Thermal Decomposition of Cu(II)-bis(8-hydroxy-5-quinolyl)methane Coordination Polymer

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Synopsis

The volatile products formed when the coordination polymer of copper(II) and bis-(8-hydroxy-5-quinolyl)methane was heated in vacuum at elevated preselected temperatures were examined. The amount of weight loss at each temperature was determined with a recording thermal balance at each fixed temperature. Infrared spectrophotometry was used to aid in the identification of the major volatile component. A sample was pyrolyzed directly into the mass spectrometer. The results show that the volatile product is for the most part the organic ligand bis(8-hydroxy-5-quinolyl)methane and not derivatives of the copper complex or fragments of the ligand. The mechanism for the decomposition previously proposed is supported.

INTRODUCTION

The thermal stability of a number of first-row transition metal coordination polymers containing bis(8-hydroxyquinoline)-type ligands has been studied in this laboratory. These studies also directed attention to a possible mechanism for the decomposition of the polymers which involved the rupture of metal-to-ligand bonds and the volatilization of organic constituents. Whereas this conclusion was based on an analysis of the residues after the polymers had been exposed to high temperatures, direct information on the decomposition products was lacking.[1,2]

This paper describes an investigation of a Cu(II)-bis(8-hydroxy-5-quinolyl)methane coordination polymer in which mass spectrometry is used to obtain more definitive information about the decomposition products when the polymer is subjected to elevated temperatures in vacuum. The data support the original hypothesis that the initial and major step in the decomposition process involves the breaking of metal-ligand bonds and the subsequent loss of organic material. While previous investigations dealt only with dynamic thermogravimetry, here the thermal stability of the polymer was also studied by determining the weight loss when a sample was heated in vacuum at fixed temperatures.

EXPERIMENTAL*

Synthesis of Cu(II)-Bis(8-hydroxy-5-quinolyl)methane

The synthesis of the ligand bis(8-hydroxy-5-quinolyl)methane and its reaction with copper acetylacetonate to give the Cu(II) coordination polymer are shown below in eqs. 1 and 2, respectively. The details of the procedures have already been described.[1]

Thermogravimetric Analysis

The TG apparatus[3] was constructed in this laboratory utilizing the weighing unit from a Cahn electrobalance. After calibration, the temperature and the weight of the sample were recorded automatically during the course of the experiment. The polymer was heated in vacuum (about 10^{-5} torr) at 50° or 100°C intervals over the temperature range 100–800°C and the weight loss was measured.

Mass Spectrometry

The mass spectra were obtained using a modified Model 21-101 Consolidated Electrodynamics Corp. mass spectrometer whose inlet system was maintained at 180°C by means of an auxiliary heater.

The pyrolysis apparatus, as shown in Figure 1, consisted of a $\frac{1}{2}$-in. diameter stainless steel combustion tube which was closed at one end, a
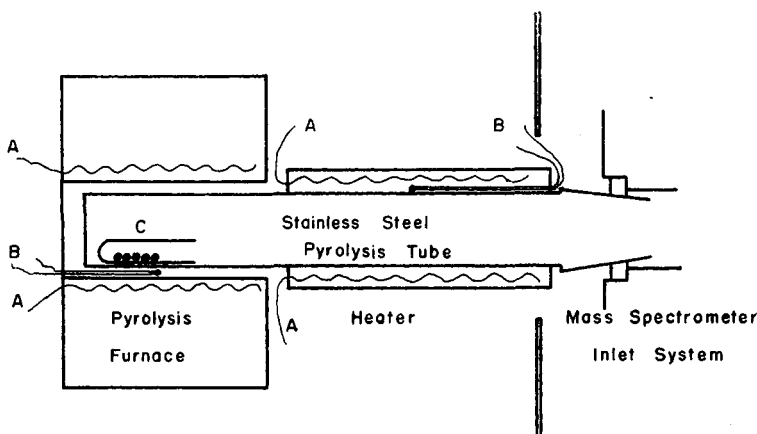

Fig. 1. Pyrolysis apparatus: A, heater wires; B, thermocouple leads; C, quartz tube and sample.

furnace for pyrolyzing the sample, and a heater for maintaining the upper portion of the tube at the same temperature as the inlet system, namely

* In order to specify adequately the experimental procedures, it has been necessary to identify commercial equipment in this paper. In no case does this identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.

