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An Investigation Of Some Complexes Of Hexafluoro-2-hydroxyisobutyric Acid And Related Compounds

John Thomas Price

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AN INVESTIGATION OF SOME COMPLEXES
OF
HEXAFLUORO-2-HYDROXYISOBUTYRIC ACID AND RELATED COMPOUNDS
by
John Thomas Price
Department of Chemistry

Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Canada
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ABSTRACT

Alkoxides of fluoro-organic alcohols have been prepared and their properties discussed throughout the literature. Perfluoro-2,3-dimethylbutane-2,3-diol (H$_2$PFP) forms a dibasic ligand that is known to chelate with main group and transition metal elements. The related ligand, perfluoro-2,3-diphenylbutane-2,3-diol has been prepared in this work. The mass spectrum, infrared spectrum, $^1$H and $^{19}$F nmr spectra, and the pK$_a$ of this compound have been measured. The diol is less reactive as a ligand than PFP but forms nickel complexes with tetramethylethylenediamine and triethylphosphine.

The majority of the text discusses the compound hexafluoro-2-hydroxyisobutyric acid (HHIB), which is structurally related to H$_2$PFP and oxalic acid. Like these compounds, HHIB forms a dibasic ligand that complexes with main group and transition elements. Infrared spectra, visible spectra, magnetic moments and molar conductances have been measured on these complexes. The ligand produces a crystal field that appears to be slightly weaker than that of an oxalate ligand. In the solid state some complexes appear to have their free carboxylate oxygen coordinate to a metal atom of a neighbouring molecule making them polymeric.
ACKNOWLEDGMENTS

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<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certificate of examination</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>iv</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td></td>
</tr>
<tr>
<td>A. General Procedure</td>
<td>19</td>
</tr>
<tr>
<td>B. Nomenclature</td>
<td>21</td>
</tr>
<tr>
<td>C. Perfluoro-2,3-diphenylbutane-2,3-diol</td>
<td>22</td>
</tr>
<tr>
<td>D. Perfluoro-2-hydroxy-2-methylpropanoic acid</td>
<td>26</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td></td>
</tr>
<tr>
<td>Part one: Perfluoro-2,3-diphenylbutane-2,3-diol</td>
<td>46</td>
</tr>
<tr>
<td>Part two: Hexafluoro-2-hydroxyisobutyric acid</td>
<td>60</td>
</tr>
<tr>
<td>A. Infrared Spectra</td>
<td>60</td>
</tr>
<tr>
<td>B. Visible Spectra</td>
<td>88</td>
</tr>
<tr>
<td>C. General Discussion and Summary</td>
<td>106</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>113</td>
</tr>
<tr>
<td>VITA</td>
<td>vii</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.</td>
<td>Infrared spectra of perfluoropinacol and perfluoro-2,3-diphenylbutane-2,3-diol</td>
</tr>
<tr>
<td>2.</td>
<td>Mass spectrum of perfluoro-2,3-diphenylbutane-2,3-diol</td>
</tr>
<tr>
<td>3.</td>
<td>pK measurements on perfluoro-2,3-diphenylbutane-2,3-diol</td>
</tr>
<tr>
<td>4.</td>
<td>Infrared spectra of complexes of hexafluoro-2-hydroxyisobutyric acid</td>
</tr>
<tr>
<td>5.</td>
<td>Far infrared spectra of some transition metal complexes of hexafluoro-2-hydroxyisobutyric acid</td>
</tr>
<tr>
<td>6.</td>
<td>Carboxylate frequencies for complexes of hexafluoro-2-hydroxyisobutyric acid</td>
</tr>
<tr>
<td>7.</td>
<td>Infrared spectra of phosphine complexes of hexafluoro-2-hydroxyisobutyric acid</td>
</tr>
<tr>
<td>8.</td>
<td>Infrared spectra of ethylenediamine complexes of hexafluoro-2-hydroxyisobutyric acid</td>
</tr>
<tr>
<td>9.</td>
<td>Infrared spectra of Group IVb complexes of hexafluoro-2-hydroxyisobutyric acid</td>
</tr>
<tr>
<td>10.</td>
<td>Crystal field splitting parameters for some nickel(II) complexes</td>
</tr>
<tr>
<td>11.</td>
<td>Crystal field splitting parameters for some chromium(III) complexes</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Mass Spectra of perfluoro-2,3-diphenylbutane-2,3-diol</td>
<td>50</td>
</tr>
<tr>
<td>2.</td>
<td>$^{19}F$ nuclear magnetic resonance spectrum of perfluoro-2,3-diphenylbutane-2,3-diol</td>
<td>52</td>
</tr>
<tr>
<td>3.</td>
<td>Splitting of free ion term for $d^2$ configuration</td>
<td>89</td>
</tr>
<tr>
<td>4.</td>
<td>Octahedral crystal field perturbation for $d^2$ configuration</td>
<td>91</td>
</tr>
<tr>
<td>5.</td>
<td>Tetragonal field perturbation on $d$ orbitals of transition metals</td>
<td>97</td>
</tr>
</tbody>
</table>
Introduction

Workers in this department have for some time been interested in fluorinated alcohols and their derivative compounds containing metal-oxygen bonds. Of particular interest to the inorganic chemist are those derivatives in which a transition metal is present, i.e. fluorinated alkoxides. Perfluoropinacol (PFP) (I) has been shown to give a number of stable derivatives whose properties are currently under investigation.

\[
\begin{align*}
&\text{(I)} & \text{(II)} \\
&(\text{CF}_3)_2\text{C}-\text{OH} & (\text{CF}_3)_2\text{C}-\text{OH} \\
&(\text{CF}_3)_2\text{C}-\text{OH} & \text{C}-\text{OH}
\end{align*}
\]

Another compound of potential application as a ligand is hexafluoro-2-hydroxyisobutyric acid (HHIB) (II) since this compound has resemblances to both perfluoropinacol and oxalic acid; and it is the study of HHIB which forms the bulk of the work reported in this thesis. As the properties of the molecule are profoundly influenced by the presence of six fluorine atoms, this introduction will begin with a brief outline of the effect on molecular properties of organic molecules by the replacement of hydrogen by fluorine.
Fluorine is the most electronegative element. The bonds formed by fluorine are among the strongest single bonds known. The carbon fluorine single bond is best described by a quantum mechanical approach but can be simply represented as a mixture of covalent and ionic bonding. Calculations\(^1\) based on Pauling electronegativities show the ionic character of the C-F bond to be 43%, compared to 12% and 2% for C-Cl and C-Br respectively. Therefore, the fluorine atom exerts a much greater inductive effect in bonding to carbon than do other groups, (except NO\(_2\), CN, S0\(_2\)). This effect is illustrated by the enhanced acidity of acetic acids when substituted by fluorine\(^2,3\).

\[
\begin{array}{ll}
\text{CH}_3\text{COOH} & K_a = 1.77 \times 10^{-5} \\
\text{CFH}_2\text{COOH} & 2.20 \times 10^{-3} \\
\text{CF}_2\text{HCOOH} & 5.70 \times 10^{-2} \\
\text{CF}_3\text{COOH} & 5.90 \times 10^{-1}
\end{array}
\]

The carbon-fluorine bond length becomes shorter when the number of fluorine atoms is increased on a saturated carbon atom. Thus in CF\(_4\) the bond length is 1.32 Å\(^1\) comparable to the C-F bond length of an sp\(^2\) hybridized carbon of 1.30 Å. (CH\(_3\)F has a C-F bond length of 1.38 Å.)

This phenomenon has been investigated by Brockway\(^4\), Pauling\(^1\), and Hine\(^5\). An argument suggested by Hine has been given the name "double bond - no bond" resonance and is similar to hyperconjugation. It suggests the C-F single bond actually has some sp\(^2\) character and shortens the C-F bond.
Streitweiser\textsuperscript{6} argues against fluorine hyperconjugation from the results of proton exchange studies. The fluorinated bicyclic compound (C\textsubscript{7}F\textsubscript{11}H) (III) is slightly more acidic than nonfluoro-t-butane (IV).

For (III), the carbanion intermediate in the base catalyzed exchange of the bridgehead proton is forced to remain pyramidal and hyperconjugation is greatly reduced. If such hyperconjugation is an important factor in stabilizing carbanions, then the base catalyzed proton exchange of (IV) should be orders of magnitude faster than that of (III). This is not observed.

In unsaturated fluoro-organic molecules the strong electron withdrawal by fluorine from the $\sigma$ and $\pi$ systems decreases the electron density and makes them more susceptible to nucleophilic attack than analogous non-fluorinated molecules (the energy of the $F_2C=CF_2$ $\pi$ bond is 40 kcal/mole compared with 60 kcal/mole for ethylene)\textsuperscript{7}. However, the relative reactivities of fluoro-olefins to nucleophilic attack is in the order $CF_2=CF_2 < CF_2=CFCF_3 < CF_2=C(CF_3)_2$. 
An explanation for this order postulates that vinyl fluorine can partially counteract its strong \( \sigma \) inductive effect by delocalization of its non-bonding \( p \) electrons to the \( \pi \) system of the olefin. 

For mono-fluorinated aromatic systems, the inductive effect of fluorine should deactivate the ring and be meta directing to electrophilic attack. In fluorobenzene, electrophilic substitution occurs at ortho and para positions. This observation once again suggests the fluorine \( p \) orbitals interact with the aromatic \( \pi \) system to activate the ortho and para positions. Highly substituted fluoro-aromatic compounds are completely deactivated, however, and subject to attack by nucleophiles. Usually a stable intermediate is formed, and, since no C-F bond breaking occurs in the rate determining step, fluoride ion is easily displaced. In saturated systems (\( sp^3 \) hybridized) however, fluorine is found to be a poorer leaving group than the other halides, due to the strength of the C-F bond and the low polarizability of the fluorine atom.\(^8\) Substitution reactions involving fluoride ion as an entering nucleophile are extremely slow in aqueous solvent systems due to the large heat of hydration of the fluoride ion. A change to a nonaqueous solvent will significantly change the relative rates, however.

The simplest perfluorinated alkoxides, \( M^+ [OCF_3]^– \) (M=K, Rb, Cs) have been prepared by the nucleophilic addition of metal fluoride to carbonyl fluoride to produce the corresponding trifluoromethoxide.\(^9\) The stability of the fluoromethoxides is influenced by the nature of

\[
MF + COF_2 \rightarrow MOCF_3
\]

the cation present. Small cations with a high charge to size ratio
cause greater polarization of the methoxide anion and displace the
above equilibrium to the left. The investigation was extended to in-
clude the preparation of ionic perfluorinated ethoxides, n-propoxides,
isopropoxides and n-butoxides.¹⁰

\[
\begin{align*}
MF + R_f \overset{\text{O}}{\overset{\text{C}}{\text{F}}} & \rightarrow \text{MOCF}_2R_f & R_f = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7 \\
MF + \overset{\text{O}}{\overset{\text{C}}{\text{F}}} & \overset{\text{CF}_3}{\text{CCF}_3} \rightarrow \text{MOCF(CF}_3\text{)}_2
\end{align*}
\]

The nature of the cation present influences the stability of
these compounds. They were also found to be considerably less stable
than the trifluoromethoxides. In the trifluoromethoxides, the large
electronenegativity of the three fluorine atoms may distribute the
electronic charge, formally on the oxygen, more evenly over the anion
and enhance its stability. Fluorinated alkoxides containing more
than one carbon atom have this effect reduced and as a result
have lower stabilities. The possibility of preparing derivatives of
these alkoxides through nucleophilic displacement reactions is
limited by the ease with which they decompose and eliminate fluoride
ion from the α-carbon. Heptafluoroisopropoxide, \( (\text{CF}_3)_2\text{CFO}^- \), is too
feeble a nucleophile to attack \( \text{C}_2\text{F}_4 \)¹¹ and undergoes nucleophilic
attack only with the more reactive alkyl halides (e.g. allylbromide)
to produce the corresponding ether. Fluoride ion abstraction
predominates with compounds of moderately electropositive elements.
perfluoroisopropoxide, upon reacting with triethyl chlorosilane,¹²
produced only triethylfluorosilane. As expected, hydrolysis
products of the α-fluorinated alkoxides did not yield the alcohol but the metal fluoride and the fluorinated acid.

\[
M^+ [R_fCF_2O^-] + H_2O \xrightarrow{\text{O}} R_f\text{CF} + MF
\]

\[
\text{H}_2\text{O} \xrightarrow{\text{O}} R_f\text{C-OH} + MF
\]

Perfluorotertiary alcohols should give any number of stable derivatives, since there is no possibility of eliminating an α-fluorine. The simplest compounds of this type are the alkoxides of perfluoro-t-butanol. Knunyants\textsuperscript{13} synthesis of the alcohol (pK\textsubscript{a} = 5.4) involved oxidation of (CF\textsubscript{3})\textsubscript{3}CNO, using N\textsubscript{2}O\textsubscript{4}, to (CF\textsubscript{3})\textsubscript{3}CONO followed by hydrolysis. The same alcohol (pK\textsubscript{a} = 5.2) was synthesized by the addition of trichloromethyl lithium to hexafluoroacetone followed by hydrolysis,\textsuperscript{14} then fluorination using SbF\textsubscript{5}. The pK\textsubscript{a} value reveals the powerful polar effect of the three trifluoromethyl groups in enhancing the acidity of the alcohol. Other fluorinated tertiary alcohols that are known include perfluorotriphenylcarbinol and perfluorotriethylcarbinol.\textsuperscript{15}

Perfluoropinacol\[(CF_3)_2COHC(F_3)_2OH\] is the simplest fluorinated ditertiary alcohol and therefore should be relatively stable since there is no possibility of eliminating an α-fluorine atom. The chemistry of perfluoropinacol has been investigated more thoroughly than the simple tertiary fluoroalcohols and many stable covalent derivatives exist.

Middleton and Lindsay first prepared the diol by the reaction of hexafluoroacetone with isopropyl alcohol\textsuperscript{16}. Other
preparative methods involve the dimolecular reduction of hexafluoroacetone by triethyl or triphenylphosphite followed by acid hydrolysis\textsuperscript{17}.

\[
2\text{(CF}_3\text{)}_2\text{C}=\text{O} + \text{P(}\text{OEt}\text{)}_3 \rightarrow \text{(CF}_3\text{)}_2\text{C}-\text{(CF}_3\text{)}_2\text{C}(\text{CF}_3\text{)}_2 \xrightarrow{\text{H}^+ \text{ acid}} \text{(CF}_3\text{)}_2\text{C}-\text{C}-(\text{CF}_3\text{)}_2
\]

The product, as expected, was considerably more stable than any primary or secondary fluorinated alcohol and was found to have a pK\textsubscript{a} of 5.95. This high acidity is only slightly lower than the value for perfluoro-\textit{t}-butanol and is attributable to the high inductive effect of the CF\textsubscript{3} groups and the formation of an anion stabilized by hydrogen bonding.

\[
\text{(CF}_3\text{)}_2\text{C}-\text{C}-(\text{CF}_3\text{)}_2
\]

The solid ionic monosubstituted potassium derivative of perfluoropinacol is readily obtained from aqueous solution. However, further neutralization to produce the dipotassium alkoxide[KOC(\text{CF}_3\text{)}\text{)}_2\text{]}_2 resulted in decomposition of the pinacol due to fluoride ion elimination. An alternative route to the ionic disubstituted alkoxides of perfluoropinacol is available by the reductive coupling of hexafluoroacetone with an alkali metal in nonaqueous donor solvents\textsuperscript{14,18}.

\[
\text{(CF}_3\text{)}_2\text{CO} + \text{Na} \xrightarrow{\text{THF}} \text{(CF}_3\text{)}_2\text{CO}^- + \text{Na}^+ \quad \text{(CF}_3\text{)}_2\text{C}^-\text{O}^- \text{Na}^+
\]
The availability of the disodium alkoxide provides a convenient route to the preparation of other alkoxides and esters of perfluoropinacol. The reaction of the disodium alkoxide with dimethyl-dichlorosilane, and trimethylchlorosilane produced a precipitate of sodium chloride and the following compounds:

\[
\begin{align*}
(CF_3)_2O & \quad O(CF_3)_2 \\
(CH_3)_3Si & \quad Si(CH_3)_3
\end{align*}
\]

The following boron, sulfur, and tellurium complexes have been prepared from disodium alkoxide and phenylborondichloride, thionyl chloride, sulfuryl chloride and tellurium tetrachloride respectively.

\[
\begin{align*}
C_6H_5B & \quad O(CF_3)_2 \\
& \quad O(CF_3)_2 \\
O &= \quad O(CF_3)_2 \\
& \quad O(CF_3)_2 \\
& \quad O(CF_3)_2
\end{align*}
\]

\[
\begin{align*}
(CF_3)_2C & \quad O \\
O & \quad C \quad O(CF_3)_2 \\
& \quad O(CF_3)_2
\end{align*}
\]

The reaction of sulfur dichloride with the alkoxide produces the orthosulfite resulting from disproportionation of sulfur(II) to sulfur(IV) and elemental sulfur.

\[
2 \quad (CF_3)_2C-O^- + 2 \quad SCl_2 \quad \rightarrow \quad (CF_3)_2C-O^- \quad O-C(F_3)_2 + S + 4 \quad Cl^- 
\]

The reaction of sodium borate with aqueous perfluoropinacol
has also been used to prepare boron perfluoropinacolate complexes.\textsuperscript{19}

\[
\text{Na}_4\text{B}_4\text{O}_7 + \text{H}_2\text{PFP} \xrightarrow{\text{Na}^+} \text{[B(PFP)\textsubscript{2}]^-}
\]

Other salts of the bis(perfluoropinacolato)borate anion have been prepared by refluxing boric acid or trimethyl borate with pinacol in an ethanol/benzene solvent mixture followed by titration of the product obtained with a metal chloride or nitrate.\textsuperscript{20}

\[
\text{B(OH)}_3 + 2 \text{H}_2\text{PFP} \xrightarrow{[H^+]} [\text{B(PFP)\textsubscript{2}]}^+ \xrightarrow{\text{Cl}^-} [\text{M}^+] \xrightarrow{[\text{B(PFP)\textsubscript{2}]}^-}
\]

The stability of perfluoropinacol in water, combined with its acidic nature ($pK_a \ 5.95$)\textsuperscript{16} suggests that a number of stable metal alkoxides might be formed in aqueous solutions. By adding the aqueous metal sulfate to perfluoropinacol and titrating with potassium hydroxide to a pH of 8, complex ions were formed according to the equation:\textsuperscript{21}

\[
n \text{H}_2\text{PFP} + M^{n+} + 2n\text{OH}^- \xrightarrow{\text{[M(PFP)\textsubscript{n}]}^{n-}} 2n \text{H}_2\text{O}
\]

$M = \text{Al}^{+3}, \text{Fe}^{+3}, \text{Mn}^{+2}, \text{Ni}^{+2}, \text{Cu}^{+2}, \text{Zn}^{+2}$

The iron and aluminum compounds have the metal atom chelated to three pinacol ligands and the structure is assumed to be basically octahedral. The Ni(PFP)$^{2-}$ complex was found to be diamagnetic which suggests it has a square planar structure. A more detailed investigation into the spectral and magnetic properties of these compounds is presently in progress by coworkers in this department.

With the success in forming stable perfluoropinacolate complexes the preparation and properties of other perfluorinated-1,2-diols and related compounds that might form stable complexes became of interest.
The ligand tetrafluorocatechol is presently under investigation. It is expected to form complexes although the \( \alpha \)-inductive effect of the fluorine leaves the catechol much less acidic than perfluoropinacol. Complications arise because tetrafluorocatechol readily oxidizes to the quinone.

More closely related to perfluoropinacol is perfluoro-2,3-diphenylbutane-2,3-diol which has been prepared and studied in this work.

\[
\begin{align*}
C_6F_5-\text{C-} & \text{OH} \\
C_6F_5-\text{C-OH} & \\
\text{CF}_3 & \\
\end{align*}
\]

The majority of the work in this thesis, however, deals with the ligand hexafluoro-2-hydroxyisobutyric acid. This acid was first prepared by the acid hydrolysis of the cyanohydrin produced from the reaction of hexafluoroacetone with hydrogen cyanide in the presence of piperidine\(^{23}\). The procedure of Filler\(^ {14} \) was followed throughout this work, however, which involved the addition of hexafluoroacetone to potassium cyanide followed by distillation of the product over concentrated sulfuric acid.

\[
(CF_3)_2C=O + \text{KCN} \xrightarrow{\text{ether}} \text{KOC(CF}_3)_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{HO-C-CO}_2\text{H} \]

The \( pK_a \) of hexafluoro-2-hydroxyisobutyric acid is 2.1, but the alcoholic hydroxyl fails to exhibit acidic properties. This behaviour is attributed to intramolecular hydrogen bonding which enhances the acidity of the carboxyl group while suppressing the acidity of the hydroxyl group. In the methyl ester of the acid,
where hydrogen bonding is reduced, the acidity of the hydroxyl group
becomes apparent ($pK_a = 7.7$). This bonding theory is similar to that

\[
\begin{array}{c}
\text{(CF}_3\text{)}_2 \text{C} - \text{C}^{0} \\
\text{O} \quad \text{H} - \text{O}
\end{array}
\]

proposed by Middleton to explain the acidity of perfluoropinacol$^{16}$. Other preparations of the acid and its esters have been reported but no study has yet been reported on the properties of this acid as a coordinating chelate ligand with either transition metals or main group elements.

Hexafluoro-2-hydroxyisobutyric acid (HHIB) is the simplest fully fluorinated α-hydroxy acid that is stable from fluoride elimination. It has a structure that can be regarded as intermediate between perfluoropinacol and oxalic acid.

\[
\begin{array}{c}
\text{(CF}_3\text{)}_2 \text{C} - \text{C}^{0} \\
\text{OH} \quad \text{OH}
\end{array} \quad \begin{array}{c}
\text{(CF}_3\text{)}_2 \text{C} - \text{C}^{0} \\
\text{OH} \quad \text{OH}
\end{array} \quad \begin{array}{c}
\text{O}=\text{C} - \text{C}^{2} \\
\text{OH} \quad \text{OH}
\end{array}
\]

The preparation of HHIB metal complexes, analogous to the perfluoropinacol complexes, would be expected for this ligand. They are expected to be dibasic and bidentate similar to the perfluoropinacolate and oxalate complexes.$^{24}$ It is possible, however, that the coordination may be similar to the simple carboxylates, and that the carboxylate group enters into either an ionic chelate structure or a bridging polymeric structure.$^{25}$
A number of studies have been made on non-fluorinated α-hydroxy-carboxylic acids and various metal complexes of these ligands. Their properties may have some important analogies with hexafluoro-2-hydroxyisobutyrate complexes.

