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# Thermogravimetric Study of Some New Transition Metal–Schiff Base Coordination Polymers

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## Synopsis

A condensation reaction between 5-amino-8-hydroxyquinoline and terephthalaldehyde yielded a bis-bifunctional Schiff base ligand, 5,5′-[*p*-phenylene-bis(methylidynenitrilo)] di-8-quinolinol, which was used to produce coordination polymers containing Mn(II), Co(II), Ni(II), Cu(II), or Zn(II) in the form of insoluble powders. The thermal stabilities of these polymers were evaluated in vacuum over the temperature range of 25–700°C. by using a newly constructed thermobalance having improved sensitivity. The results relate the decomposition of the polymers to the metal in the backbone as well as to the organic ligand to which the metal is coordinated. Some discussion is devoted to the possible modes of decomposition of these polymers.

## INTRODUCTION

Recent work[1,2] dealing with the coordination polymers of bis-8-hydroxyquinoline derivatives has shown their thermal stabilities to be related to the metal incorporated in the backbone of the polymer as well as to the organic ligand to which the metal is chelated. Initially, the ligand bis(8-hydroxy-5-quinolyl)methane, in which two 8-hydroxyquinoline molecules were linked together in the 5 5′-position through a —$CH_2$— group, was prepared. It was then demonstrated that the decomposition temperatures of the coordination polymers formed by reacting this ligand with some first-row transition metals increased linearly from Cu(II) to Mn(II) when the temperature at the start of the accelerated weight loss was plotted as a function of the atomic number of the metal. The decomposition temperature of the Zn(II) polymer deviated from linearity in a manner that could be explained on the basis of some of the periodic properties of zinc such as ionic radius and electronegativity. Subsequently, the dependence of the decomposition temperature on the nature of the ligand was assessed by evaluating the thermal stabilities of a different group of coordination polymers. These polymers contained the ligand 5,5′[methylenebis(*p*-phenylenenitrilomethylidyne)] di-8-quinolinol in which a —CH=N—$C_6H_4$—$CH_2$—$C_6H$ —N=CH— bridging group was substituted in the 5,5′-position in place of —$CH_2$—. Attempts were made to prepare bis-bifunctional derivatives of 8-hydroxyquinoline that contained 2, 3, or more —$CH_2$— groups in the bridge to help evaluate the relationship between thermal stabilities of the polymers and small consistent changes in the structure of the organic ligand. To date these have been unsuccessful.

This paper reports the synthesis of a new Schiff base ligand, 5,5′-[*p*-phenylenebis(methylidynenitrilo)] di-8-quinolinol, and a group of first-row transition metal coordination polymers derived from this compound. It also describes a recently constructed, sensitive, automatic recording thermobalance that was used to examine the thermal stabilities of the polymers. In addition, on the basis of the thermograms it discusses the thermal stabilities of the polymers and extends our understanding of the properties of these polymeric systems.

## EXPERIMENTAL

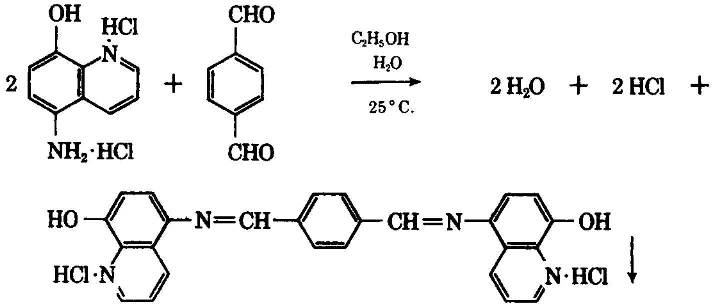
### Synthesis of 5,5′-[*p*-Phenylenebis(methylidynenitrilo)] Di-8-quinolinol

At first 5-amino-8-hydroxyquinoline dihydrochloride was synthesized by the method employed by Frühof.[3] The compound was purified and stored as the dihydrochloride because the free amine has been found to be unstable in air and in solution.[3,4]

ANAL. Calc. for $C_9H_8ON_2 \cdot 2HCl$: C, 46.6%; H, 4.39%; N, 12.1%. Found: C, 46.7%; H, 4.25%; N, 11.4%.

In subsequent condensations to form the Schiff's base the reaction with the dihydrochloride proceeded smoothly and decomposition of the 5-amino oxine compound was not a problem.

Thus, when terephthalaldehyde (0.3353 g./25 ml. $C_2H_5OH$) was added dropwise to 5-amino-8-hydroxyquinoline dihydrochloride (1.1654 g./10 ml. $H_2O$) at room temperature, small platelets formed on the surface of the solution almost immediately, and a yellow solid precipitated, in accordance with the reaction shown in eq. (1). At the end of the reaction



(1)

the product was collected and was found to be insoluble in methanol, chloroform, and ethanol, but it was soluble in boiling dimethylformamide

(DMF).* The product, in the form of the dihydrochloride, was washed with ethanol and dried in vacuum.

