

Polymetallic Complexes Part LXXXXI Dimeric and Monomeric Complexes of Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Hg^{II} with $\text{N} \cup \cup \text{N}$ and $\text{N} \cup$ Donor Bis-bidentate and Bi-dentate Azodye Ligands.

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Abstract

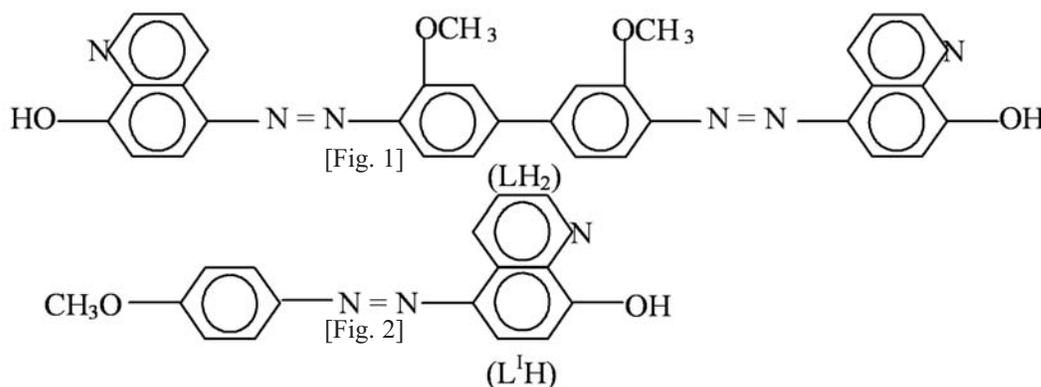
Bis-bidentate azodye, 4,4'-bis(4'-dihydroxyquinolineazo)3,3'-dimethoxydibenzene having $\text{N} \cup \cup \text{N}$ donors and bidentate azodye (4-hydroxyquinolineazo)4'-methoxybenzene having $\text{N} \cup$ donors form dimeric and monomeric complexes of the type $[\text{M}_2\text{LCl}_2(\text{H}_2\text{O})_6]$, $[\text{M}'_2\text{LCl}_2(\text{H}_2\text{O})_2]$, $[\text{ML}'_2(\text{H}_2\text{O})_2]$ and $[\text{M}'\text{L}'_2]$ where $\text{M} = \text{Co}^{\text{II}}$, Ni^{II} , Cu^{II} ; $\text{M}' = \text{Zn}^{\text{II}}$, Cd^{II} , Hg^{II} . The complexes of the first and third categories are found to be six-coordinated with an octahedral and distorted octahedral configuration and the complexes of second and fourth type are four-coordinated with a tetrahedral geometry around the metal ions. The complexes have been characterised based upon analytical, conductance, magnetic susceptibility, i.e., electronic spectra, N.M.R., E.S.R. and X-ray diffraction data. The unit cell parameters like a , b , c , α , β , γ and V (volume) have been calculated from the 2θ values. The unit cell geometry of the complex $[\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6]$ is found to be monoclinic.

Key words: Polymetallic complexes, Azodye complexes, Multidentate ligands.

Introduction

The pharmacological and chemotherapeutic activity of azodye is well recognised (Goodman and Gilman, 1970). Synthetic chemists have been inspired to prepare broad spectrum drugs from the azodyes of aromatic and heterocyclic amines. Some of the azodyes are used for dyeing food stuffs, preserving food grains and as redox indicator (Isa *et al.*). Potentiometric and Spectrophotometric studies of metal complexes with azodye ligands have been reported. Oxine and its derivatives possess antibacterial and amoebicidal

properties (Porter *et al.*, 1968). We have earlier reported the synthesis of a number of multidonor azodyes and their polymeric metal complexes (Mahapatra *et al.*, 1987). The present work reports the synthesis of one bis-bidentate and one bidentate azodye ligands containing these two potential biologically active moieties and their twelve dinuclear and mononuclear metal complexes with Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Hg^{II} ions.



