrate, evaporated to dryness and recrystallized from a methylene chloride/pet. ether (30/60) mixture to give a red crystalline product. (mp 166-167°).

The visible spectrum (MeOH) had one band at 501 nm (ε = 78) and the infrared spectrum (nujol) had peaks attributable to both ligands. The ^{19}F nmr spectrum had a multiplet at 70.5 ppm from freon 11. Attempts to detect the presence of more than one isomer through fractional recrystallization and TLC were unsuccessful.

Preparation of Ni(Dipy)(PFP)

An ethanol solution of 2,2'-dipyridyl (Dipy) (1.00 gm, 6.40 mmoles) was added slowly to an ethanol solution of nickel nitrate hexahydrate (1.86 gm, 6.40 mmoles) and perfluoropinacol (2.14 gm, 6.40 mmoles). Ethanolic potassium hydroxide was added to the solution until a pH of approximately 8 was reached. The resulting orange-brown solution was centrifuged to remove potassium nitrate and reduced in volume, precipitating a dark orange complex which was recrystallized from an ethanol/water mixture (mp 280° decomp).

Anal. Calcd. for $NiC_{16}H_8F_{12}N_2O_2$: C, 35.14; H, 1.47; F. 41.68; Ni, 10.73. Found: C, 35.03; H, 1.66; F, 41.78; Ni, 10.84. Molecular Weight Calcd. 547. Found: 480.

The compound was diamagnetic and had a singlet in the ^{19}F nmr spectrum ($CHCl_3$) at 71.33 ppm from freon 11. The infrared spectrum had peaks due to both PFP and Dipy. The diffuse reflectance spectrum had one peak at 417 nm and the solution visible spectrum (methanol) had one peak at 390 nm (ε = 1640).

Attempted Preparation of $Ni[N(Et)_3]_2(PFP)$

An excess of triethylamine $[N(Et)_3]$ (3.00 gm, 14.9 mmoles) was added dropwise to an ethanol solution of perfluoropinacol (1.66 gm, 5.00 mmoles) and nickel nitrate hexahydrate (1.45 gm, 5.00 mmoles). The resulting purple solution was centrifuged to remove potassium nitrate and evaporated to dryness. The residue was recrystallized from acetone to give a blue crystalline compound (mp 248-250° decomp).

Anal. Calcd. for $NiC_{24}H_{32}F_{24}O_2N_2$: C, 31.07; H, 3.45; F, 49.17; N, 3.02; Ni, 6.33. Found: C, 31.27; H, 3.33; F, 49.33;

N, 3.33; Ni, 6.37.

The compound was diamagnetic and had peaks in the infrared between 2500 cm^{-1} and 3000 cm^{-1} indicative of an amine salt. The diffuse reflectance spectrum and the visible spectra in various solvents were similar to those of $K_2Ni(PFP)_2$ and the compound was characterized as $(NEt_3H)_2Ni(PFP)_2$.

The use of ammonium hydroxide and tri-butyl amine also resulted in blue crystalline compounds which were identified by their infrared and visible spectra as $(NH_4)_2Ni(PFP)_2$ and $(N\text{-}bu_3H)_2Ni(PFP)_2$, respectively.

Preparation of Ni(DETA)(PFP)

Diethylenetriamine (0.71 gm) was added to a 1:1 mixture of nickel nitrate hexahydrate (2.00 gm) and perfluoropinacol (2.28 gm) in a methanol/water mixture. The resulting solution was reduced in volume and a green precipitate was collected and recrystallized from methanol (mp 242-245° decomp).

Anal. Calcd. for $NiC_{10}H_{13}F_{12}O_2N_2$: C, 24.33; H, 2.63; F, 46.16; Ni, 11.89, Found: C, 24.17; H, 3.06; F, 46.30; Ni, 12.06.

The complex had a magnetic moment of 3.14 B.M. and was a non-electrolyte in methanol.

The diffuse reflectance spectrum had the following peaks: 380, 465, 637, 781, 840, < 1,000 nm; the solution visible spectrum (MeOH) had the following peaks: 381 (65), 450 (sh), 637 (20), 781 (10), 840 (12), 14500 (15) nm (Figure 12).

Preparation of Ni(N,N'-dibenzen)(PFP)

N,N'-dibenzylethylenediamine (N,N'-dibenzen) (4.15 gm, 17.2 mmoles) was slowly added with stirring to a 1:1 ethanol/water solution of perfluoropinacol (5.75 gm, 17.2 mmoles) and nickel nitrate hexahydrate (5.00 gm, 17.2 mmoles). Ethanolic potassium hydroxide was slowly added until a pH of approximately 8 was reached and the resulting green precipitate was collected. Recrystallization from a methylene chloride/pet. ether (30/60) mixture yielded a red crystalline product (mp 101-104°). The initial green complex could be converted to the red complex under vacuum or on heating.