Cation exchange studies\textsuperscript{26,27,28,29,30,31} demonstrate that the separation of lanthanides, actinides and alkaline earth metals is possible using ammonium α-hydroxy-isobutyrate or ammonium lactate solutions as eluent. The α-hydroxy-isobutyrate produces better separation than lactate and has the advantage of producing good separation at room temperature. For the alkaline earth metals the elution was in the order magnesium, calcium, strontium, and barium for both hydroxyisobutyrate and lactate\textsuperscript{32,33}. This order agrees with the $K_2$ stability constants determined for these $ML_2$ complexes by potentiometric titrations [Ba$<$Sr$<$Ca$<$Mg]\textsuperscript{31}. The logarithms of the $K_2$ stability constants (plotted in order of decreasing atomic number) increase more rapidly for isobutyrate than for lactates. For this reason α-hydroxyisobutyrate solution is the eluent for ion exchange separations of the alkaline earth metals. These stability studies also show the average ligand number per metal ion exceeds a value of one indicating the presence of $ML^+$ and $ML_2$ species in solution. Further stability constants for divalent metal complexes\textsuperscript{34} of
hydroxyisobutyrate indicate the following order of stabilities:

\[ \text{Mn}^{2+} < \text{Cd}^{2+} < \text{Ni}^{2+} < \text{Zn}^{2+} < \text{Pb}^{2+} < \text{Ca}^{2+} < \text{UO}_2^{2+} \], in agreement with the well known Irving Williams series\(^{35}\) and Dq assignments made from visible spectra\(^{44}\). The average ligand number exceeds two, indicating the existence of \(\text{ML}^{+}\), \(\text{ML}_2\) and \(\text{ML}_3\) species in solution. For the trivalent lanthanide and yttrium\(^{36,37}\) complexes of isobutyrate, four stability constants have been measured. The average number of ligands per metal ion exceeds three, indicating the presence of \(\text{ML}_4^-\) in solution.

The preceding evidence indicates that \(\alpha\)-hydroxyisobutyric acid is monobasic; these studies do not confirm, however, if the metal-ligand bonding is mono or bidentate.

Kinetic studies\(^{38}\) on the reduction of \(\alpha\)-hydroxycarboxylate-pentaminocobalt(III) ion by chromium(II) showed specific rates to be significantly higher than with analogous simple carboxylate complexes of cobalt. It has been proposed that the carboxylate group forms a bridging group between the cobalt and chromium cations followed by ring closure to form a chelated structure with the reducing cation. If the \(\alpha\)-hydroxyl group is replaced by chlorine or methoxy groups then chelation is inhibited and the specific rates decrease. The more favorable geometry of the chelated structure presumably leads to higher specific rates than when exchange occurs only at the bound carboxylate position.
Evidence indicates α-hydroxyacids can chelate to metals and their carboxylate groups can also bridge molecules to form a polymeric complex in solution. Similar bridging structures are known for the solids of some simple carboxylates as well as 3-methoxypropionate\textsuperscript{39,40}.

Changes in free energy, enthalpy, and entropy of complexation for lanthanide ions with acetate, propionate, glycolate, lactate, isobutyrate and α-hydroxyisobutyrate ligands have been measure using calorimetric titrations\textsuperscript{41,42}. For acetate, propionate and isobutyrate complexes $\Delta H$ is endothermic (acetate $<$ propionate $<$ isobutyrate) and complex formation is stabilized by a favourable entropy factor (+ve) predominating over the unfavourable enthalpy effect. The hydroxycarboxylates have both favourable changes in enthalpy (-ve) and entropy (+ve) for complex formation. The entropy change however, is less than for the simple carboxylates. The difference in enthalpy and entropy values between analogous ligands for the formation of samarium complexes are shown below\textsuperscript{42}. 
<table>
<thead>
<tr>
<th></th>
<th>$\Delta (\Delta H)$</th>
<th>$\Delta (\Delta S)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycolate - acetate</td>
<td>-2.5</td>
<td>-6.2</td>
</tr>
<tr>
<td>acetate-propionate</td>
<td>-3.7</td>
<td>-10.4</td>
</tr>
<tr>
<td>hydroxyisobutyrate - isobutyrate</td>
<td>-4.5</td>
<td>-11.6</td>
</tr>
</tbody>
</table>

The negative $\Delta (\Delta H)$ values indicate that the complexes of the hydroxy acids are more stable than the complexes of the simple acids possibly because of their ability to chelate. This would result in a decrease in configurational entropy as substantiated by the $\Delta (\Delta S)$ values. Moreover, the increasingly negative trend of $\Delta (\Delta H)$ from glycolate to $\alpha$-hydroxyisobutyrate suggests the increasing basicity of the hydroxy group caused by the addition of methyl groups to the $\alpha$ carbon stabilizes the chelate structures. Visible spectra on glycolate, lactate and mandelate (C$_6$H$_5$CHOHCOO$^-$) complexes of manganese and nickel show a spectrochemical series for these ligands of: Dq lactate > Dq glycolate > Dq mandelate. An alternative explanation, agreeing with enthalpy and entropy changes, suggests chelation occurs by inclusion of a water molecule between the $\alpha$-hydroxy group and the cation. An infrared study of the C-OH bond for glycolate complexes indicates both structures are correct depending on the cation present. Lanthanides, nickel, and cobalt complexes contain a water molecule between the hydroxy group and the cation. Pure chelate structures are found however, for uranyl and copper complexes.

The X-ray structure of copper complexes of glycolic, DL-lactic, and $\alpha$-hydroxyisobutyric acids have been determined. All complexes have transcoplanar chelate rings with metal-oxygen bonds
formed by the hydroxyl oxygen and one of the carboxylate oxygens.
The remaining carboxylate oxygen interacts weakly with copper atoms, 
α-hydroxy groups and/or coordinated water in adjacent molecules. For 
bis(aquo)bis(2-hydroxyisobutyrate)copper(II) the complexes are joined 
together to form ribbons by hydrogen bonding of the hydroxy group to 
a coplanar carboxylate oxygen of another complex. The sheets of 
molecules formed by these bonds are held together by hydrogen bonds 
through the water molecules (O₄).

The bis(glycolate)copper(II) complexes have the copper atoms 
coordinated to two glycolate ligands forming the coplanar chelate rings. 
The octahedral coordination is completed by the two carboxy-oxygens 
of two neighbouring complexes. In addition, each carboxy-oxygen forms 
a hydrogen bond to the hydroxy-group of a second neighbouring complex 
coplanar with the chelate ring of the first complex.
The aquo-bis(d,l lactate)copper(II) complex has a structure intermediate between the two preceding structures. The copper cation is coordinated to one water molecule (O₄) and one carboxylate oxygen of the neighbouring complex.

A summary of the preceding work on α-hydroxycarboxylic acids shows:

1) α-hydroxy acids are monobasic.
2) chelated octahedral complexes are generally formed by coordination through hydroxyl and carboxylate.
3) increasing basicity of the hydroxyl group increases the stability of the metal complexes.
4) inclusion of a water molecule between the hydroxyl group and the cations occurs for some metal complexes.
5) carboxylate oxygens are capable of forming bridges between
complexes or coordinating with an hydroxyl group or water molecule associated with a neighbouring molecule.

For fluorinated α-hydroxyisobutyric acid, the inductive effects of the α-CF₃ groups should decrease the electron density in the O-H bond and hence the basicity of the hydroxyl group. This would lower the stability of an hydroxy-coordinated complex. If the inductive effect is sufficient to weaken the O-H bond (make the hydrogen acidic) forming an alkoxy anion, then this anion will be basic enough to form stable complexes.

Inclusion of a water molecule between the alkoxy anion and the central cation is still possible. Carboxylate bridging with water or the cation of neighboring molecules will also be of major importance.
Experimental Section

A. General Procedure

Instrumental

All infrared spectra were recorded on a Beckman IR-10 infrared spectrophotometer. The spectra were calibrated with a sample of polystyrene film. $^1$H nmr (nuclear magnetic resonance) spectra were recorded on a Varian T-60 spectrometer or HA-100 spectrometer and the $^{19}$F spectra on an HA-100 spectrometer at 94.1 MHz. Mass spectra were recorded on a Varian M-66 mass spectrometer. Diffuse reflectance spectra were recorded on a Unicam SP500 spectrophotometer and solution spectra recorded on the Beckman DK-1 spectrophotometer. Conductivity measurements were made on an Industrial Industries RC 18 conductivity bridge, using a dipping conductivity cell for which the cell constant was 0.1 cm$^{-1}$. Magnetic moments were measured on the solids, using a Gouy balance equipped with a permanent magnet. The molecular weights were measured on a Hitachi Perkin-Elmer Molecular Weight apparatus, Model 115.

Melting points were observed in sealed tubes in a Thomas Hoover Uni-Melt Capillary Melting Point Apparatus.

N.M.R. Spectra

$^1$H nmr measurements were made on samples in suitable solvents
with tetramethylsilane as an internal standard. \[^{19}\text{F}\] nmr measurements were taken in spectrograde chloroform solution with "freon 11" (CFCl\(_3\)) as the internal standard. Chemical shifts are recorded in p.p.m. on the low field side \(^1\text{H}\) and the high field side \(^{19}\text{F}\) of the internal standard. The probable accuracy is ±0.2 p.p.m.

**Chemicals**

Hexafluoroacetone was a commercial sample (Allied Chemical) used directly without purification. Practical triethylphosphite (Eastman), trimethylborate (K&K), pentafluorobromobenzene (Imperial Smelting), trifluoroacetic acid (Eastman), ethylenediamine (Aldrich), and tetramethylethylenediamine (Columbia) were used without purification. Manganese chloride (Analar), potassium cyanide (Fisher), ferric chloride (B.D.H.), chromic sulfate (J.T. Baker), nickel nitrate (B&A), phosphorus pentachloride (B&A), and copper sulfate (Mallinckrodt) were used directly from the bottle without purification. Benzene (B.D.H.) was refluxed and distilled from metallic sodium; tetrahydrofuran was distilled from metallic potassium; methanol and ethanol were distilled over magnesium.

**Analyses**

Microanalyses were performed by Alfred Bernhard Mikroanalitisches Laboratorium, Elbach uber Engelskirchem, West Germany. Gravimetric analyses were performed on: nickel, by precipitation with dimethylglyoxime; manganese and zinc, by precipitating as MnNH\(_4\)PO\(_4\) \(\cdot\) H\(_2\)O and ZnNH\(_4\)PO\(_4\); chromium, by precipitating as barium chromate; thorium, by precipitating as Th(C\(_2\)O\(_4\))\(_2\); iron, by ignition to form ferric oxide.
B. Nomenclature

The formal name for the diol(I) is perfluoro-2,3-dimethylbutane-2,3-diol and is abbreviated in the text as $\text{H}_2(\text{PFP})$. Diol (II) is formally named perfluoro(2,3-diphenylbutane-2,3-diol) but will be referred to in the text as diol(II).

\[
\begin{align*}
\text{diol (I)} & \quad \text{diol (II)} \\
\begin{array}{c}
\text{CF}_3 \\
\text{CF}_3 - \text{C-OH} \\
\text{CF}_3 - \text{C-OH} \\
\text{CF}_3
\end{array} & \quad \begin{array}{c}
\text{CF}_3 \\
\text{C}_6\text{F}_5 - \text{C-OH} \\
\text{C}_6\text{F}_5 - \text{C-OH} \\
\text{CF}_3
\end{array}
\end{align*}
\]

The hydroxy-acid (I) is formally called perfluoro-2-hydroxy-2-methylpropanoic acid but is commonly called hexafluoro-2-hydroxy-isobutyric acid. For convenience the ligand of the acid will be

\[
\begin{align*}
\text{hydroxyacid (I)} & \quad \text{HHIB ligand} \\
\begin{array}{c}
\text{CF}_3 \\
\text{CF}_3 - \text{C-OH} \\
\text{C-OH}
\end{array} & \quad \begin{array}{c}
\text{CF}_3 \\
\text{CF}_3 - \text{C-O-} \\
\text{C-O-}
\end{array}
\end{align*}
\]

referred to as HHIB and the hydroxy-acid as the HHIB acid throughout this text. A complex formed between a nickel salt and the potassium salt of the acid would be named potassium bis(perfluoro-2-hydroxy-2-methylpropionato)nickelate(II). The compound will be expressed in this text as $\text{K}_2\text{Ni}($HHIB$)_2$.
Other abbreviations are used throughout the text and include:

BDPPE  Bis(diphenylphosphino)ethane
PET₃    triethylphosphine
PPh₃    triphenylphosphine
En       ethylenediamine
THF     tetrahydrofuran
DMF     dimethylformamide

Formal names have been used in the experimental section but both common names and abbreviated names throughout the remainder of the text.

C. Perfluoro-2-3-diphenylbutane-2,3-diol

**Preparation of Octafluoroacetophenone**

Pentafluorobromobenzene (45 g, 0.18 moles) in diethyl ether (130 ml.) was added to magnesium (3.6 g, 0.3 moles) and allowed to react for sixty minutes. The product was added to an ethereal solution of lithium trifluoroacetate [prepared in situ from lithium hydride (1.5 g, 0.19 moles) and trifluoroacetic acid (22 g, 0.19 moles)] and stirred for six hours at room temperature. The resulting product was hydrolyzed with dilute sulfuric acid (150 ml.), then extracted with ether. Distillation gave octafluoroacetophenone (15 g, 0.05 moles, 28%) bp 131 °C.

¹⁹F nuclear magnetic resonance spectrum of octafluoroacetophenone in chloroform showed four multiplets centered at 70.6, 139.2, 150.1 and 161.0 ppm.
Preparation of perfluoro(2,3-diphenylbutane-2,3-diol)

1. Octafluoracetophenone (12 g) in 2-propanol (75 ml.) with a few drops of hydrochloric acid, was irradiated (Hg lamp) for five days. Removal of volatile materials gave a yellow solid (7 g) which was sublimed at 100 °C/0.01 mm. and recrystallized from ethanol/hexane to give the diol (II) (mp 121-123 °C.)

   Anal. Calcd. for C₁₆H₂₁₆F₁₆O₂: C, 36.3; H, 0.4; F, 57.3;
   Found C, 36.0; H, 0.3; F, 57.1

2. Octafluoroacetophenone (5 g, .02 moles) was added to cooled triethylphosphite (3.5 g, .02 moles). The product was acidified with concentrated sulfuric acid (3 ml.) and then water (5 ml.) was added. The resulting solution was refluxed (2 hrs). The organic material was extracted from the solution with methylene chloride and dried with anhydrous magnesium sulfate and filtered. The solution was evaporated to dryness and the residue crystallized from hexane to give diol(II) (1 g. 20%) mp 117-120 °C.

   The mass spectra of the preceding compounds verify that they are identical and show the following peaks and intensities:
   m/e = 511 (rel. int. = 6.1), 442 (11.3), 425 (1.7), 416 (7.9), 4.03 (7.0)
   328 (23.4), 307 (26.0), 265 (100.0) 257 (35.5), 249 (100.0), 246 (100.0)
   229 (30.4), 217 (30.4), 199 (96.0), 195 (100+), 176 (37.4), 167 (98.0),
   155 (70.5), 148 (44.1), 117 (70.0), 109 (35.2), 69 (100+).

   The following bands (cm⁻¹) were found in the infrared absorption spectrum (nujol and halocarbon mulls): 3634 (m), 1650 (m), 1530 (s),
   1480 (s), 1400 (w), 1340 (w), 1220 (s), 1200 (s), 1175 (s), 1035 (w)
   1000 (s), 950 (s), 850 (w), 785 (w), 760 (m), 715 (w), 680 (m), 550 (m),
535 (w), 440 (w), 410 (m). [s=strong, m=medium, w=weak]

The proton nmr spectrum showed a broad doublet at 4.8 p.p.m. with a coupling constant of J = 10 Hz.

The $^{19}$F nmr spectrum has six multiplets found at A, 72.6; B, 130.0; C, 141.5; D, 149.3; E, 159.8; and F, 160.7 p.p.m. from freon II. The coupling constants were found to be $J_{AB} = 26.3$, $J_{AC} = 1.5$, $J_{BF} = 22.5$, $J_{BD} = 5.7$, $J_{CF} = 7.1$, $J_{CD} = 5.7$, $J_{CE} = 21.2$ $J_{DE} = 1.2$ Hz.

The $pK_a$ of the diol(II) was measured in ethanol/water mixtures by titrating with sodium hydroxide (0.04 N.). End point readings of 7.05, 6.95, 7.14, and 6.74 ml. corresponded to molar concentrations of $2.71 \times 10^{-3}$, $2.67 \times 10^{-3}$, $2.75 \times 10^{-3}$, and $2.60 \times 10^{-3}$. The four molar concentrations are taken in 40, 50, 60, and 80% ethanol/water mixtures. Extrapolating to 0.0% ethanol yields -- $pK_a = 8.85$

At attempted reaction of perfluoro(2,3-diphenylbutane-2,3-diol) with sulfuric acid

Perfluoro(2,3-diphenylbutane-2,3-diol) (2.0 g.) was added to concentrated sulfuric acid (5 ml.) and heated to 100 °C. for 12 hours. The product was cooled, diluted with water (15 ml.), extracted with methylene chloride, dried over magnesium sulphate, filtered, and evaporated to dryness. The product (1.1 g) was identified by its infrared spectrum as the starting material, diol (II).

Attempted preparation of potassium bis[perfluoro(2,3-diphenylbutane-
2,3-diolato)] nickelate(II)

Perfluoro (2,3-diphenylbutane-2,3-diol (0.2 g, 0.4 mmoles)
was added to an ethanolic/water mixture of nickel nitrate hexahydrate (.08 g, 0.3 mmoles). Potassium hydroxide solution was added until a pH of 8 was attained. A precipitate appeared and was identified as nickel hydroxide. None of the desired product was isolated.

**Attempted preparation of potassium bis[perfluoro(2,3-diphenylbutane-2,3-diolato)] cuprate(II)**

Perfluoro(2,3-diphenylbutane-2,3-diol) (.2 g, 0.4 mmoles) was added to an ethanolic/water mixture of copper nitrate pentahydrate (.08 g, 0.3 mmoles). Potassium hydroxide solution was added until a pH of 8 was attained. A precipitate appeared and was identified as copper hydroxide. None of the desired copper complex was obtained.

**Preparation of tetramethylethylenediamine perfluoro(2,3-diphenylbutane-2,3-diolato) nickelate(II)**

Excess tetramethylethylenediamine was added to a stirred water/methanol solution containing perfluoro(2,3-diphenylbutane-2,3-diol) (0.8 g, 1.5 mmoles) and nickel nitrate hexahydrate (.54 g, 1.8 mmoles). The solution was filtered, evaporated to dryness and the pink residue recrystallized from a methanol/water mixture.

Anal. Calcd. for Ni C_{22}H_{16}F_{16}N_{2}O_2: C, 41.15; H, 3.16; F, 40.04.

Found: C, 41.17; H, 3.33; F, 40.09.

The product is diamagnetic and has one absorption band in the visible diffuse reflectance spectrum at 510 m\(\mu\).

**Preparation of bis(triethylphosphino) perfluoro(2,3-diphenylbutane-2,3-diolato) nickelate(II)**

Excess triethylphosphine was added to a methanol/water
solution containing perfluoro(2,3-diphenylbutane-2,3-diol) (0.8 g, 1.5 mmoles) and nickel nitrate hexahydrate (.54 g, 1.8 mmoles). Additional water was added and the product precipitated. The complex was recrystallized from methanol/water solution.

\[ \text{Anal. Calcd. for } \text{Ni}^{2+}_{28} \text{C}_{30} \text{H}_{16} \text{F}_{2} \text{O}_{2} \text{P}_{2}^{2-} : \text{ C, 37.60; H, 2.38; F, 43.23. Found: C, 37.44; H, 2.46; F, 43.49.} \]

The compound is diamagnetic and has one absorption band in the visible spectrum (diffuse reflectance) at 475 μm.

D. Perfluoro-2-hydroxy-2-methylpropanoic acid.

**Preparation**

Hexafluoroacetone (50 g, 0.32 moles) was bubbled into a cooled (-30 °C.) diethylether/tetrahydrofuran mixture (400 ml. 5%THF) containing potassium cyanide (17 g, 0.31 moles) under a dry nitrogen atmosphere and stirred for two hours. The resulting solution was evaporated to dryness under vacuum to yield the potassium salt of hexafluorocyanohydrin. Concentrated sulfuric acid (250 ml.) was added and the resulting solution kept at 180 °C for 48 hours. Perfluoro-2-hydroxy-2-methylpropanoic acid (38 g, 78%) was distilled from the mixture and recrystallized from benzene. mp 81 °C. bp 151 °C.

The infrared spectrum (KBr disc) of perfluoro-2-hydroxy-2-methylpropanoic acid showed the following absorption bands (cm⁻¹): 3390 (m), 1760 (s), 1380 (m), 1280 (s), 1230 (s), 1160 (s), 995 (s), 825 (m), 780 (s), 735 (w), 665 (m), 640 (w), 560 (s), 545 (w), 525 (w).
**Preparation of cesium perfluoro-2-hydroxy-2-methylpropionate**

To an aqueous solution (10 ml.) of cesium hydroxide (.7 g) was added perfluoro-2-hydroxy-2-methylpropanoic acid (1.0 g, 4.7 mmoles) Cesium chloride (1 g) was added and solution was allowed to evaporate slowly. Crystals that appeared after standing for 48 hours were filtered and recrystallized from isopropanol. (.74 g, 45%)  

Found: C,14.21; H, .60; F, 33.12.

The infrared spectrum showed the following bands (cm$^{-1}$):  
3310 (m), 3150 (w), 1660 (s-br), 1375 (m), 1280 (s), 1230 (s), 1200 (s), 1150 (s), 1005 (m), 975 (s), 800 (s), 740 (s), 675 (m), 650 (w), 555 (w), 540 (w), 515 (m).

