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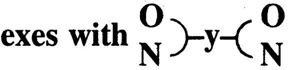
Polymetallic Complexes, Part XLIX: Synthesis Magnetic and Spectral Studies of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) Complexes with  $\overset{O}{\underset{N}{}}\rangle\text{-y-}\langle\overset{O}{\underset{N}{}}$ Donor Bis-Azodye Ligands.

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Both the bis-azodye ligands, bis [4, 4′–(8′-hydroxyquinolyl-5′)–azo-phenyl] methane and bis [4, 4′–(8′-hydroxyquinolyl-5′)–azo-phenyl] sulphone form dinuclear complexes with divalent metal ions. The Co(II) and Cu(II) complexes are either octahedral or distorted octahedral, both the Ni(II) complexes are square planar and the Zn(II), Cd(II) and Hg(II) complexes are tetrahedral in configuration basing upon analysis, conductance, magnetic moments, IR, electronic, ESR and NMR spectral studies.

INTRODUCTION

Antibacterial and amoebicidal properties of oxine and its derivatives have been well-recognised.[1] The azodyes also exhibit remarkable pharmacological activity.[2] In continuation of our earlier work[3] the present study reports the synthesis of two new bis-bidentate ligands containing these two potential biologically active moieties and their dinuclear metal complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

EXPERIMENTAL

The bis-azodye ligands were synthesized by the usual coupling reaction method. The metal chelates were prepared by reacting ethanolic solution of metal(II) chlorides with the ligand solution in dioxane.

RESULTS AND DISCUSSION

All the twelve metal complexes are amorphous in nature, have high melting points and are almost insoluble in common organic solvents but sparingly soluble in dimethyl formamide. The complexes are found to be non-electrolytes as the Ω_M values in DMF are very low (3.5–4.8 mhos $cm^2 mol^{-1}$). Analysis and conductance data indicate the composition of the complexes $[M_2L/L'Cl_2(H_2O)_6]$ 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 and $L'H_2$ are the two bis-azodye ligands.

TABLE 1

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

Sl. No.	Compound	Analysis % Found (Calcd.)		μ_{eff} B.M.	ν(C–O)	ν(C–N)
		M	N			
1.	$[Co_2LCl_2(H_2O)_6]$	14.30 (14.63)	10.20 (10.43)	5.1	1100	1315
2.	$[Co_2L'Cl_2(H_2O)_6]$	13.50 (13.78)	9.60 (9.82)	5.0	1135	1320
3.	$[Ni_2LCl_2(H_2O)_2]$	15.80 (16.02)	11.10 (11.46)	—	1105	1315
4.	$[Ni_2L'Cl_2(H_2O)_2]$	14.70 (15.00)	10.50 (10.73)	—	1130	1320
5.	$[Cu_2LCl_2(H_2O)_6]$	15.30 (15.60)	10.20 (10.31)	1.80	1100	1310
6.	$[Cu_2L'Cl_2(H_2O)_6]$	14.50 (14.69)	9.60 (9.72)	1.85	1130	1325
7.	$[Zn_2LCl_2(H_2O)_2]$	17.40 (17.52)	11.10 (11.26)	—	1110	1315
8.	$[Zn_2L'Cl_2(H_2O)_2]$	16.30 (16.42)	10.30 (10.55)	—	1135	1320
9.	$[Cd_2LCl_2(H_2O)_2]$	26.60 (26.76)	9.80 (10.00)	—	1105	1310
10.	$[Cd_2L'Cl_2(H_2O)_2]$	25.10 (25.26)	9.20 (9.44)	—	1135	1325
11.	$[Hg_2LCl_2(H_2O)_2]$	39.10 (39.47)	8.10 (8.26)	—	1110	1315
12.	$[Hg_2L'Cl_2(H_2O)_2]$	37.40 (37.62)	7.60 (7.87)	—	1130	1320

