Complexes With Polyfluorinated Ligands Part I--tetrafluorocatechol Part ii--2-amido-hexafluoro-2-propanol

Celia Anne Macdonald

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COMPLEXES WITH POLYFLUORINATED LIGANDS

PART I - TETRAFLUOROCATECHOL

PART II - 2-AMIDO-HEXAFLUORO-2-PROpanol

by

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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

This work is in two parts, the first being a study of the metal complexes of the fluorinated aromatic diol, tetrafluorocatechol, and the second, a report of the investigation of the bidentate ligands formed from the reaction of hexafluoroacetone with a series of amides.

Unlike the complexes of the fluorinated alkyl diol perfluoropinacol, complexes of tetrafluorocatechol were difficult to prepare and generally unstable. Only a few complexes could be prepared having tetrafluorocatechol as a sole ligand and other ligands with nitrogen and phosphorus donor atoms were required to stabilize the complexes. Some complexes of tetrabromocatechol were prepared for comparison purposes and these were considerably more stable than their fluorinated counterparts. It is suggested that the polar nature of the carbon-fluorine bond in systems where electron transfer processes can readily occur, leads to elimination of fluoride ion and subsequent decomposition in these complexes.

The well known susceptibility of fluorinated ketones to nucleophilic attack is utilized in the reaction of hexafluoroacetone with amides to give mononegative bidentate ligands. These have been shown to form complexes with a number of metal ions and the physical properties of these are discussed. The nature of the complex of copper(II) with 2-acetamido-hexafluoro-2-propanol permits deprotonation of the complexed ligand resulting in an anionic copper complex, which can then undergo further reactions with carbonyl containing compounds.

Some lanthanide complexes of 2-acetamido-hexafluoro-2-propanol were prepared which had the formulations NH₄⁺[M(Acfp)₄]⁻, M₂(Acfp)₄(OH)₂. acetamide and Ce(Acfp). (M = +3 lanthanide metal, Acfp = 2-acetamido-hexafluoro-2-
propoxide). The ammonium salts and the cerium complex are expected to show the lanthanide with a coordination number of eight but the exact structure of the other type of complex is still not clear.
ACKNOWLEDGMENTS

I would like to thank Professor C.J. Willis for his assistance and guidance on this thesis. I also thank my co-workers Warren Cripps, Bill Dawson, In Soon Chang and Dr. John Price for their help during the course of this work.

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GENERAL INTRODUCTION

Symbol, F. Atomic weight, 19.

This element exists in considerable quantity, in combination with calcium, forming the mineral called fluor spar, which crystallizes in fine cubes of various colours. Fluorine occurs also in small quantity as a constituent of bones and other animal substances. Its intense affinities for metals and for silicon which is a constituent of glass have hitherto baffled all attempts to isolate it in a state fit for examination, but Dr Brauner* by heating cerium tetrafluoride has obtained a lower fluoride of cerium, together with a gas smelling like chlorine or hypochlorous oxide. The reaction is probably $\text{CeF}_4 = \text{CeF}_3 + \text{F}$. Anhydrous tetrafluoride of lead is also decomposed by heat, yielding the difluoride and a gas smelling like chlorine.

*Journal of the Chemical Society, Xlii 8.

The above passage taken from a textbook entitled Fownes' Elementary Chemistry (1885) probably records the first attempts to produce fluorine although Moissan the French chemist is generally acknowledged to be the first to isolate the element in 1886.

Investigations of the reactions of fluorine proceeded slowly and cautiously for the next fifty years, a fact that could be attributed to the "frequent and often violent explosions that occur when fluorine is brought into contact with carbon." However under the motivation provided by the Second World War the field of fluorocarbon chemistry flourished and today most of the common analogues of hydrocarbon chemistry are known.
The primary concern of this thesis is a study of metal complexes derived from organic molecules which are totally or partially fluorinated. Thus the work can be conveniently divided into two parts: Part I which is mainly an investigation of complexes of a fully fluorinated diol tetrafluorocatechol (TFC) and Part II which examine the complexing properties of partially fluorinated ligands formed by reacting hexafluoroacetone with suitable nucleophiles. In the present case the nucleophiles used were a series of amides.

The characteristics of fluorine-substituted organic compounds can generally be explained in terms of the highly electronegative nature of fluorine. This is best illustrated by the classic example of the enhanced acidity of a series of fluorine substituted acetic acids.\(^2,^3\)

\[
\text{TABLE 1.}
\]

<table>
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<tr>
<th>Acid</th>
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<tr>
<td>(CH_3COOH)</td>
<td>1.77 \times 10^{-5}</td>
</tr>
<tr>
<td>(CFH_2COOH)</td>
<td>2.20 \times 10^{-3}</td>
</tr>
<tr>
<td>(CF_2HCOOH)</td>
<td>5.70 \times 10^{-2}</td>
</tr>
<tr>
<td>(CF_3COOH)</td>
<td>5.90 \times 10^{-1}</td>
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The tendency of the fluorine atom to draw \(\sigma\) electrons to it significantly reduces the negative charge density on oxygen and increases the dissociative ability of the acidic proton. The actual bond formed by carbon and fluorine is among the strongest single bonds known; 107-121 kcal.mole\(^{-1}\). According to Pauling's calculations,\(^4\) it also has considerable ionic character, namely 43\%, compared with 12\% for the carbon chlorine bond and 2\% for the carbon bromine bond. The bonding can be pictured as a mixture of covalent and ionic bonding. Qualitatively this can explain the discovery by Brockway\(^5\)
that the carbon fluorine bond distances in CF₃, CH₂F₂, CHF₂Cl, and CF₂Cl₂ are shorter than those in CH₃F, CH₂FCl and CHFCl₂. The ionic character of one C-F bond induces a double bond character in the remaining C-F bonds and resonance structures of types I and II can be written for the molecule

\[ \begin{align*}
&\text{FIGURE 1} \\
&\text{I} \\
&\text{II} \\
&\text{H} - \text{C} - \text{F} \quad \longleftrightarrow \quad \text{H} - \text{C} = \text{F}^+ \\
&\text{H} \quad \longleftrightarrow \quad \text{H} \\
&\text{H} \\
&\text{H} \\
&\text{F}^- \\
&\text{F} \\
&\text{F}^+ \\
&\text{F}^- \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
\end{align*} \]

This phenomenon was given the name double bond-no bond resonance by Hine⁶. Other theories have been advanced⁷ which explain the shortening effect by assuming that each fluorine atom removes p orbital density from the sp³ hybridized carbon in CH₄. The relative amount of s character remaining per bond is thus increased and the carbon fluorine bond length decreases.

Although the shortcomings of these theories have often been discussed² they remain useful methods of explaining many reactions in fluorocarbon chemistry.

A comparison of the properties of metal complexes formed by hydrocarbon ligands and their fluorinated analogues again clearly shows the powerful inductive effect of the fluorine atom. For example, only a few isolable complexes of pinacol (pKₐ ~ 14) have been reported with metals such as Al, Si and B while perfluoropinacol (pKₐ = 5.95) has been found to form a wide range of very stable metal complexes.⁸ The inductive effect of the fluorinated alkyl groups primarily increases the dissociation of the
ionizable protons. It must also diminish the donor ability of the negative oxygen atom formed, but not sufficiently to prevent complex formation. A good example of this increased acidity is shown by a comparison of the complexes formed by 2-hydroxyisobutyric acid and hexafluoro-2-hydroxyisobutyric acid. 9

The former gives only uninegative bidentate ligands while the latter can easily lose the ionizable proton to form complexes containing dinegative bidentate ligands. On the other hand, substituted alkyl amines which coordinate by donation of lone pair electrons have their basic properties significantly reduced, to the extent that tertiary perfluoroalkylamines will not form salts with strong mineral acids.

A report by Nyholm et.al. shows that the effect of progressive fluorination of ligands such as acetylacetone can extend to the metal atom itself
by increasing the Lewis acidity of the complex.\textsuperscript{10} Thus bis(hexafluoroacetyl-
acetonato)\textsuperscript{II}Cu forms isolable 1:2 addition complexes with pyridine at room
temperature whereas bis(acetylacetonato)\textsuperscript{II}Cu forms only an unstable 1:1
adduct which loses pyridine on exposure to air.

Fluorinated complexes are also receiving considerable attention in
the areas of biological and medicinal chemistry where their altered
electronic character, coupled with the similar steric characteristics of
their hydrocarbon analogues, often make such complexes very active in
biological systems. Since many reactions in such systems proceed via
coordination to metal containing enzymes, studies of fluorinated metal
complexes should provide additional useful information in these fields.
PART I

Metal Complexes of Tetrafluorocatechol

Experimental

General. All reactions with tetrafluorocatechol and tetrabromocatechol were carried out under an atmosphere of nitrogen using outgassed solvents. Infrared spectra were recorded as nujol mulls on a Beckman model IR-10 instrument and visible spectra on a Beckman DK-1 instrument. Abbreviations used in describing spectra are: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder. $^{19}$F n.m.r. spectra were recorded on a Varian model HA-100 spectrometer at 94.1 Mc/s. Magnetic moments were determined at 25° by the Gouy method using Hg[Co(CNS)$_4$] as standard. Micro analyses were performed by Alfred Bernhardt Laboratories. Mass spectra were recorded on a Varian M-66 instrument.

Tetrafluorocatechol.

The ligand was prepared by a modified version of the preparation reported by Tatlow et.al.\textsuperscript{11} A schematic diagram of the preparation follows

\[
\begin{align*}
\text{F} & \quad \text{NaOH} \quad \text{C}_2\text{H}_4\text{(OH)}_2 \\
\text{F} & \quad \text{O-CH}_2\text{CH}_2\text{OH} \\
\text{O-CH}_2\text{CH}_2\text{OH} & \quad \text{DMF} \quad \text{K}_2\text{CO}_3 \\
\text{F} & \quad \text{O-CH}_2\text{CH}_2\text{OH} \\
\text{O-CH}_2\text{CH}_2\text{OH} & \quad \text{AlCl}_3 \quad \text{benzene} + \text{hydrolysis} \\
\text{F} & \quad \text{OH} \\
\text{OH} & \quad \% \text{yield} = 40\% \\
\% \text{yield} & \quad \text{dioxan} = 36\% \\
\% \text{yield mono subst} & \quad 33\% 
\end{align*}
\]
The % yields are based on the product yield of the previous step. The overall % yield based on hexafluorobenzene varied from 5% to 10%. The first two steps proceeded smoothly, but isolation of the product in the final step was most difficult. The final crude mixture invariably contained large amounts of dibenzil identified by melting point, ir, and elemental analysis. The TFC cannot be separated by sublimation and extraction with dilute aqueous bases is required. The aqueous layer must be immediately neutralized however since all catechols are extremely susceptible to oxidation in basic solution. Extraction of the strongly acidic solution with diethyl ether followed by drying and removal of solvent gave a black gummy oil which after repeated sublimations gave white crystals of tetrafluorocatechol (m.p. 66-68°, lit 67-69). During the sublimations trace amounts of a transient red sublimate were observed.

Russian workers have reported the preparation of the o-quinone of TFC which they say is a red colour and decomposes rapidly. Tetrafluorocatechol appears to decompose slowly, with liberation of hydrogen fluoride, over a period of several months, the decomposition occurring more rapidly in the light. On opening a glass vial sealed for several months a strong sharp odour was noted and the inside of the glass container had been etched.

The $^{19}$F n.m.r. spectrum showed a typical AA'XX' spectrum (doublet of quartets) centred at 175.5 and 183.7 p.p.m. from CFCl$_3$. The infrared spectrum showed absorptions at 3640(s), 3550(s), 3200(br), 2700(m), 2440(w), 2340(w), 2110(w), 1750(w), 1635(s), 1520(vs), 1480(s), 1320(s), 1225(s), 1160(w), 1150(w), 1135(w), 1000(s), and 795(m) cm$^{-1}$.

Reaction of TFC with Fe$^{3+}$ and TMED

Excess TMED (2 ml) was added to TFC (0.8 g) in anhydrous methanol
(10 ml) and iron(III) acetate (0.78 g) in methanol was added dropwise. After stirring for 4 h, the deep blue solution was filtered and evaporated to give the iron complex tetramethylethlenediaminebis(tetrafluorocatechol) iron(III) as a black powder.

Analyt. Calcld. for C₁₈H₁₇F₈O₄N₂Fe: C, 40.6; H, 3.2; F, 28.5; N, 5.3; Fe, 10.5. Found: C, 40.7; H, 3.4; F, 28.9; N, 5.4; Fe, 10.3.

The electronic spectrum (MeOH solution) showed bands at 580 μ (ε = 3500) and 390 μ (ε = 2200).

The infrared spectrum showed absorptions at 2720(w), 1600(w), 1480(s), 1290(w), 1270(w), 1255(w), 1125(m), 1025(s), 1010(s), 980(s), 955(m), 805(m), 770(w) and 725(w) cm⁻¹.

The complex had a magnetic moment of 6.1 B.M. and gave a non-conducting solution in methanol. Its Mossbauer spectrum showed a centre shift of 0.68 ± 0.07 mm/sec, relative to sodium nitroprusside, a value typical of iron(III) compounds.(13)

Reaction of TFC with Ni²⁺ and TMED

TFC (1.3 g) in ethanol (10 ml) was mixed with nickel nitrate hexahydrate (2.08 g) in water (15 ml). TMED was added dropwise with stirring until the pH of the solution reached 10, by which time a green precipitate had appeared. After stirring 10 min, the mixture was filtered and the precipitate recrystallized from methanol, washed with dichloromethane, and dried briefly in vacuo at 25⁰. Analysis showed it to be tetramethylethlenediamine nickel tetrafluorocatecholate dihydrate.

Analyt. Calcld for C₁₈H₂₀F₈O₄N₂Ni: C, 36.9; H, 5.2; F, 19.4; N, 7.2; Ni, 15.0. Found: C, 36.8; H, 5.3; F, 20.7; N, 7.5; Ni, 15.6.

The electronic spectrum (diffuse reflectance) showed peaks at 400(sh), 720(br), 855(sh), and 920(w) μ; in solution (MeOH) the peaks
were at 475(sh), 650, 1054, and 1452 m\(\mu\). The magnetic moment at 25\(^\circ\) was 
3.18 B.M.

On keeping at 65\(^\circ\) in vacuo for 48 h, the green dihydrate was con-
verted to the brown anhydrous tetramethylethylenediamine nickel tetrafluoro-
catecholate.

Anal. Calcd. for \(\text{C}_{12}\text{H}_{16}\text{F}_{4}\text{O}_{2}\text{Ni}\): C, 40.6; H, 4.5; F, 21.4; N, 7.9; 
Ni, 16.5. Found: C, 40.9; H, 4.5; F, 21.5; N, 8.0; N, 8.0; Ni, 16.5.

The complex dissolved in anhydrous methanol to give a green solution 
absorbing at 475(sh), 651, 1055 and 1453 m\(\mu\). In dichloromethane, it gave 
a brown solution absorbing at 380(sh) and 475 m\(\mu\).

The infrared spectrum showed peaks at 1760(m) 1470(br,s), 1290(s), 
1243(w), 1200(w), 1132(s), 1100(w), 1077(w), 1047(w), 1000(br,s), 819(s), 
772(m), 725(m), and 628(m) cm\(^{-1}\).

This compound and the five succeeding nickel complexes were diamagnetic.

Reaction of TFC with Ni\(^{2+}\) and Triethylphosphine.

TFC(0.9 g) and nickel nitrate hexahydrate (1.4 g) were dissolved in 
methanol (10 ml) and PEt\(_3\) (0.6 g) added with stirring. Shiny brown 
crystals precipitated and were recrystallized from methanol to give 
bis(triethylphosphine) nickel tetrafluorocatecholate.

Anal. Calcd. for \(\text{C}_{18}\text{H}_{30}\text{F}_{4}\text{O}_{2}\text{NiP}_{2}\): C, 45.5; H, 6.4; F, 16.0; Ni, 12.4, 
MoL. Wt. 475. Found: C, 45.3; H, 6.0; F, 16.2; Ni, 12.5, MoL. Wt. (osmo-
metric in benzene) 520.

The electronic spectrum (CH\(_2\)Cl\(_2\) solution) showed bands at 415 m\(\mu\) 
(\(\varepsilon = 530\)) and 575 m\(\mu\) (\(\varepsilon = 170\)). A diffuse reflectance spectrum gave 
peaks at 412 and 562 m\(\mu\). The infrared spectrum showed peaks at 1470(s), 
1295(s), 1250(m), 1128(s), 1000(s,br), 776(s), 730(s), and 685(w) cm\(^{-1}\).
Reaction of TFC with Ni$^{2+}$ and 1,2-bis(diphenylphosphino)ethane (diphos).

