Preparation and Study of Polymeric Metal Chelates of Poly(8-hydroxyquinoline-7,5-diylethylene)

Bhupendra S. Patel[a]; Manhar J. Lad[a]; Shanti R. Patel[a]

[a] Department of Chemistry, Sardar Patel University Vallabh, Vidyanagar, India

PLEASE SCROLL DOWN FOR ARTICLE

Preparation and Study of Polymeric Metal Chelates of Poly(8-hydroxyquinoline-7,5-diylethylene)

BHUPENDRA S. PATEL, MANHAR J. LAD, and SHANTI R. PATEL

Department of Chemistry
Sardar Patel University
Vallabh Vidyanagar 388120, India

ABSTRACT

Polymeric chelates prepared by reacting a solution of poly(8-hydroxyquinoline-7,5-diylethylene) with various metal ions in acetic acid are characterized by elemental analysis, IR and UV reflectance spectral studies, and magnetic susceptibility measurements. These properties are explicable in terms of their expected structures. TGA and electrical conductivity of these polychelates are compared mutually and also with those of the parent polymer sample. The polymeric chelates are found to be less stable than the parent polymer sample.

INTRODUCTION

The chelating properties of 8-hydroxyquinoline have been a subject of very active investigation [1-4]. Polymers prepared from 8-hydroxyquinoline have also been extensively investigated. Pennington and Williams [5] and also DeGeiso et al. [3] synthesized 8-hydroxyquinoline-formaldehyde polymers and showed that these poly-(oxine-methylene)s were capable of forming polymeric metal chelates with metal ions in a fashion similar to that of oxine itself. A poly(8-hydroxyquinolinediyl-7,5-ethylene) (I) apparently has a steric advantage over a poly(8-

(I)
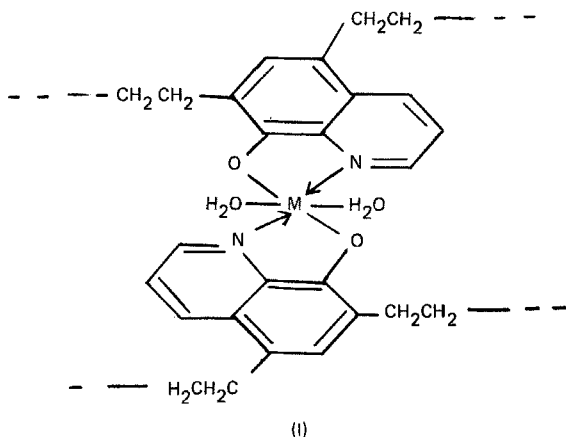
M = Ni(II), Mn(II), Zn(II), and CO(II) Co(II)

hydroxyquinolinediyl-7,5-methylene) in having a larger separation of
the 8-hydroxyquinoline units in two successive repeating units of the
polymer chain. The ion-exchange properties of I have been reported
by Patel and Patel in an earlier communication [6]. The work de-
scribed in the present communication deals with a systematic study of
the properties of polychelates of I. A sample prepared from equimolar
amounts of 8-hydroxyquinoline and 1,2-dichloroethane in the presence
of aluminum chloride having $\overline{M}_n$ = 6200 ± 100 and which is reported in
an earlier communication by Patel and Patel was selected [1]. Poly-
meric chelates listed in Table 1 are prepared by reacting this poly-
meric ligand with the required metal salts in aqueous acetic acid.
The properties of the resulting polymeric metal chelates are discussed
in relation to those of the parent polymer.

EXPERIMENTAL

Preparation of Polymeric Metal Chelates

A solution of the required metal salt (0.01 mol) in 20 mL of 3:2
(v/v) acetic acid-water was treated with a solution of the polymer sam-
ple I (0.01 mol) in 40 mL of the same type of mixed solvent. The pH
of the solution was adjusted to 5 by adding an adequate amount of 0.1
M HCl when the polymeric chelate separated out in the form of a sus-
pension. The latter was digested for about an hour on a water bath and
filtered. The solid was washed with boiling water to remove free metal
ion, then with alcohol (25 mL), and subsequently with acetone (25 mL).