The infrared spectrum of the red complex was similar to those of Ni(TMED)(PFP) and Ni(TEED)(PFP). The visible spectrum of either compound exhibited one peak in CH_2Cl_2 (500 nm, $\varepsilon = 54$). In the presence of polar solvents, the visible spectra were entirely changed (Figure 7). Visible spectra recorded in both a series of H_2O/MeOH and pyridine/CH_2Cl_2 mixtures exhibited two isosbestic points (Figures 8 and 9).

In general, the complex was red in non-polar solvents and green in polar solvents. Also, methanol solutions, which were red at room temperature, turned green on cooling while MeOH/H_2O solutions, which were green at room temperature, turned red on heating.

Preparation of Ni(N,N'-diethen)(PFP)

This complex was prepared in a similar manner to Ni(N,N'-dibenzen)(PFP), yielding both a green and red form. The visible spectrum recorded in CH_2Cl_2 exhibited one peak (503 nm, $\varepsilon = 46$) (Figure 5) but was entirely different in polar solvents (Figures 6 and 11): Two isosbestic points were observed in the visible spectra in a series of CH_2Cl_2/benzylamine mixtures. Attempts to isolate the green complexes present in polar solvents were unsuccessful except with H_2O.

Preparation of $Pd(PMe_2Ph)_2(PFP)$

Methanolic potassium hydroxide was added dropwise to a solution (methanol) of dichlorobis(dimethylphenylphosphino)palladium(II) (0.300 gm, 0.662 mmoles) and perfluoropinacol (0.220 gm, 0.660 mmoles) until a pH of approximately 8 was attained. The resulting solution was evaporated to dryness and the residue recrystallized from methylene chloride to give an off-white crystalline product (mp 157°, decomp.).

Anal. Calcd. for $PdC_{22}H_{22}F_{12}O_2P_2$: C, 36.98; H, 3.10; F, 31.89. Found: C, 36.71; H, 2.88; F, 31.90.

The infrared spectrum shows peaks due to both PFP^{2-} and PMe_2Ph. The ^1H nmr of the methyl protons shows a second order multiplet at 1.56 ppm from TMS.

Preparation of $Pt(PMe_2Ph)_2(PFP)$

Methanolic potassium hydroxide was added to a solution (methanol) of dichlorobis(dimethylphenylphosphino)platinum(II) (0.150 gm, 0.276 mmoles] and perfluoropinacol [0.092 gm, 0.276 mmoles] until a pH of 8 was attained. The solution was evaporated to dryness and the residue recrystallized from methylene chloride to give a white crystalline product (mp 174-175°).

Anal. Calcd. for $PtC_{22}H_{22}F_{12}P_2O_2$: C, 32.89; H, 2.76; F, 28.37. Found: C, 32.43; H, 3.01; F, 28.60.

The infrared spectrum of this compound is compatible with the presence of both PFP^{2-} and PMe_2Ph. The ^1H nmr spectrum of the methyl protons shows a multiplet at 1.60 ppm from TMS.

Preparation of Cu(TMED)(PFP)

An excess of tetramethylethylenediamine (1.20 gm, 10.4 mmoles) was slowly added to a methanol/water solution of copper sulphate pentahydrate (2.00 gm, 8.00 mmoles) and perfluoropinacol (2.70 gm, 8.08 mmoles). Methanolic potassium hydroxide was added until a pH of approximately 8 was attained, and a purple compound had precipitated. The compound was filtered and recrystallized from an acetone/water mixture to give a purple crystalline complex (mp 191-192°, decomp.).

Anal. Calcd. for $CuC_{12}H_{16}F_{12}O_2N_2$: C, 28.17; H, 3.13; F, 44.55; Cu, 12.42. Found: C, 28.04; H, 3.29; F, 44.49; Cu, 12.31.

The compound had a magnetic moment of 1.85 B.M. The infrared spectrum of the compound was consistent with the presence of PFP^{2-} and TMED. The diffuse reflectance spectrum of the compound had one broad band centred at approximately 600 nm. The visible spectrum had one band at 557 nm (MeOH, $\epsilon \cong 68$) and 550 nm (CH_2Cl_2, $\epsilon \cong 63$).

Preparation of Cu(TEED)(PFP)

An excess of tetraethylethylenediamine (TEED) (1.50 gm, 8.75 mmoles) was slowly added to a methanol/water solution of copper sulphate pentahydrate (2.00 gm, 8.00 mmoles) and perfluoropinacol (2.70 gm, 8.08 mmoles). Methanolic potassium hydroxide was added until a pH of approximately 8 was attained. The precipitate thus obtained was filtered and recrystallized from an acetone/water mixture to give a purple crystalline compound (mp 195-197°, decomp.).

Anal. Calcd. for $CuC_{16}H_{24}F_{12}O_2N_2$: C, 33.86; H, 4.21; F, 40.15; Cu, 11.19. Found: C, 33.93; H, 4.30; F, 40.40; Cu, 11.33.

