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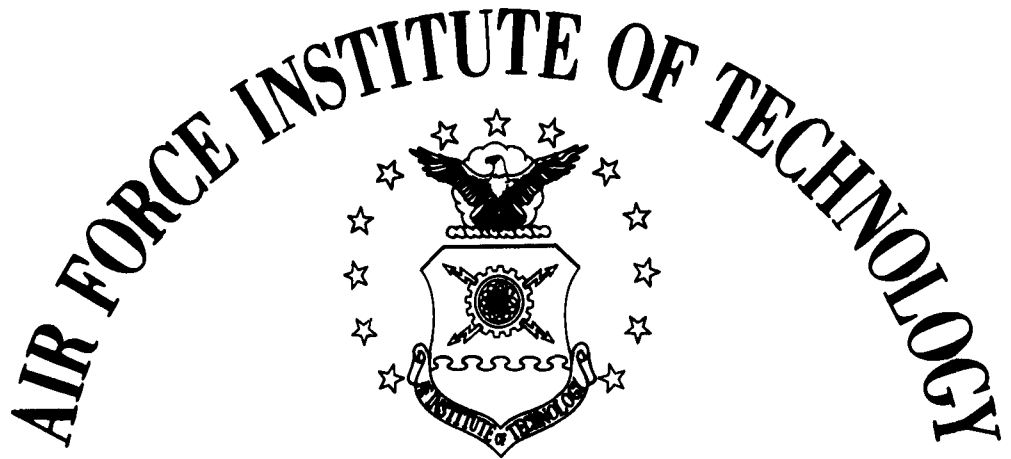
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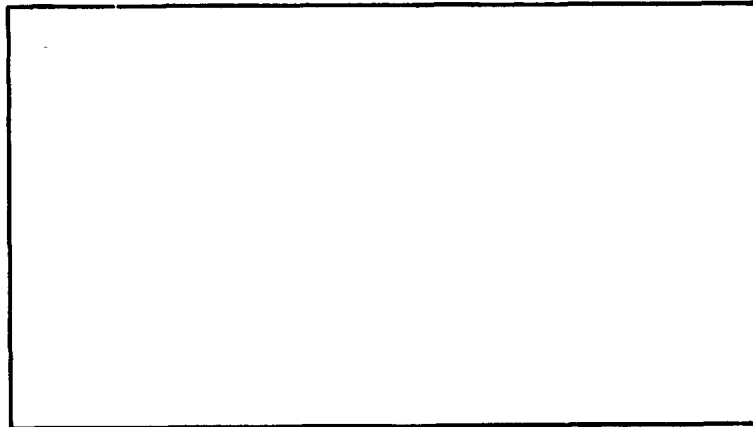
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THE SYNTHESIS OF
A VOLATILE CADMIUM CHELATE
AND
THE STUDY OF ITS VAPOR PHASE
REACTION WITH HYDROGEN SULFIDE

Capt Albert G. Cupka, Jr.

GNE/Phys/63-7

THE SYNTHESIS OF A VOLATILE CADMIUM CHELATE
AND THE STUDY OF ITS VAPOR PHASE REACTION WITH
HYDROGEN SULFIDE

THESIS

Presented to the Faculty of the School of Engineering
of the Institute of Technology
Air University
in Partial Fulfillment of the
Requirements for the Degree of
Master of Science

By

Albert George Cupka, Jr., B.Ch.E.

Capt

USAF

Graduate Nuclear Engineering

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Preface

I wish to express my appreciation to Dr. Ross Moshier and Dr. Robert Sievers of the Chemistry Branch, Aeronautical Research Laboratory, for the guidance which they so willingly gave. Dr. Sievers also deserves my gratitude for the many fruitful discussions on metal coordination chemistry. I am grateful to Dr. B. Smith and Dr. B. Ponder, also of the Aeronautical Research Laboratory, with whom I had many enlightening discussions on analytical analysis techniques.

I would like to thank my thesis advisor, Dr. George John of the Physics Department, Air Force Institute of Technology, for his encouragement, understanding, and helpful suggestions throughout this study.

In particular, I would like to thank my wife. In addition to keeping a home and caring for our new son, she spent many hours typing and retyping drafts. Her aid was invaluable.

Albert G. Cupka, Jr.

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Abstract

In this study, a chemical approach to deposition of thin films or crystals of metal compounds was investigated. It was of interest to determine whether metal chelates would undergo a vapor phase reaction to form the desired products. Reactions to produce materials of importance as semiconductors were of special interest.

Two metal derivatives of fluorinated acetylacetone containing cadmium were prepared, one ionic in nature and the other covalent. Composition and structure of the two compounds is presented, together with a few of their physical properties. The covalent cadmium chelate was reacted in the vapor phase with hydrogen sulfide. The experiments were conducted at atmospheric pressure and reaction temperatures of 140° to 240°C. Thin films of cadmium sulfide were deposited and the other gaseous reaction products were trapped and positively identified. The vapor phase reaction regenerates the free chelating agent, which may be used again for the re-synthesis of the cadmium chelate. The results indicate that this cadmium chelate, and other similar metal derivatives of fluorinated acetylacetone, look very promising for use in the vapor phase reactions to yield pure semiconductor materials.

THE SYNTHESIS OF A VOLATILE CADMIUM CHELATE
AND THE STUDY OF ITS VAPOR PHASE REACTION WITH
HYDROGEN SULFIDE

I. Introduction

Metal coordination compounds have been of interest to researchers for some time because of the unusual properties they possess. The properties of certain compounds containing organic constituents are of particular interest. These properties, normally attributed to organic compounds, are insolubility in water, solubility in non-polar solvents, and a high degree of volatility.

It is the purpose of this thesis to present the results of the synthesis of a cadmium derivative of a β -diketone, and its subsequent reaction with hydrogen sulfide both in the gaseous state and in a non-aqueous solution. An attempt is made to elucidate the chemistry of the reactions which occurred, with particular emphasis on the novel gas phase reaction of the metal chelate with hydrogen sulfide. Synthesis of pure cadmium sulfide, either in an amorphous or crystalline state was also anticipated. Properties of compounds were studied via infrared, mass spectra, nuclear magnetic resonance spectroscopy, gas chromatography and spectrographic emission techniques.

With the advent of space flights creating a demand for miniaturized, light-weight, electronic components, renewed interest is being taken in metal coordination compounds. Studies being carried on in the field of molecular electronics indicate a need for volatile metal compounds. The

desire to make thin film circuits of various metal oxides, sulfides, or nitrides creates this need. Vapor deposition of the volatile metal compounds appears to be a good approach to making the necessary thin films (Ref 2:253-254). The metal coordination compounds offer an advantage over the basic metals, or their respective salts, in that they have a higher degree of volatility, thereby making vaporization possible at much lower temperatures and with less effort. Another growing interest in these compounds, again arising from the property of volatility, is that they may be utilized as intermediates for obtaining ultra-high purity metals and metal compounds (Ref 2:129). The term "ultra-high" indicates impurity levels of about one part per billion or lower.

Not all metal coordination compounds may be suitable for vapor deposition even though they are quite volatile. The compound should be readily volatilized below the temperature of decomposition, but must undergo decomposition or reaction to form metal layers or films later in the process. That is, the compounds should possess a proper balance between volatility and thermal stability or reactivity for the particular film or coating of interest. Many metal compounds are sufficiently reactive, but lack of volatility often presents a problem. Early studies indicated that many of the metal derivatives of β -diketones exhibit a promising balance between volatility and thermal stability, thus lending themselves to a further study for their use in vapor phase deposition (Ref 3:440-444) (Ref 17:189) (Ref 31) (Ref 32:1098-1101).

Previous Studies of Metal Chelated Compounds of β -diketones

Metal chelated compounds of β -diketones have been known since 1887, when Combes (Ref 4:868-871) reported the synthesis of a few metal acetylacetonates. He recognized volatility as a definite property, especially of beryllium acetylacetonate, and used it to reconfirm the molecular weight of beryllium.

Morgan and Moss (Ref 17:189-196) looked further into the synthesis of other metal acetylacetonates, as well as their properties and possible structures. In general, the metal acetylacetonates have a non-ionizable character, good stability on heating, high solubility in anhydrous organic solvents, and in certain instances, anomalous colors. To aid in the explanation of some of these properties, they hypothesized a high degree of symmetry for the molecules. A tetrahedral or a planar configuration was used for bivalent metals and an octahedral one was used for trivalent metals. The metal atom, being centrally located in the molecule, serves as a connecting link to form six-membered rings when reacting with the univalent acetylacetonate anion.

They also reported the first synthesis of cadmium(II) acetylacetonate, wherein $\text{Cd}(\text{OH})_2$ was digested with an excess of aqueous acetylacetone. Another method is the double decomposition from cadmium acetate and sodium acetylacetonate. No melting point was reported in the early work, but Charles and Pawlikowski (Ref 3:443), have since reported it to be considerably above 191°C .



Truemper (Ref 31) substantiated Staniforth's claim of the increased volatility of the trifluoroacetylacetonate metal chelates, but found the thermal stability to be less than what was expected. He did not investigate the hexafluoroacetylacetonate metal chelates.

Since then, Moshier, et al (Ref 19) have prepared various metal chelates of hexafluoroacetylacetone in conjunction with their work in gas phase chromatography. They found, as did Staniforth and Truemper, a definite increase in volatility over the unfluorinated chelates. Cr(III) hexafluoroacetylacetonate sublimes rapidly at room temperature at 0.05 mm and can even be steam distilled from boiling water (Ref 27:966). Table II (Page 7) shows a rough comparison in volatility of three metal chelates.

TABLE I

Melting Points of Metal Derivatives of
Acetylacetone, Trifluoroacetylacetone & Hexafluoroacetylacetone

Note: All temperatures are uncorrected.

Metals	Melting Points in Degrees Centigrade of the Metal Chelates of		
	Acetylacetone	Trifluoro- acetylacetone	Hexafluoro- acetylacetone
Co(II)	200 _a *	---b	172-174 _c ***
Cu(II)	230 _a *	189 **	113-115 **
Ni(II)	290 *	230 _a *	206-208 _c ***
Mn(II)	290 *	---b	155-156 _c ***
Al(III)	193-194 **	117 **	73-74 ***
Fe(III)	179-180 *	115 *	49-50 ***
La(III)	189 **	169 **	120-125 **
Sm(III)	143-144 **	136-137 **	125 **
Zr(IV)	190-193 ****	128-130 ****	152-154 ***

a - decomposes

b - no melting point reported

c - dihydrate

* (Ref 31:8-14)

** (Ref 29:67, 68)

*** (Ref 19:411)

**** (Ref 13:5111)

TABLE II

Lowest Sublimation Temperatures of Three Metal Chelates of
Acetylacetonate and Hexafluoroacetylacetonate *

Note: The "lowest sublimation temperature" was estimated by
slowly raising the temperature of a sublimation tube
until sublimation was first observed to occur.

Metals	Lowest Sublimation Temperatures in Degrees Centigrade of the Metal Chelates of	
	Acetylacetonate	Hexafluoroacetylacetonate
Al(III)	45 _c	38 _a
Cr(III)	58 _c	25 _b
Fe(III)	44 _c	25 _b

a - Pressure .04mm

b - Pressure .05mm

c - Pressure .01mm

* - Information obtained from personal conversation with
Dr. R. E. Sievers, Research Chemist, Aeronautical Research
Laboratory, Wright-Patterson Air Force Base, Ohio.

At the time of writing this thesis, a literature search indicates that no thermal stability studies have been made on the metal chelates of hexafluoroacetylacetone, nor has the synthesis of Cd(II) trifluoroacetylacetonate or Cd(II) hexafluoroacetylacetonate been reported.

Vapor Deposition Studies

The deposition of metals or metal compounds has been known for a number of years. Over these years, a wide variety of techniques have emerged. Some of the principal techniques are (Ref 10:1):

- (1) Vacuum evaporation of metals and thermally stable compounds.
- (2) Chemical precipitation.
- (3) Thermal decomposition on a heated substrate of a metal halide or of a metal carbonyl gas.
- (4) Explosion of metal wires in an inert gas.
- (5) Cathodic sputtering of metals or metal oxides in a low pressure discharge.
- (6) Chemical reaction of a metal halide and water vapor to form a metal oxide.
- (7) Electro-deposition.