In the IR spectra of the ligands, the broad bands appear at 3350–3400 cm^{-1}, assignable to ν(OH) vibration lowered due to intramolecular O–H–N hydrogen bonding This band is found to be absent in the metal chelates which shows the bonding of oxygen atoms to the metal ions. In the ligands the bands observed at 1130 cm^{-1} (LH_2) and 1150 cm^{-1} ($L'H_2$) can be assigned to ν(C–O) vibration and in the metal complexes these bands appear at *ca.* 1100 cm^{-1} and *ca.* 1135 cm^{-1}, indicative of oxine oxygen coordination to the metal ions.[4] The bands appearing at 1380 cm^{-1} (LH_2) and 1385 cm^{-1} ($L'H_2$) can be ascribed to $\nu(C \overset{\cdots}{=} N)$ vibrations[5] and in the metal chelates these bands occur at *ca.* 1315 cm^{-1} and 1320 cm^{-1} respectively, showing oxine nitrogen atoms to the metal ions.[6] The –N = N– frequency appearing at 1580 cm^{-1} (LH_2) and at 1600 cm^{-1} ($L'H_2$) remain unchanged after complexation, indicating the non-coordination of all the four azo-nitrogen atoms of the metal ions. The presence of coordinated water molecules in all the complexes is indicated by the appearance of broad bands at *ca.* 3450 cm^{-1} followed by a sharp peak at *ca.* 820–840 cm^{-1} assignable to OH stretching and rocking vibrations respectively.[7]

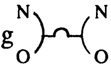
The μ_{eff} values of Co(II) and Cu(II) complexes are *ca.* 5.1 B.M. and 1.8 B.M. indicating the presence of three and one unpaired electrons respectively. Both the Ni(II) complexes are found to be diamagnetic in nature.

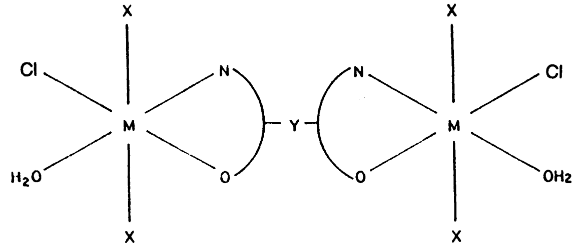
In the electronic spectra of the Co(II) complexes four bands are boserved at *ca* 8,955; 18,250; 21,460 and 33,560 cm^{-1} assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$; $\rightarrow {}^4A_{2g}(F)$; $\rightarrow {}^4T_{1g}(P)$ and CT transition respectively, indicative of octahedral stereo-chemistry around the metal ions.[8] The Ni(II) complexes show two bands at *ca* 16,350 cm^{-1} and 17,485 cm^{-1} assignable to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $\rightarrow {}^1E_{1g}$ transitions respectively in consistent with a square planar geometry around the metal ions.[9] In the Cu(II) complexes the broad asymetric ligand field band is observed at *ca* 13,445–15,475 cm^{-1} with the maxima at *ca* 14,565 cm^{-1} assignable to $^2E_g \rightarrow {}^2T_{2g}$ transition in a distroted octahedral configuration.[10]

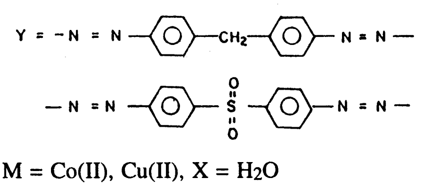
In the ^1H nmr spectrum of the ligand ($L'H_2$), an unsymmetric complex pattern appears between 6.5–9.8 due to fourteen phenyl protons and another singlet peak at 14.0 due to two phenolic protons.

The esr spectrum of the Cu(II) complexes are recorded at **X** band. The $\mathbf{g}_{av}$ values of the complexes $[Cu_2LCl_2(H_2O)_6]$ and $[Cu_2L'Cl_2(H_2O)_6]$ are found to be 2.085 and 2.090 respectively. The esr spectra are found to be isotropic consisting of a single line characterstics of regular octahedral geometry. Since the **g** values are less than 2.3, it can be suggested that both the complexes are largely covalent. Further these values are consistent with the mixed Cu–O and Cu–N bonded Cu(II) complexes.

The Zn(II), Cd(II) and Hg(II) complexes are four-coordinated with a tetrahedral geometry basing upon analytical and IR spectral data.

Considering the bis-bidentate nature of the ligands having  potential donor atoms which can hold two metal atoms on either side, the following tentative structure can be proposed for the complexes.





M = Co(II), Cu(II), X = H2O
= Ni(II), Zn(II), Cd(II), Hg(II); X = Nil

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