

Azodye ONO Donor Complexes of Co(II), Ni(II), Cu(II), Zn(II) Cd(II) and Hg(II)

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Six azodye complexes of composition $[MLCl(H_2O)_2]$ and $[M'LCI]$ have been prepared where $M = Co(II), Ni(II), Cu(II), Zn(II)$, $M' = Cd(II), Hg(II)$ and $LH = 2-(2',4'-dinitro-1-hydroxyphenylazo)-5-chlorobenzophenone$. The complexes of the first category are hexa coordinated having either octahedral or distorted octahedral geometry and the complexes of the latter type are tetracoordinated having tetrahedral stereochemistry based on analytical, conductance, magnetic susceptibility, IR, electronic spectra, ESR, NMR and X-ray diffraction data.

INTRODUCTION

In continuation of earlier studies on the preparation and characterisation of metal complexes using multidentate azodye ligands¹, the present paper reports the synthesis of a new tridentate ONO donor azodye ligand and its six mononuclear complex compounds.

RESULTS AND DISCUSSION

The complexes have the compositions $[MLCl(H_2O)_2]$ and $(M'LCI)$, $M = Co(II), Ni(II), Cu(II), Zn(II)$; $M' = Cd(II), Hg(II)$; $LH = 2-(2',4'-dinitro-1-hydroxy phenylazo)-5-chlorobenzophenone$.

All the complexes are very stable at room temperature. The complexes are mostly crystalline in nature and insoluble in common organic solvents but soluble in dimethylformamide and dimethylsulfoxide. The non-electrolytic nature of solution of complexes is indicated from the low Δ_M values ($4.7-5.9 \Omega \text{ cm}^2 \text{ mol}^{-1}$).

The IR band of the ligand at 3267 cm^{-1} can be assigned to $O-H \dots N$ intramolecular hydrogen bonding. Disappearance of this band in the metal chelates indicates the bonding of the phenolic $-OH$ group to the metal ions². In the ligand the band observed at 1536 cm^{-1} can be assigned to phenolic $C-O$ vibration and a decrease of about $10-20 \text{ cm}^{-1}$ is found in the metal complexes showing the coordination of the ligand to the metal ions through the phenolic oxygen atom. The sharp band observed in the ligand at 1598 cm^{-1} can be ascribed to $-N=N-$ band and appearance of this band at *ca.* 1567 cm^{-1} in the metal complexes indicates the bonding of one of the azo nitrogen atoms to the metal ions³. In the ligand the band observed at 1625 cm^{-1} can be assigned to $(C=O)$ vibration and in the metal

chelates it appears at *ca.* 1610 cm^{-1} indicating the bonding of carbonyl oxygen atoms to the metal ions. In case of Co(II), Ni(II), Cu(II) and Zn(II) complexes, the sharp and broad bands appeared at *ca.* 3560 and 3200 cm^{-1} followed by a sharp peak at *ca.* 839 cm^{-1} assignable to stretching, rocking and wagging vibrations respectively, thus indicating the presence of coordinated water molecules in these complexes⁴. The conclusive evidence of bonding of the ligand to the metal ion is obtained by the appearance of bands at *ca.* 422 and 529–518 cm^{-1} assignable to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ respectively in the far IR spectra of the complexes⁵.

The μ_{eff} values of Co(II), Ni(II) and Cu(II) are found to be 5.1, 3.0 and 1.8 BM respectively indicating the presence of three, two and one unpaired electrons respectively⁶.