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Materials and Methods

o-dianisidine, p-anisidine and 8-hydroxyquinoline are B.D.H. or E. Merck grade. Metal, nitrogen and chloride contents were estimated by standard methods. Conductivity measurement in DMF was made using Toshniwal CL 01-06 Conductivity Bridge. Magnetic moment was measured by Gouy method at room temperature. I.R. Spectra (KBr) were recorded on an IFS 66U Spectrophotometer, electronic spectra (10^{-2} M in DMF) using Hilger-Watt uvispeck spectrophotometer, E.S.R. spectrum on a E₄- spectrometer and N.M.R. spectra on a Jeol GSX 400 with CDCl₃ as solvent and relative to tetramethylsilane and X-ray diffraction (powder pattern) of the complex [Co₂LCl₂(H₂O)₆] was recorded on a Phillip PW 113/00 diffractometer.

Preparation of 4,4'-bis (4'-hydroxyquinolineazo)3,3'-dimethoxydibenzene

o-dianisidine (0.01 mol, 2.44 g) was dissolved in dil. HCl (10 mL) and was kept in ice cold water (0-5°C). Sodium nitrite solution was then added to it slowly with stirring when the corresponding diazonium chloride was formed. To the 8-hydroxyquinoline (Oxime) (0.02 mol, 3.18 g) solution in ethanol, sodium hydroxide solution was added and the resulting solution was then poured in to the above diazonium

chloride slowly with stirring when a red coloured azodye (LH₂) separated out. It was then filtered, washed with water and dried in vacuo.

Preparation of (4-hydroxyquinolineazo)4'-methoxybenzene

This azodye was prepared in a similar method by the coupling reaction of p-anisidine (0.01 mol, 1.23 g) with alkaline solution of 8-hydroxyquinoline (Oxime) (0.01 mol, 1.59 g). The reddish yellow azodye separated out immediately was then filtered, washed with water and dried in vacuo.

Preparation of the complexes

The metal chlorides in ethanol were mixed together with ethanolic solution of the ligands and the resulting solutions were refluxed at ~50°C for an hour on a heating mantle. The solution was then cooled down to room temperature and the pH was raised to ~7 by adding conc. ammonia drop by drop with stirring. The solid complexes thus separated were then washed with ethanol, followed by ether and dried in vacuum.

Result and Discussions

The analytical data (Table I) indicate that the metal complexes have the compositions [M₂LCl₂(H₂O)₆], [M₂LCl₂(H₂O)₂], [ML₂(H₂O)₂] and [ML₂]; where M = Co^{II}, Ni^{II},

Table I: Analytical and Physical data of the complexes

Compound	Colour	% Metal Found (Calculated)	% Nitrogen Found (Calculated)	% Chlorine Found (Calculated)	μ eff B.M.
LH ₂	Red	-	14.87 (15.10)	-	-
L ¹ H	Reddish yellow	-	14.73 (15.04)	-	-
[Co ₂ LCl ₂ (H ₂ O) ₆]	Violet	13.58 (13.76)	9.65 (9.88)	8.12 (8.35)	5.1
[CoL ₂ (H ₂ O) ₂]	Red	8.83 (9.05)	12.71 (12.90)	-	5.0
[Ni ₂ LCl ₂ (H ₂ O) ₆]	Reddish brown	13.52 (13.76)	9.79 (9.88)	8.21 (8.35)	3.1
[NiL ₂ (H ₂ O) ₂]	Reddish brown	8.88 (9.01)	12.73 (12.90)	-	3.0
[Cu ₂ LCl ₂ (H ₂ O) ₆]	Light brown	14.4 (14.76)	9.54 (9.76)	8.13 (8.25)	1.8
[CuL ₂ (H ₂ O) ₂]	Light brown	9.43 (9.69)	12.67 (12.81)	-	1.8
[Zn ₂ LCl ₂ (H ₂ O) ₂]	Brown	16.19 (16.42)	10.46 (10.61)	8.75 (8.96)	-
[ZnL ₂]	Brown	10.28 (10.52)	13.23 (13.51)	-	-
[Cd ₂ LCl ₂ (H ₂ O) ₂]	Brown	25.13 (25.31)	9.27 (9.49)	7.84 (8.02)	-
[CdL ₂]	Dark brown	16.55 (16.76)	12.36 (12.57)	-	-
[Hg ₂ LCl ₂ (H ₂ O) ₂]	Reddish brown	37.41 (37.75)	7.72 (7.90)	6.35 (6.68)	-
[HgL ₂]	Reddish brown	26.38 (26.51)	10.96 (11.10)	-	-

