Polymer Bulletin 1, 685–690 (1979)

Polymer Bulletin

Polymeric Coordination Complexes of Some Bipositive Metal Ions with 5,5′-(Benzidinebisazo)-8-hydroxyquinoline

Vishwanath Banerjie and Arun K. Dey*

Chemical Laboratories, University of Allahabad, Allahabad-211002, India

Introduction

The demand for new polymeric materials with high thermal and chemical stability has stimulated research in many areas of polymer chemistry. BAILAR et al (1959, 1961), KORSHAK et al (1960), BERG and ALAM (1962), and HOROWITZ and PERROS (1964) have been responsible for the earlier work on the coordination polymers of bis-8-hydroxyquinoline type. This communication is in continuation with previous publications from these laboratories (BANERJIE, DEY 1979, MAURYA et al 1977, 1978) and is concerned with the preparation and characterization of coordination polymers of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) with 5,5′-(benzidinebisazo)-8-hydroxyquinoline (Abbr BDHQ).

Experimental

5,5′-(benzidinebisazo)-8-hydroxyquinoline was synthesized by tetraazotizing 0.1 mol(18.4 g) of benzidine and coupling with 0.2 mol(29.0 g) of 8-hydroxyquinoline in pyridine medium. The product was filtered, washed successively with water and alcohol, and dried at 150°C. It was purified by recrystallization from dimethylsulphoxide (DMSO). Colour : orange-brown; yield: 78%; m.p. 308°C (d) (uncorrected); formula: $C_{30}H_{20}N_6O_2$ (found: C = 71.95%, H = 4.19%, N = 16.38%, calcd: C = 72.57%, H = 4.06%, N = 16.93%).

The metal complexes of BDHQ were prepared by refluxing an equimolar mixture of metal acetate hydrates and BDHQ in DMSO for 4h. The precipitates were filtered, washed with hot DMSO, and dried at 140°C.

Carbon, hydrogen and nitrogen were estimated by usual microanalytical methods. The metal contents were estimated titrimetrically against EDTA (table 1).

---

*For correspondence

0170-0839/79/0001/0685/$01.20

Infrared spectra were run using KBr pellets, in the range 4000 - 400 cm^{-1} using a Perkin Elmer Grating Infrared Spectrophotometer Model 577.

Electronic absorption spectra were studied in the solid state employing Spectrophotometer VSU-2P, in the range 220 - 1000 nm.

Magnetic measurements were done by Guoy's method.

Thermal analysis was done by heating the samples at the rate 10^{o}/min and recording the weight with increasing temperature.

Results and Discussion

The complexes are dark coloured (red-brown), amorphous solids, and insoluble in water and in most of the common organic solvents.

Phenols generally absorb sharply at 3600 - 3500, but due to hydrogen bonding, a shift to lower frequency occurs. The strong and broad band at 3280 in the i.r. spectrum of BDHQ has been assigned to bonded OH stretching frequency, which disappears in the spectra of the complexes. HOROWITZ and PERROS (1964) while discussing the spectra of coordination polymers of bis-(5,5'-8-hydroxyquinolyl)-methane assigned a weak band at 1420 to OH-in-plane deformation mode of OH bending vibration, which is reduced and shifted to 1415 -1405 region in the spectra of polymers. In BDHQ this band appears at 1440 and vanishes in the spectra of the complexes. CHARLES et al (1964) have assigned the new band appearing in the spectra of complexes of 8-hydroxyquinoline at 1100 to $>$C-O stretching at $>$C-O-M site. BERG and ALAM (1962), HOROWITZ and PERROS (1964) and PODDAR and SAHA (1970) have noted the appearance of this band at 1100 - 1135 in several polymeric complexes involving ligands of bis-8-hydroxyquinoline type. In the present case, this band appears at 1120 in the spectra of the complexes. The band at 1600 due to C=N stretching in spectrum of BDHQ, shifts to 1590 - 1585 in the spectra of complexes. The bands at 625 - 620 and 510 - 480 respectively are due to M-O and M-N bonds. The disappearance of νOH, δOH, appearance of νC-O at $>$C-O-M site, νM-O, νM-N and shifting of νC=N bands indicate the coordination through O and N of oxine units, thus forming the polymeric chain. The bands at 3400, 1640 - 1630, and 750 - 740 in the spectra of complexes have been assigned respectively to antisymmetric and symmetric OH stretching, HOH bending and M-O stretching due to coordinated water (NAKAMOTO, 1975), (All wave numbers are in cm^{-1}).

