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POLYMERIZATION THROUGH COORDINATION

JOHN C. BAILAR, JR.
K. V. MARTIN
MALCOLM L. JUDD
JOHN McLEAN

UNIVERSITY OF ILLINOIS

AUGUST 1958

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AUGUST 1958

MATERIALS LABORATORY
CONTRACT NO. AF 33(616)-3209
PROJECT NO. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

McGregor & Werner Midwest Corp., Dayton, O.
5-112-400-10-30-58

FOREWORD

This report was prepared by the Department of Chemistry and Chemical Engineering of the University of Illinois, under Contract AF 33(616)-3209. The contract was initiated under Project 7340, "Rubber, Plastic, and Composite Materials", Task number 73404, "Synthesis and Evaluation of New Polymers". It was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Lt. Robert L. Rau serving as project engineer.

This report covers work conducted from October 1, 1956 to September 30, 1957.

ABSTRACT

The study of the formation of polymers containing coordinated heavy metals has been continued.

Bis-chelating agents which are bidentate should form linear polymers by coordination with tetracoordinate metal ions. Studies have been made of polymers of this sort containing zinc, nickel, and copper (II) coordinated with bis-thiopicolinamides, bis-fluorinated 1,3-diketones, bis-amino acids and bis-8-hydroxyquinolines. The reaction of tetrahydroxy aromatic compounds with silicon tetrachloride is of this type also, and has been studied. Bis-chelating agents which are tridentate should form linear polymers by coordination with hexacoordinate metal ions. A brief study of coordination compounds of two tridentate amino acids (β-amino glutaric acid and iminodiacetic acid) showed that such polymers would not have great stability, so the matter was not pursued further.

The study of the formation of polymeric copper phthalocyanines from derivatives of pyromellitic acid has been continued, but no method for the preparation of high molecular weight polymers has yet been found.

It has been demonstrated that polymers can be formed by the condensation of monomeric coordination compounds which contain uncoordinated functional groups such as hydroxyl and carboxyl. Although the materials which have been obtained are only trimers and do not show good heat stability, their formation is encouraging, as it furnishes a tool for the study of the polymerization process.

An apparatus for the measurement of heat stabilities of polymers is described.

These studies are being continued.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. Schwartz

R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

TABLE OF CONTENTS

		Page
I	INTRODUCTION	1
II	DISCUSSION	5
	A. Attempts to Form Polymers by Coordination with Metal Ions	5
	1. Thiopicolinamide Polymers	5
	a. 4,4'-bis-Thiopicolinamido-benzophenone and related polymers	7
	b. 4,4'-bis-Thiopicolinamido-diphenylsulfone and related polymers	8
	2. Fluorinated 1,3-Diketone Polymers	10
	3. Amino Acid Polymers	12
	4. Polymers from bis-8-Hydroxyquinolines	16
	5. Silicon Containing Polymers	18
	a. Synthesis of 2,2',6,6'-tetramethoxybiphenyl	19
	b. Synthesis of 3,3',4,4'-tetramethoxybenzophenone	19
	c. Attempted demethylation of the above	20
	d. Synthesis of hydrovanilloin	20
	e. Synthesis of vanillil	20
	f. Synthesis of 3,3',4,4'-tetrahydroxybenzophenone	20
	g. Synthesis of 3,3'-dimethoxy-4,4'-dihydroxydiphenylmethane	21
	h. Synthesis of 3,3',4,4'-tetrahydroxydiphenylsulfone	21
	6. Phthalocyanine Polymers	21
	B. Attempts to Form Polymers by Linking Mononuclear Complexes Together	24
	1. Polymers from β-Hydroxyethylglycine	24
	2. Polymers from Salicylidene-ethanolamine and 2-β-Hydroxyethylaminomethyl Phenol	26
	3. Polymers from Ethylenediamine-N,N'-bis-β-Hydroxyethyl-N,N'-Diacetic Acid	28
III	EXPERIMENTAL	30
	A. Attempts to Form Polymers by Coordination with Metal Ions	30
	1. Thiopicolinamide Polymers	30
	a. 4,4'-bis-(α-Thiopicolinamido) -diphenyl	30
	b. Preparation of [4,4'-Bis-thiopicolinamido-diphenyl]-nickel polymer (Vb)	30
	c. Preparation of [4,4' Bis-thiopicolinamido-diphenyl]-copper (II) - polymer (Va)	30
	d. 4,4'-bis-(Thiopicolinamido)-benzophenone	31
	e. Polymers obtained from 4,4'-bis-(α-thiopicolinamido)-benzophenone	32
	f. 4,4'-bis-(α-Thiopicolinamido)-diphenylsulfone	32

g. Polymers derived from 4,4'-bis-(α-thiopicolinamido)-diphenylsulfone 32
2. Fluorinated 1,3-Diketone Polymers 33
a. 1,1,2,2-Tetra(trifluoro-acetyl) ethane . . 33
b. 1,1,3,3-Tetra-acetyl propane 34
3. Amino Acid Polymers 34
a. Preparation of β-aminoglutaric acid 34
b. Measurement of the stability constants of the β-aminoglutarates of zinc and nickel . . . 35
c. Preparation of copper N,N'-benzidine diacetic acid 35
4. Polymers from 8-Hydroxyquinoline 36
a. 2,2-Bis-5-(8-quinolol)propane 36
b. 2,2-bis-(3'-amino-4'-hydroxyphenyl)-propane 37
c. Synthesis of a copper 2,2-bis-(3'-amino-4'-hydroxyphenyl) propane complex of probably polymeric nature 38
5. Silicon Containing Polymers 38
a. Attempted synthesis of 2,2',6,6'-tetrahydroxybiphenyl 38
b. A second method of synthesizing 2-iodo-1,3-dimethoxybenzene(XXXVI) and its coupling to 2,2',6,6' tetramethoxybiphenyl (XXXVII) was also studied 39
c. Synthesis of 3,3',4,4'-tetramethoxybenzophenone 40
d. Attempted synthesis of 3,3',4,4'-tetrahydroxybenzophenone 41
e. Synthesis of 4,4'-dihydroxy-3,3'-dimethoxydiphenyl methane 41
6. Phthalocyanine Polymers 42
a. An improved method of preparing polymeric copper phthalocyanine 42
B. Attempts to Form Polymers by Linking Mononuclear Complexes Together 42
1. Polymers from β-Hydroxyethylglycine 42
a. Preparation of β-hydroxyethylglycine . . . 42
b. Bis-(β-hydroxyethylglycine)-copper (II) . . 43
c. Bis-(β-hydroxyethylglycine)-nickel (II) . . 43
d. O-Benzoylation of bis-(β-hydroxyethylglycine)-nickel (II) 43
e. Preparation of phthalyl-bis-(β-hydroxyethylglycine) nickel 44
f. Phthalyl-bis-(β-hydroxyethylglycine)-nickel-trimer 44
g. Attempted condensation of bis-(β-hydroxyethylglycine) nickel(II) with diethylmalonate . 44
2. Polymers from bis-(Salicylidene-ethanolamine). 44
a. Preparation of salicylidene-ethanolamine. . 44
b. Preparation of bis-(salicylidene-ethanolamine)-copper 45
c. Preparation of bis-(salicylidene-ethanolamine)-nickel 45
d. Preparation of bis-(salicylidene-ethanolamine)-zinc 45
e. Polyurethanes and polyesters prepared from bis-(salicylidene-ethanolamine)-copper . . 45

TABLE OF CONTENTS(Cont'd)

3. Polymers from Ethylenediamine-N,N'-bis-β-Hydroxyethyl-N,N'-Diacetic Acid 46
a. Preparation of nickel and copper N,N'-bis-β-hydroxyethylethylenediamine-N,N'-diacetate . 46
b. Polymerization of copper-versene-diol complex with tolylene diisocyanate 47

IV MEASUREMENT OF THE HEAT STABILITY OF POLYMERS 47
A. Thermal Stability of Polymers in Nitrogen Atmosphere 47
B. Differential Thermal Analysis of Polymeric Materials 48
C. Design and Construction of A Simple Device for Measuring Thermal Stabilities 49
D. Thermal Stability of Benzidine Disulfonato-Copper (II) 49

V CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK 51

VI BIBLIOGRAPHY 53

I. INTRODUCTION

The chief purpose of the work described in this report has been to prepare plastics which are stable to high temperatures, and which retain their plasticity over a wide temperature range. It is well known that the stability of organic materials is often markedly changed by coordination with metal ions. Sometimes it is decreased, but often it is increased. This is illustrated by the great difference in thermal stability between phthalocyanine and its copper derivative, and by the increased resistance to light and washing which is shown by azo dyes when they are metallized. This program is based upon the hope that "coordination polymers" can be formed which will show desirable physical properties, and which will be resistant to thermal and oxidative degradation.

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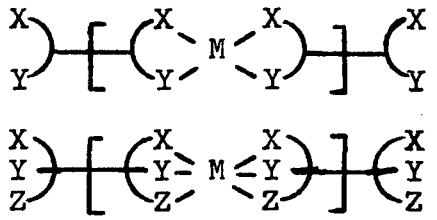
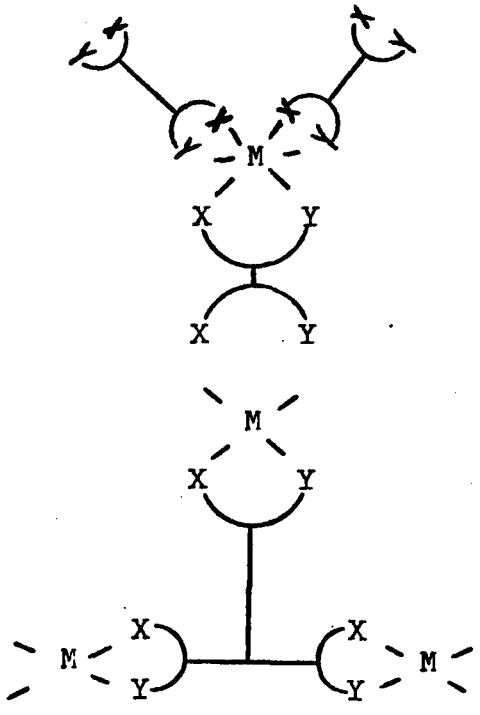
In general, it can be said that polymers containing coordinated metal atoms can be formed in three different ways:

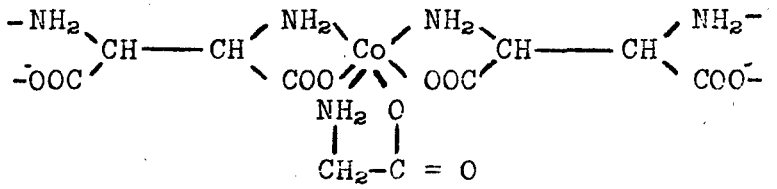
a) Coordinating agents that can combine with more than one metal ion simultaneously can be linked together by such coordination. The coordinating agent may attack the metal through monodentate groups (e.g., :CN:⁻), or, preferably, through polydentate groups. If the coordinating agent is bidentate and the metal ion is tetracoordinate, or if the coordinating agent is tridentate and the metal ion is hexacoordinate, linear polymers will result



The combination of a bidentate group with a hexacoordinate metal, or that of a polyfunctional group with a tetracoordinate metal, on the other hand, will lead to highly cross-linked polymers:

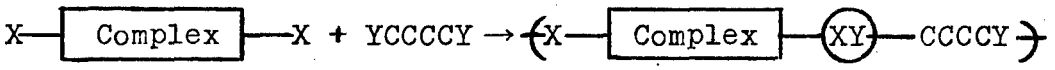


Since the chief aim of this program is to form heat-stable plastic materials, our efforts have been directed largely toward the formation of linear polymers. (The phthalocyanine polymers constitute the sole exception). Even with bidentate ligands and hexacoordinate metals, one might obtain linear polymers if two of the coordination positions of the metal are occupied by "inert" groups. We have attempted to do this in the formation of cobalt (III)-amino acid polymers,



but have found that disproportionation takes place, with the formation of mononuclear complexes and highly cross-linked ones.

b) Mononuclear complexes containing uncoordinated functional groups may be combined with each other through the agency of those functional groups. Here again, one can conceive of obtaining linear or cross-linked polymers, depending upon the number of functional groups in each mononuclear complex, and the manner in which the complexes are linked together. For example, a complex containing two uncoordinated functional groups might react with an organic molecule containing two functional groups to give a linear polymer



whereas other combinations would give cross-linked polymers. In the example given, the organic molecule might be replaced by another complex.

c) A preformed polymer may be "metallized", with consequent change in its properties and behavior. Ordinarily, coordination of a polymer with a metal ion will lead to cross linking; e.g., the union of protein and chromic ion in the tanning of leather, and probably, the union of calcium ion with polyphosphate ion. Proper stereochemical arrangement of the donor atoms in the coordinating agent, however, may avoid cross linking.

In the work described in this report, attempts were made to form polymers by methods (a) and (b), but not by method (c). In connection with method (a), five types of bis-chelating agents were used, as well as the polyfunctional octa-carboxy copper phthalocyanine unit. In the study of method (b), three mononuclear complexes were examined. None of these has yet led to the formation of polymers with useful properties. We are of the opinion that the difficulties in obtaining polymers stem from the mode of carrying out the polymerization experiments, rather than to any inherent lack of chemical reactivity. Thus, the presence of impurities, the formation of too many nuclei, or a failure to use exactly stoichiometric quantities of reactants would lead to the formation of low-molecular weight polymers. Our present efforts, therefore, are directed toward eliminating difficulties of this sort, rather than to the study of new monomers.

During the course of this work, an apparatus has been designed and built for the purpose of measuring the thermal stability of polymers in air as well as in inert atmospheres.

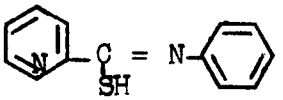
II. DISCUSSION

A. Attempts to Form Polymers by Coordination with Metal Ions.

Most of our effort during the year under review was devoted to the study of polymeric substances which may be formed by the act of coordination between metal ions and polyfunctional chelating groups. Five groups of bis-chelating agents were studied, and will be discussed in turn. The polymeric phthalocyanines are sheet like rather than linear, but they, too, are formed in the process of coordination.

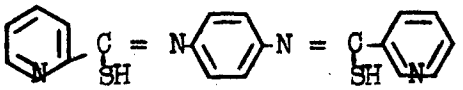
1. Thiopicolinamide Polymers. From the point of view of thermal stability, the derivatives of thiopicolinamide offer a good deal of promise, and a considerable amount of time has been spent on them by K. V. Martin (1).

Thiopicolinanilide (I) and related compounds have been shown to function as bidentate chelate



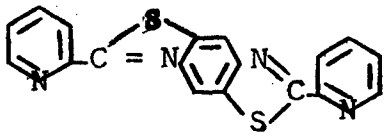
I

compounds (2). Two molecules of I coordinate with such ions as copper (II), nickel (II) and mercury (II) to form non-valent metal complexes. It appeared evident that a bis-thiopicolinanilide, such as II, would coordinate

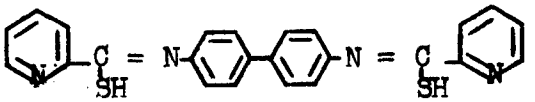


II

with suitable metals to form polymeric materials. Porter (3) has recently reported a convenient method for the preparation of thiopicolinanilides using a modified Willgerodt reaction. Application of this reaction to the synthesis of II has been shown to give 2,6-di (α-pyridyl) - benzo - (1,2,4,5) - bis-thiazole (III). Apparently the desired bis-thioamide formed initially in this reaction



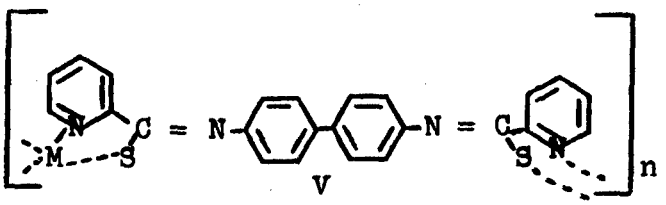
III



IV

is unstable and undergoes oxidation. When a mixture of benzidine, sulfur and α-picoline was subjected to the conditions of the Willgerodt reaction the mono-amide, 4-amino -4'- thiopicolinamido-diphenyl was obtained. Use of excess sulfur and α-picoline results in the formation of 4,4' - bis-thiopicolinamido diphenyl (IV).