TABLE 1. Results of Metal Composition and Magnetic Measurements

Polymeric metal chelate	% of metal		MW of repeat unit (g)	μ_{eff} (BM)^a	Geometry	T_d^b (°C)
	Theoretical	Observed				
[Cu(C$_{22}$H$_{18}$O$_2$N$_2$)]$_n^c$	16.50	15.55	405	2.13	Square plannar	335
[Co(C$_{22}$H$_{18}$O$_2$N$_2$)2H$_2$O]$_n$	14.77	13.48	437	4.93	Octahedral	350
[Ni(C$_{22}$H$_{18}$O$_2$N$_2$)2H$_2$O]$_n$	14.70	13.44	437	3.00	Octahedral	345
[Mn(C$_{22}$H$_{18}$O$_2$N$_2$)H$_2$O)]$_n$	13.20	13.24	433	5.88	(Penta coordinate)	360
[Zn(C$_{22}$H$_{18}$O$_2$N$_2$)2H$_2$O]$_n$	16.42	15.97	443	Dimagnetic	-	350

^{a}1 BM = 1 Bohr magneton = 9273.0×10^{-24} ml$^2 \cdot$A.
^{b}T$_d$ of 1 362°C.
^{c}Found: C, 64.0; H, 4.3; N, 6.0%. Formula requires C, 65.1; H, 4.4; N, 6.8%.

The dry polymeric chelates were finely powdered and kept at 60°C for 24 h before being analyzed for their metal content.

Polymeric metal chelates with Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) were prepared following this procedure. The metal contents of these polymeric chelates are presented in Table 1. The observed C and N% of all the polymeric chelates are found to be somewhat lower than the calculated C and N%. The results of C, H, and N analysis of polymeric copper chelate sample are shown in Table 1 in the footnote along with the expected values.

Methods of Study

IR spectra of all the polymeric metal chelates were taken in KBr on a Carl-Zeiss Model UR-10 Spectrophotometer.

Diffuse reflectance spectra were taken on a Beckman DU Spectrophotometer.

Magnetic measurements were made at room temperature using a Sartorius semimicro Gouy balance.

Thermogravimetric analysis was performed on a Linses Thermobalance (Germany) at a heating rate of 10°C/min in air. The thermobalance was calibrated with calcium oxalate monohydrate.

The electrical conductivity of the pellets prepared from finely powdered polymer samples at a hydrostatic pressure of 20,000 lb/in.^{2} was measured on Hewlett Packard 4329 high resistance meter.

RESULTS AND DISCUSSION

From analytical data (Table 1) a metal-to-ligand mole ratio of 1:2 was found as expected for a chain polymer; coordination of one or two molecules of water per metal ion is inferred, except for the copper metal ion. The association of aqua in metal complexes of the "bis-oxine" type ligand is well known [7].

The broad band due to a OH group chelated to quinoline-N appears in the polymeric ligand spectrum between 3400 to 3200 cm^{-1} [8, 9]. This band is not observed in the spectrum of the polymeric copper chelate but is observed between 3500 and 3300 cm^{-1}, with a maximum around 3400 cm^{-1}, in the spectra of the other four polymeric metal chelates. This band is attributed to OH stretching of coordinated water molecules [10]. The band around 1420 cm^{-1}, due to O–H in plane deformation [11], is observed in the spectrum of the polymeric ligand, and also in the spectra of all the polymeric metal chelates except in the spectrum of the polymeric Cu chelate. The band attributed to C–O stretching [11, 12] appears in the spectra of all the polymeric metal chelates in the expected range of 1100-1130 cm^{-1} [13]. The lowering of C=N frequency from 1600 to 1590 cm^{-1} is attributed to Met–N formation and is observed in the spectra of the polymeric chelates. The

existence of weak bands around 630 and 450 cm^{-1} in the spectra of all
the polymeric metal chelates also supports the coordination of the re-
peat unit with metal ion through both oxygen and nitrogen, respectively.

