J. Inorg. Nucl. Chem., 1964, Vol. 26, pp. 139 to 159. Pergamon Press Ltd. Printed in Northern Ireland

THERMAL STABILITY OF BIS(8-HYDROXY-5-QUINOLYL)-METHANE CO-ORDINATION POLYMERS*

E. HOROWITZ and T. P. PERROS
The Chemistry Department, The George Washington University, and the
National Bureau of Standards, Washington, D.C.

(*Received* 25 *April* 1963)

Abstract—Co-ordination polymers of bis(8-hydroxy-5-quinolyl)-methane have been prepared by reacting the ligand with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), in solution as well as by thermal polymerization. The thermal stability of each polymer in vacuum was studied by thermogravimetric analysis up to 1000°C, and the decomposition temperature was found to be closely related to such periodic properties of the metal incorporated in the backbone of the polymer as ionic potential and electronegativity. Based on an evaluation of existing data for metal 8-hydroxyquinolates it is shown that measurements in air instead of vacuum lead to erroneous conclusions about the thermal stabilities of co-ordinated systems. Infra-red spectra of the co-ordination polymers revealed that the frequency of the absorption band in the 1100 cm^{-1} region was dependent upon the ionic potential and other periodic properties of the metal ion. The infrared data provide information about the nature of the metal–ligand bond at the C—O—metal site.

IN recent years the demand for new polymeric materials with high thermal and chemical stability has stimulated research in many areas of polymer chemistry. This investigation was undertaken with the following objectives in mind:

(1) to prepare co-ordination polymers of bis(8-hydroxy-5-quinolyl)-methane that would resist thermal degradation at high temperatures and
(2) to determine some of the factors that are important in governing the thermal behaviour of co-ordination polymers and complexes at elevated temperatures.

It has been shown that the reaction of metal ions with organic ligands produces co-ordinated systems having enhanced thermal stability and frequently having improved resistance to chemical oxidation. For example, MARTIN(1) found that 4,4′-bis-α-thiopicolinamido-diphenyl sulphone–zinc(II) could be maintained at 360°C without evidence of degradation, while DENT and LINSTEAD(2) reported that copper (II)–phthalocyanine did not undergo decomposition even when heated at 500°C.

BAILAR and co-workers(3–9) initiated work on the preparation of a variety of

---

* This paper is based on a portion of a dissertation submitted by Emanuel Horowitz of the National Bureau of Standards in November 1962 in partial fulfillment of the requirements for the Degree of Doctor of Philosophy at The George Washington University. Presented at the 145th. National Meeting of the American Chemical Society in New York City, Sept. 1963.

(1) K. V. MARTIN, *J. Amer. Chem. Soc.* **80**, 233 (1958).

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

(3) J. C. BAILAR, JR., W. C. DRINKARD, JR. and M. L. JUDD, WADC Technical Report 57-391, September 1957.

(4) J. C. BAILAR, JR., J. MCLEAN, and M. L. JUDD, WADC Technical Report 58-51, pp. 124-130. April 1958.

(5) J. C. BAILAR, JR., K. V. MARTIN, M. L. JUDD and J. MCLEAN, WADC Technical Report 57-391, Part II, August 1958,

(6) J. C. BAILAR, JR., M. L. JUDD, and J. MCLEAN, WADC Technical Report 58-51, Part II, pp. 116-145. May 1959.

(7) J. C. BAILAR, JR., WADC Technical Report 59-427, pp. 353-366. January 1960.

(8) J. C. BAILAR, JR., H. A. GOODWIN, M. MORAGHAN, J. MCLEAN, C. FUJIKAWA, and LU-CHI CHEN, WADC Technical Report 58-51, Part III, pp. 66-131, April 1960.

(9) J. C. BAILAR, JR., *Inorganic Polymers*. Special Publication No. 15, The Chemical Society, London (1961).

co-ordination polymers including derivatives of bis(8-hydroxyquinoline). The thermal stabilities of the copper and zinc bis(8-hydroxyquinoline) type co-ordination polymers were examined by heating samples in a stream of nitrogen and measuring the weight losses.(6) The bis(8-hydroxy-5-quinolyl) sulphone ligand appeared to give the most stable co-ordinated systems with temperatures of decomposition of 280°C and 320°C for the copper and zinc polymers, respectively.

KORSHAK and collaborators(10) following the pattern established by BAILAR, reported the synthesis of a number of co-ordination polymers of bis(8-hydroxy-5-quinolyl)-methane as well as some mixed polymers. The thermal stability of a group of the first-row transition metal co-ordination homopolymers was evaluated by noting colour changes as the sample was heated in air in a capillary tube, and also by measuring the deformation of the sample with increasing temperature In a recent paper, BERG and ALAM(11) discussed the synthesis of co-ordination polymers of 8,8′-dihydroxy-5,5′-biquinolinol and the use of the ligand as an analytical reagent for detecting metal ions in the microgram range. These authors also studied the thermal stability of co-ordination polymers by heating samples at different temperatures in air and observing changes in colour and in the infra-red spectra.

The growing interest in the thermal properties of co-ordinated systems has made it essential that workers in this field develop some systematic approach to the problem of thermal stability. If thermal stability data reported in the literature on co-ordination systems are to have real meaning they should be accompanied by a complete description of the experimental procedure. For example, as will be demonstrated later in this paper, the thermal behaviour of metal 8-hydroxyquinolates (oxinates) in air is dependent upon the heating rate. In addition, there is no apparent correlation between data obtained in air and in vacuum; only the results in vacuum can be related to the periodic properties of the metal in the chelates. Furthermore, it will be shown that when the Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) co-ordination polymers of bis(8-hydroxy-5-quinolyl)-methane are heated in vacuum the decomposition temperature is directly related to the atomic number of the metal incorporated in the backbone of the polymer. The decomposition temperature was obtained by drawing two straight lines tangent to the thermal gravimetric curve, before and after accelerated weight-loss, and determining where their point of intersection fell on the temperature axis.

Infra-red analysis of the products of polymerization reactions gives evidence of co-ordination between the metal ions and the bis-ligand. In addition, as the atomic number of the metal in the co-ordination polymer is increased, the peak maximum of the absorption band in the 1100 cm^{-1} region is progressively shifted to higher frequencies. The infra-red data furnish useful information about the nature of the bonds at the C—O—M site.

EXPERIMENTAL

Preparation of the ligand and co-ordination polymers

Bis(8-hydroxy-5-quinolyl)-methane. The ligand was prepared, with slight modification, by the method of SCHÜLLER(12) and JUDD.(13) Reagent grade 8-hydroxyquinoline (0·5 mole) was dissolved

---

(10) V. V. KORSHAK, S. V. VINOGRADOVA, and T. M. BABCHINITSER, *Polymer Science*, USSR **2**, No. 4, 344 (1960).

(11) E. W. BERG and A. ALAM, *Analyt. Chim. Acta* **27**, 454 (1962).

(12) H. SCHÜLLER, *J. Prakt. Chem.* [2], **88**, 180 (1913).

(13) M. L. JUDD. Ph.D. Thesis, University of Illinois (1958).

in small portions, with stirring, in 250 ml of concentrated sulphuric acid maintained at 5°C. Formaldehyde (0·25 mole, 36 per cent) was then added drop-wise to the stirred solution over a 3 hr period, after which the solution was maintained at 0–5°C for 2 hr and then poured into 6 l. of distilled water maintained at room temperature. After 16 hr at 5–10°C the solution was filtered, and a bright yellow product, reported(13) as the H_2SO_4 salt of bis(8-hydroxy-5-quinolyl)-methane, was obtained. The yellow precipitate was dissolved in hot distilled water and neutralized with ammonium hydroxide to give the desired compound in approximately 40 per cent yield. Recrystallization from dimethylformamide gave a white amorphous powder that melted at 283°C. (Found: C, 75·6; H, 4·70, 4·62; N, 9·07, 9·35. Calc. for $C_{19}H_{14}O_2N_2$: C, 75·5; H, 4·64; N, 9·26%).

It is interesting to note that in a number of experiments, when the temperature was allowed to exceed 10°C, either extremely low yields were obtained or no product was isolated. While Judd(13) also reported some difficulties in preparing the pure compound no such problems are mentioned by Noelting(14) or in the patent literature.(15,16) From our experience the reaction appears to be quite sensitive to temperature, to the rates of mixing, and other factors. It should also be mentioned that in a number of experiments involving the preparation of bis(8-hydroxy-5-quinolyl)-methane·xH_2SO_4, a resinous orange material was obtained instead of the usual yellow crystals. In one instance the fine yellow precipitate formed but it changed to a resinous product over a 3 hr period while being refrigerated at 5°C. When probed with a glass rod the resinous material could be drawn out in long fibres or spun onto the rod. On being removed from solution and allowed to stand at room temperature and at a relative humidity of about 50 per cent, a portion of the resinous material became hard and brittle. However, this material could be dissolved in water at 40°C and recrystallized in the usual yellow crystalline form.