This compound has been successfully polymerized by chelation with suitable copper (II), nickel (II) and zinc (II) complexes. IV was heated under vacuo with the stoichiometric amount of the metal acetylacetonate. In each case acetylacetone was evolved and a polymer of structure V was obtained. No accurate estimation of molecular weights of these polymers has been made;



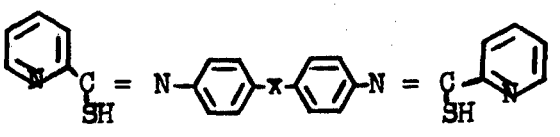
V

M = a) Cu(II)
b) Ni(II)
c) Zn(II)

however, from the analytical figures they are estimated to be greater than 5000. The polymers were obtained as dark colored powders which did not exhibit plastic properties. The thermal stabilities were measured in nitrogen, the polymers decomposing, viz.

Va : 275°
Vb : 300°
Vc : 410°

If Vc were of sufficiently high molecular weight (ca. 50,000) it would be expected to be a brittle material. In order to produce plasticity in such a high molecular weight polymer, it is necessary to introduce a bridging group between the two phenyl rings. To this end, the synthesis of thioamides of structures (VI a,b,c, d,e) was undertaken. These are accessible through the



VI

a, X = O
b, X = SO_2
c, X = $-C(Me)_2-$
d, X = $-CH_2-$
e, X = $-C(=O)-$

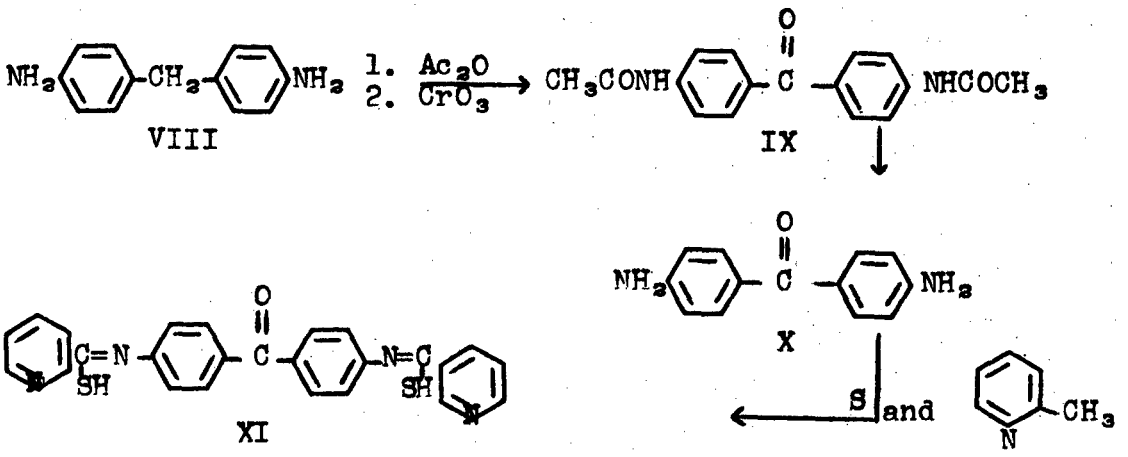
VII

amines (VII, a-e). The diamines are readily available and were purchased or synthesized, viz.

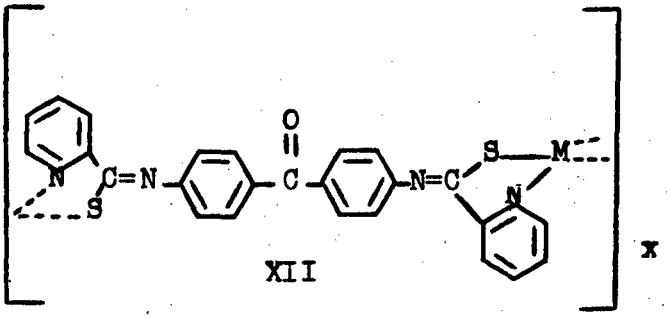
VII a) reduction of 4,4'-dinitro-diphenylether
VII b) commercially available
VII c) reaction of acetone with aniline hydrochloride
VII d) commercially available
VII e) oxidation of VII d.

a. 4,4'-bis-Thiopicolinamido-benzophenone and related polymers

Commercially available 4,4'-diamino-diphenylmethane (VIII) was acetylated and oxidized with chromic anhydride to 4,4'-diacetylamino benzophenone (IX). De-acetylation of IX gave the required 4,4' diamino benzophenone (X) in good yield. Condensation of X with sulfur and α-picoline led to the isolation of 4,4'-



bis-thiopicolinamido-benzophenone (XI), a golden crystalline material (mp. 182°), readily soluble in hot dimethylformamide. To a solution of XI (1mole) in dimethylformamide was added a solution of copper (II) acetate (1 mole) and the mixture warmed on the water bath. Almost immediately a quantitative precipitation of the copper (II) polymer (XIIa) occurred. In a similar manner the corresponding zinc (II) and nickel (II) polymers



a: Cu(II)
b: Zn(II)
c: Ni(II)

(XIIb and XIIc) were prepared. Analytical results suggest their structures are well represented by XII and that their molecular weight is of the order of at least 10 units.

Determination of Heat Stabilities

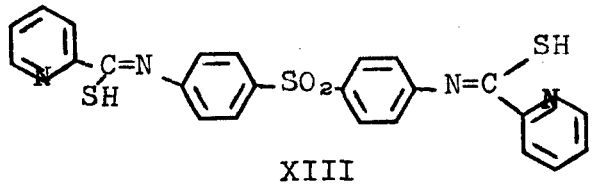
The heat stabilities of the above polymers (XIIa,b,c) were determined using the thermobalance described later in this report. Using this device, the thermal stability data obtained for the 4,4'-bis-thiopicolinamido-diphenyl-zinc(II) polymer corresponded with that obtained by differential thermal analysis and by oven-heating. Each polymer sample was maintained at a series of elevated temperatures for a period of about 1/2 hour at each temperature. At the end of each period any loss in weight was complete. The results obtained are summarized in Table I.

Table I.

% Weight Loss	190	230	270	320	350	370	390	420
Zinc(II) polymer	0	0	0	0	0	0	4%	Decom
Nickel(II) polymer	0	0	0	0	0.3%	2%	Decom.	--
Copper(II) polymer	0	0	0	2%	Decom.	--	--	--

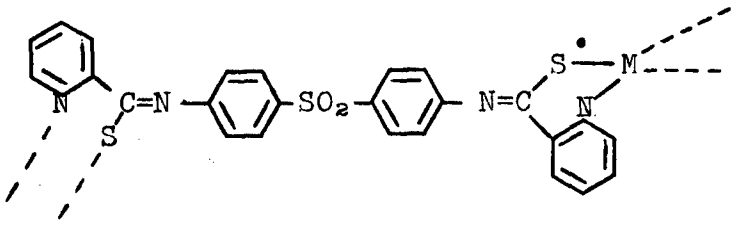
b. 4,4'-bis-Thiopicolinamido-diphenylsulfone and related polymers

Condensation of commercially available 4,4'-diamino-diphenylsulfone, sulfur and α-picoline yielded 4,4'-bis-thiopicolinamido-diphenylsulfone (XIII) in fair yield. XIII was obtained as an orange crystalline solid, readily soluble in hot cellosolve or hot dimethylformamide.



XIII

Mixture of hot dimethylformamide solutions of XIII and zinc(II) acetate led to almost immediate precipitation of the yellow zinc (II) polymer (XIVa) In a similar manner the nickel(II) and copper polymers (XIVb) and



XIV

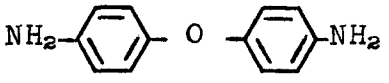
a: Zn
b: Ni
c: Cu

XIVc were prepared. In each case, after precipitation had occurred, the solutions were heated under reflux for one hour to ensure complete reaction. The thermal stabilities were determined and the data obtained are listed in Table II.

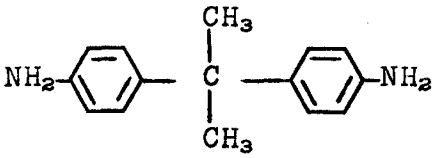
Table II.

% Weight Loss	160	200	250	290	320	350	380	430
Zinc(II) polymer	0	0	0	0	0	0.25	0.25	Decomp.
Nickel(II) polymer	0	0	0	3%	0	Decomp.	-	-
Copper(II) polymer	0	0	0	1%	3%	Decomp.	-	-

From a consideration of these data and those previously obtained with polymers derived from 4,4'-bis-thiopicolinamido-diphenyl, the zinc(II) polymers appear to be the more thermally stable. With these compounds there is little significant loss of weight on heating to 380°C. It could be, however, that some decomposition was occurring below this temperature. Thus, the infrared absorption curves of the zinc polymer XIVa, both pre- and post heating, were recorded. On heating a sample at 300°C for six hours no loss in weight could be measured and the infrared spectra remained unchanged. Heating at 360°C for six hours resulted in a 1.5% weight loss and a change in sample color from pale yellow to pale brown. However, the infrared spectra remained identical and it can therefore be inferred that no decomposition had taken place. 360°C would appear to be an upper limit with regard to thermal stability; at 390°C (see Table I) significant weight losses occur. It had been planned to synthesize the thiopicolinamides from the diamines 4,4'-diamino-diphenylether (XV) and 2,2-bis(p-aminophenyl)-propane (XVI).



XV



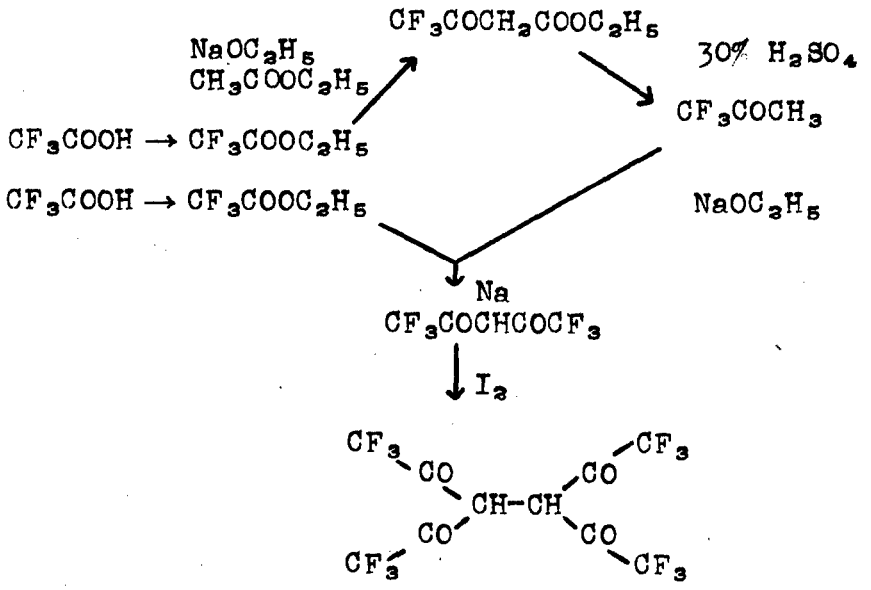
XVI

Commercially available 4,4'-dinitro-diphenylether was reduced catalytically. Syntheses of XVI have been recorded in the literature (4) using the acid catalyzed condensation of aniline and acetone. Several attempts to repeat this reaction proved abortive and this synthesis was abandoned. Also, reaction between sulfur, α-picoline and 1,5-diamino-naphthalene failed to yield any identifiable products.

Work on the thiopicolinamide polymers is being continued.

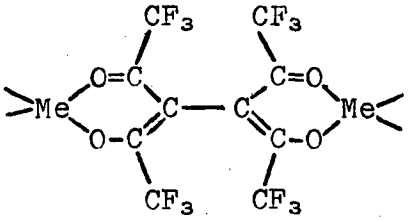
2. Fluorinated 1,3 Diketone Polymers. The work on polymers of 1,3 diketones was interrupted to allow more time for study of the thiopicolinamides. It is now under study again, but the present account can be considered to be only a progress report.

1,1,2,2- tetra-(trifluoro-acetyl)-ethane (XVII) was synthesized by the condensation of the sodium salt of 1,1,1,5,5,5- hexafluoro-acetylacetone with iodine (see reaction scheme below). It is anticipated that XVII will coordinate with suitable metal salts (divalent metals of coordination number 4) to form polymers in a similar manner to the bis (β-diketones)

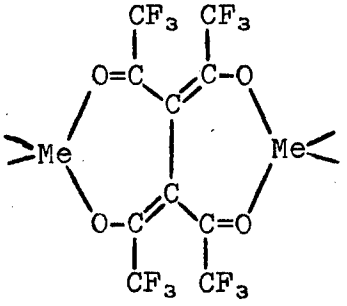


XVII

described by Fernelius and co-workers (5). The polymers so formed are expected to contain only the elements carbon, oxygen, fluorine and metal and are expected to have enhanced heat stability. It has already been reported that the substitution of fluorine for hydrogen in an organic compound results in a more thermally stable compound. Further study of the problem indicated that when XVII reacts with a metal ion, two isomeric products may form (XVIII and XIX):

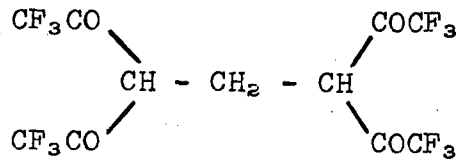


XVIII



XIX

Although XIX involves the formation of seven membered chelate rings, the possibility of its formation cannot be ruled out. Accordingly, it has been decided to use 1,1,3,3 tetra (trifluoro-acetyl)-propane (XX), and its preparation is now underway.



XX

This work is being done by Mr. Joon Suk Oh, who is not supported by the W.A.D.C. contract.

For experience with the techniques necessary for the synthesis of this compound, 1,1,3,3-tetra-acetyl propane was prepared by the reaction of sodium acetylacetonate with methylene diiodide.

$$(CH_3CO)_2CH_2 + Na \xrightarrow{ether} (CH_3CO)_2CHNa$$

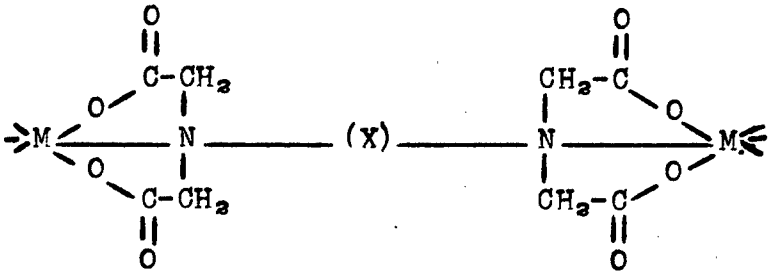
$$2(CH_3CO)_2CHNa + CH_2I_2 \rightarrow (CH_3CO)_2CH-CH_2-CH(CH_3CO)_2 + 2NaI$$

Our first attempt to prepare XX by a formal condensation was unsuccessful. The failure of this procedure is attributed to an inner condensation.

3. Amino Acid Polymers. The work on amino acid polymers has been done by M. L. Judd. It was undertaken because simple α-amino acids are known to form cobalt(III) complexes which are very stable toward heat and chemical reagents.