The compound had a magnetic moment of 1.87 B.M. and an infrared spectrum consistent with the presence of PFP^{2-} and TEED. The diffuse reflectance spectrum had a broad band centred at 610 nm and the solution visible spectrum exhibits one band (555 nm, ε ≡ 56, MeOH; 556 nm, ε ≡ 59, CH_2Cl_2).

D. Perfluoro-2,3-diphenylbutane-2,3-diol and its Metal Complexes

Preparation of Octafluoroacetophenone[96]

Pentafluorobromobenzene (50.0 gm, 0.201 moles) in diethylether (100 ml) was slowly added to magnesium (5.8 gm, 0.21 moles) and stirred for approximately one hour. The product was added dropwise to lithium trifluoroacetate [prepared under a nitrogen atmosphere from lithium hydride (1.65 gm, 0.21 moles) and trifluoroacetic acid (22.8 gm, 0.20 moles)] and the resulting mixture was stirred for 22 hours at room temperature. The product was hydrolyzed with dilute sulphuric acid, repeatedly extracted with ether and dried overnight with magnesium sulphate. Distillation gave perfluoroacetophenone (17.5 gm, .067 moles, 33%) bp 130-131°.

Preparation of Perfluoro(2,3-diphenylbutane-2,3-diol)

Octafluoroacetophenone (17.0 gm, .064 moles) in 2-propanol (85 ml), with several drops of hydrochloric acid, was irradiated for eight days in a Pyrex vessel. Removal of the volatile materials and subsequent sublimation gave a white solid (12.1 gm, .023 moles, 71%) (mp 96-115°). Fractional recrystallization from 30-60° petroleum spirits yielded two compounds in approximately equal amounts. The less soluble compound, meso-C_6F_5-diol, had a melting point of 119-120° while the more soluble rac-C_6F_5-diol had a melting point of 130-131°.

Anal. Calcd. for $C_{16}F_{16}O_2H_2$: C, 36.3; H, 0.4; F, 57.3.

Found: meso isomer: C, 36.4; H, 0.3; F, 57.6: rac isomer: C, 36.0; H, 0.3; F, 57.1.

Molecular Weights (benzene solutions): Calcd. for $C_{16}F_{16}O_2H_2$: 530. Found: meso, 535; rac, 543.

The infrared spectrum (nujol) of the meso isomer showed peaks (cm^{-1}) at: 3640(s), 1651(m), 1534(s), 1490(s); 1408(w), 1402(w), 1343(m), 1310(w), 1215(s), 1180(s), 1130(s), 1095(m), 995(s), 945(m), 853(m), 782(m), 760(m), 712(w), 677(m), 625(w), 575(w), 544(w), 490(w), 444(w), 406(m). [s ≡ strong, m ≡ medium, w ≡ weak.]

The following bands (cm^{-1}) were found in the infrared spectrum of the rac-C_6F_5-diol (nujol mull): 3627(s), 1654(m), 1535(s), 1495(s), 1465(s), 1410(m), 1315(m), 1270(s), 1250(s), 1235(s), 1210(s), 1172(s), 1135(s), 1115(s), 1098(m), 1010(s), 990(s), 873(m), 799(m), 790(m), 755(s), 745(m), 735(w), 710(m), 699(s), 650(w), 630(w), 555(w), 535(w), 519(w), 480(w), 460(w), 450(w), 440(w), 400(m).

The infrared spectra (CCl_4) above 3000 cm^{-1} exhibited an intense peak at 3610 cm^{-1} (rac) and 3625 cm^{-1} (meso) as well as a broad band at ∿ 3200 cm^{-1} (rac and meso).

The ^{19}F nmr spectrum ($CHCl_3$) of the rac-C_6F_5-diol has six multiplets at: A, 73.25; B, 129.9; C, 143.2; D, 148.7; E, 159.3; F, 160.2 ppm from freon 11. The ^1H nmr spectrum ($CDCl_3$) exhibits a doublet at 4.28 ppm (J = 12) from TMS. The ^{19}F nmr spectrum ($CHCl_3$) of the meso isomer also exhibits six multiplets at: A, 71.58; B, 129.3; C, 140.5; D, 149.6; E, 160.3; and F, 160.6 ppm from freon 11. The proton nmr spectrum ($CDCl_3$) is a doublet of doublets at 4.45 ppm (J = 5, 14) from TMS.

The ^{19}F nmr spectrum of the rac isomer in a 1:1 chloroform/

(+)-α-phenethylamine mixture, exhibited the same six peaks, very poorly resolved, with no apparent further splitting. For the meso isomer, in the same solvent system, there is a doublet of doublets at 73.92 ppm (J ≡ 35, 9) from freon 11 and a doublet of quartets at 79.14 ppm (J ≡ 42, 13) from freon 11, in the ratio of 1:1. Further multiplets occur at 127.0, 134.6, 143.2, 151.9, 160.2, 162.0 and 163.5 ppm from freon 11.

