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Polymetallic Complexes—Part XXIX : Complexes of Cobalt(II), Nickel(II), Copper(II), Zinc)(II), Cadmium(II) and Mercury(II) with Chelating ON–NO Donor Azo Dye Ligands

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The present work describes the synthesis of two bis-bidentate azodyes, 4-(2′-hydroxyphenylazo)-8-hydroxyquinoline and 4-(2′-carboxyphenylazo)-8-hydroxyquinoline containing ON–NO donor atoms and their polymeric complexes with some divalent metal ions.

INTRODUCTION

Study of polymetallic complexes containing chelating polydentate azodye ligands are of recent interest. Literature survey reveals that no systematic approach has been made earlier in this field. In continuation of our earlier work[1–5] the present paper reports the synthesis of two new bis-bidentate azodyes, 4-(2′-hydroxyphenylazo)-8-hydroxyquinoline ($HPAHQH_2$) and 4-(2′-carboxyphenylazo)-8-hydroxyquinoline ($CPAHQH_2$) containing ON–NO donor atoms and their polymeric complexes with some divalent metal ions.

EXPERIMENTAL

Preparation of the Ligands

The diazonium salt solutions obtained from *o*-aminophenol and *o*-aminobenzoic acid were separately added to the alkaline solutions of 8-hydroxyquinoline (oxine) in 1 : 1 molar proportion kept in an ice-salt bath. The red coloured azo dyes thus separated out immediately were then filtered, washed with water, dried and recrystallized from EtOH (95%) ($HPAHQH_2$) m.pt. 140°C; ($CPAHQH_2$) m.pt. > 250°C; calculated C, 67.92%, H, 4.15%, N, 15.84%; for $C_{15}H_{11}O_2N_3$ found C, 66.5%, H, 4.0%, N, 14.7%; for $C_{16}H_{11}O_3N_3$ calculated value of C, 65.52%, H, 3.75%, N, 14.33%, found C, 64.2%, H, 3.2%, N, 13.8%.

Preparation of the Complexes

The metal complexes were prepared by refluxing an EtOH solutions of the ligands (1 mol) and metal chloride (1 mol) for ½ hour. On cooling a dilute solution of sodium acetate was added dropwise with stirring when complexes separated. These were then filtered, washed with EtOH and Et_2O and finally dried in vacuum.

RESULTS AND DISCUSSION

All the twelve complexes are stable at room temperature and also at high temperature (up to *ca.* 110°C). The complexes are amorphous having high melting points and are insoluble in common organic solvents but sparingly soluble in DMF. Non-electrolytic nature of the complexes is indicated by the low conductance values in DMF [6], (2.5–4.7 mhos cm^2. mol^{-1}).

In the IR spectra of the azodye ligands the bands shown at *ca* 3250 cm^{-1} may be assigned to ν(OH) vibrations. The lowering of this band is due to intramolecular O–H . . . N hydrogen bonding[7]. Disappearance of these bands in the metal chelates is suggestive of coordination of phenolic oxygen atoms to the metal atoms. A strong and sharp band is observed at 1250 cm^{-1} ($HPAHQH_2$) which may be assigned to phenolic νC–O vibration. Another sharp band observed[8] at *ca* 1100 cm^{-1} is characteristic of phenolic νC–O. The bathochromic shift of these bands in the metal chelates indicates bonding through phenolic oxygen atom. The ν_{asym}(COO) appears at 1630 cm^{-1} ($CPAHQH_2$) and a decrease of ($\Delta\nu$)30 cm^{-1} in the metal complexes indicates the coordination of carboxylate group to the metal ions. The –N=N–frequency appears at 1580 cm^{-1} ($CPAHQH_2$) and at 1560 cm^{-1} ($HPAHQH_2$) and a bathochromic shift of 50 cm^{-1} in the metal complexes indicates the coordination of one of the azo nitrogen atom to the metal ions[9, 10]. The band observed at *ca* 1445 cm^{-1} in the ligands assignable to νC—N suffers a bathochromic shift in metal complexes because of donation of lone pair of electrons to the metal ions. In all the metal complexes one broad band appears in the 3350–3450 cm^{-1} region followed by a sharp peak at 800–850 cm^{-1} assignable to the OH stretching and rocking vibrations respectively indicating the presence of coordinated water molecules. The conclusive evidence of bonding of nitrogen and oxygen atoms to the metal atoms is shown[11] by the appearance of ν(M–N), ν(M–O) at *ca* 500 cm^{-1} and 440 cm^{-1} respectively. The μ_{eff} values of Co(II), Ni(II), and Cu(II) complexes are found out to be *ca* 5.0, *ca* 3.3 and *ca* 2.0 B.M. respectively.