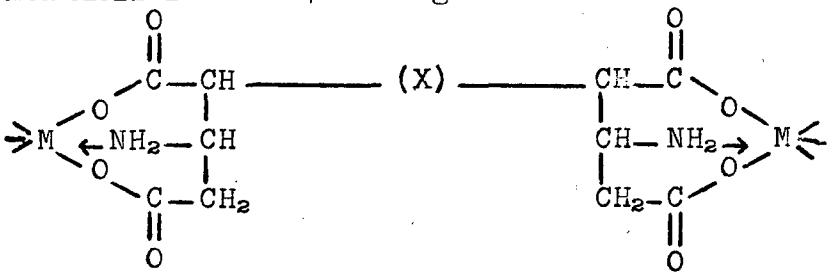
It was thought that a stable polymer might result from the reaction between a sexidentate amino acid which is tridentate to two different metal ions and a six covalent metal ion such as cobalt(III). An amino acid of the desired type might result from the linking of two β-amino glutaric acid molecules in some way that would prevent the molecule from being sexidentate to a single metal atom. Accordingly, β-amino glutaric acid was synthesized as a model compound and the stability of its complex with copper (II) was determined.

Two types of molecules were considered: compound XXI can be considered an analog of an ethylenediaminetetraacetate,



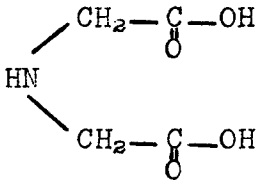
XXI

and compound XXII is a di-β-aminoglutaric acid.



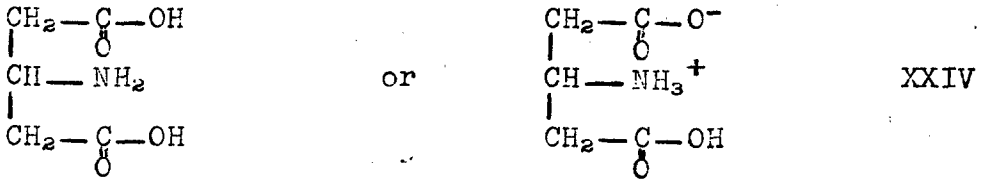
XXII

In order to determine which of these compounds would best satisfy our needs it was thought worthwhile to determine the hydrolytic and thermal stabilities of the metal-ligand bonds of the two compounds. To measure the hydrolytic stability, the formation constants of the complexes formed by a series of metals with tridentate molecules corresponding to half of the sexidentate molecule were studied. The tridentate corresponding to compound (XXI) is iminodiacetic acid (XXIII).



XXIII

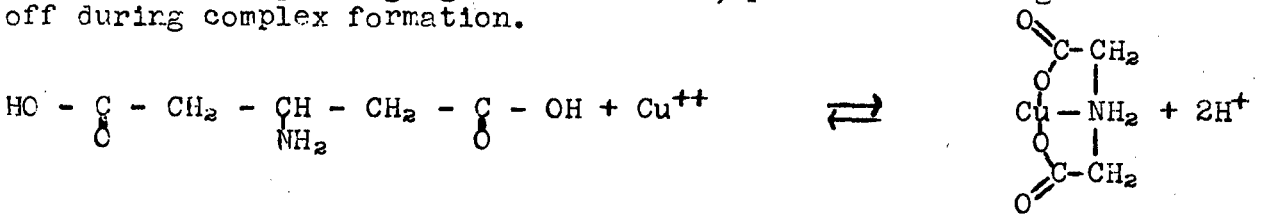
β-amino glutaric acid (XXIV) corresponds to half of compound (XXII).



XXIV

The formation constants of the complexes of compound XXIII with Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) have already been reported by Chaberek and Martell (6). Similar measurements were undertaken for complexes of compound XXIV, using the method of the above authors.

As the complexing agent is an acid, protons will be given off during complex formation.



It is possible to determine the formation constant for the complex by pH measurement. To do this, the acid dissociation constant of the acid must be known. This was determined for β-amino glutaric acid with data obtained from a pH titration, using the relationships:

$$k_1 = \frac{[H^+][a\ C_A + (H^+)]}{C_A - [(a-1)\ C_A - (OH)]}$$

$$k_2 = \frac{(H^+)\ [(a-1)\ C_A - (OH^-)]}{C_A - [(a-1)\ C_A - (OH^-)]}$$

where: a = moles of base/mole acid
C_A = initial acid concentration

The constants k_1 and k_2 may also be determined by a graphical method if they differ by several orders of magnitude. In this case p k_1 = pH at a = .5 and p k_2 = pH at a = 1.5. The values obtained for β-amino glutaric acid by this method are p k_1 = 4.20 and p k_2 = 9.07 at 26°. It should be noted that these data correct an error made in an earlier report (7) where it was reported that the k_1 and k_2 were of approximately the same magnitude.

The first formation constant for the β-amino glutaric acid-copper (II) complex was determined from data obtained from a pH titration of a solution containing a 1:1 molar ratio of acid and copper (II) ion. The following relationships are utilized in the calculations:

$$Cu^{+2} + A^{-2} \rightleftharpoons CuA$$

$$K_{form_1} = \frac{[Cu\ A]}{[A^{-2}][Cu^{+2}]}$$

$$[A^{-2}] = \frac{(2-a)\ C_A - [H^+] + [OH^-]}{\frac{2\ [H^+]^2}{k_1\ k_2} + \frac{[H^+]}{k_2}}$$

$$K_{form_1} = \frac{C_{A^-} \times [A^{-2}]}{[A^{-2}]\,[C_{Cu^{++}} + X[A^{-2}] - C_A]}$$

$$X = \frac{[H^+]^2}{k_1\, k_2} + \frac{[H^+]}{k_2} + 1$$

Where: a = moles base/mole acid
C_A = initial acid concentration
$C_{Cu^{++}}$ = total copper (II) concentration
k_1 and k_2 = dissociation constants of β-amino glutaric acid

The value obtained by this method is $k_1 = 6.1 \times 10^6$ or $\log k_1 = 6.78$.

Chaberek and Martell have reported the logarithm of the formation constant of the iminodiacetic acid copper complex to be 10.55. It is thus seen that iminodiacetic acid forms a more stable copper complex than does β-amino glutaric acid by a factor of ca. 10^4.

The question then arises as to whether any correlation can be drawn between hydrolytic and thermal stabilities. Our formation constant is essentially a measure of the difference in stability between the metal-aquo complex and the metal-amino acid complex. However, in comparing two complexes consisting of the same metal ion and the same coordinating atoms, the stabilities of the metal aquo complexes should effectively cancel out and the comparison of the respective stability constants should be a measure of the relative strengths of the metal-ligand bonds. On the other hand, the thermal stability of a complex refers to the thermal stability of the weakest link in the molecule. If the weak link in the molecule is that between the metal and the coordinating atom, the relative stability constants as measured above might indicate the relative heat stabilities.

If, however, some other link is weaker, the hydrolytic stability constant will bear no relation to the thermal stability of the complex. As it is impossible to predict which will be the thermally weak link in the complex it would seem advisable to work with the compound which stability constants indicate possesses the highest metal-ligand atom stability. Thus, when several ligands of similar type are under consideration as possible polymer formers, it would seem logical to investigate the one with the highest hydrolytic stability, assuming equal ease of preparation and manipulation.

It has to be kept in mind that the metal atom in a complex may exert an oxidizing or reducing effect upon the atoms coordinated to it, or it may catalyze atmospheric oxidation of the complex. These effects are more apt to be important in relation to thermal decomposition than in relation to hydrolytic decomposition.

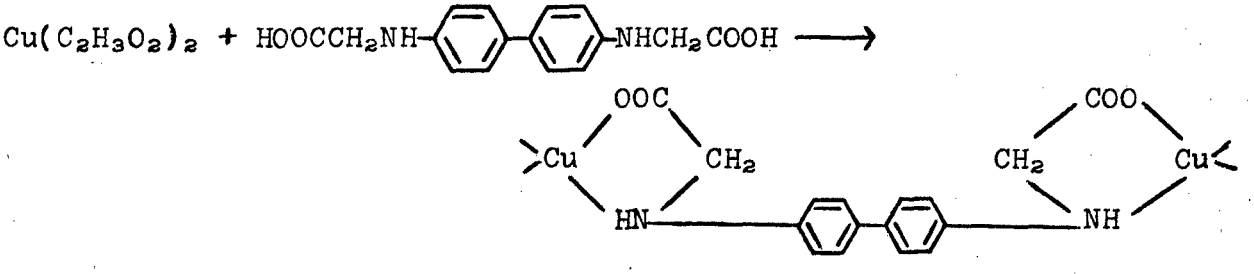
For the determination of the stability of the zinc and nickel complexes of β-aminoglutaric acid, the method was modified slightly in that the solution containing a 1:1 molar ratio of metal ion to β-amino glutaric acid was not titrated with sodium hydroxide. Instead, sufficient sodium hydroxide was added so that the ratio of base to acid was 1.5/1. This mixture was kept at 25.00°C over night and the pH measured. The calculations are the same as before. The data may be compared to those obtained for comparable complexes of iminodiacetic acid.

Metal	β-amino-glutaric acid $\log k_1$	imino-diacetic acid $\log k_1$
Cu (II)	6.78	10.55
Zn (II)	5.70	7.02
Ni (II)	5.39	8.30

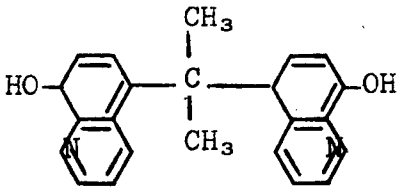
These data support the conclusion that imino diacetic acid is a more promising model compound for study than is β-amino-glutaric acid.

A study of complexes of benzidinediacetic acid was begun, and at the end of the year under review, was well under way.

Solutions of N,N' benzidinediacetic acid and copper(II) acetate in dimethyl formamide were mixed, whereupon a fine olive-drab precipitate formed. This product was isolated by filtration, dried and submitted for analysis. The analysis indicated some carbonaceous impurities to be present. Steps are underway to purify the product.

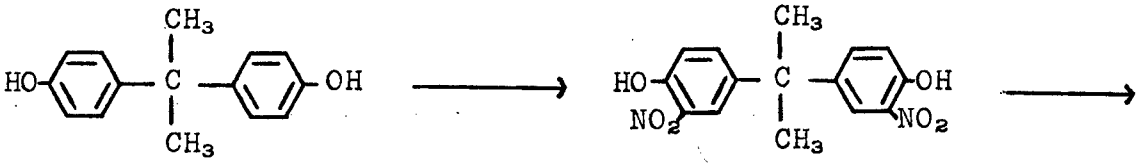


4. Polymers of bis-8-Hydroxyquinolines. Since 8-hydroxyquinoline forms stable complexes with the ions of many heavy metals, a study of polymeric substances containing bis-8-hydroxyquinolines was undertaken, the work being done by M. L. Judd. The synthesis of the chelating agents has offered several difficulties, so that metal derivatives have not yet been studied. This program is continuing. The first bis-8-hydroxyquinoline to be studied was 2,2-bis-5-(8-quinolinol) propane.

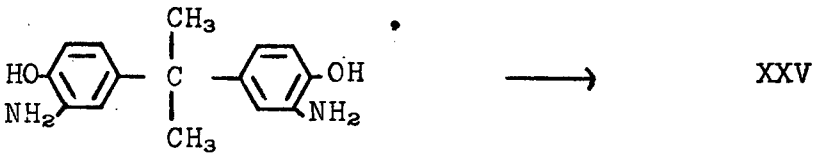


XXV

The preparation of this was attempted by the following series of reactions:



XXVI XXVII



XXVIII XXV

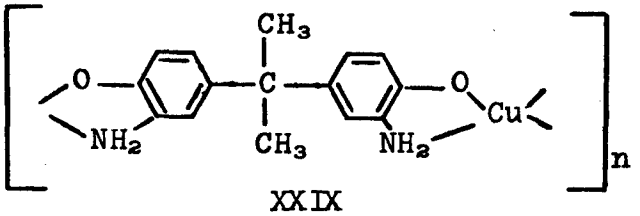
Difficulty was encountered in obtaining consistent results in the nitration of 2,2 diphenylolpropane (XXVI). A systematic study of the reactions was carried out by varying the experimental conditions followed by the isolation and identification of all products. The time of the addition of nitric acid to the reaction mixture was found to be of critical importance. A very slow addition of the nitric acid produced the nitrated phenol in excellent yield. A change in the procedure of the synthesis which shortens the time required will be mentioned in the experimental section of this report.

An extensive investigation indicated that the catalytic hydrogenation of 2,2-bis-(3'-nitro-4'-hydroxyphenyl)-propane (XXVII) is the preferred method of synthesizing the amine. Recrystallization of the crude product from absolute ethanol yields the compound as long white needles. Poisoning of the catalyst can be avoided only if the starting material is carefully purified.

Metals, such as iron and aluminum, easily reduce the nitro groups to amines, but are subsequently coordinated by the reduced form of the material, thus making separation of the metal from

the ligand difficult. An attempt to reduce the nitro groups to amines by sodium sulfide was unsuccessful. Infrared analysis identified the material obtained from a sodium reduction of a solution of the nitro compound in liquid ammonia as the desired amine. This product was less pure than that obtained by catalytic hydrogenation.

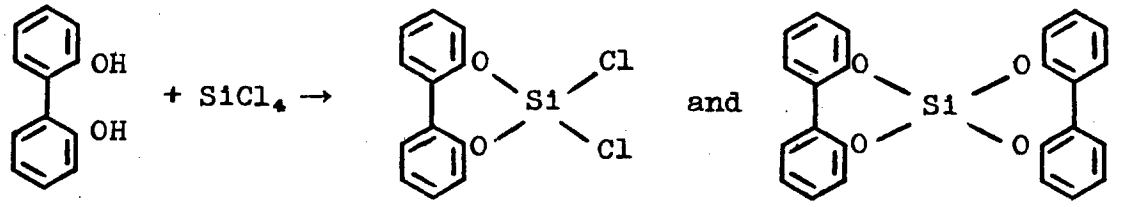
Incidentally, a polymer of composition XXIX was prepared by causing the aminophenol to react with copper (II) acetate in a solution of methanol. A very fine grey precipitate formed immediately. An investigation of the structure of this compound is presently underway.



XXIX

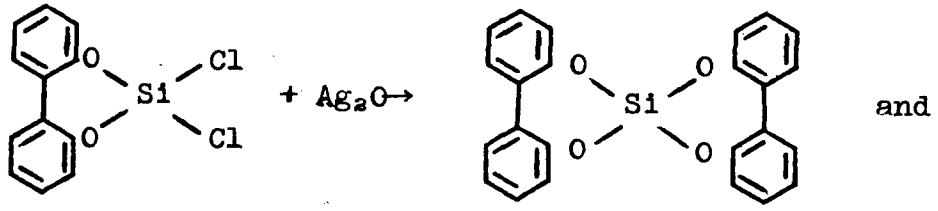
5. Silicon Containing Polymers. These have been investigated, and are still under study, by John McLean.

The reaction of o,o'-diphenol with an excess of silicon tetrachloride has been reported to yield o,o'-diphenoxy-dichloro silane (XXX) and small amounts of bis-o,o'-diphenyldioxy-silane (XXXI) (8).

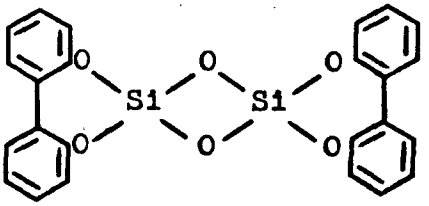


XXX XXXI

XXX reacts with metal oxides to give products XXXI and XXXII.

