

quinone, m.p. 108–110°. *Anal.* Calcd.: C, 81.4; H, 9.6. Found: C, 81.1; H, 9.3.

The reaction of benzoyl peroxide with 2,6-dimethylphenoxide ion was carried out by adding a solution of 0.05 mole of the potassium salt in 200 cc. of methanol to 0.05 mole of benzoyl peroxide suspended in 100 cc. of methanol over an hour. The peroxide dissolved during the addition, and the mixture was refluxed for five hours. Working up the mixture gave 5.5 g. of benzoic acid, 1.4 g. of 2,6-dimethylphenol and 7.9 g. of crude 2,6-dimethylphenyl benzoate. The ester was hydrolyzed to give 3.2 g. of additional phenol and 3.9 g. of acid; total recovery phenol, 75%, benzoic acid, 78%.

**Products from *t*-Butyl Perbenzoate Reactions.**—A chloroform solution, 4 *M* in *p*-methoxyphenol, and *t*-butylperbenzoate was allowed to react for 24 hours at room temperature. Extraction with sodium bicarbonate gave a 93% recovery of benzoic acid, and fractional distillation 81% *t*-butyl alcohol. In a similar experiment in the presence of *m*-cresol the yields were 92 and 84% of acid and alcohol, respectively. In neither experiment could any identifiable product be obtained from the phenol.

**Benzoyl Peroxide and Tri-*t*-butylphenol.**—A solution 2.62 g. of 2,4,6-tri-*t*-butylphenol and 2.42 g. of benzoyl peroxide in 50 cc. benzene was refluxed for 8 hours. The blue

color of the phenoxy radical appeared within 10 minutes, and faded after 5 hours. By working up the reaction mixture, 42.2% benzoic acid and 22% biphenyl were recovered, typical products of the radical decomposition of the peroxide.

**Polymerization Experiments.**—The experiments listed in Table VII were carried out under nitrogen. Peroxide disappearance and CO<sub>2</sub> evolution were determined as described above, and polymer was determined on an aliquot by precipitation with methanol, drying and weighing.

**Experiments in the Presence of I<sub>2</sub>.**—A mixture of 9.5 g. (0.069 mole) of acetyl peroxide (as a 17.6% solution in diethyl phthalate), 20.3 g. of I<sub>2</sub>, 4 cc. of water and 245 cc. of CCl<sub>4</sub> was heated for 48 hours at 80°. The evolved gases were passed through an ascarite tube and collected over water. The reaction mixture was fractionated, and the products identified as CO<sub>2</sub> (0.134 mole), CH<sub>4</sub> (0.05 mole) and CH<sub>3</sub>I (0.046 mole).

The non-involvement of iodine in the reaction of phenols with benzoyl peroxide was shown by refluxing a mixture of 6.1 g. of 2,6-dimethylphenol, 12.1 g. of benzoyl peroxide, 10 g. of iodine and 225 cc. of benzene for 8 hours. The same diphenoquinone was formed as described above and titration of an aliquot of reaction mixture with thiosulfate showed no consumption of iodine.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Polymerization through Coördination. I<sup>1a</sup>

BY KENNETH V. MARTIN<sup>1b</sup>

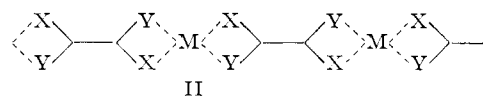
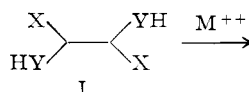
RECEIVED AUGUST 15, 1957

A number of bis- $\alpha$ -thiopicolinamido compounds have been synthesized. These have been successfully polymerized by chelation with suitable metal ions. Investigation of the thermal properties of these polymers has shown a number of them to be stable above 300°. In particular, the 4,4'-bis- $\alpha$ -thiopicolinamido-diphenyl sulfone-zinc (II) polymer can be heated at 360° without appreciable loss in weight or change in infrared spectra.