Synthesis of co-ordination polymers

1. *Thermal polymerization.* The co-ordination polymers were prepared in vacuum by heating stoichiometric amounts of the ligand and the metal acetylacetonate at 290°C. The reaction vessel and the jar containing the electrically heated silicone oil were made of glass so that it was possible to observe the entire reaction. Once formed, the polymer was quickly removed from the temperature bath after a minimum time had elapsed, thus minimizing the possibility of decomposition. By reducing the reaction time from hours to minutes, the problems encountered by other workers in preparing co-ordination polymers of bis-oxine derivatives by thermal polymerization were largely eliminated. For example, Korshak and co-workers,(10) using a heating period of 3 hr, reported the preparation of the dimer and trimer of the nickel(II) and copper(II) bis(8-hydroxy-5-quinolyl)-methane polymers, respectively. Berg and Alam(11) reported that they were unsuccessful in preparing the zinc(II) 8,8′-dihydroxy-5,5′-biquinolyl polymer by thermal polymerization.

The chelates of acetylacetonate were used in these reactions because Von Hoene *et al.*(17) reported that these compounds when heated in vacuum decomposed to give volatile products consisting of acetylacetone, acetone, acetic acid, methane, carbon monoxide and carbon dioxide. Thus in thermal polymerizations in vacuum, the by-products of the reaction could be removed while the metal would be left behind to co-ordinate with the bis-ligand.

Prior to each run, the reaction vessel was first flushed with nitrogen that had been purged of oxygen.(18) Then the reaction vessel containing the reactants was evacuated to approximately 10^{-3} mm Hg and was immersed in the silicone oil bath. After all visible signs of reactions ceased, the product was removed, either as a free-flowing powder or as clumps, wrapped in filter paper for insertion into a paper extraction thimble, and extracted overnight with reagent-grade dimethylformamide using a Soxhlet apparatus. The polymer itself was essentially insoluble in the hot solvent, but unreacted ligand, metal acetylacetonate, and other soluble materials were removed during the extraction. The solution in the extraction flask was highly coloured, and precipitated solid material was usually present. The apparatus was arranged to prevent any solid material from being physically swept into the flask. The polymer was then extracted with absolute alcohol for several hours to remove the last trace of free dimethylformamide and any non-polymeric alcohol-soluble constituents.

(14) E. Noelting, *Chim. et Indust.* **8**, 758 (1922).

(15) Swiss Pat. 208000, (1940); *Chem. Abstr.* **35**, 3649 (1941).

(16) British Pat. 536367, (1941); *Chem. Abstr.* **36**, 1617 (1942).

(17) J. Von Hoene, R. G. Charles and W. M. Hickam, *J. Phys. Chem.* **62**, 1098 (1958).

(18) L. Meites and T. Meites, *Analyt. Chem.* **20**, 984 (1948).

The polymers showed no evidence of dissolving in alcohol although some of the extracts were coloured. The extracted polymers were normally dried in vacuum over P_2O_5 at 140°C although a few polymers were also re-dried at 190°C. Based on elemental analysis there was no evidence that the polymers suffered any decomposition at these temperatures.

2. *Polymerization in solution.* The hydrated acetate of the divalent metal, dissolved in dimethylformamide, was slowly added to a stirred dimethylformamide solution containing the ligand and maintained at 120°C. In all cases precipitation occurred almost immediately upon mixing the two reactants. The contents of the reaction flask were allowed to cool overnight at room temperature, and the product was collected, extracted, and dried in the manner previously described.

TABLE 1.—ELEMENTAL ANALYSES OF CO-ORDINATION POLYMERS

Polymer*	Calculated				Found							
					Thermal†				Solution‡			
	C	H	N	M	C	H	N	M	C	H	N	M
$[MnL \cdot H_2O]_n$	61·1	3·78	7·50	14·7	62·0	3·80	7·68	14·2	—	—	—	—
$[MnL]_n$	64·4	3·42	7·85	15·4								
$[CoL \cdot H_2O]_n$	60·4	3·79	7·45	15·6	58·5	3·93	7·23	15·7	59·4	3·81	7·61	15·9
$[CoL]_n$	63·6	3·36	7·80	16·4								
$[NiL \cdot H_2O]_n$	60·5	3·74	7·43	15·6	64·0	4·39	7·11	12·0	62·3	3·78	7·76	15·1
$[NiL]_n$	63·6	3·37	7·79	16·3								
$[CuL \cdot H_2O]_n$	59·8	3·70	7·34	16·7	62·4	3·51	7·51	15·2	62·4	3·67	7·66	14·9
$[CuL]_n$	62·8	3·32	7·70	17·4								
$[ZnL \cdot H_2O]_n$	59·5	3·67	7·30	17·0	58·8	3·37	7·23	18·4	60·4	3·69	7·57	17·1
$[ZnL]_n$	62·5	3·31	7·66	17·8								

* L = $C_{19}H_{12}O_2N_2$.

† Polymers prepared by thermal polymerization.

‡ Polymers prepared in solution.

The results of the elemental analyses of the co-ordination polymers are given in Table 1 and reflect the difficulty in purifying insoluble polymers of this type.

Thermogravimetric analysis

A slightly modified Eyraud Electronic Thermobalance§ was used to study the thermal stability of the co-ordination polymers. The sample in the 50 mg range was carefully weighed in a platinum crucible, which was suspended from the balance beam and positioned in the centre of the furnace. The system was sealed and evacuated to about 10^{-3} mm Hg. Starting at room temperature the sample was heated to 1000°C at a uniform heating rate of 2·5°C per min. During the entire run the temperature in the immediate vicinity of the sample and the weight loss were automatically recorded on previously calibrated chart paper. After the furnace reached 1000°C the temperature was maintained at this level until the sample stopped losing weight, a procedure which usually required about 8 hr. Duplicate thermogravimetric analyses were made on each of the co-ordination polymers studied.

Infra-red analysis

The infra-red spectra of the ligand and the co-ordination polymers were obtained in the sodium chloride region using a Perkin-Elmer Model 21 spectrophotometer. Inasmuch as the co-ordination

§ Eyraud Recording Balance Manual, Anthony M. Kohler, 535 West 110th Street, New York, New York (25).

polymers were found to be virtually insoluble in organic solvents the Nujol mull technique was selected as a means of preparing the samples for infra-red analysis.

RESULTS AND DISCUSSION

An important property of polymers and one of high current interest is their ability to withstand degradative effects of high temperature.(19) For the present discussion thermal stability will be related to the weight loss of samples heated in air or in vacuum. The metal complexes of 8-hydroxyquinoline were selected as model compounds because it was felt that an examination of their thermal behaviour would provide considerable insight into the reactions of the co-ordination polymers when subjected to elevated temperatures. DUVAL and co-workers(20) and BORREL and PARIS(21) have reported the thermograms obtained when the 8-hydroxyquinolates were heated in air. More recently CHARLES and LANGER(22) investigated the heat stabilities of some of the metal complexes of 8-hydroxyquinoline in vacuum. The results of these investigators have been summarized in Table 2. As these data were mainly obtained directly from the thermograms reported in the literature the temperature values listed may be in error by approximately 5°C. Nevertheless such deviations would not alter the conclusions that we have reached. Also given in this table are the approximate percentage weight-loss, the composition of the residues, and the estimated heating rates. Comparing the data obtained from pyrolysis in air at 3°C/min and 5°C/min, respectively, it is evident that there is reasonably good agreement for the types of residues found and the percentage weight loss.

Although one of the principal reasons for conducting thermogravimetric analyses on these compounds was to establish the critical temperature points on the weight loss–temperature curves there is not a single case of agreement among the temperature ranges in the data shown. As the thermal stability of the complexes of 8-hydroxyquinoline was related to the larger question of the thermal properties of the bis(8-hydroxyquinoline) co-ordination polymers, data on the pyrolysis of the metal oxinates were assembled, perhaps for the first time, and evaluated from a different point of view. In Fig. 1, the temperatures at which some of the anhydrous oxinates initially began to lose weight, as indicated in Table 2, are plotted as a function of the atomic number of the metal. There is no correlation between atomic number of the metal and the temperature at which the complex begins to show a marked loss of weight. Moreover, no meaningful relationship exists between the temperature and such periodic properties as valency, group number, electronegativity, ionic potential or period classification. For example, at a heating rate of 5°C per minute in air divalent metals of the first-row transition metals Mn, Co, Ni, and Cu give a saw-tooth plot in which the manganese and nickel complexes show less thermal stability than the oxinates of cobalt and copper. On the other hand, when these samples are heated in air at 3°C per min a saw-tooth plot is obtained in which the manganese and nickel complexes are more stable than those of cobalt and copper. In addition, all four points in the latter plot are displaced toward higher values on the temperature axis as compared to the results obtained at a heating rate of 5°C per min. The points

---

(19) *Thermal Degradation of Polymers*, Society of Chemical Industry Monograph, No. 13, Macmillan, New York (1961).