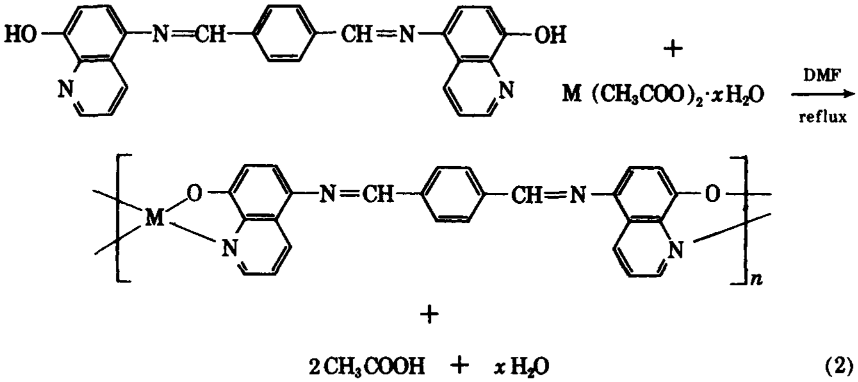
ANAL. Calc. for $C_{26}H_{18}O_2N_4{\cdot}2HCl$: C, 63.6%; H, 4.09%; N, 11.4%. Found: C, 63.8%; H, 4.31%; N, 11.1%.

The product was then recrystallized from DMF, during which the hydrochloric acid was essentially stripped from the molecule, giving a ligand in sufficient purity to be used directly in coordination polymerization reactions with metal ions.

ANAL. Calc. for $C_{26}H_{18}O_2N_4$: C, 74.7%; H, 4.34%; N, 13.4%. Found: C, 73.1%; H, 4.82%; N, 12.7%.

## Synthesis of Schiff Base Coordination Polymers

The coordination polymers were prepared, as shown in eq. (2), by dissolving the ligand in boiling DMF and adding an equimolar amount of the metal acetate in DMF solution under reflux conditions.



(2)

The addition of the cation to the solution was accompanied by a change in color and the precipitation of the polymer. The polymers, in the form of colored powders, were found to be insoluble in a wide variety of solvents and could therefore not be purified by recrystallization. Each polymer was collected, wrapped in filter paper prior to insertion in a paper thimble, and extracted with DMF for 16 hr. in a Soxhlet apparatus. This was done to purify the polymer by extracting unreacted starting materials and soluble nonpolymeric substances. After 16 hr. the solutions in the extraction flask were highly colored and sometimes contained solid materials, while the solvent in contact with the polymer in the extractor was colorless. The polymers were then extracted with absolute alcohol to remove the DMF and any alcohol-soluble constituents. The products were normally dried

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* The DMF was first treated with KOH pellets and then distilled at atmospheric pressure in the presence of CaO. The fraction that distilled at 152–154°C. was collected and used in subsequent work.

TABLE I
Comparison of Elemental Analysis Results for the Coordination Polymers with the Calculated Values

| | Calculated | | | | Found | | | |
|---|---|---|---|---|---|---|---|---|
| Polymer[a] | C, % | H, % | N, % | M, % | C,% | H, % | N, % | M, % |
| $[MnL]_n$ | 66.3 | 3.42 | 11.9 | 11.6 | 65.4 | 4.57 | 9.9 | 8.4 |
| $[MnL\cdot H_2O]_n$ | 63.8 | 3.71 | 11.4 | 11.2 | | | | |
| $[CoL]_n$ | 65.7 | 3.39 | 11.8 | 12.4 | 64.2 | 4.12 | 10.4 | 9.7 |
| $[CoL\cdot H_2O]_n$ | 63.3 | 3.68 | 11.4 | 11.9 | | | | |
| $[NiL]_n$ | 65.8 | 3.39 | 11.8 | 12.3 | 63.7 | 3.75 | 11.1 | 11.3 |
| $[NiL\cdot H_2O]_n$ | 63.5 | 3.69 | 11.4 | 11.9 | | | | |
| $[CuL]_n$ | 65.1 | 3.36 | 11.7 | 13.2 | 65.8 | 3.80 | 10.8 | 11.2 |
| $[CuL\cdot H_2O]_n$ | 62.7 | 3.64 | 11.3 | 12.8 | | | | |
| $[ZnL]_n$ | 64.8 | 3.35 | 11.6 | 13.6 | 59.9 | 3.80 | 11.1 | 12.2 |
| $[ZnL\cdot H_2O]_n$ | 62.5 | 3.64 | 11.2 | 13.1 | | | | |

[a] L = $C_{26}H_{16}O_2N_4$.

over $P_2O_5$ in vacuum at 140°C. for about 24 hr. The results of the elemental analyses are given in Table I.

## Apparatus

The thermobalance, shown in the photograph in Figure 1, was constructed with the use of the Cahn RG electrobalance as the basic unit. The balance assembly, furnace, thermocouples, diffusion pump, and cold trap were mounted on a metal frame isolated from building vibrations by butyl rubber pads. The balance controls, two-pen recorder, furnace-temperature controller, and programer, and accessory switches were located on an adjacent supporting frame mounted on casters so that the control console was mobile.

A schematic diagram of the vacuum thermobalance is given in Figure 2. A glass vacuum vessel, V, for the balance assembly, W, was supplied by the balance manufacturer complete with standard taper O-ring 40/35 male joints. The counter balance tube, A, was made by closing the tubing end of a female 40/35 O-ring joint. The vacuum line was so designed that it could be readily attached to the vacuum vessel at either the high or low sensitivity positions of the balance. Such an arrangement allowed the use of sample sizes from a few tenths of a milligram up to several hundred milligrams in weight without a major revision in the vacuum line. The sample tube, B, was constructed with a narrow-diameter section made by joining the Vycor ends of two 1.3-cm. diameter Vycor-to-Pyrex graded seals to give a 19-cm. length of Vycor tubing in the heated region. The narrow tube was terminated in a number 7 O-ring glass joint so that a Chromel–Alumel thermocouple, D, could be introduced into the heated region by means of a glass feed-through in a mating number 7 ball-O-ring joint. This arrangement permitted easy replacement and adjustment of thermocouples in the sample area. The tungsten hangdown wire, C, was adjusted in length to position the quartz crucible containing the sample in the center of the Vycor region of the sample tube. The thermocouple could be positioned to within less than 1 mm. of the bottom of the crucible. The electro-nulling principle of the balance allowed only a negligible movement of the sample during the experiment so that the relationship between the sample and the thermocouple could be maintained throughout the experiment. Temperature measurements made with a differential thermocouple showed no difference in temperature between the interior of the sample crucible and the space immediately below the crucible for a distance of several millimeters.