180°C. A commercial thermocouple temperature controller was used to select and regulate the furnace temperature. The sample, which weighed about 10 mg, was contained in a small quartz tube of 3-mm I. D. located at the closed end of the combustion tube. After assembly, the apparatus was
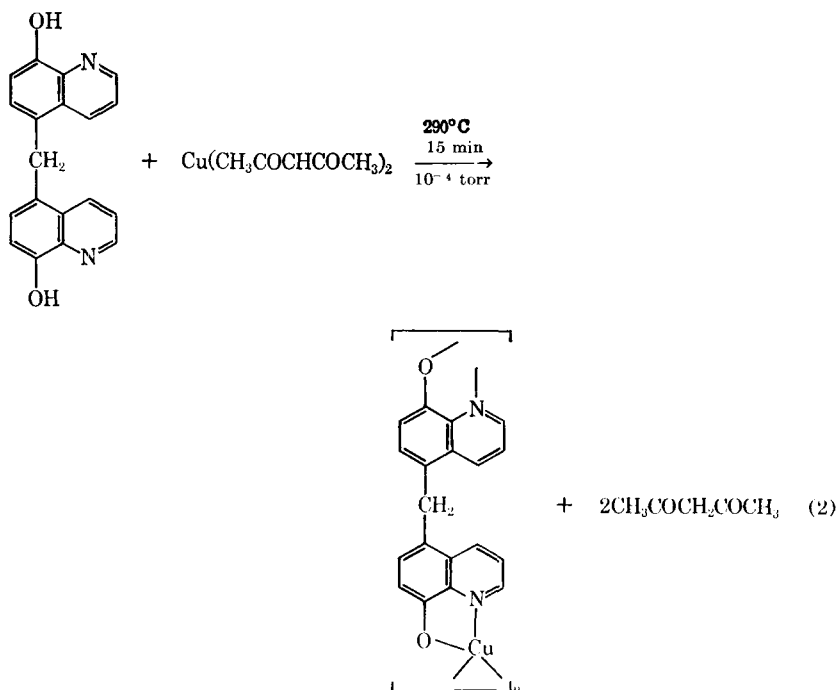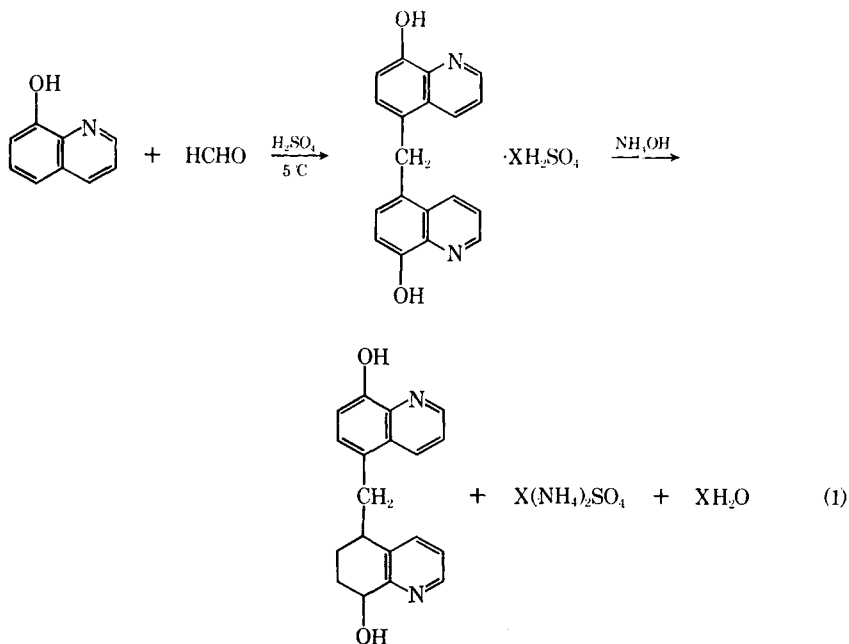

$$+ \quad X(NH_4)_2SO_4 \quad + \quad XH_2O \qquad (1)$$

$$+ \quad 2CH_3COCH_2COCH_3 \quad (2)$$

TABLE I
Weight Loss and Volatiles Detected After Heating Cu-Coordination Polymer in Vacuum