The mass spectra of the two isomers had identical peaks, differing only slightly in relative intensities. The major peaks for the rac-C_6F_5-diol and their assignment are listed below.

Mass	Fragment	Derivation
530	$C_{16}F_{16}O_2H_2$	P^+ ≡ parent ion (not observed)
510	$C_{16}F_{15}O_2H$	$(P-HF)^+$
441	$C_{15}F_{12}O_2H$	$(P-[HF, CF_3])^+$
372	$C_{14}F_9O_2H$	$(P-[HF, CF_3, CF_3])^+$
371	$C_{14}F_9O_2$	$(P-[HF, CF_3, CF_3, H])^+$
327	$C_{10}F_{10}OH$	$(P-[HF, C_6F_5O])^+$
265	C_8F_8OH	$(CF_3C_6F_5COH)^+ \equiv D$
245	C_8F_7O	$(D-HF)^+$

The pK_a values, measured in 50:50 ethanol/water mixtures, were 8.7 for the meso isomer and 9.1 for the racemic isomer.

Resolution of rac-perfluoro(2,3-diphenylbutane-2,3-diol)

Perfluoro(2,3-diphenylbutane-2,3-diol) (mp 120°, 2.0 gm, 3.7 mmoles) and l-cinchonidine (1.10 gm, 3.7 mmoles) were dissolved together in a chloroform/pet. ether (30-60°) mixture (10:1). A white precipitate, which formed after approximately five hours, was collected and dried. Although peaks due to both the diol and the cinchonidine were present, no O-H stretch was observed. The compound was treated with dilute hydrochloric acid, extracted with diethyl ether, and stripped of solvent. The infrared spectrum indicated that the diol had been regenerated but the ORD spectrum indicated no resolution. The same procedure was repeated with the higher melting isomer and the ORD spectrum showed that some resolution of the diol had occurred. Prior attempts with the alkaloids brucine, strychnine and quinine and the synthetic bases (+)-α-phenethylamine, l-α-(1-naphthyl)-ethylamine and dehydroabiethylamine were successful. Although strychnine did form a crystalline compound with the lower melting isomer, repeated attempts with the higher melting isomer yielded retractable oils. With the other reagents, either starting materials were recovered, or unmanageable oils were produced.

Perfluoro(2,3-diphenylbutane-2,3-diol) (16.1 gm, 30 mmoles, mp 130°) and l-cinchonidine (8.95 gm, 30 mmoles) were dissolved in a chloroform (150ml)/pet. ether (30-60°, 20 ml) mixture and precipitation of a white solid occurred over a period of three days. A sample was recrystallized from methylene chloride (mp 95-100°).

Anal. Calcd. for $C_{35}H_{24}F_{16}O_3N_2$: C, 50.99; H, 2.9; F, 36.86. Found: C, 51.8; H, 2.9; F, 37.9.

The following bands (cm^{-1}) were found in the infrared spectrum (nujol) of the compound: 1647(m), 1530(s), 1480(s), 1465(s), 1310(w), 1240(m), 1195(m), 1165(s), 1130(m), 1110(s), 1090(w), 1050(w), 1025(w), 1000(m), 980(s), 952(w), 920(w), 885(w), 860(w), 830(w), 805(w), 780(m), 765(m), 742(w), 720(m), 690(m), 640(w), 610(w), 580(w), 545(w), 460(w).

The compound had an equivalent conductance of 40 $ohm^{-1}\ cm^2$ in methanol and a molecular weight of 405 extrapolated to infinite dilution (Calcd. 412 for complete dissociation).

The first fraction of the salt (8.3 gm, $[\alpha]^{20}_{589} = -40.4°$, [2.09 gm/100 ml, CH_2Cl_2]) yielded 4.87 gm of diol with $[\alpha]^{20}_{589} = +62°$ (1.98 gm/100 ml, CH_2Cl_2). The last fraction, an oil, on conversion to the diol (3.30 gm), had a specific rotation at 589 nm of -42° (2.01 gm/100 ml, CH_2Cl_2). The (+)-isomer was fractionally re-crystallized from pet. ether (30-60°) to give a constant specific rotation of 96.6° at 589 nm (1.80 gm/100 ml, CH_2Cl_2) and a melting point of 89-90°.

Attempted Reaction of Perfluoro(2,3-diphenylbutane-2,3-diol) with Sulphuric Acid

Perfluoro(2,3-diphenylbutane-2,3-diol) (mixture of isomers) (0.50 gm, 0.95 mmoles) was refluxed for one hour in conc. sulphuric acid (5 ml). Water (10 ml) was added and the solution refluxed for a further thirty minutes. The solution was extracted with CH_2Cl_2, dried ($MgSO_4$) and concentrated to yield a white crystalline product. Its melting point and infrared spectrum (nujol) indicated that it was unreacted starting material.