TFC (0.6 g) and nickel(II) sulfate hexahydrate (1.65 g) in methanol (10 ml) were mixed with diphos (1.5 g) in tetrahydrofuran (15 ml) and stirred for 1 h. A brown crystalline material separated which was identified as diphos nickel tetrafluorocatecholate.

Anal. Calcd. for C$_{32}$H$_{24}$F$_{4}$O$_{2}$P$_{2}$Ni: C, 60.3; H, 3.8; F, 11.9. Found: C, 60.4; H, 3.9; F, 12.2.

The electronic spectrum (CH$_{2}$Cl$_{2}$ solution) showed one band at 570 m$\mu$ ($\epsilon = 220$). The infrared spectrum showed peaks at 2405(w), 1915(w), 1815(w), 1760(w), 1700(w), 1465(s), 1280(s), 1180(w), 1155(w), 1115(m), 1095(m), 1000(s), 865(m), 805(m), 745(s), 710(s), 700(s), 685(s), and 645(m) cm$^{-1}$.

Reaction of Tetrabromocatechol with Ni$^{2+}$ and PEt$_{3}$.

This preparation was carried out in the same manner as that of the corresponding TFC complex. The compound bis(triethylphosphine) nickel tetrabromocatecholate formed brown crystals.

Anal. Calcd. for C$_{18}$H$_{30}$Br$_{4}$O$_{2}$NiP$_{2}$: C, 30.1; H, 4.2; Br, 44.5; Ni, 8.2. Found: C, 29.9; H, 3.9; Br, 44.4; Ni, 8.3.

The electronic spectrum (CH$_{2}$Cl$_{2}$ solution) showed one band at 560 m$\mu$ ($\epsilon = 170$). The infrared spectrum showed peaks at 1450(s), 1350(m), 1275(s), 1240(s), 1220(m), 1035(s), 1010(w), 980(w), 945(s), 768(s), 750(s), 730(s), and 635(m) cm$^{-1}$.

Tetramethylammonium bis(tetrabromocatechol)nickelate(II).

Stoichiometric amounts of tetrabromocatechol and nickel nitrate were dissolved in methanol and tetramethylammonium hydroxide (15% in methanol) added dropwise with stirring. The complex precipitated as brown plates.
Anal. Calcd. for $C_{20}H_{24}O_4Br_8N_2Ni$: C, 22.8; H, 2.3; N, 2.7; Br, 60.6; Ni, 5.6. Found: C, 22.6; H, 2.5; N, 2.5; Br, 60.5; Ni, 5.6.

The infrared spectrum showed peaks at 1485(s), 1350(m), 1274(s), 1233(s), 1031(m), 950(s), 935(s), 785(s), 750(s) and 640(w) cm$^{-1}$.

**Reaction of Tetrabromocatechol, Ni$^{2+}$, and TMED.**

Tetrabromocatechol (2.0 g) and nickel nitrate (1.4 g) were dissolved in methanol (30 ml) and TMED (6.0 g) added. The dark brown precipitate was recrystallized from methanol to give tetramethylethylenediamine nickel tetrabromocatecholate.

Anal. Calcd. for $C_{12}H_{16}Br_4O_2N_2Ni$: C, 24.1; H, 2.7; N, 4.7; Br, 53.4; Ni, 9.8. Found: C, 24.3; H, 2.8; N, 4.8; Br, 53.5; Ni, 10.0.

The electronic spectrum (acetone solution) showed a band at 485 nm ($\varepsilon = 105$). The infrared spectrum showed peaks at 1435(s), 1340(m), 1270(s), 1232(s), 1205(w), 1120(w), 1040(m), 1010(m), 985(w), 940(s), 815(s), 770(s), 745(s) and 645(w) cm$^{-1}$.

**Reaction of TFC with Cu$^{2+}$.**

TFC and copper sulphate pentahydrate in a 2:1 molar ratio were dissolved in methanol and methanolic potassium hydroxide added to pH 7, at which point an olive-green solid precipitated. On drying in vacuo at 65$^\circ$ for 48 h, the solid became purple, in which state it was analyzed as potassium bis(tetrafluorocatechol) cuprate.

Anal. Calcd. for $C_{12}F_8O_4CuK_2$: C, 28.7; F, 30.3; Cu, 12.7. Found: C, 28.9; F, 30.2; Cu, 12.9.
The electronic spectrum (methanol solution) showed one band at 740 m\textmu (\epsilon = 220). In the infrared spectrum, peaks were at 1620(m), 1495(s), 1275(m), 1135(m), 1000(s), and 720(m) cm\textsuperscript{-1}.

The purple solid rapidly reverted to the green colour on exposure to atmosphere.

**Reaction of TFC with Cu\textsuperscript{2+} and TMED.**

TFC (0.4 g) and copper sulfate pentahydrate (0.55 g) in water (10 ml) were kept under vacuum and TMED (0.5 g) distilled into the flask. The resulting slurry was filtered to give a grey-green powder insoluble in common solvents. Analysis identified it as tetramethylethylene diammonium bis(tetrafluorocatechol) cuprate.

Anal. Calcd. for C\textsubscript{16}H\textsubscript{18}F\textsubscript{6}N\textsubscript{2}O\textsubscript{4}Cu: C, 39.9; H, 2.6; F, 28.1; N, 5.2. Found: C, 40.3; H, 2.7; F, 28.5; N, 5.1.

The infrared spectrum showed peaks at 2610(w), 2360(s,br), 1620(m), 1490(s), 1275(s), 1155(m), 1120(s), 1070(m), 1000(s), 790(w), and 725(m) cm\textsuperscript{-1}.

**Reaction of TFC and GeCl\textsubscript{4} in DMF.**

To TFC (1.0 g) in DMF (25 ml) was added germanium tetrachloride (0.59 g). A white solid formed initially, then redissolved. After stirring 15 min, the volume of the solution was then reduced to 5 ml, and a white solid separated. It was recrystallized from methanol to give bis(dimethylformamide) germanium bis(tetrafluorocatecholate).

Anal. Calcd. for C\textsubscript{18}H\textsubscript{14}F\textsubscript{6}O\textsubscript{4}N\textsubscript{2}Ge: C, 37.4; H, 2.4; F, 26.3; N, 4.8. Found: C, 37.3; H, 2.6; F, 26.5; N, 4.9.

The infrared spectrum showed peaks at 1760(w), 1650(s), 1510(s), 1490(s), 1350(s), 1270(m), 1250(m), 1170(w), 1150(s), 1130(w), 1080(w), 1000(s), 870(w),
760(w), 710(s), and 675(s) cm\(^{-1}\).

Reaction of TBC and Cu(II) in Methanol.

To CuSO\(_4\).6H\(_2\)O (1.2 g) in methanol was added TBC (2.0 g) in methanol. A blue powder precipitated immediately and was found to be insoluble in all ordinary solvents.

Anal. Calcd for C\(_{12}\)O\(_4\)Br\(_8\)Cu\(_2\).2CH\(_3\)OH:  C, 16.2; H, 0.77; Br, 61.6; Cu 12.3. Found C, 16.2; H, 1.3; Br, 62.5; Cu, 10.7.

The infrared spectrum had peaks at 3400(m,br), 2710(s,br), 2510(m), 1540(m), 1425(s), 1390(s), 1350(s), 1300(m), 1260(m), 1240(s), 1200(w), 1175(w), 1140(m), 1020(s), 940(s), 765(m), 745(s), 735(m), 640(w).

Reaction of Catechol with Dichlorodiphenylsilane.

The procedure of Zuckerman\(^{14}\) was followed although it was found that it was necessary to add several ml's of DMF. The above author reports that the reaction was carried out in ether which was assumed to be diethylether. However the fact that DMF was needed and presumably acted as a hydrogen halide acceptor in this case leads to the speculation that Zuckerman had used a higher boiling ether. This would allow the hydrogen chloride to be driven off during reflux.

Anal. Calcd. for C\(_{18}\)H\(_{14}\)O\(_2\)Si:  C, 74.5; H, 4.82; Si, 9.65. Found: C, 74.3; H, 4.98; Si, 9.88.

Reaction of TBC and Dichlorodiphenylsilane.

To TBC (5.32 g) in 60 ml dry ether refluxing under nitrogen was added Ph\(_2\)SiCl\(_2\) (3.16 g). After 1 1/2 h there was no evidence of reaction (colour change or evolution of HCl). DMF (10 ml) was added to the solution and a white precipitate formed immediately which redissolved in the solvent. The solution was refluxed for an additional 1 h. On partial evaporation and
cooling a white crystalline solid precipitated.

This was sublimed unchanged at 140°C under vacuum and was subsequently recrystallized from 30/60 pet ether.

Anal. Calcd. for C₃₀H₂₀Br₄O₃Si₂: C, 44.8; H, 2.49; Br, 39.8; Si, 6.97. Found: C, 45.22; H, 3.02; Br, 40.35; Si, 7.7.

Molecular weight (osmometric in benzene, 759 (mass spectrum highest peak, 80 Calcd, 803.6

Mp 187/1890

The infrared spectrum showed peaks at 3080(w), 1960(w), 1885(w), 1850(w), 1595(m), 1515(m), 1450(m,br), 1420(s), 1370(s), 1330(w), 1315(w), 1255(m), 1205(m), 1130(s), 1120(s), 1015(w), 1005(s), 975(s,br), 820(s), 800(s), 745(s), 725(s), 700(s), and 635(w) cm⁻¹.

Reaction of TFC with Dichlorodiphenylsilane.

The procedure followed was the same as that used for TBC. The white crystalline solid obtained gave no test for fluoride ion after sodium fusion and no F¹⁹ NMR, and was assumed to be a polymeric siloxane.

The same material is formed (ir, mp), in small yield when TBC and Ph₂SiCl₂ are refluxed in ether without DMF.

Reaction of TFC with Tin Tetrachloride in Pyridine.

TFC (0.4 g) was dissolved in freshly distilled pyridine (10 ml). Tin tetrachloride (0.13 ml) was added with swirling. Heat was evolved and a white solid formed. This was recrystallized from CH₂Cl₂/CCl₄.

Anal. Calcd. for C₁₇H₅F₆O₄NSn: C, 36.8; H, 0.90, F, 27.3; N, 2.51. Found: C, 39.8; H, 1.55; F, 28.04; N, 2.70.

Mp 124/125°C.
The infrared spectrum showed peaks at 1910(w), 1610(s), 1490(s),
1465(s), 1355(w), 1250(w), 1205(s), 1070(s), 1050(s), 1025(s), 955(w),
765(s), 690(s) and 655(s) cm$^{-1}$.

**Attempted Preparation of 2-2' Dihydroxyoctafluorobiphenyl.**

The 2-2' dibromo-octafluorobiphenyl was prepared via the method of
Massey et.al.\(^\text{15}\) Two methods were used to prepare the dihydroxy compound
both of which started with the dilithium salt of the dibromide. To
2-2' dibromo octafluorobiphenyl (4.0 g) in anhydrous diethyl ether
(60 ml) at -78\(^0\) was added butyl lithium (6.2 ml of 23% wt %). The
reaction was stirred at -78\(^0\) for 2 1/2 h and became a light yellow colour.
Dry oxygen gas (P\(_2\)O\(_5\)) was bubbled through the solution at -78\(^0\) and the
reaction allowed to slowly reach room temperature. After hydrolysis with
1:3 HCl and extraction with diethyl ether a yellow brown solid was
isolated and sublimed to a white crystalline compound. The compound had
no hydroxyl absorption peaks in the infrared spectrum and was probably
2-2' dihydro octafluorobiphenyl identified by analysis and comparison of
the infrared spectrum with that previously published.

Anal. Calcd. for C\(_{12}\)H\(_2\)F\(_8\): C, 48.3; H, 0.67; F, 50.9. Found: C,
48.1; H, 0.83; F, 50.6.

The second method of preparation\(^\text{16}\) involved adding trimethyl borate
(4.55 g) to the lithium salt (2.0 g dibromide, 4.9 ml BuLi) in ether at -78\(^0\).
The reaction was then allowed to warm to room temperature with stirring. The
solution was extracted with water and the two layers separated. Evaporation
of the ether layer gave a brown oil which crystallized on standing in air.
Sublimation (50\(^\circ\)C) gave a white solid mp 85/87. The ir (nujol) showed a
strong sharp absorption at 3700 cm$^{-1}$. 
Anal. Calcd. for C₁₂H₆F₈BO: C, 44.5; H, 0.0; F, 47.1; B, 3.34. Found: C, 44.4; H, 0.23; F, 47.0; B, 3.16.

The infrared spectrum showed peaks at 3680(s,sharp), 3405(s,br), 3200(s,br), 3100(s,br), 1630(s), 1530(s), 1505(s), 1475(s,br), 1465(s,br), 1415(s), 1320(m), 1280(w), 1210(m), 1165(w), 1140(m), 1095(s), 1060(s), 1020(s), 940(m), 860(s), 810(m), 745(s), 710(w), and 700(m) cm⁻¹.
RESULTS AND DISCUSSION

The success of perfluoropinacol as a ligand can be attributed to the ready formation of an inductive stabilized anion and also to the ability to form a five membered chelate ring. Tetrafluorocatechol is the simplest perfluoroaromatic diol having the same characteristics. There are numerous reports in the chemical literature of complexes of catechol\(^{17}\) (THC), however, Rohrscheid et al. in 196 were the first to isolate bis metal complexes of THC and tetrachlorocatechol (TCC) under carefully controlled and reproducible conditions. Their interest in these complexes lay in the possible existence of an electron transfer series similar to that found for the dithiolene complexes\(^{18}\):

\[
\begin{align*}
\left[ \begin{array}{c}
R \\
C \\
S \\
M/2
\end{array} \right]^{2-} & \rightarrow \left[ \begin{array}{c}
M - S_4
\end{array} \right]^- \rightarrow \left[ \begin{array}{c}
M - S_4
\end{array} \right]_0 \rightarrow \left[ \begin{array}{c}
M - S_4
\end{array} \right]^+
\end{align*}
\]

They were able to show by synthetic means and by polarographic studies that such one electron transfer reactions probably do occur for the bis catecholates although the members of such a series have very limited stability compared with their sulphur and nitrogen containing analogues.

17.
Recently in a report of reactions of tetrafluorobenzene 1,2-dithiol\textsuperscript{19}, a ligand similar to tetrafluorocatechol, it was suggested that this ligand gives complexes of metals in high oxidation states such as nickel(III) and copper(III) but as in the case of the other dithiolene complexes meaningful oxidation states cannot be assigned to the metal atom in a system of this type. Surprising reactivity is shown by this ligand as it forms complexes with finely powdered metals.

Despite many attempts under varying conditions the only complex prepared which had tetrafluorocatechol as the sole ligand on the metal ion was $K_2[Cu(TFC)_2]$, a dark purple solid reversibly forming a green dihydrate. Complex formation was evident (colour change or precipitate formation) in all attempted reactions with metal ions and the products had infrared spectra indicative of coordinated TFC. However they were in most cases too insoluble to purify and decomposed rapidly in the solid form.

Neutral, mixed ligand complexes of nickel could be prepared with nitrogen or phosphorus donors and tetrafluorocatechol, e.g. (TMED)Ni(TFC) where TMED = tetramethylethylene diamine, ($Pe_t_3$)$_2$Ni(TFC) and (diphos)Ni-(TFC) where diphos = 1,2 bis(diphenylphosphino)ethane. These three compounds were brown and diamagnetic, with similar electronic spectra and are assumed to have a square planar configuration from electronic and magnetic considerations\textsuperscript{20}. The TMED complex formed a green, paramagnetic ($\mu_{\text{eff}} = 3.18$ BM) air sensitive dihydrate, having an electronic spectrum characteristic of octahedral nickel(II). The electronic spectrum of the brown anhydrous compound in methanol was identical with that of the green dihydrate in methanol indicating axial coordination of the solvent. The spectrum of the anhydrous complex in methylene chloride
showed only two absorptions at 380 (sh) and 475 m\(\mu\) as did the previously mentioned diamagnetic nickel complexes.

The complex \((TFC)\text{Ni}(1,2 \text{ diphos})\) is light sensitive in solution. A control solution kept in the dark for one week showed only slight decomposition while the solution that was exposed to ordinary room light for the same time decomposed completely.