**Preparation of potassium bis(perfluoro-2-hydroxy-2-methylpropionato) nickelate(II)**

1. Potassium hydroxide (0.52 g, .01 moles) was added to methanol (10 ml.) containing perfluoro-2-hydroxy-2-methylpropanoic acid (1.0 g., .005 moles) and nickel nitrate hexahydrate (.9 g., .003 moles). Potassium nitrate was filtered and the filtrate evaporated to dryness. The solid product was recrystallized from ethanol.

2. Perfluoro-2-hydroxy-2-methylpropanoic acid (5 g., .022 moles) was added to an excess of nickel hydroxide solution. Potassium hydroxide was added until a pH of 8 was attained. Excess nickel hydroxide was centrifuged from solution which was evaporated to dryness. The residue was recrystallized from ethanol (4.8 g. 73%)
and dried under vacuum to give the yellow-green product.

Anal. Cld. for K₂NiC₈F₁₂O₆ C, 17.3; H, 0.0; F, 40.9; Ni, 10.5. Found C, 16.81; H, 0.22; F, 40.35; Ni, 10.44.

The compound has a magnetic moment of 3.06 B.M. at room temperature.

The diffuse reflectance spectra has bands at 410, 475 (shoulder) 725 μ (with a shoulder at 735 μ). The solution spectra (methanol) has bands at 405 μ (ε = 15.6), 700 μ (5.9), 1125 μ (5.3).

The infrared spectrum (KBr disc) has bands at: 3660 (w), 3440 (w), 1650 (s), 1400 (m), 1270 (s), 1210 (s), 1160 (s), 1015 (s), 972 (s), 830 (m), 800 (m), 740 (s), 665 (m), 530 (m), 465 (m), 360 (w) cm⁻¹.

The molar conductance of the complex taken in aqueous solution is 193 at 10⁻³ molar concentration.

The dried nickel complex (.6721 g.) when exposed to the atmosphere gains weight (.0518 g.) and changes to a bright green color. The process is reversible and suggests a dihydrate (molar ratio of complex to water is 1: 2.3). This complex has a magnetic moment of 2.99 B.M. Its diffuse reflectance spectrum is similar to the anhydrous complex but the shoulder at 475 μ is weaker in intensity.

The cesium salt of bis (perfluoro-2-alkoxy-2-methylpropionate) nickel (II) was prepared by method 1. Attempts to prepare barium and nickel salts of this cation failed.
Preparation of potassium bis(perfluoro-2-hydroxy-2-methylpropionato)-cuprate(II)

1. Potassium hydroxide (.52 g, .01 moles) was added to a methanolic solution (10 ml.) of perfluoro-2-hydroxy-2-methylpropanoic acid (1 g, .005 moles) and copper sulfate pentahydrate (0.65 g, .0026 moles). The solution was filtered free of potassium sulfate and evaporated to dryness, the residue was recrystallized from ethanol.

2. Perfluoro-2-hydroxy-2-methylpropanoic acid (5 g, 0.024 moles) was added to an excess of cupric hydroxide suspended in water. Potassium hydroxide solution was added until a pH of 8 was attained. The solution was centrifuged, the clear blue liquid evaporated to dryness, and the resulting blue residue (5.6 g, 85%) recrystallized from ethanol/hexane. The product was dried under vacuum at 50 °C.

Anal. Calcd. for $K_2CuC_8F_{12}O_6$: C, 17.10; H, 0.00; F, 40.6; Cu, 11.3. Found: C, 17.04; H, 0.14; F, 39.65; Cu, 11.28.

The complex has a magnetic moment of 1.85 B.M. and a conductivity of 240 mhos at infinite dilution in water. The diffuse reflectance spectrum has a broad absorption band at 650 μm while the solution spectrum (methanol) has a similar band at 675 μm (ε= 27.8).

The infrared spectrum of $K_2Cu(HHIB)_2$ has the following bands:

3340 (w), 1665 (s), 1380 (m), 1276 (s), 1210 (s), 1160 (s), 1140 (s), 1020 (s), 970 (s), 825 (m), 790 (w), 745 (s), 660 (m), 590 (w), 525 (m), 445 (m–w), 365 (w) cm$^{-1}$.

The cesium derivative of this compound was prepared by method 1. Its diffuse reflectance spectrum has a band at 650 μm; its solution spectrum has a band at 680 μm (ε=29.7); and its infrared spectrum has
the following bands: 3410 (w), 1665 (s), 1375 (m), 1270 (s) 1210 (s),
1160 (s), 1140 (s), 1020 (s), 970 (s), 825 (m), 790 (w), 745 (s),
660 (m), 585 (w), 450 (w) cm\(^{-1}\).

**Preparation of cesium bis(perfluoro-2-hydroxy-2-methylpropionato)-
  cobaltate(II)**

Cesium hydroxide (1 g, 0.0075 moles) was added to an
ethanolic solution containing perfluoro-2-hydroxy-2-methylpropanoic
acid (.7 g, 3.2 mmoles) and cobaltous sulfate heptahydrate (0.47 g,
1.6 mmoles). The resulting precipitate was filtered and the filtrate
evaporated to dryness under vacuum. The residue was recrystallized
from isopropanol to give a purple-pink solid (.8 g., 70%).

Anal. Calcd. for Cs\(_2\)CoC\(_8\)H\(_4\)F\(_{12}\)O\(_8\): C, 12.17; H, 0.51; F, 29.19;
Co, 7.60. Found C, 11.73; H, 0.22; F, 28.99; Co, 8.02.

The compound has a magnetic moment of 3.88 B.M. and a molar
conductivity of 275 mhos at infinite dilution (water.). The diffuse
reflectance spectrum has bands at: 500, 560, 590, 950 µm. The solution
spectrum has bands at; 478 µm(ε=8.3), 520 µm(8.6), 578 (8.7), 850 (3.8).

The infrared spectrum shows the following bands: 3400 (w),
1630 (s), 1430 (w), 1375 (m), 1270 (s), 1205 (s), 1165 (s), 1135 (m−s),
1020 (s), 980 (s), 820 (m), 750 (m), 670 (m), 560 (w), 530 (m) cm\(^{-1}\).

**Preparation of cesium tris(perfluoro-2-hydroxy-2-methylpropionato)-
manganate(III)**

Cesium hydroxide (1.4 g, 0.011 moles) was added slowly to an
ethanolic solution containing perfluoro-2-hydroxy-2-methylpropanoic
acid (1.0 g, 5.0 mmoles) and manganous chloride tetrahydrate (0.46 g,
2.2 mmoles). The solution turned black in color. Cesium chloride
was filtered from solution and the filtrate cooled under vacuum. Black crystals appeared, were filtered, and dried under vacuum (0.6 g).

Anal. Calcd. for Cs$_3$MnC$_{12}$F$_{18}$O$_9$: C, 13.28; H, 0.00; F, 31.55; Mn, 5.06. Found: C, 13.14; H, 0.32; F, 31.83; Mn, 4.99.

The magnetic moment was found to be 4.97 B.M.

The infrared spectrum of the solid (KBr disc) was recorded and has the following bands: 3450 (w), 1650 (s-br), 1340 (m), 1270 (s), 1205 (s), 1155 (s), 1032 (m), 1015 (s), 975 (s), 825 (m), 810 (m), 755 (s), 665 (m), 585 (m-w), 545 (m-w), 445 (w) cm$^{-1}$.

Preparation of cesium tris(perfluoro-2-hydroxy-2-methylpropionato)ferrate(III).

Cesium hydroxide (1.0 g, 7 mmoles) was added to an ethanolic solution containing perfluoro-2-hydroxy-2-methylpropanoic acid (0.7 g, 3.3 mmoles) and ferric chloride (.18 g, 1 mmole). Cesium chloride was filtered from the solution; the filtrate was evaporated to dryness; and the residue was recrystallized from 2-propanol. (.9 g, 82%).

Anal. Calcd. for Cs$_3$FeC$_{12}$H$_2$F$_{18}$O$_{10}$: C, 13.08; H, 0.18; F, 31.01; Fe, 5.06. Found C, 12.90; H, 0.10; F, 30.83; Fe, 4.70.

The magnetic moment of the compound is 5.84 B.M. Its equivalent conductance at infinite dilution (water) is 305 mhos. The diffuse reflectance spectrum has very weak bands at 580, 670, 700, and 920 m$_{\nu}$. The solution spectra (methanol) has one band at 455 m$_{\nu}$ ($\varepsilon$=4.0).

The infrared spectrum has the following bands: 3370 (w), 1655 (s), 1365 (m), 1275 (s), 1160 (s), 1020 (s), 975 (s), 825 (m),
755 (s), 670 (m), 565 (w), 540 (m), 445 (w).

**Preparation of Cesium tris(perfluoro-2-hydroxy-2-methylpropionato)-chromate(III)**

Cesium hydroxide (0.9 g, 6 mmoles) was added to an ethanolic solution containing perfluoro-2-hydroxy-2-methylpropanoic acid (0.6 g, 0.03 moles) and Cr₂(SO₄)₃·15 H₂O (0.3 g, 0.5mmoles). Cesium sulfate was filtered from the solution, the filtrate evaporated to dryness, and the residue (1.0 g, 91%) was recrystallized from 2-propanol.

Anal. Calcd. for Cs₃CrC₁₂H₂F₁₈O₁₀: C, 13.11; H, 0.18; F, 31.10; Fe, 4.72. Found: C, 13.07; H, 0.17; F, 30.65; Cr, 5.20.

The magnetic moment of the compound is 3.85 B.M. Its molar conductance is 319 mhos at infinite dilution (water). The diffuse reflectance spectrum has visible absorptions at 480, and 680 μ and the solution spectrum (methanol) has bands at 440 (ε=55.0) and 595 (ε=51.1) μ. In water, the bands appear at 438 and 598μμ.

The infrared spectrum (KBr disc) has the following bands:
3400 (s), 1655 (s), 1365 (m), 1270 (s), 1220 (s), 1160 (s), 1020 (s), 985 (s), 835 (m), 755 (s), 665 (m), 565 (w), 540 (m), 445 (w) cm⁻¹.

**Preparation of potassium bis(perfluoro-2-hydroxy-2-methylpropionato)-vanadate(IV)**

Potassium hydroxide (1.2 g, 0.02 moles) was added to an ethanolic solution containing perfluoro-2-hydroxy-2-methylpropanoic acid (2.0 g, 0.01 moles) and vanadyl sulfate (1.6 g, 0.01 moles). Potassium sulfate was centrifuged, the solution evaporated to dryness and the residue (2.2 g, 95%) was recrystallized from isopropanol.
Anal. Calcd. for $K_2V_8H_2F_{12}O_8$: C, 16.50; H, 0.35; F, 39.05. Found: C, 17.20; H, 0.53; F, 38.66. The compound appears to contain a trace of solvent.

The molar conductance is 251 mhos when extrapolated to infinite dilution, and the magnetic moment is 1.76 B.M. The diffuse reflectance spectrum has a band at 420 m$, and a broad band extending from 500-900 m$. The solution spectrum (methanol) has bands at 540 m$ ($\varepsilon=16$), 620 m$ ($\varepsilon=15$), 730 m$ ($\varepsilon=9.9$).

The infrared spectrum of the compound has the following bands: 3560 (w, sharp); 1680 (s), 1350 (m), 1270 (m), 1215 (s), 1160(s), 1090 (w), 1025 (s), 1000 (s), 950 (s), 840 (s), 765 (s) 675 (m), 600(m), 560 (s), 530 (m), 514 (m), 440 (s).

The cesium salt of the vanadyl complex has also been prepared in an analogous manner and has similar properties to the potassium derivative.

**Preparation of an ethylenediamine complex of perfluoro-2-hydroxy-2-methylpropionato)nickelate(II).**

Perfluoro-2-hydroxy-2-methylpropanoic acid (2.1 g, .011 moles) was added to an aqueous solution containing nickel nitrate hexahydrate (2.9 g, .01 moles). Upon the addition of ethylenediamine the solution
turned from green to blue at which point a blue-violet precipitate formed. The solid was filtered and recrystallized from ethanol.

Anal. Calcd. for NiC_{12}H_{18}F_{12}N_{4}O_{6}: Ni, 9.77; C, 23.96; H, 3.01; F, 37.90; N, 9.33. Found: Ni, 10.17; C, 23.41; H, 3.09; F, 36.65; N, 9.70.

The compound has a molar conductance of 133 mhos at infinite dilution in water. The diffuse reflectance spectrum has bands at 355 μm, 550 μm, and 890 μm; the solution spectrum in methanol has bands at 364 μm (ε=13.3), 381 μm (8.68), 950 μm (8.82).

The infrared spectrum (KBr disc) has bands at: 3360 (s), 3290 (m), 3190 (w), 2980 (w), 2960 (w), 2900 (w), 1660 (s), 1610 (m), 1595 (m), 1380 (m), 1355 (m), 1270 (s), 1200 (s), 1150 (s), 1065 (w), 1000 (m), 970 (s), 695 (w), 510 (m), 530 (m), 380 (m) cm⁻¹.

Addition of ethylenediamine to a solution of K₂Ni(HHIB)₂ produced a blue-violet compound which has an infrared spectrum identical to that of the preceding compound. The reaction appeared to be reversible.

**Attempted preparation of tris(ethylenediamine)perfluoro-2-hydroxy-2-methylpropionato-nickelate(II).**

1. Ethylenediamine was added to the preceding compound, H₂En₂Ni(HHIB)₂ (1.0 g, 1.6 mmoles) until the blue-violet color changed to purple. The solution was evaporated to dryness and recrystallized from ethanol/pentane mixture. The analysis indicated an excess of the HHIB acid to be present. The molar conductivity is 200 mhos at infinite dilution. Its magnetic moment is 3.01 B.M. The diffuse reflectance spectrum has bands at 340, 550, and 875 μm. The solution
spectrum has bands at 335 μ (ε=9.6), 554μ (6.2), 890 μ (6.2).

2. A tris(ethylenediamine)nickelate(II) sulfate suspension in methanol was shaken with perfluoro-2-hydroxy-2-methylpropanoic acid (1 g, 5.0 mmoles). The excess tris(ethylenediamine)nickelate(II) sulfate was centrifuged and the remaining solution evaporated to dryness and identified by its color and infrared as the \( \text{H}_2\text{En}_2\text{Ni(HHIB)}_2 \) compound.

**Preparation of potassium (perfluoro-2,3-dimethylbutane-2,3-diol)-(perfluoro-2-hydroxy-2-methylpropionato)nickelate(II)**

Perfluoropinacol (1g, 3.0 mmoles), perfluoro-2-hydroxy-2-methylpropanoic acid (.65 g, 3.0 mmoles) and nickel nitrate hexahydrate were dissolved in methanol. Addition of potassium hydroxide produced a white precipitate which was filtered; the filtrate was evaporated to dryness and the orange residue recrystallized from 2-propanol. (1.5 g, 75%).

**Anal. Calcd. for K₂NiC₁₀F₁₈O₅:** C, 17.67; H, 0.0; F, 50.37; Ni, 8.69; Found: C, 18.03; H, 0.18; F, 49.55; Ni, 8.59.

The molar conductance of the compound is 233 mhos at infinite dilution (water). The diffuse reflectance spectrum has bands at: 415, 760, and 1150 μ. The solution spectrum has bands at 405 μ (ε=31.4), 760 (10.7), 1150 μ (2.7). The magnetic moment is 3.21 B.M.

The infrared spectrum (KBr disc) has the following bands:

3680 (w), 1645 (s), 1610 (s), 1380 (m), 1265 (s), 1205 (s), 1150 (s), 1120 (m), 1010 (m), 980 (m), 940 (m), 870 (m), 830 (m), 745 (m), 720 (m), 670 (w), 560 (w), 535 (m), 435 (m) cm⁻¹.
The cesium salt of this compound was prepared by a similar procedure. It has a molar conductance of 254 mhos, and a magnetic moment of 3.18 B.M.

**Preparation of bis(triethylphosphino)(perfluoro-2-hydroxy-2-methylpropionato)nickelate(II).**

1. Nickel nitrate hexahydrate (1.4 g, 5 mmol) and perfluoro 2-hydroxy-2-methylpropanoic acid (1.0 g, 5 mmol) were dissolved in a methanol/water mixture (15%). Triethylphosphine (1.18 g, 10 mmol) was dropped into solution (under an atmosphere of dry nitrogen) until the solution turned orange. Water (10 ml.) was added and the solution evaporated slowly under vacuum. Orange crystals precipitated (1.8 g, 70%) and were recrystallized from an ethanol/water mixture.

   Anal. Calcd. for NiP₂C₁₆H₃₀F₁₆O₃: Ni, 11.62; P, 12.25; C, 38.0; H, 5.97; F, 22.56. Found: Ni, 11.70; P, 12.18; C, 37.95; H, 6.06; F, 22.59.

2. The compound has also been prepared by the reaction of triethyl phosphine (.1g) with a solution (methanol) of potassium bis(perfluoro-2-hydroxy-2-methylpropionato)nickelate(II) (0.25 g) and the orange complex recrystallized from water. The reaction is reversible if excess acid and potassium hydroxide are added.

   A molecular weight of 500 was obtained in benzene solution when extrapolated to infinite dilution. (Calcd. M\(_\text{wt}\)=504.7) The molar conductivity is 12.2 mhos taken in ethanol at a concentration of \(6 \times 10^{-4}\) M. The compound has a band at 450 \(\mu\) in the diffuse reflectance spectrum and a band at 460 \(\mu\) (\(\epsilon=193\)) in the solution spectrum (methanol). The compound is diamagnetic.
The infrared spectrum has bands at: 2880 (w), 1685 (s),
1410 (w), 1360 (w), 1330 (m), 1260 (s), 1205 (s), 1185 (s), 1155 (s),
1130 (m-s), 1025 (s), 970 (s), 820 (s), 760 (s), 740 (s), 660 (m),
575 (m), 520 (m), 470 (m), 425 (m), 385 (m) cm⁻¹.

Preparation of [bis(diphenylphosphino)ethane](perfluoro-2-hydroxy-
2-methylpropionato)nickelate(II)

1. Nickel nitrate hexahydrate (.6 g, 2 mmole) and perfluoro-
2-hydroxy-2-methylpropanoic acid (0.4 g, 1.9 mmole) were dissolved
in a methanol/water mixture (15 ml.). Bis(diphenylphosphino)ethane
(0.74 g, 1.8 mmole) dissolved in methanol/tetrahydrofuran mixture
was added slowly. The solution was heated gently for one hour,
the water (10 ml.) was added to the orange brown solution, and
the solution evaporated slowly under vacuum. Bright yellow
 crystals (.9 g, 75%) were filtered from the solution, recrystallized
from an ethanol/water mixture and dried under vacuum.

Anal. Calcd. for NiC_{30}H_{24}F_{6}O_{3}P_{2}: Ni, 8.79; C, 54.10;
H, 3.62; F, 17.08; P, 9.28. Found: Ni, 8.70; C, 55.48; H, 3.67;
F, 17.57; P, 9.30.

2. The compound has also been prepared by the reaction of bis-
(diphenylphosphino)ethane with a solution (methanol) of potassium
bis(perfluoro-2-hydroxy-2-methylpropionato)nickelate(II). The
reaction was not reversible however, even with an excess of the
hydroxy acid.

The molar conductance is 2.8 mhos at 4 x 10⁻⁴ M. concentrations
in methanol. The compound has an absorption band at 400 μ. In the
solution spectra the band appears at 425 μ (ε=200). The compound is diamagnetic.

The infrared spectrum (nujol and halocarbon mulls) has the following bands: 3060 (w), 1680 (s), 1435 (m), 1415 (w), 1365 (m), 1312 (s), 1285 (s), 1240 (s), 1215 (s), 1185 (s), 1155 (s), 975 (s), 810 (w), 785 (m), 755 (m-w), 735 (m), 720 (m-w), 705 (m), 690 (m), 670 (m), 525 (s), 505 (s), 480 (m), 430 (w) cm⁻¹.

Attempts were made at preparing other nickelate(II) complexes containing the HHIB ligand but were unsuccessful. These complexes include K₂Ni(CN)₂(HHIB), K₂(C₂O₄)(HHIB), K₂NiCl₂(HHIB), (bipyryl)Ni(HHIB), (TMED)Ni(HHIB), (PPh₃)₂Ni(HHIB).

**Reaction of ethylenediamine with perfluoro-2-hydroxy-2-methylproanoic acid and copper sulfate**

Ethylenediamine was slowly added to aqueous perfluoro-2-hydroxy-2-methylproanoic acid (2.1 g, 0.01 moles) and copper sulfate pentahydrate (2.7 g, 0.01 moles). A blue precipitate appeared which was filtered and recrystallized from methanol.

Anal. Calcd. for CuC₁₀H₁₀F₁₂N₂O₃: Cu, 11.69; C, 22.08; H, 1.83; F, 41.93; N, 5.15. Found: Cu, 12.72; C, 21.93; H, 2.10; F, 41.38; N, 5.78.

The molar conductivity is 133 mhos at infinite dilution. The magnetic moment is 1.90 B.M. The diffuse reflectance spectrum has a band at 650 μ with a shoulder 550 μ. The solution spectrum (methanol) has a band at 635 μ(ε=25.2).

The infrared spectrum has the following bands: 3150 (m-s), 2980 (m-s), 2740 (m), 2690 (s), 2590 (s), 2460 (s), 2100 (m), 1686 (s),
1615 (s), 1525 (s), 1330 (w), 1280 (s), 1265 (s), 1200 (s), 1150 (s), 1080 (w), 1020 (s), 970 (s), 695 (m), 580 (m), 540 (w), 530 (w), 496 (m), 460 (w), 340 (w), 205 (w) cm$^{-1}$.

**Preparation of bis(ethylenediamine)bis(perfluoro-2-hydroxy-2-methylpropionato)cuprate(II).**

Ethylenediamine was slowly added to a suspension of the preceding complex [H$_2$EnCu(HHIB)$_2$](91.0 g. 2mmoles) until the complex dissolved and a violet colored solution appeared. The solution was evaporated to dryness and the residue recrystallized from an ethanol/hexane mixture.