Attempted Preparation of $K_2Ni(rac-C_6F_5-diol)_2$

Rac-C_6F_5-diol (1.00 gm, 1.88 mmoles) and nickel nitrate hexahydrate (0.27 gm, 0.93 mmoles) were dissolved in methanol and potassium hydroxide (in methanol) was slowly added until a pH of approximately 8.5 was attained. The only metal containing product isolated from the reaction mixture was $Ni(OH)_2$. Attempts to prepare the tetramethyl-, tetraethyl- and tetrabutylammonium salts were also unsuccessful. Similar reactions using the meso-C_6F_5-diol were also unsuccessful. Also, ORD spectra were recorded of mixtures of (+)-C_6F_5-diol and Ni^{2+} in which the ratio of ligand to metal was varied from 1.0:0.5 to 1.0:5.0 and no sign of interaction between the two species was detected.

Attempted Preparation of $K_2Cu(rac-C_6F_5-diol)_2$

Attempts to prepare bis-diol complexes with Cu^{2+} were undertaken as previously described for the analogous Ni^{2+} compounds. Efforts to prepare the potassium, tetramethyl-, tetraethyl- and tetrabutylammonium salts with both the meso- and rac-diols were unsuccessful.

Preparation of Ni(TMED)[(+)-C_6F_5-diol]

An excess of tetramethylethylenediamine (TMED) (0.15 gm, 1.30 mmoles) was slowly added to an ethanol solution (15 ml) of (+)-C_6F_5-diol (0.300 gm, 0.57 mmoles, $[\alpha]_{589}^{20} = 96.6°$) and nickel nitrate hexahydrate (0.165 gm, 0.57 mmoles). Potassium hydroxide in ethanol was added until a pH of approximately 8 was reached. The resulting red solution was centrifuged, evaporated to dryness and the product was recrystallized from ethanol to give a red crystalline compound (mp 148°, decomp.).

Anal. Calcd. for $NiC_{22}H_{16}F_{16}O_2N_2$: C, 41.15; H, 3.16; F, 40.04. Found: C, 41.17; H, 3.33; F, 40.09. Molecular Weight (benzene). Calcd: 759. Found: 765.

The infrared spectrum (nujol) of the complex exhibited peaks due to both TMED and (+)-C_6F_5-diol. The visible, circular dichroism (CD) and optical rotatory dispersion (ORD) spectra (1.44 x 10^{2-} M in methanol) exhibited the following bands (nm).

Visible Spectrum		ORD Spectrum		CD Spectrum	
λ(max)	ε	λ(max)	[α]λ(max)	(max)	Δε
510	82	438	-598	474	+1.07
		504	+144	527	-.42
		554	-407	576	+.82
		618	+121		

Preparation of Ni(TMED)[(-)-C_6F_5-diol]

The compound was prepared as described for Ni(TMED)[(+)-C_6F_5-diol], using ligand with $[\alpha]_{589}$ = -54°. The product was fractionally recrystallized from methylene chloride/pet. ether (30-60°) to give a red crystalline complex. The data for the ORD and CD spectra are presented below (in methanol, 10^{-2} M).

ORD Spectrum		CD Spectrum	
λ(max)	[α]λ	λ(max)	Δε
439	+546	474	-0.91
504	-134	527	+0.28
554	+382	576	-0.72
618	-114		

Preparation of Ni(TMED)(meso-C_6F_5-diol)

A slight excess of TMED was added slowly to a methanol/water solution of meso-C_6F_5-diol (0.50 gm, 9.4 mmoles) and nickel nitrate hexahydrate (0.27 gm, 9.3 mmoles). Methanolic KOH was added slowly until a pH of 8 was attained. The resulting red precipitate was recrystallized from a methylene chloride/pet. ether (30-60°) solution, yielding a red crystalline complex (mp 130-131°). The visible spectrum (methanol) showed a single band at 525 nm ($\varepsilon = 80$).

Preparation of Ni(TMED)(rac-C_6F_5-diol)

The compound was prepared by the identical procedure as used for the analogous meso-compound. The product was recrystallized from a methylene chloride/pet. ether (30-60°) mixture to give a red crystalline complex (mp 138-139°). The visible spectrum (methanol) exhibited one band at 510 nm ($\varepsilon = 78$).

Preparation of Ni[P(Et)$_3$]$_2$[(+)-C_6F_5-diol]

Triethylphosphine (0.095 gm, 0.80 mmoles) was slowly added under an atmosphere of nitrogen to a methanol solution containing (+)-C_6F_5-diol (0.200 gm, 0.38 mmoles) and nickel nitrate hexahydrate

(0.110 gm, 0.38 mmoles). Methanolic potassium hydroxide was slowly added until a pH of ~ 8.5 was attained. The resulting orange solution was evaporated to dryness, dissolved in methylene chloride, filtered and recrystallized from a methylene chloride/pet. ether mixture.(mp 137-138°).

Anal. Calcd. for $NiC_{28}H_{30}F_{16}P_2O_2$: C, 37.60; H, 2.28; F, 43.23. Found: C, 37.44; H, 2.46; F, 43.49.