Electronic spectra and magnetic moment data of the complexes suggest that the stereochemistry around the central metal is octahedral. This furnishes support for the presence of water in coordination sphere of the metal and two out of six coordination sites are occupied by H_2O.

TABLE 1

Analytical results of BDHQ (L)-metal complexes

Complexes	Elemental analysis, Found (Calc)			
	C%	H%	N%	M%
$(MnL.2H_2O)_n$	61.32 (61.53)	3.65 (3.76)	14.05 (14.35)	9.29 (9.40)
$(FeL.2H_2O)_n$	61.37 (61.51)	3.59 (3.75)	14.07 (14.34)	9.22 (9.39)
$(CoL.2H_2O)_n$	61.06 (61.12)	3.68 (3.73)	14.09 (14.24)	9.89 (10.01)
$(NiL.2H_2O)_n$	60.48 (61.12)	4.16 (3.72)	14.15 (14.24)	9.88 (10.00)
$(CuL.2H_2O)_n$	59.00 (60.65)	4.10 (3.70)	13.93 (14.15)	10.62 (10.69)
$(ZnL.2H_2O)_n$	60.19 (60.50)	3.75 (3.69)	13.72 (14.11)	10.89 (10.92)
$(CdL.2H_2O)_n$	55.82 (56.07)	3.52 (3.42)	13.23 (13.08)	17.33 (17.44)

Metal to BDHQ ratio is 1:1 (table 1) and suggests the coordination of $2H_2O$ in the polymeric complexes. Such an association of aqua ligands in coordination polymers of bis-oxine type compounds is already known. (PODDAR and SAHA 1970; BERG and ALAM 1962; BAILAR et al 1960; KORSHAK et al 1960).

TGA data (table 2) indicate that the complexes decompose in a gradual manner as contrasted to the sharp decomposition reported for other 8-hydroxyquinoline complexes. Water is lost between 80° - 260°C, the weight loss due to water approaching the theoretical amounts for dihydrates. The chelates begin to lose weight at an accelerated rate at 300°-360°C. Below this temperature, the weight loss percentage is 15-25%. Zn(II)-oxinate is known to lose approximately 90% weight at 375°C; thus BDHQ complexes are much more stable than simple oxinates, and this further supports their polymerization. Before the onset of decomposition the weight loss represents the volatilization of

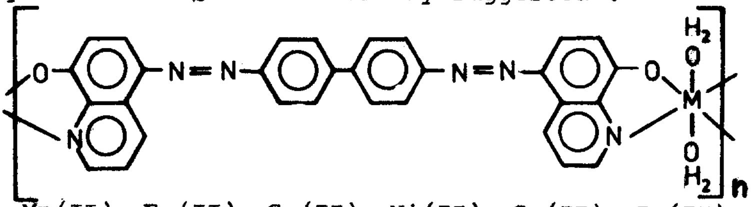
TABLE 2

TGA data of complexes

Temperature ($^{\circ}$C)	Percent weight loss						
	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
80	0.50	0.0	1.63	0.35	0.65	1.02	0.71
120	2.51	0.0	4.91	3.16	2.61	3.42	2.14
160	4.77	0.0	7.37	6.69	5.88	5.13	3.57
200	7.03	0.0	9.83	9.50	6.53	6.16	4.28
240	9.79	12.30	11.80	11.61	7.51	8.90	4.28
280	16.58	15.38	16.39	16.54	9.80	14.38	7.85
300	20.10	18.46	21.31	25.00	13.07	19.86	12.14
320	22.15	20.00	24.26	28.16	16.99	21.91	15.00
340	23.36	23.07	27.04	31.69	17.64	23.63	17.14
360	24.12	27.23	27.86	35.91	21.56	25.34	19.64
380	25.62	30.00	33.14	39.08	24.18	26.71	22.50
400	27.38	32.30	36.06	42.95	26.79	28.76	26.42
500	37.43	47.69	57.37	55.28	39.54	40.41	46.42
600	47.23	75.38	85.24	66.54	52.28	53.76	60.00
700	60.80	80.61	84.42	80.28	65.03	67.80	72.85
800	73.86	81.63	85.24	85.21	76.47	80.82	75.00
900	79.64	81.53	84.42	85.21	84.96	85.60	75.00