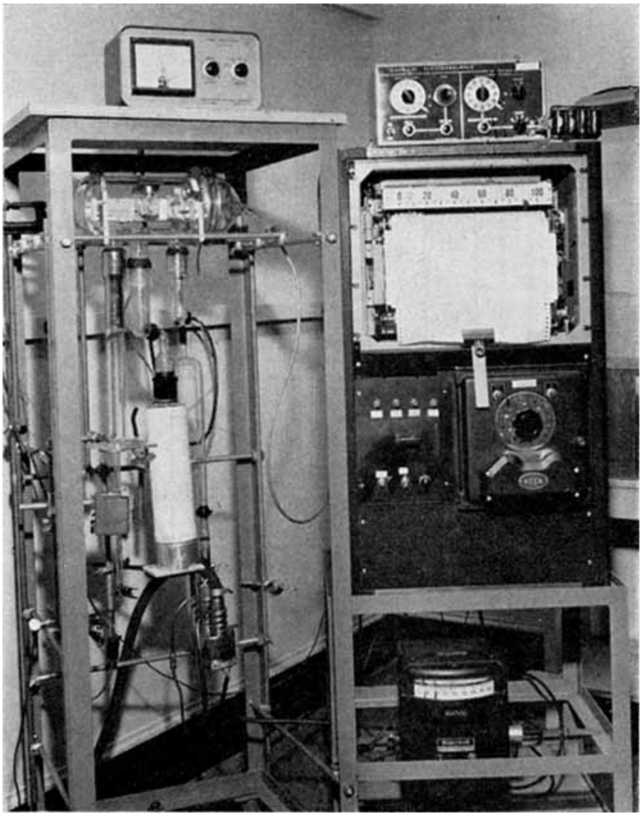


Fig. 1. General view of thermobalance, recorder, and control console.

The system was evacuated with an oil diffusion pump backed up with a mechanical oil pump. The decomposition products evolved during the pyrolysis were collected in the glass trap, E, which was cooled with liquid nitrogen. A Pirani gage, P, was used to monitor the mechanical pump prior to starting the diffusion pump. The pressure usually obtained in this system with both pumps operating was of the order of $10^{-5}$ torr as measured with an ionization gage.

The furnace, F, was a Sargent, Model 5679-M5, with a side opening and modified with a rod support so that it could be easily brought up to or removed from the sample tube without disturbing the vacuum.

A Minneapolis-Honeywell Pyrovane temperature controller and a Beck programer were adapted as shown in the circuit in Figure 3. A Wheatstone bridge arrangement was used to generate a voltage difference between the temperature indicated by the recorder–thermocouple combination and that called for by the Beck programer. One pair of bridge arms was composed of a second independent (retransmitting) slidewire in the temperature recorder, and the other two arms were the programed rheostat in the Beck programer. The Minneapolis-Honeywell Pvrovane controller was used for the error sensor.

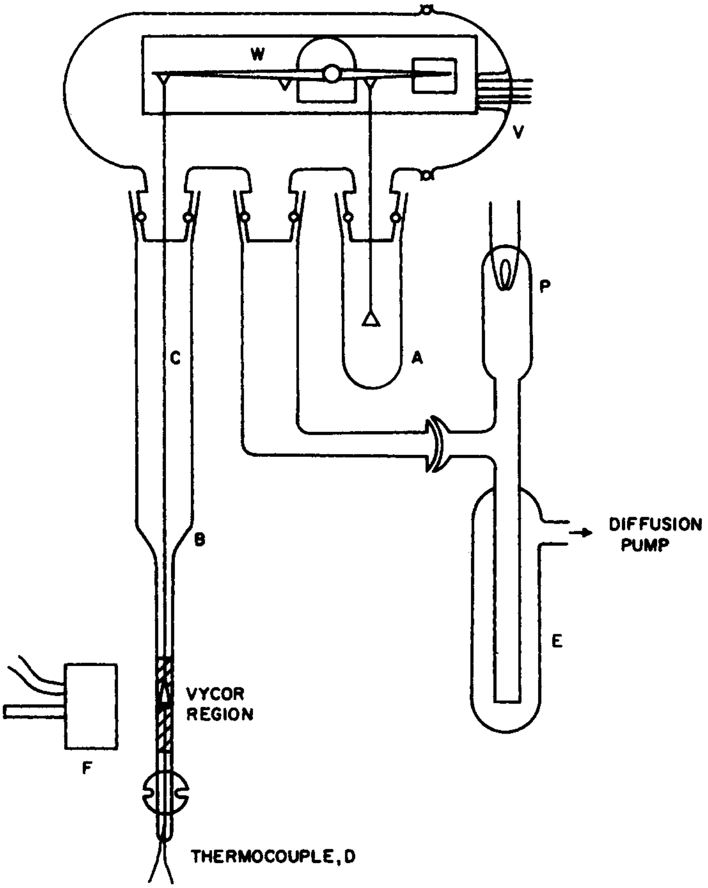


Fig. 2. Schematic of vacuum thermobalance: (W) Cahn balance mechanism; (V) vacuum bottle with O-ring seals and electric wire feed-through; (A) counter-balance tube; (B) sample tube; (C) tungsten hand-down wire; (D) thermocouple sealed in O-ring joint; (E) trap; (F) furnace.