Recent advances in jet-aircraft manufacture have shown that there is a need for new rubbers, oils and plastics that will not decompose at 400°. Thus, over the last several years a number of people have directed research toward the synthesis of polymers which would be stable at elevated temperatures. It appeared probable that this property might be realized in a polymer containing recurring chelated metal atoms. Many coördination compounds exhibit marked stability. For example, copper(II)-phthalocyanine can be heated at 500° without decomposition.<sup>2</sup>

It is apparent that three approaches are available for the preparation of such "coördination polymers," *viz.* (a) preformed metal complexes may be polymerized through the functional groups which they contain; (b) an organic polymer containing a recurring chelate group can be treated with suitable metal salts to form the metal derivative; (c) a polymer may be formed by the reaction of metal atom-donor atom coördination. In this paper approach (c) has been followed. It should be mentioned, however, that "coördination polymers" have been obtained by methods a<sup>3</sup> and b.<sup>4</sup>

In order to form a linear polymer using method (c) a molecule of molecular structure I is required. X and Y represent suitable donor atoms, two of



these donor atoms being associated with acidic hydrogen atoms. Then, on reaction with a bivalent metal atom of coördination number four (copper(II), nickel(II), etc.) two protons are lost from each molecule of I and a non-charged linear polymer II is formed. It is obvious that many variations of I are possible; however, use of different donor atoms and other metal ions may result in the formation of a charged or a cross-linked polymer. This is not desirable. Several examples of reactions of this type have been described. Wilkins and Wittbecker<sup>5</sup> treated a number of tetraketones with beryllium(II) salts and polymers were obtained having structures similar to II. Also, coördination polymers have been formed from 4-hydroxy-5-formyl-salicylaldehyde,<sup>6</sup> rubeanic acid<sup>7</sup>

(1) (a) This research was supported in whole by the United States Air Force Contract No. AF 33(616)-3209, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. (b) Polychemicals Dept., E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, Delaware.

(2) C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, 1027 (1934).

(3) J. C. Bailar, Jr., and K. V. Martin, unpublished results.

(4) F. Lions and K. V. Martin, *THIS JOURNAL*, **79**, 2733 (1957).

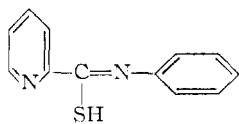
(5) J. P. Wilkins and E. L. Wittbecker, U. S. Patent 2,659,711, Nov. 17, 1953.

(6) R. H. Bailes and M. Calvin, *THIS JOURNAL*, **69**, 1892 (1947).

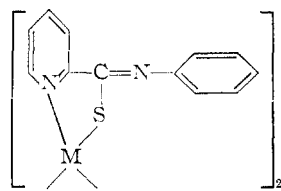
(7) J. C. Bailar, Jr., "Advances in Chelate Chemistry," Polytechnic Institute of Brooklyn, Brooklyn, N. Y., 1955, p. 52.

and certain bis-( $\alpha$ -aminoacids).<sup>8</sup> None of these polymers were reported as being stable at elevated temperatures. This is not unusual as almost all metal-chelate compounds which exhibit pronounced heat-stability possess a set of  $\pi$ -orbitals into which electrons can be delocalized. This factor must be considered when designing a potentially thermally stable polymer.

In 1954, Porter<sup>9</sup> showed that  $\alpha$ -picoline, sulfur and aniline undergo a Willgerodt reaction<sup>10</sup> to form  $\alpha$ -thiopicolinanilide (III) in good yield. A number of  $\alpha$ -thiopicolinamides were prepared later and their reaction with metal ions was studied.<sup>11</sup> The base III was shown to function as a mono-acido-bidentate chelate compound. Chelation occurred with copper(II), nickel(II), zinc(II) and mercury(II) ions to form complexes of structure IV. These did not decompose at their melting