The choice of a technique depends, of course, upon several factors. A few of these factors are the film structure, thickness, or distribution required, substance to be deposited, or the nature of the base material. These requirements, along with definite characteristics of each technique, impose certain limitations upon a process. Films produced by vacuum deposition tend to contain tiny pinholes through which corrosive agents

may penetrate. Therefore, where resistance to corrosion or abrasion is necessary in the films, electro-deposition might best be employed.

For the formation of semiconducting films where crystalline or ordered films are required, or the more amorphorous dielectric films where porosity and adhesion are more important, vapor phase deposition may afford the best approach. Inorganic compounds, or the separate elements of the compounds may, in certain instances, be vaporized to yield the desired films. Cadmium sulfide crystals can be grown from cadmium vapor in hydrogen sulfide gas at 1000°C (Ref 5:932). Another way of obtaining cadmium sulfide crystals is to heat cadmium sulfide powder to 1250°C in an atmosphere of hydrogen sulfide or an inert gas. The crystals form in large grains on a substrate maintained at a temperature of 1150°C (Ref 24:559). Extremely high temperatures are usually encountered when the inorganic compounds or the separate elements are used, as seen in the cited example of cadmium sulfide. As a result, at elevated temperatures trace contamination is introduced from the apparatus or crucible materials of construction. This then, is where organometallic compounds may play an important role. These compounds are much more volatile and so the reactions to form the desired deposits may be carried out at substantially lower temperatures than are otherwise possible. The volatile compounds may undergo reaction in the gas phase to form a deposit of a metal compound or of the metal in its elemental form.

Marboe, in 1947, patented a process for the deposition of metals on glass (Ref 22). The method involves volatilizing a suitable metallo-organic compound in a vacuum and decomposing the vapor of that compound at a hot glass surface. The hot surface of the glass, which is freed of absorbed gases and vapors, is highly active and an adherent deposit results. Some of the volatile compounds used in the process were metal acetylacetonates.

In 1962, Podall, et al (Ref 22) reported the use of organometallic compounds in vapor depositions. For dielectric films of metal oxides, nitrides, or sulfides, two approaches are used. The films may be made either from a single compound containing both elements, or by reacting two or more compounds in the vapor phase at a heated substrate. The first method results in more uniform film or coating because the control of the stoichiometry of the deposits is built right into the starting compound. This greatly reduces the requirement for careful control of flow rates that is encountered in the second method. However, it is necessary that the compound used in the first approach decomposes cleanly to give the desired film or coating. In either approach, the by-products of the decomposition may well contaminate the films, so this might be listed as a disadvantage to the approaches. Contamination is minimized, however, if the by-products are gaseous. They further reported that the optimum temperature for the processes is a function of many variables, and consequently must be determined empirically.

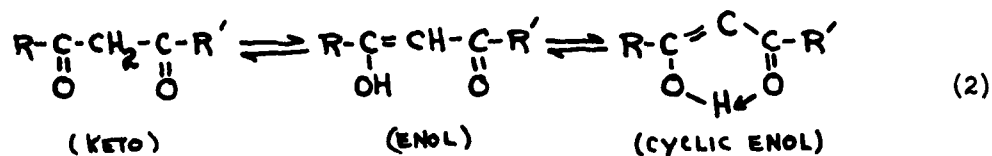
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Format of Report

The first portion of this report is a review of those aspects of metal chelation and vapor phase deposition theory pertinent to this investigation. The second division presents experimental techniques, equipment, and results. A discussion of the results and a presentation of conclusions is made in the third section. Areas for further study are proposed in the fourth section. The appendices contain the experiment on the reaction between hexafluoroacetylacetone and hydrogen sulfide and the infrared spectra and gas chromatograms of a few compounds studied in the investigation.

II. TheoryChelating Agent

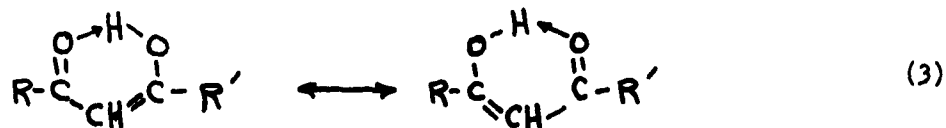
The β -diketones, in general, exist in tautomeric equilibrium between the keto and enol form. The enolic form is favored in the equilibrium to an unusually great extent, especially in the vapor phase where it may be as much as 100% (Ref 12:143). It undoubtedly has a cyclic structure, with the hydroxyl hydrogen coordinated to the carbonyl oxygen (Ref 1:29). The equilibria are illustrated by



where R and R' may be CH_3 , CF_3 , C_2H_5 , C_6H_5 , etc.

An essential requirement for the ligand to readily enter into chelation is that it be capable of being enolized. If both hydrogen atoms on the central carbon between the two carbonyl groups are replaced by two other groups, such as fluorines or chlorines, then there can be no enolization, and chelation does not occur.

It is further postulated that the enol form of the β -diketones may exist in a resonance state, which has the tendency to increase the chelating power of the carbonyl group (Ref 29:30). The resonance state is as follows:



The above equilibrium representation is used primarily for the sake of convenience. Modern theory holds that only one compound is actually present wherein the bonding becomes identical and is represented as follows:



The dotted line represents the even distribution of bonds throughout the ring. The same representation may be made for the metal chelates, where the hydrogen between the two oxygen atoms is replaced by a metal ion.

The chelating agents of the β -diketones which are of primary interest are the acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone. They are shown in their respective anion forms as follows:



For the sake of simplicity, the three ligands will be referred to hereafter as AcAc, TFA, and HFA. Table III (Page 14) lists some physical properties of these β -diketones.

TABLE III

Some Physical Properties of
Acetylacetone and Its Fluorine-Substituted Derivatives

Note: Wave length of the maximum of the absorption bands is represented by $\lambda_{\max}$, and the corresponding molar extinction coefficient is represented by $\epsilon_{\max}$.

β -diketone	Boiling Point °C	*** Density Grams/ml	Ultra-Violet Absorption in CHCl ₃ Solutions ****	
			$\lambda_{\max}$ m μ	$\epsilon_{\max}$
Acetylacetone	134-136 _a *	.98	280	9500
Trifluoro- acetylacetone	107 **	1.27	284	10500
Hexafluoro- acetylacetone	63-65 **	1.33	273	7800

a - Pressure at boiling point is 740mm; others are at 760mm.

* (Ref 12:148)

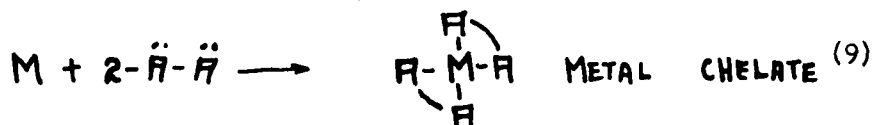
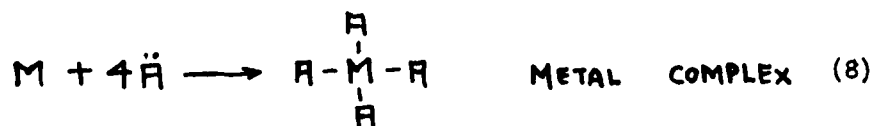
** (Ref 8:1820)

*** (Ref 9:49)

**** (Ref 1:17)

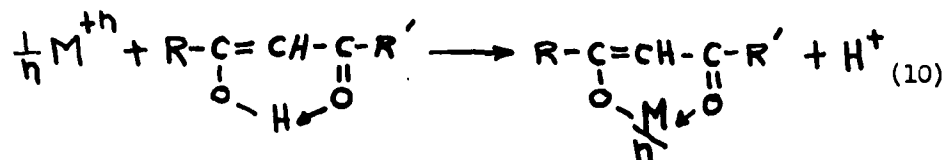
Formation of the Chelate Compounds

A complex or coordination compound is one in which a metal ion combines with an electron donor. If this electron donor contains two or more groups which combine with the metal to form one or more rings, then the resulting molecule is termed a metal chelate. To emphasize the difference between a metal complex and a metal chelate, consider the following general reactions (Ref 15:1):



M is a metal ion, $\ddot{A}$ is a complexing agent, and $\ddot{A}-\ddot{A}$ is a chelating agent.

For the metal chelates of AcAc and its derivatives, the chelation takes place from the enolic form of the β -diketone. The hydrogen atom of the hydroxyl group is replaced by the metal ion, and the ring is completed by coordination with two unshared pair of electrons of the other oxygen atom. The general reaction is



where M is a metal ion, n is the ionic charge, and R and R' may be CH_3 , CF_3 , C_2H_5 , C_6H_5 , etc.

Metal ions which have appreciable tendencies toward the formation of covalent bonds usually enter readily into chelation. In a covalent bond the interacting atoms combine through the agency of shared electron pairs. In the classical theory, the principal valence is the number of electrons utilized by a given atom in the formation of the bonding electron pairs, and the secondary valence is reduced to the filling of energetically suitable electron orbitals of the atom, with electron pairs loaned by neutral or charged addenda. For primary covalent bonding, the directional distribution of the donor groups will depend on the angular distribution of the metal orbitals which are available for bond formation (Ref 7:174-175). The actual bonding of the metal with the chelate, however, may occur through two principal valences, through two auxiliary valences, or through one principal and one auxiliary, as in inner complex compounds.

The idea of two types of valences used in the bonding of a metal with an organic ligand was exhaustively studied by Alfred Werner and he was given extensive credit for the correct explanation of the characteristics of these compounds. Many of our more modern theories rely heavily on his early work. The fundamental postulates of his theory may be summarized as follows (Ref 16:229-230):

- (1) Metals possess two types of valence, so-called principal or ionizable valence and secondary or non-ionizable valence.
- (2) Every metal has a fixed number of secondary valences, or coordination number.

- (3) Principal valences are satisfied by negative ions, whereas secondary valences may be satisfied by either negative groups or neutral molecules. In some instances, a given negative group may satisfy both, but in every case fulfillment of the coordination number of the metal appears essential.
- (4) Secondary valences are directed in space about the central metal ion. Therefore, six such valences were regarded as directed to the apexes of a regular octahedron circumscribed about the metal ion, whereas four such bonds might be arranged in either a planar or a tetrahedral manner.

Thus, we see that Werner takes into account the bonding of the chelate as well as proposing structures, where the metal exists in the center of the molecule, totally or partially surrounded by the organic ligand.

There are many factors which will influence chelation. Some of these are:

- (1) The size of the rings affects chelation, in that they may be large and interfere with each other in the build-up of the molecule, since they may arrange themselves more or less independently about the metal ion. This could cause distortion and strain in the chelate ring and affect the molecular stability (Ref 11:1838).

- (2) An increase in the number of rings within a particular chelate structure results in a greater stability. If two donor groups are linked together to form an additional ring in which the donor groups are not materially altered, then the increased stability of the chelate, as indicated by an increase in the formation constant of the molecule, arises almost entirely from an increase in entropy (Ref 15:143, 149).
- (3) For the alkaline-earth and alkali metals, it was found that there is generally an increase in the stability constant of the metal chelate with increased values of e^2/r , where e is the charge of the metal ion and r is the radius of the metal ion (Ref 15:191).
- (4) Geometric considerations alone may limit the number of donor groups around a metal ion. The ratio of the radius of a metal ion to that of a donor must be equal to, or greater than, a certain limiting value for each geometric configuration. If the ratio is less, it is considered that the bond between the donor and the metal, if it exists at all, is somewhat longer than normal and considerably weakened. Therefore, metals usually form a structure with a lower coordination number which indicates a lower radius ratio restriction (Ref 15:243).
- (5) Substitutions made on the ligand in the R and R' groups in equation 3, may influence the acidity of the donor group, or it may interfere with or enhance the resonance of the chelate ring. The substitution of fluorine for hydrogen on the methyl

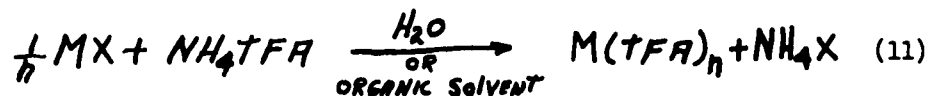
groups of AcAc showed that the rare earth chelates possess an increase in thermal stability, a decrease in melting point, and an increase in organic solubility (Ref 15:180). The carbon-fluorine bond cannot interfere with the resonance of the chelate ring, so it should have a greater chelate stability. However, the stability constants are reduced by about thirty percent (Ref 15:152). The inductive electron withdrawal of fluorine is very great, rendering the oxygen donor atom of the compound much less basic. Thus, its lower stability is substantiated from the general case where the less basic donor atoms should exhibit a weaker covalent bond with a metal ion, by virtue of the lower electron density about them (Ref 11:1838).