Several attempts were made to perform an oxidation of the coordinated ligand to tetrafluoro-0-quinone, i.e.

\[
\begin{align*}
\text{F} & \quad \text{O} \quad \text{Ni} \quad \text{PET}_3 \\
\text{O} & \quad \text{PET}_3 \\
\text{PET}_3 & \quad \text{Br}_2 \\
\text{F} & \quad \text{O} \quad \text{Ni} \quad \text{PET}_3 \\
\text{O} & \quad \text{PET}_3 \\
\text{PET}_3 & \quad \text{Br}
\end{align*}
\]

Reactions did occur but the products were too unstable for further investigation.

Efforts were made to produce copper complexes comparable to the nickel compounds. However when tetramethylethylenediamine was added to a copper(II) solution containing TFC in an attempt to prepare \((\text{TMED})\text{Cu}(\text{TFC})\) the amine acted as a base rather than a ligand and the product was characterized as \([\text{H}_2\text{TMED}]^{2+}\text{Cu}(\text{TFC})_2]^{2-}\). (This grey-green complex is insoluble in all common organic solvents.) The elemental analysis allows two other possible formulations; I and II.

The mechanism for ligand oxidation in I is not obvious and the only justification for such a structure would be the infrared absorption at
1620 cm\(^{-1}\) which could be interpreted as a \(C = O\) stretch. However the infrared spectrum of the complex \([(TFC)_2Cu]^+\) also has a peak at 1620 cm\(^{-1}\) and these are best assigned\(^{21}\) to a \(C = C\) mode of the aromatic ring. The structure labelled II is possible although the infrared absorptions above 2300 cm\(^{-1}\) seem to exclude the presence of a hydroxyl group and fall rather in the region expected for amine salts.

Reaction of copper(II) and TFC with triethylphosphine gave a brown oil which could not be crystallized. The infrared spectrum was similar to that of the nickel complex and it is probable that complex formation did occur. Other workers have experienced difficulties in the preparation of copper complexes of phosphines.\(^{22}\)

Tetrafluorocatechol appears to produce a smaller ligand field splitting than similar ligands. The first absorption maximum for \((TFC)_2Cu^+\) occurs at 13,500 cm\(^{-1}\) compared with 14,800 cm\(^{-1}\) for \((TCIC)_2Cu^+\) and \((THC)_2Cu^+\), 15,100 cm\(^{-1}\).\(^{17}\)

On a purely electrostatic ligand field model the above results would be expected, fluorine having a larger inductive effect than chlorine which in turn is more electron withdrawing than hydrogen. However studies on
halogenated phenols\textsuperscript{23} have shown that pentafluorophenol, while it is more acidic than phenol is less acidic than pentachlorophenol. This discrepancy is attributed to the ability of fluorine to donate $\rho$ electron density back into the $\pi$ electron ring system. Although a complete range of compounds is lacking, the substituted phenols and thiophenol\textsuperscript{24} metal complexes reflect this back donation ability of the fluorine atom. Thus thiophenol has a larger Dq value than pentafluorothiophenol (a result of the inductive effect of fluorine) while the Dq value for pentafluorophenol is greater than that for pentachlorophenol illustrating the back donation ability of fluorine. The low value obtained here for TFC is probably the result of a tetragonal field about the copper atom because of the polar nature of the solvent required. The TFC complex has properties similar to those of bis(hexafluoroacetylacetonato)copper(II) which also forms a green hydrated species that can be reversibly dehydrated to a purple compound. Studies by Funck and Ortolano\textsuperscript{25} show that if the visible spectrum of anhydrous bis(hexafluoroacetylacetonato)copper(II) is recorded in chloroform containing trace amounts of ethanol the overall maximum of the band envelope is shifted to lower energy.

For purposes of comparison a brief investigation was made of the properties of tetrabromoacetate (TBC) as a ligand since no report of such complexes has yet appeared. With nickel(II), the complexes $[\text{Me}_4\text{N}]_2^+ [\text{Ni(TBC)}_2]^{2-}$, (TMED)Ni(TBC) and (PET$_3$)Ni(TBC) were isolated as brown diamagnetic crystalline solids considerably more stable\textsuperscript{*} than

\textsuperscript{*} The word stable is used in a general way throughout this thesis to mean resistant to hydrolysis and air oxidation under normal conditions.
either the catechol or TFC nickel complexes. The bis tetrabromocatecholate appears to be able to coordinate two molecules of methanol (the only solvent in which it is even sparingly soluble) to form a yellow paramagnetic solid. The adduct formation is not reversible to the original diamagnetic complex, however, and the abnormally high value for $\mu_{\text{eff}}$ of the yellow compound (5.1 BM) suggests that some decomposition takes place. For the similar complexes (TFC)Ni(TMED) and (TBC)Ni(TMED), the metal atom in the TFC complex apparently carries a larger residual positive charge. No evidence of adduct formation of (TBC)Ni(TMED) with water was noted.

The reaction of TBC with copper sulphate in methanol caused instantaneous precipitation of an insoluble blue solid. Further treatment with base left the complex unchanged. Analysis gave a copper to TBC ratio of 1:1 suggesting a polymeric structure of TBC and copper atoms with solvent present as an impurity.

No compound could be prepared in which three tetrafluorocatechol molecules were chelated around a metal ion, whereas perfluoropinacol readily forms such complexes with $\text{Fe}^{3+}$ and $\text{Al}^{3+}$. Tetrafluorocatechol did, as previously reported, give a blue colouration with iron(III), which provided a sensitive test for the presence of the ligand, but it was difficult to isolate a stable solid adduct. However, addition of tetramethylethylenediamine gave a black complex, soluble in methanol to give an intensely coloured blue solution. Elemental analysis showed the compound to be (TMED)Fe(TFC)$_2$. The magnetic moment (6.1 BM) is close to that of the perfluoropinacol complex of iron(III) (6.0 BM) and in the region usually found for high-spin iron III complexes. The Mössbauer spectrum was also consistent with the presence of iron(III).
To preserve charge balance, the molecule must therefore contain an additional proton. From examination of the infrared spectrum it does not appear that the amine is protonated as complexes of this type, such as \([H_2\text{TMED}]^{2+}[\text{Cu(TFC)}]\)^{2-} described previously together with analogous perfluoropinacol complexes, which have a strong characteristic absorption in the region 2300-2700 cm\(^{-1}\). It is possible that the proton is attached to the oxygen atom of a TFC molecule and probably hydrogen-bonded to a second oxygen atom as shown below.

\[
\begin{align*}
\text{Fe} & \quad \text{(CH}_3\text{)}_2 \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{F} & \quad \text{F}
\end{align*}
\]

The infrared spectrum does not show any absorption assignable with certainty to such a grouping but this is frequently the case with hydrogen bonded hydroxyl groups, e.g. in nickel bis(dimethylglyoxime). Attempts to remove the proton by treatment with base to give an anionic iron complex resulted only in decomposition.

**Non Transition Metals.**

Zuckerman et al. have reported the preparation of diphenylsilicon-catecholate which they claim to be very easily hydrolysed if handled in air. In the present work this reaction was repeated and a good yield of the expected product was obtained. Tetrafluorocatechol was reacted under the same conditions with dichlorodiphenylsilane, dichlorodimethylsilane and silicon tetrachloride. None of the desired products were obtained
with or without the use of an organic base. Reaction of TFC with germanium tetrachloride in dry ether with a hydrogen chloride acceptor (dimethylformamide) gave a completely air stable, almost insoluble white compound which was identified as \((\text{TFC})_2\text{Ge} \cdot 2\text{DMF}\). Germanium complexes of perfluoro-2-hydroxyisobutyric acid also have greater stability than the silicon derivatives.\(^9\) The dimethylformamide molecule is probably coordinated via the carbonyl oxygen atom since the infrared band observed at 1650 cm\(^{-1}\) and assigned to the carbonyl stretch of the DMF molecule has been lowered in energy from the non coordinated position, 1660 cm\(^{-1}\).

A tin derivative could not be prepared by the same method but a product was isolated using pyridine as a solvent. The pale yellow crystalline compound decomposed over a period of days. By analogy with known reactions of THC\(^{30}\) to yield a bis(catechol) tin IV pyridine adduct the compound is expected to be five coordinate, square pyramidal tin(IV).

The reaction of TBC with dichlorodiphenylsilane gave a stable white crystalline compound whose formulation remains an enigma. The elemental analysis would indicate a structure such as:

![Diagram](image)

M.W. 803.6

The additional oxygen required for such a species could have arisen
from inadvertent hydrolysis of a chloro-silane intermediate during the workup. The calculated and observed mass spectrum is in good agreement as to the position of the molecular ion although the observed and predicted percentages of isotopic abundances do not agree. (Table 2)

Overlapping spectra of the molecular ion and other species resulting from loss or gain of a proton could explain this discrepancy. A comparison of the best fit spectrum of composition 72.8%, C₃₀H₂₀O₃Si₂Br₄ and 27.2%, C₃₀H₂₁O₃Si₂Br₄ with the observed spectrum is shown in Table 2.

The rather limited success of TFC as a ligand led to the decision to prepare 2,2′ dihydroxyoctafluorobiphenyl.

This compound should have all the enhanced acidity of pentafluorophenol with extra stability to be gained by chelate ring formation. Also the compound should not be as susceptible to oxidation as TFC. Complexes of the similar ligand 4,4′ dithiooctafluorobiphenyl have been reported. A Two different preparative methods were investigated but neither gave the desired product. However a compound was obtained in small yield by the reaction of the 2,2′ dilithium salt of octafluorobiphenyl with trimethylborate.

Similar derivatives could probably be formed through the reaction of the
### TABLE 2

A Comparison of Observed and Calculated Patterns of Isotopic Abundances for $C_{30}H_{2o}Br_{4}O_{3}Si_{2}$ Spectrum

<table>
<thead>
<tr>
<th>Mass</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>800</td>
<td>13.7</td>
<td>15.6</td>
</tr>
<tr>
<td>801</td>
<td>10.7</td>
<td>6.92</td>
</tr>
<tr>
<td>802</td>
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</tr>
<tr>
<td>810</td>
<td>7.41</td>
<td>2.89</td>
</tr>
</tbody>
</table>

* 100% $C_{30}H_{20}Br_{4}O_{3}Si_{2}$

** 72.8% $C_{30}H_{20}O_{3}Si_{2}Br_{4}$

27.7% $C_{30}H_{21}O_{3}Si_{2}Br_{4}$
dilithium salt with different alkoxides even though the ligand itself is not isolated.
CONCLUSION

The very limited stability of the tetrafluorocatehol complexes was unexpected as previous workers had shown that complete replacement of hydrogen by chlorine in a catechol complex leads to much greater stability. This was found to be true here also for the bromine substituted complexes. Fluorinated aromatic systems are well known for their susceptibility to nucleophilic attack but the difficulties encountered in this study do not seem to result from this since compounds were isolated from alcoholic solutions containing hydroxyl ions. In many cases a complex could be isolated from the reaction but decomposed in the course of a few hours, even when kept under vacuum in the dark. One explanation can be found in the highly polar nature of the carbon-fluorine bond, which, in a system where electron transfer processes may readily occur, could very well lead to elimination of a fluoride ion and consequent decomposition of the complex. It was mentioned previously that the ligand itself decomposes slowly, with evidence of hydrogen fluoride elimination. In view of the limited stability and number of the complexes of tetrafluorocatehol prepared here, it is unlikely that further research would be of benefit.
PART II

Complexes of 2-Amido-hexafluoro-2-propanol
INTRODUCTION

Among the most extensively studied classes of chelating ligands are those of the β-diketones. These ligands, the simplest of which is acetylacetone, form very stable well defined metal complexes eminently suited to the study of magnetic and spectral phenomena related to the electronic configuration of the metal atom. These complexes have also often been used as model systems for studies in kinetics, in structure and in modes of bonding in transition metal complexes. Much of the interest in these ligands is a result of the ability of the molecule to coordinate to a metal in several different ways. These are shown diagramatically below:

![Diagram of ligands]

Diacetamide is a molecule that is isoelectronic and isostructural with acetylacetone with the exception that the central carbon atom has been exchanged for a nitrogen atom. A few complexes of these ligands (diacetamide and dibenzamide) have been reported by Stehly and Kraihanzel.34,35

30.
The sodium salt of the diamide was prepared by reacting the ligand with finely divided sodium metal and to this was added the appropriate anhydrous metal salt. Basing their inferences mainly on infrared data, the authors claim that the ligands are coordinated to the metal atom by the two oxygen atoms. The complexes are air stable but show signs of decomposition in wet solvents. Measurements of the electronic spectra of these complexes show the ligand field generated gave $Dq$ values similar to those found for the acetylacetonates. Other authors have reported in a series of rather curious papers$^{36}$, the preparation of diacetamide complexes with alkali and alkaline earth metals. These compounds appear to contain diacetamide in the keto form, coordinated as a neutral ligand by the carbonyl oxygen atoms.

Originally it was intended to study the complex formation of 1,1,1,5,5,5-hexafluorodiacetamide.$^{37}$ However some preparative difficulties were encountered, namely the apparent decomposition of the diacetamide in mildly basic solution and attention was therefore switched to a similar compound which incorporated the acetamido group of diacetamide with the well known$^{8,9,27}$ complexing ability of a fluorinated alkoxide group. This new compound, 2-acetamido-hexafluoro-2-propanol, was first prepared by Newallis and Rumano wski$^{38}$ by the reaction of hexafluoroacetone with acetamide but they did not investigate its potential as a chelating agent.
The reaction is reversible but the strong inductive effect of the trifluoromethyl groups increases the electrophilicity of the ketone causing the equilibrium to lie to the right. The reaction is a general one and can be extended to include most nucleophiles with reactive protons such as amines, alcohols and hydrogen cyanide. By choosing a nucleophile with an additional functional group capable of metal coordination, various types of chelating ligands could possibly be prepared having donor sets of O₆, S₂O₄ and N₂O₄. A convenient route to ligands with the latter properties would be useful to the study of the depolymerization and stabilization of planar structures reported to come with the replacement of oxygen atoms by sulphur and nitrogen atoms in bis chelate acetylacetone complexes.

In the present work the ligands studied were restricted to the acetamide adduct and the previously unreported benzamide and formamide complexes. There are several methods of bonding available to such ligands, since they have the potential to act either as a mononegative or a dinegative chelate. For example in Figure 3, structure I shows the ligand as bidentate and mononegative with coordination through the oxygen atoms. Enolization with subsequent deprotonation (or loss of the nitrogen proton and electronic rearrangement) gives a ligand which is bidentate and dinegative, as in structure II. Although coordination through the nitrogen atom is less probable since it would involve a strained four membered ring, structure III and the deprotonated structure IV are also possible. By having the advantage of the strongly coordinating fluorine alkoxide group it was hoped that there would be ready formation of a chelate ring. The ability of these complexes to undergo further deprotonation could then be investigated. This type of reaction has been studied by Lions and co-workers with complexes of ligands with extended π systems such as pyridine-2-aldehyde-2 -
FIGURE 3

I

II

III

IV
Treatment of the positively charged complex ion with aqueous base leads to the isolation of the neutral complex.

The recent interest\textsuperscript{41} in lanthanide complexes prompted investigations in this field also.

Most of the early work with the lanthanides was aimed toward the very difficult separation of the elements within the series. The nature of the complexes was of little concern other than their solubility and volatility characteristics since the excellent shielding of the 4f orbitals by the outer filled 5s and 5p electrons left the properties of the metal ion unaffected by changes in environment due to a ligand field. Unlike the transition metal ions, spectral and magnetic measurements of the lanthanide complexes do not yield much information about the compounds themselves. However the lanthanides have the ability to form complexes with unusual structure and coordination numbers of six through ten have been reported.

It has also recently been shown by Forsberg and Wathen\textsuperscript{42} that lanthanide complexes with nitrogen donor ligands are considerably more
stable than was previously supposed, so that there is some need for more data in this field.

The following section is divided into four main parts which discuss the properties of the ligands themselves, complexes of the ligands with first row transition metals, further reactions of the transition metal complexes, and complexes of some lanthanide metals.
PART II
Metal Complexes of Amide-Hexafluorocetone Ligands

Experimental

General. Reactions were carried out according to standard procedures, a nitrogen atmosphere being used where noted. The i.r. spectra were recorded as mulls or as solution on a Beckman model IR-10 instrument. Visible spectra were recorded on a Beckman DK-1 instrument or a Cary model 14. Abbreviations used in describing spectra are: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder. $^{19}$F and $^1$H n.m.r. spectra were recorded on a Varian model HA-100 spectrometer at 100 and 94.1 mHz with reference compounds Freon II and tetramethylsilane. Magnetic moments were determined at room temperature by the Gouy method using Hg[Co(CNS)$_4$] as standard. Melting points are reported uncorrected unless noted. Mass spectra were recorded on a Varian M-66 instrument.