water and of low molecular weight moeities. PODDAR and SAHA (1970), and HOROWITZ and PERROS (1964) have found their coordination polymers lose 6.5 - 35% and 5.2 - 18.6% respectively of the weights at the onset of decomposition. The order of stability $Cd(360^{\circ}) \sim Zn(360^{\circ}) > Mn(340^{\circ}) > Co(320^{\circ}) \sim Ni(320^{\circ}) \sim Cu(320^{\circ}) > Fe(300^{\circ})$ is in agreement with that of other 8-hydroxyquinoline type compounds, except that the behaviour of Fe complex is anomalous, (HOROWITZ, PERROS 1964). The state associated with the half-filled d^5 electronic configuration of Mn(II) is quantum mechanically the most stable energy state. There is a progressive decrease in the thermal stability of the coordinated systems of Co(II), Ni(II), and Cu(II) ions, whose 3d configurations depart in a regular manner from a stable half-filled state. Cd(II) and Zn(II) with completely filled d-orbitals are thermally more stable. Either the complexes decompose into MO, H_2O and bis-ligand ether as suggested by MILLER and McLENNAN (1940), or the organic part breaks into small fragments and then volatilizes leaving the metal alone which then gets oxidised as found by DUVAL (1953) and by BORREL and PARIS (1950). In the present complexes, the residues do not conform to the metal oxides alone, indicating that the decomposition of the organic moeity remains incomplete even at $900^{\circ}C$.

The following structure for the coordination polymers of BDHQ is tentatively suggested :



M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), n = degree of polymerization.

The positions of coordination sites in the ligand, 1:1 metal to BDHQ ratio, i.r. spectra of ligand and the complexes, the high insolubility, and thermal stability are evidences for their polymeric nature.

Summary

Coordination chain polymers of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) with 5,5-(benzidinebisazo)-8-hydroxyquinoline were synthesized by refluxing a mixture of metal acetate hydrates and ligand (1:1) in DMSO. From analytical data an empirical formula of $ML.2H_2O$ is indicated. Ir spectra reveal coordination through O and N of oxine units, thus forming the polymeric chain; presence of coordinated water is also indicated. Magnetic moments and electronic spectra suggest octahedral geometry around the central metal ion. Besides the presence of $2H_2O$, TGA shows the order of thermal stability as : Cd$\sim$Zn$>$ Mn$>$Co$\sim$Ni$\sim$Cu$>$Fe.

Acknowledgement

The work was supported by the Council of Scientific & Industrial Research, New Delhi, and the authors are thankful for the same.

References

J.C. BAILAR Jr. :
Inorganic Polymers, London : The Chemical Society 1961

J.C. BAILAR, M.L. JUDD, and J. McLEAN :
WACD Tech.Rept. No. 57 - 391 May (1959)

V. BANERJIE, and A.K. DEY :
Makromol. Chem. 180, (1979) (in press)

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

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

R.G. CHARLES, and A. PERROTTO :
Analyt. Chim. Acta 30, 131 (1964)

E. DUVAL :
Inorganic Thermogravimetric Analysis :
Oxford : Elsevier 1953

E. HOROWITZ and T.P. PERROS :
J. Inorg. Nucl. Chem. 26, 139 (1964)

V.V. KORSHAK, S.V. VINOGRADOVA and T.M. BABCHINISTER:
Polymer Sci. USSR 2, 4, 344 (1960)

P.L. MAURYA, B.V. AGARWALA and A.K. DEY :
Inorg. Nucl. Chem. Lett. 13, 147 (1977)

P.L. MAURYA, B.V. AGARWALA and A.K. DEY :
Indian J. Chem. 16A, 358 (1978)

C.C. MILLER and I.C. McLENNAN :
J. Chem. Soc. 656 (1940)

K. NAKAMOTO :
Infrared Spectra of Inorganic and Coordination compounds, New York : Wiley Interscience 1975

S.N. PODDAR and N. SAHA :
Indian J. Appl. Chem. 33, 242 (1970)

Received July 19, 1979