The greatest tendency for chelation results when the requirements of both donor and acceptor are mutually satisfied to the greatest extent (Ref 15:149).

The actual preparation of the metal chelate usually involves the addition of a chelating agent to a solution of an inorganic metal salt in water. An aqueous solution of the chelating agent which has been buffered or neutralized may be added in place of the chelating agent itself. The pH of the combined solutions must be substantially controlled, since basic solutions have a strong tendency to form the metal hydroxides, and in acid solutions chelation is repressed. If the metal inorganic salts are soluble, the reactions can also be conducted in organic solvents; this reduces the probability of the ligand undergoing

hydrolysis. Other variations in the synthesis of the metal chelates have been reported and, in some instances, are necessary because all metal ions do not exhibit the same tendency to form coordination compounds under the same conditions.

In some cases, it may be desirable to synthesize the chelates by the use of an intermediary such as the ammonium trifluoroacetylacetonate or hexafluoroacetylacetonate. Spendlove (Ref 28) has shown this method to be quite successful with a number of metal ions. The general reaction for the synthesis of metal chelates of TFA is shown below, and applies as well for the synthesis of the metal chelates of HFA.

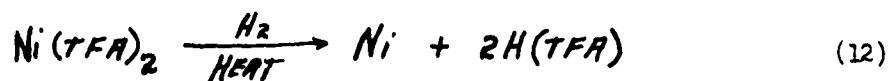


M is a metal, X may be P, Cl, N, etc., and n is the ionic charge of the metal.

Reactions of Chelate Compounds in the Gaseous Phase

Very little is known about the chemistry of the metal acetylacetonates and fluorinated derivatives in the gas phase reactions. Thermal decomposition studies of metal acetylacetonates by Van Hoene and co-workers (Ref 32:1098) showed the two major decomposition products to be acetone and carbon dioxide. It may be postulated, however, that the ligand could be regenerated intact if temperatures are kept relatively low. The ligand, carrying a negative charge when it is cleaved from the metal ion, will combine with a proton to form a gaseous neutral species.

If hydrogen is introduced into the system, a reduction reaction occurs yielding protons which recombine with the anion of the chelating agent. In decomposition reactions, the chemistry is not clearly defined and numerous decomposition products result. The reduction reaction would proceed as follows:

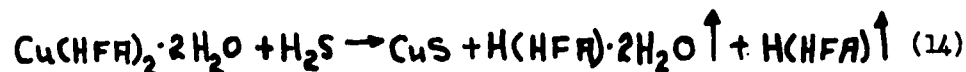


It may be further postulated that if the metal acetylacetonate is a hydrate, as is often the case in the HFA chelates prepared in aqueous solutions, then hexafluoroacetylacetone dihydrate will be formed in place of anhydrous H(HFA). Schultz and Larsen (Ref 25:3250) have reported evidence of the HFA dihydrate, stating that it may exist in an equilibrium form, as follows:



The HFA dihydrate is very volatile, showing substantial sublimation at room temperature. Therefore, at elevated temperatures in the gas phase, it would be given off as a gas in much the same manner as the free ligand.

In metathetical gas phase reactions not involving reduction or thermal decomposition, it is to be expected that the metal would be free to react. The ligand or its dihydrate would be carried off as a gas and another metal bearing compound formed. To illustrate this, let us consider the reaction of copper hexafluoroacetylacetonate dihydrate with hydrogen sulfide.



If there is excess water present or the vapors of H(HFA) come in contact with moist air, the dihydrate will be formed exclusively. The mere exposure of a small quantity of HFA liquid to the atmosphere for a very short period of time will result in the HFA dihydrate being formed.

Since the ligands or hydrates of the ligands come off as gases, they may be trapped and re-used to synthesize more of the metal chelates. The sulfides or other metal inorganic compounds that are formed should be reasonably pure because the reaction by-products are gaseous.

Vapor Phase Deposition

Organo-metallic compounds, metal chelates, and some metal complexes are promising compounds to consider for use in vapor phase deposition of the metal since they usually possess a vaporization point below that of their decomposition point. These compounds generally have vaporization temperatures much lower than the corresponding metals themselves, which further allows the process to be carried on at greatly reduced temperatures. Care must be taken in the selection of the proper compound to be used, since it is extremely important that the reaction products or thermal decomposition products do not contaminate the deposited metal or metal compound. It is equally important that the organic metal compound lend itself to be easily controlled in the vapor state so that the reaction occurs at the desired place.

Malvern and Jenkin (Ref 14:4-18) reported some of the more important parameters they studied on aluminum deposition and the effects these parameters may have on the process. The temperature of the substrate must be above a lower limit below which the vaporizable compound will not deposit, and below an upper limit above which the metal will deposit as a powder. Between these two limits, the deposition proceeds at a rate which depends on the temperature level used. The temperature for vaporization must be at an optimum which is below the decomposition point, yet sufficient to accomplish good volatilization. In a reduced pressure system, which would allow vaporization to occur at a much lower temperature, there is a better opportunity of reaching the optimum temperature. Reduced pressures also increase the mean-free path of the vaporized molecule in the residual gas in the system, so that only a limited number of collisions between vapor and gas molecules will occur. Thus, the rate of deposition at a given vaporization temperature will be increased. If it is necessary or desired to operate at atmospheric pressure, a carrier gas may be utilized which will aid in vaporization. The carrier gas may also function as a means of sweeping out decomposition products, and may dilute the metal plating compound, which allows for better control of the plating operation. Along with the carrier gas, other agents may be added which might serve to suppress undesirable side reactions, stabilize the metal-bearing compound, promote the plating reaction by reacting with one of the decomposition products, or affect the quality of the deposit. Finally, the condition of the substrate should be taken into account. It must be absolutely clean for best adhesion. A wide variety of techniques, depending on the material of the

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substrate, are employed to prepare the surface. They may vary from using abrasive paper followed by hydrogen reduction to degreasing with trichloroethylene vapor.

Though the parameters discussed above apply to the deposition of a metal by thermal decomposition, they could very well be extended to include chemical reactions in the gaseous phase to deposit metal oxides, sulfides, or nitrides.

III. Experimental and Results

Introduction

Many experiments were undertaken in order to explain as completely as possible, the vapor phase deposition reaction of the cadmium chelate with hydrogen sulfide. All of the experimental work was performed in the Inorganic and Analytical Chemistry Branch of the Aeronautical Research Laboratory, Wright-Patterson Air Force Base, Ohio. Necessary analyses which could not be obtained in the laboratory, because of a lack of special equipment items, were performed by commercial laboratories.

A preliminary experiment established the fact that the crude cadmium chelate and hydrogen sulfide react in various organic solvents to produce cadmium sulfide. The reaction occurring in solutions enhanced the possibility that the reaction would also take place in the vapor phase. An experiment was also conducted to see what effects, if any, the anticipated vapor phase reaction temperatures would have on hydrogen sulfide. Only one minor effect was observed. This effect is that hydrogen sulfide reacts moderately with water. Therefore, the amount of moisture in the vapor phase reaction system must be reduced to a minimum. Another experiment to investigate a possible reaction between hydrogen sulfide and hexafluoroacetylacetone was performed and is presented in Appendix A. This particular experiment was initiated in an attempt to identify one of the products of the cadmium chelate-hydrogen sulfide vapor phase reaction. The main experiments, however, which are presented in detail in this report are the synthesis of the

cadmium chelate, the vapor phase reaction of hydrogen sulfide with the cadmium chelate and the gas solid reaction of hydrogen sulfide with the cadmium chelate.

The primary synthesis of the cadmium chelate closely followed the procedure used in the synthesis of other metal hexafluoroacetylacetonate chelates whose identities have been firmly established. Infrared spectra of the synthesized cadmium chelate and basic chemical analyses of this compound, indicated that the cadmium derivative of hexafluoroacetylacetonate was the synthesized compound. It was therefore initially accepted that cadmium(II) hexafluoroacetylacetonate or one of its hydrated forms was synthesized.

However, fluctuations in the melting point of the cadmium chelate taken in conjunction with the fact that the vapor phase reaction products were not consistent with the initially accepted structure, prompted further detailed investigations. Since the gas solid reaction of the cadmium chelate with hydrogen sulfide yielded the same reaction products as the vapor phase reaction, the gas solid reaction was utilized to obtain large quantities of the reaction products. Many analyses techniques such as infrared studies, mass spectra, nuclear magnetic resonance spectroscopy and gas chromatography were performed on these products to establish their identity. At the same time, another means of synthesizing the cadmium chelate was established. This method yielded the same crude compound that was previously synthesized. Close analysis of the crude and sublimed synthesized cadmium chelates correlated with the identities of the gas solid reaction products ultimately led to the

proposed composition and structure of the crude and sublimed cadmium chelates presented in Section IV. The chemical reaction for the vapor phase is also presented in Section IV.

Synthesis of the Cadmium Chelate

The cadmium chelate was prepared by two different methods. The first method followed the approach reported by Young in his synthesis of Aluminum (III) acetylacetonate, where the ligand itself was used to form a metal chelate compound (Ref 6:25). The second method is not, at the present time, reported in the literature and makes use of an intermediary compound, ammonium hexafluoroacetylacetonate, to form the metal chelate. In both methods, the HFA and the cadmium chloride starting compounds were obtained commercially. The HFA was obtained from Columbia Organic Chemical Co., Inc., Columbia, South Carolina. The anhydrous reagent grade cadmium chloride was obtained from Fisher Scientific Co., Fairlawn, New Jersey. The ammonium hexafluoroacetylacetonate, however, was synthesized according to a method reported by Spendlove (Ref 28).

In the first method, 4.97 g (0.0238 moles) of HFA was added to 20 ml of distilled water. The solution was heated and partially neutralized by the addition of 6N ammonium hydroxide dropwise with constant stirring until the HFA was completely in solution. This was indicated by the disappearance of the oily glob initially present when HFA was added to the water. The pH of the solution at this point was about five to six. This solution was then added dropwise with constant

stirring to a second solution containing two grams (0.0109 moles) of cadmium chloride dissolved in 20 ml of water. The cadmium chelate precipitated out slowly in a small yield, approximately thirty percent of the theoretically calculated yield. The yield may be increased to 80% by stepwise addition of 6N ammonium hydroxide to the filtrate and repeated filtration of the cadmium chelate. The formation of the cadmium hydroxide is greatly favored if the pH exceeds seven. Therefore, if the pH becomes too high, the hydroxide may form rather than the cadmium chelate.

In the second method, 4.91 g (0.0218 moles) of freshly prepared NH_4 (HFA) was dissolved in 35 ml of distilled water. The water was added slowly with constant stirring to the NH_4 (HFA). The solution may be filtered if it is evident that not all of the NH_4 (HFA) has gone into solution. This, however, was usually not necessary. The aqueous NH_4 (HFA) solution was then added slowly with constant stirring to a second solution containing two grams (0.0109 moles) of cadmium chloride dissolved in 10 ml of distilled water. The cadmium chelate precipitated immediately to give a yield of approximately eighty percent.

To study the synthesis on a quantitative basis, it is necessary to achieve complete recovery of the cadmium chelate derived from the reaction. In general, water can be used as a recovery agent, since the metal HFA's have been found to be insoluble in it. It was discovered, however, that the cadmium chelate is soluble in water. Consequently, a liquid such as carbon tetrachloride was used to achieve the recovery.