Microanalyses were performed by Alfred Bernhardt Laboratories.

Preparation of 2-Acetamido-hexafluoro-2-propanol.

The ligand was prepared by the method of Newallis and Rumanowski. Hexafluoroacetone was bubbled through a cooled ($\sim 10^0$) solution of acetamide in THF until slightly more than an equimolar ratio had been added. The reaction proceeds quickly and can be monitored by the escape of excess hexafluoroacetone through an outlet oil bubbler. The yield of product is virtually 100% after partial removal of solvent. m.p. 90-92$^0$ corr. $^{19}$F n.m.r. (acetone) spectrum shows a single peak at 82.5 Hz relative to Freon 11. Hereafter the ligand is abbreviated as HAcfp to denote free ligand and Acfp as the complexed form. The infrared spectrum run as a Nujol mull
showed peaks at: 3260(s), 3200(s), 3090(s), 1640(s), 1560(s), 1440(s), 1285(s,br), 1220(s,br), 1190(s), 1160(s), 1070(s), 975(s), 935(s), 810(w), 745(m), 725(s), 640(w), 620(w). When the infrared was run in diethyl ether the bands at 1640 and 1560 cm\(^{-1}\) changed position to 1675 and 1575 cm\(^{-1}\).

Titration of the ligand with standard NaOH in a 50% methanol water solution showed only one removable proton. Equivalent wt. 226, molecular weight calculated, 225. The molar diamagnetic susceptibility \(X_M\) was found to be 61.0 x 10\(^{-6}\).

**Preparation of the Disodium salt of HAcfp.**

Dry THF (20 ml) was added to NaH (1.0 g) in a two necked flask fitted with a nitrogen bubbler and a magnetic stir bar. To this was added HAcfp (40 g) in dry THF (30 ml) slowly with stirring. The reaction was stirred until bubbles of gas were no longer evolved (ca 2 hr). The slurry was filtered and the precipitate collected, redissolved in dry THF and filtered again. Solvent was removed under vacuum until a white crystalline precipitate formed. This was filtered, dried and stored under vacuum. The compound decomposes in moist air.

Anal. Calcd. for \((C_6H_5F_6NO_2)^{2-}Na_2\)\(^+\): C, 22.3; H, 1.12; F, 42.4

Found: C, 22.3; H, 1.38; F, 42.0.

The infrared spectrum had peaks at, 1715(sh), 1670(s,br), 1560(m), 1525(m), 1310(s), 1270(m), 1190(s,br), 1130(m), 1045(s), 1010(w), 960(s), 900(s), 830(w), 800(w), 730(w) and 710(s) cm\(^{-1}\). The \(^{19}\)F n.m.r. showed a single absorption at 75.2 Hz.

**Reaction of Copper(II) with HAcfp.**

Methanolic potassium hydroxide was added with stirring to a solution of HAcfp (4.0 g) and copper sulphate (2.2 g) until the pH reached 8.
The solution was evaporated to dryness, redissolved in THF and filtered, thereby removing the potassium sulphate. The filtrate was partially evaporated and 30-60° pet ether added dropwise to precipitate bright blue crystals. m.p. 180 dec.

Anal. Calcd. for Cu(Acfp)$_2$: C, 23.5; H, 1.56; F, 44.6. Found: C, 23.3; H, 1.35; F, 44.1. The electronic spectrum showed a single broad peak at 640 mμ (ε = 26) when run in acetone and two resolvable bands at 652 mμ and 724(sh) mμ when run as a diffuse reflectance spectrum. The F$^{19}$ n.m.r. spectrum (acetone) showed a single broad peak at 75.2 Hz. Magnetic data, χ = 2.238 x 10^-6, χ_m = 1145 x 10^-6, χ_m' = 1257 x 10^-6 (diamagnetic correction for Acfp made by direct measurement of χ_m for pure ligand in all instances.) μ_{eff} = 1.73 BM (230°).

The infrared spectrum showed peaks at 3580(w), 3420(w), 3200(m), 1615(m), 1585(s), 1530(m,sh), 1345(m), 1305(m), 1285(m), 1210(s), 1110(m), 1075(m), 1025(w), 985(m), 970(s), 920(s), 845(w), 820(m), 750(m), 730(s), 640(w) cm$^{-1}$.

Major peaks found in the mass spectrum were identified as follows:

<table>
<thead>
<tr>
<th>Mass</th>
<th>Fragment</th>
<th>Derivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>444</td>
<td>C$<em>9$H$</em>{10}$F$_6$N$_2$O$_4$Cu$^{63}$</td>
<td>Cu(AcfpH)$_2$-CF$_3$</td>
</tr>
<tr>
<td>442</td>
<td>C$_9$H$_6$F$_3$N$_2$O$_4$Cu$^{63}$</td>
<td>Cu(Acfp)$_2$-CF$_3$</td>
</tr>
<tr>
<td>220</td>
<td>C$_4$H$_6$F$_3$NO$_2$Cu$^{63}$</td>
<td>M(444)-C$_5$H$_4$F$_6$O$_2$N</td>
</tr>
<tr>
<td>218</td>
<td>C$_4$H$_4$F$_3$NO$_2$Cu$^{63}$</td>
<td>M(442)-C$_5$H$_4$F$_6$O$_2$N</td>
</tr>
<tr>
<td>155</td>
<td>C$_4$H$_6$F$_3$NO$_2$</td>
<td>M(218)-Cu$^{63}$</td>
</tr>
</tbody>
</table>

Reaction of Nickel(II) with HAcfp.

The method followed was the same as that used for the copper complex with nickel nitrate the source of nickel ions. The pale green product is
considerably less soluble in methanol and acetone than the copper and cobalt complexes and is almost completely insoluble in THF. Thus it was necessary to recrystallize the crude product repeatedly from methanol. m.p. 190 dec.

Anal. Calcd. for Ni(Acfp)₂: C, 23.2; H, 1.55; F, 44.2. Found: C, 23.2; H, 1.29; F, 44.2. The electronic spectrum, run in acetone, had peaks at 400(s) (ε = 61), 710(br) (ε = 23), and 1135(br) (ε = 11) μ. As a solid the complex had a diffuse reflectance spectrum with peaks at 408, 709 and 1224 μ. The F¹9 n.m.r. spectrum run in acetone showed a single broad peak at 81.3 Hz.

Magnetic data: \( \chi = 6.442 \times 10^{-6} \), \( \chi_m = 3264 \times 10^{-6} \), \( \chi_m' = 3370 \times 10^{-6} \). \( \mu_{\text{eff}} = 2.84 \) BM (23⁰).

The infrared spectrum showed peaks at 3615(w,br), 3440(s), 3300(w,br), 1690(m,sh), 1660(s), 1540(s), 1315(m), 1275(w), 1200(s,br), 1130(m), 1050(s), 960(s), 915(s), 820(m), 740(m), 720(s), 630(w). The mass spectrum showed no peaks assignable to nickel-containing fragments.

**Reaction of Cobalt(II) with H\text{Acfp}**.

The procedure was the same as that for the copper complex with cobalt nitrate as the source of cobalt ions. The initial pink solid obtained from this reaction was found to be a mixture of two components. These could be separated by dissolving the crude product in isopropanol and filtering the insoluble portion (pink solid) from the solution.

Recrystallization from acetone/pet ether yields a pink crystalline solid m.p. 195 dec.

Anal. Calcd. for Co(Acfp)₂: C, 23.2; H, 1.55; F, 44.2. Found: C, 23.1; H, 1.33, F, 43.7. The electronic spectrum run in acetone showed peaks at 490 (ε = 20), 525 (ε = 17), 590 (ε = 13). The diffuse reflectance
FIGURE 4
Molecular Weight Studies of
Cu(Acfp)$_2$ and Co(Acfp)$_2$
spectrum showed poorly resolved peaks at 434, 527 and 584 m\(\mu\). Magnetic data: \(\chi = 19.19 \times 10^{-6}\), \(\chi_m = 9728 \times 10^{-6}\), \(\chi_m' = 9840 \times 10^{-6}\), \(\mu_{\text{eff}} = 4.85\) BM (23\(^0\)).

The infrared spectrum showed peaks at 3440(s), 1655(s), 1534(s), 1314(s), 1275(m), 1200(s,br), 1117(m), 1042(s), 960(s), 813(w), 716(m), 717(s), and 626(w) cm\(^{-1}\).

The mass spectrum contained major peaks assignable as follows:

<table>
<thead>
<tr>
<th>Mass</th>
<th>Fragment</th>
<th>Derivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>507</td>
<td>(\text{C}_{16}\text{H}<em>8\text{F}</em>{12}\text{N}_2\text{O}_4\text{Co})</td>
<td>parent ion</td>
</tr>
<tr>
<td>438</td>
<td>(\text{C}_{9}\text{H}_8\text{F}_9\text{N}_2\text{O}_4\text{Co})</td>
<td>(\text{M(507)-CF}_3)</td>
</tr>
<tr>
<td>272</td>
<td>(\text{C}_{6}\text{H}_8\text{F}_3\text{N}_2\text{O}_2\text{Co})</td>
<td>(\text{M(438)-(CF}_3\text{)}_2\text{CO})</td>
</tr>
<tr>
<td>229</td>
<td>(\text{C}_4\text{H}_5\text{F}_3\text{N}_2\text{O}_2\text{Co})</td>
<td>(\text{M(272)-CH}_3\text{CO})</td>
</tr>
<tr>
<td>156</td>
<td>(\text{C}_2\text{F}_3\text{OCO})</td>
<td>(\text{M(229)-C}_2\text{H}_5\text{N}_2\text{O})</td>
</tr>
</tbody>
</table>

During the preparation of \(\text{Co(Acftp)}_2\) it was noted that the crude product was a mixture of pink \(\text{Co(Acftp)}_2\) and a mauve compound. This was thought to be a cobalt(III) compound produced by air oxidation during the reaction and work up. In order to get a better yield, the cobalt salt and excess ligand were dissolved in methanol and a methanolic potassium hydroxide solution was added to pH 8. Air was then bubbled through the solution for twelve hours. The solution was then evaporated to dryness, redissolved in tetrahydrofuran and filtered. The filtrate was concentrated and 30-60 pet ether added to precipitate a mauve compound.

The analysis corresponded to a compound of composition \([\text{Co(Acftp)}_3]^-\text{K}^+\cdot\text{THF}\)

Calcd: C, 27.1; H, 2.38; F, 40.6. Found: C, 27.6; H, 2.71; F, 40.4.

m.p. 108-110 dec.

The electronic spectrum run in acetone had peaks at 485 (\(\varepsilon = 13\)) 515 (\(\varepsilon = 13\)), 595 (\(\varepsilon = 14\)) m\(\mu\). Magnetic Data: The compound was para-
magnetic but the magnetic moment was not reproducible.

The infrared spectrum had peaks at 3315(s,br), 3030(w), 1630(s,br), 1535(s), 1310(s), 1275(s), 1200(s,br), 1140(w), 1050(s), 965(s), 916(s), 880(m), 815(m), 740(m), and 720(s) cm\(^{-1}\).

**Reaction of HAcfp with Zinc(II).**

The procedure followed was similar to that used for Cu(Acfp)\(_2\). The crude material usually contains a gummy impurity which can be sublimed out of the white solid at 60° under vacuum. The residue can then be re-crystallized from tetrahydrofuran/pet ether.

**Anal. Calcd. for Zn(Acfp)\(_2\):** C, 23.5; H, 1.56; F, 44.6. **Found:** C, 23.6; H, 1.71; F, 44.8. The F\(^{19}\) n.m.r. showed a single peak at 81.6 Hz.

The infrared spectrum showed peaks at 3450(m), 3170(m), 3080(m), 1680(s,br), 1575(s), 1530(s), 1315(s), 1275(m), 1200(s,br), 1135(s), 1050(s), 965(s), 905(s), 830(w), 810(m), 735(m) and 715(s) cm\(^{-1}\).

**Reaction of HAcfp with Iron(III).**

To a solution of FeCl\(_3\) (0.43 g) and HAcfp (2.0 g) in methanol (20 ml) was added a 50% ammonium hydroxide-methanol solution dropwise with stirring to a pH of 9. Diethyl ether was then added to precipitate ammonium chloride and the solution was filtered. The filtrate was evaporated to dryness under vacuum, redissolved in diethyl ether and filtered through anhydrous magnesium sulphate. Pet ether (30-60) was added to the cloud point and pale green crystals formed on standing. These were collected on a glass filter and dried briefly under vacuum. m.p. dec. begins 130°.

**Anal. Calcd. for Fe(Acfp)\(_2\):** C, 24.7; H, 1.65; F, 47.0. **Found:** C, 24.8; H, 1.71; F, 46.7. The electronic spectrum run in methanol showed a peak 450 m\(_{\mu}\). The remainder of the spectrum was obscured by a charge transfer band.
Magnetic data: $\chi = 18.32 \times 10^{-6}$, $\chi_m = 13330 \times 10^{-6}$, $\chi_m' = 13500 \times 10^{-6}$, $\mu_{\text{eff}} = 5.68$ BM (23°).

The infrared spectrum had peaks at 3440(s), 1620(s,br), 1535(s,br), 1320(s), 1200(s,br), 1070(s), 1035(w), 970(s), 935(s), 830(m), 750(m), 725(s), 670(w), and 645(w) cm$^{-1}$.

Major peaks in the mass spectrum were found as follows:

<table>
<thead>
<tr>
<th>Mass</th>
<th>Fragment</th>
<th>Derivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>504</td>
<td>Fe(Acfp)$_2$</td>
<td>Fe(Acfp)$_3$-Acfp</td>
</tr>
<tr>
<td>338</td>
<td>Fe(Acfp)C$_2$H$_4$NO</td>
<td>M(504)-HFA</td>
</tr>
<tr>
<td>172</td>
<td>Fe(C$<em>4$H$</em>{10}$N$_2$O$_2$)</td>
<td>M(338)-HFA</td>
</tr>
</tbody>
</table>

Reaction of HAcfp with Tetrakis-triphenylphosphine Platinum (0).

Tetrakis-triphenylphosphine platinum (1.0 g) was dissolved in dry tetrahydrofuran. To this was added dropwise under a nitrogen atmosphere HAcfp (4.0 g) in tetrahydrofuran. The reaction mixture was warmed to 60°C and allowed to react for 48 h during which time the original deep yellow colour faded. After partial evaporation of the solvent, 30-60 petroleum ether was added to cause precipitation of a white solid. Successive crops were obtained by cooling and adding more ether. The complex was recrystallized from a benzene/pentane mixture m.p. 183 dec. The $F^{19}$ n.m.r. spectrum showed a triplet of doublets with additional fine structure, centred at 67.0 ppm. The molecular weight determined osmometrically in benzene was 920. The infrared spectrum had peaks at 1950(w), 1895(w), 1815(w), 1760(w), 1665(m), 1605(m), 1590(m), 1570(m), 1480(s), 1430(s), 1375(m), 1300(s), 1270(s), 1150(s,br), 1095(s), 1030(m), 1000(m), 970(m), 970(m), 970(s), 850(s), 740(s), 700(s), 620(w), and 630(w) cm$^{-1}$.

Anal. Calcd. for C$_{39}$H$_{30}$F$_6$OP$_2$Pt: C, 52.8; H, 3.39; F, 12.89; N, 0.0;
P, 7.00. Found: C, 52.8; H, 3.59; F, 12.6; N, 0.38; P, 6.59.

**Attempted Reaction of HAcfp with Chromium(III), Iron(II), and Manganese(III).**

The previously used methods did not give complexes of HAcfp with chromium(III), iron(II), or manganese(III). Thus standard methods for reactions of acetylacetone with metals were tried. Chromium(III) chloride was heated with HAcfp in the presence of aqueous urea for 48 h. The starting materials were unchanged. Ferrous chloride and HAcfp were dissolved in a sodium acetate buffer. Addition of ammonia caused precipitation of ferric hydroxide.

A solution of manganese(II) chloride and HAcfp was treated with potassium permanganate in an attempt to prepare Mn^{III}(Acfp)$_3$. Only manganese dioxide was produced.

HAcfp was reacted with both nickel tetracarbonyl and chromium hexacarbonyl but no isolable products were obtained.