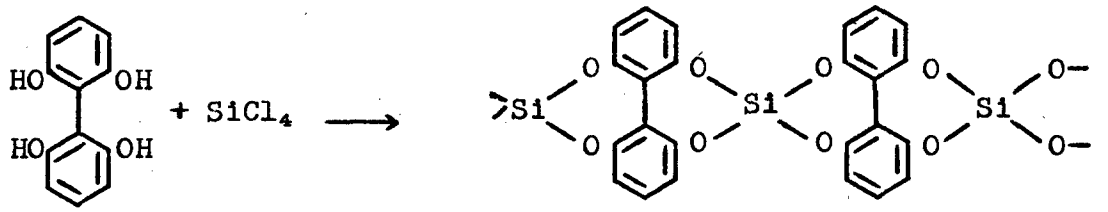


XXX XXXI



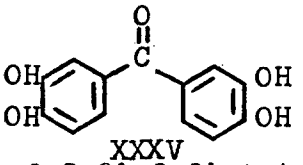
XXXII

It has been shown that when XXXII is heated in a high boiling solvent it rearranges to a resinous four-fold polymeric molecule. These reactions suggest that silicon tetrachloride might react with a phenol containing four hydroxyl groups suitably arranged to give a polymer. Thus, reaction between 2,2',6,6'-tetrahydroxy-biphenyl (XXIII) and silicon tetrachloride might lead to the polymer (XXIV). Accordingly, the syntheses of 2,2',6,6'-tetrahydroxy biphenyl (XXXIII) and 3,3',4,4'



XXXIII XXXIV

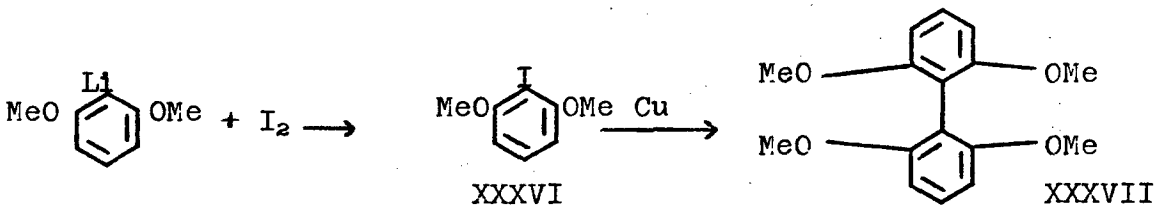
tetrahydroxy-benzophenone (XXXV) were undertaken.



XXXV

a) Synthesis of 2,2',6,6'-tetramethoxy-biphenyl (XXXVII)

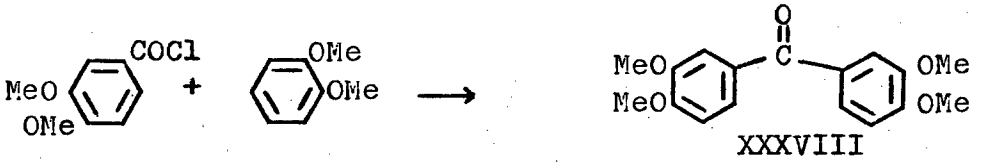
2-Iodo-1,3-dimethoxy benzene (XXXVI) was conveniently prepared by reaction of iodine with 1,3-dimethoxy-phenyl lithium (yield 90%). Reaction of XXXVI with activated copper produced the desired tetramethoxy compound in 90% yield.



XXXVI XXXVII

b) Synthesis of 3,3',4,4'-tetramethoxy-benzophenone

3,3',4,4'-tetramethoxy-benzophenone (XXXVIII) was conveniently prepared using the Friedel-Craft reaction between veratroyl chloride and veratrole.



XXXVIII

c) Attempted demethylation of XXXVII and XXXVIII.

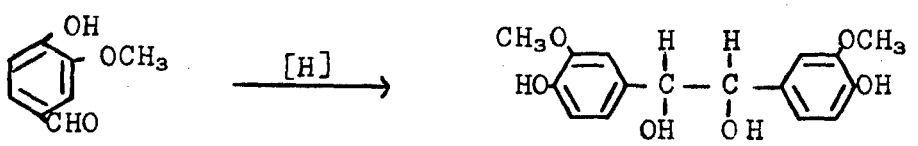
Many attempts have been made to demethylate XXXVII and XXXVIII. These compounds appear to be resistant to the methods commonly used for demethylation. XXXVII has been reported to demethylate upon heating under reflux with hydrogen iodide (9). This reaction could not be repeated. Other methods which were attempted unsuccessfully include

a) Heating with a solution of sodium hydroxide in diethylene glycol.
b) Heating with a solution of aluminum chloride in carbon tetrachloride.
c) Heating with a solution of aluminum bromide in benzene.
d) Heating in aqueous hydrogen iodide with iodine and red phosphorus catalyst.
e) Heating with hydrogen iodide in acetic acid.
f) Heating with aqueous hydrogen iodide with phosphonium iodide catalyst.
g) Heating with aniline hydrochloride.
h) Heating with a solution of aluminum bromide in nitrobenzene.

Failure of the demethylation procedures is believed to be a steric problem. Since optimum conditions could not be found to overcome these factors, an alternate procedure has been carried out for XXXVIII.

d) Synthesis of Hydrovanilloin

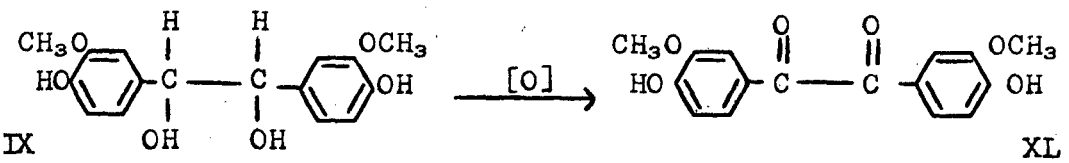
Hydrovanilloin (XXXIX) was prepared by the electrolytic reduction of vanallin (10).



XXXIX

e) Synthesis of Vanillil

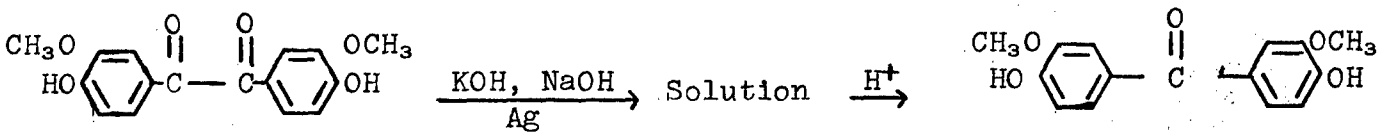
Vanillil (XL) was prepared by oxidizing hydrovanilloin with copper (II) hydroxide in acetic acid.



XXXIX XL

f) Synthesis of 3,3'-4,4'-Tetrahydroxy-benzophenone

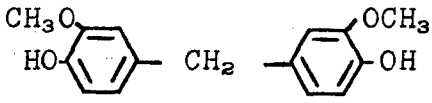
Attempts to prepare 3,3',4,4' tetrahydroxy-benzophenone gave the 3,3'-dimethoxy, 4,4'-dihydroxy derivative. Since Pearl reports no analysis for his products, he may well have had this same material.



XLI XLII

g) Synthesis of 3,3'-dimethoxy-4,4'-dihydroxy-diphenyl-methane.

Treatment of XLI with sodium hydroxide and silver oxide leads to 3,3'-dimethoxy-4,4'-dihydroxydiphenylmethane, XLIII (12).

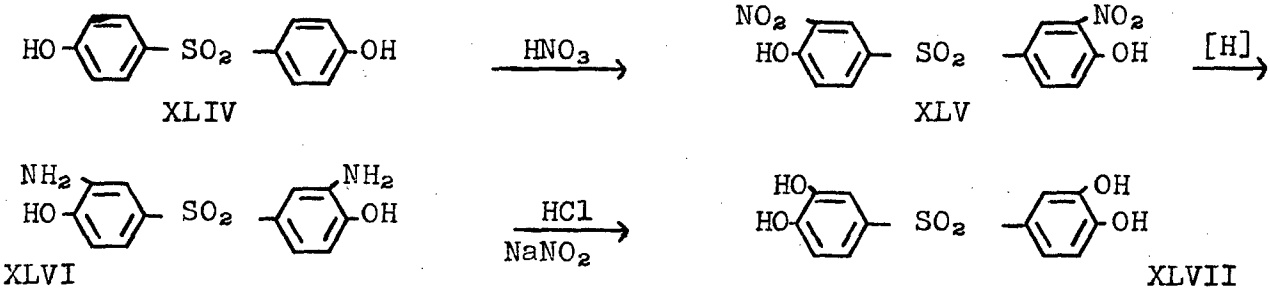


XLIII

Attempts to demethylate this are in progress.

h) Synthesis of 3,3',4,4' tetrahydroxydiphenyl sulfone

Dihydroxydiphenyl sulfone is commercially available and can easily be nitrated. If this product is reduced and the diazonium salt formed, hydrolysis to the 3,3', 4,4'-tetrahydroxydiphenyl (XLVII) should be easily accomplished. This synthesis is now in progress.



XLIV XLV XLVI XLVII

6. Phthalocyanine Polymers. During the past year, the earlier work on phthalocyanine polymers has been extended by John McLean. Efforts have been made to obtain polymers of higher molecular weight and greater stability.

Variation of reaction conditions, e.g., temperature, amount of reactants, and time of reaction appears to have little effect on increasing the molecular weights beyond a limit of ca. 5,000 for a given reaction. In the past the amount of ancillary reagent used in the synthesis has been kept small. This precaution was based on the assumption that traces of the ancillary actually replace the coordinating metal in the phthalocyanine unit. It is

possible that this assumption is invalid because ancillary content of the product has not been determined directly. Ancillary metals have been identified in the solutions which remain after electrolytic deposition of copper. Inasmuch as this is not conclusive evidence, future plans include increasing the amount of ancillary reagent in the synthesis. A direct analysis of the samples for ancillary metals will be necessary to check copper replacement by ancillary metals.

"Recycling", or subjecting the largest polymers to polymerization processes has been the only method employed thus far which increases polymer size. Analysis indicates that the first cycle increases the molecular weight by a factor greater than ten. Products obtained from additional cycles have not been analyzed but are much darker (black) which indicates that the molecular weight is larger. The only draw back to this process is the fact that yields become surprisingly smaller with each successive recyclization. After four cycles the yield of the polymer is too small to allow the process to be efficiently repeated.

Previously, end group titration of the free carboxyl groups has been employed to determine equivalent weights. The insolubility of the polymeric complex in water made this process very slow and difficult. Additions of 0.1N sodium hydroxide had to be made in small increments and twelve hours allowed for reaction after each addition. Presently this method has been improved by adding an excess of 0.1N sodium hydroxide, allowing the solution to stand for twelve hours and back-titrating this excess with 0.1N hydrochloric acid. This method gives comparable results with the former and is many times faster. The validity of this procedure rests on the assumption that decarboxylation of the peripheral carboxyl groups does not occur during preparation of the polymer. As yet no method has been devised to check the possibility of decarboxylation or the extent of decarboxylation of these peripheral groups.

The various methods which have been employed in attempts to synthesize heat stable phthalocyanine polymers have all involved the reaction of pyromellitic dianhydride, copper, urea and an ancillary reagent. The numerous variations of this reaction can be described under three general types. Synthesis in which (1) a copper (II) salt is used and molten urea serves as the reaction medium; (2) a copper (II) salt is used and the reaction mixture is refluxed in a dichlorobenzene suspension; (3) copper powder is used with an oxidizing agent and the reaction mixture is refluxed in a trichlorobenzene solution.

The heat stabilities of samples prepared by the above methods have been found by heating these samples in a nitrogen atmosphere and recording weight losses periodically. The temperatures at which weight losses were greater than 2% were abitrarily used as

points of thermal decomposition. The mean decomposition temperatures of samples prepared by the three methods cited above were found to be as follows:

Method	Decomposition Temperature
1	218°
2	324°
3	242°

Extended heating of the reaction mixture had little or no effect on increasing the thermal stability of the products obtained. The stabilities of these polymeric substances are surprisingly low when compared with the high thermal stability of copper phthalocyanine itself. If copper phthalocyanine is heated under reduced pressure, sublimation commences at 550°C and is rapid at 580°C (13). On the basis of this observation it is concluded that attempts to form the polymer result in drastic losses in heat stability. There seem to be two possible explanations for this odd behavior of the polymer.

(1) It has been reported that the monochloro- derivative of copper phthalocyanine cannot be sublimed but is decomposed on heating at a much lower temperature than the parent compound (13). This decomposition occurs with the evolution of hydrogen chloride. This would seem to indicate that if there is any chlorination of the polymer in the course of the synthesis, great losses in thermal stability are to be expected.

(2) A decrease in resonance stability of the polymer due to cross linkage could subsequently cause a decrease in thermal stability. The difficulties involved in the synthesis of a phthalocyanine polymer have led to a broader approach to polymer synthesis. Other possibilities in polymer formation are also being presently investigated.

The substitution of zirconium tetrachloride for zirconium oxychloride to prevent possible chlorination failed to increase the heat stability of the product. Using a mixture of solvents as reaction media did not aid in the growth of larger polymeric units.

One of the difficulties encountered in the synthesis of phthalocyanine polymers has been that of finding a suitable solvent for the reactants. Orthodichloro benzene, trichloro benzene, and mixtures of these two solvents have previously been employed as reaction media. Since the reaction mixture was only sparingly soluble in these solvents, it was necessary to reflux a suspension of starting materials for varying periods of time. Maximum thermal stability for products obtained from the above reaction was 253°C. Weight losses were greater than 3% when this temperature was exceeded.

Solubility difficulties have been overcome in the synthesis of phthalocyanine polymers by employing dimethyl formamide as a solvent. All of the starting materials are completely soluble in this compound and the thermal stabilities of the products obtained are increased considerably. Reaction conditions were varied employing dimethyl formamide as a solvent for the synthesis. Three samples were obtained. First, the thermal stabilities were determined for the crude samples. Sample I decomposed at 277°C, and samples II and III decomposed at 300°C (3% loss or more). Secondly, the stabilities were redetermined for these samples after treatment with warm dilute sulfuric acid. These data are recorded in Table III.

Table III

Percent weight loss from purified samples on heating

Temperature	224	250	280	290	316	330	348	360
Sample I	2.3%	1.6%	0.8%	1.2%	Decom.	-	-	-
Sample II	0.3%	0.23%	0.85%	0.75%	0.97%	Decom.	-	-
Sample III	1.1%	0.6%	0.67%	0.91%	0.47%	-	0.9%	Decom.

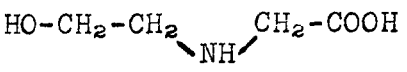
These data indicate that decomposition is catalyzed by impurities. If the purification procedure which was employed can be improved, thermal stability should also increase.

B. Attempts to Form Polymers by Linking Mononuclear Complexes Together.

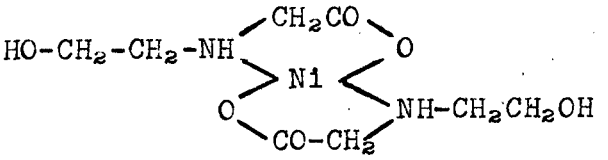
The general method of forming polymers by condensation with organic materials has not been studied as extensively as the formation of polymers by direct coordination. However, some of the results which have been obtained show promise, and the work will be given increased emphasis.

1. Polymers from β-Hydroxyethylglycine. Previous workers (14) on this program had attempted to utilize the free hydroxyl groups in tris(β-hydroxyethylethylenediamine)-cobalt(III) salts in polyesterification. No proven examples of polymer formation were obtained, the hydroxyl groups being inert to attack by a wide variety of chemical reagents (15). It was postulated that this inertness is due to the proximity of the hydroxyl group to the charged cobalt atom. It appeared evident that the metal complex compounds which would be formed by reaction between β-hydroxyethyl-glycine (XLVIII) and copper (II), nickel (II) and co-

balt (III) salts would be similar in constitution to the above described cobalt (III) salt. Such compounds would be non-valent and appeared to be more suitable for polyesterification studies.