Anal. Calcd. for CuC$_{12}$H$_{18}$F$_{12}$N$_4$O$_3$: Cu, 10.52; C, 23.87; H, 2.67; F, 37.76; N, 9.27. Found: Cu, 10.85; C, 24.61, H, 3.11; F, 37.98; N, 9.52.

The compound has a molar conductance of 160 mhos at infinite dilution (water). The magnetic moment is 1.86 B.M. Its diffuse reflectance spectrum has a band at 575 m$\mu$ and a weaker band at 790 m$\mu$. The visible spectrum in methanol has a broad absorption band at 573 m$\mu$ ($\epsilon$=25).

The infrared spectrum has the following bands: 3350 (s), 3250 (m), 3180 (m), 2980 (w), 2960 (w), 2800 (w), 1660 (s), 1605 (s), 1465 (m), 1380 (m), 1355 (m), 1275 (s), 1255 (s), 1195 (s), 1145 (s), 1080 (w), 1020 (s), 970 (s), 705 (m), 630 (w), 590 (m), 535 (m), 505 (m), 450 (w), 380 (m) cm$^{-1}$.

**Reaction of tetramethylethylenediamine with perfluoro-2-hydroxy-2-methylpropanoic acid and copper sulfate**

Copper sulfate pentahydrate (1.3 g, 5.0 mmoles) and perfluoro-2-hydroxy-2-methylpropanoic acid (1.0 g, 5.0 mmoles) were dissolved
in water (10 ml.) and titrated with potassium hydroxide until a pH of 6 was obtained. Tetramethylethylenediamine (0.3 g, 5 mmoles) was added slowly. The deep blue solution was evaporated to dryness, dissolved in ethanol, filtered, and evaporated to dryness again. The residue was recrystallized from 2-propanol.

Anal. Calcd. for CuC_{14}H_{18}F_{12}N_{2}O: Cu, 10.6; C, 27.97; H, 3.01; F, 37.87; N, 4.65. Found: Cu, 11.73; C, 27.97; H, 3.07; F, 41.19; N, 4.91.

The molar conductance in water at 10^{-4} M (water) is 91 mhos. The diffuse reflectance spectrum has a very broad band with two maxima at 640 μm and 530 μm. The solution spectrum (methanol) has one maximum at 633 μm (ε=26.8).

The infrared spectrum has bands at: 3030 (w), 2960 (m), 2680 (m), 2650 (m), 2600 (m), 2530 (m), 2460 (m), 1695 (s), 1485 (m-w) 1470 (m-2), 1355 (w), 1330 (m), 1275 (s), 1265 (s), 1205 (s), 1185 (s), 1150 (s), 1075 (w), 1020 (s), 975 (s), 830 (m), 780 (w), 750 (w), 695 (w), 660 (m), 585 (m), 550 (w), 530 (w), 465 (w), 395 (m).

Attempts to prepare phosphine complexes of copper with the HHIB ligand proved unsuccessful. These include (PET_{3})_{2}Cu(HHIB), (BDPPE)Cu(HHIB), and (PPh_{3})_{2}Cu(HHIB).

**Preparation of potassium tris(perfluoro-2-alkoxy-2-methylpropionato)-thorate(IV)**

Potassium hydroxide (0.65 g, 0.01 moles) was dissolved in ethanol containing thorium nitrate hexahydrate (1.05 g, 2.0 mmoles) and perfluoro-2-hydroxy-2-methyl propanoic acid (1.2 g, 6.0 mmoles).
The solution was filtered, the filtrate evaporated to dryness, then
the residue recrystallized from 2-propanol and dried under vacuum.

Anal. Calcd. For K₂ThC₁₂F₁₈O₉: Th, 24.6; C, 15.3; F, 36.4:
0, 15.3. Found: Th, 23.46. Calculated for K₂Th(C₄F₆O₃)₃·2H₂O:
Th, 23.7.

The molar conductivity is 254 mhos at 10⁻³ M. (water).

The infrared spectrum has the following bands; 3460 (m),
1660 (s), 1270 (s), 1210 (s), 1190 (s), 1130 (s), 1010 (s), 810 (s),
747 (m), 685 (w), 665 (m), 555 (w), 532 (w), 520 (w), 450 (s), 356(m).

Preparation of bis(dimethylformamide)bis(perfluoro-2-hydroxy-2-
methylpropionato)germanium(IV)

Germanium tetrachloride (0.75 g, 3.5 mmole) was added to an
anhydrous diethylether/dimethylformamide mixture containing perfluoro-
2-hydroxy-2-methylpropanoic acid (1.5 g, 7.1 mmole) under a dry
nitrogen atmosphere. The solution was filtered, the filtrate evapor-
ated to dryness and the residue (2. g) washed with methylene
chloride. mp 268-272 °C.

Anal. Calcd. for GeC₁₄H₁₄F₁₂N₂O₈: Ge,11.36; C, 26.30;
H, 2.19; F, 35.72. Found: Ge, 10.76; C, 27.17; H, 2.31; F, 37.82.

The infrared spectrum of the compound has the following
bands: 2950 (w), 2860 (w), 1735 (s), 1655 (s), 1480 (m), 1345 (s),
1275 (s), 1215 (s), 1175 (s), 1040 (s), 980 (s), 830 (m), 765 (m),
735 (m), 720 (m), 660 (m), 620 (w), 535 (w), 445 (m), 405 (m),
365 (m).
**Attempted preparation of bis(dimethylformamide)bis(perfluoro-2-hydroxy-2-methylpropionato)silicon(IV)**

Silicon tetrachloride (0.7 g, 4.1 mmoles) was added to anhydrous diethylether/dimethylformamide solution containing perfluoro-2-hydroxy-2-methylpropanoic acid (1.7 g, 8.2 mmoles) under a dry nitrogen atmosphere. The solution was filtered, the filtrate evaporated to dryness, and the residue washed with methylene chloride.

Analysis indicated the compound had partially hydrolyzed.

The infrared spectrum (nujol mull) is similar to the spectrum of the germanium complex with bands at: 3380 (m-br.), 1750 (s), 2950(w) 2860 (w), 1690 (s), 1480 (w), 1345 (s), 1285 (s), 1225 (s), 1170 (s), 1050 (m), 995 (m), 670 (m), 565 (s), 550 (s), 515 (w), 420 (w)cm\(^{-1}\).

Attempts to prepare pure perfluoro-2-hydroxy-2-methylpropionato- chelate complexes of the group (IVb) elements failed.

**Preparation of trimethylsilyl-2-trimethylsiloxy(perfluoro-2-methylpropionate).**

Perfluoro-2-hydroxy-2-methylpropanoic acid (2.1 g, 0.01 moles) was added to excess hexamethyldisilazane and heated (80 °C.) for four hours. The solution was distilled under vacuum to obtain the product (40 °C, 0.1 mm)

Anal. Calcd. for \(\text{Si}_2\text{C}_2\text{H}_{18}\text{F}_6\text{O}_3\): Si, 15.7; C, 33.7; H, 5.05; F, 32.0. Found: C, 33.81; H, 5.26.

The infrared spectrum has the following bands: 2980 (m), 2910 (m) 1750 (s), 1410 (w), 1340 (m), 1255 (s), 1230 (s), 1200 (m), 1160 (m), 1025 (s), 980 (s), 850 (s), 760 (s), 735 (m), 635 (w), 545(w)
450 (w) cm\(^{-1}\).

**Preparation of potassium tris(perfluoro-2-hydroxy-2-methylpropionato)aluminate(III).**

Potassium hydroxide (1.0 g, 0.02 moles) was added to an ethanolic solution of perfluoro-2-hydroxy-2-methylpropanoic acid (2.1 g, .01 moles) and aluminium chloride (0.45 g, .003 moles). The potassium chloride precipitate was filtered, the filtrate evaporated to dryness, and the residue recrystallized from 2-propanol.

Anal. Calcd. for K\(_3\)AlC\(_{12}\)F\(_{18}\)O\(_9\): C, 18.61; H, 0.00; F, 44.17 Al, 3.49. Found: C, 17.66; H, 0.39; F, 44.84; Al, 3.76.

The molar conductance taken in water at infinite dilution is 380 mhos.

The infrared spectrum of the complex has the following absorption bands: 3350 (w), 1710 (w), 1685 (s), 1385 (m), 1280 (s), 1215(s), 1180 (s), 1030 (s), 975 (s), 845 (m), 760 (m), 670 (w), 600 (s), 540 (m), 490 (m), 460 (s), 420 (s) cm\(^{-1}\).

**Preparation of cesium bis(perfluoro-2-hydroxy-2-methylpropionato)borate**

Trimethylborate (0.5 g, .005 moles) was added to a methanol/benzene solution (15 ml.) containing perfluoro-2-hydroxy-2-methylpropanoic acid (2.1 g, 0.01 moles) and heated gently for two hours.

After evaporating to dryness, the gelatinous product was added to an aqueous cesium hydroxide (.75 g, .005 moles) solution containing cesium chloride (1.0 g). Evaporation of this solution produced crystals that were filtered and recrystallized from 2-propanol.
Anal. Calcd. for CsBC$_{8}$ F$_{12}$ O$_{6}$: Cs, 23.57; C, 17.04; H, 0.00; F, 40.44; B, 1.92; O, 11.02. Found: C, 17.30; H, 0.19; F, 40.21.

The molar conductance of the compound was found to be 123 mhos when extrapolated to infinite dilution (water).

The infrared spectrum has the following prominent bands: 1770 (s), 1280 (s), 1230 (s), 1210 (m), 1155 (s), 1140 (m), 780 (m), 745 (m), 670 (s), 655 (s), 560 (w), 530 (m), 470 (w), 435 (m) cm$^{-1}$.

All attempts to prepare this compound using sodium borate or boric acid failed.

Attempted preparation of cesium tris(perfluoro-2-hydroxy-2-methylpropionato)phosphorus(V).

Solid phosphorus pentachloride (0.9 g, 4.3 mmoles) was added to perfluoro-2-hydroxy-2-methylpropanoic acid (2.7 g, 12.9 mmoles) and heated gently. Aqueous cesium hydroxide was added to the product and the resulting solution evaporated for 24 hours. A solid precipitate was filtered and identified by infrared spectroscopy as cesium perfluoro-2-hydroxy-2-methylpropionate.

Preparation of perfluoro-2-hydroxy-2-methylpropionato-phosphorus-trichloride

Solid phosphorus pentachloride (2.0 g, 0.01 moles) was added to perfluoro-2-hydroxy-2-methylpropanoic acid (2.0 g, 0.01 moles) and heated gently. A vigorous reaction ensued and liberated hydrogen chloride. The remaining liquid was distilled to yield the product (2.5 g, 66%) bp 151 °C.

The product reacts vigorously with water or alcohols to release
Anal. Calcd. for CsBC$_8$F$_{12}$O$_6$: Cs, 23.57; C, 17.04; H, 0.00; F, 40.44; B, 1.92; O, 11.02. Found: C, 17.30; H, 0.19; F, 40.21.

The molar conductance of the compound was found to be 123 mhos when extrapolated to infinite dilution (water).

The infrared spectrum has the following prominent bands: 1770 (s), 1280 (s), 1230 (s), 1210 (m), 1155 (s), 1140 (m), 780 (m), 745 (m), 670 (s), 655 (s), 560 (w), 530 (m), 470 (w), 435 (m) cm$^{-1}$.

All attempts to prepare this compound using sodium borate or boric acid failed.

**Attempted preparation of cesium tris(perfluoro-2-hydroxy-2-methyl-propionato)phosphorus(V).**

Solid phosphorus pentachloride (0.9 g, 4.3 mmoles) was added to perfluoro-2-hydroxy-2-methylpropanoic acid (2.7 g, 12.9 mmoles) and heated gently. Aqueous cesium hydroxide was added to the product and the resulting solution evaporated for 24 hours. A solid precipitate was filtered and identified by infrared spectroscopy as cesium perfluoro-2-hydroxy-2-methylpropionate.

**Preparation of perfluoro-2-hydroxy-2-methylpropionato-phosphorus-trichloride**

Solid phosphorus pentachloride (2.0 g, 0.01 moles) was added to perfluoro-2-hydroxy-2-methylpropanoic acid (2.0 g, 0.01 moles) and heated gently. A vigorous reaction ensued and liberated hydrogen chloride. The remaining liquid was distilled to yield the product (2.5 g, 66%) bp 151 °C.

The product reacts vigorously with water or alcohols to release
hydrogen chloride.

Anal. Calcd. for $\text{C}_6\text{F}_3\text{O}_3\text{PCl}_3$: C, 13.8; F, 32.9; O, 13.8;
P, 8.95; Cl, 30.5. Found: C, 14.52; Cl, 27.45.

The analysis is consistent with a mixture of the desired product and
its hydrolysis product, $[(\text{HHIB})_2\text{Cl}_2\text{P}]_2\text{O}$. A mixture containing 25% of
the latter compound would analyze for $\text{C}_6\text{F}_3\text{O}_{1.25}\text{PCl}_{2.6}$: C, 14.2;
Cl, 27.41.

The infrared spectrum of the compound showed the following
prominent bands: 1825 (s), 1310 (s), 1245 (s), 1185 (m), 1120 (s),
1050 (s), 990 (s), 915 (w), 870 (s), 840 (s), 830 (m), 750 (w), 650 (m),
605 (s), 565 (w), 535 (s), 505 (s), 460 (m) cm$^{-1}$. 
Results and Discussion

Part one: Perfluoro-2,3-diphenylbutane-2,3-diol, (II)

This compound can be made, like perfluoropinacol, by the reaction of a perfluorinated ketone with triethylphosphite to form a cyclic phosphorane which can be hydrolyzed to the diol. Best yields were obtained however, by the photolytic reductive dimerisation of octafluoroacetophenone with 2-propanol.

\[
\begin{align*}
2\text{CF}_3\text{COC}_6\text{F}_5 & \xrightarrow{\text{PrOH/H}^+} \text{CF}_3\text{CF}_3 \\
\text{C}_6\text{F}_5\text{C}-\text{C}_6\text{F}_5 & \quad \text{diol (II)}
\end{align*}
\]

Like perfluoropinacol and 2,3-diphenyl-hexafluorobutane-2,3-diol\(^48\), this diol did not undergo pinacol-pinacolone rearrangement, even in conditions much more acidic than those normally required (conc. H\(_2\)SO\(_4\)/100 °C.). The presence of the electrophilic CF\(_3\) and C\(_6\)F\(_5\) groups precludes the development of the carbonium ion necessary for rearrangement to take place.

The diol (II), differs from perfluoropinacol since it contains two asymmetric carbon atoms and can exist in three isomeric forms; a meso isomer and two optically active enantiomers. The compound was purified by sublimation and recrystallization (mp 121-125 °C) and was assumed to be either the meso isomer or the racemic mixture.
Infrared spectrum

A sharp band observed at 3635 cm\(^{-1}\) is similar to that in the hydroxyl stretching region of perfluoropinacol. Strong bands are observed in the 1300-1100 cm\(^{-1}\) region, indicating the presence of CF\(_3\) and aryl-F in the compound. Skeletal modes characteristic of C\(_6\)F\(_5\) groups are observed at 1650, 1530, and 1000 cm\(^{-1}\). Bands at 1000 and 1130 cm\(^{-1}\) might be the C-O stretching vibrations, although aryl-F stretching bands are also expected in this region.

The region between 1000 and 600 cm\(^{-1}\) is more complicated than for perfluoropinacol. Common bands appear at 860 and 715 cm\(^{-1}\). Diol (II) has bands at 950, 785, and 680 cm\(^{-1}\) while perfluoropinacol has bands at 920 and 740 cm\(^{-1}\). A few of these bands have been tentatively assigned as shown in Table 1.

It is difficult to detect the presence of more than one isomer since the spectrum is complicated. More than two C-O vibrations would indicate both the meso and the racemic isomers to be present. These bands are in the same stretching region as F-aryl bands however, and could couple with C-C vibrations to further distort their stretching frequencies. As a result the infrared evidence is not sufficient to determine if the meso and optically active isomers are both present.
Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>O-H</th>
<th>CF₃</th>
<th>aryl-F</th>
<th>C=C</th>
<th>C-O</th>
<th>CF₃</th>
<th>C-C cm⁻¹</th>
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<tbody>
<tr>
<td>[(CF₃)₂COH]₂</td>
<td>3635</td>
<td>1280</td>
<td></td>
<td>1110</td>
<td>710</td>
<td>920</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3600</td>
<td>1260</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1165</td>
</tr>
<tr>
<td>[C₆F₅(CF₃)COH]₂</td>
<td>3635</td>
<td>1220</td>
<td>1135</td>
<td>1650</td>
<td>1100</td>
<td></td>
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<tr>
<td></td>
<td>1200</td>
<td></td>
<td></td>
<td>1530</td>
<td>950</td>
<td>760</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1175</td>
<td></td>
<td></td>
<td>1480</td>
<td></td>
<td>1000</td>
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</tr>
</tbody>
</table>

Mass spectrum

Table 2 shows the mass spectrum of diol (II). The molecular ion peak is not observed, presumably reflecting the low stability of the compound. The largest m/e value is observed at 511, produced by the loss of fluorine from the parent ion. The loss of CF₄ from the parent ion produces the next peak at m/e of 442. The peaks between 511 and 265 have relatively low intensity. No peaks are observed corresponding to the loss of CF₃ or C₆F₅ from the parent ion, although intense peaks are observed at 69 and 167 corresponding to CF₃⁺ and C₆F₅⁺ ions. The intense peak at 265 has half the m/e value of the molecular ion indicating a large portion of the diol decomposes to C₆F₅C(CF₃)OH⁺ ion. Loss of F and CF₃H from this ion may produce the intense peaks at 247 and 195 corresponding to C₆F₅CCF₂OH⁺ and C₆F₅CO⁺ respectively. The latter ion represents the very stable perfluorotropolone cation C₇F₅CO⁺ commonly observed in other pentafluorophenyl...
alcohols. Peaks of lesser intensity represent the series of ions 
$C_9F_{10}^+$, $C_8F_7^+$, $C_7F_5^+$, and $C_6F_4^+$.

Table 2.

<table>
<thead>
<tr>
<th>Peak</th>
<th>m/e</th>
<th>relative intensity</th>
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</thead>
<tbody>
<tr>
<td>$C_6F_5CCF_3O^+$</td>
<td>265</td>
<td>100.0</td>
</tr>
<tr>
<td>$C_6F_5CCF_3H^+$</td>
<td>249</td>
<td>100.0</td>
</tr>
<tr>
<td>$C_6F_5CCF_2OH^+$</td>
<td>246</td>
<td>100.0</td>
</tr>
<tr>
<td>$C_6F_5^+$</td>
<td>229</td>
<td>30.4</td>
</tr>
<tr>
<td>$C_8F_7^+$</td>
<td>217</td>
<td>30.4</td>
</tr>
<tr>
<td>$C_7F_6^+$</td>
<td>199</td>
<td>96.0</td>
</tr>
<tr>
<td>$C_6F_5CO^+$</td>
<td>195</td>
<td>*</td>
</tr>
<tr>
<td>$C_6F_5C^+$</td>
<td>176</td>
<td>37.4</td>
</tr>
<tr>
<td>$C_6F_5^+$</td>
<td>167</td>
<td>98.0</td>
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<tr>
<td>$C_4F_5^+$</td>
<td>155</td>
<td>70.5</td>
</tr>
<tr>
<td>$C_4F_4^+$</td>
<td>148</td>
<td>44.1</td>
</tr>
<tr>
<td>$C_4F_3^+$</td>
<td>117</td>
<td>70.0</td>
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<td>$C_3F_2^+$</td>
<td>109</td>
<td>35.2</td>
</tr>
<tr>
<td>$CF_3^+$</td>
<td>69</td>
<td>*</td>
</tr>
<tr>
<td>$CF_2OH^+$</td>
<td>67</td>
<td>*</td>
</tr>
</tbody>
</table>

* very strong, not estimated.
The means by which the peaks listed in table 2 might be formed are shown in the following figure. The drawing is not really valid however, since no metastable peaks were observed in the spectrum.

\[
\begin{align*}
[C_6F_5C(CF_3)OH]_2 & \rightarrow \text{C}_6\text{F}\text{C}(CF_3)OH^+ & \text{C}_6\text{F}_{15}^+0^2\text{H}_2^- \\
-C_6F_0 & \quad & -CF_3 \\
C_{10}F_{10}OH^- & \rightarrow \text{C}_6\text{F}_5C(CF_3)OH^+ & \text{C}_{15}F_{12}^+0^2\text{H}_2^+ \\
-H_2F & \quad & -CF_2H \\
C_{10}F_9OH^+ & \rightarrow \text{C}_6\text{F}_5CCF_3H & \text{C}_7F_5^+0^2 \\
-HF & \quad & -C \\
C_{10}F_9OH^+ & \rightarrow \text{C}_6\text{F}_5CCF_2OH_2 & \text{C}_7F_5^+0^2 \\
-CF_2 & \quad & -CO \\
C_{9}F_7OH^+ & \rightarrow \text{C}_6\text{F}_5CCF_2OH_2 & \text{C}_7F_5^+0^2 \\
-CF & \quad & -F \\
C_{8}F_7 & \rightarrow \text{C}_7F_5^+0^2 \\
-CO & \quad & \text{C}_6\text{F}_5^+0^2 \\
\end{align*}
\]

\text{figure 1.}

**Nuclear magnetic resonance spectra**

The $^{19}F$ nmr spectrum of the diol (II) does not show the simple pattern of four peaks. In fact six lines, of intensity 3:1:1:1:1:1, are present, the second and third being in the ortho-region, the fourth in the para-region, and the fifth and sixth in the meta-region. This suggested that the $C_6F_5$ groups were in some way unsymmetrical, and was investigated by means of decoupling experiments, which are described below.

A) 72.6 ppm from CF$Cl_3$, CF$^3$. A second order doublet of triplets ($J=26.3$ cps, $J=1.5$ cps). Irradiation of B causes collapse to a broad singlet while irradiation of C removes the small triplets.

B) 130.0 ppm, ortho-F, width 100 cps, broad.

C) 141.5 ppm, ortho-F, width 60 cps, broad.
D) 149.3 ppm, para-F. Triplet of triplets \( (J_{D-E} = J_{D-F} = 21.2 \text{ cps}, J_{D-B} = J_{C-D} = 5.7 \text{ cps}) \) which on irradiation at either B or C, collapses to a triplet of doublets.