The diffuse reflectance spectrum of Cu(II) polychelate shows bands
at 17,240 and 22,730 cm^{-1}, diagnostic of a square planar geometry.
The probable assignments for these bands are $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow$
^2E_g transitions, respectively. The absence of bands below 10,000 cm^{-1}
may be considered to rule out the possibility of a tetrahedral structure
for the Cu(II) polychelate [15]. The observed magnetic moment of 2.13
BM (Table 1) is also consistent with the presence of a single unpaired
electron, although no stereochemical information can be deduced from
this in contrast to some of the other divalent metal complexes of the
first series [16, 17].

The spectrum of Mn(II) polychelate exhibits bands at 11,900, 15,620,
and 21,050 cm^{-1}, indicating a penta- or hexa-coordinated structure [18].
Results of TGA indicate the presence of only one water molecule. Hence
a penta-coordinated structure appears most likely for the present Mn(II)
polychelate.

The spectrum of Ni(II) polychelate is characteristic of an octahedral
stereochemistry consisting of three bands at 10,870, 17,240, and 27,400
cm^{-1}. These bands may be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow$
$^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transitions, respectively. The octa-
hedral geometry is also supported by the observation that the Ni(II)
polychelate has a magnetic moment equal to 3.00 BM.

The spectrum of Co(II) polychelate shows bands at 8,470, 17,540,
20,000, and 23,810 cm^{-1}. The first three bands may be assigned to
$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transi-
tions, respectively, in an idealized octahedral stereochemistry sup-
ported by the observed magnetic moment 4.93 BM at room temperature,
which is in the range required for high spin octahedral complex. The
high energy band at 23,810 cm^{-1} may be due to tetragonal distortion
[19, 20]. Thus the band patterns and the observed values of the mag-
netic moments (Table 1) indicate octahedral geometry around the cen-
tral metal, which would require coordination of two H_2O molecules for
completing the octahedral environment in Co(II) and Ni(II) polychelates.
This is supported by IR and TGA data.

TGA data in air (Table 2) indicate that these polymeric metal che-
lates decompose in a gradual manner in contrast to the sharp decompo-
sition reported for other 8-quinolinol complexes [7, 11]. The observed
loss between 100 and 160°C is most probably due to loss of water. The
observed weight loss agrees with the weight loss calculated on the basis
of the molecular formulas of the repeat unit shown in Table 1. The
polymeric metal chelates begin to lose weight at an accelerated rate at
about 300°C. Below this, the percentage weight loss is about 10 to 12%.
Poddar and Saha [13] and Horowitz and Perros [11] have found their
coordination polymers to lose 6.5 to 35% weight and 5.2 to 18.6% weight,

TABLE 2. Results of Thermogravimetric Analysis[a]

Temperature (°C)	Polymeric ligand I	% Weight loss in				
		Polymeric metal chelate of				
		Cu(II)	Co(II)	Ni(II)	Mn(II)	Zn(II)
100	2	-	2	1	2	1
160	2	2	9[b]	8[b]	4[b]	9[b]
280	4	4	13	12	10	10
340	8	8	18	14	10	12
380	16	18	27	18	16	15
400	25	25	32	26	22	17
420	32	28	65	33	25	18
440	36	30	80	40	26	20
460	40	32	82	77	28	22
500	55	35	82	77	30	25

[a]In air at a heating rate of 10°C/min.
[b]Weight loss due to loss of associated water.

respectively, at the beginning of decomposition. The polymeric metal chelates usually decompose either into a metal oxide or the organic part breaks into small fragments and volatizes, leaving the metal which is then oxidized. In the present case the weight of the residue does not conform to the metal oxide alone, except in the case of Co(II) polychelate, indicating that the decomposition of the organic moiety remains incomplete even at 500°C or that a portion of the residue at 500°C is due to carbon formed during decomposition.