**Reaction of HAcfp with Copper Sulphate and Tetramethylethylenediamine.**

Copper sulphate (2.22 g) and HAcfp (2.0 g) were dissolved in methanol (60 ml). Tetramethylethylenediamine was added dropwise with stirring to pH 8. The solution was then filtered, evaporated to dryness and redissolved in dry methanol. Undissolved solids were filtered from the solution. After reducing the volume of solution by half, the concentrated solution was added dropwise to a large quantity of rapidly stirred dry acetone. The hydroscopic blue crystals that precipitated were quickly filtered from the solution and dried under vacuum. The material gave a white precipitate when treated in methanol with aqueous barium chloride.
Anal. Calcd. for C$_{22}$H$_{20}$O$_8$F$_{12}$N$_6$SCu: C, 29.2; H, 4.43; F, 25.3. Found: C, 29.1; H, 4.53; F, 24.9. The electronic spectrum run in acetone showed a single peak at 630 m$_
u$.

The infrared spectrum showed peaks at 3220(s,b), 1680(m), 1635(s,br), 1575(m), 1525(m), 1320(w), 1300(w), 1275(w), 1180(s,br), 1130(m), 1045(s), 965(s), 920(s), 800(m), 760(w), and 710(s) cm$^{-1}$.

When the anion was exchanged for PF$_6^-$, dark purple crystals of [(TMED)Cu(Acfp)]$^+$PF$_6^-$ were obtained. The electronic spectrum showed a single peak at 620 m$_
u$ (methanol)(ε = 11).

Anal. Calcd. for C$_{11}$H$_{20}$O$_2$F$_{12}$N$_3$PCu: C, 24.1; H, 3.65; F, 41.6. Found: C, 24.3; H, 3.77; F, 41.4.

Reaction of Cu(Acfp)$_2$ with Sodium Hydride.

Cu(Acfp)$_2$ (10 g) in dry tetrahydrofuran was added slowly with stirring to a slurry of excess sodium hydride in tetrahydrofuran. Bubbles of gas evolved vigorously while the solution was allowed to stir under nitrogen for two hours. As the reaction proceeded the blue colour of the copper complex faded and a dark blue precipitate formed. When the reaction was complete the blue solid was filtered from the solution, washed with dry tetrahydrofuran and dried immediately under vacuum. The compound decomposes quickly in moist air to a black solid.
Anal. Calcd. for C_{14}H_{14}O_{5}F_{12}N_{2}Na_{2}Cu: C, 28.2; H, 2.35; F, 38.4. Found: C, 28.6; H, 2.56; F, 39.9.

The infrared spectrum showed peaks at 1665(s), 1595(s), 1335(s), 1285(s), 1160(s,br), 1105(s), 1050(s), 960(s), 910(s), 805(w), 735(w), 715(s) cm\(^{-1}\).

**Attempted Reaction of Ni(Acfp)\(_2\) and Zn(Acfp)\(_2\) with Sodium Hydride.**

To a slurry of Ni(Acfp)\(_2\) in dry tetrahydrofuran was added a 10% excess of sodium hydride. The reaction was stirred under nitrogen for three hours. The solution was then filtered and the yellowish filtrate evaporated to dryness. Acetone was added to dissolve the solid and more insoluble material filtered from the solution. The filtrate was again evaporated to dryness and redissolved in tetrahydrofuran. The addition of 30-60 pet ether caused a white solid to precipitate. The infrared spectrum was the same as that for (C\(_5\)H\(_5\)F\(_6\)NO\(_2\))\(^{2+}\)Na\(^+\) and the coloured solution obtained when added to copper sulphate in methanol was also identical with the colour obtained with (C\(_5\)H\(_5\)F\(_6\)NO\(_2\))\(^{2+}\)Na\(^+\). The white compound did not give a positive test with dimethylglyoxime for nickel(II).

The zinc complex decomposed when treated in a similar manner.

**Reaction of Cu(Acfp)\(_2\)Na\(_2\).THF with Acetone.**

The copper complex was dissolved in acetone and the insoluble material filtered from the solution. (This appeared to be mainly copper hydroxide). The blue filtrate was concentrated and pet ether added dropwise to induce precipitation of a pale blue solid. The material could be recrystallized unchanged only from acetone. m.p. 147 dec.

The infrared spectrum had peaks at 1720(s), 1600(s), 1390(s), 1345(s), 1300(s), 1225(w), 1208(m), 1170(s,br), 1105(s), 1020(w), 955(s), 912(s), 810(w), 722(m), 711(s), and 630(w) cm\(^{-1}\).

The same reaction could be carried out using methyl ethyl ketone in place of acetone. m.p. 180 dec.

Anal. Calcd. for C\(_{16}\)H\(_{11}\)O\(_6\)F\(_{12}\)N\(_2\)Na\(_2\)Cu: C, 30.9; H, 3.15; F, 32.6. Found: C, 30.7; H, 3.28; F, 32.2.

The infrared spectrum had peaks at 1715(s), 1600(s), 1460(m), 1385(m), 1340(m), 1290(m), 1210(m), 1180(s,br), 1110(s), 1020(w), 960(s), 920(s), 810(w), 740(w), and 720(s) cm\(^{-1}\).

The reaction was repeated using ethylacetate and although a analysis was not carried out, the infrared spectrum indicated a compound essentially the same as the previous ones, with peaks at 1735(s), 1635(w), 1600(s), 1460(s), 1380(s), 1350(s), 1300(s), 1270(s), 1210(s), 1175(s,br), 1110(s), 960(s), 920(s), 845(w), 815(w), 740(w) and 720(s) cm\(^{-1}\).

In order to react hexafluoroacetone with the copper complex it was necessary to use a sealed glass tube. The copper complex suspended in tetrahydrofuran was placed in the tube and excess hexafluoroacetone was distilled into the reaction vessel. This was then sealed and allowed to warm to room temperature with occasional shaking. After four hours the tube was opened and the solution removed and filtered. Pentane saturated with hexafluoroacetone was added to cause precipitation of a blue complex. In order to recrystallize the complex it was necessary to use solvents (THF and pentane) saturated with hexafluoroacetone. m.p. 114-115.

Anal. Calcd. for C\(_{16}\)H\(_6\)F\(_{24}\)O\(_6\)N\(_2\)Na\(_2\)Cu: C, 21.6; H, 0.68; F, 51.4. Found: C, 21.4; H, 1.65; F, 54.5.
The infrared spectrum had peaks at 3440(w), 1680(s), 1630(w), 1530(s), 1310(m,br), 1275(w), 1200(s,br), 1100(w), 1050(m), 965(s), 910(s), 845(w), 805(w), 735(m), and 715(s) cm\(^{-1}\).

**Reaction of Formamide with Hexafluoroacetone.**

The method was identical to that used in the preparation of 2-acetamido-hexafluoro-2-propanol. The yield was virtually 100% of the white crystalline solid. Titration with .1N potassium hydroxide showed an equivalent weight of 215, molecular weight, 211. m.p. 119/121.

Anal. Calcd. for \(\text{C}_4\text{H}_3\text{O}_2\text{F}_6\text{N}\): C, 22.7; H, 1.42; F, 54.1. Found: C, 22.6; H, 1.54; F, 54.3.

Infrared peaks were found at 3240(s,br), 3110(s,br), 2600(m), 1675(s), 1500(s), 1415(w), 1350(m), 1280(s,br), 1200(s,br), 1060(s), 965(s), 840(m), 795(m), 740(m), 715(m), and 640(m) cm\(^{-1}\).

Preliminary investigations indicated that the ligand also forms a salt with sodium hydride.

**Reaction of 2-Formamido-hexafluoro-2-propanol with Copper(II).**

The method followed was the same as that used for the preparation of \(\text{Cu(Acfp)}_2\). The blue solid isolated was insoluble in THF but could be recrystallized from methanol.

Anal. Calcd. for \(\text{C}_6\text{H}_4\text{O}_4\text{F}_{12}\text{N}_2\text{Cu}\): C, 19.9; H, 0.83; F, 47.2. Found: C, 19.5; H, 0.67; F, 46.9.

Magnetic data: \(\chi = 2.85 \times 10^{-6}\), \(\chi_m = 1383.0 \times 10^{-6}\), \(\chi_m' = 1553.9 \times 10^{-6}\) (diamagnetic correction by Pascals' constants); \(\mu_{\text{eff}} = 1.92\) BM (21\(^{\circ}\)).

The infrared spectrum had peaks at 3400(m,br), 3190(m), 2640(s,br), 1640(s), 1585(s,br), 1405(m), 1310(s,br), 1270(s,br), 1200(v,s,br), 1050(s), 1025(s), 970(s), 870(m), 850(m), 760(w), 725(s), and 670 cm\(^{-1}\).
The compound was allowed to react with sodium hydride in the presence of acetone (the complex being insoluble in tetrahydrofuran). The blue compound isolated decomposed very rapidly preventing further investigation. **Reaction of N-Methyl-Acetamide with Hexafluoroacetone.**

In the paper by Newallis and Rumanowski it was stated that adduct formation does not occur with secondary amides. This was found to be the case in the present instance also. **Attempted Reaction of Trifluoroacetamide by Hexafluoroacetone.**

Trifluoroacetamide was reacted with hexafluoroacetone both by bubbling the gas through a solution of the amide and by a sealed tube reaction. No product could be isolated and only starting materials were recovered. N-methyl trifluoroacetamide prepared by the method of Husted and Ahlbrechts also did not condense with hexafluoroacetone. **Reaction of Benzamide with Hexafluoroacetone.**

The reaction was carried out in dry tetrahydrofuran in the same manner as for HAcfp. The crude product was obtained in 80% yield but recrystallization caused decomposition of the ligand to hexafluoroacetone and benzamide. The ligand is also not stable at room temperature but slowly evolves hexafluoroacetone. m.p. sealed tube 69-70°.

Anal. Calcd. for C₁₀H₁₈O₂NF₆: C, 41.8; H, 2.44; F, 39.8. Found: C, 43.5; H, 2.40; F, 30.2. Equivalent weight: calcd. 287; found 293. It is obvious that the ligand had partially decomposed during the above measurements.

By reacting the ligand 2-benzamido-hexafluoro-2-propanol with metal ions in basic methanol solution, compounds analogous to those of Acfp were obtained. However these were considerably less stable and, reflecting the nature of the ligand used, decomposed over several days. The analysis
figures for these complexes indicate their unstable nature.

<table>
<thead>
<tr>
<th></th>
<th>Expected</th>
<th></th>
<th></th>
<th>Found</th>
</tr>
</thead>
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<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>F</td>
<td>C</td>
</tr>
<tr>
<td>Cu(Bzfp)$_2$</td>
<td>37.8</td>
<td>1.89</td>
<td>35.8</td>
<td>38.7</td>
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<tr>
<td>Co(Bzfp)$_2$</td>
<td>38.0</td>
<td>1.90</td>
<td>36.2</td>
<td>34.11</td>
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<tr>
<td>Ni(Bzfp)$_2$</td>
<td>38.01</td>
<td>1.90</td>
<td>36.2</td>
<td>35.3</td>
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</table>

Infrared spectra were similar to those of the Acfp complexes.

When the copper complex was heated under vacuum, the volatile portion collected had an infrared spectrum with peaks at 3100(w), 1740(s), 1450(m,br), 1380(s), and 1210(s,br) cm$^{-1}$.

**Reaction of HAcfp in Methanol with the Lanthanides La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm and Yb.**

The following general method was found to be applicable to the formation of complexes of all of the above lanthanides. Erbium chloride (1.0 g) was dissolved in methanol (20 ml) and HAcfp (1.8 g) added with stirring. A 50% solution of ammonium hydroxide in methanol was added to pH9. Ammonium chloride was precipitated by the addition of diethyl ether to the solution. After filtration the solution was evaporated to dryness, redissolved in diethyl ether and the remaining ammonium chloride filtered from the solution. The addition of benzene to the cloud point with subsequent slow evaporation gave long needles of a pale pink crystalline complex. All of the complexes appeared to be of the same type except the cerium complex. Analyses, melting points and colours are given in Table 3. Magnetic data are reported where there was a sufficient amount of complex available for study. The infrared spectrum of the erbium complex, shown
<table>
<thead>
<tr>
<th>Complex</th>
<th>Calculated</th>
<th>Found</th>
<th>Colour</th>
<th>M.P.</th>
<th>Comments</th>
<th>F/C</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>C  H  F  N</td>
<td>C  H  F  N</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>La</td>
<td>20.9 1.82 36.0 5.54</td>
<td>21.2 2.13 36.2 6.02</td>
<td>white</td>
<td>67-68</td>
<td>hygroscopic diamagnetic</td>
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<tr>
<td>Pr</td>
<td>21.3 1.78 35.7 -</td>
<td>21.5 1.80 37.2 -</td>
<td>pale green</td>
<td>70-71</td>
<td>hygroscopic</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>μ = 3.03 BM</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>20.7 1.80 35.7 -</td>
<td>20.8 1.95 35.9 -</td>
<td>pale blue</td>
<td>102</td>
<td>hygroscopic</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>μ = 3.08 BM</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>20.5 1.78 35.4 -</td>
<td>20.6 2.13 35.5 -</td>
<td>cream</td>
<td>64-65</td>
<td>hygroscopic</td>
<td>1.09</td>
</tr>
<tr>
<td>Eu</td>
<td>20.4 1.78 35.3 5.41</td>
<td>20.6 1.65 35.5 4.80</td>
<td>white</td>
<td>92-94</td>
<td></td>
<td>1.09</td>
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<tr>
<td>Tb</td>
<td>20.1 1.98 34.8 -</td>
<td>20.1 1.81 35.1 -</td>
<td>white</td>
<td>235d</td>
<td></td>
<td>1.09</td>
</tr>
<tr>
<td>Dy</td>
<td>20.1 1.75 34.7 -</td>
<td>20.3 1.61 36.3 -</td>
<td>white</td>
<td>143-145</td>
<td>μ = 10.8</td>
<td>1.12</td>
</tr>
<tr>
<td>Ho</td>
<td>20.0 1.75 34.6 -</td>
<td>20.1 1.57 35.5 -</td>
<td>pale orange</td>
<td>250d</td>
<td></td>
<td>1.11</td>
</tr>
<tr>
<td>Er</td>
<td>19.9 1.74 34.4 -</td>
<td>19.6 1.93 34.2 -</td>
<td>pink</td>
<td>250d</td>
<td>μ_{eff} = 9.80</td>
<td>1.10</td>
</tr>
<tr>
<td>Yb</td>
<td>19.8 1.72 34.2 -</td>
<td>20.0 1.63 35.4 -</td>
<td>white</td>
<td>255d</td>
<td></td>
<td>1.12</td>
</tr>
</tbody>
</table>

Average Calcd. 1.10
FIGURE 5

Molecular Weight Studies of Er₂(Acfp)₄(OH)₂ acetamide

M.Wt.

1400

1300

1200

1100

1000

900

800

700

600

500

(x x 10³)

concentration gm/gm
in Figure 14 is typical of the spectra for the lanthanide complexes. The lanthanum complex had a F\(^{19}\) n.m.r. spectrum which showed 2 peaks centred at 81.4 and 82.1 ppm.

A cerium complex prepared in the same way as the other lanthanides using cerium(III) nitrate was isolated as pale yellow crystals. m.p. 118.

Anal. Calcd. for Ce(Acfp)\(_4\): C, 23.2; H, 1.55; F, 44.1. Found: C, 23.4; H, 1.69; F, 43.9. The complex was diamagnetic and the F\(^{19}\) n.m.r. spectrum showed a single peak at 80.7 Hz. The H\(^1\) spectrum showed a poorly resolved peak at 2.75 ppm. The infrared spectrum showed peaks at 3440(s), 1650(s,br), 1570(m), 1530(s,br), 1430(m), 1310(s), 1280(s), 1200(s,br), 1070(s), 1020(w), 965(s), 925(s), 825(m), 740(s), 720(s), 650(m) and 615(w) cm\(^{-1}\).

Preparation of [M(Acfp)\(_4\)]\(^{-}\)NH\(_4\)\(^+\)  M = Er, Dy.

2-Acetamido-hexafluoro-2-propanol (0.94 g) was added to 20 ml of distilled water. Ammonium hydroxide was added dropwise with stirring until solution was complete. This was then added very slowly with stirring to an aqueous solution of erbium chloride (0.2 g). The pale pink precipitate was filtered from the solution and dried under vacuum. The compound could not be recrystallized unchanged from acetone or methanol and was not readily soluble in diethyl ether. The white dysprosium complex was prepared in a similar manner.