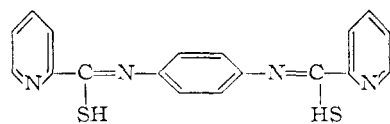


III

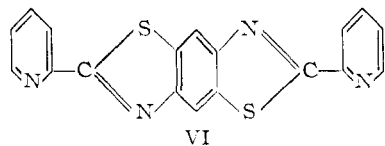


IV

points (ca. 250°). It appeared probable that a bis- $\alpha$ -thiopicolinamide might be formed by the reaction between sulfur,  $\alpha$ -picoline and an aromatic diamine. Use of a suitable diamine, such as *p*-phenylenediamine, was expected to lead to a thioamide V. This base has a molecular structure similar to I and it would be suitable for polymerization by metal atom-donor atom coordination. The reaction between  $\alpha$ -picoline, sulfur and *p*-phenylenediamine has now been shown to give 2,6-di- $\alpha$ -pyridyl-benzo-(1,2,4,5)-bis-thiazole (VI). Apparently the desired bis-thioamide V, which would be formed initially in this reaction, is unstable and undergoes oxidation. A similar reaction has been observed<sup>11</sup> with several substituted  $\alpha$ -thiopicolinanilides. When benzidine



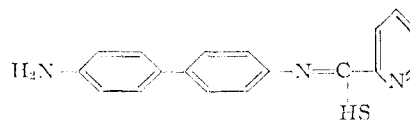
V



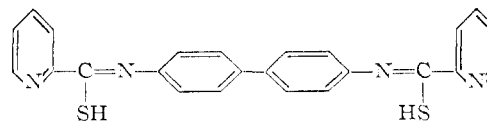
VI

was used instead of *p*-phenylenediamine the mono-substituted compound 4-amino-4'- $\alpha$ -thiopicolin-amido-biphenyl (VII) was obtained. Use of excess  $\alpha$ -picoline and sulfur led to the isolation of 4,4'-bis- $\alpha$ -thiopicolinamido-biphenyl (VIII), a

golden crystalline solid, m.p. 227°. Also, treatment of VII with sulfur and  $\alpha$ -picoline resulted in the formation of VIII.

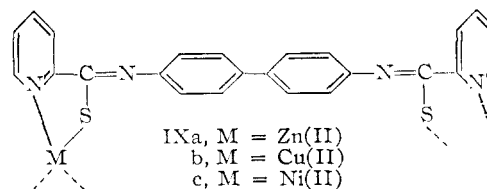


VII



VIII

Polymerizations of VIII were successfully effected by chelation with zinc(II), copper(II) and nickel(II) ions. These reactions were carried out by heating a stoichiometric mixture of the appropriate metal acetylacetonate and VIII *in vacuo*. In each case the theoretical quantity of acetylacetonate was collected in a cooled receiver, the polymeric product remaining in the reaction vessel. Both the copper(II) and nickel(II) polymers were obtained as brown powders, the zinc(II) polymer was yellow. The analyses and the infrared spectra obtained for these compounds are in agreement with their formulation as polymers of structure IX (a,b and c), the chain length being at least 15 units. No end groups could be detected in the infrared spectra and the analyses corresponded with those for theoretical polymers of infinite chain length. The polymers were found to be insoluble in a wide variety of organic solvents. It was impossible, therefore, to determine their molecular weights



IXa, M = Zn(II)  
b, M = Cu(II)  
c, M = Ni(II)

using the viscosity method. Accurate and reproducible determinations of thermal stabilities were made using a thermogravimetric balance. The results obtained are listed in Table I (see Experi-

TABLE I

Thio- amide	Metal	Temperature, °C.								
		220	250	270	290	310	340	370	390	420
		Weight loss, %								
VIII	Cu(II)	2	1	1	d. <sup>a</sup>					
VIII	Ni(II)	0.3	0.1	0	0	0.2	6	d.		
VIII	Zn(II)	0	0	0	0	0	0	0.5	0.2	d.
Xa	Cu(II)	0	0	2	2	3	d.			
Xa	Ni(II)	0	0	0	0	0	0.5	3	d.	
Xa	Zn(II)	0	0	0	0	0	0	0.5	3	d.
Xb	Cu(II)	0	0	0	0	2	d.			
Xb	Ni(II)	0	0	0	0	2	d.			
Xb	Zn(II)	0	0	0	0	0	0	0	4	d.
Xc	Cu(II)	0	0	0	1	3	d.			
Xc	Ni(II)	0	0	0	3	0	d.			
Xc	Zn(II)	0	0	0	0	0	0.2	0.3	0	d.