The point of intersection of the two lines drawn through the points on the TG curve before and after the major change in the slope was arbitrarily taken as the decomposition temperature (T_d). These data, presented in Table 1, reveal that the thermal stability of the polymeric metal chelates is less than that of the parent polymeric ligand. The order of the thermal stability is the same as that of the thermal stability of the corresponding metal 8-hydroxyquinolinates [3, 11].

Horowitz and Perros [11] have shown an excellent relationship between the decomposition temperature of metal 8-hydroxyquinolinates and the properties of the central metal ion (e.g., atomic number, electronegativity, and ionic potential). Such relationships are also observed with the polymeric metal chelates reported here. The plot of the de-
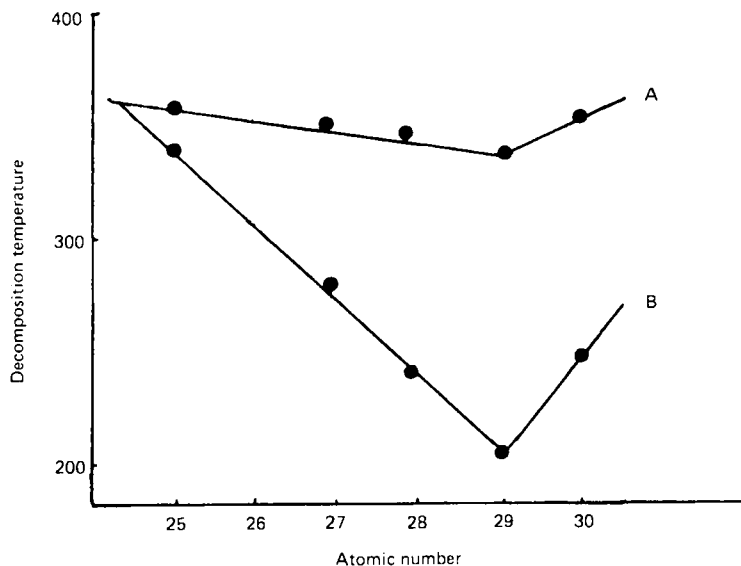
FIG. 1. Plot of thermal stability as a function of atomic number.
A: Poly(oxine-ethylene) metal chelates. B: 8-Hydroxyquinolinate
metal chelates.

composition temperature of the polymeric metal chelate and that of
the corresponding metal 8-hydroxyquinolinate against the atomic num-
ber of the central metal ion are shown in Fig. 1. If one considers a
metal-8-hydroxyquinolinate as a monomeric unit and the correspond-
ing polymeric metal chelate as a succession of these units linked to-
gether by ethylene bridges, then Fig. 1 depicts the increase in the
thermal stability that has been conferred on the different polymeric
metal chelates by virtue of the polymerization process. A compari-
son of these Plots A and B reveals a close similarity. The decreas-
ing trend in the decomposition temperature with an increase in the
atomic number from 25(Mn) to 29(Cu) and the deviation of the point
of the Zn species are observed in both plots. This type of variation
is also observed in the plots of T_d against the electronegativity and
the ionic potential of the central metal atom. Only one such plot of
T_d against electronegativity is shown in Fig. 2.