E) 159.8 ppm, meta-F. Triplet of doublets of doublets. \( (J_{E-D} = J_{E-C} = 21.2 \text{ cps}, J_{E-B} = 5.7 \text{ cps}, J_{E-F} = 1.2 \text{ cps}) \)

F) 160.7 ppm, meta-F. Overlapping doublet of doublets, each further split to doublets of doublets. \( (J_{F-B} = 22.5 \text{ cps}, J_{F-D} = 21.2 \text{ cps}, J_{F-C} = 7.1 \text{ cps}, J_{F-E} = 1.2 \text{ cps}) \).

Irradiation of C simplifies F to a broad triplet and E to a broad doublet of doublets, while irradiating B simplifies E to a triplet and F to a broad doublet of doublets. Both peaks simplify to doublets of doublets of doublets on irradiating D. Irradiation of E and F caused the collapse of the small 1.5 cps doublet coupling from the other.

The structure of the diol is therefore considered on the following model:

![Diagram](image)

E and F are then chemically different meta-fluorine atoms whose couplings to the ortho- and para-fluorines next to them are nearly, but not quite, the same. B and C are chemically different ortho fluorine atoms, B adjacent to F and C adjacent to E.

It is suggested that the reason for this unusual spectrum is
$J_{AB} = 26.3$

Peak A, irr. of C

$J_{AC} = 1.5 \text{ Hz}$

Peak A, no irr.

CF$_3$ fluorine

$^{19}$F nmr spectrum of diol(II)

Figure 2.
Peak B, no irr.  

Peak C, no irr.  

$J_{DE} = J_{DF} = 21.2$  

$J_{CD} = 5.7$  

$J_{BD} = 5.7$  

Peak D, Irr. B  

Peak D, Irr. C  

Peak D, no irr.
Peak F, Irr. of D

Peak E, Irr. of D

Peak F, Irr. of C.

Peak E, Irr. of C.
that $F_C$ is hydrogen-bonded or otherwise associated with the hydroxyl group, while $F_B$ is then spatially closer to the CF$_3$ group and is coupled with it (presumably by a through-space mechanism) to a much greater extent. The spectrum of the CF$_3$ groups is second-order, containing three low-intensity broad peaks between two high-intensity triplets. Since these groups, as deduced from the decoupling experiments, appear to couple only to $F_B$ and $F_C$, this spectrum is probably complicated by coupling between the two chemically equivalent but magnetically non-equivalent halves of the molecule.

The $^1$H nmr spectrum, run at 60 MHz in chloroform solution, shows a broad doublet at 4.8 ppm ($J=10$ cps), in agreement with the proposed rigid association of the hydroxyl proton with one aromatic ortho-fluorine atom. A possible reason why the hydroxyl group should preferentially hydrogen-bond to (or associate with) a fluorine atom in the C$_6$F$_5$ group, rather than to the more electronegative CF$_3$ group, is that the ortho fluorine atoms are in a preferential spatial orientation.

**Acidity measurements**

The pK$_a$ of diol (II) was measured in a range of ethanol/water mixtures using the half end point method. The diol, like other pentafluorophenyl containing alcohols$^{49}$ has limited solubility in water, which necessitated an extrapolation from ethanol/water mixtures to obtain aqueous pK$_a$ values. The diol dissolved in a minimum of 40% ethanol and was found to be only weakly acidic; both factors reducing the accuracy of the pK$_a$ value obtained. A plot of the mole fraction of ethanol versus the pK at various concentrations produced
the linear relationship:
\[ pK = 2.0(\text{mf}) + 8.85 \]
giving an extrapolated \( pK_a \) of 8.85.

Table 3

<table>
<thead>
<tr>
<th>Vol. % ETOH</th>
<th>mf</th>
<th>pK</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>.171</td>
<td>9.17</td>
</tr>
<tr>
<td>50</td>
<td>.236</td>
<td>9.34</td>
</tr>
<tr>
<td>60</td>
<td>.317</td>
<td>9.47</td>
</tr>
<tr>
<td>80</td>
<td>.514</td>
<td>9.93</td>
</tr>
</tbody>
</table>

Knunyants\textsuperscript{50,51} found the acidity of fluorinated alcohols can be related to the sum of the Taft polar substitution constants \( \sigma^* \), the applicable equation for \( \text{CF}_3 \)-containing alcohols:
\[ pK_a = -1.44\Sigma\sigma^* + 16.67 \] (A)
For primary and secondary alcohols they found \( \sigma^*(\text{CF}_3) = 2.6 \)
assuming \( \sigma^*(\text{H}) = 0 \). [According to Taft\textsuperscript{52} \( \sigma^*(\text{H}) = 0.48 \) on a scale based on \( \sigma^*(\text{CH}_3) = 0 \).

Using equation (A), \( \sigma^*(\text{CF}_3) = 2.6 \), and the \( pK_a \)'s of perfluoro-(2-phenylpropane-2-ol) and perfluoro(1,1 diphenylethanol) the \( \sigma^*(\text{C}_6\text{F}_5) \) value was established to be 1.1.\textsuperscript{49} Using this value and Knunyants equation, the \( \sigma^* \) value for the \( \text{CF}_3(\text{C}_6\text{F}_5)\text{C-OH} \) group was determined to be 1.7. For perfluoropinacol \( \sigma^*[(\text{CF}_3)_2\text{OH}] \) is 2.25.

Filler and Schure\textsuperscript{14} related the \( pK_a \) of several fluorinated alcohols to the difference \( \Delta \lambda \) in O-H stretching frequencies in solutions of \( \text{CCl}_4 \) (free O-H) and THF (H bonded O-H) obtaining a linear expression:
\[ pK_a = -25.7\Delta\lambda + 18.15. \]
Points obtained by plotting $pK_a$ versus $\Delta \lambda$ for diol (II) and pentafluorophenyl alcohols $C_6F_5C(CF_3)_2OH$ and $C_F_3C(C_6F_5)_2OH$ do not lie on the line. The $pK_a$ value in each case was high relative to $\Delta \lambda$ indicating alcohols and diols containing pentafluorophenyl groups behave as weaker acids than expected. Hence it appears that the hydrogen bonding between ortho-fluorine and the hydroxyl group observed in nmr studies of the diol is sufficiently strong to have a marked weakening effect on the acidity of the perfluorophenyl alcohols.

**Metal complexes.**

Diol (II), as mentioned in the previous section, is a much weaker acid than expected. It is therefore, probably a poorer chelating ligand than its perfluoropinacol analogue since the formation of chelate complexes requires a donor atom (Lewis base) to coordinate to the metal. Perfluoropinacol can be readily changed to an anion (good Lewis base) enabling metal complexes to be easily prepared. The reaction of diol (II) with copper and nickel nitrates in a basic ethanol/water mixture produced no bis-diol metal complexes as does perfluoropinacol. The only products obtained were the copper and nickel hydroxides which must be formed before the correct pH can be attained.

Subsequent work has shown that nickel and copper complexes of diol (II) may be prepared by employing a second ligand (triethylphosphine, tetramethylethylenediamine) to stabilize the entire complex. These compounds are diamagnetic and have one band in the
visible spectrum characteristic of square planar complexes of nickel.

These compounds and corresponding copper compounds are currently being studied and compared with analogous perfluoropinacol complexes.
Part two: Hexafluoro-2-hydroxyisobutyric acid

A. Infrared Spectra

**Hexafluoro-2-hydroxyisobutyric acid**

The molecule hexafluoro-2-hydroxyisobutyric acid has very low symmetry, possessing \( \text{CF}_3 \), \( \text{COOH} \), and \( \text{COH} \) as functional groups. An examination of the infrared spectrum of this compound shows prominent bands at 3390, 1768, 1300-1150, and 995 cm\(^{-1}\). The 3390 and 1768 bands are the most easily identified; being assigned to the O-H stretching of the hydrogen bonded hydroxyl and carboxylate groups, and the C=O stretching respectively.

A number of prominent bands are observed in the C-F stretching region and may be assigned to C-F stretching of the \((\text{CF}_3)_2\text{C}\) group. Other bands may appear in this region. The carboxylate C-O stretching band is known to be found at 1315-1280 cm\(^{-1}\) for nonfluorinated organic acids. Tertiary substituted carbon atoms may show a C-C skeletal vibration near 1200 cm\(^{-1}\). Four bands appear in the CF\(_3\) stretching region at 1160, 1220, 1230, and 1280 cm\(^{-1}\). Due to the low symmetry of HHIB, six infrared active CF\(_3\) stretching bands are expected. Hexafluoroacetone has five infrared active C-F stretching bands at 1344, 1275, 1252, 1220, and 1200 cm\(^{-1}\) plus a Raman active band at 1162 cm\(^{-1}\).

Perfluoropinacol has twelve possible C-F stretching modes, nine of which are infrared active if \( C_{2v} \) symmetry is assumed for the ligand. All possible bands are not observed for perfluoropinacol. The band
observed at 1160 cm\(^{-1}\) is much weaker than its analogue in HHIB, and suggests it is infrared inactive in PFP as it is for hexafluoroacetone. The symmetry of HHIB causes this CF\(_3\) band to be more intense since all stretching vibrations are infrared active. The carboxylate C-O stretch should occur around 1200 cm\(^{-1}\) for this compound making it impossible to distinguish from the C-F stretching modes.

The strong band found at 995 cm\(^{-1}\) might be attributed to the C-O stretch of this hydroxyl group. This band, however, is found at a lower frequency than expected for the C-O stretch of a tertiary alcohol. The hydrocarbon analogues have C-O stretches found in the 1210-1100 cm\(^{-1}\) region\(^4^4\). The inductive effect of the CF\(_3\) group is not expected to lower the frequency. The band at 995 cm\(^{-1}\) is probably a mode involving C-C or C-C-O vibrations. Strong bands have been observed at 972 and 991 for CF\(_3\)COCF\(_3\) and (CF\(_3\))\(_2\)C=O\(^5^6\)\(^5^7\) and assigned to C-C stretching vibrations.

Bands of major intensity are found at 830, 780, 735, 670, and 640 cm\(^{-1}\). The bands at 830 and 780 cm\(^{-1}\) probably involve C-C stretching frequencies while the bands at 735 and 640 cm\(^{-1}\) may be assigned to CF\(_3\) deformation modes\(^5^6\)\(^5^7\). Hexafluoroacetone has these deformation bands at 720 and 635 cm\(^{-1}\). Other C-F deformation modes have been assigned to bands in the far infrared at 560, 545, and 525 cm\(^{-1}\). The band observed at 670 cm\(^{-1}\) is in the same region as that found for an in-plane deformation mode of a carboxylate group in metal glycollate complexes.

The ligand hexafluoro-2-hydroxyisobutyric acid, upon chelating to metals, is expected to show changes (if any) in the O-H, carboxylate,
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$ C-O$_2$</th>
<th>OH</th>
<th>$\nu$C-O</th>
<th>$\nu$C-F</th>
<th>$\nu$C-C</th>
<th>$\delta$C-O$_2$</th>
<th>$\delta$CF$_3$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHIB acid</td>
<td>1760</td>
<td>3390</td>
<td>995</td>
<td>1280, 1230</td>
<td>825</td>
<td>665</td>
<td>525, 545, 560, 640, 735</td>
</tr>
<tr>
<td>Cs(HHIB)</td>
<td>1660, 1375</td>
<td>3310</td>
<td>1005, 975</td>
<td>1280, 1230, 1200, 1150</td>
<td>800</td>
<td>675</td>
<td>555, 540, 515</td>
</tr>
<tr>
<td>K$_2$Ni(HHIB)$_2$</td>
<td>1650, 1400</td>
<td>3660</td>
<td>1015, 972</td>
<td>1276, 1210, 1160</td>
<td>1140</td>
<td>825</td>
<td>660, 790</td>
</tr>
<tr>
<td>K$_2$Cu(HHIB)$_2$</td>
<td>1665</td>
<td>1380</td>
<td>1020, 970</td>
<td>1276, 1210, 1160</td>
<td>1140</td>
<td>825</td>
<td>660, 790</td>
</tr>
<tr>
<td>Cs$_3$Fe(HHIB)$_3$</td>
<td>1655</td>
<td>1365</td>
<td>1020, 975</td>
<td>1275, 1215, 1160</td>
<td>755</td>
<td>670</td>
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<tr>
<td>Cs$_3$Mn(HHIB)$_3$</td>
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<td>1340</td>
<td>1032, 1015</td>
<td>1270, 1205, 1160</td>
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<td>665</td>
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<tr>
<td>Cs$_2$Co(HHIB)$_2$</td>
<td>1630</td>
<td>1375</td>
<td>1020, 980</td>
<td>1270, 1205, 1165</td>
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<td>820</td>
<td>670</td>
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<td>Cs$_3$Cr(HHIB)$_3$</td>
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<td>1270, 1205, 1165</td>
<td>755</td>
<td>665</td>
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<tr>
<td>K$_3$Al(HHIB)$_3$</td>
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<td>1030, 975</td>
<td>1280, 1215, 1180</td>
<td>760</td>
<td>675</td>
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<tr>
<td>CsB(HHIB)$_2$</td>
<td>1770</td>
<td>980</td>
<td>1065, 1110</td>
<td>1280, 1230, 1210, 1155</td>
<td>780</td>
<td>670</td>
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</tbody>
</table>
and the C-O modes of the hydroxyl group.

- Metal Complexes

Metal complexes of HHIB may have a number of possible structures. Bis-HHIB metal complexes may have two configurations surrounding the metal atom, tetrahedral and square planar. A tetrahedral configuration has two optical enantiomers for HHIB complexes.

If a square planar configuration exists about the central metal then cis and trans geometric isomers are possible for the compound. Even if an octahedral configuration is attained by trans coordination of water or some other donor molecule only two isomers are possible for these bis-HHIB complexes. The cis isomers belong to the point group $C_{2v}$ while the trans isomer belongs to the point group $C_{2h}$.

The tris HHIB metal complexes are more complicated since three geometric isomers are possible each having an optically active isomer.
Structure (C) has the highest symmetry of the isomers belonging to the $D_3$ point group.

It was hoped a study of the infrared spectra of bis and tris HHIB complexes could determine the configuration of the product obtained and hence the mechanism by which HHIB chelates by metals.

**Hydroxyl C-O and C-C stretching bands**

As mentioned previously there is some confusion as to where the C-O stretching frequency occurs in HHIB acid. Upon formation of the mono cesium salt of HHIB, the 1160 cm.$^{-1}$ band previously assigned as a C-F stretching vibration has increased in intensity and has a shoulder at 1140 cm.$^{-1}$. The 995 cm.$^{-1}$ band, present in the acid, now exhibits a shoulder at 1005 cm.$^{-1}$. The 780 cm.$^{-1}$ band present in the acid has shifted to 800 cm.$^{-1}$.

The bis HHIB complex of copper has an infrared spectrum showing a shoulder at 1140 cm.$^{-1}$ on the 1160 cm.$^{-1}$ band. The 995 cm.$^{-1}$ band is split into two bands of equal intensity at 1020 and 970 cm.$^{-1}$. The 780 cm.$^{-1}$ of HHIB has disappeared and a new band has appeared at 830 cm.$^{-1}$.

It seems the bands assigned to C-C stretching frequencies shift upon coordination with metals. These bands are probably coupled with C-O stretching modes and as a result have their frequencies
shifted.

The splitting of the 975 cm.\(^{-1}\) band may be the result of both cis and trans isomers being present for the bis chelate compounds, or it may be the result of a coupling of the C-O bands across the metal atom. For the trans isomer \((C_{2h} \text{ symmetry})\) the two C-O modes are of different symmetry \(A_g\) and \(B_u\), only one of these bands being infrared active. The cis isomer, having \(C_{2v}\) symmetry, would have two C-O modes of symmetry \(A_1\) and \(B_2\) both infrared active. The evidence therefore suggests the cis isomer has been formed or possibly a mixture of both cis and trans isomers.

For the mono cesium salt of HHIB, the 975 cm.\(^{-1}\) band is split unevenly and probably indicates the presence of both hydrogen bonded and free hydroxyl groups.

For the tris HHIB complexes, two bands are observed in the 1000 cm.\(^{-1}\) region. Since three geometric isomers are possible, each with an optical isomer, the splitting does not appear to be caused by isomerism. If the molecule is assumed to have \(D_3\) symmetry two infrared active bands of \(A\) and \(E\) symmetry are expected. The other isomers with lower symmetry would each produce three C-O stretching vibrations. Thus the splitting of the 975 cm.\(^{-1}\) band may be caused by the existence of a preferred isomer having \(D_3\) symmetry.

**CF\(_3\) region**

Bis-HHIB complexes of nickel and copper have a higher order of symmetry than does the acid itself. Both the \(C_{2h}\) and \(C_{2v}\) symmetry groups have nine of the twelve possible C-F vibrational modes infrared active. Some of these bands must be superimposed upon one another since fewer than nine bands are observed in the infrared spectra. In fact, the
CF$_3$ stretching region changes very little upon the formation of both bis and tris HHIB complexes. As a result little useful information can be obtained from this region of the infrared spectrum which can help distinguish the structures of the complexes.

**Metal-oxygen region**

With the exception of the boron complex, the majority of the complexes of HHIB are square planar or octahedral. The tris HHIB complexes are presumably octahedral while the bis HHIB complexes can be square planar or octahedral. Water molecules, or the non-bonding carboxylate oxygens may complete the octahedral coordination by interacting with a metal atom of an adjacent molecule.

By observing the number of M-O bands and correlating with the number expected for various point groups some evidence may be obtained concerning the isomer present.

If the coordination is octahedral, the local symmetry around the metal is approximately $O_h$. Depending upon the distortion the local symmetry may be lowered to $D_{4h}$, $D_{2h}$, $C_{2h}$, or $C_{2v}$ symmetry. Similar symmetry is possible for the square planar complexes. If the local symmetry surrounding the metal is $O_h$ then the M-O stretching modes have $A_{1g}$, $E_g$, and $F_{1u}$ symmetry. Only the $F_{1u}$ mode is infrared active and only one band is expected in the infrared spectrum.

If the bis HHIB complexes are distorted octahedral, such that the local symmetry about the metal atom is $D_{4h}$, then two $A_{2u}$ and three $E_u$ M-O modes are infrared active. The vibrational modes are attributed to $A_{2u}$, $B_{2g}$, $E_u$ and two $A_{1g}$ symmetry types. Only the $A_{2u}$ and $E_u$ bands
are infrared active. Thus, two bands would be observed. If the structure is square planar with $D_{4h}$ symmetry only one band of $E_u$ symmetry would be observed.

If chelation affects the metal oxygen vibrations then the symmetry for the bis HHIB complexes is further reduced to the $D_{2h}$ point group.

For octahedral coordination eight modes are infrared active (two $B_{1u}$, three $B_{2u}$, and three $B_{3u}$). The M-O vibrations should produce three infrared active bands ($B_{1u}$, $B_{2u}$, and $B_{3u}$). The square planar configuration would have two bands ($B_{2u}$ and $B_{3u}$).

The M-O stretching vibrations may be sensitive to the different types of oxygen that coordinate to the metal in bis HHIB complexes, then the local symmetry around the metal becomes equivalent to the molecular symmetry of the geometric isomer present. The cis chelate structures have $C_{2v}$ symmetry while the trans structures have $C_{2h}$ symmetry.

Octahedral structures of $C_{2h}$ symmetry would have three infrared
M-O stretches (A_u and two B_{2u}) while the square planar configuration
would have two modes of B_{2u} symmetry. Octahedral structures of C_{2v}
symmetry would have all six M-O stretching frequencies infrared active
(three A_1, two B_1, and one B_2 modes) while the square planar struc-
ture would have four infrared active modes (two A_1 and two B_2).

The tris HHIB metal complexes have three geometric isomers.
The isomer of highest symmetry (D_3) would have four M-O stretching
vibrations infrared active (A_1, A_2 and two E modes). The other two
isomers have C_1 symmetry and should exhibit six M-O vibrations.

The number of bands actually observed in the far infrared of
bis and tris HHIB complexes are fewer than expected for structures
with the point groups C_{2v}, C_1 or D_3 symmetry. The bis HHIB complexes
may therefore exist as trans isomers. It is also possible, however,
that the symmetry controlling the M-O stretching modes is much higher
than the point groups of any specific isomers.

Studies involving normal vibrational analysis for acetylacet-
tonate and oxylate and hydroxyisobutyrate complexes of Fe(III), V(III)
Cr(III), Co(III), Al(III), Cu(II), Zn(II), Pd(II), and Pt(II) have
assigned M-O stretching vibrations in their spectra
59 60 61. Bands
between 350 and 600 cm^{-1} previously assigned to M-O modes are now
thought to show not only M-O frequencies but combination bands of M-O
and other group frequencies. Some differences are observed among
1:1, 2:1, and 3:1 oxalate-metal complexes. The far infrared region
shows bands shifted to higher frequencies for the 2:1 and 3:1 complexes
with band splitting more extensive in the latter complexes.

The tris HHIB metal complexes in general have a more complicated
far infrared spectrum than the bis-HHIB complexes.

Table 5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequency</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cs}_2\text{Co(HHIB)}_2 \cdot 2\text{H}_2\text{O}$</td>
<td>530 (m-w) cm.$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$\text{K}_2\text{Ni(HHIB)}_2$</td>
<td>530 (m)</td>
<td>465 (m)</td>
</tr>
<tr>
<td>$\text{K}_2\text{Cu(HHIB)}_2$</td>
<td>525 (m)</td>
<td>445 (m-w)</td>
</tr>
<tr>
<td>$\text{Cs}_3\text{Fe(HHIB)}_3 \cdot \text{H}_2\text{O}$</td>
<td>565 (w)</td>
<td>540 (m)</td>
</tr>
<tr>
<td>$\text{Cs}_3\text{Cr(HHIB)}_3 \cdot \text{H}_2\text{O}$</td>
<td>570 (m-w)</td>
<td>535 (m-w)</td>
</tr>
<tr>
<td>$\text{Cs}_3\text{Mn(HHIB)}_3$</td>
<td>585 (m-w)</td>
<td>543 (m-w)</td>
</tr>
<tr>
<td>$\text{K}_3\text{Al(HHIB)}_3$</td>
<td>595 (m)</td>
<td>535 (w)</td>
</tr>
</tbody>
</table>

The chelated ring system for HHIB complexes is similar to that of oxalate complexes. A band occurring near 380 cm.$^{-1}$ may be assigned to O-C=O out of plane deformation. The bands observed from 520-600 cm.$^{-1}$ are more intense than those attributed to CF$_3$ deformations. They are probably M-O vibrations but could be the ring skeletal modes found in the metal glycolates at 540 cm.$^{-1}$.