In the electronic spectra of the Ni(II) complexes, three bands are observed at *ca* 11850, 18470 and 27760 cm^{-1} attributable to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $\rightarrow {}^3T_{1g}(F)$ and $\rightarrow {}^3T_{1g}(P)$ transitions respectively. The ligand field parameters like ν_2/ν_1, 10 Dq, B, β_{35} and σ suggest an octahedral geometry[12] for the complexes. The Co(II) complexes show three ligand field bands at 8785 cm^{-1}, 18150 cm^{-1} and 21980 cm^{-1} assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) \rightarrow$ $^4A_{2g}(F)$ and $\rightarrow {}^4T_{1g}(P)$ transitions respectively. The values of ligand field parameters are suggestive of an octahedral stereochemistry for the complexes. The Cu(II) complexes show broad assymmetric ligand field band in the region 13320–15750 cm^{-1} with the maxima at *ca* 14450 cm^{-1} assignable to $^2E_g \rightarrow {}^2T_{2g}$ transitions in a distorted-octahedral geometry.

The polycrystalline ESR spectra have been recorded at X-band. The principal 'g' values have been calculated using Kheubuhl's method[13]. The 'g_{av}' value for the complex $[CuL\,2H_2O]_n$ is found to be 2.102. This may be

TABLE 1

ANALYSIS OF METAL-COMPLEXES AND I.R. SPECTRAL DATA (cm^{-1})

Compound colour	% (Found/calcd.)		$\nu(C-O)$ $\nu\left(C\overset{O}{\underset{O}{\lessgtr}}\right)$	$\nu(-N=N-)$
	Metal	Nitrogen		
H_2L Chocolate red	—	15.4 (15.84)	1100	1560
H_2L' Violet	—	13.8 (14.00)	1630	1580
$[CoL\cdot 2H_2O]_n$ Coffee	16.1 (16.46)	11.2 (11.73)	1080	1520
$[NiL\cdot 2H_2O]_n$ Dark brown	15.9 (16.41)	11.5 (11.74)	1075	1515
$[CuL\cdot 2H_2O]_n$ Brown	17.2 (17.52)	11.1 (11.58)	1085	1520
$[ZnL\cdot 2H_2O]_n$ Coffee	17.6 (17.94)	11.2 (11.52)	1070	1525
$[CdL]_n$ Grey	29.2 (29.94)	11.1 (11.18)	1080	1520
$[HgL]_n$ Red	42.5 (43.26)	8.7 (8.05)	1080	1525
$[CoL\cdot 2H_2O]_n$ Reddish brown	16.1 (16.54)	11.2 (11.80)	1435	1530
$[NiL'\cdot 2H_2O]_n$ Yellow	14.9 (15.22)	10.2 (10.88)	1430	1535
$[CuL'\cdot 2H_2O]_n$ Orange	16.1 (16.26)	10.5 (10.75)	1420	1545
$[ZnL'\cdot 2H_2O]$ White	16.2 (16.66)	10.5 (10.70)	1410	1540
$[CdL']_n$ Yellow	27.2 (27.86)	10.1 (10.41)	1415	1535
$[HgL']_n$ Grey	40.2 (40.80)	8.3 (8.54)	1415	1540

H_2L = 4-(2′-hydroxyphenylazo)-8-hydroxyquinoline.
H_2L' = 4-(2′-carboxyphenylazo)-8-hydroxyquinoline.

due to random orientation of the axes. The g_1, g_2 and g_3 values for the complex $[CuL'2H_2O]_n$ is found to be 2.04, 2.05, and 2.20 respectively indicative of an rhombic symmetry around the metal ion. In order to obtain information about the ground state an useful parameter **R** has been calculated using the relation.

$$R = \frac{g_2 - g_1}{g_3 - g_2}$$

The **R** value for the complex is found out to be 0.0632 which indicates that the ground state is predominantly $d_{x^2-y^2}$. In the complex the **g** values are less than 2.3 which show that the complex is largely covalent. Further these values are consistent with the mixed Cu–N, and Cu–O bonded copper complexes[14]. Basing upon above experimental evidences two possible structures A and B can be suggested for the complexes with the ligands ($HPAHQH_2$) and ($CPAHQH_2$) with MO_2N_2 ligand arrangement respectively.

TABLE 2

SPECTRAL PARAMETERS OF METAL COMPLEXES

Compound	Band Positions cm^{-1}	Dq(cm^{-1})	B cm^{-1}	β_{35}	ν_2/ν_1	σ
$[CoL \cdot 2H_2O]_n$	8785 18150 21980	936	918	0.94	2.06	6.38
$[NiL \cdot 2H_2O]_n$	11850 18470 27760	1185	712	0.68	1.55	47.05
$[CuL \cdot 2H_2O]_n$	13320	1332	—	—	—	—
$[CoL'2H_2O]_n$	8780 18200 21950	942	927	0.95	0.07	5.26
$[NiL'2H_2O]_n$	11800 18450 27750	1180	720	0.69	1.56	44.92
$[CuL'2H_2O]_n$	13250	1335	—	—	—	—

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