	Pyrolysis temp., °C									
	110	140	200	250	300	400	500	600	700	800
I. Thermogravimetry										
time of heating, hr	3.5	16	8	4	8	32	18	4.5	15	4
incremental weight loss, %	0.7	3.4	6.8	5.4	9.2	21.8	2.8	2.1	2.0	1.5
cumulative weight loss, %	0.7	4.1	10.9	16.3	25.5	47.3	50.1	52.2	54.2	55.7
II. Mass Spectrometry[a]										
DMF	+	+	+	−	−	−	−	−	−	−
H$_2$O	+	+	+	−	−	−	−	−	−	−
Organic decomposition products	−	−	−	+	+	+	−	−	−	−

[a] Time of heating for mass spectrometer experiments was approximately 30 min at each temperature for the mass run. TG times as shown were generally much longer (heated to no detectable further weight loss) and cumulative. A plus sign indicates the presence of the species while a minus sign indicates that no material was detected.

evacuated at room temperature for several hours to remove any easily volatilized materials. Then the combustion apparatus was isolated from the vacuum pumps and the mass spectrometer expansion volume by closing the valves in the inlet system. The temperature of the furnace was quickly raised and the sample was heated at the selected temperature for 30 min, after which the volatile products were allowed to enter the 3-liter expansion volume. The pressure of the expanded gas was measured with a micromanometer and the gas was then fed into the analyzer for examination. After the spectrum was obtained, the heating and evacuation of the pyrolysis tube was continued until the micromanometer indicated no additional volatile products at the selected temperature. The temperature of the furnace was raised stepwise and at each new level the decomposition products were examined in the manner described above.

An earlier study[1] using a dynamic thermogravimetric technique indicated that the accelerated weight loss for this polymer started at about 420°C. This is in good agreement with the temperature of maximum incremental weight loss in the present experiment, which is 400°C. The difference in the two results arises from the nature of the two runs, dynamic and progressive isothermal.

RESULTS

The loss in weight of the Cu(II) coordination polymer when heated in vacuum to constant weight at fixed temperatures is given in Table I and shown graphically for the major part of the reaction at each temperature in Figure 2. In some cases the actual weight loss curve was continued for more than 4 hr to obtain constant weight. The curves are not shown beyond 4 hr for the sake of graphical presentation. A negligible loss in weight, 0.7%, occurred at 100°C while the maximum incremental weight loss, 21.8%, took place at 400°C. Approximately 47%, by weight, of the polymer was volatilized over the temperature range 100–400°C and only 8.4% was lost between 500° and 800°C. The cumulative weight loss at the end of the progressive isothermal experiment amounted to 55.7%. In a previous paper,[1] which dealt with a dynamic thermogravimetric analysis of this polymer, where the temperature was increased at a rate of 2.5°C/min, the cumulative weight loss at 800°C was 51.2%.

Table I also indicates the volatile products that were detected by the mass spectrometer when the polymer was heated at the specified temperatures in the furnace shown in Figure 1. Below 200°C, the volatiles consisted solely of water and dimethylformamide; neither of these compounds was detected above this temperature. Between 250° and 400°C, organic decomposition products were found to be present and the nature of these products will be discussed subsequently. Although the polymer sample was then subjected to further continuous stepwise heating as previously described, no organic products were detected by the mass spectrometer at each step over the temperature range 500° to 800°C. The apparent dis-
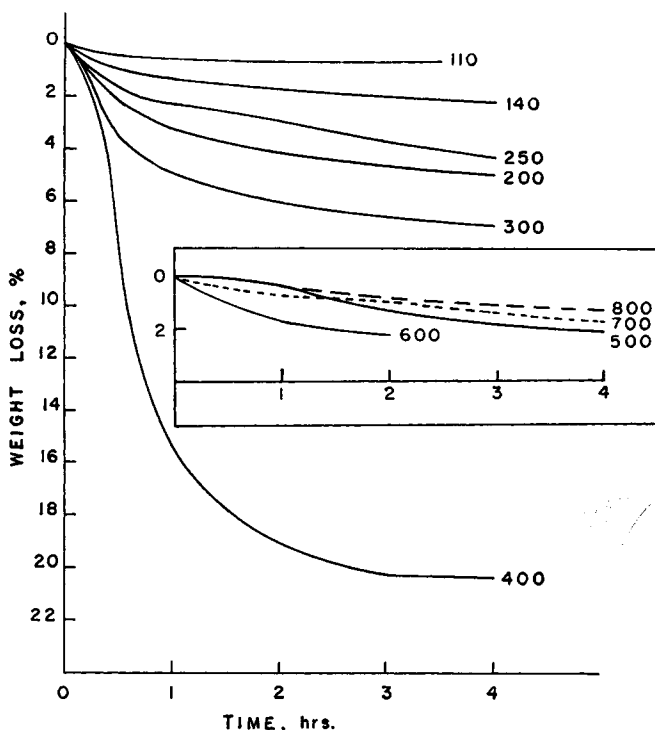
Fig. 2. Weight loss of the Cu(II)-coordination polymer versus time in isothermal intervals from 110 to 800°C. Temperature of each interval is noted at the end of each isotherm.