The nickel complex does not show any water coordinated to the nickel atom as bands would be expected at 645 and 405 cm.$^{-1}$. The bands in the copper complex at 525 and 445 cm.$^{-1}$ may be attributed to coordinated H$_2$O but more probably are M-O vibrations.

The far infrared spectrum thus reveals that the bis and tris HHIB complexes have higher symmetry about the central metal atom than for the C$_{2v}$, D$_3$ or C$_1$ point groups. The bis-HHIB complexes may have C$_{2h}$ symmetry and thus the reaction mechanism may preferentially form trans complexes. The metal-oxygen vibrations may
not be influenced by the different types of oxygen and hence this region of the infrared may reflect even a higher symmetry for the molecule than actually exists.

**Carboxylate region**

The carboxylate group of hexafluoro-2-hydroxyisobutyric acid is subject to a high degree of hydrogen bonding but has a carboxylate stretching band at 1768 cm\(^{-1}\). The corresponding band in the mono cesium salt of the acid is broadened and appears at 1660 cm\(^{-1}\). The band is lowered in energy because the ionic salt has a symmetrical carboxylate group with each carbon-oxygen band having a formal bond order of 1.5. Additional hydrogen bonding between hydroxyl groups and the carboxylate groups may broaden the observed band and also contribute to the reduced stretching frequency. The strong inductive effect of the CF\(_3\) group still influences the carboxylate frequency. Metal glycolate complexes have C=O stretching bands at 1595 cm\(^{-1}\).\(^{63}\) Trifluoroacetates of copper, cobalt, and nickel,\(^{64}\) which are reported to be ionic, have asymmetric stretching frequencies centred at 1762, 1698, and 1697 cm\(^{-1}\) respectively. If the carboxylate bond formed upon chelation with the metals is covalent the carboxylate stretching frequencies should alter only slightly with respect to the parent acid's absorption frequency. The asymmetric carboxylate frequency is therefore at higher wave numbers than the anionic form.
The transition metal complexes of hexafluoro-2-hydroxy-isobutyric acid have stretching frequencies about 100 cm.\(^{-1}\) lower than the pure acid, suggesting an ionic carboxylate bond is involved between the metal and the carboxylate oxygen. The lower stretching frequency may be caused, however, by the interaction of the non-bonded carboxylate oxygen to a central metal atom of an adjacent molecule, to a hydrogen atom of a hydrated water molecule, or to the metal cation that exists as a counterion for the bis and tris HHIB complexes. Back bonding of the filled orbitals of \(t_{2g}\) symmetry with \(p^\pi\) antibonding orbitals of the carboxylate oxygen could also explain the low absorption frequency of the carboxylate group.

The carboxylate group of the tris-HHIB complexes is unable to bond to the metal ion on an adjacent molecule since the coordination sites on the metals are all occupied. These compounds have broad asymmetric carboxylate stretching frequencies at low wave numbers not unlike the bis-HHIB complexes. Interaction of the carboxylate with water or a counterion, formation of an ionic complex and/or formation of a back bond must be involved to cause the low stretching frequency of the carboxylate group. The compound \(K_3\text{Al(HHIB)}_3\) has no low energy d orbitals that can participate in the formation of a back bond. The asymmetric stretching band is split and appears at 1710-1680 cm.\(^{-1}\)
which is lower than pure HHIB but raised relative to the mono-
cesium salt. Thus the lowering is not solely caused by back bonding.
The high resonance frequency of the aluminum complex relative to the
cesium salt suggests that the complex has some covalent character.
The difference in energy between the asymmetric carboxylate stretching
absorption of the aluminum complex and the transition metal complexes
may be contributed to by back bonding, but is more probably caused by
the difference in the electronegativity of the metals. The cesium
bis-HHIB boron complex, like the aluminum complex, has all available
coordination sites occupied and no d orbitals available for back bond-
ing. The asymmetric carboxylate stretch absorbs at 1770 cm.$^{-1}$ The bis
trimethylsilyl-HHIB complex has a sharp carboxylate stretching band
at 1750 cm.$^{-1}$ Thus, as the electronegativity of the metal increases
a stronger covalent bond is formed between the metal and the carboxyl-
ate group which increases the carboxylate stretching frequency.

The bis chelate complexes of Cu, Ni, and Co may have the
non-bonding carboxylate oxygen interact with a metal atom of another
molecule and reduce the asymmetric carboxylate stretching frequency.
If interaction of this type does contribute to a lowering of the
asymmetric carboxylate stretch, then the symmetric stretching absorp-
tion would be expected to be raised in energy. Acids and their

\[
\begin{align*}
\text{OO} & \quad M \\
\text{C} & \quad M \\
\text{O} & \quad M
\end{align*}
\]
esters have their symmetric carboxylate stretching frequency at 1250-1150 cm.\(^{-1}\) which unfortunately is the same region as the strong CF\(_3\) absorptions.

Trifluoroacetates having ionic carboxylate groups have symmetric stretching frequencies increased in energy to 1450 cm.\(^{-1}\)\(^ {64} \). The monocesium salt of HHIB has a band at 1375 cm.\(^{-1}\) which can be assigned to the O-H deformation mode and/or the symmetric carboxylate stretch. The band appears too intense to be only the O-H deformation mode. Similar bands are observed in transition metal complexes of HHIB at frequencies between 1350 and 1420 cm.\(^{-1}\) suggesting an ionic carboxylate group.

If a copper acetate type structure existed for transition metal HHIB complexes then the stronger the M-O bond, the higher would be the absorption energy for both symmetric and asymmetric carboxylate stretching frequencies.\(^ {65} \) No such trend is observed for M(II) complexes of HHIB. Therefore it seems justified to suggest that transition metal complexes of HHIB are of the type shown in figure B and are largely ionic. Interaction of the carboxylate oxygen with other atoms would

(A) \[ \begin{array}{c}
\text{O} \\
\text{M}
\end{array} \]

(B) \[ \begin{array}{c}
\text{C} \\
\text{O} \\
\text{M}
\end{array} \]

be of secondary importance but can not be overlooked completely.

A weak interaction of this type would further lower the asymmetric carboxylate stretching frequency while raising the symmetric carboxylate stretching frequency, similar to the effect shown in complexes of
carboxylic acid esters of tin.\textsuperscript{66}

The differences between the absorption energies of the asymmetric and symmetric stretching modes of the carboxylate group might be a measure of the interaction between metals and the carboxylate oxygen not involved in chelation.

The $\nu_{CO \text{ asym}} - \nu_{CO \text{ sym}}$ ($\Delta \nu$) are listed below according to the positive charge on the central atom.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$\Delta \nu_{cm^{-1}}$</th>
<th>$\Delta \nu_{cm^{-1}}$</th>
<th>$\Delta \nu_{cm^{-1}}$</th>
<th>$\Delta \nu_{cm^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>CsHHIB</td>
<td>250</td>
<td>Cs$_2$Co(HHIB)$_2$·2H$_2$O</td>
<td>255</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cs$_3$Cr(HHIB)$_3$·H$_2$O</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td>Cs$_2$Ni(HHIB)$_2$</td>
<td>250</td>
<td>Cs$_3$Fe(HHIB)$_3$·H$_2$O</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td>K$_2$Ni(HHIB)$_2$</td>
<td>250</td>
<td>K$_3$Fe(HHIB)$_3$</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td>K$_2$Cu(HHIB)$_2$</td>
<td>285</td>
<td>Cs$_3$Mn(HHIB)$_3$</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>Cs$_2$Cu(HHIB)$_2$</td>
<td>290</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cs$_2$Ni(HHIB)(PFP)</td>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>K$_2$Ni(HHIB)(PFP)</td>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>($PET_3$)Ni(HHIB)</td>
<td>355</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(BDPPE)Ni(HHIB)</td>
<td>315</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The energy difference of the CsHHIB complex is only slightly smaller than the value for the metal(III) complexes. The metal(II) complexes, with the exception of Cu(II), have even smaller $\Delta \nu$ values and indicates the possibility of interaction of the non-chelating carboxylate oxygen with adjacent central metal atoms.

The HHIB nickel complexes of bis triethylphosphine and bis (diphenylphosphino)ethane have larger $\Delta \nu$ values than bis HHIB nickel(II). The complexes are diamagnetic and therefore are assumed to have a square
planar configuration. Therefore, the nickel atom cannot interact with water of a free carboxylate oxygen. It might therefore be reasoned that the $\Delta v_{CO}$ values would be larger than for the corresponding bis HHIB nickel complexes. The values are larger than the value for the ionic mono-cesium salt of HHIB and suggests the presence of a phosphino group in the complex makes the metal oxygen bond more covalent. Conversely, the bis HHIB complexes have a carboxylate oxygen that is at least partially ionic and probably has the nonbonding carboxylate oxygen interacting with either water or a metal atom.

Infrared spectra of Mixed Ligand Complexes of transition metals

**Phospheine Complexes**

The nickel HHIB complexes of bis(triethylphosphine) and bis(diphenylphosphino)ethane have bands of 1415 and 1410 cm.$^{-1}$ respectively, characteristic of P-CH$_2$ linkage. The 1440 cm.$^{-1}$ band in the latter complex is characteristic of phenylphosphine complexes. The 1350-1150 cm.$^{-1}$ region is complicated for the phenylphosphine complex because both CF$_3$ vibrations and in-plane hydrogen rocking of the phenyl hydrogen atoms absorb here. The 700-800 cm.$^{-1}$ region has a number of bands due to the C-H wag of the phenyl and CH$_2$ hydrogen atoms. The far infrared has a strong band at 525 cm.$^{-1}$ assigned to out of plane deformation of the aromatic ring. The other bands observed in this region are CF$_3$, CO$_2$, or HHIB deformations. The Ni-O stretching vibrations also occur in this region. The triethylphosphine complex has five bands in this region. The carboxylate bands have been discussed previously.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$-\text{CO}_2(\nu)$</th>
<th>CH$_2$</th>
<th>CH$_3$</th>
<th>$\phi$</th>
<th>C-O $\nu$</th>
<th>CF$_3(\nu)$</th>
<th>C-C($\nu$)</th>
<th>$\text{CO}_2\delta$</th>
<th>Below 600 cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BDPPE)Ni(HHIB)</td>
<td>1680(s)</td>
<td>1415(w)</td>
<td></td>
<td>3060(w) 975(s)</td>
<td>1312(w) 810(w)</td>
<td>1285(m) 785(m) 670(m)</td>
<td>525(s)</td>
<td>505(m)</td>
<td>480(m) 430(w)</td>
</tr>
<tr>
<td></td>
<td>1365(m)</td>
<td></td>
<td></td>
<td>1585(w) 1480(w) 1435(m)</td>
<td>1240(s) 755(mw) 1215(s) 735(m) 1185(s) 720(mw) 1155(s) 705(m)</td>
<td>690(m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PEt$_3$)$_2$Ni(HHIB)</td>
<td>1685(s)</td>
<td>2880(w) 2976(mw)</td>
<td></td>
<td>1025(s) 1260(s) 820(s) 660(m)</td>
<td>1025(s) 1260(s) 820(s) 660(m)</td>
<td>575(m)</td>
<td>520(m)</td>
<td>470(m) 425(m) 385(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1330(m)</td>
<td>1410(m) 2930(mw)</td>
<td></td>
<td>970(s) 1185(s) 740(s) 1155(s)</td>
<td>970(s) 1205(s) 760(s) 1185(s) 740(s) 1155(s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1360(w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Ethylenediamine Complexes

(a) $\text{H}_2\text{En Cu(HHIB)}_2$

This complex has five bands in the $2700 \text{ cm}^{-1}$ to $2000 \text{ cm}^{-1}$ region which suggests an amine salt is present. The simplest possible structure for an amine salt is illustrated below.

\[
\begin{align*}
\text{CH}_2\text{NH}_3^+ & \quad \text{[CH}_2\text{NH}_3^-]_2^2- \\
\end{align*}
\]

This complex is similar to $\text{K}_2\text{Cu(HHIB)}_2$ and any differences in their infrared spectra must be attributed to the ethylenediamine cation. Bands found at $1020 \text{ cm}^{-1}$ and $970 \text{ cm}^{-1}$ are identical with those in $\text{K}_2\text{Cu(HHIB)}_2$. Bands found at $1070$ and $695 \text{ cm}^{-1}$ are not observed in $\text{K}_2\text{Cu(HHIB)}_2$ but can be assigned to C-C-N stretch and N-H wag respectively. The asymmetric carboxylate stretch is shifted to $1680 \text{ cm}^{-1}$, compared with $1665 \text{ cm}^{-1}$ for $\text{K}_2\text{Cu(HHIB)}_2$. The steric effect of the ethylenediamine salt may prevent the free carboxylate oxygen from interacting with other copper atoms and thus increasing the stretching frequency.

A number of other models are possible but involve metal nitrogen interaction. The far infrared region has a band at $490 \text{ cm}^{-1}$ not observed in $\text{K}_2\text{Cu(HHIB)}_2$. This band could indicate metal-nitrogen bonding is involved. It could also be assigned as an $\text{NH}_2$ rocking mode (which appears as a broader, weaker band in a liquid film of
ethylene diamine) or as an \( \text{NH}_3^+ \) torsional oscillation. The latter assignment is in agreement with the model illustrated. The far infrared spectrum has changed slightly from the \( \text{K}_2\text{Cu(HHIB)}_2 \) complex, the major change being a shift in the 365 cm.\(^{-1}\) band to 380 cm.\(^{-1}\) for the ethylene diamine copper complex.

Amine salt complexes that involve metal-nitrogen bonds cannot be ruled out because minor changes are observed between \( \text{H}_2\text{EnCu(HHIB)}_2 \) and \( \text{K}_2\text{Cu(HHIB)}_2 \) in the carboxylate and far infrared regions. A model of this type would be in closer agreement with the conductance measurements (1:1 electrolyte) than the model illustrated.

(b) \( \text{H}_2\text{En}_2\text{Cu(HHIB)}_2 \)

The asymmetric carboxylate stretch in this compound absorbs at 1660 cm.\(^{-1}\), lower in energy than for \( \text{H}_2\text{EnCu(HHIB)}_2 \). Bands at 1020 and 970 cm.\(^{-1}\) are identical with bands observed in \( \text{K}_2\text{Cu(HHIB)}_2 \) and \( \text{H}_2\text{EnCu(HHIB)}_2 \). The band found at 705 cm.\(^{-1}\) attributed to N-H wag is more intense and at a higher wave number than for \( \text{H}_2\text{EnCu(HHIB)}_2 \).

The far infrared region for \( \text{H}_2\text{En}_2\text{Cu(HHIB)}_2 \) has bands at 590, 505, and 380 cm.\(^{-1}\) corresponding to bands found in \( \text{H}_2\text{En}_2\text{Cu(HHIB)}_2 \). A strong band is also found at 535 cm.\(^{-1}\) which is more intense than the band at this wave number for \( \text{K}_2\text{Cu(HHIB)}_2 \) or \( \text{H}_2\text{EnCu(HHIB)}_2 \) complexes. It suggests a different type of coordination exists and possibly a copper-nitrogen linkage is involved.

The absence of bands between 2800-2000 cm.\(^{-1}\) as well as the 1525 cm.\(^{-1}\) band indicates the complex is not an amine salt. Since this complex is prepared by the addition of ethylene diamine to the amine salt \( \text{H}_2\text{EnCu(HHIB)}_2 \) and the product \( \text{H}_2\text{En}_2\text{Cu(HHIB)}_2 \) is not an
amine salt, then copper must either become eight coordinate or one end of the HHIB group must be displaced. The N-H and O-H stretching region has three bands which can be assigned as symmetric, and asymmetric N-H stretching, and an overtone of the $1615 \text{ cm}^{-1}$ NH deformation band. Any O-H vibration is concealed by these bands. No bands can be assigned definitely to the O-H deformation although bands occur at 1410 and 1380 cm.$^{-1}$ It is felt, however, that the complex formed is illustrated below.

![Chemical Structure](image)

(c) $\text{H}_2\text{TMEDCu(HHIB)}_2$

The infrared spectrum of this compound is somewhat similar to the $\text{K}_2\text{Cu(HHIB)}_2$ complex in the far infrared region. The band at 530 cm.$^{-1}$ has been reduced in intensity, however. The asymmetric carboxylate stretching frequency is sharper and at higher energy (1695 cm.$^{-1}$) than for $\text{K}_2\text{Cu(HHIB)}_2$. The 2600-2400 cm.$^{-1}$ region shows a number of bands characteristic of a tertiary amine salt. The 3600-3100 cm.$^{-1}$ region is free of bands indicating that no O-H group is present in the molecule. This suggests both HHIB ligands are chelated to copper. The presence of the large tetramethylethylenediamine
group in the molecule may prevent the free carboxylate oxygen from interacting with a copper atom of a neighboring molecule. As a result, the carboxylate stretching frequency is found to be sharper and at higher wave numbers than it is for the K$_2$Cu(HHIB)$_2$ complex.

(d) H$_2$En$_2$Ni(HHIB)$_2$

This compound has an infrared spectrum similar to that of H$_2$En$_2$Cu(HHIB)$_2$. The bands observed at 1020 cm.$^{-1}$ and 920 cm.$^{-1}$ in the copper compound have disappeared in the nickel complex which has a band at 970 cm.$^{-1}$ with a shoulder at 1000 cm.$^{-1}$ The CF$_3$ stretching region is not as sharp as for the copper complex and only three bands can be distinguished.

The far infrared region shows major bands at 510, 430, and 380 cm.$^{-1}$ This region differs from the spectrum of K$_2$Ni(HHIB)$_2$ and suggests the coordination about the nickel atom has changed. The similarity with the spectrum of H$_2$En$_2$Cu(HHIB)$_2$ suggests both compounds have a similar structure. No infrared evidence exists for the presence of a hydroxyl group in H$_2$En$_2$Ni(HHIB)$_2$. The O-H bands may be hidden by the N-H absorption bands.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$ OH</th>
<th>$\nu$ CH$_2$</th>
<th>$\nu$ C=O</th>
<th>$\delta$ NH</th>
<th>$\delta$ CH$_2$</th>
<th>$\nu$ CF$_3$</th>
<th>$\nu$ C-C-N</th>
<th>$\nu$ C-O</th>
<th>NH wag</th>
<th>far I.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$EnCu(HHIB)$_2$</td>
<td>3150 (ms)</td>
<td>2980 (ms)</td>
<td>1680 (s)</td>
<td>1615</td>
<td>1330 (w)</td>
<td>1280 (s)</td>
<td>1265 (s)</td>
<td>1150 (s)</td>
<td>1080 (w)</td>
<td>1020 (s)</td>
</tr>
<tr>
<td>$H_2$En$_2$Cu(HHIB)$_2$</td>
<td>3350 (s)</td>
<td>2980 (w)</td>
<td>1660 (s)</td>
<td>1605</td>
<td>1380 (m)</td>
<td>1275 (s)</td>
<td>1255 (s)</td>
<td>1195 (s)</td>
<td>1145 (s)</td>
<td>1080 (w)</td>
</tr>
<tr>
<td>$H_2$TMEDCu(HHIB)$_2$</td>
<td>3030 (w)</td>
<td>3030 (w)</td>
<td>1695 (s)</td>
<td>1485 (w)</td>
<td>1355 (w)</td>
<td>1275 (s)</td>
<td>1265 (s)</td>
<td>1205 (s)</td>
<td>1185 (s)</td>
<td>1075 (w)</td>
</tr>
<tr>
<td>$H_2$En$_2$Ni(HHIB)$_2$</td>
<td>3360 (s)</td>
<td>2980 (w)</td>
<td>1660 (s)</td>
<td>1610 (m)</td>
<td>1380 (w)</td>
<td>1270 (s)</td>
<td>1200 (s)</td>
<td>1150 (s)</td>
<td>1065 (w)</td>
<td>1000 (s)</td>
</tr>
<tr>
<td>$H_2$TMEDNi(HHIB)$_2$</td>
<td>3415 (w)</td>
<td>1690 (s)</td>
<td>1660 (sh)</td>
<td></td>
<td></td>
<td>1260 (s)</td>
<td>1220 (s)</td>
<td>1155 (s)</td>
<td>1040 (w)</td>
<td>985 (s)</td>
</tr>
</tbody>
</table>
The infrared spectrum of this compound has bands at 1645, 1020 and 980 cm\(^{-1}\) characteristic of the HHIB ligand and bands at 940, 870, 740 and 720 cm\(^{-1}\) characteristic of perfluoropinacol. The far infrared spectrum has main bands at 535 and 435 cm\(^{-1}\).

The asymmetric carboxylate stretching band is split into two sharp bands at 1645 cm\(^{-1}\) and 1610 cm\(^{-1}\). Since only one geometric isomer is possible, the two carboxylate bands are probably caused by a crystal lattice effect with two carboxylate groups existing in different environments. Some of the free carboxylate oxygens may coordinate to a nickel atom in an adjacent molecule and as a result produce two asymmetric carboxylate stretching bands. This argument is in accord with the tetragonal structure suggested by the compound's magnetic moment (3.23 B.M.). The 1645 cm\(^{-1}\) and 1610 cm\(^{-1}\) bands are both at lower frequencies than for K\(_2\)Ni(HHIB)\(_2\) and suggests that both bands can be attributed to carboxylate groups coordinating through both oxygen atoms but in different chemical environments.

Non Metal Complexes

CsB(HHIB)\(_2\)

The infrared spectrum of this compound shows an asymmetric stretch at 1770 cm\(^{-1}\) for the carboxylate group indicating a covalent B-O bond. The relatively high frequency suggests no interaction between free carboxylate oxygen and other boron atoms. The strong B-O stretching frequency observed in trialkylborates at 1380-1320 cm\(^{-1}\) is not observed and suggests the boron atom is probably four
coordinate. This coordination would lower the B-O stretching
cfrequency, possibly to 1110 and 1060 cm$^{-1}$ where two strong bands are
observed.