<sup>a</sup> d. here denotes decomposition.

mental). It can be seen that the zinc(II) polymer is the more heat stable, no decomposition occurring below 380°. In order to obtain some other measurement of thermal stability and to see if this

(8) J. R. Elliot, Thesis, Doctor of Philosophy, University of Illinois, 1943.

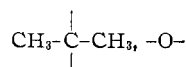
(9) H. D. Porter, THIS JOURNAL, **76**, 127 (1954).

(10) M. Carmack and M. A. Spielman, "Organic Reactions," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 83.

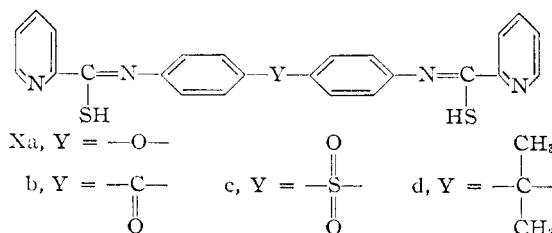
(11) F. Lions and K. V. Martin, in process of preparing manuscript for publication.

other value was consistent with those in Table I, IXa was subjected to differential thermal analysis. The analysis was carried out by measuring the thermal differential in heating samples of the zinc(II) polymer and alumina in the air. Decomposition occurred at 400°.

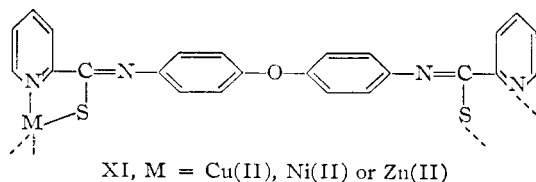
As a result of the preparation methods used, the polymers obtained in this research were all, most probably, of low molecular weight (*ca.* 15,000). The physical properties (plasticity, etc.) of a polymer can be predicted with some precision by an examination of the gross molecular structure. If IXa, IXb and IXc were of high molecular weight they would be expected to be hard, brittle materials. It was thought possible that plasticity might be introduced into polymers of this type by the introduction of a bridging group between the two phenyl rings, *e.g.*



etc. Thus attempts were made to introduce certain of these groups into polymers in order that plastic properties might be found in the high molecular weight species, though probably not to be observed in those of low molecular weight. With this end in view the synthesis of  $\alpha$ -thiopicolinamides of structure X and related metal derivatives was undertaken.



The reaction between 4,4'-diamino-diphenyl ether, sulfur and  $\alpha$ -picoline proceeded smoothly, Xa being isolated as a golden crystalline solid in 85% yield. This compound was readily soluble in dimethylformamide, in which solution polymerization reactions were carried out. Addition of dimethylformamide-methanol solutions of the metal acetates (zinc(II), nickel(II) and copper(II)) to hot dimethylformamide solutions of Xa resulted in almost immediate precipitation of polymeric materials. They were isolated as solid materials which were insoluble in a wide variety of organic solvents and did not melt below 300°. Analytical results and infrared spectra suggest that the structures of these polymers are well represented by XI. The thermal stability data for these compounds are given in Table I.



In a similar manner 4,4'-bis- $\alpha$ -thiopicolinamido-benzophenone (Xb) and 4,4'-bis- $\alpha$ -thiopicolinamidodiphenyl sulfone (Xc) were prepared from

the appropriate diamines. The thermal stabilities of the derived metal chelate polymers are shown in Table I.