The value of electrical conductivity σ of the parent polymer I and
its five metal chelates at 25°C are around 10^{-12} ohm^{-1} cm^{-1}, indi-
cating that these are semiconducting materials with high resistance.
It is observed that the conductivity increases with an increase in
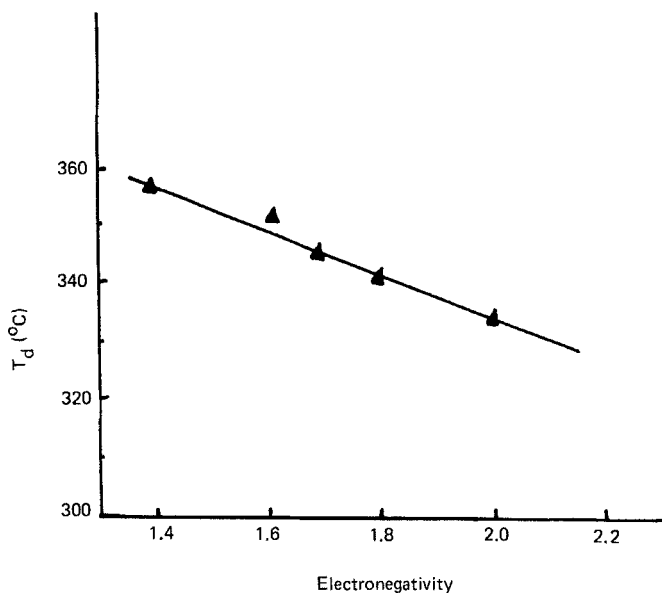temperature. Plots of log σ against $1/T$ are found to be linear only

FIG. 2. Plot of decomposition temperature vs electronegativity for polymeric chelates.

over a very limited range of temperature from 250 to 280°C. This indicates that the exponential relation $\sigma = \sigma_0 e^{E/RT}$ [22] is not obeyed from room temperature up to about 250°C.

REFERENCES

[1] B. S. Patel, G. S. Choxi, and S. R. Patel, Makromol. Chem., 180, 897 (1979).

[2] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, Anal. Chem., 34, 845 (1962).

[3] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, J. Appl. Polym. Sci., 2, 411 (1965).

[4] L. I. Aristov and V. V. Kostantinov, Izy Tomsk. Politekh. Inst., 111, 104 (1961); Chem. Abstr., 57, 13967g (1962).

[5] L. D. Pennington and M. B. Williams, Ind. Eng. Chem., 51, 759 (1959).

[6] B. S. Patel and S. R. Patel, Makromol. Chem., 180, 1159 (1979).

[7] E. N. Berg and A. Alam, Anal. Chim. Acta, 27, 454 (1962).

[8]   L. J. Bellamy, Infrared Spectra of Complex Molecules, Wiley,
      New York, 1959, p. 279.
[9]   J. P. Phillips and L. Merritt, J. Am. Chem. Soc., 71, 3984
      (1949).
[10] K. Nakamoto, Infrared Spectra of Inorganic and Coordination
      Compounds, Wiley-Interscience, New York, 1975.
[11] E. Horowitz and T. P. Perros, J. Inorg. Nucl. Chem., 26, 139
      (1954).
[12] R. G. Charles, H. Friser, R. Frieldel, L. E. Hilliard, and R. D.
      Johnson, Spectrochim. Acta, 8, 1 (1956).
[13] S. N. Poddar and N. Saha, Indian J. Appl. Chem., 33, 242 (1970).
[14] M. A. Ali and R. Bose, J. Inorg. Nucl. Chem., 39, 265 (1977).
[15] L. W. Lane and L. T. Taylor, J. Coord. Chem., 2, 295 (1973).
[16] P. Ray and D. Sen, J. Indian Chem. Soc., 25, 473 (1948).
[17] A. K. Mukherjee and P. Ray, Ibid., 32, 604 (1955).
[18] A. N. Speca, N. M. Karayannis, and L. L. Pyflewski, J. Inorg.
      Nucl. Chem., 35, 3113 (1973).
[19] B. Sing, Lakshmi, and G. Agraval, Inorg. Chem., 8, 2341 (1969).
[20] A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier,
      Amsterdam, 1968.
[21] L. E. Maley and D. P. Mellor, Aust. J. Sci. Res., 2A, 92 (1949).