The infrared spectrum of the compound was consistent with the presence of both (+)-C_6F_5-diol and $P(Et)_3$. The data for the visible, ORD and CD spectra are tabulated below.

(i) Methanol solution (6.8 x 10^{-3} M)

Visible		ORD		CD	
λ(max)	ε	λ(max)	[α]λ	λ(max)	Δε
470	205	387	-1200	421	+2.31
		453	+550	478	-1.00
		505	-340	531	+0.14

(ii) Methylene chloride (5.8 x 10^{-3} M)

Visible		ORD		CD	
λ(max)	ε	λ(max)	[α]λ	λ(max)	Δε
470	210	390	-1300	425	+2.72
		455	+650	482	-1.05
		508	-376	533	+0.19

Preparation of $Ni[P(Et)_3]_2[meso-C_6F_5-diol]$

This compound was prepared in the same manner as $Ni(PEt_3)_2[(+)-C_6F_5-diol]$. Recrystallization from a methylene chloride/pet. ether solution produced a bright orange crystalline compound (mp 124-125°, decomp.). The infrared spectrum of the compound was consistent with the presence of meso-C_6F_5-diol and PEt_3. The visible spectrum (methanol) exhibited one band at 480 nm (ε = 215).

Preparation of $Ni(PMe_2Ph)_2([+]-C_6F_5-diol)$

Dimethylphenylphosphine (0.200 gm, 1.45 mmoles) was slowly added under nitrogen to an ethanol solution containing (+)-C_6F_5-diol (0.300 gm, 0.57 mmoles) and nickel nitrate hexahydrate (0.165 gm, 0.57 mmoles). Ethanolic potassium hydroxide was added until a pH of approximately 8 was attained. The resulting orange solution was centrifuged, the filtrate evaporated to dryness, and the residue recrystallized from ethanol to give an orange crystalline complex (mp 143°).

Anal. Calcd. for $NiC_{32}H_{22}F_{16}P_2O_2$: C, 44.53; H, 2.57; F, 35.22. Found: C, 44.87; H, 2.77; F, 34.24.

Molecular Weight (benzene). Calcd: 861. Found: 846.

Data for the visible, circular dichroism, and optical rotatory dispersion spectra (8.55×10^{-3} M in methanol) are listed below.

Electronic Spectrum		ORD Spectrum		CD Spectrum	
λ(max)	ε	λ(max)	[α]λ(max)	λ(max)	Δε
460	286	502	−272	520	+0.22
		446	+598	472	−0.98
		380	−1110	412	+2.52

Preparation of Ni$(PMe_2Ph)_2$(meso-C_6F_5-diol)

The compound was prepared by a similar method to Ni$(PMe_2Ph)_2$[(+)-C_6F_5-diol]. It was recrystallized from a methylene chloride/pet. ether (30-60°) mixture to yield an orange crystalline compound (mp 115-116°). The infrared spectrum (nujol) confirmed the presence of PMe_2Ph and meso-C_6F_5-diol. The visible spectrum (methanol) exhibited one band at 474 nm (ε = 226).

Preparation of Cu(TMED)([+]-C_6F_5-diol)

An excess of tetramethylethylenediamine (0.200 gm, 1.70 mmoles) was added to an ethanol/water mixture containing (+)-C_6F_5-diol (0.30 gm, 0.57 mmoles) and copper sulphate pentahydrate (0.15 gm, 0.60 mmoles). Potassium hydroxide (ethanolic) was slowly added until a pH of approximately 8 was attained. The solution was concentrated and a solid product was collected and recrystallized from ethanol to give a purple, light sensitive compound (mp 88-90°, decomp.).

Anal. Calcd. for $CuC_{22}H_{16}F_{16}O_2N_2$: C, 37.23; H, 2.27; F, 42.81. Found: C, 36.70; H, 2.24; F, 42.65.

The data for the visible, ORD, and CD spectra (methanol, 10^{-2} M) are listed below.

Electronic Spectrum		ORD Spectrum		CD Spectrum	
λ(max)	ε	λ(max)	[α]λ(max)	λ(max)	Δε
561	77	616	+50.6	654	-0.12
		544	-202	577	+0.24
				503	-0.22

Reaction between rac-C_6F_5-diol, meso-C_6F_5-diol, TMED and Nickel Nitrate

A slight excess of TMED was slowly added with stirring to a methanol/water mixture of rac-C_6F_5-diol (0.530 gm, 1.00 mmoles), meso-C_6F_5-diol (0.530 gm, 1.00 mmoles) and nickel nitrate hexahydrate (0.290 gm, 1.00 mmoles). A methanolic potassium hydroxide solution was slowly added until a pH of approximately 8.5 was reached. The red precipitate produced was filtered, redissolved in methylene chloride, refiltered and recrystallized from a methylene chloride/pet. ether mixture. The complex was identified by its infrared spectrum as being exclusively Ni(TMED)(rac-C_6F_5-diol).