In practice, the Beck programer was dialed to the desired starting temperature. The thermocouple in the vacuum chamber was at ambient temperature, and the temperature recorder was at the low end of the scale, which also set the retransmitting slidewire at the low end. Thus an imbalance resulted between the arms of the bridge, composed of the Beck rheostat and the recorder retransmitting slidewire. This imbalance generated a voltage to actuate the Pyrovane controller. (The Pyrovane scale is arbitrary in this application, and its control point can be set anywhere that is convenient.) The set point rheostat was adjusted to cancel out the error signal, i.e., the voltage difference mentioned above, at the Pyrovane when the furnace temperature came to the temperature set on the Beck programer. This calibrated the Beck slidewire with the temperature-indicating slidewire in the recorder. The Beck programer motor was then started, and as it called for increased temperature the resulting bridge imbalance imposed a voltage on the Pyrovane controller, which caused the controller to turn on the furnace. The furnace raised the temperature of the sample and the thermocouple, which caused the recorder pen to indicate a higher temperature. The movement of the recorder pen shifted the position of the pickoff of the retransmitting slidewire, which brought the bridge back to balance and once again turned off the furnace through the Pyrovane controller. The sensitivity of this temperature-control circuit was very high, since less than a millivolt was necessary to actuate the Pyrovane controller, and the use of a 1.5-v. potential on the bridge slidewires meant that very little motion of either slidewire was needed to supply the necessary error voltage.

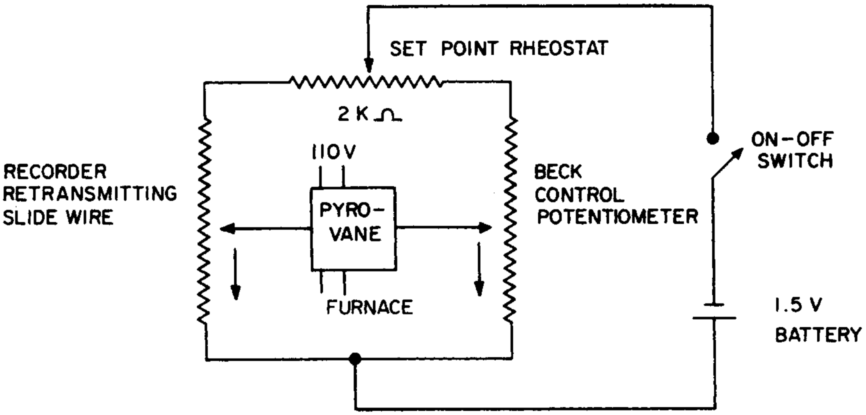


Fig. 3. Schematic of furnace temperature controller-programer circuit.

The heating scheme used here produced a nearly linear heating rate from 0.25°C./min. to 10°C./min. from room temperature to approximately 700°C. The same system can also be used for isothermal work in this temperature range by setting the temperature on the Beck programer manually. In this mode the temperature of the crucible can be held to within ±0.5°C. of the control temperature.

In operation, the crucible and hangdown wire were counterbalanced by placing weights on the pan on the right side of the balance. A 1–3-mg. sample of finely powdered polymer was placed in the micro quartz crucible and the system was evacuated until constant weight readings were obtained on the 0.1-mg. range of the balance, as indicated on the 1-mv. range of the recorder. The sensitivity of the weighing system in this mode was of the order of $\pm 0.1$ $\mu$g. The range of the balance was then set at 1 mg., and the Cahn recorder controls were adjusted to place the weight pen of the two-pen recorder at the upper weight limit on the chart. The furnace was brought into position, and the temperature programer and the recorder were actuated to start the run. During the entire run the temperature and the weight of the sample were continuously recorded on calibrated chart paper. Two separate thermogravimetric analyses were made for each of the polymers studied.

## RESULTS AND DISCUSSION

Table II lists the percentage weight loss of the 5,5′-[*p*-phenylenebis(methylidynenitrilo)] di-8-quinolinol Schiff base coordination polymers when heated in vacuum in the range of 25–700°C. at a heating rate of 3°C./min. The results obtained in duplicate analyses for a given polymer were in good agreement, and only the average values of both runs are reported. Under the conditions employed in these analyses, the polymers lost weight gradually during the early phase of the experiment. Then the samples underwent an accelerated weight loss, and finally in the temperature range of about 500–700°C. the loss of weight became much more moderate. Over the temperature range of 25–700°C. the polymers lost between 34 and 46% of their weight. This means, considering the metal content of the polymers, that 40–50% by weight of the organic portion of the polymers was not volatilized. In work already cited[2] on a group of coordination polymers derived from another Schiff base ligand, it was shown that about 39–54% of the polymers volatilized by the time the temperature reached 700°C. These results do not differ appreciably from those obtained in the current study, even though the experimental conditions were not the same in both sets of experiments.

