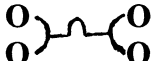


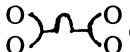
**Polymetallic Complexes, Part XLVIII Complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with Chelating Bis-bidentate  Donor Azodye Ligand.**

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Bis-bidentate chelating azodye ligand, 4,4'-bis[(acetylacetylonyl-3')-azo]-3,3'-dimethyldiphenyl form binuclear complexes with divalent metal ions. The Co(II), Cu(II) and Zn(II) complexes are found to be either octahedral or distorted octahedral, Ni(II) complex square planar and Cd(II) and Hg(II) complexes are tetrahedral as inferred from analysis, conductance, magnetic moments and spectral studies.

### INTRODUCTION

The study of metal complexes containing multidentate chelating azo dye ligands is of recent interest. In continuation of our earlier work<sup>1</sup>, the present study reports the preparation and characterisation of a new  donor bis-bidentate bid bis-azo dye ligand and its dinuclear metal complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

### EXPERIMENTAL

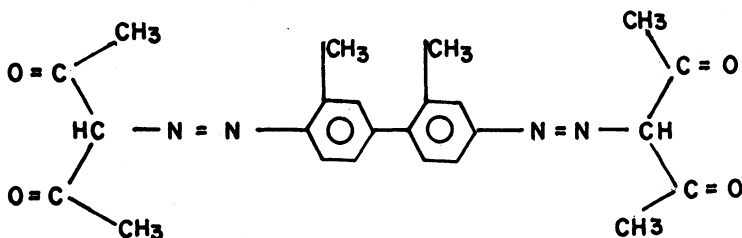
The ligand was synthesized by the coupling reaction of the diazonium chloride obtained from 3,3'-dimethylbenzidine with alkaline solution of acetylacetone at 0°C in 1:2 ratio when the reddish brown coloured azo dye separated out. The metal complexes were prepared by reacting ethanolic solution of metal(II) chlorides with the ligand solution in dioxane in 2:1 ratio. On raising pH of the solution to around 7, the metal complexes separated out, which were then filtered, washed with ethanol followed by ether and dried under reduced pressure.

### RESULTS AND DISCUSSION

The complexes have the composition  $[M_2LCl_2(H_2O)_6]$  and  $[M'_2LCl_2(H_2O)_2]$  were  $M = Co(II), Cu(II), Zn(II)$ ;  $M' = Ni(II), Cd(II), Hg(II)$ ;  $LH_2 = 4, 4'$ -bis-

[(acetylacetylonyl-3'-azo)-3, 3'-dimethyldiphenyl]. All the six complexes are quite stable at room temperature. They are amorphous in nature, have high melting points and are insoluble in common organic solvents but sparingly soluble in dimethylformamide. Nonelectrolytic nature of the complexes is indicated from their low conductance values in DMF ( $3.7\text{--}6.8\text{ mhos cm}^2\text{ mol}^{-1}$ ).

In the IR spectrum of the ligand, the broad band observed at *ca.*  $3440\text{ cm}^{-1}$  can be attributed to  $\nu(\text{OH})$  vibration lowered due to  $\text{O—H} \cdots \text{O}$  intramolecular hydrogen bonding.<sup>2</sup> Disappearance of this band in the metal chelates indicates deprotonation of both the enolic OH groups thereby indicating their coordination to the metal ions. The ligand can exist in two tautomeric keto and enol forms. In the ligand four important bands at  $1670\text{ (C=C)}$ ,  $1610\text{ (C=O)}$ ,  $1180\text{ (C—O enolic)}$  and  $1620\text{ cm}^{-1}\text{ (—N=N—)}$  have been assigned. In the complexes the former three frequencies show negative shifts indicating the coordination of carbonyl and enolic oxygen atoms to the metal ions. The fourth band remains unaffected in the metal chelates showing non-coordination of the azo nitrogen atoms.<sup>4</sup> The presence of coordinated water molecules in all the complexes is indicated by the appearance of a broad band (*ca.*  $3300\text{--}3500\text{ cm}^{-1}$ ) followed by a sharp peak between  $835\text{--}845\text{ cm}^{-1}$  assignable to OH stretching and rocking vibrations respectively.<sup>5</sup>



The  $\mu_{\text{eff}}$  values of Co(II) and Cu(II) complexes are found to be 5.1 and 1.8 B.M. respectively indicating the presence of three and one unpaired electrons. The Ni(II) complex is found to be diamagnetic in nature.