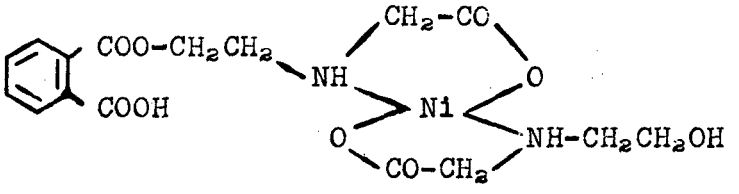


XLVIII



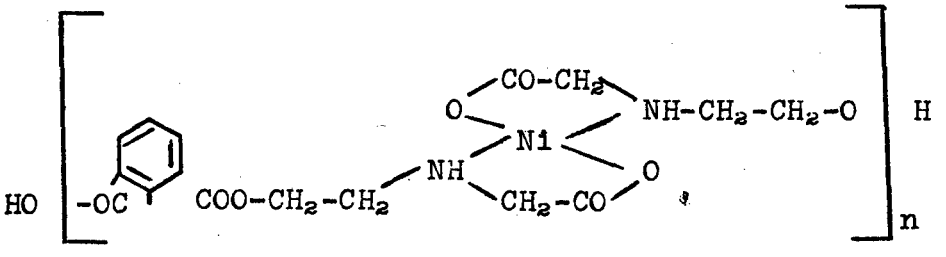
XLIX

β-Hydroxyethylglycine has been synthesized in 67% yield and the copper (II) and nickel (II) complexes prepared. The copper (II) complex melts with decomposition at 220°. However, the nickel (II) complex (XLIX) was found to be reasonably heat stable. It can be heated to 320° without melting or decomposition and was therefore selected for polyesterification studies. These metal complexes were found to be completely insoluble in a wide range of organic solvents and to be soluble only in water. Hence, polyesterification reactions are rendered difficult. There was no reaction observed between XLIX and sebacic or terephthalic acid, nor could ester-interchange reactions between XLIX and dimethyl sebacate, diethyl malonate or dimethyl terephthalate be effected in the presence of selected catalysts. Fusion of XLIX with phthalic anhydride at 170° was shown to give the monophthalate ester (L). L is a blue-green solid which is heat stable at 320°. When a finely powdered sample of L was heated in vacuo at 170° for four



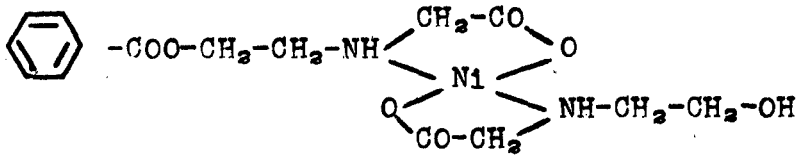
L

hours, self-condensation occurred and the polymer LI (n=2 or 3) was obtained.



LI

It is evident that if metal complex compounds similar to XLIX, but soluble in organic solvents, could be prepared, then high molecular weight polyesters of composition similar to LI might be accessible. Also, when an aqueous solution of XLIX is agitated with a carbon tetrachloride solution of benzoyl chloride, O-benzoylation occurs, the monobenzoyl-ester (LII) being obtained. This reaction is of interest, as use of a

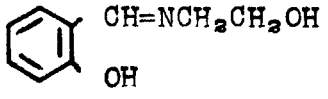


LII

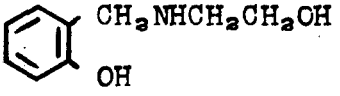
bis-acylchloride (such as succinoyl chloride) may result in polymer formation.

2. Polymers from Salicylidene ethanolamine and 2-β-Hydroxyethylaminomethyl Phenol.

In order to obtain metal complex compounds which would be soluble in organic solvents and yet similar in structure to XLIX, salicylidene ethanolamine (LIII) and 2-β-hydroxyethylaminomethylphenol (LIV) have been studied. LIII condenses readily with suitable

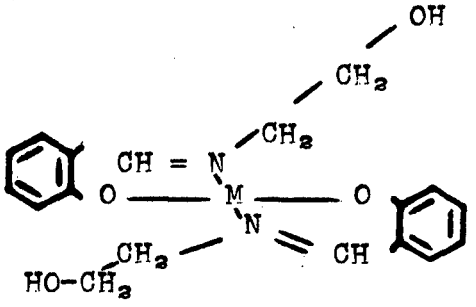


LIII



LIV

zinc (II), copper (II) and nickel (II) salts to form metal chelate compounds of composition LV. These metal

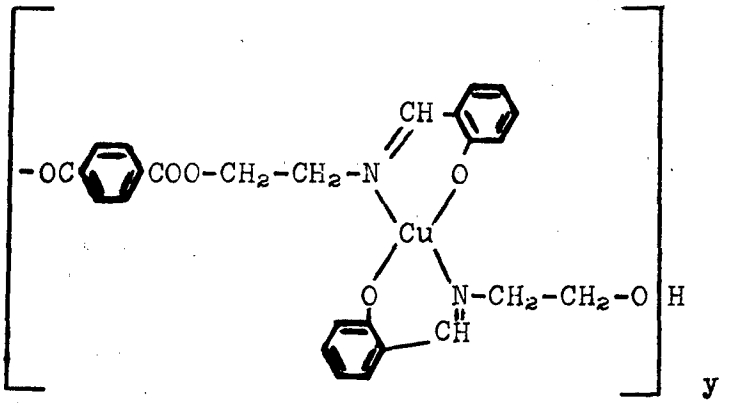


LV

LVa: M = Cu (II)
LVb: M = Ni (II)
LVc: M = Zn (II)

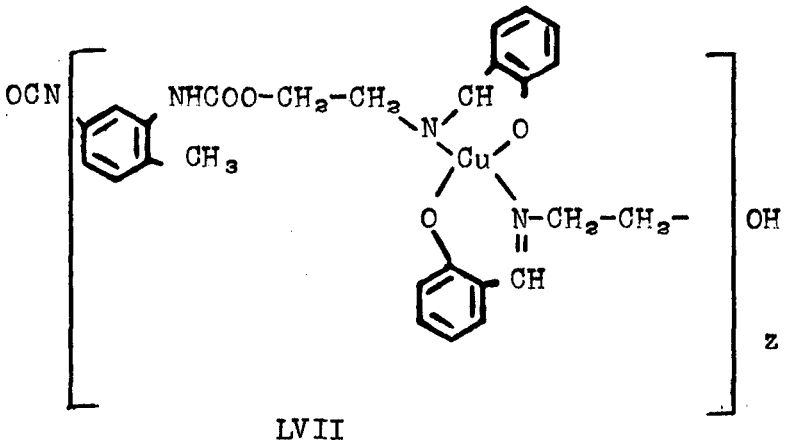
complexes are insoluble in water and are soluble in a wide range of organic solvents. The copper (II) complex (LVa) appears to be most stable toward heat, melting at 177° and being stable to 300°. Fusion of LVa with phthalic anhydride at 170° resulted in the formation of polymeric material. During the course of the reaction a small amount of salicylaldehyde was liberated, due to fission of the azo-methine linkage. In order to circumvent this, experiments will be conducted using metal chelate compounds derived from the reduced form (LIV) of LIII. Hydrogenation of the imine linkage confers a stronger donor power on the nitrogen atom and should result in the formation of very stable metal complexes. Catalytic hydrogenation of LIII using Raney-Nickel catalyst was expected to give LIV, a similar reduction having been observed with allied Schiff's bases (16). No reduction took place, even under higher pressures than those reported in the literature. This can probably be attributed to deactivation of the catalyst by chelation with LIII. The reduction was successfully carried out using a platinum oxide catalyst at 1000 lbs. pressure.

Under the supposition that the fission of the azomethine linkage mentioned above was due to hydrolysis by the water liberated in the reaction, attempts were made to form polymers by ester interchange between LVa and dimethyl terphthalate. The polymeric material so obtained may be melt drawn but is brittle in the solid state. Analytical results suggest the polymer has structure LVI.



LVI

Also, LVa was caused to react with 2,4-tolylene-diissocyanate by heating under reflux in chlorobenzene. The polymer LVII precipitated from solution. After these two experiments had been

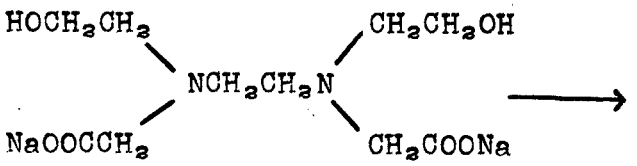


LVII

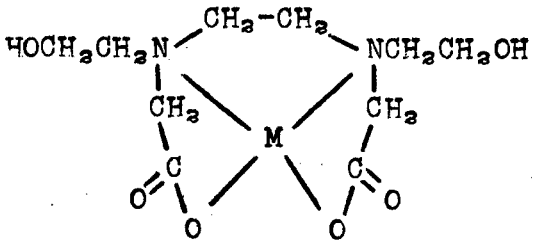
carried out the thermal stability of LVI and LVII was determined. In each case decomposition occurred below 200°. It was evident that heat stability would not be found in polymers of these types. Accordingly, this project, as well as that using metal complexes of β-hydroxyethyl-glycine, was temporarily abandoned.

3. Polymers from Ethylenediamine-N,N'-bis-β-Hydroxyethyl-N,N'-Diacetic Acid.

Before the lack of heat stability of polymers formed by condensation was discovered, some effort was made to prepare the monomer LIX.



LVIII



LIX

Treatment of the appropriate metal salt with a solution of versene-diol (LVIII) forms a complex immediately. Isolation of these complexes in pure form, however, proved difficult. Attempts were then made to eliminate the impurities by allowing the acid form of versene-diol to react with the appropriate metal carbonate. The acid form was prepared by passing the sodium salt through a cation exchange resin in the hydrogen cycle.

The complex between copper (II) and versene-diol (LVIII) was prepared by treating the acid form of versene-diol with copper powder. An attempt has been made to produce a polyurethane by causing the monomer to react with tolylene diissocynate. This work is not yet complete.

III. EXPERIMENTAL

A. Attempts to Form Polymers by Coordination with Metal Ions

1. Thiopicolinamide Polymers

a) 4,4'-Bis-(α-thiopicolinamido)-diphenyl (IV)

Benzidine (18.4 g., 0.1 mole), sulphur (19.2 g., 0.6 mole) and α-picoline (18.6 g., 0.2 mole) were mixed and heated at 140° for 6 hours. After cooling, the solid residue was recrystallized several times from an ethanol-methyl cellosolve mixture. 4-Amino-4'-β-thiopicolinamido-diphenyl crystallized as orange prisms, mp. 175°. Anal.: Calcd. for $C_{18}H_{15}N_3S$; C, 70.7; H, 4.9. Found: C, 70.2; H, 4.8.

An intimate mixture of 4-amino-4'-α-thiopicolinamido-diphenyl (3.05 g., 0.01 mole), sulfur (0.96 g., 0.03 mole) and α-picoline (1.39 g., 0.015 mole) was heated at 160° until hydrogen sulfide was no longer evolved (about six hours). The residual solid was washed with carbon disulfide to remove any remaining sulfur, and was then recrystallized several times from pyridine. The bis-thioamide crystallized in orange needles, mp. 237°. Anal.: Calcd. for $C_{24}H_{18}N_4S_2$; C, 67.6; H, 4.2; N, 13.1. Found: C, 67.8; H, 4.1; N, 13.0.

α-Picoline (75.0 g., 0.8 mole), sulfur (72.8g., 2.2 mole) and benzidine (36.8 g., 0.2 mole) were intimately mixed and heated under reflux for fifteen hours. Excess α-picoline was removed by distillation and the solid residue was recrystallized several times from pyridine, being first washed with carbon disulfide to remove excess sulfur. The thioamide crystallized in orange needles, mp. 236-7°.

b) Preparation of [4,4'-Bis-thiopicolinamido-diphenyl]-nickel polymer (Vb)

An intimate mixture of 4,4'-bis-thiopicolinamido-diphenyl (2.13 g., 0.005 mole) and bis(pentane-2,4-dione)-nickel (II) (1.28 g., 0.005 mole) was heated at 270°/1 mm. After four hours a red-brown solid, insoluble in many organic solvents, had formed and 2,4-pentanedione (0.96 g) had collected in the receiver. The polymer did not melt below 300°. Anal.: Calcd. for $C_{24}H_{16}N_2S_2Ni$; C, 59.6; H, 3.3. Found: C, 61.7; H, 3.6.

c) Preparation of [4,4'-Bis-thiopicolinamido-diphenyl]-copper (II) - polymer (Va)

The copper (II) polymer was prepared in a similar manner to that described above for the nickel (II) compound, using 4,4'-bis-thiopicolinamido-diphenyl (2.13 g., 0.005 mole) and bis-(pentane 2,4-dione)-copper (II) (1.31 g., 0.005 mole). It was

obtained as a brown powder which did not melt below 300°. Anal.: Calcd. for $C_{24}H_{16}N_2S_2Cu$; C, 59.0; H, 3.2. Found C, 59.4; H, 3.5.

d) 4,4'-bis-thiopicolinamido-benzophenone (XI)

4,4-diacetylamino-diphenylmethane

Acetic anhydride (102 g.) was slowly added to a solution of 4,4'-diamino-diphenylmethane (100 g.) in glacial acetic acid (150 ml.) and the mixture warmed on the steam bath for 1 hour. The solution was cooled, water (300 ml.) added and the white solid collected. The crude product, 4,4-diacetylamino-diphenylmethane, melted 234°.

4,4'-diacetylamino-benzophenone (IX)

To a solution of the acetyl compound (28.2 g.) in glacial acetic acid (100 ml.) was added chromic oxide solution (36 mls. of a solution containing 100 g. of chromic oxide in 50 ml. of water and 240 ml. of glacial acetic acid). The mixture was warmed on the steam bath for one hour, then cooled and 500 ml. of water was added. The precipitated 4,4'-diacetylamino-benzophenone (IX) was collected and dried. It melted at 220°.

4,4'-diamino-benzophenone (X)

The acetylated ketone (100 g.) was mixed with sulfuric acid (300 ml. of 30% acid) and warmed on the water bath for four hours. The solution was then filtered, and the filtrate was cooled and made alkaline with ammonia. The precipitated 4,4'-diamino-benzophenone (X) was collected and dried. It melted at 180-230°C. The crude product could be purified by precipitation from hydrochloric acid solution with ammonia. It was eventually obtained as light brown needles, mp. 245°.

4,4'-bis-thiopicolinamido-benzophenone (XI)

An intimate mixture of α-picoline (19 g., 0.2 mole), sulfur (17.5 g., 0.55 mole) and 4,4'-diamino-benzophenone (10.g, 0.05 mole) was heated under reflux for 15 hours. Hydrogen sulfide was evolved. After this time, excess α-picoline was removed by vacuum distillation and the residue was dissolved in pyridine (150 ml.) by heating. On cooling, sulfur (10 g.) crystallized. This was removed by filtration and the filtrate was evaporated under reduced pressure. The residual orange colored 4,4'-bis-thiopicolinamido-benzophenone (XI) was recrystallized many times from a mixture of dimethyl formamide and ethanol and was eventually obtained in golden plates, mp. 181°.

Anal.: Calcd. for $C_{25}H_{18}N_4S_2O$; C, 66.1; H, 4.0; N, 12.3.
Found: C, 66.2; H, 3.9; N, 11.8.

e) Polymers derived from 4,4'-bis-thiopicolinamido-benzophenone

These polymers were prepared by addition of a methanol solution of the appropriate metal acetate (1 mole) to a solution of XI (1 mole) in dimethyl formamide. In each case, the polymeric material precipitated immediately from solution. The mixture was usually heated under reflux for one-half hour to ensure complete reaction.

Copper (II) polymer (XIIa)

Red brown solid

Anal.: Calcd. for $C_{25}H_{16}N_4S_2OCu$; Cu, 58.2; H, 3.1; N, 10.9
Found: C, 57.1; H, 3.1; N, 10.4

Zinc (II) polymer (XIIb)

Pale yellow solid, mp. 300°

Anal.: Calcd. for $C_{25}H_{16}N_4S_2OZn$; C, 58.0; H, 3.1; N, 10.8
Found: C, 57.0; H, 3.1; N, 10.5

Nickel (II) polymer (XIIc)

Brown solid

Anal.: Calcd. for $C_{25}H_{16}N_4S_2ONi$; C, 58.7; H, 3.1; N, 11.0
Found: C, 58.4; H, 3.4; N, 11.0

f) 4,4'-bis-thiopicolinamido-diphenylsulfone (XIII)

4,4'-Diamino-diphenylsulfone (24.8 g.), sulfur (38.4 g.) and α-picoline (100 g.) were heated under reflux for 12 hours, hydrogen sulfide being evolved. The excess α-picoline was removed by distillation in vacuo and the residue was recrystallized from pyridine. The solid which settled out was washed with carbon disulfide and then recrystallized several times from dimethyl formamide. The thioamide was obtained as an orange micro-crystalline solid, mp. 265.6°.