The results in Table II have been plotted in Figure 4 and more clearly depict the relationship between the temperature and the weight loss of the polymers. The decomposition temperature, defined as the temperature at which the accelerated weight loss of the polymer began and determined as previously described,[1] was used as a measure of thermal stability. Thus, when the decomposition temperatures of the polymers were plotted as a function of the atomic numbers of the coordinated metals, curve *A* shown in Figure 5 was obtained. This figure also gives similar plots for coordination polymers made in this laboratory which contain different bridging groups in the 5,5′-position of the organic ligand. First, with respect to

TABLE II
Percentage Weight Loss of Coordination Polymers (25–700°C., Heating Rate in Vacuum: 3°C./Min).

| | Weight loss of polymer, %[a] | | | | |
|---|---|---|---|---|---|
| Temp., °C | Mn | Co | Ni | Cu | Zn |
| 25 | 0 | 0 | 0 | 0 | 0 |
| 50 | 0.5 | 0.4 | 0 | 0 | 0 |
| 75 | 1.4 | 0.8 | 0.5 | 0 | 0.3 |
| 100 | 1.8 | 1.3 | 0.8 | 0 | 0.7 |
| 125 | 2.4 | 1.8 | 1.0 | 0 | 1.0 |
| 150 | 2.9 | 2.0 | 1.1 | 0.1 | 1.4 |
| 175 | 3.7 | 2.2 | 1.4 | 0.1 | 1.8 |
| 200 | 4.3 | 2.5 | 1.6 | 0.3 | 2.3 |
| 225 | 4.7 | 2.9 | 1.9 | 0.5 | 3.0 |
| 250 | 5.3 | 3.4 | 2.4 | 1.2 | 3.7 |
| 275 | 5.8 | 4.1 | 2.8 | 2.2 | 4.7 |
| 300 | 6.5 | 5.3 | 3.3 | 3.7 | 5.7 |
| 325 | 7.3 | 6.5 | 3.9 | 5.5 | 6.9 |
| 350 | 8.4 | 7.8 | 4.8 | 7.6 | 8.1 |
| 375 | 9.4 | 9.1 | 5.8 | 10.3 | 9.0 |
| 400 | 10.4 | 10.2 | 7.1 | 13.1 | 10.4 |
| 425 | 11.6 | 12.0 | 9.3 | 16.8 | 12.3 |
| 450 | 13.5 | 15.5 | 12.0 | 22.4 | 16.1 |
| 475 | 17.6 | 20.3 | 16.7 | 29.3 | 21.8 |
| 500 | 22.2 | 23.4 | 23.3 | 33.4 | 26.9 |
| 525 | 24.6 | 25.1 | 30.6 | 34.4 | 30.0 |
| 550 | 25.8 | 26.4 | 32.8 | 35.2 | 32.6 |
| 575 | 26.9 | 27.9 | 34.2 | 36.2 | 35.0 |
| 600 | 28.0 | 29.8 | 35.9 | 37.2 | 37.2 |
| 625 | 29.3 | 31.9 | 37.7 | 38.4 | 39.9 |
| 650 | 30.9 | 33.9 | 39.4 | 39.1 | 42.0 |
| 675 | 32.6 | 35.2 | 40.9 | 40.2 | 44.2 |
| 700 | 34.4 | 38.0 | 42.2 | 41.0 | 46.1 |

[a] Average of two analyses.

curve *A*, representing the polymers containing 5,5′-[*p*-phenylenebis(methylidynenitrilo)] di-8-quinolinol, the trend in thermal stability is of the order Mn > Co > Ni > Cu < Zn. It should be stated that some of the decomposition temperatures could not be located with great accuracy because there were no sharp breaks in the thermograms near the temperature at which the weight loss became more rapid. Nevertheless, the trend in thermal stability for the Ni > Cu < Zn polymers is unmistakable and in excellent agreement with data for the other bis-8-hydroxyquinoline coordination polymers containing these metals, which are also shown in Figure 5, curves *B* and *C*. While there is evidence that the decomposition temperatures of the Mn, Co, and Ni 5,5′-[*p*-phenylenebis(methylidynenitrilo)] di-8-quinolinol coordination polymers decrease in the sequence given, the trend is not as pronounced as it is in curves *B* and *C*, nor is it as clear-cut as in the case of the nonpolymeric metal chelates of 8-hydroxyquinoline. The absence

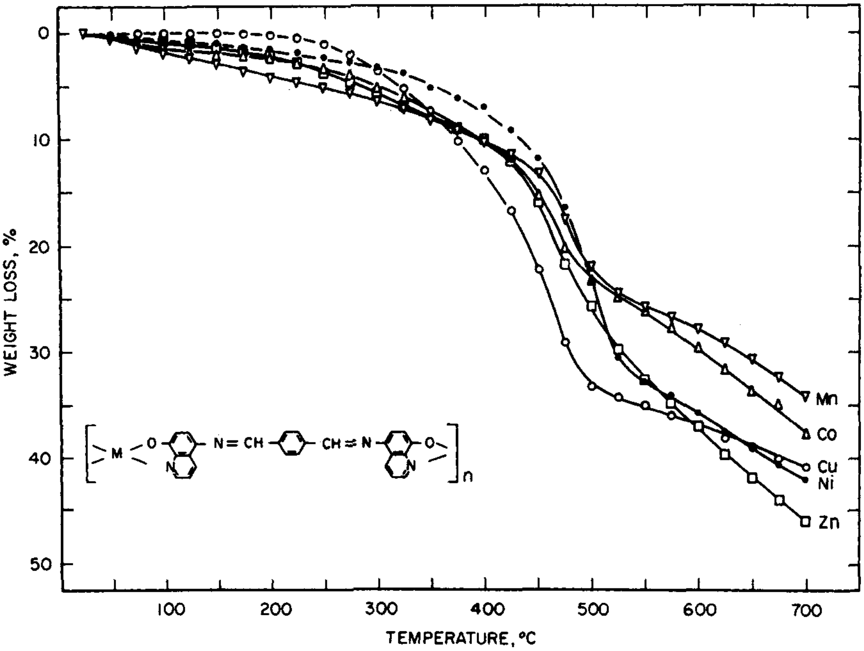


Fig. 4. Thermograms for Schiff base coordination polymers of 5,5′-[*p*-phenylenebis-(methylidynenitrilo)] di-8-quinolinol in which M is: (▽) Mn; (△) Co; (●) Ni; (○) Cu; (□) Zn.