agreement between this observation and the thermogravimetric results over the same temperature range may be explained by the facts that (1) the heating time intervals were much shorter for the mass spectrometer measurements than the thermogravimetric analysis measurement and (2) the thermogravimetric analysis results are cumulative while the mass spectrometric results are not.

Table II gives a tabulation of the relative peak heights obtained from mass spectra of the volatile components of 8-hydroxyquinoline (oxine), the bismethylene ligand, and the copper-coordination polymer. The volatile components which resulted from heating the sample to 400°C in vacuum (10^{-7} torr) were evolved directly into the mass spectrometer using the furnace system previously shown. Only mass values above 84 are given, as they were found to be adequate in evaluating the major components of decomposition; however, some smaller fragments were also detected. The oxine and the bis-ligand sublime at the pressure of this experiment at temperatures below 400°C; thus, very little if any fragmentation of these materials would be expected until they reach the ionization chamber of the mass spectrometer. The polymer, on the other hand, must decompose thermally to form fragments volatile under these conditions. Therefore,

some differences between the relative peak heights and possibly mass number of peaks would be expected for the polymer fragments as compared to the oxine and the bis-ligand sublimates.

TABLE II
Comparison of Mass Spectral Data Obtained on Volatiles

Mass no.	Relative peak heights		
	Oxine	Ligand	Polymer
173	0	1.6	0.4
172	0	1.2	0.3
160	0	2.6	2.7
159	0	24.4	24.6
158	0	17.6	19.7
147	0.7	0.7	0.7
146	10.3	10.3	10.3
145[a]	100	100	100
144	1.8	2.6	2.2
143	—[b]	2.9	1.3
142	—	1.6	1.2
141	—	0.6	0.3
131	0	2.1	2.0
130	0	13.5	13.9
129	0	1.4	2.5
128	0	2.2	1.3
118	6.4	6.2	6.5
117	68.5	64.9	69.7
116	11.2	10.8	3.0
115	1.4	2.3	1.8
114	0.8	1.2	1.0
105	0	2.9	0.4
104	0	4.1	1.7
103	0	2.9	2.4
102	0	2.1	2.3
101	0	0.9	1.0
92	0.3	2.0	0.5
91	3.4	7.4	3.9
90	21.2	18.8	21.7
89	24.0	21.7	25.2
88	2.9	3.0	3.4
87	2.8	3.1	3.4
86	1.9	2.1	2.2
85	1.0	0.8	2.5
84	0.2	1.0	0.3

[a] All data normalized to mass 145 as 100%.
[b] Dash indicates less than 0.1.

The major results obtained in these experiments are the following: (a) There was no evidence of mass peaks at masses higher than 173, for any of the samples studied. (b) The bis-ligand (MW 302.3) and 8-hydroxyquinoline (MW 145.2) are known to be volatile under the conditions used, and the organic fragments detected in runs involving these substances must

come from fragmentation of the parent compounds in the ionization chamber.   (c) The major mass peak obtained for 8-hydroxyquinoline, the bis-ligand, and the polymer is the one at 145, corresponding to the 8-hydroxy-quinoline ion (Fig. 3A).   The peaks at about 90 and 117 are also due to organic fragments coming from this species.   (d) The mass peak at 158, which is not present in the 8-hydroxyquinoline spectrum, can be attributed to the cleaved portion of the bis-ligand containing the methylene bridge
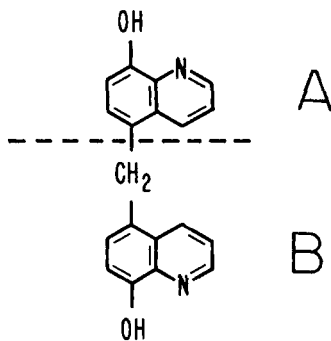

Fig. 3. Organic fragments arising from cleavage of the bis-ligand at the methylene bridge.