Anal.: Calcd. for $C_{24}H_{18}N_4S_3O_2$; C, 58.8; H, 3.7.
Found: C, 58.9; H, 3.6.

g) Polymers derived from 4,4'-bis-thiopicolinamido-diphenylsulfone (XIII)

Zinc (II) polymer (XIVa)

Hot solutions of zinc (II) acetate (0.44 g., 1 mole) in dimethyl formamide (20 ml.) and XIII (0.98 g., 0.002 mole) in dimethyl formamide (35 ml.) were mixed and warmed on the water bath.

After 15 minutes, a yellow solid precipitated from solution. After 30 minutes, this was filtered, washed well with ethanol and dried in vacuo.

Anal.: Calcd. for $C_{24}H_{18}N_4S_3O_2Zn$; C, 51.9; H, 3.2; N, 10.1
Found: C, 51.5; H, 3.0; N, 10.4

Nickel (II) polymer (XIVb)

Hot solutions of nickel (II) acetate (0.496 g., 1 mole) in methanol (40 ml.) and XIII (0.98 g., 1 mol.) in dimethyl formamide (30 ml.) were mixed. A brown solid precipitated immediately from solution. The mixture was heated under reflux for one-half hour. The brown polymer was collected, washed well with ethanol and dried in vacuo.

Anal.: Calcd. for $C_{24}H_{18}N_4S_3O_2Ni$; C, 52.6; H, 3.3; N, 10.2
Found: C, 52.9; H, 3.6; N, 10.3

Copper (II) polymer (XIVc)

Hot solutions of XIII (0.98 g., 1 mol.) in dimethyl formamide (30 ml.) and copper (II) acetate (0.4 g., 1 mol.) in dimethyl formamide (15 ml.) were mixed and warmed on the water bath. The solution immediately became deep brown and after ten minutes a brown solid crystallized from solution. This was collected, washed well with ethanol and dried in vacuo.

Anal.: Calcd. for $C_{24}H_{18}N_4S_3O_2Cu$; C, 52.0; H, 3.3; N, 10.1
Found: C, 51.9; H, 3.5; N, 10.1

2. Fluorinated 1,3-Diketone Polymers

a) 1,1,2,2-Tetra(trifluoro-acetyl)ethane (XVII).
This was prepared according to the scheme shown on page 10.

Trifluoro-acetic acid (114 g., 1 mole) was added with stirring to a solution of sodium hydroxide (40 g., 1 mole) in water (100 ml.). The resulting sirup was evaporated to dryness in a vacuum desiccator (sulfuric acid desiccant). The anhydrous sodium salt was added to a cold mixture of ethanol (120 ml.) and sulfuric acid (150 g. of 36%) and allowed to stand at room temperature for three hours. The mixture was heated on a water bath and the liquid distilling at 58°-62° was collected. The distillate was dried over calcium chloride and distilled from phosphorus pentoxide. The ethyl trifluoroacetate distilled as a colorless liquid, b.p. 59-61.5°.

To prepare 1,1,1-trifluoro-acetone, ethanol (23 g., 0.5 mole) was added to a suspension of sodium sand (11.5 g., 0.5 mole) in ether (300 ml.) After the exothermic reaction had abated, ethyl acetate (44 g., 0.5 mole) was added and then, over a period of one hour, an equimolecular quantity of ethyl trifluoro acetate (71 g.). The mixture was heated under reflux for forty-eight hours and then the volatile solvents were removed in vacuo. The residual solid

was dissolved in sulfuric acid (300 ml. of 30%) and the solution was heated under reflux until the organic layer had completely disappeared. The vapors passing through the reflux condenser were directed to a dry ice trap which collected trifluoro-acetone (44 g., 80%).

1, 1,2,2-Tetra(trifluoro-acetyl)-ethane (XVII) was prepared as follows:

Ethanol (8.6 g., 0.187 mole) was slowly added to a suspension of sodium sand (4.3 g., 0.187 mole) in ether (100 ml.) contained in a 1-liter 3-necked round-bottomed flask equipped with stirrer, dropping funnel and reflux condenser. Trifluoro-acetic ester (26.6 g., 0.187 mole) was then added, the suspended sodium ethoxide dissolving to give a clear solution. Trifluoro-acetone (21 g., 0.187 mole) was added and the solution was heated under reflux for twenty hours. The reaction mixture was evaporated to dryness in vacuo and the solid residue was dissolved in ether (500 ml.) A solution of iodine (23 g., 0.187 mole) in ether (200 ml.) was added and the solution was heated under reflux for 20 hours. The ethereal solution was washed twice with 200 ml. of 10% aqueous sodium thiosulfate solution, dried over sodium sulfate and evaporated. The solid residue was recrystallized several times from a benzene-petroleum ether mixture. 1,1,2,2-Tetra(trifluoro-acetyl)-ethane crystallized in pale yellow needles, mp. 144°.

Anal.: Calcd. for $C_{10}H_2F_{12}O_4 2H_2O$; C, 26.7; H, 1.1.
Found: C, 26.5; H, 1.3.

b) 1,1,3,3-Tetra-Acetyl Propane

Dry sodium acetylacetonate (24.4 g., 0.2 mole) (prepared by the reaction of equivalent amounts of acetylacetone and divided sodium in absolute ether) was mixed with an excess of methylene iodide (117 g., 0.4 mole) and heated at 130° for twenty-four hours. The reaction mixture was filtered and the solid washed with ether. The wash liquid and filtrate were combined. Upon standing, the ether evaporated off, leaving an oil. The product was made to crystallize by allowing it to stand in the presence of ether. The material was recrystallized from ethanol. The product has been submitted for analysis. Yield 6 g. (28.3% of theoretical). Pale yellow needles, mp. 80°.

3. Amino Acid Polymers

a) Preparation of β-aminoglutaric acid (17)

A mixture of 56 g. of ethyl acetone dicarboxylate dissolved in 150 cc of ethyl ether and 30 g. of phenyl hydrazine was left at 0-5°C for 24 hours. Then the separated water was decanted and the ethereal solution was dried over sodium sulfate. The solution was evaporated under vacuum at 15-20°C. The phenyl hydrazone did not crystallize, but remained as an oil.

To this phenyl hydrazone of 56 g. of ethyl acetone dicarboxylate in 400 cc of ethanol at 25°-30° was added 40 g. of amalgamated aluminum and 150 cc H_2O. The mixture was stirred for sixteen hours, after which another two grams of aluminum amalgam was added. The mixture was stirred 10 hours more, 1600 cc water was added and the alumina was filtered off. To the solution was added 187 g. of barium hydroxide. After three days an equivalent amount of sulfuric acid was added. The solution was filtered and concentrated to yield 5 g. of β-aminoglutaric acid. mp. = 280°. Anal.: Calcd. C, 40.82; N, 9.52; H, 6.12. Found: C, 41.12; N, 9.43; H, 6.17.

b) Measurement of the stability constants of the β-aminoglutarates of zinc and nickel

A solution of zinc sulfate was prepared by dissolving 0.3269 g. of pure zinc metal in sulfuric acid and diluting the neutralized solution to one liter. This gave a 0.005M solution.

A solution of nickel perchlorate was prepared by dissolving 1.8285 g. of nickel perchlorate in water and diluting to one liter. This solution was standardized by titration with the disodium salt of ethylenediamine tetracetic acid, and was found to be 0.005M.

β-Amino glutaric acid was purified by three recrystallizations from water. A standard solution of sodium hydroxide was made up from an "Acculate"sample and checked against standard hydrochloric acid.

The procedure used for the pH measurements is as follows:

1) A 0.0147 g. (10^{-4} moles) sample of acid was diluted volumetrically to 100 ml. with 0.1N KCl.
2) Into a 100 ml. volumetric flask was put 10 ml. of the acid -KCl solution, 2 ml. of metal ion solution and 1.50 cc of .01N of sodium hydroxide. This solution was diluted to 100 cc with 0.1N KCl.
3) The solution was kept overnight at 25° and the pH was measured. The pH of the solution containing zinc ion was 7.84; the pH of solution containing nickel ion was 8.01.

c) Preparation of a copper-N,N' benzidine diacetic acid

A solution of 0.630 g. (0.00315 mole) of cupric acetate monohydrate in 20 ml. of dimethyl formamide (DMF) was added to a solution of 1.0 g. (0.00315 mole) of N,N'-benzidine diacetic acid in 100 ml. of DMF. A fine olive-drab precipitate formed immediately. This was allowed to stand overnight. The precipitate was removed by vacuum filtration, washed with ethanol, ether and submitted for analysis. The analysis indicated impurities to be present. Anal.: Calcd. for $C_{16}H_{14}O_4N_2Cu$; C, 53.1; H, 3.87; N, 7.74. Found: C, 55.5; H, 5.14; N, 7.75.

4. Polymers from 8-Hydroxyquinoline

a) 2,2-Bis-5-(8-quinolol)-propane (XXV)

The synthesis of this bis-hydroxyquinoline as outlined on page 17 was begun, but was not complete at the end of the period under review.

2,2-bis(3'-nitro-4'-hydroxyphenyl)-propane (XXVII). Nitric acid (sp.g 1.42, 45 ml.) was added dropwise with stirring to a solution of bis-phenol A (45 g.) in benzene (225 ml.) and acetic acid (150 ml.), the temperature of the solution being maintained between 0-6°. After the addition was complete, the stirring was maintained for a further 30 minutes. Water (500 ml.) and benzene (300 ml.) were added and the benzene layer was separated. The extracts were washed well with water, dried over calcium chloride and evaporated. The solid residue recrystallized from ethyl acetate in yellow needles, mp. 135°. Yield, 45 g., 70%. Anal.: Calcd. for $C_{15}H_{14}N_2O_6$; C, 56.6; H, 4.4; N, 8.8. Found: C, 56.6; H, 4.7; N, 8.7.

In the course of this investigation, it was found that the product could be obtained directly from the reaction mixture by cooling it to ca. 5°. Upon standing at this temperature, the product crystallized from the reaction mixture in the form of needles. These were isolated by vacuum filtration, washed with water, ethanol and ether.

Table IV summarizes the results of a study of several variables on the nitration of bis-phenol A. It was concluded from this study that the rate of addition of the nitric acid to the reaction mixture is of critical importance. It also appears that cracked ice is the best coolant and that rapid top stirring is desirable.

Table IV
Effect of Variables on Nitration of Bis-Phenol A.

Variable	Trial A	Trial B	Trial C	Trial D
Stirring	Slow Magnetic St.	Rapid Top St.	Rapid Top St.	Rapid Top St.
Coolant	Dry Ice Acetone	Salt-Ice	Salt-Ice	Ice
Time of HNO_3 Add'n.	ca. 20 min.	ca. 1 hr.	ca. 1 hr.	ca. 2 hr.
Time of Standing After Add'n.	1/2 hr.	1/2 hr.	4 hr.	4 hr.
% of Total Yield which was Mon-nitrated	72.5	100		
% of Total Yield which was Bi-nitrated	14.5			100
% of Total Yield which was Tri-nitrated	13		100	

b) 2,2-bis-(3'-amino-4'-hydroxy-phenyl)-propane (XXVIII)

A suspension of the above described nitro compound in ethanol was catalytically reduced over PtO_2, at 1000 lbs. pressure, at 80°, six mols. of hydrogen being absorbed. The catalyst was removed by filtration and the ethanol was evaporated. The residue which remained was eluted with petroleum ether and dried in vacuo. The diamine was obtained as a brown colored solid. Anal.: Calcd. for $C_{15}H_{18}N_2O_2$; C, 69.7; H, 7.0. Found: C, 69.5; H, 7.1.

The amino phenol melts at 265°, is soluble in formamide, hot ethanol, hot acetone and hot ethylacetate and is insoluble in water, chloroform and ether.

The reduction using sodium in liquid ammonia was carried out as follows:

Into ca. 500 ml. of liquid ammonia was put 10 g. of 2,2'-bis-(3'-nitro-4'-hydroxy-phenyl)-propane (0.0314 mole) which dissolved to form a dark red solution. To this solution was added 21.0 g. of ammonium chloride (0.276 mole). To the stirred solution was added 6.64 g. of sodium (0.276 mole) in small pieces over a period of an hour. The ammonia was allowed to evaporate, leaving a red-brown solid. The solid was extracted several times with boiling ethanol to separate the reduced amine from the sodium chloride produced in the reaction. The evaporation of these extracts yielded a brown powder which gave the same infrared spectrum as the material previously identified as the amino-phenol. The dissolution and subsequent precipitation of this material from ethanol failed to produce crystals; this was taken as an indication that the material was impure.

c) Synthesis of a copper 2,2-bis-(3'-amino-4'-hydroxy-phenyl)-propane complex of probably polymeric nature (XXIX)

Into a solution of 0.7760 g. of cupric acetate monohydrate (0.00388 mole) in 100 ml. of methyl alcohol was poured a solution of 1 g. of 2,2-bis-(3'-amino-4'-hydroxy-phenyl)propane (0.00388 mole). Immediately, a very fine grey precipitate formed; this remained in suspension. The suspension was refluxed for ten minutes and allowed to stand overnight. The precipitate was removed by filtration and digested in hot water overnight. The material was again isolated by vacuum filtration, washed with ethanol and ether and submitted for analysis.
Anal.: Calcd. for $C_{15}H_{16}O_2N_2Cu$: C, 56.2; H, 5.00; N, 8.75; Cu, 25.0
Found: C, 56.5; H, 5.01; N, 8.21; Cu, 24.1

5. Silicon Containing Polymers

a) Attempted synthesis of 2,2',6,6'-tetrahydroxybiphenyl (XXXIII)

From 2-nitroresorcinol

2-Nitroresorcinol was prepared by a modification of the method of Kauffman and DePay (18). 176 g. of resorcinol in fine crystals was stirred into 1200 g. of 20% oleum at 30-70°. The paste was cooled to 0° and a mixture of 120 g. of 98% nitric acid and 320 g. of 20% oleum was added with agitation and cooling. Steam distillation of the mixture yielded 50 g. of 2-nitroresorcinol as orange red crystals, mp. 84°. This was converted to 2,6-dimethoxynitrobenzene by the method of Bayer (19). 100 g. of nitroresorcinol was dissolved in 300 cc of 20% sodium hydroxide and 300 cc of water. After cooling, 200 g. of dimethyl sulfate was added and the mixture was shaken for two hours. The product was separated and recrystallized from ethanol. Yield, 100%; mp. 118-25°.

Reduction of the dimethoxynitrobenzene gave 2,6-dimethoxyaniline (20). 120 g. of 2,6 dimethoxynitrobenzene was dissolved in 600 cc of hot ethanol and was hydrogenated at 80° and a hydrogen pressure of 75 kg/cm^2 in the presence of Raney nickel. The solution was evaporated to 200 ml., and after standing overnight the crystals were collected. Yield, 75 g; mp. 75-77°.

2,6-Dimethoxydiazonium sulfate. A solution of 20 g. of dimethoxyaniline in 80 g. of absolute alcohol was mixed with 20 g. of concentrated sulfuric acid and 20 g. of amyl nitrite. The temperature was kept below 20°C during this addition. The mixture was allowed to stand thirty minutes and then 50 ml. of ether was added. After thirty more minutes the precipitation of 2,6-dimethoxydiazonium sulfate was complete. It was filtered and washed with ether. Yield; 28 g.