Anal. Calcd. for C\(_{20}\)H\(_{20}\)F\(_{24}\)N\(_5\)O\(_8\)Er: C, 22.2; H, 1.86; F, 42.2; N, 6.46. Found: C, 22.9; H, 1.75; F, 42.9; N, 6.74. The complex had a magnetic moment of 9.80 B.M. Infrared peaks were found at 3440(s), 3380(m,br), 3280(m), 1670(s,br), 1540(s,br), 1450(s,br), 1310(s,br), 1280(s,br), 1175(s,br), 1090(m), 1050(s), 950(s), 910(s), 805(w), 730(w) and 710(s) cm\(^{-1}\).

Anal. Calcd. for C\(_{20}\)H\(_{20}\)F\(_{24}\)N\(_5\)O\(_8\)Dy: C, 22.3; H, 1.84; F, 42.3; N, 6.50.
Found: C, 22.3; H, 1.46; F, 41.9; N, 6.33. The complex had a magnetic moment of 10.6 B.M. The infrared spectrum was the same as for the erbium complex.
RESULTS AND DISCUSSION

A. Investigation of Ligands.

Before attempting to prepare metal complexes the properties of the ligands were investigated since little more than analysis figures were given in the report of their synthesis. All three of the compounds 2-acetamido, 2-formamido and 2-benzamido-hexafluoro-2-propanol (HAcfp, HFmfp and HBzfp) were isolated from the reaction of the amide and hexafluoroacetone as white, crystalline, hygroscopic solids. The general properties of HAcfp are representative of all three and will be discussed first.

Titration of HAcfp with standard aqueous potassium hydroxide solution revealed that the compound acted as a mono basic acid with an approximate pKa of 8.3 Several structures can be drawn for HAcfp and these are shown in Figure 7.

The infrared spectrum of HAcfp run in nujol indicates that in the solid both the hydroxyl group and the nitrogen-hydrogen group are hydrogen bonded. Free hydroxyl stretching vibrations are generally found as sharp absorptions occurring at 3640-3610 cm\(^{-1}\). Free nitrogen hydrogen stretching modes are also sharp and are found at 3500-3400 cm\(^{-1}\).\(^{43}\) Hydrogen bonding lowers and broadens both of these characteristic absorptions so that complete identification is impossible. It is probable that the peak observed at 3260 cm\(^{-1}\) corresponds to the hydrogen bonded hydroxyl stretch and the absorption at 3090 cm\(^{-1}\) indicates a hydrogen bonded N-H stretch (Figure 6). Of the structures shown in Figure 7 structure I can be discarded as chemically unrealistic. Structure III does not contain a nitrogen-hydrogen bond which was found to be present by the infrared spectrum.
FIGURE 7

I

II

III

IV
FIGURE 7 (continued)

\[ \text{di-Na salt} \]

\[
\begin{align*}
\text{VI} & \quad \text{VII} \\
\begin{array}{c}
\text{CH}_3 - \overset{\text{C}}{\text{N}} - \overset{\text{O}}{\text{C}} - \overset{\text{N}}{\text{C}} - \overset{\text{CF}_3}{\text{CF}_3} \\
\text{CH}_3 - \overset{\text{C}}{\text{C}} - \overset{\text{N}}{\text{C}} - \overset{\text{O}}{\text{O}} - \overset{\text{CF}_3}{\text{CF}_3}
\end{array}
\end{align*}
\]

\[
\text{VIII}
\]

\[
\begin{array}{c}
\text{CH}_3 - \overset{\text{C}}{\text{C}} - \overset{\text{N}}{\text{C}} - \overset{\text{O}}{\text{O}} - \overset{\text{CF}_3}{\text{CF}_3}
\end{array}
\]
Structure IV contains a strained four membered ring and would not be energetically favourable. The second structure would appear to be the most probable. The formation of the six membered ring would help to stabilize the adduct and the proton on the nitrogen atom could well be hydrogen bonded to an adjacent molecule.

Infrared studies of amides are usually carried out to study the effects of the combination of the carbonyl group with the amido group. Three distinct features can be identified in the infrared spectra of secondary amides,\textsuperscript{43} the amide I, II and III vibrations which refer to the carbonyl stretching frequency (1680-1640 cm\textsuperscript{-1}), the nitrogen-hydrogen bending absorption (1570-1530 cm\textsuperscript{-1}) and the carbon-nitrogen stretch (1300-1260 cm\textsuperscript{-1}) respectively. In the present case the strong absorption at 1640 cm\textsuperscript{-1} can be identified as the amide I band while the peak at 1560 cm\textsuperscript{-1} corresponds to the amide II band. Bands in the 1200-1300 cm\textsuperscript{-1} region overlap with the very strong carbon-fluorine stretching region and cannot be assigned with any authority. The ligand is not soluble in non polar and weakly polar solvents which prevented a more complete study of the infrared spectrum. However a dilute solution of HAcfp in diethyl ether gave somewhat better resolution in the 3000 cm\textsuperscript{-1} region (Figure 8). The weak band at 3540 cm\textsuperscript{-1} must belong to an intra-molecular weakly hydrogen bonded hydroxyl stretch since it occurs at too great an energy to be a free nitrogen stretch. The next highest peak at 3410 cm\textsuperscript{-1} is only slightly decreased from a free nitrogen hydrogen stretch (3440 cm\textsuperscript{-1}). The amide I band has increased to 1675 cm\textsuperscript{-1} indicating a decrease in the amount of intermolecular hydrogen bonding although the value is still considerably lower than the values for free carbonyl groups. On the basis of this infrared data it can be assumed that in dilute solution the molecule
exists as a 6 membered ring with the hydroxyl proton hydrogen bonded to the carbonyl oxygen, a structure commonly found in the \( \beta \)-diketones.\(^{33}\)

\[
\begin{align*}
\text{CH}_3 & \text{C} \quad \text{N} \quad \text{CF}_3 \\
\text{O} & \quad \text{O} \quad \text{C} \quad \text{CF}_3
\end{align*}
\]

Treatment of HAcfp with sodium hydride in dry tetrahydrofuran gave the desired disodium salt. The infrared spectrum revealed very little absorption in the 4000-3000 cm\(^{-1}\) region indicating that both protons had been removed. Referring again to Figure 7, two structures (VI) and (VII) can be drawn for the disodium salt which are resonance hybrids. Structure (VIII) is probably the best representation of these two. The amido grouping has been shown twisted away from the negative oxygen atom to minimize electrostatic repulsion. The 1500-1750 cm\(^{-1}\) region in the infrared spectrum is complicated by the presence of two peaks in the carbonyl region (1715 and 1670 cm\(^{-1}\)) and two peaks in the amido resonance region (1560 and 1525 cm\(^{-1}\)). A more complete assignment is not possible.

The disodium salt appeared to be stable under anhydrous conditions although the ligand itself lost hexafluoroacetone over a period of several months.

The reaction with hexafluoroacetone was next extended to include a number of different amides, the most successful of which was the reaction with formamide. The resulting product 2-formamido-hexafluoro-2-propanol was a white crystalline solid that decomposed considerably more slowly than the acetamide adduct. The infrared spectrum run in nujol showed the typical
pattern of hydrogen bonded nitrogen-hydrogen and hydroxyl stretches in the region 3000-3300 cm\(^{-1}\). The amide I band (the carbonyl stretch) occurred at a slightly higher frequency, 1675 cm\(^{-1}\), than in the acetamide adduct, possibly a result of the difference in inductive effect of a hydrogen atom versus a methyl group. The amide II band is found at 1500 cm\(^{-1}\) in this case at a slightly lower frequency than in the acetamide complex. The molecule acted as a mono-basic acid upon titration with aqueous base and so was expected to serve as a suitable bidentate ligand with metal atoms. Treatment of the ligand with sodium hydride gave the expected disodium salt.

The reaction of benzamide with hexafluoroacetone was somewhat less encouraging. The product could be isolated as a crystalline solid but analytical figures indicate that the compound lost hexafluoroacetone rapidly. Titration with base gave a definite but irreproducible endpoint, corresponding roughly to the molecular weight. However, it was hoped that complex formation once achieved would stabilize the adduct.

Newallis and Rumanowski had stated in their earlier work\(^{38}\) that secondary amides did not undergo the reaction with hexafluoroacetone and this was confirmed in the present work. Neither N-methyl acetamide nor N-methyl-trifluoroacetamide formed an adduct with hexafluoroacetone. It has been reported\(^{44}\) that the major effect of alkylation on an amide nitrogen is steric hindrance to further reaction at the nitrogen atom rather than enhancement of the donor properties of the amide. The attempted reaction of trifluoroacetamide with hexafluoroacetone also resulted in failure which could be expected, since the strong inductive effect of the trifluoromethyl group would also greatly decrease the donor ability of the nitrogen atom.
B. Transition Metal Complexes.

The most extensive study reported in this work centered on the metal complexes which 2-acetamido-hexafluoro-2-propanol formed with Fe(III), Co(II), Ni(II), Cu(II), and Zn(II). Some effort was made to prepare complexes with metals from the first half of the transition series but these did not form as readily. Lanthanide complexes are discussed separately in the last section of this thesis.

(i) Preparation

The neutral complexes Fe(Acfp)$_3$, Co(Acfp)$_2$, Ni(Acfp)$_2$, Cu(Acfp)$_2$ Zn(Acfp)$_2$, Co(Bzfp)$_2$, Ni(Bzfp)$_2$, Cu(Bzfp)$_2$, and Cu(Fmfp)$_2$ were prepared by dissolving the ligand and the appropriate metal ion in methanol and adjusting the pH to approximately 9 with methanolic potassium hydroxide. The complexes of 2-benzamido-hexafluoro-2-propanol could be isolated from the reaction but decomposed over a few days. This reaction was not generally applicable to the metals in the first half of the series. Various other methods of obtaining these complexes were tried such as refluxing metal carbonyls with HAcfp$^{45}$ and oxidation of metal ions Co(II) and Mn(II) in the presence of the ligand$^{46}$ but these reactions were not successful. However it is probable that complexes would be formed under the proper conditions. The attempted preparation of a Co(III) complex by air oxidation of Co(II) in the presence of base and excess HAcfp gave only a tris chelated Co(II) complex. This well known preparative route to Co(III) complexes failed also in the synthesis of a tris (hexafluoro-2-hydroxy-isobutyrate) Co(III)$^{47}$ complex. The reason for this is not apparent.

The reaction of tetrakis-triphenylphosphine platinum with HAcfp in tetrahydrofuran was expected to give a platinum(II) derivative containing the ligand in a bidentate dinegative form, and two coordinated triphenyl-
phosphine groups. The formulation was found to be incorrect for the product isolated and the complex is discussed further in the last section of this chapter.

A number of attempts were made to synthesize a mixed ligand complex containing Acfp and a neutral, bidentate ligand. By the addition of excess tetramethylethylenediamine (TMED) to a methanol solution of copper sulphate and HAcfp, a bright blue compound with the formulation \([\text{Cu(Acfp)(TMED)}]^+ \text{SO}_4^-\) was prepared. The anion could be exchanged for \(\text{PF}_6^-\) by adding potassium hexafluorophosphate to an acetone solution of the sulphate from which purple crystals of \([\text{Cu(Acfp)(TMED)}]^+\text{PF}_6^-\) could be isolated. Similar attempts at preparing mixed ligand complexes with Ni(II) gave only nickel hydroxide.

The reaction of Co(II), Ni(II) and Cu(II) with HAcfp in basic methanol in the presence of phosphine (1,2 bisdiphosphinoethane and dimethylphenylphosphine) gave only a metal phosphine complex containing no Acfp even when the phosphine, metal ion, and HAcfp ratio was 1:1:1.

(ii) **Infrared Spectra.**

Previous discussion has led to the conclusion that several sites are available in the ligand HAcfp for coordination with metal ions. The infrared spectra should give some information concerning the method of bonding.

The Acfp complexes of Fe(III), Co(II), Ni(II) and Zn(II) all had similar infrared spectra, their most prominent feature being the very strong sharp absorption at 3440 cm\(^{-1}\) characteristic of a free nitrogen hydrogen stretching mode. The Cu(II) complex on the other hand always showed several broad bands below 3400 cm\(^{-1}\) in the infrared spectrum. This anomaly could be interpreted as either hydrogen bonding of the nitrogen proton to an adjacent oxygen or nitrogen atom, or as coordination of the nitrogen atom
to the metal ion. However some workers have discarded this nitrogen hydrogen stretching criterion for nitrogen coordination entirely. They suggest instead that inter- and intramolecular hydrogen bonding plays such an important role in such solid compounds as to cause a marked lowering of the nitrogen hydrogen frequencies whether or not the nitrogen atom is coordinated. To emphasize the point they quote a series of approximately thirty amine complexes, all of which were shown by other means to have coordinated nitrogen, and in which the nitrogen hydrogen stretches ranged from 3340 to 3100 cm$^{-1}$.

In spite of these findings, however, the shape and position (Figure 9) of these absorption bands in the complexes Ni(Acfp)$_2$, Fe(Acfp)$_3$, Co(Acfp)$_2$ and Zn(Acfp)$_2$ leave little doubt that the ligand is not coordinated by the nitrogen atom. These complexes represent one of the few instances where the nitrogen hydrogen stretch in the complex has the "free ligand value", which in practice is never found for the ligand itself due to intramolecular hydrogen bonding.

Table 4 is a list of the amide I and II bands for each neutral complex of Acfp and of HAcfp itself.

<table>
<thead>
<tr>
<th></th>
<th>Amide I (cm$^{-1}$)</th>
<th>Amide II (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAcfp</td>
<td>1675</td>
<td>1575</td>
</tr>
<tr>
<td>Fe(Acfp)$_3$</td>
<td>1620</td>
<td>1535</td>
</tr>
<tr>
<td>Co(Acfp)$_2$</td>
<td>1655</td>
<td>1535</td>
</tr>
<tr>
<td>Ni(Acfp)$_2$</td>
<td>1660</td>
<td>1540</td>
</tr>
<tr>
<td>Cu(Acfp)$_2$</td>
<td>1615</td>
<td>1530</td>
</tr>
<tr>
<td>Zn(Acfp)$_2$</td>
<td>1680</td>
<td>1530</td>
</tr>
</tbody>
</table>
Infrared Spectra

FIGURE 9

Co(Actf)₂

Fe(Actf)₃
As expected, there is a general reduction in the carbonyl stretching frequency on complex formation indicating a lowering of the carbonyl bond order. However the copper complex again does not fit in well with the established order having a value of carbonyl frequency closer to that of the Fe(III) complex than the complexes in the +2 oxidation state. There is also a general lowering of the nitrogen hydrogen deformation mode, possibly a result of decreased hydrogen bonding.

The sum of the infrared data would seem to indicate that ligand coordination for Acfp in complexes of Co(II), Fe(III), Ni(II) and Zn(II) is through the two oxygen atoms as shown by: (i) the decrease in carbonyl stretching frequency (ii) the free nitrogen hydrogen value for this absorption and (iii) by the absence of any bands assignable to a hydroxyl group. The infrared spectrum of the copper complex shares features (i) and (iii) with the other complexes but no decision can be made as to the coordination of the nitrogen atom on the basis of the decreased value of the nitrogen hydrogen stretch. If the nitrogen atom is coordinated however it would almost certainly be associated with a nearby copper atom as steric limitations would prevent the ligand from becoming tridentate with respect to one copper atom.

The copper(II) complex of Fmfp also had a nitrogen hydrogen stretch lower in energy than the free value of 3440 cm\(^{-1}\) as did the mixed ligand complex \([\text{Cu(Acfp)(TMED)}]_2\text{SO}_4^–\). In the latter compound the infrared spectrum showed only a broad peak at 3220 cm\(^{-1}\). When the sulphate ion is exchanged for
hexafluorophosphate giving the complex \([\text{Cu(ACf)}(\text{TMED})]^+\text{PF}_6^-\) the nitrogen hydrogen absorption is found as a sharp peak at 3400 cm\(^{-1}\) indicating that hydrogen bonding to the sulphate oxygen atoms occurs in the previous complex. This conclusion is substantiated by the observation that although the compounds should be the same colour since they contain the same metal complex ion the sulphate containing complex is blue while the other is purple. (Separate solutions of the compounds have the same blue colour.)

(iii) **Interpretation of Magnetic and Spectral Data.**

Although the infrared spectrum can give information on the method of coordination of the ligands it cannot, in the present case, reveal much about the actual geometry of the complex. Inferences on bonding in the preceding section were based on the concept of group frequency but even the ligand itself is too complicated to attempt a complete infrared analysis. The magnetic and electronic spectral properties are much more useful for determining structure in this case and accordingly each metal complex will be discussed separately with regard to possible geometries.