(20) E. DUVAL, *Inorganic Thermogravimetric Analysis*, Elsevier, New York (1953).

(21) M. BORREL and R. PARIS, *Analyt. Chim. Acta* **4**, 267 (1950).

(22) R. G. CHARLES and A. LANGER, *J. Phys. Chem.* **63**, 603 (1959).

TABLE 2.—THERMAL STABILITY OF METAL OXINATES*

Element and Valence	BORREL and PARIS(21)			DUVAL(20)			CHARLES and LANGER(22)		
	Heating rate, 3°C/min			Heating rate, 5°C/min			Heating rate, 2·5°C/min		
	In air, °C	Wt. loss (%)	Residue	In air, °C	Wt. loss (%)	Residue	In vac., °C	Wt. loss (%)	Residue
Al(III)	375–700	$\cong 90$	Al_2O_3	220–1000	$\cong 90$	Al_2O_3	265–350	$\cong 100$	Trace
Ca(II)	—	—	—	300–880	$\cong 85$	CaO	490–540	< 100	Significant
Cr(III)	—	—	—	360–500	$\cong 85$	Cr_2O_3	265–355	$\cong 100$	Trace
Mn(II)	320–700	$\cong 80$	Mn_3O_4	250–890	$\cong 80$	Mn_3O_4 + C†	355–450	< 100	Small, Black
Fe(III)	335–700	$\cong 85$	Fe_2O_3	285–395	$\cong 85$	Fe_2O_3	265–360	$\cong 100$	Trace
Co(II)	305–700	$\cong 80$	CoO	295–960	$\cong 80$	Co_3O_4+C†	280–375	$\cong 100$	Trace
Ni(II)	340–700	$\cong 80$	NiO	230–690	$\cong 80$	Ni + NiO	250–325	$\cong 100$	Trace
Cu(II)	305–700	$\cong 80$	CuO	270–835	$\cong 80$	CuO	200–260	$\cong 100$	Trace
Zn(II)	390–700	$\cong 80$	ZnO	285–960	$\cong 70$	ZnO + $ZnCO_3$	255–320	$\cong 100$	Trace
Ga(III)	—	—	—	50–180	—	GaO + C†	265–325	$\cong 100$	Trace
Cd(II)	345–900	$\cong 70$	CdO	385–950	100	None	340–450	$\cong 100$	Trace
In(III)	—	—	—	285–1000	$\cong 75$	In_2O_3	265–350	$\cong 100$	Trace
Ba(II)	—	—	—	—	—	—	425–650	$\cong 5$	Large, Black

---

* As characterized by weight loss of the anhydrous metal oxinate.

† Carbonaceous materials.

for the trivalent metal oxinates, Al, Cr, Ga, and In, are widely dispersed with no apparent interrelationship. Furthermore, the Group III metals, Al, Ga, and In, give a V-shaped plot.

Figure 2 presents the pyrolysis data of Charles and Langer from Table 2, obtained on metal oxinates in vacuum at a heating rate of about 2·5°C per min. Here, when the atomic number of the metal is plotted as a function of the temperature at the start of the weight-loss, for the anhydrous oxinates there is excellent agreement between the thermal stability of the complexes and the periodicity of the central metal. The oxinates of the divalent transition metals Mn, Co, Ni, and Cu give a perfectly straight line, almost vertical, in which there is a decrease in thermal stability of approximately 155°C in going from atomic number 25 (Mn) to 29 (Cu). In contrast to the plots obtained for the trivalent metal and Group III metal complexes heated in air, the points for the oxinates of Al, Cr, Fe, Ga, and In give an almost perfectly horizontal straight line in vacuum. This line, which intersects the temperature axis at 265°C,

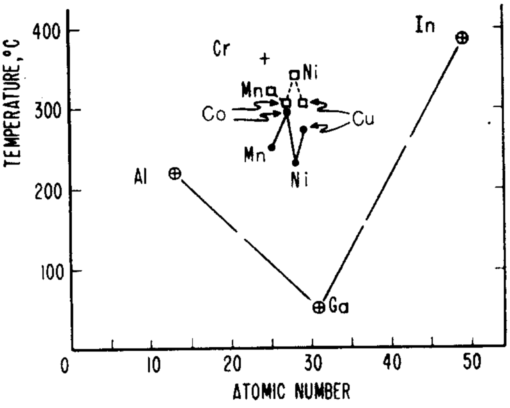


Fig. 1.—Temperature at start of weight-loss of metal oxinates versus atomic number of metal.

	Heating rate in air	
	3°C/min	*5°C/min*
Divalent transition metal	□	●
Trivalent Cr		+
Group III metals		⊕

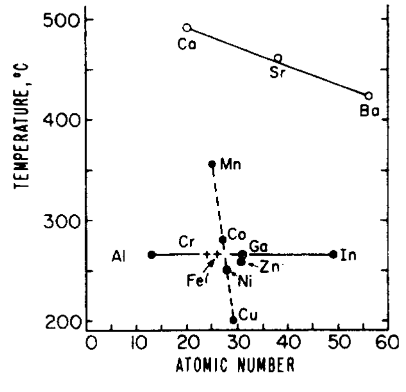


Fig. 2.—Correlation between temperature at start of weight-loss of metal oxinates and atomic number of metal.

Heating rate in vacuo., ≃ *2·5°C/min*

Divalent transition metals	●
Trivalent Cr and Fe	+
Group II metals	○
Group III metals	⊕

indicates that for these trivalent metal oxinates the thermal stability is independent of the position of metal in the periodic table. The data for the Ba, Sr and Ca oxinates are also presented and show reasonably good conformance to a straight line fit. Of special interest with respect to the thermal stability of these compounds is the fact that the Group II metal oxinates listed show a pronounced increase in the temperature required to initiate weight-loss. For the barium oxinate, this temperature is approximately 425°C and for the calcium oxinate it is close to 490°C.

The relationship between the electronegativity of the metal and the temperature at which the anhydrous metal oxinates begin to lose weight is shown in Fig. 3. The

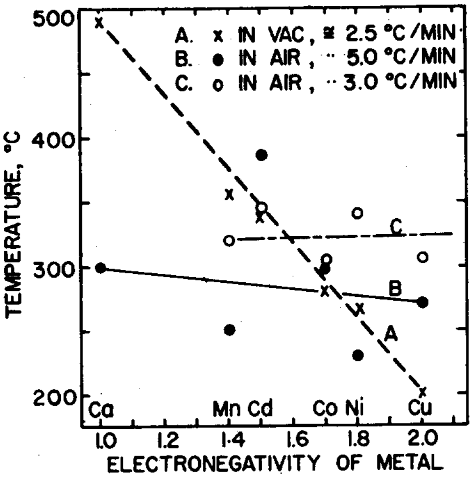


Fig. 3.—Temperature at start of weight-loss of metal oxinates versus electronegativity of metal.

electronegativity values for the metals have been taken from the work of Gordy,(23) Pauling,(24) and Haissinsky.(25) It is interesting to note that for the metal oxinates heated in vacuum a straight line is obtained when the electronegativity of the metal is plotted as a function of the temperature at which weight-loss was initiated (Curve A). Thus, for the divalent metal oxinates of Cu, Ni, Co, Cd, Mn, and Ca, covering the electronegativity range of 2·0–1·0, there is a marked increase in temperature with decreasing electronegativity. In the case of the copper oxinate the weight loss begins at 200°C, while calcium oxinate starts to lose weight at 490°C. When these oxinates are heated in air no such linear relationship is apparent. The data in Fig. 3 also indicate that the thermal stability of the metal oxinates in air is dependent on the rate of heating the samples.

In general, samples heated in air at 5°C/min (Curve B) start to lose weight at a temperature somewhat below those heated in air at 3°C/min (Curve C). From examination of data in the literature this trend also appears to hold for the oxime and cupferron

(23) W. Gordy, *J. Chem. Phys.* **14**, 305 (1946).