It was not found possible to effect a facile synthesis of 2,2-bis-(*p*-aminophenyl)-propane. The reported condensation<sup>12</sup> between acetone and aniline could not be repeated. Also attempts to prepare  $\alpha$ -thiopicolinamides from 1,5-diaminonaphthalene and 4,4'-diamino-diphenylmethane proved abortive.

An examination of the thermal stability data reveals the zinc(II) polymers to be the most promising materials. Marvel and his co-workers<sup>13</sup> prepared a number of metal complexes from a series of salicidimines and also found the zinc(II) complexes to be the more thermally stable. This is to be associated with the electronic structure of the zinc(II) ion. Zinc(II) possesses only one oxidation state. The other transition metals used can be oxidized to higher states and this reaction may catalyze thermal decomposition.

In order to ascertain whether weight loss is a good criterion of the thermal properties of these materials, a sample of the 4,4'-bis- $\alpha$ -thiopicolinamido-diphenyl-sulfone-zinc(II) polymer was heated for six hours at 300°, and at 360° for a further six hours. Examination of the pre- and post-heating infrared spectra of this compound revealed that they are identical. It can therefore be inferred that this polymer is stable to at least 360°, and that the data recorded in Table I are reliable.

The infrared spectra of the thioamides VII, VIII, Xa, Xb, and Xc together with several of the derived polymers were recorded. The principal interest lay in the position of the  $-\text{C}=\text{N}-$  vibration of the pyridine ring and the band caused by the thioureide group ( $-\text{NH}-\text{C}=\text{S}$ ).

These were found in the regions 1575-1600 and 1515-1526  $\text{cm}^{-1}$ , respectively. In the chelated species the bands are displaced to 1560-1570 and 1470-1480  $\text{cm}^{-1}$ , respectively.

#### Experimental<sup>14</sup>

**2,6-Di- $\alpha$ -pyridyl-benzo-(1,2,4,5)-bis-thiazole.**—A mixture of *p*-phenylenediamine (10.8 g., 0.1 mole), sulfur (19.2 g., 0.6 mole) and  $\alpha$ -picoline (18.6 g., 0.2 mole) was heated at 140° for ten hours. After this time hydrogen sulfide had ceased to be evolved. The resulting solid was recrystallized several times from pyridine and thus obtained in pale yellow needles, m.p. 260°.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{10}\text{N}_4\text{S}_2$ : N, 16.1. Found: N, 15.8.

**4-Amino-4'- $\alpha$ -thiopicolinamido-diphenyl.**—4,4'-Diaminodiphenyl (18.4 g., 0.1 mole), sulfur (19.2 g., 0.6 mole), and  $\alpha$ -picoline (18.6 g., 0.2 mole) were mixed and heated at 140° for six hours. After cooling, the solid residue was collected and recrystallized several times from an ethanol-dimethylformamide mixture. The amide crystallized in orange prisms, m.p. 175°.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{S}$ : C, 70.7; H, 4.9. Found: C, 70.2; H, 4.8.

**4,4'-Bis-( $\alpha$ -thiopicolinamido)-biphenyl.**—(a) An intimate mixture of 4-amino-4'- $\alpha$ -thiopicolinamido-biphenyl (3.05 g., 0.01 mole), sulfur (0.96 g., 0.03 mole) and  $\alpha$ -picoline (1.39 g., 0.01 mole) was heated at 160° for six hours. After this

(12) B. Homolka, German Patent, 399,149; *Frdl.*, Vol. XIV, p. 721 (1924).

(13) C. S. Marvel, S. A. Asprey and E. A. Dudley, *THIS JOURNAL*, **78**, 4905 (1956).

(14) The melting points are uncorrected.

time hydrogen sulfide had ceased to be evolved. The residual solid was washed with carbon disulfide and then recrystallized several times from pyridine. The bis-thioamide crystallized in orange needles (70%), m.p. 237°.