The electronic spectrum of the Co(II) complex shows four bands at  $8,920$ ,  $18,155$ ,  $21,585$  and  $33,310\text{ cm}^{-1}$  which can be assigned to  $4T_{1g}(\text{F}) \rightarrow 4T_{2g}(\text{F}) \rightarrow 4A_{2g}(\text{F}) \rightarrow 4T_{1g}(\text{P})$  and CT bands respectively in conformity with an octahedral stereochemistry around the metal ions.<sup>6</sup> The Ni(II) complexes show two bands at  $16,250$  and  $17,435\text{ cm}^{-1}$  attributable to the  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1E_{1g}$  transitions respectively supporting a square-planar geometry.<sup>7</sup> Distorted octahedral stereochemistry is suggested to the Cu(II) complex as the broad band appears at  $13,210\text{--}15,350\text{ cm}^{-1}$  with the maxima at  $14,470\text{ cm}^{-1}$  assignable to  ${}^2E_g \rightarrow {}^2T_{2g}$  transition.<sup>8</sup>

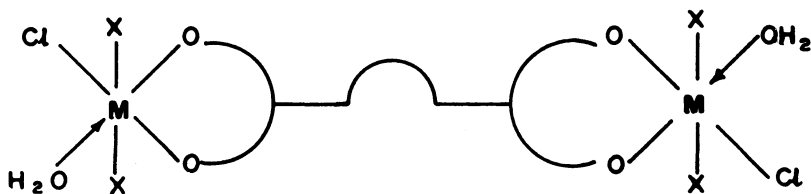
TABLE I  
ANALYTICAL, MAGNETIC AND IR SPECTRAL DATA ( $\text{cm}^{-1}$ )

Sl. No.	Compound and colour	Analysis % Found (Calcd.)		$\mu_{\text{eff}}$ B.M.	$\nu(\text{C}=\text{O})/\nu(\text{C}-\text{O})$
		M	N		
1.	$[\text{CO}_2\text{LCl}_2(\text{H}_2\text{O})_6]$ (Yellow)	15.90 (16.12)	7.60 (7.79)	5.1	1600, 1170
2.	$\text{Ni}_2\text{LCl}_2(\text{H}_2\text{O})_2$ (Reddish brown)	17.60 (17.83)	8.30 (8.56)	—	1595, 1170
3.	$[\text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_6]$ (Green)	16.90 (17.16)	7.50 (7.69)	1.8	1600, 1165
4.	$[\text{Zn}_2\text{LCl}_2(\text{H}_2\text{O})_6]$ (Grey)	17.40 (17.58)	7.40 (7.66)	—	1605, 1170
5.	$[\text{Cd}_2\text{LCl}_2(\text{H}_2\text{O})_2]$ (White)	29.10 (29.35)	7.10 (7.35)	—	1600, 1160
6.	$[\text{Hg}_2\text{LCl}_2(\text{H}_2\text{O})_2]$ (White)	42.20 (42.58)	5.80 (5.97)	—	1595, 1170

In the ESR spectrum of the Cu(II) complex, the " $g_{\text{av}}$ " value is found to be 2.123. The spectrum is isotropic consisting of a single line, characteristic of a regular octahedral geometry. This type of spectrum may result due to the fact that a regular octahedral stereochemistry undergoes a dynamic or pseudo-rotational type of Jahn-Teller distortion.<sup>9</sup>

The  $^1\text{H}$  NMR spectrum of the ligand shows unsymmetric complex patterns between 6.6–8.0 which corresponds to six phenyl protons. The sharp singlet peak observed at 3.2 $\delta$  shows the presence of twelve methyl protons of acetylacetonate moiety ( $-\text{CO}-\text{CH}_3$ ) and another peak at 2.3 $\delta$  for six methyl protons attached to two benzene nuclei (Ar-Me).

The Zn(II) complex is found to be octahedral and Cd(II) and Hg(II) complexes are tetrahedral based upon analytical and IR spectral data. The following structure can be proposed for the Complexes.



$\text{M} = \text{Co(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{X} = \text{H}_2\text{O}$

$\text{M} = \text{Ni(II)}, \text{Cd(II)}, \text{Hg(II)}, \text{X} = \text{Nil}$

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