It was also desired that the cadmium chelate be purified after its synthesis in order to reduce, as much as possible, any side reactions which might occur when it is reacted with the hydrogen sulfide. Since the cadmium chelate is not soluble in a suitable organic solvent, purification by recrystallizing the compound could not be achieved. The compound was therefore sublimed at temperatures of 120-130°C, and a pressure of 0.1 mm Hg. In these sublimations, a water cooled cold finger was used. Sublimations were also carried out by the use of a cold finger cooled by a mixture of dry ice and acetone. However, the first approach was used strictly for the sake of convenience, because it was not necessary to maintain a close vigilance over the cold finger to insure that the coolant was not expended. Three or four sublimations were performed on each synthesized cadmium chelate. A melting point determination of the cadmium chelate after each sublimation disclosed a decrease in the melting point rather than the increase expected with purification. The compound of interest that is to be purified through sublimation is usually the major constituent. A minority of contaminants will thus cause the melting point of the compound of interest to be lower. Therefore, through sublimation where the minor contaminants are removed, the compound of interest should then exhibit a higher melting point. The opposite may be true, however, if the compound of interest is in the minority before the start of the sublimation. The observation of the decrease in melting points naturally prompted further investigation and ultimately led to the conclusion that either another cadmium chelate

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compound was formed during the sublimation or resulted from the method of synthesis. Some physical properties of the two proposed compounds are given in Table IV.

TABLE IV
Determined Physical Constants of Investigated Compounds

Chemical Compound	Molecular Weight	Physical State	Melting Point °C	Solubility at Room Temperature	
				Solvents compound is soluble in	Solvents compound is insoluble in
NH_4HFA	225.09	White crystalline solid	138-140 ^c	Water, Acetone, Ethanol, Pyridine	Hexane, Benzene, Carbon Tetrachloride, Chloroform
$\text{Cd}(\text{HFA})_2 \cdot \text{H}_2\text{O} \cdot \text{NH}_3$ ^a	561.57	White crystalline solid	163-165 ^d	Ethanol, Carbon Tetrachloride, Slightly in Benzene, Pyridine	Chloroform, Water, Acetone
$\text{NH}_4^+ [\text{Cd}(\text{HFA})_3]^- \cdot \text{H}_2\text{O}$ ^b	769.56	White crystalline solid	177-181	Water, Acetone, Ethanol, Pyridine	Hexane, Benzene, Chloroform, Carbon Tetrachloride
$\text{HFA} \cdot 2\text{H}_2\text{O}$	244.10	White crystalline solid	102-103	Acetone, Ethanol, Ether, Slowly in Water	Toluene

^a - Proposed compound of sublimed cadmium chelate

^b - Proposed compound of crude cadmium chelate (unsublimed)

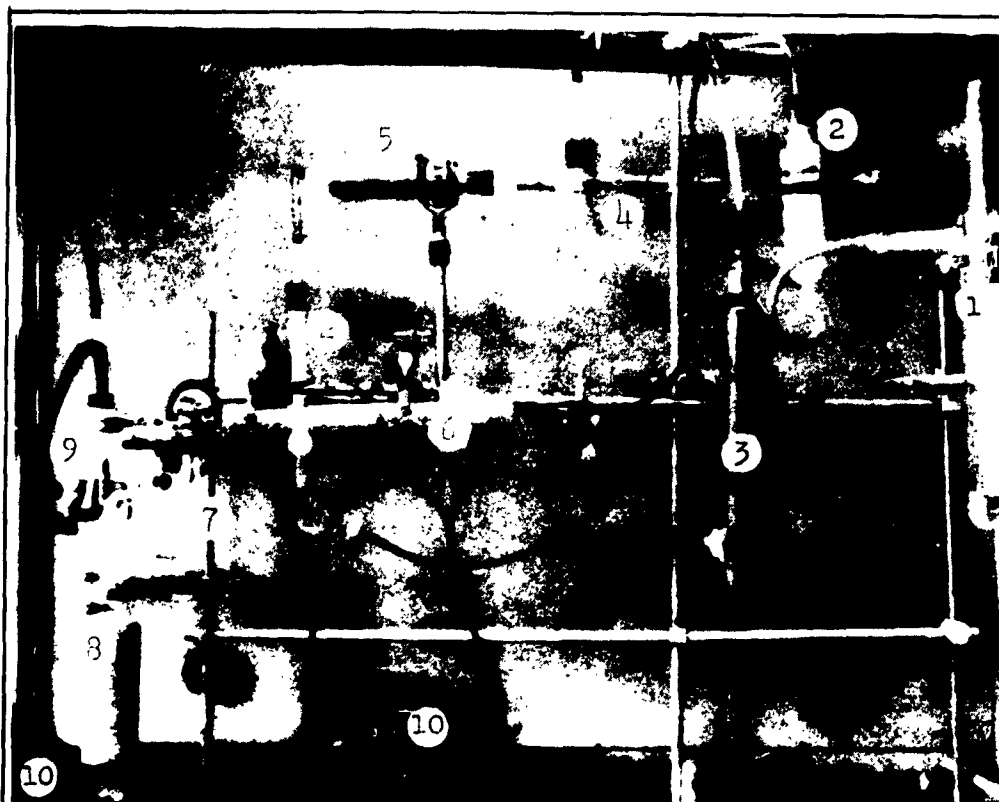
^c - Compound sublimes

^d - Melting point after four sublimations made at 120°-130°C and 0.1 mm pressure of Hg

Vapor Phase Reaction of Hydrogen Sulfide With the Cadmium Chelate

The sublimed cadmium chelate was vaporized and then transported, by nitrogen, acting as a carrier gas, into a heated glass tube. Hydrogen sulfide flowed into the heated reaction tube and reacted with the cadmium chelate. This reaction caused a deposit of cadmium sulfide to be formed on the sides of the glass tube. The other products of the reaction were swept out of the reaction tube by the carrier gas and collected in cold traps. In an effort to understand this vapor phase reaction and thereby be able to write out the balanced chemical reaction, analyses were performed on the trapped products and the cadmium sulfide. Many different arrangements of the experimental apparatus, as well as modifications in the reaction tube, were used throughout this experiment. Only one reaction tube and one arrangement, however, is presented in this thesis, since they yielded the best control of the parameters which were necessary to investigate the reaction.

Apparatus. Figure 1 is a photograph of the experimental apparatus. The hydrogen sulfide was bubbled into a silicone oil bath to check its flow rate and was then passed through two drying tubes containing silica gel and cadmium chloride. The two drying tubes were used to extract any water which the hydrogen sulfide might contain. After the hydrogen sulfide passed through the last drying tube, it entered the vaporization-reaction tube where it came into contact with the vaporized cadmium chelate. A very thin glass probe was used as an inlet for the hydrogen sulfide to make sure that it only came in contact with the vaporized cadmium chelate. Figure 2 shows the vaporization-reaction tube with the inserted hydrogen sulfide probe.



1. Sulfuric Acid Flow Rate Indicator
2. Calcium Chloride Drying Tube
3. Hydrogen Sulfide Cylinder
4. Silicone Oil Flow Rate Indicator
5. Silica Gel Drying Tube
6. Furnace and the Vaporization-Reaction Tube
7. Cold Trap
8. Dry Ice-Acetone Cold Trap
9. Copper Chloride Solution
10. Powerstats

Figure 1

Experimental Apparatus for the Vapor Phase Reaction

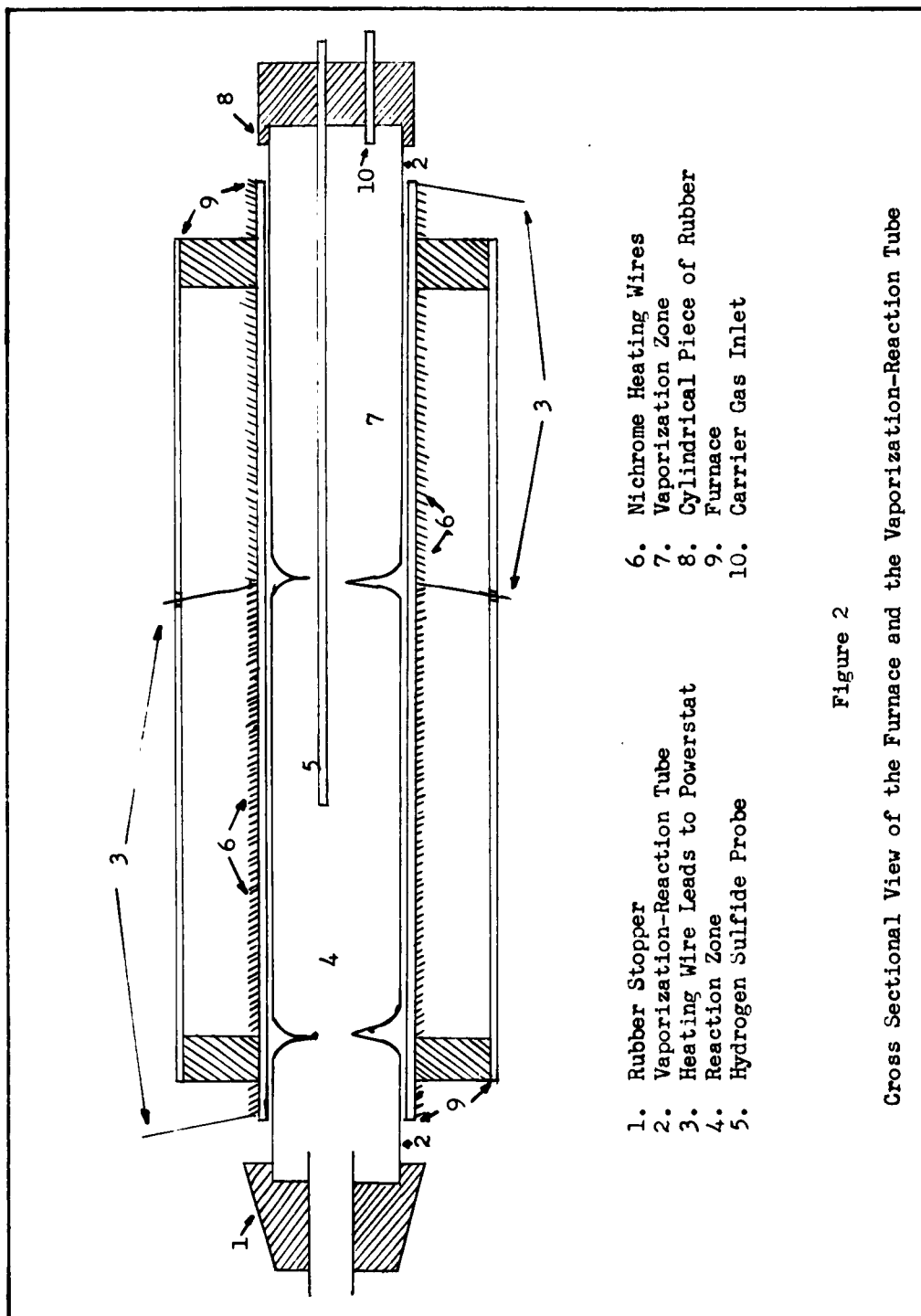


Figure 2

Cross Sectional View of the Furnace and the Vaporization-Reaction Tube

The nitrogen carrier gas was dried in three drying towers which are not shown in Figure 1. The towers contained calcium sulfate, calcium chloride, and phosphorous pentoxide. After passing through these three drying towers, the nitrogen gas then entered the sulfuric acid flow rate indicator. Aside from being used as a flow rate indicator, the concentrated sulfuric acid was an additional drying agent for the nitrogen. To prevent the possible spraying of the sulfuric acid into the vaporization-reaction tube, another drying tube, containing calcium chloride, was inserted into the system. The nitrogen entered the vaporization-reaction tube upon exiting from this last drying tube.

Two cold traps and an aqueous copper chloride solution were located on the exit end of the vaporization-reaction tube. The first cold trap was maintained at 0°C and trapped most of the reaction products but not the unreacted hydrogen sulfide. The second trap, maintained at a dry ice and acetone mixture temperature of -85°C, collected most of the unreacted hydrogen sulfide and any reaction products which escaped the first trap. The aqueous copper chloride solution prevented the escape of any untrapped hydrogen sulfide by reacting with it to precipitate out copper sulfide. It should be noted that extreme caution was taken to prevent the escape of the toxic hydrogen sulfide. In addition to the cold trap and the copper chloride solution, the complete experiment was conducted in a well ventilated hood.

The furnace and the vaporization-reaction tube are represented in a cross-sectional view in Figure 2. The former is reusable and the latter is replaceable. The replaceable vaporization-reaction tube allows

the cadmium sulfide to be maintained as it was deposited, so that a visual comparison of such deposits is possible when various parameters of the vapor phase reaction are studied.