(24) L. Pauling, *J. Amer. Chem. Soc.* **54**, 3570 (1932); *The Nature of the Chemical Bond*, Cornell, Ithica, New York (1960).

(25) M. Haissinsky, *J. Phys. Radium* **7**, 7 (1946).

complexes in which the critical temperature is lower when the heating rate is faster. Returning to Fig. 1 momentarily, it will be recalled that at the slower heating rate the critical temperatures of the oxinates of the Cu, Ni, Co, and Mn are also higher than at the more rapid heating rate. It is worthwhile to notice in Fig. 3 that when the oxinates were heated in air no straight-line plots were actually obtained, although "average" straight lines have been drawn for comparative purposes. Furthermore, at the faster heating rate the scatter of experimental points is considerably greater than at the slower rate. It is now apparent that the reason for the disagreements in the literature over the correctness of the thermograms reported may be explained on the basis of the different rates of heating the samples in air.

On the basis of the assembled information it may be possible to draw some inferences concerning the mechanisms involved in the weight-loss of the samples. In general, at least two mechanisms appear to be operative. Examination of Table 2 reveals that except for cadmium oxinate heated at 5°C/min some metallic oxide is left in the residue after pyrolysis in air. MILLER and MCLENNAN(26) who studied the thermal degradation of the dihydrated magnesium oxinate proposed that the oxinate decomposed to give MgO, H_2O, and the bis-oxine ether, $NH_6C_9—O—C_9H_6N$, and perhaps other products. The work of DUVAL(20) on the pyrolysis of nickel oxinate suggests that the organic portions of the molecules are decomposed to smaller fragments and volatilized leaving metallic nickel which is then oxidized to nickel oxide. His thermogram of this complex shows a minimum in the weight-loss–temperature curve at 365°C and an increase in weight of the residue as the temerature is raised to above 370°C. The residue was analyzed as a mixture of Ni and NiO. The presence of NiO in this type of pyrolysis was also confirmed by the results of BORREL and PARIS.(21) For the oxinates of Mn, Co, and Ga there is evidence, based on analysis of the residue, that the ligand is also decomposed into smaller carbonaceous units.

The cleavage at the metal–ligand site is strongly suggested because of the presence of metal oxide in the residues. Here the metal could abstract an oxygen atom from the ligand in the process of separation, leading to the formation of a metal oxide and perhaps a bis-oxine ether molecule, as has been proposed for the magnesium oxinate.(26) On the other hand the ligand could break free of the co-ordinated metal entirely, as the evidence of Duval suggests for the nickel oxinate. In this case the metal might be oxidized to the oxide by the oxygen in the air.

The gallium oxinate is interesting in that it starts to decompose at 50°C while all the remaining oxinates heated in air at 3°C/min began to lose weight between 220°C and 385°C. This complex merits further study, particularly in light of the interesting report by SIEVERS and collaborators(27) that chromium complexes of 2,4-pentanedione derivatives may be analyzed by gas chromatography at 35°C.

For the experiments run in vacuum, still another mechanism may be prevalent. CHARLES and LANGER(22) have suggested that volatilization of the metal oxinates that leave no residue on pyrolysis, proceeds by a simple sublimation mechanism. However, where significant residues remained after heating, as in the case of calcium and barium oxinates, the major process may be one of decomposition. The presence

---

(26) C. C. MILLER and I. C. MCLENNAN, *J. Chem. Soc.* **656** (1940).

(27) E. SIEVERS, R. W. MOSHIER, and B. W. PONDER, Paper presented at the American Chemical Society Meeting, Washington, D.C., March 1962.

of large amounts of carbon, nitrogen, metal and metal oxide in these residues supports this view.

Prior to initiating the thermogravimetric analyses of the co-ordination polymers it was important to evaluate the reliability and reproducibility of the experimental values obtained with the Eyraud balance and auxiliary recording apparatus. This was done by analysing zinc oxinate under conditions similar to those used by CHARLES and LANGER.(22) There was very good agreement between the two sets of data, and furthermore duplicate runs on zinc oxinate with the Eyraud balance gave almost identical thermograms.

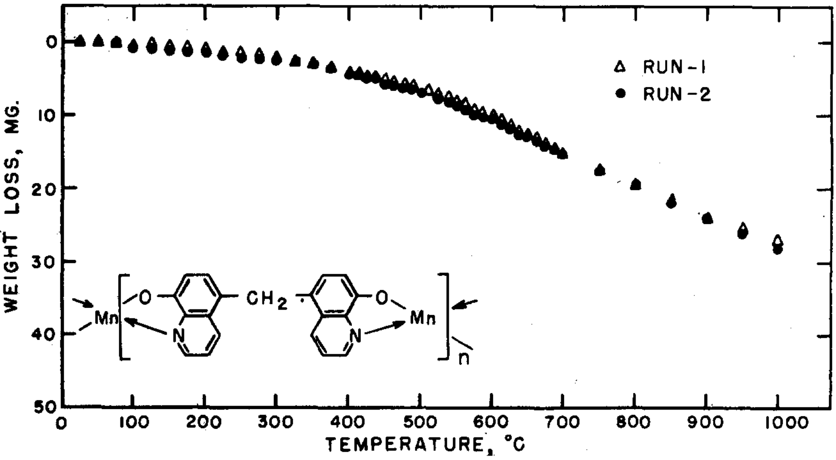


FIG. 4.—Thermograms for Mn-bis(8-hydroxy-5-quinolyl)-methane polymer.

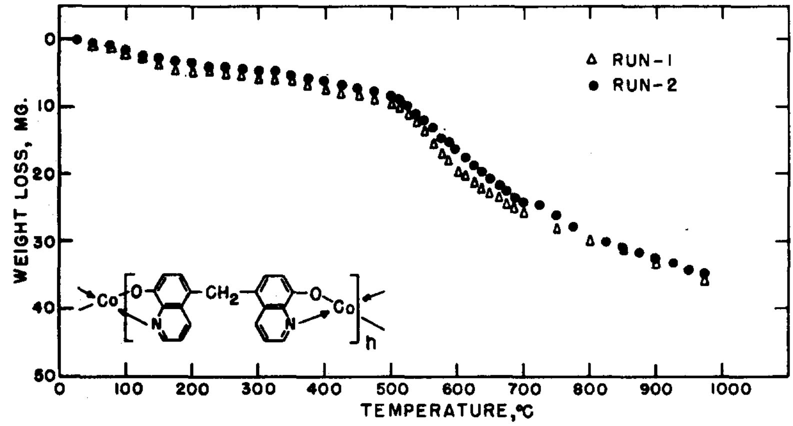


FIG. 5.—Thermograms for Co-bis(8-hydroxy-5-quinolyl)-methane polymer.

The thermograms obtained in our laboratory for the Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) co-ordination polymers of the bis(8-hydroxy-5-quinolyl)-methane are shown in Figs. 4–8, respectively. Each figure contains the weight-loss data as a function of temperature obtained during two separate experiments performed on different days. The data have been summarized in Fig. 9, where each of the curves

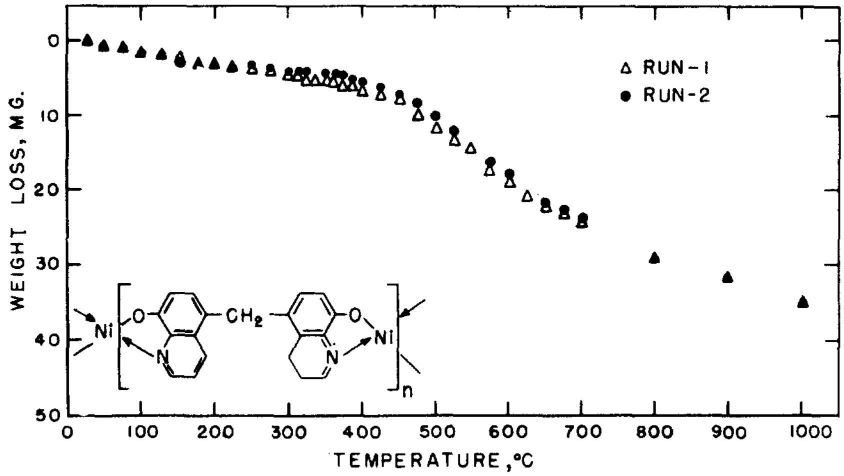


FIG. 6.—Thermograms for Ni-bis(8-hydroxy-5-quinolyl)-methane polymer.