Reaction between H_2PFP, rac-C_6F_5-diol, TMED and Nickel Nitrate

A slight excess of TMED was slowly added with stirring to a methanol/water mixture of rac-C_6F_5-diol (.530 gm, 1.00 mmoles) PFP (0.334 gm, 1.00 mmoles) and nickel nitrate hexahydrate. Methanolic potassium hydroxide was added to the stirring solution until a red compound precipitated. The precipitate was collected, redissolved in methylene chloride, refiltered and recrystallized from a methylene chloride/pet. ether mixture. The compound was identified by infrared spectroscopy as being exclusively Ni(TMED)(PFP).

The reaction was repeated with meso-C_6F_5-diol in place of rac-C_6F_5-diol. The product was identified as Ni(TMED)(PFP).

Determination of Absolute Configuration by Cupra A Method

A solution of Cupra A was prepared by dissolving copper(II) hydroxide (0.487 gm) in ammonium hydroxide (98.0 ml) and ethanol (5.0 ml). The resulting solution was diluted to 500 ml to yield a solution 0.010 M in Cu^{2+} and 3.0 M in NH_3. CD spectra of both (+)-C_6F_5-diol and (-)-C_6F_5-diol were recorded in ethanol/Cupra A solutions with 10%, 20%, 30% and 40% ethanol by volume, since the ligands were insoluble in pure Cupra A solutions. No change in the position or sign of the CD bands was observed as the ethanol content of the solvent was increased. The (+)-isomer had one positive band in the visible region (600-610 nm) and a more intense band of opposite sign below 300 nm. The (-)-isomer had bands in the same positions with the signs reversed. No intensity values are reported due to incomplete knowledge of the extent of complex formation and of the nature of the complex formed in solution.

E. Partially Fluorinated Diols and Their Transition Metal Complexes

Preparation of 1,1,1-trifluoroacetophenone[96]

Bromobenzene (157.0 gm, 1.00 mole) in anhydrous diethyl ether (180 ml) was slowly added to magnesium (24.3 gm, 1.00 mole) over a period of 1 hour and stirred for 1 hour further. Trifluoroacetic acid (57.0 gm, 0.50 mole) in diethyl ether (40 ml) was added dropwise at -5°C and the mixture was stirred for approximately 90 minutes. Water (100 ml) and then dilute hydrochloric acid were added to the reaction mixture. After repeated extractions with diethyl ether, the ethereal solution was reduced in volume to approximately 200 ml and dried with magnesium sulphate. Fractional distillation gave trifluoroacetophenone (53.6 gm, 62%, b.p. 151-153°).

Preparation of 1,1,1,4,4,4-hexafluoro-2,3-diphenylbutane-2,3-diol

Trifluoroacetophenone (10.0 gm), in 2-propanol (22 ml), with several drops of hydrochloric acid, was degassed and irradiated (quartz tube) for 8 days. The solvent was removed and the solid residue was recrystallized from a benzene/pet. ether (30-60°) mixture to give a white crystalline product (7.0 gm, mp 154-155°, lit. mp 155-156°). Fractional recrystallization of the product from a variety of solvents gave no evidence of the presence of more than one isomer. Attempts to prepare the diol through reactions of trifluoroacetophenone with triethylphosphite or with sodium in THF did not produce the desired product.

The infrared spectrum of the diol (nujol) had the following peaks: 3550(m), 3480(m), 1500(w), 1240(m), 1150-1200(s), 1065(m), 1030(m), 960(w), 870(m), 840(m), 750(s), 710(s), 690(m), 635(m), 565(w), 470(m)~~, 420(w)~~.

The ^{19}F nmr spectrum exhibited a singlet, both in $CHCl_3$ (70.2 ppm from freon 11) and in (+)-α-phenethylamine (67.8 ppm). A peak due to the parent ion was absent in the mass spectrum; the most intense peak in the mass spectrum occurred at 175 amu, which is one-half the calculated molecular weight. The pK_a, determined in a 1:1 ethanol/water mixture, was 11.4.

When equimolar quantities of the diol and strychnine were dissolved in a $CHCl_3$/pet. ether (30-60°) mixture, a white crystalline precipitate formed. Its infrared spectrum lacked an O-H stretching band

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1165(m), 1125(s), 1085(m), 1055(m), 980(s), 920(w), 870(s), 780(w), 770(w), 740(m), 680(m).

The parent peak was not observed in the mass spectrum of the compound. The most intense peak observed occurred at 211 amu, exactly one-half of the theoretical mass of 422.

Titration of the diol in a 1:1 methanol/water mixture with KOH did not produce a discernible end point.

The ^{19}F nmr spectrum ($CHCl_3$) shows 3 peaks, a broad unresolved multiplet at 138.0 ppm, a triplet of triplets at 154.7 ppm and an apparent doublet of triplets at 162.3 ppm from freon 11.

