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Polymetallic Complexes : Part XXXVI $^{O}_{N}\supset$-Z-$\subset^{O}_{N}$ Donor Bis-Bidentate Chelating Azodye Complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)

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4,4′-Bis[5-(8′-hydroxyquinolyl)-azo] benzene and bis[4-(8′-hydroxyquinolyl-5′)-azo-3-methylphenyl] methane act as bis-bidentate $^{O}_{N}\supset$-Z-$\subset^{O}_{N}$ donor chelating ligands and form polymeric complexes with divalent metal ions. The characterisation of the complexes has been made basing upon elemental analysis, conductivity measurements, magnetic moments and spectral (electronic, IR, and ESR) studies. The antibacterial activities of the ligands and a few representative complexes have been determined.

INTRODUCTION

The azodyes possess[1–3] immense pharmacological properties. Some of these dyes are also used as food preservants[4] and dyeing food grains. Azodyes exhibit the property of an indicator[5], in both strong and weak acid-base titration. Potentiometric and spectrophotometric studies of Co(II), Ni(II) and Cu(II) chelates with azodyes have been reported. The azodyes are also used for spectrophotometric determination of vanadium in steel[6]. The pharmacological activity and the chelating ability of the azodyes prompted us to synthesize new azodyes and their metal complexes with divalent metal ions[7–10]. The present work reports the preparation and characterisation of two chelating azodyes (Fig. 1) and their metal chelates with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

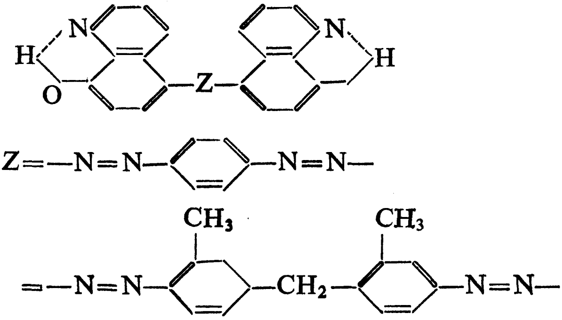


Fig. 1

EXPERIMENTAL

The ligands were prepared by the coupling reaction of diazonium chlorides obtained from *p*-phenylene-diamine and 4,4′-diamino-,3 3′-dimethylphenylmethane separately with alkaline solution of 8-hydroxyquinoline at 0°C, when the reddish-brown coloured azodyes separated out. The metal complexes were prepared by reacting ethanolic solution metal(II) chlorides with the ligand solution in dioxane. The pH of the resulting solution was then raised to around 7 when the metal compounds separated out. These were then filtered, washed in ethanol, ether and dried in vacuo.

RESULTS AND DISCUSSION

All the complexes were stable at room temperature and also at high temperature. They are amorphous in nature and have high melting points and are insoluble in common organic solvents but sparingly soluble in DMF and dioxane. Analysis and conductance data show the composition of the complexes to be $[M_2L/L'\ Cl_2(H_2O)_6]$ and $[M'_2L/L'\ Cl_2(H_2O)_2]$ where M=Co(II), Cu(II) and M′=Ni(II), Zn(II), Cd(II), Hg(II), LH_2=4,4′-Bis [5-(8-hydroxyquinolyl)-azo] benzene and $L'H_2$=Bis[4-(8-hydroxyquinolyl)-azo-3-methylphenyl] methane. Non-electrolytic nature of the complexes is indicated by the low conductance values in DMF (4.6–7.2) mhos cm^2 mol^{-1}.

In the IR spectra of the ligands, the bands observed at around 3400 cm^{-1} can be assigned to ν(OH) vibration lowered due to intramolecular O—H$\cdots$N hydrogen bonding, The disappearance of this band in the metal chelates is indicative of co-ordination of oxygen atoms to the metal atoms. The —N=N—frequency appearing at *ca.* 1560 cm^{-1} in the ligands remains unaffected in the metal chelates showing non-coordination of all the four azo nitrogen atoms to the metal atoms[11]. The band observed at 1130 cm^{-1} (LH_2) and 1140 cm^{-1} ($L'H_2$) in the ligands can be assigned to ν(C–O) vibration and the bathochromic shift of around 10–20 cm^{-1} in the metal complexes indicating co-ordination of oxine oxygen atoms to the metal atoms[12]. In the spectra of the complexes, an intense band is observed at *ca.* 1330 cm^{-1} due to vibration of the $C\overset{\cdots}{=}N$ bond in the oxinate group[13,14]. In the ligands this band occurs[15] at *ca.* 1450 cm^{-1}. The shift to lower frequency regions in the complexes shows considerably lower double bond character of the $C\overset{\cdots}{=}N$ bond due to involvement of the ring nitrogen on complexation. One broad band appears in the region 3200–3450 cm^{-1} in case of all the metal complexes followed by sharp peaks at *ca.* 840 cm^{-1} assignable to OH stretching and rocking vibrations respectively indicating the presence of co-ordinated water molecules in the complexes. The evidence of bonding of phenolic oxygen and quinolyl nitrogen atom is further substantiated by the appearence[16] of bands at *ca.* 500 cm^{-1} and *ca.* 450 cm^{-1} assignable to ν(M—O) and ν(M—N) vibrations respectively.

The cobalt(II) and copper(II) complexes exhibit magnetic moments *ca* 5.0 B.M. and 1.9 B.M. indicating the presence of three and one unpaired electrons respectively. The Ni(II) complexes are found to be diamagnetic in nature.