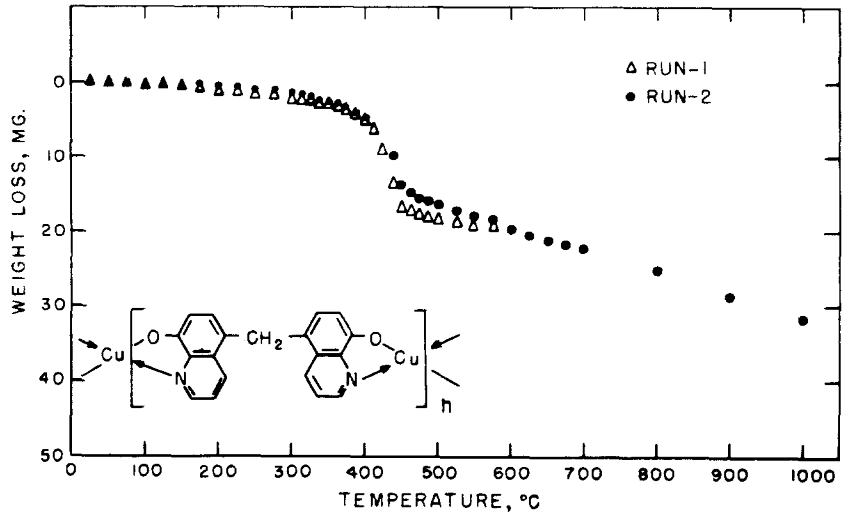


FIG. 7.—Thermograms for Cu-bis(8-hydroxy-5-quinolyl)-methane polymer.

represents the average of two independent runs. The thermogram of zinc-8-hydroxyquinolate is included in this figure for the sake of comparison. The marked stabilization that occurs in going from zinc-8-hydroxyquinolate to the zinc co-ordination polymer of bis(8-hydroxy-5-quinolyl)-methane is immediately apparent from the two curves shown in Fig. 9. The zinc polymer begins to lose weight at an accelerated rate at a temperature approximately 250°C above that of zinc oxinate. Another significant difference is that the loss in weight of zinc oxinate amounts to approximately 90 per cent, even at 375°C, while at this temperature the zinc co-ordination polymer has lost less than 5 per cent of its original weight. On continued heating at somewhat higher temperatures essentially 100 per cent of the zinc oxinate is volatilized through a sublimation mechanism. Evidence of sublimation was obtained by analysing a portion of the volatile products collected during the run. The sublimed

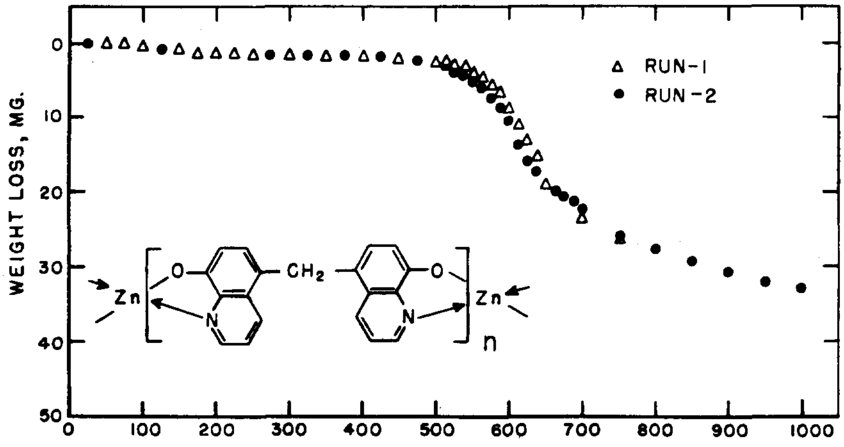


FIG. 8.—Thermograms for Zn-bis(8-hydroxy-5-quinolyl)-methane polymer.

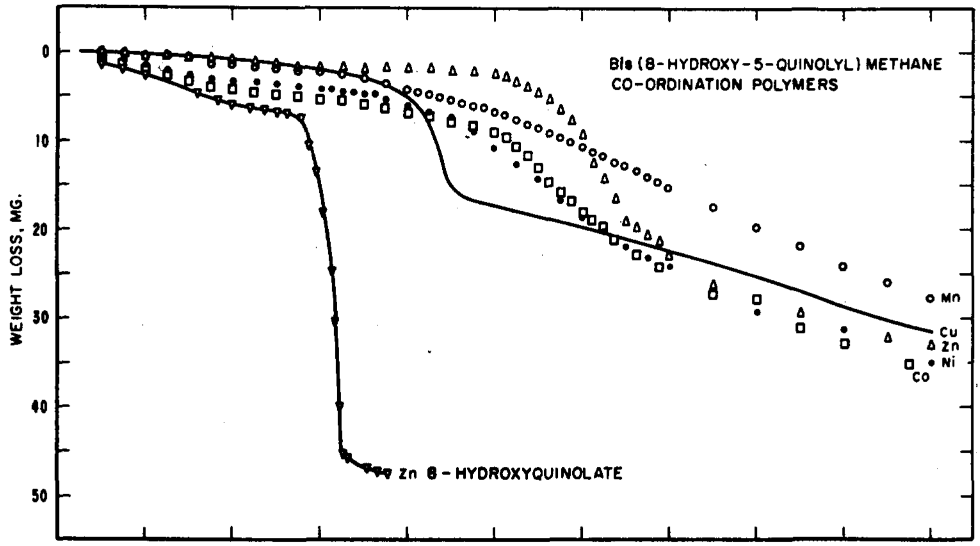


FIG. 9.—Thermograms for bis(8-hydroxy-5-quinolyl)-methane co-ordination polymers and zinc 8-hydroxyquinolate.

yellow powder gave an infra-red spectrum that was identical with a pattern obtained on a sample of the zinc oxinate. Interestingly enough, at 1000°C about 70 per cent by weight of the zinc polymer has been volatilized. The remaining residue was heated at this fixed temperature for another 10 hr. The weight-loss curve for this portion of the experiment is given in Fig. 10. As may be seen from this figure, the residue lost weight at a uniform rate during the first 5 hr at 1000°C. After this time the rate of weight loss decreased markedly, and no further change in weight was detected after 7 hr. In all, there was a weight-loss of about 99 per cent of the original sample. Examination of the platinum crucible after the run showed only a trace of residue.

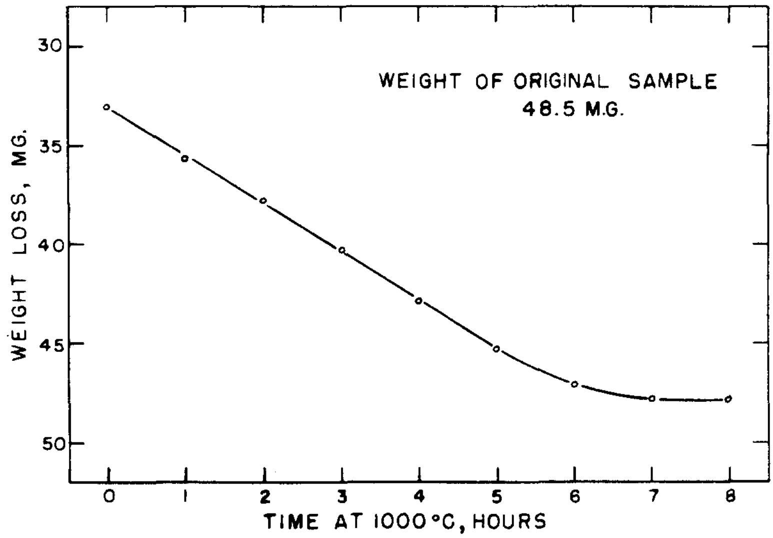


FIG. 10.—Weight-loss of residue from Zn-bis(8-hydroxy-5-quinolyl)methane polymer.

TABLE 3.—PERCENTAGE OF SAMPLE VOLATILIZED DURING PYROLYSIS OF CO-ORDINATION POLYMERS
(Heating Rate: 2·5°C/min in vacuum)

Temp. (°C)	Percentage volatilized				
	Bis(8-hydroxy-5-quinolyl)-methane polymers				
	Zn	Cu	Ni	Co	Mn
100	1·2	0·5	3·6	4·2	0·8
200	2·5	1·8	6·8	8·9	2·7
300	3·4	3·7	8·9	10·8	4·5
325	3·4	4·8	9·5	11·1	5·3
350	3·4	5·9	10·0	12·0	5·9
375	3·4	7·8	11·2	13·0	7·0
400	3·8	10·8	12·6	14·1	8·1
425	4·0	16·7	14·2	15·1	9·2
450	4·1	32·0	15·6	16·2	10·8
475	4·4	35·2	18·7	17·0	11·9
500	5·2	36·3	22·9	18·6	13·3
525	6·8	37·6	26·7	21·6	15·0
550	9·4	39·0	29·9	26·6	17·2
575	13·2	40·4	35·1	32·6	19·3
600	19·8	40·5	38·9	37·4	21·5
625	32·4	42·0	42·7	41·3	23·6
650	39·5	43·3	45·9	45·2	25·9
675	44·7	44·6	48·4	48·4	28·5
700	47·8	46·0	51·0	51·2	31·1
800	57·4	51·2	61·4	61·0	39·9
900	63·9	48·8	66·6	67·8	48·9
1000	68·0	64·5	73·1	73·0	56·1

These findings suggest that the polymer may have decomposed to give volatile organic fragments and finally metallic zinc or ZnO which volatilized at 1000°C. There was no evidence of the polymer's decomposing to zinc oxinate which then sublimed.