Cu^{II} ; $\text{M} = \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}, \text{Hg}^{\text{II}}$; $\text{LH}_2 = \text{C}_{32} \text{H}_{24} \text{O}_4 \text{N}_6$ (Fig. 1) (Calcd. (%) C, 69.06; H, 4.35; N, 15.1; Found (%) C, 69.02; H, 4.31; N, 14.87); $\text{L}^1\text{H} = \text{C}_{16} \text{H}_{13} \text{O}_2 \text{N}_3$ (Fig. 2) (Calcd. (%) C, 68.81; H, 4.69; N, 15.04; Found (%) C, 68.63; H, 4.54; N, 14.73). All the six complexes with ligand (LH_2) are powdery in nature having high melting points and are insoluble in common organic solvents but the six complexes with ligand (L^1H) are crystalline, soluble in organic solvents and have low melting points. The non-electrolytic nature of all the twelve complexes are correlated with the low μ_M values ($4.3\text{--}6.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$).

In the IR spectra of the ligands, (Table II) one broad band appears at $3431(\text{LH}_2)$ and the other at $3411(\text{L}^1\text{H})$ which might be due to O-H...N intramolecular hydrogen bonding. These bands are non-existent in the metal complexes, indicating the bonding of the phenolic -OH groups to the metal ions (Mishra and Keshari, 1981). The $\nu_{(\text{C}=\text{N})}$ band observed at $1595 \text{cm}^{-1}(\text{LH}_2)$ and $1600 \text{cm}^{-1}(\text{L}^1\text{H})$ remain unaffected in the metal chelates showing non-coordination of the azo nitrogen atoms to the metal atoms (King and Bisnette, 1966). The bands observed at $1168 \text{cm}^{-1}(\text{LH}_2)$ and $1152 \text{cm}^{-1}(\text{L}^1\text{H})$ in the ligands are attributable to $\nu_{(\text{C}-\text{O})}$ vibration and the bathochromic shift of $\sim 40 \text{cm}^{-1}$ in the metal complexes indicates the bonding of oxine oxygen to the metal atom. In the spectra of the ligands, an intense band is observed at 1400

$\text{cm}^{-1}(\text{LH}_2)$ and at $1403 \text{cm}^{-1}(\text{L}^1\text{H})$ due to C—N Vibration of the oxinate (Magee and Gorden) group. In the metal complexes this band occurs at $\sim 1320 \text{cm}^{-1}$. The shift of this band to lower frequency regions show considerably lower double bond character of the C—N bond due to involvement of the ring nitrogen on complexation. One broad band appears in the region $3400\text{--}3412 \text{cm}^{-1}$ for LH_2 complexes and the other peaks at $\sim 837\text{--}842 \text{cm}^{-1}$ for $\text{Co}^{\text{II}}, \text{Ni}^{\text{II}}$ and Cu^{II} , L^1H complexes which are assignable to -OH stretching and rocking vibrations respectively indicating the presence of coordinated water molecules in the complexes (Nakamoto, 1978 and Gamo, 1961). The evidence of bonding of oxygen and nitrogen atoms in oxine is further substantiated by the appearance (Ferraro, 1971) of bands at $\sim 603 \text{cm}^{-1}$ and $\sim 516 \text{cm}^{-1}$ assignable to $\nu_{(\text{M}-\text{O})}$ and $\nu_{(\text{M}-\text{N})}$ vibrations respectively.

The cobalt(II), nickel(II) and copper(II) complexes exhibit magnetic moments at $\sim 5.1, 3.1$ and 1.8B.M. indicating the presence of three, two and one unpaired electron respectively (Cotton and Wilkinson, 1988).