Both optical isomers of this molecule have distorted tetrahedral
symmetry and will have identical infrared spectra. If the local
symmetry about boron is $T_d$ then only one B-O stretching frequency would
be observed. If chelation lowers the symmetry about boron to $C_{2v}$ or
lower symmetry then four B-O bands might be expected ($2A_1$, $B_1$ and $B_2$).
Only the $B_1$ and $B_2$ bands might be observed, however, since $A_1$ bands are
infrared inactive for $T_d$ symmetry and would absorb only weakly for
lower symmetry. The B-O stretching vibrations may be coupled to the
C-O vibrations of the carboxylate. The C-O carboxylate and alkoxy
stretching modes each have one doubly degenerate mode for the
CsB(HHIB)$_2$ complex. These C-O vibrations may be coupled to the B-O
stretching vibrations and be represented by the bands at 1110, 1075,
1060 and 998 cm$^{-1}$

Although twelve C-F stretching modes are possible for the
boron complex only three prominent bands are observed. The two ligands
must produce a number of degenerate C-F bands.

$K_3Al(HHIB)_3$

The spectrum of this compound is quite similar to the tris
HHIB transition metal complexes. The major differences are observed
in the asymmetric carboxylate stretch and the far infrared region.
The carboxylate stretching frequency of 1685 cm$^{-1}$ indicates the Al-O
bond is more ionic than the B-O bond of the preceding complex but more
covalent than the transition metal complexes. The far infrared has a
number of sharp bands which involve CO$_2$ deformation, CF$_3$ deformation,
ring skeletal vibrations, and Al-O stretching vibrations. The 490 cm. \(^{-1}\) band coincides with a band found at 494 cm. \(^{-1}\) in aluminum acetylaltonate assigned as M-O stretch.

**Group(IV) HHIB complexes**

Attempts to prepare bis or tris HHIB complexes of silicon, germanium, and tin failed. The preparation of bis(dimethylformamide)-bis(hexafluoro-2-hydroxyisobutyrate) complexes of silicon and germanium seemed more successful. The compounds have similar infrared spectra except for an hydroxyl stretching band in the silicon complex which suggests some hydrolysis may have occurred.

The silicon and germanium complexes have infrared spectra with two bands in the C=O stretching region, four bands in the CF \(_3\) stretching region and two bands in the C-O stretching region. The germanium complex has an additional band between 900 and 700 cm. \(^{-1}\) which is the region characteristic of Ge-O linkages. \(^{71}\) The far infrared spectrum has bands at 620, 535, and 445 cm. \(^{-1}\) The silicon compound has bands at 565, 550, and 515 cm. \(^{-1}\); the last may indicate an Si-N linkage. \(^{68}\)

The germanium complex has its two C=O bands at 1735 cm. \(^{-1}\) and 1655 cm. \(^{-1}\) Dimethylformamide has its broad C=O band at 1660 cm. \(^{-1}\). The mono-cesium salt of HHIB has an asymmetric carboxylate stretch at 1660 cm. \(^{-1}\) also.

Two resonance forms can be written for dimethylformamide.

\[
\begin{align*}
\text{(a)} & \quad \text{O} \quad \text{H-C-N(CH}_3\text{)}_2 \\
\text{(b)} & \quad \text{O}^- \quad \text{H-C=N(CH}_3\text{)}_2
\end{align*}
\]
<table>
<thead>
<tr>
<th>Compound</th>
<th>C=O cm(^{-1})</th>
<th>C-N cm(^{-1})</th>
<th>CH(_3)</th>
<th>CF(_3)</th>
<th>C-O</th>
<th>N-C=O bend</th>
<th>Below 600 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge(HHIB(_2))·2DMF</td>
<td>1735(s)</td>
<td>1480(w)</td>
<td>2950(w)</td>
<td>1275(s)</td>
<td>1040(s)</td>
<td>660(m)</td>
<td>620, 535(w)</td>
</tr>
<tr>
<td></td>
<td>2860(w)</td>
<td></td>
<td>1215(s)</td>
<td></td>
<td>980(s)</td>
<td></td>
<td>445, 405(m)</td>
</tr>
<tr>
<td></td>
<td>1430(m)</td>
<td></td>
<td>1175(s)</td>
<td></td>
<td></td>
<td></td>
<td>365(s)</td>
</tr>
<tr>
<td>(CF(_3))(_2)O[Si(CH(_3))](_3)</td>
<td>1750(s)</td>
<td>2980(m)</td>
<td>1255(s)</td>
<td>1025(s)</td>
<td>850(s)</td>
<td></td>
<td>Si-CH(_3)</td>
</tr>
<tr>
<td></td>
<td>665(w)</td>
<td>2910(m)</td>
<td>1230(s)</td>
<td></td>
<td>980(s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C[OSi(CH(_3))](_3)</td>
<td>1410(w)</td>
<td>1200(m)</td>
<td>1160(m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
If dimethylformamide coordinates to germanium through nitrogen, then the resonance structure (b) is precluded and the C=O stretching frequency of dimethylformamide should increase upon coordination. The 1735 cm\(^{-1}\) band would then be attributed to DMF and the 1655 cm\(^{-1}\) band to the asymmetric carboxylate stretch of an ionic \textit{NHIB} ligand. The asymmetric carboxylate stretch in the compound \((\text{CF}_3)_2\text{C}[(\text{OSi(CH}_3)_3]\text{CO}_2\text{Si(CH}_3)_3\text{ appears at 1750 cm}\(^{-1}\) and suggests a covalent silicon-carboxylate bond. The difference in the asymmetric carboxylate stretching frequencies of this silicon compound and the germanium compound is surprising, because of the similarity in the two group IV elements. Neither the difference in electronegativities of the group IV elements, nor the type of coordination can account for the discrepancy in the stretching frequencies. The C=O band in the germanium complex would, therefore, be assigned to the 1735 cm\(^{-1}\) absorption.

The \((\text{CF}_3)_2\text{C}[(\text{OSi(CH}_3)_3]\text{CO}_2\text{Si(CH}_3)_3\text{ compound has four bands in the CF}_3\text{ stretching region, one of which is probably the C=O stretching frequency of the carboxylate group. Bands at 1025 and 980 cm}\(^{-1}\) are probably asymmetric and symmetric Si-O-C stretching frequencies. The far infrared has two prominent bands at 545 and 450 cm\(^{-1}\) No O-H stretching bands are present in the near infrared.
$\text{HHIBP} \text{C}_3$

The asymmetric carboxylate stretching frequency is very strong at $1825 \text{ cm}^{-1}$ and has a shoulder at $1870 \text{ cm}^{-1}$. The absorption is at higher energy than for HHIB acid ($1760 \text{ cm}^{-1}$) indicating a complex has been formed which has a covalent carboxylate –phosphorus linkage.

The suggested compound may exist as five coordinate (square pyramid, or trigonal bipyramid) structures or a four coordinate-tetrahedral-ionic complex.

The P-Cl stretching region ($600-435 \text{ cm}^{-1}$) has three strong bands at 605, 535, and $505 \text{ cm}^{-1}$ and a band of medium intensity at $460 \text{ cm}^{-1}$. The five coordinate structures should exhibit three P-Cl stretching frequencies while the tetrahedral structure would only exhibit two bands.

The P-O-C vibrations should show symmetric bands in the $740-900 \text{ cm}^{-1}$ region and asymmetric bands in the $1150-970 \text{ cm}^{-1}$ region. One structure would produce a maximum of four bands in these regions although coupling with C-C vibrations would produce additional bands. Five bands are observed suggesting more than one structure is present.

The number of bands in the P-Cl stretching region suggests the complex is probably five coordinate but conclusions of this type are of limited value because some hydrolysis product may be present as indicated in the analysis.
B. Visible Spectra

The visible spectra of the transition metal complexes of HHIB have been recorded to gather additional information concerning the properties of the HHIB ligand.

The configuration of an element is the assignment of a given number of electrons to a certain set of orbitals. A transition element, having two electrons in the d orbitals would have a configuration d^2. Each electronic configuration gives rise to a number of energy levels each of which is called a term. Electrons in an unfilled shell have no interaction with electrons in a filled shell, apart from the shielding of the nuclear charge by the latter. The electrons within an unfilled shell of a free ion are subject to two perturbations. Firstly, the electrons within an unfilled shell repel each other and the energy levels arise from the manner in which the electrons occupy the orbitals of the shell relative to one another. This produces terms of various multiplicities (spin angular momentum) each of which is subdivided into one or more terms each having a given angular momentum. The energy separation between these terms is generally in the order of 10,000 cm\(^{-1}\).

Secondly, there is a weaker interaction of electron spin and orbital angular momentum that further splits the orbital angular momentum states (spin-orbit coupling). This interaction is an order of magnitude
smaller than the electron repulsion terms and as a result attention is focused mainly on the latter.

The splitting of the $d^2$ configuration into terms and states is illustrated below. With the aid of Hund's rule (of the terms with highest multiplicity the one with the highest orbital angular momentum is the ground state) it is easy to find the ground state of any configuration. Thus, for a $d^2$ configuration the ground term is $3_F$.

<table>
<thead>
<tr>
<th>Terms</th>
<th>States</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1S$</td>
<td></td>
</tr>
<tr>
<td><strong>singlet</strong> terms</td>
<td></td>
</tr>
<tr>
<td>$^1D$</td>
<td></td>
</tr>
<tr>
<td>$^1G$</td>
<td></td>
</tr>
<tr>
<td>$d^2$</td>
<td></td>
</tr>
<tr>
<td>$^3P$</td>
<td></td>
</tr>
<tr>
<td><strong>triplet</strong> term</td>
<td></td>
</tr>
<tr>
<td>$^3F$</td>
<td></td>
</tr>
</tbody>
</table>

The theory of interelectronic repulsion can be extended to
give the energies of the terms above the ground term for any configuration. The energies are a function of two electron repulsion parameters (usually Racah parameters B and C). The Condon and Shortley parameters, $F_2$ and $F_4$, can also be used and are related to the Racah parameters by the equations:

\[
B = F_2 - 5F_4 \\
C = 35F_4
\]

The Racah parameter B and the ratio C/B are available for various oxidation states for most transition metal free ions.

Upon the formation of a metal complex, a number of additional perturbations act upon the terms of the free ion. The term in the crystal field complex is usually stabilized by an amount $E^0_b$ relative to the free ion. The complex is further stabilized by an amount called the crystal field stabilization energy caused by splitting of the lowest energy level by an anisotropic crystal field. The difference between the lowest energy level of a term split by a crystal field and the center of gravity of the term in the crystal field is the crystal field stabilization energy (c.f.s.e.). The total stability of the complex is therefore $E^0_b$ plus the c.f.s.e. and is assigned the symbol $E_b$. In figure 4, the diagram indicates the crystal field stabilization for the $d^2$ configuration ($^3F$ term) in an octahedral crystal field. The magnitude of Dq is a measure of the crystal field splitting and enables chemists to establish an order for both ligands and transition metals called the spectrochemical series.
(a) attraction between central ion charge and ligand charges
(b) repulsion of central ion electrons by ligand charges and themselves
(c) splitting of $^{3}F$ term

Figure 4.

For the transition metal complexes of HHIB the energy terms for the free transition ion are perturbed according to the type of crystal field that surrounds the ion. For the tris-HHIB complexes the complex anion isomer with highest symmetry belongs to the $C_{3}$ point group, although the crystal field perturbing the free ion terms may be more closely related to $D_{3}$ or $O_{h}$ symmetry. The bis-HHIB complexes have cis- and trans-isomers which belong to $C_{2v}$ and $C_{2h}$ point groups respectively. The spectrum, however, may have a closer resemblance to compounds having $D_{2h}$, $D_{4h}$, or even $O_{h}$ symmetry depending upon the effect of the crystal field on the free ion terms.

Electronic transitions can only occur if $\Delta S$, the change in spin from the ground state to the excited state, is zero. Spin forbidden
bands are, in fact observed in some complexes but have extinction coefficients of $\epsilon \approx 0.1$. Spin allowed, but Laporte forbidden (g$\leftrightarrow$g, u$\leftrightarrow$u) transitions have extinction coefficients of $\epsilon \approx 10$. and are normally the d-d transitions associated with transition metal complexes. Square planar and octahedral bis(HHIB) complexes have two possible geometric isomers that belong to the $C_{2v}$ (cis) and $C_{2h}$ (trans) point groups. All $d^n$ electronic configurations for $C_{2v}$ symmetry have the same number of energy states and therefore electronic transitions as for $C_{2h}$ symmetry. Therefore, it is difficult to distinguish between the cis and trans HHIB complexes by the number of bands in their visible spectra. In fact, the higher point group $D_{2h}$ would also show the same number of electronic transitions for a given electronic configuration. Only the $D_{4h}$ and $O_h$ point groups, which have one or more doubly degenerate and triply degenerate energy states respectively, can be distinguished from each other and the $D_{2h}$, $C_{2h}$, or $C_{2v}$ point groups.

The tris(HHIB) complexes belong to the $C_3$ or $C_1$ point groups. Molecules belonging to the $C_1$ point group have more electronic transitions than molecules with $C_3$ or the $D_3$ points groups; these, in turn, have more electronic transitions than molecules with an $O_h$ point group. Therefore it is theoretically possible to distinguish one of the isomers of the tris(HHIB) transition metal complexes from the others.

Practically, however, fewer bands than calculated for a given point group are observed in the visible spectrum for both bis- and tris-HHIB complexes. The symmetry about the central metal
appears higher than the point group of the molecule. In most cases, the complexes appear to have octahedral or distorted octahedral configurations. Visible spectroscopy appears of limited value in determining any preferred geometric configuration for either the bis- or tris-HHIB transition metal complexes.

The simplification of the spectra does, however, make it easier to determine Dq and Racah B parameters for the HHIB ligand with a given transition metal ion. The Dq values can be determined readily using the appropriate Orgel or Tanabe-Sugano diagram for the electronic configuration involved. The Racah B parameter can be obtained using the correct secular equation and the Dq value determined from the Orgel diagram, and it can also be determined directly from the Tanabe-Sugano diagram. The ratio of the Racah B parameter for the complex to the Racah B parameter of the free ion is a measure of the amount by which the interelectronic repulsion has decreased by complexing with that ligand. The effectiveness of ligands in reducing the electronic repulsion have been measured and placed in a series called the nephalauxetic series.

The following discussion also comments upon the magnetic moment of various HHIB transition metal complexes. The magnetic moment is a measure of the angular momentum of the central transition metal ion. The spin angular momentum is the major component of the angular momentum. Consequently, the magnetic moment is a measure of the number of unpaired electrons. Crystal fields that have orbitally degenerate ground states give an orbital contribution to the magnetic moment that augments the spin only value.
Manganese complexes

In a weak octahedral crystal field the Mn(III) ion (d⁴ configuration) has an energy level diagram with a \( ^5E_g \) ground state and a \( ^5T_{2g} \) excited state. The magnetic moment of Mn(III) complexes should have a value of 4.90 B.M. (4 unpaired electrons) or slightly higher because of the orbitally degenerate \( ^5E_g \) ground state. The \( \text{Cs}_3\text{Mn(HHIB)}_3 \) complex was found to have a magnetic moment of 4.97 B.M., slightly higher than the spin only value of 4.90 B.M. for four unpaired electrons.

Copper complexes

All copper complexes in this study have a d⁹ electronic configuration and can therefore have only one unpaired electron regardless of the type or strength of crystal field. The magnetic moment of these complexes should be 1.73 B.M. Assuming the \( \text{bis(HHIB)copper(II)} \) complexes have a square planar configuration (\( D_{4h} \) symmetry about the copper ion) three electronic transitions are possible from the \( ^2A_{1g} \) ground state. If free carboxylate oxygens or solvent molecules complete the octahedral coordination about copper and raise the local symmetry to \( O_h \), then the ground state will become \( ^2E_g \) and one electronic transition to the \( ^2T_{2g} \) excited state is possible (10 Dq).

The visible spectra of \( \text{Cs}_2\text{Cu(HHIB)}_2 \) and \( \text{K}_2\text{Cu(HHIB)}_2 \) in methanol are almost identical, having one broad absorption band at 680 μ. The diffuse reflectance spectrum has its absorption band shifted to 650 μ. Assuming the broad absorption bands are centered at 10 Dq then the HHIB copper complex has a Dq value between 1470 cm.⁻¹ and 1530 cm.⁻¹.
The methanolic solution spectra of $\text{H}_2\text{En(Cu(HHIB)\textsubscript{2})}$ and $\text{H}_2(\text{TMED})\text{Cu(HHIB)\textsubscript{2}}$ show single bands at 635 m\(\mu\) and 633 m\(\mu\) respectively. The Dq value for these complexes is 1580 cm\(^{-1}\). The diffuse reflectance spectrum of these compounds show evidence of the energy band splitting, probably caused by some distortion in the solid state.

The $\text{H}_2\text{En}_2\text{Cu(HHIB)\textsubscript{2}}$ complex, which is purple in colour, has a band at 575 cm\(^{-1}\) in both the diffuse reflectance and solution spectra. This yields 1,700 cm\(^{-1}\) for the Dq parameter of this complex. The shift in absorption energy to a higher frequency in relation to the other copper complexes suggests a change in coordination has occurred about the copper atom. Both ethylenediamine ligands are probably coordinated to the copper ion and have displaced one end of the HHIB ligand.

The Dq values although only approximate, indicate that HHIB is definitely lower in the spectrochemical series than ethylenediamine and is probably between water and ammonia in the series.

All magnetic moments of the copper complexes are in the region of 1.8 - 2.0 B.M. and agree with a $^2D$ ground term.

Vanadyl complexes

The vanadyl ion (VO\(^{+2}\)) gives the vanadium atom the formal oxidation number of four. It therefore, has a $^1d$ electronic configuration and a $^2D$ ground term. This term splits into a $^2T_{2g}$ ground state and a $^2E_g$ excited state when placed in an octahedral crystal field. The very nature of the vanadyl ion makes for tetragonal distortion about the vanadium atom in the HHIB complex, and the orbital degeneracy of both doublet energy states must be lowered. The
magnetic moment of the compound is 1.76 B.M., almost identical to the spin only value, and verifies that the orbital degeneracy of the ground state has been lowered. The diffuse reflectance spectrum shows two bands, a band centred at 420 m\(\mu\) and an extremely broad band extending from 500 m\(\mu\) to 900 m\(\mu\). The broad band in the solution spectrum shows evidence of separating into three bands at 540 m\(\mu\), 620 m\(\mu\), and 730 m\(\mu\). The \(K_2VO(HHIB)_2\) complex probably has a structure similar to the square pyramidal structure of bis(acetylacetonato)vanadate complex. A solvent molecule may coordinate in the vacant site to make the vanadium atom six coordinate.

**Nickel complexes**

The nickel(II) has the \(d^8\) electronic configuration with \(3^2F\) free ion ground term. In the presence of an octahedral crystal field the triply degenerate \(t_{2g}\) orbitals are filled and the \(e_g\) orbitals have an electron in each orbital to give a \(3^3A_{2g}\) ground state. The triplet excited states are \(3^3T_{2g}(F)\), \(3^3T_{1g}(F)\), and \(3^3T_{1g}(P)\). Three transitions should be observed in the visible spectrum. With the \(3^3A_{2g}\) ground state, the magnetic moment of octahedral nickel is expected to be near the spin only value of 2.84 B.M. for two unpaired electrons.

Tetragonal distortion from the octahedral configuration removes some of the degeneracy of the \(e_g\) and \(t_{2g}\) orbitals and increases, theoretically, the number of electronic transitions. Infinite distortion produces the square planar structure which has so completely removed the \(e_g\) orbital degeneracy that spin pairing occurs and forms the \(1^1A_{1g}\) ground state. Square planar complexes of nickel(II) are therefore expected to be diamagnetic.
The bis(perfluoropinacol) derivatives of nickel are expected to have square planar configurations and have been found to be diamagnetic.

The bis(HHIB) complexes of nickel might also be expected to be square planar, but their colours are green in contrast to the purple colour of the perfluoropinacol complexes. The magnetic moment of 3.06 B.M. taken at room temperature indicates the crystal field about the nickel ion is probably octahedral. The visible spectra of the complexes show three main absorption bands characteristic of octahedral nickel complexes, although the high energy band shows evidence of splitting, indicating some distortion from the octahedral configuration. A distorted octahedron supports the infrared evidence of an interaction occurring between the free carboxylate oxygen and nickel ions of an adjacent molecule.

Using a Tanabe-Sugano diagram and assuming a pseudo-octahedral crystal field, Dq values have been calculated for the nickel complexes. The solution spectrum of \( \text{K}_2\text{Ni(HHIB)}_2 \) agreed well with the Tanabe-Sugano diagram to yield a Dq value of 873 cm\(^{-1}\) and an almost identical value for the Racah B parameter. The diffuse reflectance spectrum gave a Dq
value of 860 cm\(^{-1}\). The simplified nature of the present treatment, where vibrations, spin-orbit coupling, and low symmetry ligand field components have been neglected, probably produces a somewhat questionable value for Dq. The values obtained however, may serve as an approximate measure of the crystal field stabilization energy. The crystal field stabilization energy is less than for a hexamino-nickel(II) complex (Dq=1080 cm\(^{-1}\)) and greater than hexabromo-nickel(II) (Dq=680 cm\(^{-1}\))\(^{75}\). It is slightly greater than that of the hexaquo-nickel(II) ion (Dq=850 cm\(^{-1}\)).

The Racah B parameter of the HHIB ligand is slightly lower than that of water (B=905 cm\(^{-1}\))\(^{72}\) indicating HHIB is more effective at reducing interelectronic repulsion on nickel(II). The diffuse reflectance spectrum of K\(_2\)Ni(C\(_2\)O\(_4\))\(_2\)·4H\(_2\)O\(^{76}\) has been measured in this study and compared with K\(_2\)Ni(HHIB)\(_2\) since the HHIB acid has a structure intermediate to oxalic acid and perfluoropinacol. The oxalate complex has a spectrum consistent with octahedral nickel complexes and has bands at 395 \(\mu\)m, 640 \(\mu\)m, 1020 \(\mu\)m which yield a Dq value of 980 cm\(^{-1}\) and a B value of 745 cm\(^{-1}\).