The thermogravimetric data in Figs. 4–9 have been presented on an absolute weight-loss basis in keeping with the widespread practice of reporting the results of thermogravimetric analysis of inorganic and co-ordination compounds. However, there is advantage in expressing thermogravimetric analysis data as a percentage weight-loss, and Table 3 presents the results of the relative thermal stability of the co-ordination polymers in these terms. These data have been plotted in Fig. 11 on the basis of the percentage of the sample volatilized. It is interesting to note that while there are significant differences among the curves in the temperature range of approximately 400–700°C, above 800°C the slopes of all the co-ordination polymers are quite similar. At a 1000°C the percentage weight loss of the Zn, Cu, Ni, Co, and Mn co-ordination polymers are 68·0, 64·5, 73·1, 73·0 and 56·1, respectively.

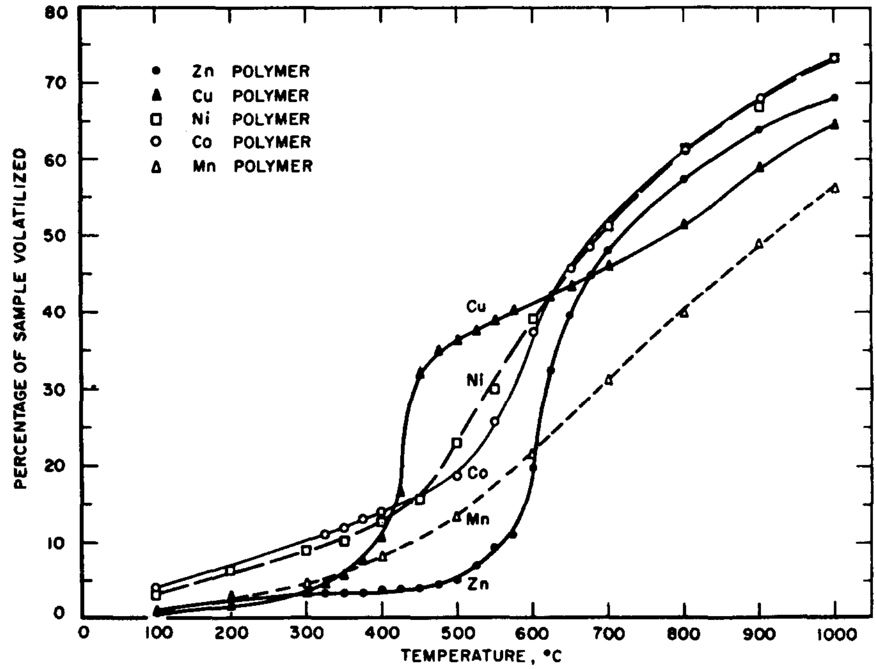


FIG. 11.—Relative thermal stability of co-ordination polymers of bis(8-hydroxy-5-quinolyl)-methane.

The data for each of the duplicate runs indicated in Figs. 4–8 were plotted on a ten-fold expanded scale in order to locate more precisely the decomposition temperature. The intersection of the two lines drawn through the points on the curve before and after the major change in slope was arbitrarily taken as the decomposition temperature. These data are reported in Table 4, where the results of each run and the average values for each polymer are listed. From the columns headed Run 1 and Run 2 one may obtain a rough measure of the precision of the measurement. The differences between runs range from 10°C for the Cu and Co polymers to a maximum of 20°C for the Zn and the Ni polymers. No detectable break in the thermogram curve for the Mn co-ordination polymer was observed by the technique used and thus no decomposition temperature is listed for this polymer. Based on the decomposition temperature and the thermograms the thermal stability of the transition metal co-ordination polymers studied may be arranged in the order of increasing stability: Cu $<$ Ni $<$ Co $<$ Mn. As will be shown shortly, this is also the sequence for the thermal stability of the chelates of 8-hydroxyquinoline.

MALEY and MELLOR[28] have reported on the hydrolytic stability constants of the 8-hydroxyquinolates in 70 per cent dioxane–water solution. These authors determined the order of stability for transition metal oxinates to be Cu $>$ Ni $>$ Co $>$ Mn, just opposite to that reported here for thermal stability. These results point up one of the dilemmas facing polymer chemists, that in attempting to synthesize a polymer having high thermal stability one may be forced to sacrifice, to some extent at least, other important physical and chemical properties. Until a co-ordination polymer is prepared that will provide general stability to the system, including thermal and hydrolytic stability, the use of different polymers may be needed to satisfy diverse and seemingly conflicting requirements.

TABLE 4.—TEMPERATURE AT START OF ACCELERATED WEIGHT LOSS FOR CO-ORDINATION POLYMERS

Co-ordination polymer	Temperature (°C)		
	Run 1	Run 2	Average
a. Zn(II)	500	520	510
b. Cu(II)	415	425	420
c. Ni(II)	450	470	460
d. Co(II)	505	515	510
e. Mn(II)	*	*	—

* Because of the smooth curvature of the thermogram, Fig. 9, the decomposition temperature as defined in the text could not be detected.

It is interesting to note that the order of the stability constants for some of the transition metal complexes coincides with the second ionization potentials for these metals; Cu (20·29 eV) $>$ Ni (18·15 eV) $>$ Co (17·05 eV) $>$ Mn (15·64 eV). In addition, MALEY and MELLOR reported that the stability constants for the zinc and cobalt oxinates were just about equal. One finds a similar situation in comparing the second ionization potentials of these two metals, Zn (17·96 eV) and Co (17·05 eV). The behaviour of the chelates of 8-hydroxyquinoline as measured by the stability constants may also be related to the electron configurations in the $3d$ orbitals. In proceeding from the d^5 case of Mn(II) to the d^9 case of Cu(II) the electron density in the $3d$ orbitals is increased, a condition which could make it more difficult for the oxinate to undergo nucleophilic reactions.

The state associated with the half-filled d^5 electron configuration of Mn(II) is quantum mechanically the most stable energy state, and the 8-hydroxyquinolines containing this element are found to be thermally the most stable.

---

(28) L. E. MALEY and D. P. MELLOR, *Austral. J. Sci. Res.* **2** A, 92 (1949).

progressive decrease in the thermal stability of the co-ordinated systems containing Co(II), Ni(II), and Cu(II), metallic ions whose 3*d* configurations depart in a regular manner from the stable half-filled state. Zinc(II) with completely filled 3*d* orbitals is known to be in a more stable energy state than Cu(II), and one finds that the zinc 8-hydroxyquinolates also have greater thermal stability than the copper compounds. Of course, these relationships are qualitative in nature, but they are consistent with the observed behaviour of these systems.

The average values for the decomposition temperatures of the co-ordination polymers listed in Table 4 have been plotted in Fig. 12, Curve A, as a function of the atomic number of the central metal atom. It should be restated that the atomic number is used here to index more fundamental periodic properties of the metal such as the charge-to-radius ratio. When Curve A is compared with Curve B, representing the data taken from literature on the metal chelates of 8-hydroxyquinoline, a number of significant relationships between the two systems emerge. First, the shapes of the two curves are quite similar, with the points for the zinc species in each curve departing from the straight line plot obtained for the other transition metals. Secondly, as mentioned earlier, an unmistakable trend is apparent in each curve such that the thermal stability of the system decreases with an increase in atomic number in going from Mn to Cu.