2,6-Dimethoxyiodobenzene. 2,6-Dimethoxydiazonium sulfate (28 g.) was dissolved in 30 ml. of water and poured into 60 ml. of a cool 50% solution of potassium iodide. The mixture was heated to 40°, held at this temperature until evolution of nitrogen ceased, and then heated on a steam bath for thirty minutes. Enough chloroform was added to dissolve the crystalline mass which had formed. The solution was washed successively with dilute solutions of sodium bisulfate and sodium hydroxide, and was allowed to stand overnight. The iodine compound crystallized. It was filtered and washed with ether. Yield; 70 g. or 100%, mp. 103°.

b) A second method of synthesizing 2-iodo-1,3-dimethoxybenzene(XXXVI) and its coupling to 2,2',6,6' tetramethoxybiphenyl (XXXVII) was also studied

Into a 1 liter, 3 necked flask, equipped with magnetic stirrer, reflux condenser, powder funnel and swept with dry nitrogen, was placed 230 ml. of anhydrous ether. Finely divided lithium metal (7.35 g., 1.05 ml.) was added and the powder funnel was replaced by a dropping funnel. Bromobenzene (52.6 ml., 78.5 g., 0.5 mole) was slowly added to the stirred mixture at such a rate as to maintain the solution under steady reflux. After 2 hours, all of the bromobenzene had been added and almost all the lithium metal had dissolved. The solution was decanted into a one-liter flask and m-dimethoxybenzene (94 g., 0.6 mole) was added. The solution was allowed to stand 60 hours, after which time the lithio-derivative had crystallized from solution in large crystals. Iodine (127 g., 1 mole) was slowly added. An exothermic reaction immediately occurred with the iodine dissolving with decoloration. After 80% of the iodine had been added the reaction abated and was completed by heating under reflux for two hours. Fifty percent of the ether was removed by distillation and chloroform (250 ml.) was added. The solution was washed well with aqueous sodium bisulfite (2 lots of 300 ml. (20%)) and water (500 ml.) The extracts were then dried over calcium chloride and evaporated.

The residual solid was eluted and washed well with petroleum ether (b.p. 40-60°). The 2-iodo-1,3-dimethoxy-benzene (105 g., 80%) melted at 106°C, the melting point being undepressed when the material was mixed with an authentic sample.

A mixture of 3.5 grams of pure powdered 2-iodo-1,3-resorcinol dimethyl ether and 45 grams of very finely divided copper bronze was tightly packed in a large pyrex test tube and covered with a layer of copper bronze. A closely fitting cork stopper was then inserted into the tube directly above the reaction mixture. The tube was heated in an oil bath at a temperature of 170°-200° for three hours and finally at 210° for 15 minutes. After cooling, the reaction mixture was extracted in a Soxhlet apparatus with acetone for 20 hours. The tetramethoxydiphenyl crystallized from acetone on cooling. It was easily purified by recrystallization from acetone containing a little water. Yield, 1.2 grams (68%) mp. 162-165°.

The above synthesis was repeated using an iodo- compound prepared by the reaction of iodine on the corresponding lithium compound. The yields and properties of the products are almost identical in the two cases. The first product is slightly darker than the second.

c) Synthesis of 3,3',4,4'-tetramethoxy-benzophenone

Veratraldehyde. Vanillin (250 g.) was melted on the water bath. Solutions of potassium hydroxide (123 g.) in water (180 ml.) and dimethyl sulfate (180 g.) were added simultaneously with stirring. After thirty minutes the reaction mixture was poured into ice. Water (500 ml.) was added and the solid product collected; mp. 44°.

Veratric Acid. A solution of potassium permanganate (34 g.) in water (1 liter) was added with stirring to a suspension of veratraldehyde (50 g.) in water (300 ml.), the solution temperature being maintained at 60°. The reaction mixture was cooled and filtered. Acidification of the filtrate precipitated the veratric acid as a colorless solid; mp, 179°.

Veratroyl Chloride. To a solution of veratric acid (256 g.) in carbon disulfide (510 g.) was added phosphorous pentachloride (340 g.) and the mixture heated under reflux for one hour. Evaporation of the carbon disulfide and vacuum distillation of the residue yielded veratroyl chloride (mp. 71°) in 90% yield.

3,3'4,4'-tetramethoxy-benzophenone. Veratroyl chloride (113 g.) and veratrole (79 g.) were dissolved in carbon disulfide (400 ml.). Aluminum chloride (141 g.) was added slowly and the mixture was heated under reflux for three hours. After this time, the reaction complex was decomposed by the addition of ice and hydrochloric acid (2N). The precipitated solid was collected and recrystallized several times from methanol. The ketone melted at 144°.

d) Attempted synthesis of 3,3',4,4'-tetrahydroxybenzophenone.

Hydrovanilloin (XXXIX). A solution of 100 grams of vanillin and 100 grams of sodium hydroxide in 1500 ml. of water was heated to 60°C. This solution was placed in an electrolysis apparatus consisting of a 3-liter beaker and a 70x190 mm. porous cup. Forty millimeter and 140 mm. lead cylinders served as electrodes. The porous cup was filled with the alkaline solution and the remainder of the solution was placed in the beaker. A current of 3 amperes was maintained across the cell for 5 hours. The catholyte was filtered and acidified with sulfur dioxide and the crystalline material was filtered and washed with water. The precipitate was dried overnight and recrystallized from glacial acetic acid. Yield 50 grams, (69%), mp. 225-226.

Vanillil (XL). A mixture of 30.6 grams of hydrovanilloin, 39.0 grams of cupric hydroxide and 600 ml. of glacial acetic acid was boiled under reflux for one hour. The blue color of the hot solution turned to green after a few minutes of boiling and a bluish precipitate separated upon cooling. The entire mixture was filtered and washed with a large volume of water. The precipitate was then leached with dilute sodium hydroxide solution and the alkaline solution was acidified. The resulting precipitate was recrystallized from glacial acetic acid to give very light yellow needles of vanillil melting at 233-234°. Yield 12 grams (46%).

Attempted synthesis of 3,3',4,4' Tetrahydroxybenzophenone. A vigorously stirred mixture of 70 grams of sodium hydroxide, 70 grams of potassium hydroxide, 17.5 grams of silver powder and 30 ml. of water at 140°C was treated with 9.8 grams of vanillil. The temperature was raised gradually to 220°, maintained for 15 min. and allowed to drop. When it reached 120°, the solution was diluted with 210 ml. of water. The solution was then acidified with concentrated hydrochloric acid and filtered. White crystals separated upon cooling. The crystalline material was filtered and recrystallized from water and activated carbon. Yield 5 grams, mp. 230-231°C.

Further study and analysis of the product indicated that it was not the desired product, but was 4,4'-dihydroxy-3,3'-dimethoxybenzophenone.

e) Synthesis of 4,4'-dihydroxy-3,3'-dimethoxydiphenyl methane

Freshly prepared silver oxide (4 grams) was covered with 100 ml. of water and treated in succession with 16 grams of sodium hydroxide and 15 grams of vanillin with vigorous stirring. When the reaction mixture began to cool, heat was applied and the mixture was boiled under reflux for one hour. After filtering and washing the precipitate, the filtrate was cooled and saturated

with carbon dioxide. A yellow semi-solid precipitate separated while the solution was still strongly alkaline. The mixture was extracted with ether, and the ether was dried with sodium sulfate. The ether was removed by vacuum distillation to give four grams of 4,4'-dihydroxy-3,3'-dimethoxydiphenyl-methane. After recrystallization from water the mp. was 108-9°.

6. Phthalocyanine Polymers.

a) An improved method of preparing polymeric copper phthalocyanine.

Previous attempts have been made to synthesize phthalocyanine polymers by heating mixtures of pyromellitic dianhydride, urea, anhydrous copper halides and an ancillary reagent. This method included reactions in molten urea as well as refluxing of suspension of the reagents in orthodichlorobenzene (22). Attempts to produce large polymers proved unsuccessful when the above synthesis was tried under various conditions. The following method seems to offer some advantages.

A mixture of 50 grams of powdered urea, 36 grams of pyromellitic dianhydride, 2.25 grams of 300 mesh copper powder, 8.5 grams of zirconium oxychloride and 1.12 grams of powdered ammonium perchlorate was added to 473 grams of trichlorobenzene. This mixture was agitated for one hour at room temperature. The temperature was raised uniformly to 165° and held at 165°-175° for one hour, then at 175°-180° for one hour and a half. The product was filtered while hot and washed with trichlorobenzene and then with isopropanol. The crude filter cake was dried at 110°. This crude product was purified by grinding, adding 250 grams of water and then 44 grams of concentrated sulfuric acid. This mixture was stirred at 60°-70° for one hour and a half. The solution was filtered and the residues washed with dilute sulfuric acid followed by six washings with water. The final product was dried overnight at 110°. This reaction is much more efficient than any previously tried, as yields are ca. 90% of the amount theoretically possible. The polymer which was recovered, however, appeared to be no larger than those prepared by previous methods.

B. Attempts to Form Polymers by Linking Mononuclear Complexes Together.

1. Polymers from β-Hydroxyethylglycine (XLVIII)

a) Preparation of β-hydroxyethylglycine

Formaldehyde (42 ml. of 38% aqueous solution, 0.5 mole) was added to a chilled mixture of ethanolamine (61 g., 1 mole) and hydrogen cyanide (27 g., (40 ml.), 1 mole) at such a rate that the temperature did not rise above 10°. After standing thirty minutes at room temperature, a solution of barium hydroxide (171 g., 1 mole) in water (500 ml.) was added and the mixture

was heated under reflux for 12 hours. After this time ammonia had ceased to be evolved. Carbon dioxide was then passed into the cooled solution until the pH was ca. 8. Sufficient sulphuric acid (ca. 5 ml. of 5%) was added to precipitate any remaining barium ions. The precipitated barium salts were removed by filtration. Water was removed from the filtrates by distillation at reduced pressure and the residual oil was allowed to stand at 0°C for 10 hours. The β-hydroxyethylglycine (40 g., 67%) which crystallized was collected and washed well with alcohol. It could be recrystallized from ethanol/water in colorless hexagonal plates, mp. 181°. Literature (21) gives up 175°. Anal.: Calcd. for $C_4H_9NO_3$: C, 40.3; H, 7.6. Found: C, 39.9; H, 7.7.

b) Bis-(β-hydroxyethylglycine)-copper (II). Basic copper carbonate (5.0 g.) was added to a solution of β-hydroxyethylglycine (5.0 g.) in water (25 ml.) and the mixture was warmed on the steam bath. After 20 minutes the blue solution was filtered. On cooling the filtrate, the blue copper (II) complex (4.0 g.) crystallized from solution. By repeated evaporation and cooling a further 0.4 g. was obtained. The copper (II) complex was recrystallized from water and thus obtained in deep blue prisms which decomposed at 229°. Anal.: Calcd. for $C_8H_{16}N_2O_6Cu$: C, 32.1; H, 5.4; N, 9.3. Found: C, 31.7; H, 5.4; N, 9.0.

c) Bis-(β-hydroxyethylglycine)-nickel (II). Nickel carbonate (2.0 g.) was added to a hot solution of β-hydroxyethylglycine (4.0 g.) in water (20 ml.). The nickel (II) complex formed almost immediately, giving an intense blue color to the solution. On cooling, the nickel (II) complex (3.0 g.) crystallized from solution. A further 0.8 g. was obtained by repeated evaporation and cooling. The bis-(β-hydroxyethylglycine)-nickel (II) was recrystallized from water and thus obtained in pale blue plates which did not melt at 305°. It was found to be insoluble in a wide variety of organic solvents. Anal.: Calcd. for $C_8H_{16}N_2O_6Ni$: C, 32.6; H, 5.4; N, 9.5. Found: C, 33.4; H, 5.5; N, 9.2.

d) O-Benzoylation of bis-(β-hydroxyethylglycine)-nickel (II) This reaction was carried out to give experience in the formation of esters from coordinated donor groups. Solutions of bis-(β-hydroxyethylglycine)-nickel (XLIX) (1.0 g., 0.003 mole) in water (20 ml.) and benzoyl chloride (1.0 g., 0.006 mole) in carbon tetrachloride (50 ml.) were agitated together for 3 hours, pyridine (2 ml.) being added to the solution. After this time the initially blue aqueous layer had become green. Evaporation of the aqueous layer yielded mono-O-benzoyl-bis-(β-hydroxyethylglycine)-nickel (II) as a green hydroscopic solid, mp. 300°. Anal.: Calcd. for $C_{15}H_{22}N_2O_7Ni$: C, 45.1; H, 5.0; N, 7.0. Found: C, 45.0; H, 3.3; N, 7.3.

e) Preparation of phthalyl-bis-(β-hydroxyethylglycine)-nickel (L)

An intimate mixture of bis-(β-hydroxyethylglycine)-nickel (II) [1.18 g., 0.04 mole] and finely powdered phthalic anhydride [0.59 g., 0.04 mole] contained in a vacuum adaptable test tube, was heated at 170° for one hour. The tube was then evacuated (1 mm.) and heated at 180° for a further 3 hours. The residual solid was dissolved in water by boiling, and the solution was filtered and evaporated to dryness on the steam bath. The blue-green solid which remained began to decolorize at 260°, but did not melt below 310°.

Anal.: Calcd. for $C_{16}H_{20}N_2O_8Ni$; C, 43.3; H, 4.5; N, 6.3.
Found: C, 42.9; H, 4.8; N, 6.7.
Equivalent weight Calcd. 443
Found 425

f) Phthalyl-bis-(β-hydroxyethylglycine)-nickel-trimer (LI)

Finely powdered phthalyl-bis-(β-hydroxyethylglycine)-nickel (1.1 g.), contained in a vacuum adaptable test tube, was heated at 180° for four hours, the tube being evacuated to 5 mms. After fifteen minutes the solid had become light green. The residual solid was purified by solution in water and evaporation. The trimer was obtained as a pale green solid which did not melt at 300°. Anal.: Calcd. for monomer; C, 43.4; H, 4.3; N, 6.3. Calcd. for trimer; C, 44.3; H, 4.3; N, 6.5. Found; C, 44.3; H, 4.4; N, 6.5.

Equivalent Weight (titration with N/100 Sodium hydroxide).	Calcd. for trimer,	1329
	Found	1393

g) Attempted condensation of bis-(β-hydroxyethylglycine)-nickel (II) with diethylmalonate

Bis-(β-hydroxyethylglycine)-nickel (II) [2.95 g., 0.01 mole], freshly distilled diethylmalonate (1.76 g., 0.01 mole) and litharge (0.02 g.) were heated at 150° for 5 hours in an atmosphere of nitrogen. After this time the bis-(β-hydroxyethylglycine)-nickel (II) was recovered by solution of the reaction mixture in water and evaporation.

2. Polymers from bis-salicylidene-ethanolamine (LIII)

a) Preparation of salicylidene-ethanolamine

Salicylaldehyde (12.2 g., 1 mole) and ethanolamine (61 g., 1 mole) were mixed and heated on the steam bath for one hour. After cooling, the solution was extracted with ether (600 ml.), dried over sodium sulfate, and evaporated. The residual oil was subjected to vacuum distillation, salicylidene-ethanolamine (130 g., 80%) distilling as a yellow oil, b.p. 138°/0.4 mm. Anal.: Calcd. for $C_9H_{11}NO_2$; C, 65.4; H, 6.7. Found: C, 65.8; H, 6.9.

b) Preparation of bis-(salicylidene-ethanolamine)-copper (LVa)

A solution of copper (II) acetate monohydrate crystals (1.0 g., 0.005 mole) in methanol (25 ml.) was added to a boiling solution of salicylidene-ethanolamine (1.65 g., 0.01 mole) in alcohol (10 ml.) The solution acquired a deep olive brown color. Most of the alcohol was distilled and then ethyl acetate (10 ml.) was added. The copper (II) complex which settled out on cooling was recrystallized from an ethanol-ethyl acetate mixture and obtained in olive needles, mp. 177-8°. Anal.: Calcd. for $C_{18}H_{20}N_2O_4Cu$; C, 55.1; H, 5.1; N, 7.2. Found: C, 55.3; H, 5.2; N, 7.4.

c) Preparation of bis-(salicylidene-ethanolamine)-nickel (LVb)

A solution of nickel (II) acetate tetrahydrate crystals (1.25 g., 0.005 mole) in methanol (20 ml.) was added to a boiling solution of salicylidene-ethanolamine (1.65 g., 0.01 mole) in ethanol (10 ml.). Chloroform (100 ml.) was added and water soluble materials were washed out by several treatments with water. The chloroform extract was then dried over sodium sulfate and the solvent was removed. The residual solid was recrystallized from ethanol, the nickel (II) complex crystallizing in green needles, mp. 237°. Anal.: Calcd. for $C_{18}H_{20}N_2O_4Ni$; C, 55.8; H, 5.2. Found: C, 55.9; H, 5.1.

d) Preparation of bis-(salicylidene-ethanolamine)-zinc (LVc)

To a solution of salicylidene-ethanolamine (1.65 g., 0.01 mole) in ethanol (10 ml.) was added a solution of zinc acetate dihydrate (1.05 g., 0.005 mole) in methanol (100 ml.). The resulting yellow solution was concentrated to small volume (10 ml.), chloroform (20 ml.) was added and water-soluble materials were washed out by several treatments with water. The chloroform extract was dried over sodium sulfate and the solvent was removed. The residual solid was recrystallized from ethanol, the zinc complex crystallizing in yellow needles, mp. 221°. Anal.: Calcd. for $C_{18}H_{20}N_2O_4Zn$; C, 55.0; H, 5.1. Found: C, 54.8; H, 5.1.

e) Polyurethanes and polyesters prepared from bis-(salicylidene-ethanolamine)-copper.