Attempted Preparation of Metal Complexes of bis(pentafluorophenyl)-butane-2,3-diol [CH_3-C_6F_5-diol]

A slight excess of TMED was slowly added to a methanolic solution of nickel nitrate hexahydrate (.066 gm, 0.23 mmole) and the CH_3-C_6F_5-diol. No colour change was observed, even on addition of alcoholic KOH and the only metal containing product isolated was nickel hydroxide. Attempts using triethylphosphine and dimethylphenylphosphine as the secondary ligand were also unsuccessful. Similar attempts using Cu^{2+} and TMED as the secondary ligand were unsuccessful.

Preparation of Ni(TMED)(CH_3-CF_3-diol)

A solution of 1,1,1-trifluoroacetone (12.2 gm) and 2-propanol (28 ml) was repeatedly degassed and irradiated (quartz tube) for 8 days. Unreacted starting material (∿ 11 gm) and 2-propanol were removed under vacuum, leaving behind a small amount of oily residue, which was used without further purification. Nickel nitrate hexahydrate (0.050 gm) in ethanol (5 ml) was added to the residue, followed by TMED, until a colour change from green to red had occurred. The resulting solution was evaporated to dryness, and the residue was recrystallized from a methylene chloride/pet. ether (30-60°) solution to give a red crystalline complex (≈ 10 mg). There was one band in the visible spectrum (505 nm, $\varepsilon = 74$, methanol); the infrared spectrum (nujol) exhibited strong bands in the 1200 cm^{-1} region. Elemental analysis was not performed on the compound due to insufficient sample.

Repeated attempts to prepare the diol in better yields, both photolytically and through the reaction of the ketone with $P(OEt)_3$, were unsuccessful; no reaction was detected in the latter reaction.

Preparation of $K_2Ni(CF_3-C_6H_5\text{-diol})_2$

Initially, alcoholic KOH was slowly added to a 2:1 stoichiometric mixture of the diol and nickel nitrate in ethanol until a pH of ≈ 11 was attained. The only metal containing product isolated was $Ni(OH)_2$. Alternatively, the diol (3.00 gm, 8.5 mmole) and nickel nitrate hexahydrate (0.95 gm, 3.2 mmole) were dissolved in ethanol (30 ml) and solid KOH was added (7.5 gm). The green precipitate, which initially formed, slowly redissolved over a period of 30 minutes, leaving a clear, deep blue solution. The visible spectrum of this solution had peaks at 550 nm and 620 nm(sh). Repeated attempts to isolate this complex were unsuccessful.

Preparation of $Ni(TMED)(CF_3-C_6H_5\text{-diol})$

This complex was prepared by the same method as for Ni(TMED)(PFP), and was recrystallized from ethanol to give a red crystalline complex (mp 196-200°, decomp.).

Anal. Calcd. for $NiC_{22}H_{26}F_6N_2O_2$: C, 50.52; H, 5.01; F, 21.78. Found: C, 50.42; H, 4.91; F, 22.05.

The infrared spectrum was consistent with the presence of both ligands. There was one band in the visible spectrum (MeOH) at 502 nm (ϵ = 58).

Preparation of Complexes of the Type $Ni(PR_3)_2(CF_3-C_6H_5-diol)$

All attempts to prepare complexes of this type involved the same procedures as those employed for the $Ni(PR_3)_2(PFP)$ complexes. With the phosphines PEt_3, PMe_2Ph and $PMePh_2$, complexes were readily formed in solution whose visible spectra contained one band in the 450-500 nm region but repeated attempts to get pure crystalline solids from these solutions were not successful. No evidence of complexation was observed with PPh_3.

Attempted Preparation of Ni^{2+} Complexes with Perfluoro Alcohols as Ligands

Attempts were made to prepare complexes of the type $Ni(TMED)(L)_2$ where L ≡ the anion of $(CF_3)_3COH$, $(CF_3)_2C_6F_5COH$, $CF_3(C_6F_5)_2COH$ or $(C_6F_5)_3COH$, using similar methods as for the analogous PFP^{2-} compounds. No metal complexes were isolated with these alcohols as ligands. Also, attempts to prepare compounds of the type $Ni(L)_4^{2-}$ by the method used for $Ni(PFP)_2^{2-}$ were not successful.

Reactions of CF_3-C_6H_5-diol and CH_3-C_6F_5-diol with H_2SO_4

The reactions of these diols with sulphuric acid were carried out as described for the CF_3-C_6F_5-diol. In both instances, unreacted starting material was recovered, as identified by their infrared spectra.

Competitive Reactions of CF_3-C_6H_5-diol

A series of competitive reactions were carried out between the CF_3-C_6H_5-diol and PFP^{2-}, meso-CF_3-C_6F_5-diol and rac-CF_3-C_6F_5-diol as previously described. The products were identified by their infrared spectra as Ni(TMED)(PFP), Ni(TMED)(meso-CF_3-C_6F_5-diol) and Ni(TMED)(rac-CF_3-C_6F_5-diol) respectively.

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