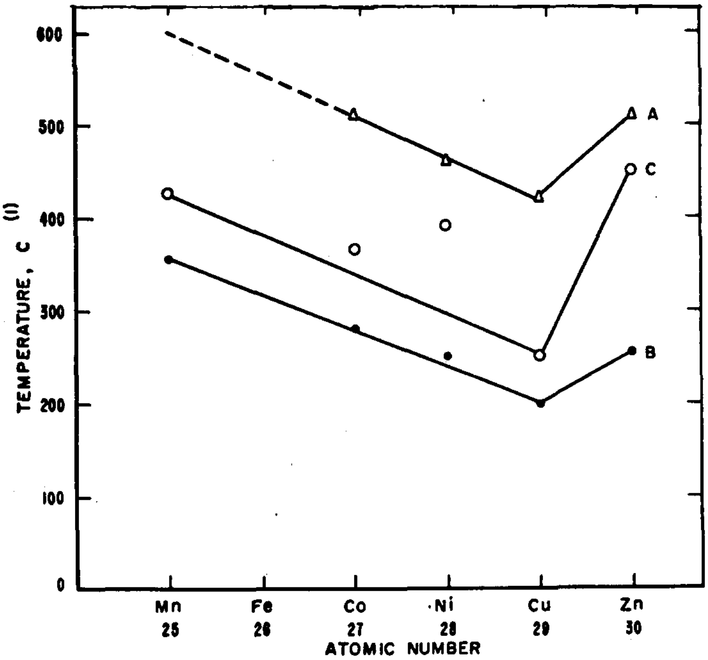


Fig. 12.—Thermal stability as a function of atomic number.
(1) Temperature at start of accelerated weight-loss.
A. Bis(8-hydroxy-5-quinolyl)methane co-ordination polymers.
B. 8-hydroxyquinolates
C. Polyvinylphthalic acid metal polymers.

If one considers the 8-hydroxyquinolates designated in Curve B as monomer units, and the co-ordination polymers represented in Curve A as a succession of these units linked together by methylene bridges, then Fig. 12 depicts the increase in thermal stability that has been conferred on the different co-ordination complexes by virtue of the polymerization process. The results reflected in Curve A support the hypothesis that the weight-loss measures the volatilization of products arising from decomposition at the metal–ligand site. Furthermore, evidence for cleavage at the metal–ligand position is provided by the data in Table 5, which give the percentage residue remaining after the sample had been heated in vacuum at 1000°C for 8 hr. For example, the zinc co-ordination polymer, whose weight-loss at 1000°C is depicted in Fig. 10, yielded a residue of only 1·5 per cent. Decomposition of the polymer by the above process could give rise to metallic zinc or zinc oxide, each capable of volatilization under the pyrolysis conditions. The weight-loss data do not appear to be related to the formation of zinc oxinate through rupture of the methylene bridge because in such a case the decomposition temperature would have been that reported for the zinc oxinate. The percentage residue from the nickel polymer after prolonged heating at 1000°C was within 0·1 per cent of the nickel content of the original sample based on the formula $[NiL]_n$ and within 0·8 per cent nickel content assuming $[NiL{\cdot}H_2O]_n$, where L represents the ligand. The results shown in Table 5 for the remaining co-ordination polymers do not agree with the calculated values as well as those for the nickel sample but the results are of the right order of magnitude.

TABLE 5.—TOTAL PERCENTAGE OF SAMPLE VOLATILIZED AFTER PYROLYSIS AT 1000°C FOR 8 hr

Co-ordination polymer	Elemental analysis, calc.		After pyrolysis at 1000°C	
	Metal (%)	C, H, N, O (%)	Residue (%)	Volatilized (%)
Zn	17·8	82·2	1·5	98·5*
Cu	17·4	82·6	14·2	85·8
Ni	16·3	83·7	16·4	83·6
Co	16·4	83·6	18·8	81·2
Mn	15·4	84·6	17·0	83·0

* May include metallic zinc or zinc oxide formed during decomposition of the co-ordination polymer.

The fact that analysis of the residues revealed the presence of metal oxides may lend support to the idea that oxides are formed during thermal decomposition. However, it may be that these oxides were formed at the end of the thermogravimetric run when the system was exposed to the atmosphere. Special precautions that had not been employed at the end of the thermogravimetric runs will be taken in subsequent work to prevent the possible conversion of metal residues to metallic oxides as a result of atmospheric oxidation. It is also planned to employ thermogravimetric equipment that will permit the collection of decomposition products, the detailed analysis of which should provide more definite information about the decomposition mechanism.

The data in Curve C, Fig. 12, for polyvinylphthalic acid metal polymers, taken from a recent paper by WINSLOW and LAFERRIERE(29) shows how this polymer compares with the co-ordination polymers of the bis-8-hydroxyquinolines. Although the precision for each point in Curve C could not be ascertained the general trend is in agreement with the plots obtained for the hydroxyquinoline systems. It is worth-

---

(29) E. C. WINSLOW and A. LAFERRIERE, *J. Polymer Sci.* **60**, 65 (1962).

while to report that the co-ordination polymers of bis(8-hydroxy-8-quinolyl)-methane are more stable to heat than are those of polyvinylphthalic acid, the difference being in the order of about 150°C for the copper and cobalt polymers. Fig. 12 clearly demonstrates the relationship that exists between the thermal stability of these co-ordination complexes and polymers and the atomic number of the central metals. This information may be used to advantage in attempting to predict the thermal behaviour of co-ordination systems when only a minimum of experimental data are available and to evaluate the accuracy of thermogravimetrically derived decomposition temperatures of co-ordination compounds by noting the magnitude of the departure of one or more points from a linear plot.

Infra-red analysis

References in the literature to infra-red spectra of the chelates of 8-hydroxyquinoline are extremely scarce, in contrast to the vast amount of data that have been published on the spectra of other compounds. In what appears to be the first paper on this subject, STONE(30) reported the infra-red spectra of the anhydrous and dihydrated magnesium-8-quinolate as well as those for the anhydrous and monohydrated bismuth-8-quinolate. He concluded that the magnesium and bismuth-8-quinolates had about the same types of bonding because of the similarity of the two spectra. COTTON(31) has pointed out that while this may be correct, the magnesium oxinate dihydrate probably is characterized by a co-ordination number 6 with two water molecules functioning as ligands. COPELAND and collaborators(32) studied the infra-red spectrum of zinc oxinate and ascribed the reduction in intensity or disappearance of the absorption bands at 1408 and 1351 cm^{-1} upon chelation of zinc with 8-hydroxyquinoline to the replacement of the phenolic hydrogen by zinc. The infra-red spectra of the metal complexes of 8-hydroxyquinoline and some of its methyl-substituted derivatives have been reported by CHARLES and co-workers(33) who perhaps have made the most extensive infra-red spectroscopic study of the oxine-type co-ordination compounds. The effect of the metal atom in the complex on the position of the absorption band in the 1100 cm^{-1} region was noted, and a correlation was shown to exist between the position of this band and the atomic number of the metal.

The spectra of the ligand and the divalent transition metal co-ordination polymers of bis(8-hydroxy-5-quinolyl)-methane are given in Fig. 13 for the systems containing Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). While the spectrum of the ligand contains a moderately strong absorption band at about 3340 cm^{-1}, the region of the OH vibration frequency, this band has virtually disappeared in the co-ordination polymers, indicating that co-ordination has taken place. The patterns of all the polymers show an absorption band at 1573–1575 cm^{-1}, somewhat displaced from the 1580 cm^{-1} frequency which occurs in the ligand. For the ligand 8,8′-dihydroxy-5,5′-biquinolyl,

---

(30) K. G. STONE, *J. Amer. Chem. Soc.* **76**, 4997 (1954).

(31) F. A. COTTON, *Infra-red Spectra of Transitional Metal Complexes*, Chap. 5, p. 391, *Modern Co-Ordination Chemistry* (Edited by J. LEWIS and R. G. WILKINS) Interscience, New York (1960).

(32) H. I. COPELAND, G. M. BRAUER, W. T. SWEENEY and A. F. FORZIATI, *J. Res. Natl. Bur. Standards* **55**, 133 (1955).

(33) R. G. CHARLES, H. FREISER, R. FRIEDEL, L. E. HILLIARD, and W. D. JOHNSTON, *Spectrochim. Acta* **8**, 1 (1956).