Polyurethane derived from bis-(salicylidene-ethanolamine)-copper (LVII)

2,4-Tolylene-diisocyanate [0.72 ml. (0.87 g.), 0.005 mole] was added to a solution of bis-[salicylidene-ethanolamine]-copper (II) [1.96 g., 0.005 mole] in hot chlorobenzene (100 ml.) and pyridine [0.1 ml]. An exothermic reaction occurred. The solution was heated under reflux for eight hours. The brown solid which settled on cooling was collected and submitted for analysis. The compound sintered at 170° and appeared to decompose at 240°.
Anal.: Calcd. for $C_{27}H_{26}N_4O_4Cu$; C, 60.6; H, 4.9.
Found: C, 58.0; H, 4.6.

Terephthalate polymer of bis-(salicylidene-ethanolamine)-copper (II)

An intimate mixture of bis-(salicylidene-ethanolamine)-copper (II) (3.9g., 0.01 mole), dimethyl terephthalate (1.7 g., 0.01 mole) and sodium methoxide (0.01 g) was heated at 210° for three hours, a stream of nitrogen being continually passed through the mixture. The resulting material could be melt drawn but was brittle in the solid state.

Anal.: Calcd. for $C_{28}H_{26}N_2O_6Cu$; C, 59.8; H, 4.2.
Found: C, 58.1; 4.7.

3. Polymers from Ethylenediamine-N,N'-bis-β-Hydroxyethyl-N,N'-Diacetic Acid (LVIII)

a) Preparation of nickel and copper N,N'-bis-β-hydroxyethyl ethylenediamine-N,N'-diacetate

Nickel complex. To a solution of 118.85 g. of nickel chloride hexahydrate (0.5 mole) in hot water was added 500 cc. (estimated to contain 0.5 mole) of an aqueous solution of disodium-N,N'-diacetate-N,N'-bis-β-hydroxyethyl-ethylenediamine. A blue precipitate formed immediately. After filtering and drying, the precipitate was extracted overnight with boiling ethanol. Evaporation of the extract yielded a precipitate, which upon standing for one day in vacuum became a light blue powder. Its behavior on melting and microscopic examination indicated that the product was impure.

Copper complex. To a solution of 14.5 g. of copper (II) chloride dihydrate (0.085 M) dissolved in 50 cc. of water was added 100 ml. of an aqueous solution of disodium N,N'-diacetate-N,N'-bis-β-hydroxyethyl-ethylenediamine (found by analysis to contain 0.085 mole). A dark blue oil formed immediately. Thus far no way has been found to separate the complex from the sodium chloride which is also formed in the reaction.

Better success in preparing the copper derivative was achieved by the use of cupric acetate.

A solution of 0.0425 moles of versene-diol and 8.5 g. (0.00425 moles) of cupric acetate monohydrate in methanol was refluxed for a few hours on the steam bath. The volume of the solution was reduced to about fifty ml. Upon standing, sodium acetate precipitated from the solution. The sodium acetate was removed by vacuum filtration and the filtrate evaporated to dryness under reduced pressure (ca. 2 mm.). The green powder obtained was mixed with 200 ml. of absolute ethanol and heated on the steam bath with reflux. The ethanol was removed under diminished pressure and the product stored in a dessiccator over phosphorous pentoxide as the product is extremely hygroscopic.

b) Polymerization of copper-versene-diol complex with tolylene diisocyanate

A solution of 1.74 g. (0.001 mole) tolylene diisocyanate and 3.26 g. (0.001 mole) of the copper-versene-diol complex was heated on the steam bath with reflux overnight. To prevent the destruction of the isocyanate by moisture, the reactants were weighed and mixed in a dry box and the condenser was fitted with a drying tube. During the reflux, the solution changed color from green to brown. The identification of the products is not complete.

IV. THE MEASUREMENT OF HEAT STABILITY OF POLYMERS

In reports to W.A.D.C. by Marvel and his associates (23), these workers described the determination of heat stabilities of a series of polymeric metal chelate compounds. The method used involved the prolonged heating of a polymer sample in the air. The loss in weight incurred was then correlated with temperature and duration of heating. More recently, it has been ascertained that this method is inadequate (24), the rate of decomposition or loss in weight being dependent on variables such as sample size. It appeared probable that more accurate and reproducible results could be obtained by prolonged heating in an inert atmosphere (nitrogen) and by the method of differential thermal analysis.

A. Thermal Stability of Polymers in Nitrogen Atmosphere

Weighed samples of the polymers (ca. 0.4 g.), contained in porcelain boats, were heated in a tube furnace, a stream of nitrogen (ca. 4 bubbles/second) being flushed through the apparatus. Generally, each sample was heated at each of $[220 + n \times 40]^{\circ}$ (n = 1,2,3, etc.) for periods of two to three hours. After each period of heating the weight loss and any change in appearance were noted. The results obtained for a series of polymers derived from 4,4'-bis-thiopicolinamindo-diphenyl are listed in Table V. In amplification, the zinc polymer was found to be

Table V

Temperature and time of heating

% wt. loss	6 hrs. at 225°	3 hrs. at 275°	3.5 hrs. at 300°	3.5 hrs. at 340°	2.5 hrs. at 390°	2.5 hrs. at 435°
M = Cu(II)	2%	3%	18%(a)			
= Ni(II)	1%	0.5%	7%	6%	30%(b)	
= Zn(II)	0.3%(c)	0.1%	0.2%	0.4%	3.2%	18%(d)

(a) decomposition to a black powder occurred.
(b) decomposition to a black powder occurred.
(c) color change from yellow to orange.
(d) complete decomposition.

the more heat stable, no loss in weight occurring below 400°. The results obtained for several polymers described in this report are given in Table VI.

Table VI

Temperature and time of heating

% Weight Loss

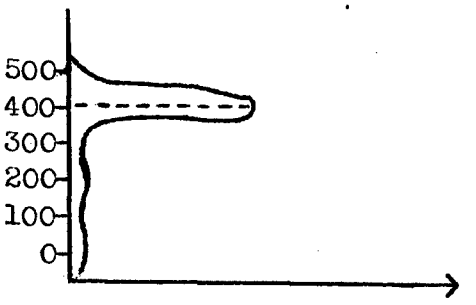
	1 hr. at 200°	2 hrs. at 250°	1.5 hrs. at 300°
Bis-(salicylidene-ethanolamine) copper (II)-2,4-tolylene-di-urethane	5%	12%	25%
Bis-(salicylidene-ethanolamine)-copper (II) -terphthalate polyester	27%		
Bis-(β-hydroxyethylglycine)-nickel (II) -phthalate trimer	1.6%	10%	50%

It can be seen that in the latter series (Table VI) none of the polymers possess any thermal stability above 200°. This lack of thermal stability is to be correlated with the localization of electrons in the organic residues of the polymers. Almost all metal chelate compounds which show pronounced thermal stability possess orbitals into which electrons can be delocalized (e.g., ferrocene, phthalocyanine derivatives, etc.). Also, such delocalization is encountered in the polymers listed in Table II. It appears evident that in the design of polymeric materials, this factor must be considered and incorporated into any new structures.

B. Differential Thermal Analysis of Polymeric Materials

In order to obtain some other measurement of thermal stability and to see if this new value is consistent with those just described, 4,4'-bis-(thiopicolinamido)-diphenyl-zinc (II) polymer was subjected to differential thermal analysis. The apparatus was provided by the Department of Ceramic Engineering of the University of Illinois. The analysis was carried out by measuring the thermal differential in heating samples of the zinc polymer (0.3 g.) and alumina (the reference standard, 0.5 g.) in the presence of air. The differential curve obtained is shown in Graph I. It can be interpreted as indicating decomposition of the polymer at 420°. This is in good agreement with the previously described result.

Graph I



After the run just described had been completed it was found that the chromel/alumel thermocouple had been burnt out. This could be circumvented by using a platinum/platinum, 10% rhodium thermocouple or by using a platinum heating vessel.

Differential thermal analysis appears to be a convenient method for the determination of heat stabilities. Its use would, however, necessitate the construction of a D.T.A. apparatus. The apparatus used had been specially built for use with clay minerals and does not have the required sensitivity. Thus, further research along these lines could not be undertaken.

It is evident that the method of heating in a nitrogen atmosphere provides a reasonable guide toward thermal stability. However, it is somewhat tedious to weigh samples in the cold after having maintained them at raised temperatures. Moreover, it is difficult to prevent the uptake of moisture by the substance between the end of heating and of weighing. Use of a "thermobalance" (for detailed review, see ref. 25) should give good results with ease of operation. These instruments are, of necessity, rather complex in construction.

C. The Design and Construction of A Simple Device for Measuring Thermal Stabilities

A relatively simple thermobalance has been constructed, following the suggestions of Winslow and Matyerik (26), and has been found to be very useful in the evaluation of our polymers. It is built from a semi-micro balance and a heating furnace. One pan of the balance is replaced by a platinum chain, to one end of which is attached a pyrex container. This container is so arranged that it can be heated. The weight loss of a sample in the container can be readily followed, without interrupting the heating. The design is shown in Figure 1.

D. Thermal Stability of **Benzidine** Disulfonato-Copper (II)

The preparation of this complex was described in an earlier report (27). A sample was heated in the thermogravimetric balance in a stream of nitrogen. The sample showed less than 1% weight

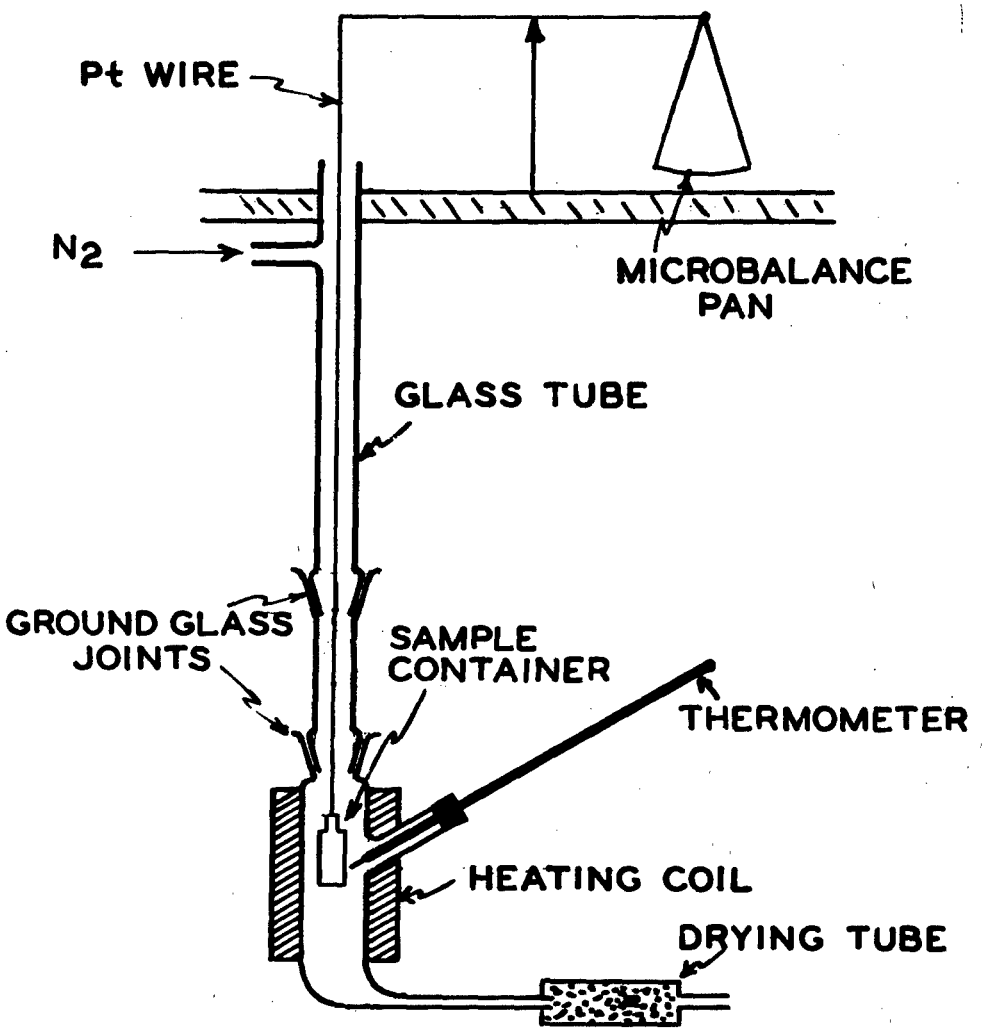


FIGURE 1 - Schematic Diagram of Thermobalance

loss up to 290°C, but at 300°C is slowly decomposed. (See Table VII)

Table VII

Thermal Stability of Benzidine Disulfonato-Copper (II)

Temperature	Period of Heating in hours	% Weight Loss
140	0.33	1%
200	0.7	1%
220	21	1%
250	22	1%
290	65	1%
300	66	4%
300	90	Decomposition

V. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

It is still not possible to report the formation of useful coordination polymers, but a great deal of valuable information has been obtained, and will serve as a guide in future work. In the past, there has been little quantitative work done on the thermal stabilities of coordination compounds, so some of our predictions have not been borne out by experiment. It is now evident that stability toward hydrolysis or other chemical attack in solution cannot be taken as an accurate guide to thermal stability. Copper in the divalent state forms many complexes which are extremely stable toward hydrolysis, but which are not thermally stable because the copper is readily reduced by the coordinating agents. However, it does not follow that all copper (II) complexes are thermally unstable. The relationship between strength of coordinate bond and thermal stability is doubtless a complex one, and is not yet clearly understood.

It has been shown possible to form polymers of low molecular weight by linking coordinating monomers together through condensation reactions. Even though the polymers so obtained are not thermally stable, their study should be continued, as it may lead to a better understanding of the factors which are important in such polymerization.

The metal derivatives of the bis-thiopicolinamides, of benzidene disulfonic acid, and of a polymeric phthalocyanine have been shown to possess good thermal stability, but it has not yet been found possible to get useful polymers from them. Efforts to do so will be continued.

The work on polymers from fluorinated bis-1,3-diketones, from bis-8-hydroxyquinolines and from cyclic siloxanes has not gone far enough to allow us to draw any conclusions as to the ease of their formation or their heat stabilities.

Since almost no work on the formation of coordination polymers has been reported in the literature, that which has been done under this contract has of necessity been highly exploratory. It is believed, however, that a sufficient understanding of the subject has now been gained that a more thorough study is justified. Work undertaken in the next few months will therefore be devoted to a more thorough study of those substances which have shown a good tendency to polymerize, or which have high heat stability. No new substances will be studied at present.

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