of a precipitous break in the thermograms (Fig. 4) near the region of accelerated weight loss, as well as the gradual change in slope of curve *A* from atomic number 25 to 28 (Fig. 5), may be due to several factors that tend to obscure the decomposition temperature of the polymers. For example, the thermograms may reflect the slow volatilization of bound solvent, water, or low molecular weight moieties during the initial phase of the pyrolysis. In addition, the thermal behavior of the samples is greatly influenced by the purity of the polymers, and because of their insoluble nature the purification of coordination polymers has been a serious problem. Additional attempts to obtain purer coordination polymers will be made in order better to characterize these systems.

In the work on the coordination polymers that has already been reported[1,2] an Eyraud thermogravimetric balance was used to evaluate their thermal stabilities. This apparatus had a temperature range of 25–1000°C., but it was less sensitive to changes in weight than the present equipment using the Cahn balance. Also, considerably larger samples were required with the Eyraud balance. For the purpose of comparing the results obtained with the Eyraud and the Cahn balances the Ni-5,5′-[*p*-phenylenebis(methylidynenitrilo)] di-8-quinolinol polymer was selected for separate analysis on each of the units. Table III gives the results of these analyses in terms of the percentage weight loss of the polymer as a function

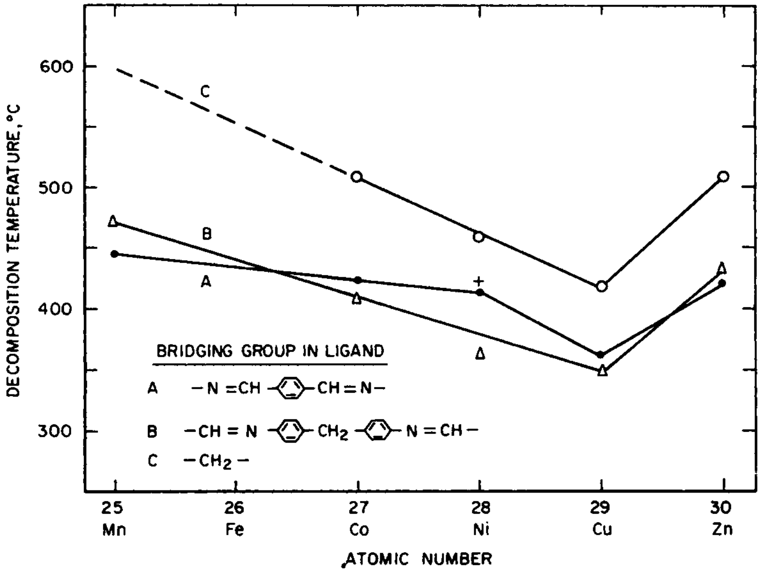


Fig. 5. Relationship between the thermal stability (decomposition temperature) of the coordination polymer and atomic number of the metal for bis-8-hydroxyquinoline ligands containing different bridging groups. The symbol (+) represents a value obtained with the use of the Eyraud balance. All other points on curve *A* were obtained with the balance described in this paper.

of temperature. Limitations on the furnace assembly employed in conjunction with the Cahn balance at the time this work was in progress did not permit these thermogravimetric analyses to be extended beyond 700°C. These two sets of results have been plotted in Figure 6 and are in good agreement up to about 550°C. However, in the thermogram obtained on the Cahn balance, there is a pronounced change in slope at approximately 500°C., accompanied by a reduction in the rate of volatilization. On the other hand, the Eyraud thermogram does not show any such definite and consistent departure from the established slope in this region, and in fact, the slope becomes more gradual only above 700°C. Thus, at 700°C. the weight losses of the Ni polymer samples were about 42 and 53% when analyzed with the Cahn and the Eyraud balances, respectively. It is known that sample size, the geometry of the sample, and other factors may influence the thermal behavior of compounds and polymers undergoing thermogravimetric analysis. In this investigation the samples analyzed with the Cahn equipment weighed about 2 mg. and were contained in a micro quartz crucible, while those analyzed with the Eyraud apparatus weighed 50 mg. and were pyrolyzed in a cylindrical platinum crucible.

The residues remaining after heating the Schiff base coordination polymers up to 700°C. consisted of approximately 25% metal and about 75% organic material, by weight. As mentioned earlier, samples of the Ni-5,5′-[*p*-phenylenebis(methylidynenitrilo)] di-8-quinolinol polymer were