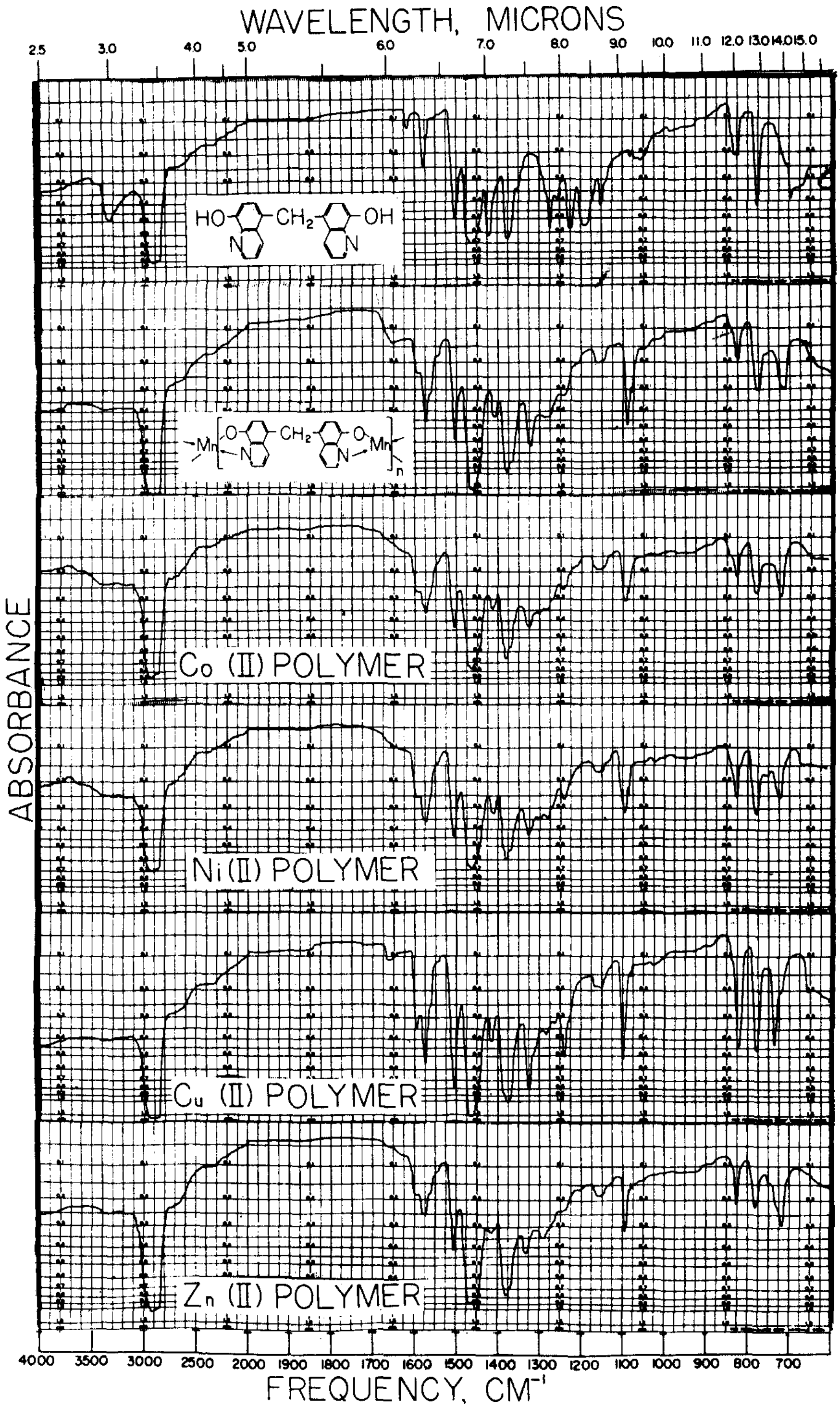


FIG. 13.—Infra-red spectra of bis(8-hydroxy-5-quinolyl)-methane and the Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) co-ordination polymers.

the absorption bands in this region have been assigned to the vibrations in the —C═N— group in the quinoline ring.[11] Although qualitatively the shapes of many of the absorption bands in the spectra of the polymers differ somewhat, examination of Fig. 13 indicates that their peak frequencies are actually very similar.

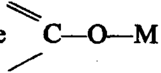
The spectrum of bis(8-hydroxy-5-quinolyl)-methane has a strong band at 1420 cm^{-1}, due in all likelihood to the OH vibration, but none of the co-ördination polymers have a band at this frequency. All spectra show a reduced absorption band in the 1405–1415 cm^{-1} region. CHARLES and co-workers[33] have suggested that the absorption band at approximately 1100 cm^{-1} may be assigned to C—O stretching vibration frequencies at the  $C{-}O{-}M$ site in chelates of 8-hydroxyquinoline. For the co-ordination polymers of Mn, Co, Ni, and Cu this absorption band is shifted to slightly higher frequencies with increasing atomic number of the central metal.

TABLE 6.—FREQUENCIES OF THE INFRA-RED ABSORPTION BANDS IN THE 1080–1100 CM^{-1} REGION

Polymer	Peak max. of polymer (cm^{-1})		Ionic Radius (A°)	Ionic potential q/r	Electro-negativity
	Original spectrum	Expanded scale			
Mn(II)	1088·5	1089·8	0·91	2·2	1·4
Co(II)	1094·0	1093·5	0·82	2·4	1·7
Ni(II)	1094·5	1094·8	0·78	2·6	1·8
Cu(II)	1098·0	1098·3	0·69	2·9	2·0
Zn(II)	1094·5	1094·6	0·83	2·4	1·5

In the 1080–1100 cm^{-1} region, where the metal in the co-ordination polymer is apparently influencing the stretching vibration frequency of the absorption band attributed to the C—O group, the scale was quite reduced on the original spectrum and it was somewhat difficult to locate precisely the band frequency. Using a four-fold scale expansion these frequencies were essentially confirmed, as shown in Table 6. These data are plotted in Fig. 14 where the frequency of the absorption band peaks are shown as a function of the atomic number of the central metal. Except for Mn and Ni the two sets of data are in good agreement. The points for Mn, Co, Ni, and Cu fall essentially on a straight line while Zn deviates from the line and occurs at a lower frequency than Cu. The shape of this plot is remarkably similar to the one obtained for these same co-ordination polymers when the decomposition temperatures were plotted versus the atomic number.

The data in Table 6 show that the frequencies of the infra-red absorption bands of the co-ordination polymers in the 1100 cm^{-1} region are related to such fundamental periodic properties of the metals as ionic radii, ionic potentials, and electronegativities. For example, because Cu(II) is more electronegative than Mn(II) it would be expected to attract the electrons in oxygen more strongly and give rise to a bond with more covalent character. The q/r ratio is also a measure of the tendency of the cations to attract electrons, those with high q/r values exhibiting this tendency to a larger extent and forming bonds with enhanced covalency. These factors, as well as the presence of the metal-nitrogen bond in the five-membered ring formed on chelation,

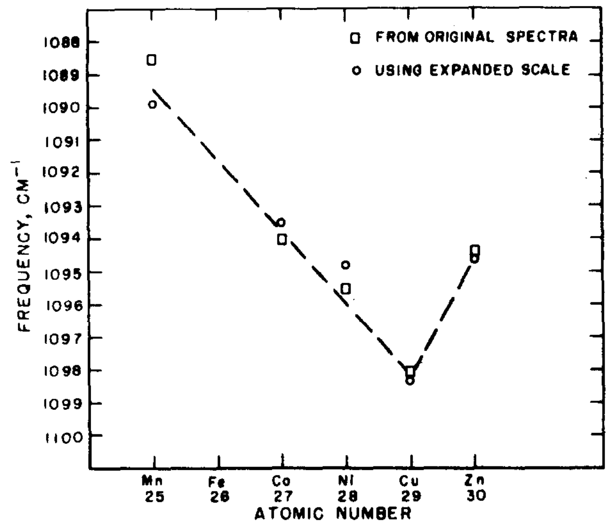
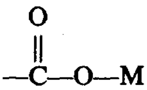


FIG. 14.—Effect of central metal on infra-red absorption of bis(8-hydroxy-5-quinolyl)-methane polymers.

could account for the increase in the frequency of the peak maximum from 1089·8 to 1098·3 cm^{-1} for the Mn(II) and the Cu(II) co-ordination polymers respectively.

SIEVERS and BAILAR[34] have recently reported that as the O—M bond in the  $\overset{\overset{\displaystyle O}{\|}}{—C}—O—M$ group in the chelates of polyaminocarboxylic acids becomes more covalent there is a shift to higher frequencies in the infra-red absorption band due to the carbonyl group. Thus in the potassium salt of ethylenediaminetetraacetic acid the peak maximum was measured at 1595 cm^{-1} while in the Co(III) chelate of EDTA the absorption maximum occurred at 1650 cm^{-1}. An examination of the infra-red and thermogravimetric data on the co-ordination polymers of bis(8-hydroxy-5-quinolyl)-methane indicates that as the absorption band maximum in the 1100 cm^{-1} region shifts to higher frequencies there is a decrease in the decomposition temperatures of the polymers. As more data become available it should be possible to formulate a more complete explanation for the thermal behaviour of the co-ordination polymers.

Acknowledgement—The valuable discussions with Professor J. C. BAILAR, JR. of the University of Illinois, and his generous co-operation in the course of this work are gratefully acknowledged.

[34] R. E. SIEVERS and J. C. BAILAR, JR., *Inorg. Chem.* **1**, 174 (1962).