It is impossible to compare the crystal field stabilization energy of the HHIB ligand with perfluoropinacol, since the latter forms square planar complexes with nickel(II). In a 4:1 aqueous-methanol solution, Cs\(_2\)Ni(PFP)\(_2\) has a spectrum characteristic of an octahedral complex; the Dq and B values have been calculated to be 832 and 815 cm\(^{-1}\) respectively (the solvent is assumed to complete the octahedral coordination). The K\(_2\)Ni(PFP)(HHIB) complex has also been prepared and has a magnetic moment of 3.21 B.M. suggesting octahedral coordination. The visible spectrum in methanol is charac-
teristic of a slightly distorted octahedral complex (the high energy)
band at 405 m\(\mu\) shows some evidence of splitting). The crystal field
stabilization parameter Dq, was calculated to be 808 cm\(^{-1}\) and the
Racah B parameter 848 cm\(^{-1}\). The diffuse reflectance spectrum of
this solid orange complex has the high energy band, characteristic
of the \(3^3T_{1g}(P) \leftrightarrow 3^3A_{2g}(F)\) transition, split into three bands. The
symmetry about the nickel atom has been lowered below that of \(D_{4h}\)
symmetry. A calculation to obtain a pseudo-octahedral Dq parameter
produced the value 660 cm\(^{-1}\), but the distortion from a true octahedral
structure makes the significance of this value doubtful.

The Dq and Racah B values obtained for \(K_2Ni(PFP)(HHIB)\) and
Cs\(_2\)Ni(PFP)\(_2\) are lower than the value obtained for \(K_2Ni(HHIB)\)\(_2\). The
preceding information indicates the HHIB ligand is higher in the
spectrochemical series than perfluoropinacol but lower than oxalic
acid when complexing with nickel (II). The following ethylenediamine
complex provides further evidence that HHIB is relatively low in the
spectrochemical series.

The compound, analytically found to have the formula
\(H_2En_2Ni(HHIB)\)\(_2\), has a magnetic moment of 3.07 B.M. and has a
visible spectrum characteristic of an octahedral complex. (Both
ethylenediamine probably coordinate to nickel with one end of each
HHIB ligand completing the octahedral environment about the metal.)
The Dq and Racah B parameters were found to be 1150 cm\(^{-1}\) and
787 cm\(^{-1}\) respectively.
Table 10.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Diffuse Reflectance</th>
<th>Solution (methanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dq cm$^{-1}$</td>
<td>B cm$^{-1}$</td>
</tr>
<tr>
<td>Ni(H$_2$O)$_6^{72}$</td>
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<td></td>
</tr>
<tr>
<td>K$_2$Ni(HHIB)$_2$</td>
<td>860</td>
<td>860</td>
</tr>
<tr>
<td>Cs$_2$Ni(PFP)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$Ni(C$_2$O$_4$)$_2$</td>
<td>980</td>
<td>745</td>
</tr>
<tr>
<td>K$_2$Ni(PFP)(HHIB)</td>
<td>660</td>
<td>812</td>
</tr>
<tr>
<td>Ni(Br)$_6^{4-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(NH$_3$)$_6^{2+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$En$_2$Ni(HHIB)$_2$</td>
<td>1190</td>
<td>740</td>
</tr>
</tbody>
</table>

The Dq and B values are summarized in Table 10 and indicate the following spectrochemical series:

$\text{Br}<\text{PFP}<\text{H}_2\text{O}<\text{HHIB}<\text{C}_2\text{O}_4<\text{NH}_3<\text{En}$.

The nephalauxetic series is:

$\text{H}_2\text{O}<\text{HHIB}<\text{PFP}<\text{En}<\text{C}_2\text{O}_4$.

and places HHIB surprisingly high in the series. It must be remembered, however, that the conclusions drawn from the Dq and B values are based upon the assumption that similar structures exist for K$_2$Ni(HHIB)$_2$, K$_2$Ni(C$_2$O$_4$) and K$_2$Ni(PFP)(HHIB). The pseudo-octahedral crystal fields about the nickel ion may be produced by various structures, and the Dq and B values cannot be compared quantitatively with much significance.
The Dq and B parameters have not been calculated for phosphine complexes of HHIB-nickelate(II). These compounds are unlike the other nickel complexes of HHIB, being diamagnetic. The yellow-orange \((\text{PEt}_3)_2\text{Ni(HHIB)}\) has only one very broad intense band in the visible spectrum at 450 \(\text{mu}\). The bis(diphenylphosphino)ethane complex of HHIB-nickelate(II), \((\text{BDPPE})\text{Ni(HHIB)}\), has similar magnetic and visible spectral properties. These two phosphine complexes are the only HHIB complexes in this work that have the square planar configuration. The added stability due to \(d\pi\) bonding between phosphine and nickel and the bulkiness of the phosphine ligands must inhibit octahedral coordination.

**Chromium complexes.**

The chromium(III) ion has a \(d^3\) electronic configuration and a \(^4F\) ground term caused by interelectronic repulsion. When placed in an octahedral crystal field the ground term will be perturbed in the same manner as that of the \(d^8\) configuration. The ground state is therefore the \(^4A_{2g}\) (F) term, while the excited states are (in order of increasing energy) the \(^4T_{2g}\) (F), \(^4T_{1g}\) (F), and \(^4T_{1g}\) (P) terms. The magnetic moment of 3.85 B.M. for \(\text{Cs}_3\text{Cr(HHIB)}_3\cdot\text{H}_2\text{O}\) is consistent with the \(^4A_{2g}\) ground state. Doublet energy states also exist in this energy diagram but are not considered because transitions to these levels are spin forbidden. Three spin allowed transitions are therefore expected. The tris-HHIB chromiunate(III) complexes are expected to be of higher symmetry than the bis-chelate complex of nickel(II), and have visible spectra that can be fitted to the Tanabe-
Sugano diagram for $d^3$ ions in octahedral crystal fields. The spectrum of the $\text{Cs}_3\text{Cr(HHIB)}_3\cdot\text{H}_2\text{O}$ complex closely resembles that of aqueous chromium(III), with two bands observed in the visible region. The ratio of the energies of these bands when matched with the Tanabe–Sugano diagram showed these bands to be the $^4T_{2g}(F)\leftrightarrow^4A_{2g}$ and $^4T_{1g}(F)\leftrightarrow^4A_{2g}$. A Dq value of 1685 cm$^{-1}$ is obtained for the $\text{Cs}_3\text{Cr(HHIB)}_3\cdot\text{H}_2\text{O}$ complex in methanol solution and a B value of 550 cm$^{-1}$. In aqueous solution the values are 1700 cm$^{-1}$ and 554 cm$^{-1}$. The Dq value of HHIB is almost identical to the value for the aqueous chromium(III) ion (1700 cm$^{-1}$). This result verifies those results obtained from the nickel(II) complexes; that the crystal field stabilization energy for the HHIB ligand is very similar to that of water. The tris(oxalato)chromium(III) anion also has a similar visible spectrum. Its interpretation gives a Dq value of 1740 cm$^{-1}$ and a B value of 600 cm$^{-1}$. The Dq and Racah B values are summarized in Table 11. The same relative order of the spectro-chemical series is obtained as was for the nickel complexes:

$$\text{H}_2\text{O}<\text{HHIB}<\text{C}_2\text{O}_4<\text{en.}$$

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Dq cm$^{-1}$</th>
<th>B cm$^{-1}$</th>
<th>f</th>
<th>h</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 oxalate</td>
<td>1740</td>
<td>640</td>
<td>1.02</td>
<td>1.8</td>
</tr>
<tr>
<td>6 (\text{H}_2\text{O})</td>
<td>1700</td>
<td>695</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>3 HHIB</td>
<td>1700</td>
<td>554</td>
<td>.97</td>
<td>2.2</td>
</tr>
<tr>
<td>3 En</td>
<td></td>
<td></td>
<td>1.28</td>
<td>1.5</td>
</tr>
</tbody>
</table>

For Cr(III)-- $B_o=1030$ cm$^{-1}$, $g=17.0$, $k=0.21$
The B values do not follow the same order as for the nickel complexes. The nephalauxetic order is:

$$H_2O > C_2O_4 > HHIB.$$

These results are probably more reliable than those obtained from nickel(II) complexes because three chelate ligands or six water molecules produce the ligand field. The nickel(II) complexes require extending results of octahedral molecules to complexes that are tetragonally distorted.

It is unfortunate $K_3Cr(PFP)_3$ has not yet been prepared or a $D_q$ value obtained for the PFP ligand.

Parameters for the empirical estimation of $10D_q$ and $B$ for various combinations of ligand groups and metal ions are given by the equations:

$$10D_q = f \cdot g \text{ cm} \cdot 10^{-3}$$

$$B = B_0 (1 - hk)$$

$B_0$ is the free ion interelectronic parameter while $g$ and $k$ are parameters associated with the metal ion and $f$ and $h$ parameters associated with the ligand. Since $B_0$, $g$, and $k$ are known for the chromium(III) ion and $10D_q$ and $B$ have been calculated, the $f$ and $h$ parameters can be calculated for HHIB. The results obtained from the chromium(III) complex gives $f$ and $h$ values of .98 and 1.5 respectively. They are compared with a few $f$ and $h$ values for other ligands in Table 11.

Using parameters for the nickel(II) ion, $f$ and $h$ parameters of .97 and 1.7 are obtained. The $f$ parameter, associated with the $D_q$ value is almost identical with the value obtained from the chromium(III) complex.
Cobalt complexes

Cobalt(II) has a \( d^7 \) electronic configuration and a \( ^4F \) ground term. Perturbation by an octahedral crystal field would split the free ion terms and give a \( ^4T_{1g}(F) \) ground term. For the compound \( \text{Cs}_2\text{Co(HHIB)}_2 \cdot 2\text{H}_2\text{O} \), the magnetic moment of 3.88 B.M. is in excellent agreement with three unpaired electrons, but is low for an octahedral complex because of orbital contribution to the angular momentum by the \( ^4T_{1g} \) ground state. A distortion in the crystal field may remove the orbital degeneracy to give an A or B ground state. Three electronic transitions should occur for octahedral cobalt(II) complexes: \( T_{2g}(F) \leftrightarrow T_{1g}, T_{1g}(P) \leftrightarrow T_{1g}(F), A_{2g}(F) \leftrightarrow T_{1g}(F) \). Four absorption bands are observed in the visible region of a spectrum run in methanol. The bands at 485 m\( \mu \), 520 m\( \mu \) and 578 m\( \mu \) may be caused by the splitting of an excited T orbital state. The fourth band in the spectrum at 800 m\( \mu \) is extremely broad. A similar spectrum is observed for the solid but the high energy band is not so obviously split.

The energies of the absorption bands in this complex do not fit well with any of the absorption ratios on the Tanabe-Sugano diagram for octahedral complexes. The structure of the compound is very different from a slightly distorted octahedral complex, but the possibility of the compound having tetrahedral symmetry can be ruled out. Although the relative energies of the electronic transitions are suited to the appropriate Tanabe-Sugano diagram, the magnitudes of the extinction coefficients are much too low for the molecule to be tetrahedral. (Molecules with \( T_d \) symmetry have d-p orbital mixing and as a result higher absorptivity).
Iron(III) complexes

The iron(III) ion has the d<sup>5</sup> electronic configuration and has a 6<sup>S</sup> ground term. If placed in an octahedral crystal field the ground state becomes 6<sub>ALG</sub> and is the only sextet term for the d<sup>5</sup> electronic configuration. Consequently, there can be no spin allowed transitions. Any transition observed is spin forbidden and therefore is very weak in intensity. For the compound Cs<sub>3</sub>Fe(HHIB)<sub>3</sub>·H<sub>2</sub>O, the diffuse reflectance spectrum has four weak electronic transitions at 480 mμ, 670 mμ, 700 mμ, and 920 mμ. These results, when applied to the Tanabe-Sugano diagram for a d<sup>5</sup> electronic configuration indicate the high energy band at 480 mμ is the 4<sub>2G</sub>→6<sub>ALG</sub> transition. These energy states lie parallel to each other in agreement with the extremely sharp band observed. The three other bands in order of increasing energy probably involve transitions from the 6<sub>ALG</sub> ground state to the 4<sub>T1G</sub>, 2<sub>T2G</sub>, and 4<sub>T2G</sub> levels. A DQ value of 1050 cm<sup>-1</sup> was calculated from these transitions using the Tanabe-Sugano diagram. It has limited significance however, since the diagram is only valid for spin forbidden transitions when the Racah C and B parameters are in the ratio of 4.48 to 1. Since these parameters are not known for the Cs<sub>3</sub>Fe(HHIB)<sub>3</sub>·H<sub>2</sub>O complex any quantitative information obtained from the diagram is of little value.

The magnetic moment of Cs<sub>3</sub>Fe(HHIB)<sub>3</sub>·H<sub>2</sub>O was determined to be 5.84 B.M. slightly lower than the spin free value of 5.92 B.M. expected for the 6<sub>ALG</sub> ground state.
Discussion and Summary.

This work was undertaken with the object of determining whether HHIB could form complexes with metals and if so, how the properties of these complexes compared with those complexes of similar ligands. The isolation of numerous stable HHIB complexes has obviously established that complexes can be prepared. The properties of the ligand and its complexes are summarised and discussed in the following sections.

Reactivity of the ligand.

The HHIB acid, like PFP readily forms transition metal complexes as indicated by the color changes observed during their preparation. Bis- or tris-HHIB complexes have been made with the majority of the first row transition elements. HHIB and PFP are both more reactive than diol(II) which requires another ligand to be present to form stable complexes. Metal complexes of HHIB with En, TMED, PFP, and phosphine ligands have also been prepared. Nickel complexes of HHIB with other ligands (bipyridil, cyanide) showed color changes indicative of complex formation but their products were difficult to purify. In fact, the majority of compounds were difficult to crystallize and formed gelatinous looking solids which suggested the complexes were polymeric. Attempts to produce HHIB complexes of nickel oxalate or nickel dichloride failed. In both attempts $K_2Ni(HHIB)_2$ was isolated. The En and $PET_3$ ligands can displace HHIB from $K_2Ni(HHIB)_2$. The equilibrium for these reactions can be reversed if excess HHIB is used.
HHIB did not, however, displace BDPPE from (BDPPE)Ni(HHIB) even in excess HHIB. These reactions indicate that phosphines stabilize metal complexes more than En or HHIB. All attempts to prepare En$_3$Ni(HHIB) however, resulted in the formation of H$_2$En$_2$Ni(HHIB)$_2$.

The preparation of main group complexes of HHIB is more difficult than PFP complexes which are readily available by reacting Na$_2$PFP with the metal chloride in THF. The disodium salt of HHIB is not available and complexes must be prepared from the hydroxy acid. HHIB complexes of boron and aluminum can be prepared from the acid, trimethylborate and aluminum chloride. Group IVb and Vb complexes are difficult to prepare and appear to hydrolyze easily. The infrared spectra of the complexes that were obtained showed changes in the carboxylate stretching frequency (relative to the pure acid) which suggested complexes of these elements had been made.

Stabilization of oxidation states

HHIB forms stable complexes of Cu(II), Ni(II), Co(II), Fe(III), Cr(III), and Mn(III). The preparation of the Cs$_3$Mn(HHIB)$_3$ complex showed HHIB could stabilize the Mn(III) oxidation state. Molecular oxygen will oxidize Mn(II) to Mn(III) in basic solution (-1.1 V) and is most certainly the oxidizing agent involved.

$$0_2 + 4\text{Mn}^{2+} + 12\text{HHIB} = 2\text{HOEt} \rightarrow 4\text{Mn(HHIB)}_3 + 2\text{OH}^- + 20\text{Et}^-$$

The magnetic moment of 4.92 B.M. is consistent with a Mn(III) complex. Attempts to obtain a molar conductance by dissolving the complex in water caused decomposition and suggested disproportionation occurs in aqueous solution which is in agreement with Mn(III) complexes.
It was surprising that molecular oxygen did not oxidize Co(II) to Co(III) since the oxidation potential of this reaction is only slightly larger than that for the manganese (-1.17 v). The compound isolated was a red-pink color and paramagnetic which indicated that oxidation had not occurred. (With the exception of Cobalt(III) hexafluoride all known octahedral Co(III) compounds are low spin and diamagnetic).

Mode of attachment

Transition elements are known to form complexes with non-fluorinated α-hydroxyisobutyric acid. Kinetic and thermodynamic studies indicated the ligand forms chelate complexes and stability studies showed the ligand to be monobasic. An X-ray study of copper complexes of α-hydroxyisobutyric and glycolic acids substantiated these results and showed the free carboxylate oxygen coordinated to neighbouring molecules in the solid state.

The analyses of transition metal HHIB complexes indicated the ligand differs from its non-fluorinated analogue and is dibasic like the PFP and oxalate ligands. The inductive effect of the two CF₃ groups must enhance the acidity of the hydroxyl hydrogen of HHIB relative to the non-fluorinated acid. The HHIB ligand is assumed to chelate to the transition metal elements bonding through both carboxylate and alkoxide oxygens to form the bis- or tris- complexes. The infrared spectra of the HHIB-transition metal complexes suggests an ionic carboxylate-metal linkage while the more electronegative B, Al, and P elements have covalent linkages. The free carboxylate oxygen appears to be associated with some electron acceptor in the
bis-HHIB transition metal complexes. In this respect the HHIB complexes are like the bis-non-fluorinated α-hydroxy carboxylates of copper\(^{39}\) and may be polymeric.

**Geometry and Coordination.**

The HHIB complex of boron(III) is assumed to be similar to the PFP complex and have tetrahedral coordination. The infrared spectrum indicates the boron complex is four coordinate which agrees with this tetrahedral configuration. The tris-HHIB aluminum complex and Ge(HHIB)\(_2\).2DMF most probably have octahedral coordination. The HHIBPCl\(_3\) complex could be four or five coordinate. Its infrared spectrum suggests a five coordinate complex because of three strong P-Cl bands but the possibility of an hydrolysis product being present makes conclusions of this type of limited significance.

The majority of the transition metal complexes of HHIB appear to have octahedral coordination. The tris-HHIB complexes are most probably octahedral as indicated by the magnetic moment and visible spectrum of Cs\(_3\)Cr(HHIB)\(_3\). Even the bis-HHIB complex, K\(_2\)Ni(HHIB)\(_2\), has a diffuse reflectance spectrum characteristic of octahedral coordination. The most satisfactory explanation suggests that two non-chelating carboxylate oxygens complete the octahedral coordination about nickel much as is observed in the non-fluorinated bis(glycolate) copper complex. This model would agree with the infrared evidence that suggested free carboxylate oxygens associate with some electron acceptor.

Neither infrared nor visible spectroscopy is able to establish
if a preferred geometric isomer is formed in bis- or tris-HHIB complexes.

The HHIB-nickel complex of ethylenediamine, $H_2En_2Ni(HHIB)_2$, is also octahedral. The infrared spectrum suggests the carboxylate end of each HHIB molecule is coordinated to nickel and two ethylenediamine groups complete the octahedral coordination. This structure would suggest that the carboxylate metal-oxygen bond is stronger than that of a fluorinated alkoxide-metal linkage.

The HHIB-nickel complexes differ from the PFP and diol(II) derivatives of nickel that have properties characteristic of square planar complexes. The phosphine nickelate(II) complexes of HHIB are the only nickel compounds of HHIB that have the square planar configuration. The size of the phosphine ligand and the stability of the resulting complex presumably inhibits octahedral coordination.

Conductivity measurements show the majority of the complexes are ionic in aqueous solution. Molar conductance values were plotted against the square root of the concentrations to obtain molar conductance values at infinite dilution. The graphs in general were straight lines and gave values for 1:1, 2:1, or 3:1 electrolytes. The phosphine complexes of HHIB-nickel were exceptions and had molar conductivities suggesting they are non-electrolytes in agreement with a square planar configuration.

The molecular weight measurement on $(PET_3)_2Ni(HHIB)$ (m wt=505) in benzene produced high molecular weight values indicating this complex is associated in solution. A value of 500 was obtained when the readings were extrapolated to infinite dilution. Molecular weight
measurements on the complexes that were electrolytic gave low molecular weight values.

Ethylenediamine and tetramethylethylenediamine complexes of copper have molar conductances indicative of 1:1 electrolytes. The infrared spectra of $H_2EnCu\text{(HHIB)}_2$ and $H_2\text{(TMED)}Cu\text{(HHIB)}_2$ indicate both complexes are amine salts. The TMED complex has no bands above 3100 cm$^{-1}$ and suggests no O-H bond is present although a weak band is observed at 3030 cm$^{-1}$. It is difficult to describe any adequate model that is a 1:1 electrolyte and an amine salt, but has no C-OH bond. Possibly the amine salts do not dissociate completely which causes the molar conductances to be lower than expected. Only an X-ray investigation will be able to determine the exact bonding in these amine salts.

**Position in the spectrochemical series**

A comparison of the Dq values for $Cr\text{(HHIB)}_3^{-3}$ and $Cr\text{(C}_2\text{O}_4)_3^{-3}$ indicated HHIB to be slightly lower in the spectrochemical series than the oxalate ligand. A study of the visible spectra of $K_2\text{Ni(HHIB)}_2$, $K_2\text{Ni(PFP)(HHIB)}_2$, $K_2\text{Ni(C}_2\text{O}_4)_2$, and $H_2\text{En}_2\text{Ni(HHIB)}_2$ indicated HHIB is slightly higher in the spectrochemical series than PFP but lower than oxalate, ethylenediamine or triethyl phosphine. HHIB–nickel complexes with ligands that produce weak ligand fields (chloride, bromide) were not isolated and no ligand field parameters obtained. The order for the spectrochemical series including PFP and HHIB would be:

$F < Cl < Br < PFP < HHIB = H_2O < C_2O_4^{-2} < NH_3 < En < PEr_3$

**Summary**

The HHIB acid forms stable chelate complexes with the majority of the transition elements and also with some of the main group elements.
The acid forms a dibasic ligand which produces, like PFP and oxalic acid a weak (high-spin) ligand field about the first row transition metal ions. The carboxylate group has an ionic metal linkage which appears to be slightly stronger than the metal alkoxide linkage. The free carboxylate oxygens are capable of coordinating to available coordination sites on adjacent metal atoms. This is most prevalent for the bis-HHIB complexes of the transition elements and enables them to be octahedral but makes them polymeric.
REFERENCES


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