(b) Sulfur (72.8 g., 2.2 moles),  $\alpha$ -picoline (75.0 g., 0.8 mole) and 4,4'-diaminobiphenyl (36.8 g., 0.2 mole) were mixed intimately and heated under reflux for 15 hours. Excess  $\alpha$ -picoline was removed by distillation *in vacuo*. The solid residue was recrystallized several times from pyridine after washing with carbon disulfide. The base crystallized in orange needles, m.p. 237°; melting point undepressed on mixture with a sample prepared by method a.

*Anal.* Calcd. for  $C_{24}H_{18}N_4S$ : C, 67.6; H, 4.2; N, 13.1. Found: C, 67.8; H, 4.1; N, 13.0.

**Polymers Derived from 4,4'-Bis-( $\alpha$ -thiopicolinamido)-biphenyl.**—The zinc(II), nickel(II) and copper(II) chelate polymers were prepared by heating mixtures of the metal acetylacetonate (1 mol) and VIII (1 mol) *in vacuo* at 250°. In each case the calculated quantity of acetylacetone was displaced and collected in a cooled receiver. The polymers which remained in the reaction vessel (yld. 100%) were found to be insoluble in a wide variety of organic solvents.

**Elementary Analyses of Polymers.**—Calculated values are based on those for a theoretical polymer of infinite chain length,  $C_{24}H_{18}N_4S_2M$  ( $M = Cu, Zn$  or  $Ni$ ).

Metal	Color of polymer	Carbon, %		Hydrogen, %		Nitrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Cu(II)	Brown	59.0	59.4	3.2	3.5	11.3	11.1
Ni(II)	Red-br.	59.6	59.7	3.3	3.5	11.6	11.4
Zn(II)	Yell.	58.9	58.6	3.3	3.3	11.5	11.3

**4,4'-Bis-( $\alpha$ -thiopicolinamido)-benzophenone** was prepared using the chromic oxide-acetic acid oxidation of 4,4'-diamino-diphenylmethane.<sup>15</sup>

**4,4'-Bis-( $\alpha$ -thiopicolinamido)-benzophenone.**—An intimate mixture of  $\alpha$ -picoline (19 g., 0.2 mole), sulfur (17.5 g., 0.55 mole) and 4,4'-diamino-benzophenone (10.6 g., 0.05 mole) was heated under reflux for 15 hours. Hydrogen sulfide was evolved. The excess  $\alpha$ -picoline was removed by vacuum distillation and the residue dissolved in pyridine (150 ml.) by heating. On cooling sulfur (10 g.) crystallized. This was removed by filtration and the filtrate evaporated under reduced pressure. The residual orange solid was recrystallized many times from a dimethylformamide-ethanol mixture and eventually obtained in golden plates (7 g., 25%), m.p. 181°.

*Anal.* Calcd. for  $C_{28}H_{18}N_4S_2O$ : C, 66.1; H, 4.0; N, 12.3. Found: C, 66.2; H, 3.9; N, 11.8.

**Polymers Derived from 4,4'-Bis-( $\alpha$ -thiopicolinamido)-benzophenone.**—These polymers were prepared by addition of a solution of the appropriate metal acetate (1 mol) in dimethylformamide-methanol to a solution of the thioamide (1 mol) in dimethylformamide. In each case the polymeric material precipitated immediately from solution. The mixture was heated under reflux one-half hour to ensure complete reaction. The yields in each case were quantitative.

**Elementary Analyses of Polymers.**—Calculated values are based on those for a theoretical polymer of infinite chain length,  $C_{28}H_{18}N_4S_2OM$  ( $M = Cu, Zn$  or  $Ni$ ).

Metal	Color of polymer	Carbon, %		Hydrogen, %		Nitrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Cu(II)	Red-br.	58.2	57.1	3.1	3.1	10.9	10.4
Ni(II)	Brown	58.7	58.4	3.1	3.4	11.0	11.4
Zn(II)	Yell.	58.0	57.0	3.1	3.1	10.9	10.4

(15) H. Rivier and A. Farine, *Helv. Chim. Acta*, **12**, 865 (1929).