TABLE III
Comparison of Data Obtained with the Cahn and Eyraud Thermogravimetric Balances

| | Weight loss, % (average of two runs) | |
|---|---|---|
| Temperature, °C. | Eyraud balance[a] | Cahn balance[b] |
| 25 | 0.4 | 0 |
| 50 | 0.8 | 0 |
| 75 | 1.1 | 0.5 |
| 100 | 1.2 | 0.8 |
| 125 | 1.8 | 1.0 |
| 150 | 2.1 | 1.1 |
| 175 | 2.7 | 1.4 |
| 200 | 3.2 | 1.6 |
| 225 | 3.3 | 1.9 |
| 250 | 3.6 | 2.4 |
| 275 | 3.9 | 2.8 |
| 300 | 4.5 | 3.3 |
| 325 | 5.0 | 3.9 |
| 350 | 5.4 | 4.8 |
| 375 | 5.8 | 5.8 |
| 400 | 7.6 | 7.1 |
| 425 | 9.8 | 9.3 |
| 450 | 11.9 | 12.0 |
| 475 | 15.5 | 16.7 |
| 500 | 22.0 | 23.3 |
| 525 | 28.2 | 30.6 |
| 550 | 31.0 | 32.8 |
| 575 | 34.8 | 34.2 |
| 600 | 38.8 | 35.9 |
| 625 | 42.5 | 37.7 |
| 650 | 45.9 | 39.4 |
| 675 | 49.3 | 40.9 |
| 700 | 52.7 | 42.2 |
| 800 | 61.2 | — |
| 900 | 67.9 | — |
| 1000 | 72.6 | — |

[a] Sample weight 50 mg., heating rate 2.5°C./min., Pt crucible.
[b] Sample weight 2 mg. heating rate 3°C./min., quartz crucible.

also heated in the Eyraud unit up to 1000°C., during which about 75% of the original polymer was volatilized. At this point the metal content amounted to about 45% of the total residue. This residue was then heated at 1000°C., and it was found that it continued to lose weight at a uniform rate until essentially all the organic material derived from the ligand had volatilized. The thermograms in Figure 7 indicate the weight loss of the Ni polymer residue while the temperature was maintained at 1000°C. It can be seen that there is a very sharp break in the weight-loss curve after approximately 2.5 hr. When the weight of the residue at this point was determined and used to calculate the percentage volatiles a value of 86.6% was obtained. This compares very well with the amount of organic mate-

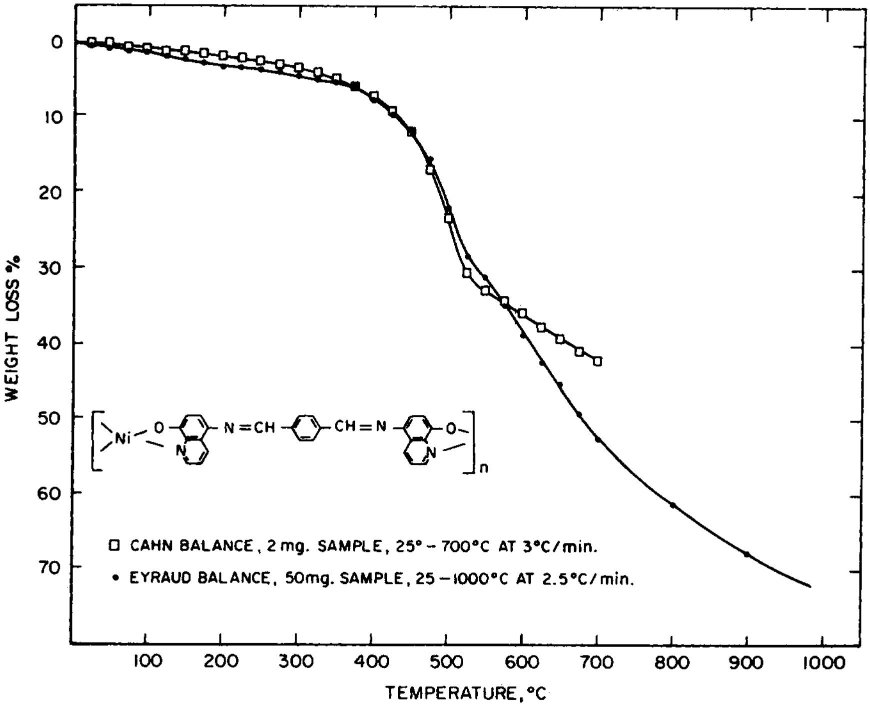


Fig. 6. Comparison of thermograms of Ni polymer obtained in vacuum on two different thermogravimetric balances.

rial contained in the original polymer, 87.7%, based on the formula $(NiL)_n$, where L represents the ligand. In both curves in Figure 7, representing two separate runs conducted on different days, there is evidence of an apparent increase in the weight of the residues after about 2.5–3 hr. This trend continues, although less markedly, until there is no detectable change in the weight of the residues after 7 hr. The reason for this behavior is not entirely clear, but a re-examination of some data dealing with this aspect of the analysis for a different Ni-Schiff base coordination polymer reported previously[2] indicated the same characteristic. On the other hand, the residue from the Cu polymer of that series showed no tendency to increase in weight once the low point in the thermogram was obtained.

In order that the coordination polymers undergo appreciable weight loss (and this rules out loss of bound solvent and low molecular weight species), a large number of chemical bonds must be broken to account for the volatile products that are generated. All the data accumulated thus far on the thermal stability of the bis-8-hydroxyquinoline type coordination polymers, based on weight loss and chemical and x-ray analyses of residues, indicate that no metal is lost as part of the decomposition reaction. As discussed in former papers,[1,2] zinc is lost when its coordination polymers are heated to 1000°C. because of the volatile nature of the metal