(Fig. 3B).   Furthermore, the mass peak detected at mass 130, which is also absent in the 8-hydroxyquinoline spectrum, must arise from further disruption of the moiety shown in Figure 3B.   (e) Virtually identical mass spectra were obtained in the 80 to 173 mass peak region when the bis-ligand was heated at 200 and 400°C.   (f) No metal-containing compounds were detected by the mass spectrometer when the polymer was heated over the temperature range 100 to 800°C.   (g) The Cu(II)-coordination polymer, when heated at 400°C, yielded organic products which gave a mass pattern that was nearly identical to that obtained for the bis-ligand.

The great similarity between the mass spectra for the bis-ligand and the polymer leads one to conclude that the polymer degradation must initiate with the preferential rupture of bonds at the metal-ligand sites, giving rise to the free bis-ligand.   There is little likelihood that the thermal decomposition of the polymer is initiated by cleavage of methylene bridges in the ligand, because this would have given rise to some Cu(II)-8-hydroxyquinolate which is known to sublime under some of the conditions described. No such compound or copper-containing derivative was detected.   It is also unlikely indeed for the remarkable spectral similarity to exist if the thermal degradation of the Cu(II)-coordination polymer involved the scission at the methylene bridge prior to the cleavage of the metal-ligand bonds.   In this latter case, the mass spectrum obtained would have been that of the volatile fragments of the bis-ligand (Fig. 3A and 3B) rather than the intact bridged bis-ligand.   Furthermore, when the bis-ligand itself was heated in vacuum at 200°C, a temperature far below its decomposition point, it also

gave a mass spectrum between masses 80 to 173, which was virtually identical to those obtained for the polymer.

In a separate experiment the bis-ligand was heated in vacuum in the thermobalance by raising the temperature to 400°C and the volatile product was collected and identified by infrared absorption measurements (Fig. 4) as the starting material. Finally, when the Cu(II)-coordination polymer was subjected to the same treatment, it gave a compound whose infrared absorption spectrum resembled the bis-ligand and not 8-hydroxyquinoline (Fig. 4).
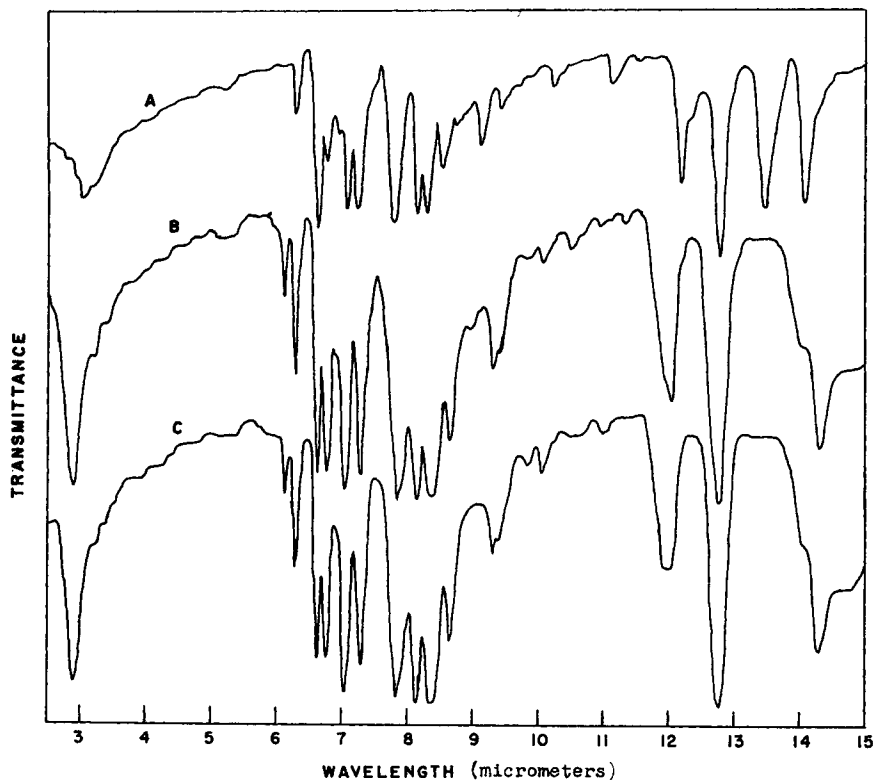

Fig. 4. Infrared absorption spectra: samples prepared as powder dispersions in potassium bromide and pressed into pellets. Curve A, 8-hydroxyquinoline; curve B, parent ligand, bis(8-hydroxy-5-quinolyl)methane; curve C, pyrolyzate from Cu(II)-coordination polymer obtained at 400°C, 10^{-5} torr.