The furnace is constructed from two pieces of glass tubing which are concentric. The inner glass tube is eleven inches long and twelve millimeters in diameter. It is wound with nichrome wire in such a manner as to allow two independently heated sections inside the furnace. An asbestos tape which serves as an insulator and spacer, separates the inner tube from the outer one. The outer tube is ten inches long and twenty-five millimeters in diameter. It has two 1/8 inch diameter holes oppositely positioned from one another, and located four inches from one end of the furnace. The holes provide a means of attaching the nichrome heating wires to the powerstats.

The vaporization-reaction tube is twelve inches long and fits snugly inside the furnace. It is constricted in two places. The constriction between the vaporization zone and the reaction zone serves to hinder the backward flow of hydrogen sulfide. The other constriction serves the purpose of momentarily containing the hydrogen sulfide and the vaporized cadmium chelate. This allows the two gases to react with each other for a longer period of time. The hydrogen sulfide probe, shown inserted in the vaporization-reaction tube in Figure 2, is two millimeters in diameter and extends well into the reaction zone. The carrier gas inlet is also two millimeters in diameter and enters only into the vaporization zone.

Procedure

A clean vaporization-reaction tube was inserted into the furnace and the exit end of the tube connected into the system and sealed off from the atmosphere. Only the reaction zone of the tube was then preheated to the selected operating temperature for 15 minutes. This procedure tends to bake out any absorbed gases which might be present in the glass tubing of the reaction zone. A quartz boat, filled with the sublimed cadmium chelate was inserted into the vaporization zone and the entrance end of the vaporization-reaction tube was connected to the system and sealed off from the atmosphere. The nitrogen carrier gas was then introduced. Once its flow rate was adjusted and remained steady, the vaporization zone was heated to the selected operating temperature. While the temperature was increasing inside the vaporization zone, the hydrogen sulfide flow was initiated and adjusted to maintain a selected flow rate. The reaction was allowed to proceed until it was observed that all of the cadmium chelate had vaporized out of the quartz boat or had started to decompose. The hydrogen sulfide was then disconnected from the system. The nitrogen gas was allowed to flow for an additional fifteen minutes before it was disconnected, to flush out any remaining hydrogen sulfide or gaseous reaction products. The vaporization-reaction tube was cooled to room temperature and removed from the system to recover the cadmium sulfide. The condensed gaseous products were recovered from the cold traps.

The temperatures in each zone were measured with the vaporization-reaction tube in place and the nitrogen carried gas flowing. Measurements were made with a chromel-alumel thermocouple connected to a Leeds-Northrup potentiometer. The temperatures were correlated to settings on a powerstat in order that certain conditions may be duplicated without having to recheck the temperatures in the two zones.

The nitrogen and hydrogen sulfide gas flow rate were determined by use of their respective flow rate indicators. That is, the number of bubbles, caused by the flowing of the gases through either the silicone oil or the sulfuric acid, were counted as a function of time. These counts were later correlated to a flow rate in ml per minute. A simple Burrell Corporation flowmeter was used to accomplish this. This principle of operation is that a soap bubble is introduced into the flowing gas, whose flow rate is to be measured. The gas carries the soap bubble through a glass tube of calibrated length, which is related to the volume. Therefore, the time it takes the bubble to travel the calibrated length is the flow rate of the gas in the specific volume units per length of time measured.

Table V shows the results obtained in the vapor phase reaction.

TABLE V
Results of Vapor Phase Reactions

Vaporization Zone Temperature °C	Reaction Zone Tempera- ture °C	H ₂ S Flow Rate ml/min	N ₂ Flow Rate ml/min	Observations
158-170	227-240	5-10	10-15	Very little deposit formed since H ₂ S back-tracked to the solid cadmium chelate. This is a poor combination of parameters. At the temperatures used, the N ₂ flow rate should be at least three times that of the H ₂ S.
158-170	227-240	5-10	65-70	Good film of CdS was deposited. The combination of parameters, however, is poor for trapping the pure gaseous products. They become contaminated because of the high N ₂ flow rate. A lower N ₂ flow rate decreases the quality of the CdS.
150-160	140-150	2-3	6-10	Yellow crystals formed which gave a positive lead acetate test. There is doubt if crystals are pure CdS because of the low reaction temperature. The collection of gaseous products was very difficult.
164-174	180-195	15-20	33-40	This is a good combination of parameters for collecting the gaseous products. The film of CdS, however, was rather poor.

Gas Solid Reaction of Hydrogen Sulfide With the Cadmium Chelate

In the vapor phase reaction of the cadmium chelate with hydrogen sulfide, the trapped white crystalline products were obtained in insufficient amounts to be chemically analyzed. Therefore, since this reaction could be carried out on a larger scale, sufficient samples could then be obtained. A sample from the batch of sublimed cadmium chelate, which was used in the vapor phase reaction, was used in the gas solid reaction. Subsequent samples of the cadmium chelate used were purified in the same manner as the sublimed cadmium chelate initially used in the vapor phase reaction.

The reaction took place in a simple glass trap. Six hundred to eight hundred milligrams of the cadmium chelate were placed in the bottom of the trap. Great pains were taken not to spill any of the metal chelate on the sides of the trap. This would cause contamination of the reaction product or products that were to be collected. One end of the trap was connected to a regulated hydrogen sulfide source and the other end was connected to an aqueous copper chloride solution. The function of the aqueous copper chloride solution was to trap any excess hydrogen sulfide which did not enter into the reaction. A stopcock was inserted between the copper chloride solution and the trap. This was done so that with the stopcock closed, the hydrogen sulfide might be contained inside the trap to permit as complete a reaction as possible. The system was initially purged with nitrogen and then, with the stopcock in the closed position, a small amount of hydrogen sulfide was allowed to enter the trap. An immediate reaction was observed,

whereby the white cadmium chelate turned a bright yellow but no gaseous products were obtained. The trap was then immersed in a preheated oil bath, maintained at a temperature of 170° to 180°C. It was quite evident at this time that a volatile product resulted from the reaction, since white needlelike crystals started to condense on the sides of the trap. The deposit appeared in two zones, one near the hot oil and the other in the cooler region near the top of the trap. The reaction was allowed to proceed for three minutes without introducing anymore hydrogen sulfide and then the stopcock was opened to the copper chloride solution for an additional two minutes. The trap was removed from the oil bath, cooled to room temperature and the stopcock again closed. Hydrogen sulfide was re-emitted into the trap and the procedure repeated.

A small quantity of the product in both zones was carefully removed from the sides of the trap. The melting point and infrared spectra of the product in the two zones was determined. The results showed that there were two distinct products and they exactly compared with that of the products from the vapor phase reaction. This experiment was performed many times to obtain large quantities of the reaction products to be used in further tests to establish their identity.

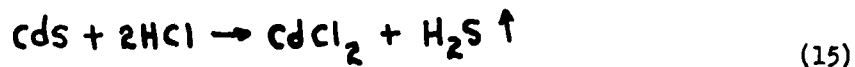
The same reaction was initially attempted at reduced pressure, whereby the aqueous copper chloride solution was replaced by a dry ice acetone cold trap which was, in turn, connected to the vacuum pump. This procedure was not utilized, however, since the gaseous products were

carried over into the cold trap which made for difficult recovery. At the same time, the products were being contaminated by each other.

Analyses

Of the many analysis techniques employed, only qualitative analysis, gas chromatography, and infrared could be performed in the laboratory. The mass spectra, nuclear magnetic resonance, and spectrographic emission studies were performed by the Analytical Laboratories of the Monsanto Research Corporation, Dayton, Ohio. The quantitative chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Qualitative and Quantitative Analyses. Cadmium sulfide is detectable by the lead acetate test (Ref 30:70). This test makes use of the reaction of a sulfide with hydrochloric acid. The reaction releases hydrogen sulfide gas, which when brought into contact with a saturated filter paper of lead acetate, gives it a brown-black discoloration. This is due to the formation of lead sulfide. The two reactions are as follows:



The elements, sulfur and nitrogen, may be detected in organic compounds by a sodium fusion test (Ref 26:52-55). This test depends upon the fusion of an organic compound with sodium, which converts the elements

into water soluble ionic compounds. The reactions for nitrogen and sulfur are



where X represents the rest of the organic compound, and is not indicated on the right hand side of the reaction since the products into which it is converted are not well known. Thionapthenequinone (C_6H_4SCOCO) and 8-hydroxyquinoline ($HOC_6H_3N:CHCH:CH$) were used as standard organic compounds to check the sodium fusion analysis reagents.

The quantitative analyses, as mentioned previously, were performed by the Galbraith Laboratories and the results are presented in Table VI. The limit of error tolerated for an actual positive confirmation of a chemical compound is plus or minus 0.30% deviation from the theoretically calculated values of each element in the compound. As noted from Table VI, the cadmium and fluorine analysis for both proposed compounds of the cadmium chelates did not fall within the limit of error.

Gas Chromatography. The gas chromatography analyses were performed on an F & M Scientific Corporation, Model 500, gas chromatograph. This particular model employs a thermal conductivity cell for its detection (Ref 20:764).

A two foot glass column, having an inner diameter of 4mm, was used for the separation of the vaporized samples. It was packed with a composition of 5% Dow-Corning Silicone 7-10 oil on Cromsorb-W. The column was maintained at a temperature of 25°C and the helium gas flow rate

TABLE VI
Results of Chemical Analyses

Note: Chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Chemical Compounds	Elements	Calculated Values for Compound in Percent	Found Analyses for Compound in Percent
NH_4HFA	C	26.68	26.41
	H	2.24	2.43
	F	50.65	50.38
	N	6.21	6.39
^a $\text{Cd}(\text{HFA})_2 \cdot \text{H}_2\text{O} \cdot \text{NH}_3$	C	21.39	21.52
	H	1.36	1.19
	F	40.60	41.65
	N	2.49	2.54
	Cd	20.02	20.62
^b $\text{NH}_4^+ \left[\text{Cd}(\text{HFA})_3 \right]^- \cdot \text{H}_2\text{O}$	C	23.39	23.57
	H	1.17	1.07
	F	44.50	42.46
	Cd	14.62	13.74
$\text{HFA} \cdot 2\text{H}_2\text{O}$	C	24.62	24.71
	H	2.48	2.69
	F	46.70	46.63

a - Proposed compound of sublimed cadmium chelate

b - Proposed compound of crude cadmium chelate (unsublimed)

through it was measured at 16 ml per minute. One lambda (1 micro liter) samples of individual solutions of HFA, $\text{HFA} \cdot 2\text{H}_2\text{O}$, and $\text{NH}_4(\text{HFA})$ in absolute ethanol were injected into the port which was set at 95°C. Appendix B contains copies of the chromatograms.

The gas chromatography technique was used to compare the retention time and the purity of the three compounds mentioned. The HFA and $\text{HFA} \cdot 2\text{H}_2\text{O}$ were detected as anticipated, and the chromatograms showed no signs of impurities. The ammonium HFA, however, could not be detected under the above mentioned conditions. Therefore, the column temperature was changed. It was programmed at an increasing temperature rise of 11°C per minute up to a maximum temperature of 130°C. This procedure also showed that the ammonium HFA was still not being detected and further attempts were not made.

Infrared. Infrared studies were carried out on a Perkin-Elmer Infracord Spectrophotometer, Model 21. It employs a sensitive gas thermocouple as its detector (Ref 21:1183).

Samples whose spectra are to be investigated may be prepared in a variety of ways. Only two methods, however, were utilized in this study. The first method was to take a minute quantity of sample, about 1/2 milligram, and mix it with 200 to 400 milligrams of spectrograde potassium bromide. This mixture was then pressed into a pellet under 15,000 psi pressure. The prepared pellet should be as transparent as possible, to allow transmission of 85 to 90%.

The second method was to take about 50-100 milligrams of sample and grind it up in one drop of nujol (white mineral oil) to form a mull. That is, the solid particles of the sample are suspended in the liquid medium. Nujol has a refractive index higher than that of air, so that light scattering is reduced to a minimum, which allows for high transmission and good peak resolution.

Infrared studies were conducted to look into the structure of compounds and to detect organic contaminate in cadmium sulfide. Table VII shows the assignments of the absorbed peaks of the investigated compounds. The actual spectra are in Appendix B.