**Iron(III).**

The Fe(III) ion has a d\(^5\) electron configuration which gives a ground term of \(^6S\) according to Hund's rules. The magnetic moment would thus be expected to be close to the spin only value of 5.92 B.M. since the orbital contribution is quenched. The magnetic moment of Fe(ACf\(_3\)) was 5.68 ± 0.05 B.M. which is in the range of experimental values usually found for iron(III). By analogy with most tris iron(III) chelates, e.g. the \(\beta\)-diketone complexes,\(^{51}\) it is probable that the complex has an octahedral structure and the presence of an octahedral ligand field would give a ground state of \(A_{1g}\). All higher energy states must have lower spin multiplicity, hence all spectroscopic transitions are spin forbidden.
As is the case for many iron(III) complexes these weak transitions in the electronic spectrum of Fe(Acfp)$_3$ are obscured by intense charge transfer bands. Only one band was observed at 450 m\(\mu\) with \(\varepsilon \approx 6\).

**Cobalt(II).**

It was noted in the experimental section that two different complexes of cobalt were isolated from the reaction of cobalt(II) with HAcfp. Initially it was thought that one of these complexes contained cobalt in the +3 oxidation state, the metal having been oxidized by exposure to the atmosphere during the preparation. However, analysis of the complexes indicated that both were cobalt(II) complexes, one having the formulation Co(Acfp)$_2$ and the other Co(Acfp)$_3$\(^{-}K^{+}\cdot THF$. The latter compound was difficult to isolate and decomposed over a few weeks. A magnetic study verified the presence of Co(II) since both substances were paramagnetic. (Virtually all Co(III) complexes known are diamagnetic.\(^{52}\)) The pink complex Co(Acfp)$_2$ had a magnetic moment of 4.85 B.M. and this could be identified with a tetrahedral geometry, moments of tetrahedrally co-ordinated cobalt(II) being about 4.1 to 4.9 B.M. However cobalt(II) ions in an octahedral environment also have magnetic moments that overlap into this region i.e. 4.7 to 5.2 B.M. The best indicator of geometry would be the molar extinction coefficient which is generally found to be approximately one hundred times larger for tetrahedral complexes than for octahedral complexes. The molar extinction coefficient of Co(Acfp)$_2$ was found to be ~20 and confirms the assignment of octahedral configuration in solution.

The diffuse reflectance spectrum showed a broad band from which three poorly resolved bands at 434, 527 and 584 m\(\mu\) could be distinguished. The
solution spectra peaks occurred at 490, 525 and 590 m\(\mu\). (None of these could be assigned to a particular transition with any confidence.) It can be concluded that solvent coordination helps to achieve octahedral coordination in solution since the difference between ligand metal and solvent metal interaction could explain the observed differences in spectra. Molecular weight measurements when extrapolated to infinite dilution gave a value of 510 compared with the calculated value of 507. However the evidence that the complex is associated at higher concentrations supports an assignment of octahedral configuration in the solid. The mass spectrum of Co(Acfp)\(_2\) did show a molecular ion peak at 507 mass units but no higher peaks.

**Nickel(II)**

Complexes of nickel(II) can have either tetrahedral, octahedral, or square planar geometries. The magnetic moment of 2.84 ± 0.05 B.M. for Ni(Acfp)\(_2\) suggests that this complex is octahedrally coordinated. However it has been shown\(^5\) that a weak square planar crystal field can also give a paramagnetic complex. The assumption of octahedral symmetry for Ni(Acfp)\(_2\) was tested in the following way. The three absorptions in the diffuse reflectance spectrum were assigned to the transitions as follows; (Ni(II) is a d\(^8\) system with a ground term of \(^3\)F which is split by the ligand field to give an \(^3\)\(A\sub{2g}\) spectral ground state), \(^3\)\(A\sub{2g} \rightarrow ^3T\sub{2g}\) (6160 cm\(^{-1}\)); \(^3\)\(A\sub{2g} \rightarrow ^3T\sub{1g}\) (F) (14,100 cm\(^{-1}\)); \(^3\)\(A\sub{2g} \rightarrow ^3T\sub{1g}\) (P), (24,500 cm\(^{-1}\)). Assuming the lowest energy band to be equal to 10 Dq, calculations\(^5\) were carried out to determine \(\beta = 0.861\), Dq = 816 cm\(^{-1}\). The \(\beta\) value expresses the amount of interelectronic repulsion in the complexed metal ion compared to that found in a free gaseous metal ion. For Ni(Acfp)\(_2\) it was found that the nephelauxetic effect of the ligands has reduced the interelectonic
repulsion by about 14%. By resubstituting the values obtained for Dq (816 cm\(^{-1}\)) and the energy of the next highest state, \(^3\mathrm{P}\) (13,640 cm\(^{-1}\)) into the equation \[ [6 \text{Dqp} - 16 (\text{Dq})^2] + [-6\text{Dq} - p]E + E^2 = 0 \] the values of the energy of the \(\text{T}_{1g}(F)\) and \(\text{T}_{1g}(P)\) can be obtained. The results predict that the transitions \(^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(F)\) and \(^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(P)\) will be found at 13,610 cm\(^{-1}\) and 24,554 cm\(^{-1}\) respectively. These values agree quite well with the experimentally determined values for Ni(Acfp)\(_2\) and this is convincing evidence that the assumption of an octahedral structure is quite a valid one considering the latitude in peak position for broad bands.

Although little can be said about the actual formation of an octahedral structure, polymeric structures such as the trimers in the solid form of nickel(II) bis-acetylacetone might be present (Figure 10).

A complete study of the concentration dependence of the molecular weight was limited by the solubility of the complex but the compound did appear to be monomeric in dilute solutions.

The Dq value of 816 cm\(^{-1}\) is close to the average value (832 cm\(^{-1}\)) found for the complex Cs\(_2\)Ni(PFP)\(_2\) (PFP = perfluoropinacol) in methanol solution\(^8\). The Racah B value for the complex Ni(Acfp)\(_2\) is 910 cm\(^{-1}\) which is slightly higher than the value for Cs\(_2\)Ni(PFP)\(_2\). In a spectrochemical series of common ligands Acfp would have the following position

\[ \text{Br}^- < \text{Acfp}^- < \text{PFP}^2^- < \text{H}_2\text{O} < \text{HHIB}^2^- \] (2 hydroxy perfluoroisobutyrate)\(^9\) < \(\text{C}_2\text{O}_4^{2-}\)

The nephelauxetic series is Acfp\(^-\) > \(\text{H}_2\text{O} > \text{HHIB}^2^- > \text{PFP}^2^- > \text{C}_2\text{O}_4^{2-}\).

The complex Cs\(_2\)Ni(PFP)\(_2\) is diamagnetic and presumably square planar in the solid but gives a typical octahedral electronic spectrum in methanol which evidently complete the axial coordination sites.
FIGURE 10

Possible Structures of Acfp Complexes

I

II
Copper(II).

The magnetic moment of Cu(Ac fp)₂ was determined to be 1.73 ± 0.05 B.M., which is close to the spin only value for a d⁸ electronic system. The ground state for octahedral symmetry in Cu(II) is ²Eg. The only transition possible is one to the excited state ²T₂g. This sequence is reversed for tetrahedral symmetry, Cu(II) being electronically equivalent to a d¹ system. It appears that no copper-copper interaction of the sort found in the copper acetate complexes occurs to couple the electron spins although variable temperature studies would be needed to confirm this. The diffuse reflectance spectrum shows a broad band at 652 m𝜇 with a shoulder at 724 m𝜇. This kind of splitting is typical of Jahn-Teller distortion which can be found for copper(II) spectra. However, this assignment is tentative since well documented cases of Jahn-Teller splitting in Cu(II) complexes are rare.⁵³

The assumption that the centre of the broad band is a good approximation to the value of the ²E → ²T₂g transition leads to a Dq (octahedral) value of 1530 cm⁻¹. This number falls in the range commonly found for octahedrally coordinated Cu(II). The Dq values for tetrahedral geometries are approximately 4/9 of the octahedral values.

Molecular weight studies in solution showed that the compound was dissociated at low concentrations.

If the complex is octahedral or pseudo-octahedral two possible structures can be drawn (Figure 10). In structure I polymerization occurs by having each metal atom share an oxygen donor with its neighbour atom. This diagram is in fact the structure of Ni(II) bis-acetylacetone⁵² but as noted earlier for the cobalt and nickel Ac fp complexes the structural
principle could apply for Acfp complexes also. Structure II also represents a method of polymerization but here the nitrogen atoms are coordinated by long bonds to adjacent metal atoms. In this structure a copper atom could more easily achieve its preferred tetragonally distorted geometry. The infrared evidence also supports the features present in structure II for Cu(Acfp)_2, i.e. the low value for the nitrogen hydrogen stretching frequency.

Zn(II).

This complex is expected to have the tetrahedral geometry normally found in Zn(II) complexes. Molecular weight measurements were impossible because the complex decomposed in solution. The fluorine n.m.r. spectrum contained a single sharp peak at 81.6 Hz but a much smaller peak at 82.2 Hz was continually present also. This was attributed to decomposition of the ligand in solution to give hexafluoroacetone. However Zn(Acfp)_2 can be heated to 80°C in the solid form under vacuum with no evidence of decomposition.

Platinum(II).

It was mentioned in the earlier section on preparation of complexes that HAcfp reacted with tetrakis-triphenylphosphine platinum (0) to give a white crystalline air stable solid. The infrared spectrum had peaks characteristic of triphenylphosphine, trifluoromethyl groups and a peak at 1665 cm\(^{-1}\) which could be assigned to either a carbonyl stretch or an imine stretch. There were no absorptions in the region above 3000 cm\(^{-1}\), expected for a nitrogen hydrogen stretch. The compound was at first thought to be a platinum(II) complex with two triphenylphosphine groups and one dinegative bidentate ligand arranged as shown below.
The molecular weight determined osmotically in benzene was 920. The calculated figure for the above complex is 944. The analytical data was consistent with the above formulation except that the percent nitrogen was slightly lower than calculated. However no other zero valent metals gave a similar reaction and so the complex was investigated further. An F\textsuperscript{19} n.m.r. showed a surprisingly well resolved triplet of doublets with each peak split again into a doublet. If one considers the molecule to be planar with two equivalent trifluoromethyl groups above and below the plane, the spectrum can be interpreted in the following way: $J_{\text{Pt-F}} = 69.8$ Hz, $J_{\text{Trans F-P}} = 11.0$ Hz, $J_{\text{Cis F-P}} \approx 2$Hz. These coupling constants are in the region usually found\textsuperscript{55} for trifluoromethyl groups attached to a carbon atom which is directly bonded to a platinum atom. In the present case there is an oxygen atom interspaced between the carbon and platinum atoms which would certainly affect the coupling constants. It was then found that all the physical characteristics including melting point corresponded to a complex reported earlier with the formulation
Evidently the ligand had decomposed in solution during the lengthy reaction and the liberated hexafluoroacetone then reacted with the tetrakis-triphenylphosphine platinum.

C. Reactions of Coordinated Ligands.

It was part of the intent of this study to investigate the ability of HAcfp to act as both a mononegative and dinegative chelate ligand. Two approaches can be taken, the first being the preparation of the ligand in its dinegative form with subsequent reaction with metal ions and the second approach being the preparation of a mononegative ligand chelate complex which would then be converted to the dinegative form. An example of this type of reaction was reported in the introduction to Part II which referred to a complex which could be deprotonated with dilute base. As noted earlier the disodium salt of HAcfp can be prepared by reaction of the ligand with sodium hydride in dry tetrahydrofuran. The exact structure of this compound is not clear but it is expected that the negative charge will be shared by the acetamido grouping by a resonance mechanism. However since both the sodium salt and the metal salts have limited solubility in organic solvents it was decided to react a bis metal complex with base and in this way form an anionic complex.

![Chemical Structure Diagram]

The copper complex was chosen first for the reaction because of its greater solubility in tetrahydrofuran and this proved to be a fortunate choice since
the reaction appears to be peculiar to the copper complex.

Although deprotonation can be achieved in some cases by treatment of the complex with aqueous base \(^{40,56,57}\) this was not true for the Cu(Acfp)\(_2\) complex. The addition of even alcoholic potassium hydroxide to a solution of Cu(Acfp)\(_2\) caused the complex to decompose. In the examples listed above the reaction sequence proceeded from a positively charged complex ion to a neutral compound while the reaction with Cu(Acfp)\(_2\) is an attempt to start with a neutral molecule and proceed to a negatively charged complex ion. In the latter case the complex ion formation would not only be less favourable energetically but the product would also react readily with available protons to reverse the reaction with base. However deprotonation did occur when Cu(Acfp)\(_2\) was treated with sodium hydride in tetrahydrofuran. The pale blue powder decomposes to a black solid on exposure to moist air. Satisfactory analysis figures were obtained for the formulation,

\[
\begin{align*}
\text{2/Cu} & \quad \text{CF}_3 \\
\text{O} & \quad \text{C} \\
\text{CF}_3 & \quad \text{N} \\
\text{O} & \quad \text{C} \\
\text{CH}_3 & \quad \text{Na}^+ 
\end{align*}
\]

No absorptions were present in the infrared region 4000 to 3000 cm\(^{-1}\) indicating that both protons had been removed. The carbonyl stretching absorption was shifted to 1665 cm\(^{-1}\) from its position in Cu(Acfp)\(_2\) of 1615 cm\(^{-1}\) although with no information on the actual distribution of the negative charge this absorption is best assigned to the acetamido grouping as a whole.
None of the other metal complexes gave this type of product with sodium hydride. The nickel complex is not soluble in tetrahydrofuran. The white solid isolated from its reaction did not contain nickel and was identified as the sodium salt of the ligand from its infrared spectrum. Both Zn(Acfp)₂ and Co(Acfp)₂ decomposed during the course of the reaction. The previous assumption that the nitrogen atom takes part in coordination in the copper complex but not in the others is consistent with these results since the negative charge formally left on the nitrogen atom could be reduced by bonding to the copper atom.

When recrystallization from acetone was attempted it was found that the complex had reacted with the solvent to form a new compound which analysed as having the stoichiometry of the sodium salt of the complex with the addition of two molecules of acetone per unit of complex. The infrared spectrum of the blue crystals did not show any absorption in the nitrogen-hydrogen or hydroxyl stretching region but two new peaks appeared at 1720 cm⁻¹ and 1600 cm⁻¹. Prolonged pumping under vacuum (24 h) at a temperature of 70°C left the compound unchanged indicating that a simple adduct of acetone was unlikely. In conjunction with this stability towards heat and vacuum, such a strong adduct would probably have a carbonyl frequency well below the free value of ~1720 cm⁻¹.

By dissolving the sodium salt of the copper complex in methyl ethyl ketone or ethyl acetate similar complexes were formed although less readily than with acetone. Similarly, reaction of the complex with hexafluoroacetone was accomplished by a sealed tube reaction with subsequent re-crystallization from solvents saturated with hexafluoroacetone. In the solid state all these complexes were air stable and non-hygrosopic unlike either Cu(Acfp)₂ or its sodium salt. In solvents other than the parent,
decomposition to Cu(Acfp)$_2$ occurred unless the solvents were very dry although the carbonyl containing solvents could be quite wet.

All of the solvent containing compounds had strong absorptions in the ~1725 region and no peaks above 3000 cm$^{-1}$. The hexafluoroacetone containing complex showed weak absorptions in the infrared spectrum at 3240 cm$^{-1}$ and 3440 cm$^{-1}$ indicating some hydrolysis had taken place. There was no absorption in the 1700 cm$^{-1}$ region but there was a peak at 1680 cm$^{-1}$ for this complex.