**4,4'-Bis-( $\alpha$ -thiopicolinamido)-diphenyl Sulfone.**—Sulfur (38.4 g., 1.2 moles), 4,4'-diamino-diphenyl sulfone (24.8 g., 0.1 mole) and  $\alpha$ -picoline (100 g.) were heated under reflux for 12 hours, hydrogen sulfide being evolved. The excess  $\alpha$ -picoline was removed by distillation *in vacuo* and the residue recrystallized from pyridine. The solid which settled out on cooling was washed with carbon disulfide and then recrystallized several times from dimethylformamide. The thioamide crystallized in orange micro-crystals (15 g., 30%), m.p. 265–266°.

*Anal.* Calcd. for  $C_{24}H_{18}N_4S_2O_2$ : C, 58.8; H, 3.7. Found: C, 58.9; H, 3.6.

**Polymers Derived from 4,4'-Bis-( $\alpha$ -thiopicolinamido)-diphenyl Sulfone.**—These were prepared in a similar manner to that described for the benzophenone derivative.

#### ELEMENTARY ANALYSES OF POLYMERS

Metal	Color of polymer	Carbon, %		Hydrogen, %		Nitrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Cu(II)	Brown	52.0	51.9	3.3	3.5	10.1	10.1
Ni(II)	Brown	52.6	52.9	3.3	3.5	10.2	10.3
Zn(II)	Yell.	51.9	51.5	3.2	3.0	10.1	10.4

**4,4'-Diamino-diphenyl ether** was synthesized by reduction ( $PtO_2$ , 1000 lb.) of the commercially available 4,4'-dinitro-diphenyl ether (yld. 90%). It crystallized from ethanol in colorless needles, m.p. 187°.

**4,4'-Bis-( $\alpha$ -thiopicolinamido)-diphenyl Ether.**—An intimate mixture of 4,4'-diamino-diphenyl ether (10.0 g., 0.046 mole), sulfur (24 g., 0.75 mole) and  $\alpha$ -picoline (25 g., 0.27 mole) was heated under reflux for 15 hours. The excess  $\alpha$ -picoline was removed by vacuum distillation and the residue dissolved in pyridine by warming. The sulfur (9 g.) which crystallized was collected and the pyridine solution evaporated. The solid residue was recrystallized several times from a dimethylformamide-ethanol mixture and obtained in golden prisms (14 g., 60%), m.p. 143°.

*Anal.* Calcd. for  $C_{24}H_{18}N_4S_2O$ : C, 65.2; H, 4.1. Found: C, 65.4; H, 4.1.

**Polymers Derived from 4,4'-Bis-( $\alpha$ -thiopicolinamido)-diphenyl Ether.**—These were prepared in a similar manner to the polymers derived from 4,4'-bis-( $\alpha$ -thiopicolinamido)-benzophenone.

Calculated values are based on theoretical polymer of infinite chain length,  $C_{24}H_{18}N_4S_2OM$  ( $M = Cu, Zn$  or  $Ni$ ).

Metal	Color of polymer	Carbon, %		Hydrogen, %		Nitrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Cu(II)	Dark br.	57.2	57.4	3.2	3.6	11.1	10.7
Ni(II)	Brown	57.8	57.9	3.2	3.2	11.2	11.1
Zn(II)	Yellow	57.0	56.6	3.2	3.3	11.1	11.0

**Thermal stability data** were obtained using a simple thermobalance, similar in design to that described by Winslow and Matreyek.<sup>16</sup> In each case the samples were heated at each of a series of temperatures for one hour or until any loss in weight was complete (nitrogen atmosphere).

**Acknowledgment.**—The author gratefully acknowledges his indebtedness to Dr. J. C. Bailar, Jr., for helpful discussion, to Mr. J. Nemeth for all the C, H and N micro-analyses recorded in this paper and to Mr. J. Brader for the infrared spectra.

URBANA, ILLINOIS

(16) F. H. Winslow and W. Matreyek, *J. Polymer Sci.*, **22**, 315 (1956).