Mass Spectra. Table VIII shows the results of the mass peaks observed, together with assignments of molecular fragments corresponding to the mass peaks. For the two cadmium chelates, two mass peaks were not given assignments because they could not be correlated with the proposed structures. It is possible that recombination of molecular fragments occurred.

TABLE VII

Infrared Absorption Bands of Investigated Compounds

a, b

Region	HFA·2H ₂ O	NH ₄ HFA	NH ₄ ⁺ [Cd(HFA) ₃] ⁻ ·H ₂ O ^c	H ₂ O·Cd(HFA) ₂ ·NH ₃ ^d
OH Stretch	3240	3330	3400	3450
NH Stretch		3090	3125	3200
C=O and C=C Stretch	(1620)	1670 1650	(1670) 1655	(1700) 1670
C=O Stretch CH Bend	1460	1565 (1540) (1500)	1565 1540 (1520)	1580 1555 (1540)
C-C Stretch CF ₃ Stretch	1350 (1335)	1400	1400 1340	1420 1360
CF ₃ Stretch	1275 (1220) 1205	1260 1225 1200	1262 1230 (1190)	1275 1255 (1200)
CH in Plane Bend	1185 1145	1140	1160	1160
OH out of Plane	992 975 914	.	(1095) (950)	1100 (950)
CH out of Plane Bend C-CF ₃ Stretch	828	801 .	(815)	(810)
C-CF ₃ Stretch	743	790 (765) (740)	798 (767) 745	795 (765) 741

a - Infrared Spectra made on samples in KBR and weak or doubtful bands are enclosed in parentheses.

b - Infrared absorption frequencies given in units of cm⁻¹.

c - Proposed structure of crude cadmium chelate (unsublimed).

d - Proposed structure of sublimed cadmium chelate.

TABLE VIII

Mass Spectrometric Data ^a

Compound	Masses Observed	Molecular Fragments Corresponding to Observed Masses
NH ₄ HFA	69	F ₃ C-
	139	-C(O)-CH ₂ -C(O)-CF ₃
	16	NH ₂ -
	17	NH ₃ -
	18	NH ₄ -
HFA	69	F ₃ C-
	139	-C(OH)=CH-C(O)-CF ₃
	69	F ₃ C-
HFA · 2H ₂ O	139	C(OH)=CH-C(O)-CF ₃
	16	O-
	17	O·H-
	18	H-O-H
	69	F ₃ C-
^b Cd(HFA) ₂ · 2H ₂ O · NH ₃ + [NH ₄ [Cd(HFA) ₃] ⁻ · H ₂ O]	139	-C(OH)=CH-C(O)-CF ₃
	208	CF ₃ -C(OH)=CH-C(O)-CF ₃
	409	----- c
	484	----- c
	484	----- c

^a - Only Major Masses are indicated.^b - Proposed Compounds of Sublimed and Crude Cadmium Chelates.^c - Molecular Fragments for Proposed Chelates Not Possible Without Recombination.

Nuclear Magnetic Resonance Spectroscopy. Table IX and Table X show the results for the proton and fluorine resonances respectively. The proton resonances were also determined in pyridine under the same operating conditions when ethanol was used as the solvent. The results are not represented in a table, since pyridine has many peaks in the 7 to 8 parts per million range which would need assignments, and this would serve no useful purpose. It is sufficient to say that the $\text{NH}_4(\text{HFA})$ sample had a resonance at 5.8 parts per million, and the proposed sublimed cadmium chelate had a resonance at 5.7 parts per million. These single peaks correspond to those determined in the ethanol solvent. The proton resonances were both assigned to CH of the respective compounds. This is because it is the only position where a single proton exists. The other proton resonances were not observed, and would possibly require different operating conditions to be detected.

Spectrographic Emission. A sample of cadmium sulfide obtained from the vapor phase reaction gave the following analysis:

- (1) Cadmium and Silicon - major constituents.
- (2) Sodium - minor constituent.
- (3) Aluminum and Zirconium - traces.
- (4) Boron and Iron - traces.
- (5) Magnesium - trace.

TABLE IX
Nuclear Magnetic Resonance Data For Proton Identification

Sample	Peaks Observed - Reported in Parts Per Million	Assignment of Peaks
NH ₄ HFA 17% by weight in ethanol diluted with 8 drops of Carbon Tetrachloride	Triplet at 1.19	CH ₃ of Ethanol
	Quartet at 3.64	CH ₂ of Ethanol
	Single at 5.42	OH of Ethanol
	Single at 5.70	CH of NH ₄ HFA a
Cd(HFA) ₂ · H ₂ O · NH ₃ 23% by weight in ethanol	Triplet at 1.19	CH ₃ of Ethanol
	Quartet at 3.60	CH ₂ of Ethanol
	Single at 5.20	OH of Ethanol
	Single at 5.85	CH of Cd(HFA) ₂ · H ₂ O · NH ₃ b

a - No Peaks Observed for NH₄.

b - No Peaks Observed for H₂O or NH₃.

c - Proposed Compound of Sublimed Cadmium Chelate.

TABLE X
Nuclear Magnetic Resonance for Fluorine Identification ^b

Sample	Peaks Observed - Reported in Parts Per Million	Assignment of Peaks
NH_4HFA 17% by weight in Ethanol	Single - 0.49	CF_3 of NH_4HFA
^a $\text{Cd}(\text{HFA})_2 \cdot \text{H}_2\text{O} \cdot \text{NH}_3$ 23.9% by weight in Ethanol	Single - 0.45	CF_3 of $\text{Cd}(\text{HFA})_2 \cdot \text{H}_2\text{O} \cdot \text{NH}_3$

^a - Proposed Compound of Sublimed Cadmium Chelate.

^b - Reference Material was Trifluoroacetic Acid and RF Frequency was 40.0 Megacycles.

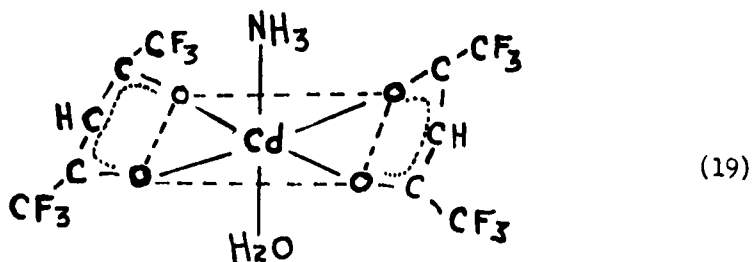
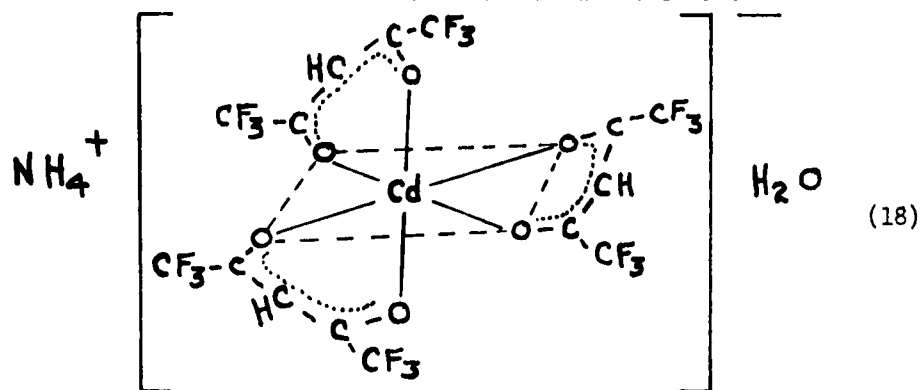
IV. Discussion and Conclusion

The Chemical Compositions of the Synthesized Cadmium Chelates

When initial experiments were undertaken, previously prepared samples of a cadmium chelate were used. The cadmium chelate was prepared by the first method explained in the thesis on Page 27. A chemical analysis of one of the samples indicated that it might be Cadmium(II) hexafluoroacetylacetonate, or possibly its dihydrate. Variations in the melting points of the various cadmium chelate samples, however, led to the possible speculation that water might also be trapped inside the crystal lattice of the compound. Preliminary tests on the vapor phase reaction were initiated on the assumption that the metal compound contained one of these three possible compositions. Observations of the vapor phase reaction led to an element of doubt that the cadmium chelate could have one of the proposed compositions. The vapor phase reaction was yielding a product which was not compatible with the anticipated results. It is possible, but not probable, that this could happen. Therefore, in addition to trying to identify the product of the vapor phase reaction, a closer look was taken at other possible compositions of the cadmium chelate.

Samples of the sublimed and crude cadmium chelates were prepared and investigated. Solubility tests showed that the crude cadmium chelate was reasonably soluble in water which indicated that it should be an ionic molecule. The sublimed cadmium chelate was minutely soluble in water, indicative of a non-ionic molecule.

The infrared spectra of the sublimed and crude cadmium chelates were practically identical but slight differences were noted in a shift of the absorption peaks. Both spectra showed strong carbonyl, carbon-fluorine and ammonium absorption peaks. The ammonium absorption peak might also be interpreted as the OH stretch since both fall within the same frequency range. The spectra, therefore, indicated that in addition to the basic ligand being present, there was the possibility of nitrogen being contained in the composition of the molecule. The sodium fusion test of both chelates proved that nitrogen was present in each and this was substantiated by the chemical analysis. These findings, along with the actual determination that ammonium hexafluoroacetylacetonate was a product of the vapor phase reaction of the sublimed cadmium chelate with hydrogen sulfide, led to the following proposed composition and structure of the crude and sublimed cadmium chelates:



The Nuclear Magnetic Resonance analysis, performed only on the sublimed sample, did not completely substantiate the proposed structure. The single sharp fluorine resonance is in agreement with the proposed structure, but there should be more than one proton resonance. It might be possible for the proposed structure to be in a fast equilibrium state with itself, or with the solvent used in the analysis, so as not to pick up the other resonances. More than likely, an inadequate analysis was performed. Other operating conditions for the analysis might be necessary to bring out the missing resonances. A known sample of ammonium hexafluoroacetylacetonate also showed one proton resonance where there should be two.

The mass spectrographic data could not totally substantiate either proposed structure but did indicate that there were sufficient differences in the spectra to state that the samples were not the same. None of the mass peaks observed corresponded to the molecular weights of the proposed molecules. However, the proposed molecules are very large and the rate of decomposition of a molecular ion increases with molecular size so that only molecular fragments may have been observed. It is also true that certain fluorocarbons give either no parent peak or a very weak one.

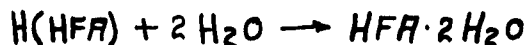
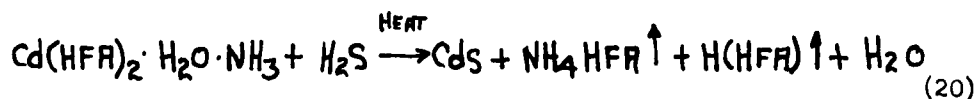
If the proposed structures are correct, it would follow that when the crude cadmium chelate is sublimed, the molecule should undergo an orientation to the second proposed structure. This would release one of the HFA ligands to possibly form H(HFA) or NH_4HFA , which could be detected in the cold trap. Instead, the HFA dihydrate was detected in the cold trap in very small quantities. It is suspected then, that when one of the HFA ligands broke loose from the cadmium metal and started to

escape out of the sublimator, it acquired a little moisture and some crystallized out as the dihydrate. This is reasonable, since liquid HFA, exposed to the atmosphere, readily converts to the solid dihydrate.

The sublimed cadmium chelate should also possess different physical properties because of its different composition and structure. This was found to be true. The melting point in particular, was observed to decrease after each sublimation, and was always different, even after four such sublimations. This possibly rules out the chances of having a pure compound, and this is indeed indicated in other analyses. The chemical analysis showed that the determined percentages of some elements did not agree within experimental error of the theoretically calculated values for the proposed cadmium structures. It is therefore, possible that both compounds are present in the sublimed and crude samples. If this is true, experimental results still substantiate the fact that the first proposed compound is highly dominant in the crude synthesized product and the second proposed compound highly dominant in the sublimed synthesized product.