In the electronic spectra of cobalt(II) complexes three bands are noticed at *ca* 9105, 18320 and 21580 cm^{-1} assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $\rightarrow {}^4A_{2g}(F)$ (ν_2) and $\rightarrow {}^4T_{1g}(P)$ (ν_3) transitions respectively. The values of spectral parameters Dq(910.5, 912.0) cm^{-1}, B(839, 840) cm^{-1}, β(0.864, 0.865), ν_2/ν_1(2.01, 2.01) and σ(15.74, 15.60) of the complexes $[Co_2L\ Cl_2(H_2O)_6]$ and $[Co_2L'\ Cl_2(H_2O)_6]$ respectively are suggestive of an octahedral stereochemistry around the metal ions[17]. Both the Cu(II) complexes show one broad asymmetric ligand field band in the region 13,340-15,670 cm^{-1} with the maxima at *ca* 14, 445 cm^{-1} assignable to $^2E_g \rightarrow {}^2T_{2g}$ transition in a distorted octahedral geometry[18]. The Ni(II) complexes exhibit two bands at *ca* 16,450 and 17,550 cm^{-1} attributable to the transitions $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ respectively which are inconsistent with a square planar configuration[19,20].

The ESR spectrum of the complex $[Cu_2L\ Cl_2(H_2O)_6]$ was recorded at X-band. The "g_{av}" value (2·05) was evaluated using Kneubuhl's method[22]. The ESR spectrum is found to be isotropic consisting of a single line characteristic of regular octahedral geometry. This type of spectrum may result either due to the fact that a regular octahedral stereochemistry undergoing a dynamic or pseudo-rotational type of Jahn-Teller distortion or due to grossly misaligned tetragonal axes which may be reducing the symmetry or a chromophore of symmetry lower than octahedral may undergo free rotation[22].

The molecular weight data of the complexes agree fairly well with the dimeric structures.

Biological Screening

The compounds have been screened for their antibacterial activity by vincent and vincent filter paper disc diffusion method[23]. Five gram +ve and gram −ve bacteria employed for the tests are *staphylococci aureus, escherichia coli, proteus mirabilis, pseudomonas aureus* and *klebsiella aureus.* The ligand 4,4′-bis [5-(8′-hydroxyquinolyl)-azo] benzene has been found to be active against the bacteria *staphylococci aureus* (coagulage +ve) with sensitivity pattern +ve and the diameter of zone of inhibition 10mm and 3mm in two different patients respectively. The sensitivity pattern has been found to be −ve in case of rest of the compounds.

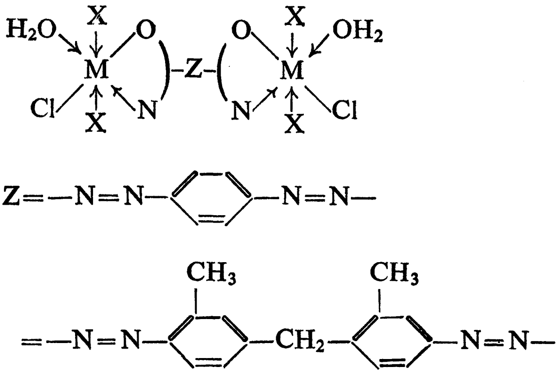
A tetrahedral stereochemistry has been assigned to Zn(II), Cd(II) and Hg(II) complexes on the basis of analysis, conductance and I.R. spectral data.

TABLE 1

ANALYTICAL, MAGNETIC, MOLECULAR WEIGHT AND IR SPECTRAL DATA (cm^{-1})

Sl. No.	Compound	Analysis % Found (calcd)		μ_{eff} B. M.	Mol. Wt. found	ν(C–O)/ ν(C–N)	ν(M–O)/ ν(M–N)
		M	N				
1.	$[Co_2LCl_2(H_2O)_6]$	16.1 (16.40)	11.2 (11.70)	5.00	615	1120/1330	500/450
2.	$[Co_2L'Cl_2(H_2O)_6]$	13.8 (14.11)	9.7 (10.06)	5.10	780	1130/1325	505/460
3.	$[Ni_2LCl_2(H_2O)_2]$	17.6 (18.22)	12.7 (13.03)	—	510	1115/1330	500/445
4.	$[Ni_2L'Cl_2(H_2O)_2]$	15.1 (15.40)	10.8 (11.01)	—	690	1125/1330	505/450
5.	$[Cu_2LCl_2(H_2O)_6]$	17.2 (17.50)	11.2 (11.56)	1.90	665	1110/1325	500/545
6.	$[Cu_2L'Cl_2(H_2O)_6]$	14.6 (15.05)	9.5 (9.95)	1.85	780	1130/1325	505/450
7.	$[Zn_2LCl_2(H_2O)_2]$	19.2 (19.85)	12.2 (10.82)	—	585	1120/1330	510/455.
8.	$[Zn_2L'Cl_2(H_2O)_2]$	16.3 (16.85)	10.4 (10.85)	—	692	1130/1325	500/450
9.	$[Cd_2LCl_2(H_2O)_2]$	29.2 (29.93)	10.7 (11.17)	—	675	1151/1330	505/450
10.	$[Cd_2L'Cl_2(H_2O)_2]$	25.3 (25.84)	9.3 (9.65)	—	795	1125/1375	500/460
11.	$[Hg_2LCl_2(H_2O)_2]$	42.7 (43.22)	8.7 (9.04)	—	842	1120/1330	505/450
12.	$[Hg_2L'Cl_2(H_2O)_2]$	37.7 (38.34)	7.7 (8.02)	—	945	1130/1330	500/460

Basing upon the above experimental evidences it is concluded that both the azodyes behave as bis-bidentate chelating ligands having $^{O}_{N}\supset\text{-}Z\text{-}\subset^{O}_{N}$ donor atoms which can hold metal atoms on either side thus forming dimeric complexes. (Fig. 2).



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