Three bands appear at $9100(9090), 18315(18280)$ and $21560(21470) \text{cm}^{-1}$ in the electronic spectra of Co^{II} complexes, which could be attributed to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F}) (\nu_1), \rightarrow {}^4\text{A}_{2g}(\text{F}) (\nu_2)$ and $\rightarrow {}^4\text{T}_{1g}(\text{P}) (\nu_3)$ transitions respectively. The value of the spectral parameters like $\text{Dq} = 921.5(919) \text{cm}^{-1}$, $\text{B} = 838.3(832.0) \text{cm}^{-1}$, $\beta_{35} = 0.863(0.856) \text{cm}^{-1}$, $\nu_2/\nu_1 = 2.01(2.01)$ and $\sigma = 15.87\%(16.82\%)$ of Co^{II} complexes are suggestive of an octahedral stereochemistry around the metal ion (Lever 1968). In the electronic spectra of Ni^{II} complexes, four bands appear at $10250(10282), 17122(17315), 24980(24992)$ and $32240(31355) \text{cm}^{-1}$ which may be assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F}) (\nu_1), \rightarrow {}^3\text{T}_{1g}(\text{F}) (\nu_2), \rightarrow {}^3\text{T}_{1g}(\text{P}) (\nu_3)$ and CT transition respectively. Spectral parameters like $\text{Dq} = 1025.0(1028.2) \text{cm}^{-1}$, $\text{B} = 756.80(764.06) \text{cm}^{-1}$, $\beta_{35} = 0.726(0.773) \text{cm}^{-1}$, $\nu_2/\nu_1 = 1.67(1.68)$ and $\sigma = 37.74\%(36.42\%)$ indicates the octahedral symmetry. In the case of the copper (II) complexes one broad asymmetry band appears at $12750\text{--}12980 \text{cm}^{-1}$ characteristic of distorted octahedral stereochemistry with D_{4h} symmetry (Procter *et al.*, 1968). The broadness of the bands might be due to Jahn-Teller distortion.

Table II: Infrared spectra of the ligands and the complexes

Compounds	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
LH_2	1168	1400	-	-
L^1H	1152	1403	-	-
$[\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6]$	1130	1321	603	516
$[\text{CoL}^1_2(\text{H}_2\text{O})_2]$	1112	1313	603	517
$[\text{Ni}_2\text{LCl}_2(\text{H}_2\text{O})_6]$	1130	1321	602	515
$[\text{NiL}^1_2(\text{H}_2\text{O})_2]$	1115	1315	602	516
$[\text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_6]$	1132	1320	603	515
$[\text{CuL}^1_2(\text{H}_2\text{O})_2]$	1112	1313	603	517
$[\text{Zn}_2\text{LCl}_2(\text{H}_2\text{O})_2]$	1130	1322	603	516
$[\text{ZnL}^1_2]$	1115	1315	603	517
$[\text{Cd}_2\text{LCl}_2(\text{H}_2\text{O})_2]$	1130	1320	602	515
$[\text{CdL}^1_2]$	1110	1313	602	515
$[\text{Hg}_2\text{LCl}_2(\text{H}_2\text{O})_2]$	1132	1321	601	516
$[\text{HgL}^1_2]$	1115	1315	602	516

In the E.S.R. spectra of the copper complexes $[\text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_6]$ and $[\text{Cu}_2\text{L}^1_2(\text{H}_2\text{O})_2]$ were recorded at Q-band and the ' g_{av} ' values were found to be 2.05554 and 2.05848 respectively by Kneubuhl's method (Kneubuhl 1960). These spectra are found to be isotropic, consisting of a single line which is a characteristic of complexes having regular octahedral geometry. This type of spectrum may also result due to regular octahedral stereochemistry undergoing a dynamic or pseudo-rotational type of Jahn-Teller distortion.

The ^1H NMR spectra of the ligands LH_2 and L^1H were recorded in CDCl_3 solvent with TMS as internal standard. The complex pattern observed at δ 6.797 - 8.198 (LH_2) and δ 6.983 - 8.186 (L^1H) corresponds to 16 and 8 aromatic protons each. The sharp singlet peak observed at δ 4.019 (LH_2) and δ 3.972 (L^1H) corresponds to six and three methoxy ($-\text{OCH}_3$) protons respectively. The phenolic protons could not be detected as it was beyond the range of the instrument.