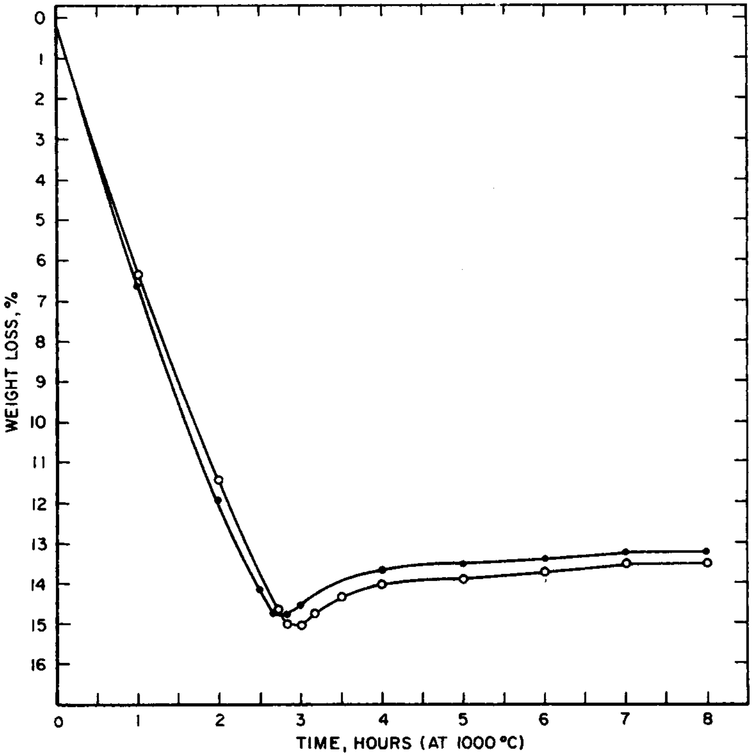
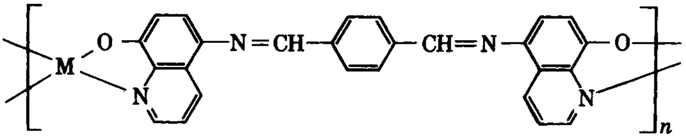


Fig. 7. Duplicate curves of weight loss of Ni polymer residue when heated in vacuum at 1000°C. after thermogravimetric analysis at 25–1000°C. (Eyraud balance).

at this elevated temperature. Therefore, any decomposition mechanism which involves the formation of bis-8-hydroxyquinoline (nonpolymeric) chelates may be ruled out as a major process because these chelates are volatile under the conditions used in the thermogravimetric analyses and no metal would have remained after the runs. In work that will be reported subsequently dealing with an analysis of the decomposition products by mass spectrometry, it will be demonstrated that no metal or metal containing compounds are lost and that the volatile products arising as a direct result of the polymer degradation process are organic materials formed by bond cleavages within the polymer. Accordingly, this eliminates the possibility that there is widespread cleavage of the 5,5′-nitrogen bonds, which attach the Schiff base bridges to the aromatic rings insofar as the initiation of the accelerated weight loss is concerned, and probably also rules out a decomposition mechanism based on the rupture of a single bond in many sequential Schiff base bridges. In the case of the bis-8-hydroxy-5-quinolyl methane coordination polymers,[1] which contained a —$CH_2$— bridge in the 5,5′-position, the only reasonable explanation for the accelerated weight loss involved rupture of the metal–ligand bonds as at least one step in the decomposition mechanism.

Likewise, in the present work, the loss in weight of the polymers may be attributed to a mechanism that depends to some extent upon the breaking of the metal–ligand bonds. One simple model assumes that when some critical temperature is reached there is a widespread rupturing of the bonds that anchor the metal to the ligand, giving rise to volatile products. From attempts to determine the activation energies of these reactions and also from other evidence, it is already known that the decomposition mechanism is very much more complicated than in this simple model. Nevertheless, if one assigns a prominent role to the step involving the thermal cleavage of the metal–ligand bonds within the polymer unit (I) it follows that a minimum of three chemical bonds must be broken before volatile organic fragments are generated:



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The nature of the decomposition products and the manner in which they are formed, including the sequence of bond rupture, are questions that have been raised in these recent studies and will require attention in subsequent work.

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## Résumé

Une réaction de condensation entre la 5-amino-8-hydroxyquinoléine et le téréphtaldéhyde fournit une base dé Schiff bis-bifonctionnelle possédant des propriétés de coordination, le 5,5'-[*p*-phénylène-bis(méthylidine-nitrilo)] di-8-quinoléinol, et qui a été utilisée pour produire des polymères de coordination sous forme de poudres insolubles contenant du Mn(II), Co(II), Ni(II), Cu(II) ou Zn(II). Les stabilités thermiques de ces polymères ont été étudiées sous vide dans un domaine de température situé entre 25 et 700°C au moyen d'une nouvelle thermobalance possédant une meilleure sensibilité. Les résultats se rapportent à la décomposition des polymères en métal dans la chaîne principale aussi bien qu'en produit de coordination organique. On discute des modes possibles de décomposition de ces polymères.

## Zusammenfassung

Die Kondensationsreaktion zwischen 5-Amino-8-hydroxychinolin und Terephthalaldehyd liefert eine bisfunktionelle Schiff'sche Base 5,5'-*p*-Phenylen-bis(methylidynnitril)-di-8-chinolinol, welche zur Erzeugung von Kondensationspolymerem verwendet wurde, die Mn(II), Co(II), Ni(II), Cu(II) oder Zn(II) in Form unlöslicher Pulver enthielten. Die thermische Stabilität dieser Polymeren wurde im Vakuum im Temperaturbereich 25–700°C mit einer neu gebauten Thermowaage mit verbesserter Empfindlichkeit ermittelt. Die Ergebnisse lassen eine Beziehung der Zersetzung dieser Polymeren sowohl zum Metall in der Hauptkette als auch zu den organischen Liganden, an welchen das Metall koordiniert ist, erkennen. Zersetzungsmöglichkeiten für diese Polymeren werden diskutiert.

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