The possibility that the complexes are simple adducts was considered and discarded earlier. There are two other possibilities involving condensation reactions at either the methyl group or the nitrogen atom. In the former case the reaction scheme could proceed as shown in Figure 11. However this involves an unlikely proton transfer from a methyl group to an alkoxide oxygen atom to form the carbanion. In addition the product would be expected to show some signs of hydroxyl stretching in the infrared spectrum. The following theory was found to be consistent with all the physical data and follows certain precedents put forward by other authors.$^{58,59}$

The anionic copper salt can be thought of as existing in the form I in Figure 12, although the negative charge is delocalized over the nitrogen, carbon and oxygen atoms. On dissolving the complex in a carbonyl containing solvent, the nucleophilic nitrogen atom attacks the carbonyl carbon (structure II). The complex could now account for all the physical data except the infrared peak at 1720 cm$^{-1}$. However these complexes are probably quite labile in solution and by a simple rotation about the nitrogen carbon bond structure III can be obtained. This structure can now explain the appearance of a peak in the range where free carbonyl groups are usually found. Condensation reactions between metal complexes with coordinated amines
FIGURE 12

I

II

III

\[ \text{CH}_3 \]

\[ \text{CF}_3 \]

\[ \text{Cu} \]

\[ \text{N}^{\text{Na}^+} \]

\[ \text{R}^1 \]

\[ \text{R}^2 \]

\[ \text{C} \equiv \text{O} \]

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FIGURE 12 (cont'd)
and carbonyl containing compounds have been known for some time. The final step in such reactions was a dehydration whereby an imine complex could be formed, i.e.

\[
\begin{align*}
\text{M} & \quad \text{NH}_2 \quad \text{CH}_2 \\
\text{NH}_2 & \quad \text{CH}_2 \\
\text{C} & \quad \text{C} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[\text{M} \quad \text{NH}_2 \quad \text{CH}_2 \quad \text{C} \quad \text{N} \quad \text{CH}_2 \quad \text{NH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \quad \text{CH}_3 + \text{H}_2\text{O}\]

In the present case this reaction cannot occur but the general mechanism is quite analogous. The puckering of the ring in what is most likely a slightly distorted chair structure IV prevents the structure from being as sterically hindered as might first seem the case, especially if \(R^1\) is the methyl group.

Since the achievement of a less strained ring structure (both the reactant and product have six membered rings) does not seem to be the driving force of the reaction, condensation with a carbonyl group probably occurs simply because the oxygen atom can accommodate the negative charge better than the nitrogen atom.

The hexafluoroacetone complex does not show the spectrum of the other complexes, yet with regard to the analysis results also contains two molecules of hexafluoroacetone. This discrepancy can be rationalized by noting structure IV. If \(R^1\) and \(R^2\) were trifluoromethyl groups there might be enough electrostatic repulsion to prevent the ring formation, in which case the complex would precipitate out of solution as structure II and would not contain a free carbonyl group.

At the beginning of this section it was noted that the deprotonation of the neutral complex \(\text{Cu(Acfp)}_2\) required a strong base and anhydrous
conditions to give the anionic complex. If the starting product were cationic the deprotonation would be expected to proceed under milder conditions to give a neutral compound. Preliminary investigations with the complex ion [Cu(TMED)(Acfp)]\(^+\) indicate that this compound can be deprotonated with dilute alcoholic potassium hydroxide as evidenced by a definite colour change from blue to purple on addition of the base and a white precipitate of KPF\(_6\). An infrared spectrum of the product does not show an absorption for a nitrogen hydrogen stretch and a peak is present which could be assigned to an imine stretch.

Preliminary investigations with bis-2-formamido hexafluoro-2-propanol copper(II) indicate that a sodium salt is formed with sodium hydride but reaction with acetone does not occur as the compound is insoluble in all solvents.

D. Lanthanide Complexes.

Until recently there were a few well characterized lanthanide complexes known. Since the discovery by Hinckley\(^6\) that certain lanthanide complexes can be used as n.m.r. shift reagents to simplify the spectra of complicated organic systems, a number of these complexes have been prepared and their properties investigated.\(^6\) Structural aspects of lanthanide complexes are also becoming of interest to many researchers because of the capacity of
the metal ion to accommodate anywhere from six to ten ligand donor atoms. It has also been shown that for the β-diketone chelates the most volatile and thermally stable compounds are those in which the ligands are best able to shield the metal atom from solvation effects and interactions between molecules. Bulky fluorine substituted ligands appear to suit these requirements. Hence it was thought worthwhile to investigate the reactions of HAacfp with the trivalent lanthanide ions in the expectation of making neutral complexes of the type M(Acfp)₃. However, this was not achieved in practice and two different types of lanthanide complexes were formed. The simpler type, which had the stoicheometry M(Acfp)₄NH₄, will be discussed first. The two representative complexes, Dy(Acfp)₄NH₄ and Er(Acfp)₄NH₄ precipitated from solution when dilute ammonium hydroxide was added to a solution containing the metal ion and a large excess of ligand. The infrared spectra were identical as expected and showed absorptions in the 3000 to 3300 cm⁻¹ region characteristic of the ammonium ion. A very strong sharp peak at 3440 cm⁻¹ (Figure 13) was assigned to the nitrogen hydrogen stretch of the ligand and, as before, was taken to indicate that the nitrogen atom was not coordinated. The carbonyl stretching band appeared at 1650 cm⁻¹ and a strong nitrogen hydrogen bending mode at 1525 cm⁻¹. The compounds could be sublimed ca. 90°C with no decomposition. This is surprising but not unknown among lanthanide tetrakis chelates. Hexafluoroacetylacetone and decafluoro-4,6-heptanedione both form volatile tetrakis chelates.

The magnetic moments of the complexes were characteristic of the metal ions present.

Based on infrared data which indicates that no free carbonyl or
FIGURE 13

Infrared Spectrum of Er(Acfp)$_4$NH$_4$ (mull)
hydroxyl is present it is likely that the erbium and dysprosium ions are eight coordinate in these compounds. Although the complexes could be polymeric their volatility suggests that they are monomeric, in which case the complex metal ion is likely to have the symmetry $S_4$. Other more complex geometries are possible but a cube about the central metal ion with alternating positions for the trifluoromethyl groups would be both compact and sterically feasible.

Despite their thermal stability and precipitation from aqueous solution during preparation, the tetrakis complexes decompose during attempted recrystallizations from organic solvents. Excess HAcfp in the solution does not suppress the solvolysis. The product that does crystallize out of solution can also be synthesized directly by the reaction of lanthanide ion with HAcfp in a lower ratio in methanol solution. (A lower ratio of metal ion to HAcfp in aqueous media gives a mixture of the two products.)

This second type of complex was prepared for the tervalent ions of La, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, and Yb.

The exact formulation of these trivalent lanthanide complexes is difficult to determine. Although the fluorine to carbon ratio in the ligand
* Peaks absent in non-deuterated complex.

FIGURE 14
Infrared Spectrum of $\text{Er}_2(\text{Acfr})_4(\text{OH})_2$ acetamide.
itself is 6:5 (1.20) the fluorine to carbon atom ratio in the complexes is on average 1.10 ± 0.01 (Table 3) and the deviation from the value 1.20 is clearly greater than the experimental error. This value of 1.10 could be obtained for the complexes by assuming either a fluorine to carbon ratio of 12:11 or 11:10. The second value was rejected since this would mean that fluorine atoms were lost during the reactions, and as the reaction conditions were quite mild it is unlikely that a fluorine atom would be lost from a trifluoromethyl group. Consideration of the remaining value 12:11 leads to the conclusion that for every two ligands in the complex there must be an extra carbon atom. Incorporation of a solvent molecule was suggested and an examination of the representative infrared spectrum (Figure 14) shows a sharp peak at 3660 cm⁻¹ which was initially attributed a methanol adduct. However, when the reaction was repeated using isopropanol as a solvent throughout the preparation and work up*, the product obtained was identical in colour, melting point, infrared spectrum and analysis to the complex prepared in methanol. Partial deuteration of the complex identified the peaks at 3660 cm⁻¹ and 3440 cm⁻¹ as O-H and N-H stretches. Coordinated water generally shows a broad absorption at 3510 cm⁻¹ but hydroxyl absorptions can be sharp. (Any water bending mode (1630 cm⁻¹) would be obscured by the strong carbonyl absorption.) Measurement of the molecular weight revealed only that very complicated behavior exists in solution. (Figure 5).

The only formulation which seemed to fit the available data was M₂(AcFp)₄(OH)₂·acetamide (M = lanthanide). Recrystallization of these

* Throughout these investigations the erbium complex was used as a representative sample.
complexes from pyridine, diethyl amine and concentrated acetone solutions of triethylphosphine does not cause either adduct formation or decomposition. Absorptions in the infrared spectrum due to the acetamide molecules would be masked by the strong absorptions of the ligand itself. The only vibrations that could substantiate the presence of a primary amide would be in the N-H stretching region. Close examination of band at 3440 cm$^{-1}$ assigned to the N-H stretch of the ligand reveals a slight but consistent asymmetry of this very sharp peak. This could mean that the N-H stretching modes of acetamide (i.e. symmetric and antisymmetric) were hidden under the band of the ligand N-H stretch, since these would all occur in the same region. However this evidence is slight at best. The n.m.r. spectrum was little use since the molecular weight determinations showed that the complexes were dissociated in solution.

A cerium complex prepared by the same method gave, instead of a cerium(III) complex, a cerium(IV) complex. The pale yellow compound was found by analysis to have a stoicheometry of one metal atom to four ligand ions. Consistent with its formulation as a neutral complex of cerium(IV) was its diamagnetism and failure to show any evidence of hydroxyl groups in the infrared spectrum. There are several precedents in the literature for such an oxidation reaction, one of these being the isolation of a Ce(IV) complex of dipivaloylmethane using Ce(III) as a starting material. Although these workers did offer other supporting evidence (infrared, magnetic and analysis) for obtaining a Ce(IV) complex they also put forth colour (red) and high melting point (276°C) as criteria for distinguishing the +4 oxidation state. The complex reported in this work was pale yellow and melted at 118°C.
The oxidizing agent in this reaction is presumably atmospheric oxygen since the ligand itself did not prove to be a strong oxidizing agent with Co(II). Cerium(IV) in solution is generally obtained by treatment of Ce(III) solutions with very powerful oxidizing agents and concentrated aqueous HCl is oxidized to Cl\(_2\) by Ce(IV).

Previous authors commented only that (a) there is a greater ease of oxidation \([\text{Ce(III)} \rightarrow \text{Ce(IV)}]\) in the case of cerium and (b) there might be more favourable total bond energy associated with the utilization of four rather than three bidentate ligands.

Table 5 compares the carbonyl and hydroxyl stretching frequencies of the various complexes with increasing atomic weight. The cerium complex is included also although it contains the metal atom in a +4 oxidation state. The carbonyl stretching absorption is invariant with the increase in atomic number along this series. The hydroxyl peaks on the other hand show a small increase in energy from praesodymium to ytterbium. It is generally accepted that the bonding in the rare earths is primarily ionic in nature as a result of the electronically shielded 4f orbitals and this is substantiated by the list of similar carbonyl frequencies. The fact that the carbonyl frequency is less than in the free ligand by about 25 cm\(^{-1}\) could result from simple polarization of the oxygen atom. By this argument the hydroxyl frequencies should change in the opposite direction to that which was found experimentally. The explanation is not obvious and the trend, if it is actually significant, may depend on steric or other factors.
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$ C=O cm$^{-1}$</th>
<th>$\nu$ O-H cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>1655</td>
<td>-</td>
</tr>
<tr>
<td>Ce$^{4+}$</td>
<td>1650</td>
<td>-</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>1655</td>
<td>3620</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>1655</td>
<td>3630</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>1660</td>
<td>3650</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>1655</td>
<td>3650</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>1655</td>
<td>3650</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
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<td>3650</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>1650</td>
<td>3650</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>1660</td>
<td>3670</td>
</tr>
</tbody>
</table>

* No sharp OH peak
CONCLUSION

The susceptibility of the carbonyl group to nucleophilic attack is well known and this effect is greatly increased in fluorinated ketones by the strong inductive effect of fluoroalkyl groups. Thus hexafluoroacetone forms isolable hydrates, hemiketals and amine adducts whereas its hydrocarbon counterpart does not. This type of reaction between hexafluoroacetone and molecules with reactive protons has been used in this work to synthesize a new class of chelate ligands. These compounds were produced by the nucleophilic attack of an amide on hexafluoroacetone, giving the following products

![Chemical structure](attachment:chemical_structure.png)

The reaction is reversible with the order of stability of the products 2->formamido->2-acetamido->2- benzamido-hexafluoro-2-propanol. The preparation of a larger series of ligands with bulkier alkyl groups would help determine if the observed order is a result of electronic or steric factors. Hydrogen bonding of the hydroxyl hydrogen to the carbonyl oxygen atom probably helps to stabilize the adduct in a six membered ring system. Substitution of fluorine for hydrogen on the R group decreases the nucleophilicity of the nitrogen atom and prevents isolation of a stable product. N-alkyl amides also do not undergo the reaction, probably as a result of steric hindrance.

95.
It was the aim of this work to determine whether or not the above compounds could act as ligands and if so, to investigate the nature of the complexes, particularly with regard to further reactions of the ligands. It was found that these compounds, with the exception of 2-benzamido hexafluoro-2-propanol, formed stable complexes with ions of the second half of the first row transition metals, and with the trivalent lanthanide metals. Coordination to the metal ion was found to be through the oxygen atoms alone for the Fe(III), Co(II), Ni(II), Zn(II) and lanthanide metals but coordination of the nitrogen atom is also suspected in the Cu(II) complexes. This theory is based largely on infrared evidence which shows that all of the complexes but the copper ones have very high, sharp nitrogen hydrogen stretching frequencies. The copper complexes Cu(Acftp)$_2$ and Cu(Fmfp)$_2$ had N-H stretching absorptions that were lower in frequency and broader than those of the other complexes. The nickel Acftp complex was found to have octahedral coordination by comparison of the observed and calculated values of the $A_{2g} \rightarrow T$ transitions. The structure of Co(Acftp)$_2$ could not be determined with certainty because of the difficulty of assigning the bands in the visible spectrum, although the magnetic moment together with the position of the peaks in the visible spectrum indicate octahedral coordination also. The copper complex is thought to be essentially planar with tetragonal distortions along the long axis due to interaction with the nitrogen atom of a neighbouring ligand thus lowering the N-H peak from its normal sharp position of 3440 cm$^{-1}$ to a broader band at $\sim$ 3300 cm$^{-1}$.

Coordination of the high spin iron chelate is presumably octahedral as is typical for six coordinate iron(III) complexes.
No conclusions were reached on the reasons for the instability of the complexes of HBzfp. However the formamide adduct appeared to be an excellent ligand but the insoluble nature of the complexes made purification of the compound more difficult than for the acetamide complexes.

Further reactions of the complexed ligand occurred only for the copper complexes. These could be deprotonated by treatment with sodium hydride to give anionic metal complexes but the product was very easily hydrolysed back to the starting material. The complex formulated as *\([\text{Cu}(\text{Acfp})_2]^{2+}\) reacted with carbonyl-containing compounds to incorporate one molecule of the reactant into each unit of Acfp. The reaction is thought to proceed as shown in Figure 12 and to give compounds with structure III with acetone, methyl ethyl ketone and ethylacetate and structure IV with hexafluoroacetone.

Preliminary studies show that a cationic complex of Acfp Cu(TMED)Acfp\(^+\) will undergo deprotonation with milder conditions to give an air stable neutral complex.

Reaction of the trivalent lanthanide ions Dy\(^3+\) and Er\(^3+\) with ammonical solution of HAcfp gave complexes which have the stoicheometry M(Acfp)\(_4\)NH\(_4\). The complexes decompose in organic solvents to give products which according to analysis have the formula M\(_2\)(Acfp)\(_4\)(OH)\(_2\).acetamide. These complexes can be synthesized directly by using methanol as a solvent and were prepared for most of the lanthanide metals. The cerium(III) ions used in the latter reaction did not give a similar complex but rather were oxidized to cerium(IV) and the compound isolated was characterized as

* Acfp indicates the ligand has lost a proton from the nitrogen atom.
Ce(Acfp)₄. The paramagnetic complexes were found to have little application as n.m.r. shift reagents due to their low solubility in aprotic and weakly polar solvents.

The successful synthesis of metal complexes of HAcfp and HFmfp suggests several new topics for investigation.

Recent work⁶⁶ on some glycine and leucine peptide complexes indicate bonding of the peptide-amide nitrogen in copper complexes and peptide-amide oxygen in zinc and nickel complexes. These complexes have a number of functional groups and the infrared spectra are complicated. The peptide linkage in HAcfp and related ligands provides a much simpler model for the investigations of the coordinative ability of this grouping. Motekaitis and Martell⁶⁵ have also recently reported on the difficulty of synthesizing amide-containing ligands for studies on the coordinating characteristics of the amibdent amido group.

By choosing an appropriate nucleophile a variety of bidentate ligands could also be prepared having different donor sets i.e. S₂O₂, N₂O₂ etc. Depending on the nucleophile chosen these complexes will have reactive protons which may be removed with strong base to give neutral or anionic complexes. Interesting mixed metal complexes could then be prepared by coordination of the anionic complex to a different metal ion through the amidic nitrogen atom.

The reaction of the sodium hydride derivative of Cu(Acfp)₂ with carbonyl containing solvents was unexpected and further work in this area is clearly indicated.
REFERENCES


99.
REFERENCES (continued)


27. W.S. Cripps, private communication.


REFERENCES (continued)


REFERENCES (continued)