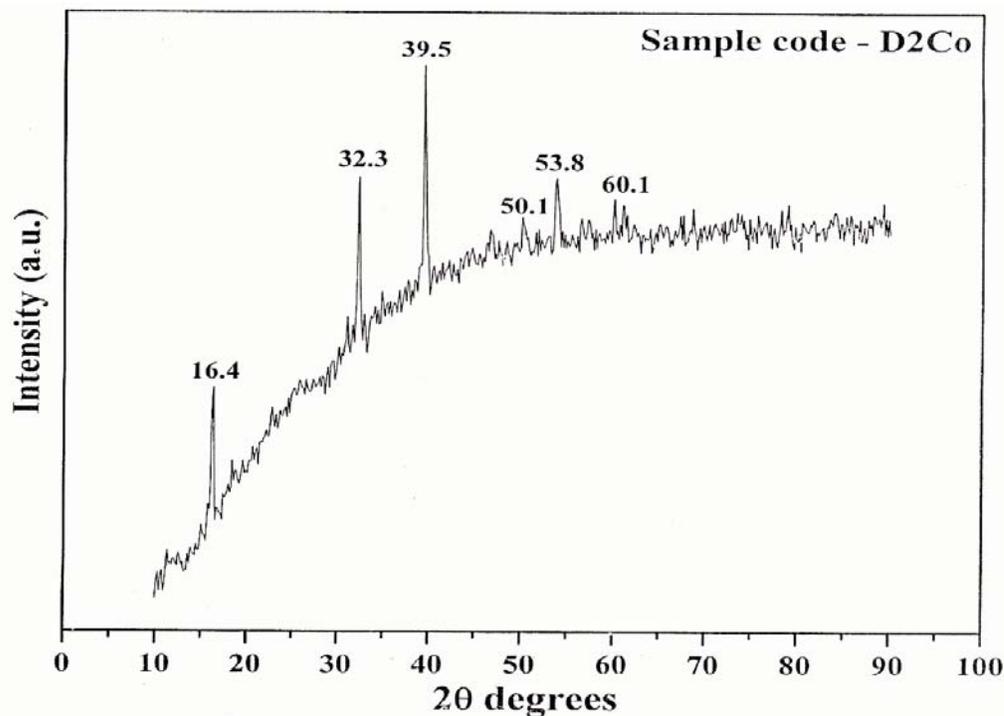
The XRD study (powder pattern) of the complex $[\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6]$ was shown in graph-1. The unit cell parameters a , b , c , α , β , γ and V (volume) have been calculated from the 2θ

values. The density (d) of the complex was determined by floatation method. The number of formula units (n) per unit cell is calculated from the relation $n = dNV / M$ where d = density of the compound, N = Avogadro's number, V = Volume of the unit cell and M = molecular weight of the compound. The value of ' n ' is found to be 1.0 for the complex corresponding to the volume of the unit cell 414.95 \AA^3 . The unit cell is found to be 'monoclinic', based upon the unit cell parameters (Puri *et al.*, 1993) (Table III).

The Zn^{II} , Cd^{II} and Hg^{II} complexes are suggested to be four-coordinated having tetrahedral geometry based on analytical, IR and conductance data.

Conclusion

The azodye LH_2 having O N-N O donor atoms behaves as a bis-bidentate ligand and the azodye L^1H behaves as a bidentate ligand having O N donor atoms. The former ligand binds two metal atoms on either side forming dimeric complexes whereas the latter ligand forms monomeric complexes with the metal ions. Both the azodyes coordinate to the metal atoms through the quinolyl oxygen and nitrogen atoms.



Graph-1: XRD Graph for $[\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6]$ complex

Table III: X-ray diffraction data of the complex

Compound	2 θ -Values in degrees	Unit cell parameters	Density, (g/cm ³)	N	Possible crystal system
[Co ₂ LCl ₂ (H ₂ O) ₆]	10.897,12.991,14.935, 16.430,18.975,21.964, 28.993,32.300,39.313, 39.462,39.521,39.612, 50.137,53.670,53.820, 60.101,60.998,61.148, 68.626,73.411,73.860, 78.197,83.881,84.030, 85.675,88.218,89.265	a = 11.843 Å b = 4.925 Å c = 7.127 Å α = 90.00 ° β = 93.425 ° γ = 90.00 ° V = 414.95 cc	2.04	1.0	Monoclinic

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