Vapor Phase Reaction

The chemical reaction for the vapor phase is as follows:



The cadmium sulfide, ammonium hexafluoroacetylacetonate, and the hexafluoroacetylacetone dihydrate were all detected and verified as products of the reaction. The ammonium hexafluoroacetylacetonate was the most difficult compound to identify and many analysis techniques had to be employed before it was substantiated that it was ammonium hexafluoroacetylacetonate.

In addition to the use of analysis techniques for the positive identification of NH_4HFA , possible secondary reactions which might occur were also investigated. Primarily, the possible reaction between HFA and hydrogen sulfide to yield a sulfur containing compound. The experiment for this possible secondary reaction is described in Appendix A. The results of the experiment showed that no products of the reaction had the same physical characteristics as the products which resulted from the vapor phase reaction. It was thus concluded that the proposed secondary reaction did not occur. At the same time other possible reactions were being investigated, a closer look was taken at the method of synthesizing the cadmium chelate. It was noted that ammonium hydroxide was used to neutralize the solution. This led to the possibility of ammonia being included in the cadmium chelate molecule. The vapor phase reaction products were checked for nitrogen content and one of the products did contain nitrogen, as shown in the results of the analyses. The analyses offered strong support that the compound was NH_4HFA .

The HFA dihydrate, obtained from the vapor phase reaction, also showed a good chemical analysis. It's infrared spectrum, along with other physical properties, agreed with values found in the literature.

The results concerning the cadmium sulfide were not as good as had been anticipated. Problems were encountered in designing a suitable reaction apparatus to prevent the hydrogen sulfide from coming into contact with the cadmium chelate before the cadmium chelate was vaporized. The mere contact of hydrogen sulfide with the cadmium chelate at room temperature causes a reaction. Cadmium sulfide is formed on the surface of the cadmium chelate particles. Consequently, only a few parameters of the gas phase reaction to yield highly pure cadmium sulfide crystals could be studied. The one spectrographic analysis made showed cadmium as the main constituent. Silicon and sodium were main contaminants, along with traces of a few other metals. These results could be misleading, however, because the cadmium sulfide had to be scraped off the surface of the glass reaction tube. This alone could cause contamination. The cadmium sulfide formed in the vapor phase reaction usually deposited in thin amorphous films rather than as crystals. A few crystals of cadmium sulfide were obtained when the vapor phase reaction was carried out at a low temperature. There is doubt, however, as to whether the crystals actually resulted from the vapor phase reaction. This is because uniform heating could not be achieved in the reaction zone, and the cadmium chelate may have crystallized and then reacted with the hydrogen sulfide to give the appearance of yellow cadmium sulfide crystals.

The experimental work does show that cadmium sulfide is formed in the vapor phase reaction. The two other products are gaseous at the reaction temperatures, so that if the right conditions are met, pure cadmium sulfide should be obtained.

Summary

Though it cannot be stated with absolute certainty that the two molecules exist as proposed, the majority of analyses tend to indicate that the proposed compositions are extremely likely. Not enough work has been done to completely substantiate the structure of the molecules. However, it should be pointed out that other known metal chelates have structures similarly designated.

The vapor phase reaction looks feasible for forming pure cadmium sulfide since the other reaction products are gaseous and are easily swept out of the reaction zone. These gaseous products may be trapped and re-used in the synthesis of another metal chelate, which is an added benefit of the process. The vapor phase reaction of the cadmium chelate may be extended to include other metal chelates. This then, makes the metal derivatives of fluorinated acetylacetone potentially important compounds for future use in making pure semiconductor materials.

V. Recommendations

In the course of this investigation, several areas were uncovered which could be studied in future research. These areas are stated below.

- (1) The sublimed cadmium chelate used in the vapor phase reaction never did exhibit one distinct melting point after repeated sublimations, but rather continued to decrease. It is possible, however, that if enough sublimations were carried out, the cadmium chelate's melting point might stabilize. This is postulated since the difference in melting points taken after each sublimation continued to decrease. A suitable solvent for recrystallization might be found and used on the cadmium compound after two sublimations to possibly achieve the same purpose. At the same time, other approaches to the synthesis of a cadmium chelate other than neutralizing with NH_4OH or using the NH_4HFA intermediary might be investigated. This could lead to the synthesis of Cadmium(II) hexafluoroacetylacetonate ($\text{Cd}(\text{HFA})_2$), which was initially thought to be the cadmium chelate used in this study.
- (2) The vapor phase reaction of other metal chelates, which could be used in the synthesis of semiconductor material should be studied. Reduced pressure systems might be investigated to achieve better volatility, but the main emphasis of the study should be directed toward obtaining a very pure semiconductor material. This means that the metal chelates will initially

have to be extremely pure. Gas chromatography might be utilized in this respect. Precautions will have to be taken to insure that the carrier gas and the reaction gas being used are very dry and uncontaminated, and the substrate surface extremely clean.

- (3) When a thin film is deposited on a substrate, a problem then arises on how the film is to be removed without introducing possible contamination. Otherwise, analyses on the film might indicate many contaminants whose source cannot be precisely determined. Methods for relieving this situation in the form of new analysis techniques must be obtained.

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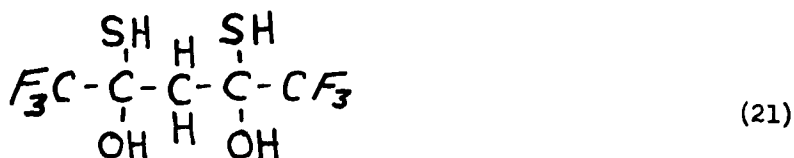
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APPENDIX A

Hexafluoroacetylacetone Reaction With Hydrogen Sulfide

HFA Reaction With Hydrogen Sulfide

This particular experiment was initiated in an attempt to identify one of the products of the cadmium chelate hydrogen sulfide vapor phase reaction. If HFA reacted with hydrogen sulfide, then it is possible that when the ligand is separated from the cadmium chelate in the vapor phase reaction, the ligand might enter into a secondary side reaction rather than being carried off intact or as other decomposition products. The structure of a possible compound containing sulfur that could be formed is



where the SH groups are placed in the positions normally occupied by the (OH) hydroxyl groups in HFA dihydrate. The experiment was conducted with the HFA in the normal liquid phase and in the gaseous phase.

Hydrogen sulfide was passed into a silicone oil bath to check its flow rate and then into a round bottom flask where it was bubbled into the HFA liquid. A dry ice cold trap was connected after the reaction flask to trap any products or unreacted hydrogen sulfide. An aqueous copper chloride solution was also connected to the exit of the cold trap to prevent the escape of hydrogen sulfide which was not trapped. When no reaction between H_2S and the HFA liquid was visibly apparent after a period of ten minutes, the hydrogen sulfide flow was discontinued and the reaction flask was immersed into a beaker of warm water for five

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minutes. Hydrogen sulfide was then bubbled into the warm HFA liquid for an additional five minutes. Still no reaction was visible in the round bottom flask. The experiment was therefore concluded and the collector U-shaped tube in the cold trap was sealed off from the atmosphere and left in the cold trap overnight. The reaction flask was likewise sealed and left to stand at room temperature overnight.

The following morning the liquid inside the reaction flask had an orange tinted color and a few small clear crystals had formed. The liquid inside the cold trap, however, was still very clear. Since the crystals formed in the reaction flask might have been hygroscopic, a vacuum pump was used in the filtration of the liquid. This created greater suction, whereby the filtration time was greatly reduced and the crystals were exposed to the atmosphere for a minimum amount of time. The crystals were collected on a sintered-glass filter and immediately placed in a glass ampule, sealed off, and sent to be analyzed. The filtrate solidified because of the reduced pressure system. It was a brown pasty substance and had a foul odor. The compound was exposed to the atmosphere to dry for twenty-four hours but it remained in the same pasty state. It was, therefore, placed in a capped container and observed over a period of 30 days. At the end of this period, the compound was still pasty. Because its physical characteristics differed greatly from the compound of interest, whose identity was not known at the time, no attempt was made to identify the pasty filtrate. Attention was then focused on the liquid inside the cold trap.

When the U-shaped tube was slowly brought to room temperature, an effervescence was noted, followed by the distinct odor of hydrogen sulfide. The hydrogen sulfide was allowed to escape into the copper chloride solution. After all the hydrogen sulfide escaped, some liquid still remained behind in the U-shaped tube and had an odor characteristic of HFA. A small quantity of the liquid was placed on a watch glass and exposed to the atmosphere. It immediately turned to a white solid, whose identity was verified by infrared to be that of the $\text{HFA} \cdot 2\text{H}_2\text{O}$. The analysis of the clear crystals in the reaction flask showed that they also were the $\text{HFA} \cdot 2\text{H}_2\text{O}$.

Table VI, Page 44, shows the results of the analysis of the $\text{HFA} \cdot 2\text{H}_2\text{O}$ which were the same as that of the $\text{HFA} \cdot 2\text{H}_2\text{O}$ obtained from the vapor phase reaction.

The same experimental arrangement was used in the gaseous phase reaction, except that the hydrogen sulfide was passed into a separate reaction flask into which gaseous HFA was also being admitted. Again, no compound other than the dihydrate was formed which had the same physical characteristics of the products formed in the vapor phase reaction of the cadmium chelate with hydrogen sulfide.