The overall mechanism of the thermal reaction in vacuum for the copper-coordination polymer appears to be as follows: (a) At temperatures up to 250°C, the major weight loss is due to the evolution of entrapped, adsorbed, or even coordinated solvent, i.e., DMF, H_2O; (b) At temperatures between 250 and 450°C, the major decomposition product is the bis-ligand with lesser amounts of smaller organic species (at the higher temperatures,

some of the ligand may crack before it escapes from the high temperature zone). Between 450 and 800°C there is some weight loss on prolonged heating and this may very well be small amounts of much lighter fragments due to stripping of polycondensed ring structures left as pyrolytic residues. It should be borne in mind that at 800°C only 55.7% of the polymer was volatiled in the electrobalance furnace, and approximately 27% of the remaining residue was carbonaceous matter.

DISCUSSION

Inasmuch as the initial and principal step in the decomposition of the Cu(II)-bis(8-hydroxy-5-quinolyl)methane polymer is breaking of the Cu—O and Cu—N bonds, it is worthwhile to consider the configuration at the metal-ligand site. While data on the structure of the polymer are not yet available, there have been several interesting studies of the copper–8-hydroxyquinolate complex. Mundy[4] studied both the anhydrous and dihydrated copper–8-hydroxyquinolate and found that the hydrated form was a distorted octahedral while he considered that the anhydrous complex could be tetrahedral. Kruh and Dwiggins[5] performed an X-ray analysis of the dihydrated copper complex and concluded that the compound was isomorphous with the distorted octahedral zinc dihydrate 8-hydroxyquinolate examined by Merritt et al.[6] However, Kruh and Dwiggins predicted that the anhydrous copper complex would be found to have a square planar configuration and that the compound was not tetrahedral. In a later and more detailed study Kanamura et al.[7] investigated the crystal structure of anhydrous Cu(II)-8-hydroxyquinolate and confirmed the prediction that each copper atom was bonded to two oxygen atoms and two nitrogen atoms in a square planar configuration. There is every reason to believe that the anhydrous copper coordination polymer will also be shown to be square planar and that the solvated polymer will be a distorted octahedral. Furthermore, it is unlikely that the bond distances and bond angles in these two polymers, particularly in the coordinated five-membered rings, will be found to differ significantly from those in the respective metal complexes. Also, one would expect that in the polymer the two 8-hydroxyquinolines are in one plane and are coplanar with the coordinated copper atom. With respect to the nature of the metal-ligand bonds, Kokoszka et al.[8] have reported values for the sigma and pi bonding in copper 8-hydroxyquinolate dihydrate and stated that the Cu—O and Cu—N bonds are covalent in character. The Cu—O metal-ligand bond distance in this complex has been estimated as 2.0 Å, while the Cu—O distance between copper and water is about 2.3 Å.[5] In the anhydrous copper complex, the Cu—O bond distance is given as 2.01–2.07 A while the Cu—N bond distance is 1.90–1.92 Å.[7] An examination of the bond angles in the five-membered ring of this complex reveals that the ring formed when copper and 8-hydroxyquinoline coordinate are under strain. Similarly, the five-membered ring in the polymer must be under strain, and thus the Cu—O and Cu—N bonds are

most susceptible to cleavage when the polymer is subjected to pyrolysis. This releases the bis-ligand and accounts for the weight loss and the mass peaks detected in the mass spectrometer experiment.   We are convinced that no intact bis-ligand is detected in the mass spectrometry experiment because this compound is fragmented in the ionization chamber.   Based on the relationships established between the thermal stability and the properties of the central metal atom in previous studies, it is very likely that the same general decomposition mechanism may be applied to the other first-row, divalent transition coordination polymers of bis-8-hydroxyquinolines.

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