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APPENDIX B

Infrared Spectra and Gas Chromatograms

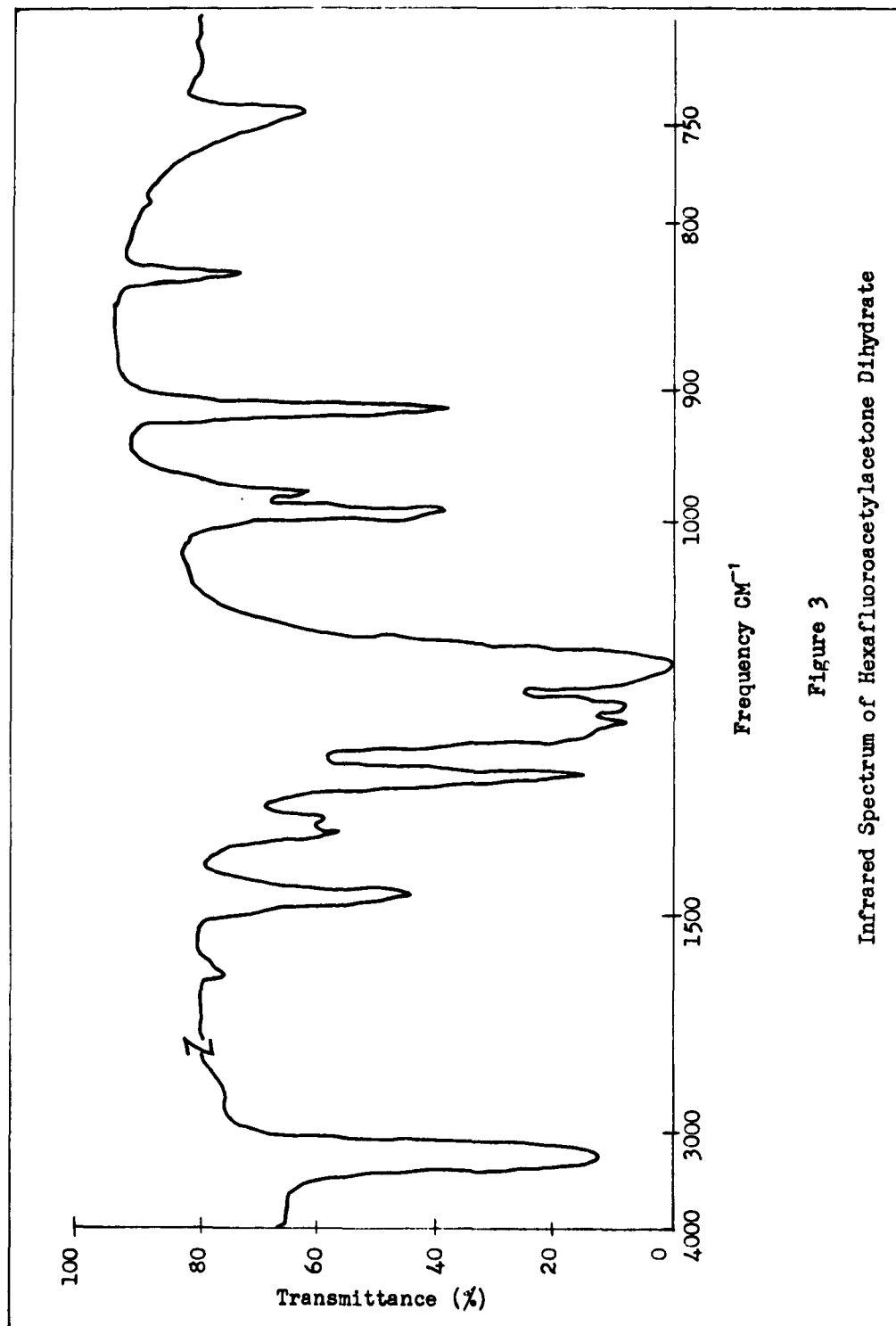
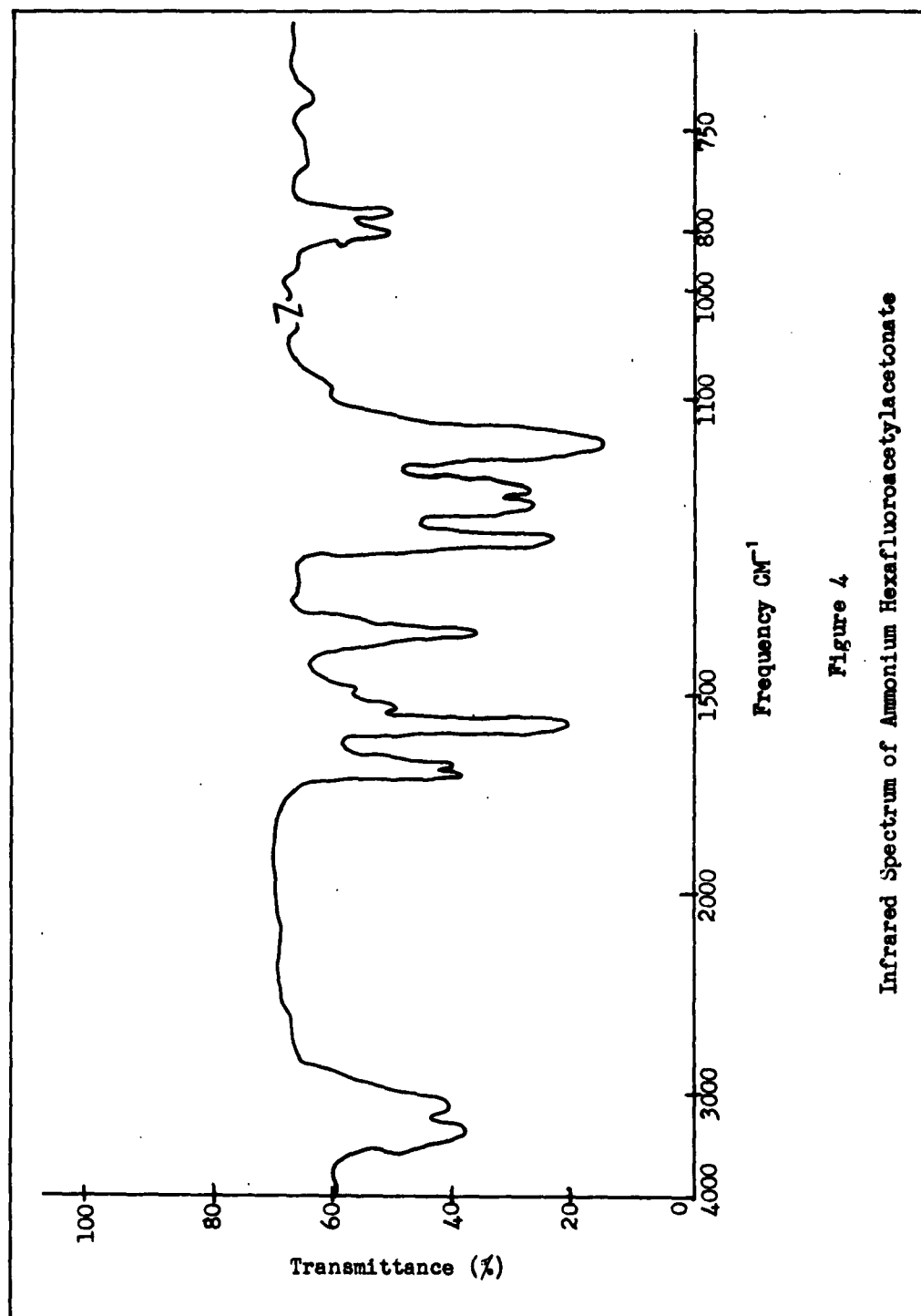


Figure 3
Infrared Spectrum of Hexafluoroacetylacetonone Dihydrate



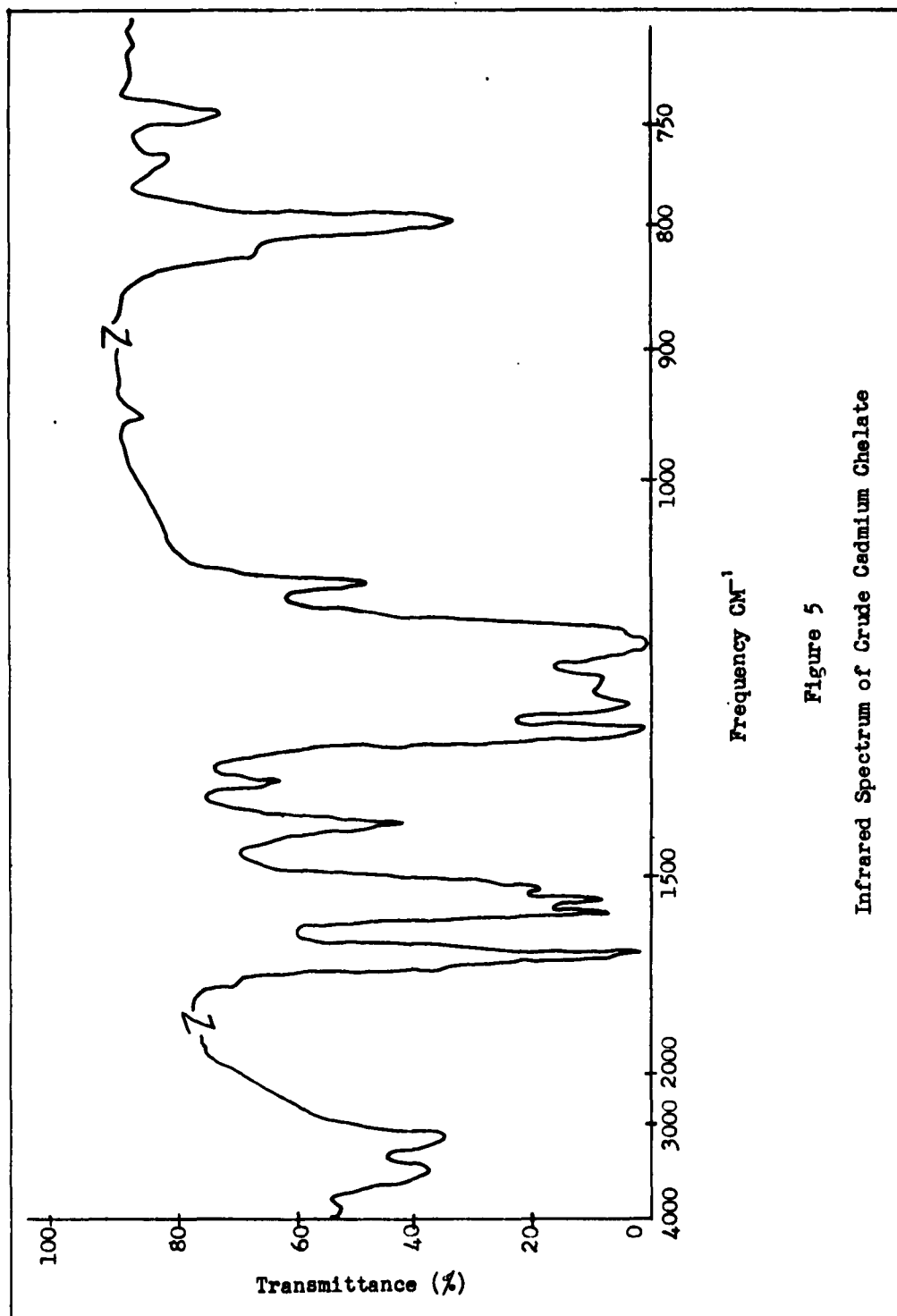


Figure 5
Infrared Spectrum of Crude Cadmium Chelate

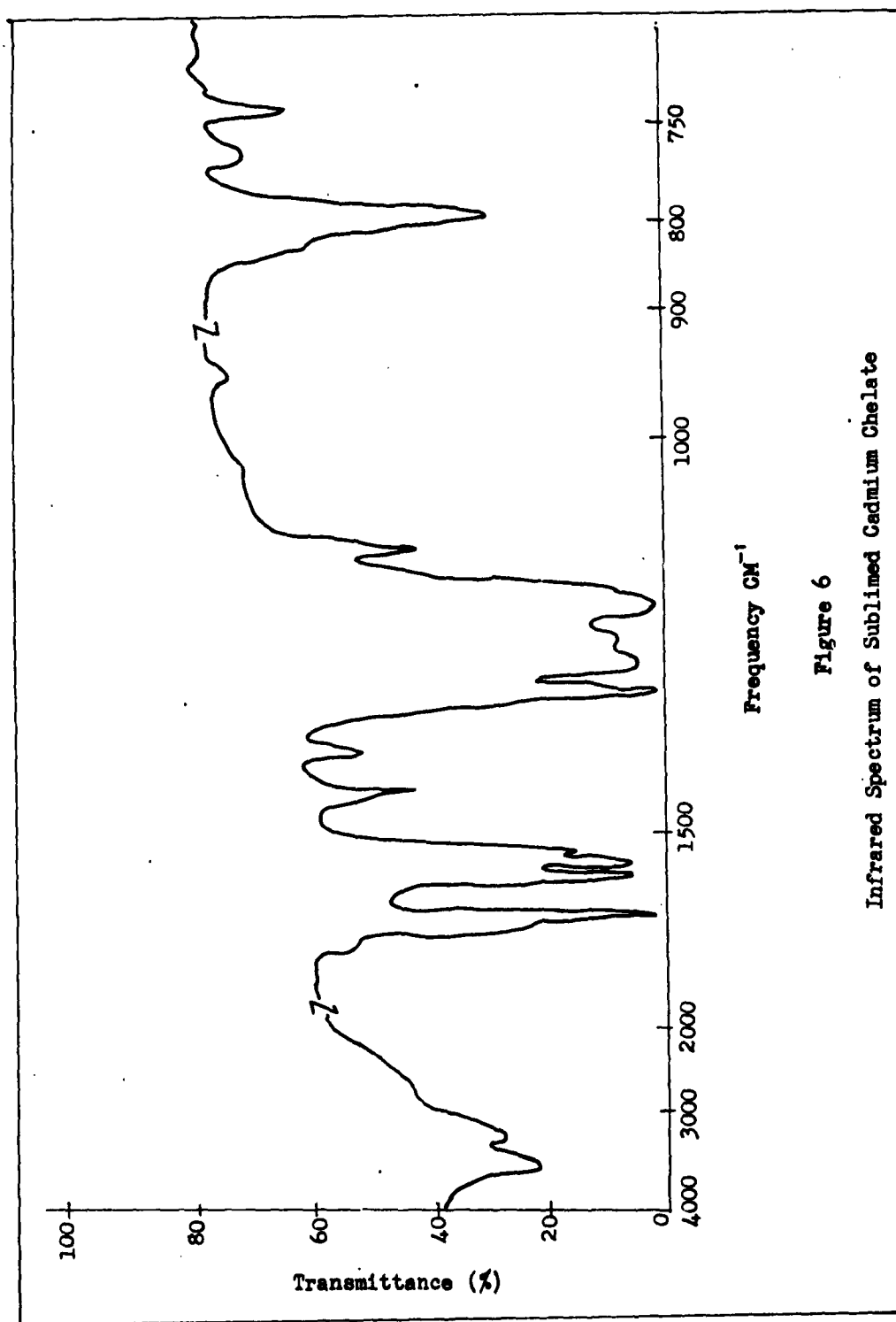


Figure 6
Infrared Spectrum of Sublimed Cadmium Chelate