The electronic spectrum of the cobalt complex consists of four bands at 8670, 17215, 18890 and 32100 cm^{-1} . The last band may be a CT band and the first three bands may be assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, $\rightarrow {}^4\text{A}_{2g}(\text{F})$ and $\rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions respectively in conformity with an octahedral stereochemistry. The ligand field parameters like $D_q = 854.5 \text{ cm}^{-1}$, $B = 739.6 \text{ cm}^{-1}$, $\beta_{35} = 0.761$, $\nu_2/\nu_1 = 1.98$ and $\sigma = 31.40$ suggest an octahedral geometry for the Co(II) complex⁷. In the electronic spectrum of copper complex, one broad asymmetrical band appears at 13555, 14685 cm^{-1} with maxima at 14370 cm^{-1} attributable to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition which is suggestive of a distorted octahedral geometry⁸. In the nickel complex four bands are observed at 10120, 16250, 26690 and 32250 cm^{-1} assignable to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, $\rightarrow {}^3\text{T}_{1g}(\text{F})$, $\rightarrow {}^3\text{T}_{1g}(\text{P})$ and CT transitions respectively in a distorted octahedral (D_4 symmetry) field. The ligand field parameters like $D_q = 1012 \text{ cm}^{-1}$, $B = 838.6 \text{ cm}^{-1}$, $\beta_{35} = 0.805$, $\nu_2/\nu_1 = 1.60$, $\sigma = 24.22$ show an octahedral stereochemistry for the complex⁹.

In the complex $[\text{CuLCl}(\text{H}_2\text{O})_2]$, the ' g_{av} ' is found to be 2.0634 by applying Kneubuhl's method¹⁰. The type of spectrum may be due to dynamic or pseudo-rotational type of Jahn-Teller distortion.

The ${}^1\text{H}$ NMR spectrum of the ligand displays sharp peak at δ 11.0 and a complex pattern at δ 7.4–9.0 due to one phenolic and ten aromatic protons respectively.

The X-ray diffraction study (powdered pattern) of the complex $[\text{ZnLCl}(\text{H}_2\text{O})_2]$ has been indexed and the unit cell parameters like a , b , c , α , β , γ and volume of the unit cell have been calculated with the help of computer to be 9.068 Å, 9.465 Å, 7.843 Å, 90.058 Å, 94.493 Å, 90.906 Å and 668.34 (Å)³ respectively which are suggestive of the triclinic nature of the complex. In addition to it, we can infer the number of formula units per unit cell which is compatible with the triclinic system. The number of formula units (n) per unit cell is calculated from the relation $n = \frac{dNV}{M}$, where d = density of the compound,

N = Avogadro's number, V = volume of the triclinic unit cell, M = molecular weight of the compound. We found the density of the compound to be 1.39. The

number of formula units is found to be 1 which is compatible with triclinic unit cell. We observe that there is no centre of symmetry in the molecule and the structure of the complex corresponds to the triclinic system.

The Zn(II) complex is six coordinated and Cd(II) and Hg(II) complexes are four coordinated with an octahedral and tetrahedral geometries respectively basing upon analytical and IR spectral data, Table-1.

TABLE-1
ANALYTICAL DATA OF THE LIGAND AND THE COMPELXES

Compounds	Colour	% Analysis, Found (Calcd.)		
		M	N	Cl
LH	Pink	–	12.70 (13.13)	8.10 (8.32)
[CuLCl(H ₂ O) ₂]	Green	10.80 (11.33)	9.50 (9.99)	12.50 (12.66)
[NiLCl(H ₂ O) ₂]	Light green	10.20 (10.56)	9.70 (10.07)	12.20 (12.77)
[CoLCl(H ₂ O) ₂]	Light green	10.40 (10.60)	9.80 (10.07)	12.50 (12.77)
[ZnLCl(H ₂ O) ₂]	Light yellow	11.20 (11.62)	9.50 (9.95)	12.20 (12.62)
[CdLCl]	Yellow	19.30 (19.60)	9.60 (9.76)	12.10 (12.38)
[HgLCl]	White	29.80 (30.30)	8.20 (8.46)	10.20 (10.73)

LH = 2-(2',4'-dinitro-1'-hydroxy-phenylazo)-5-chlorobenzophenone.

Hence the azodye (LH) behaves as ONO donor tridentate ligand, coordinating to the metal ions through phenolic oxygen, carbonyl oxygen and azo nitrogen atoms. The most probable structure of the complexes can be represented by Fig. 1.

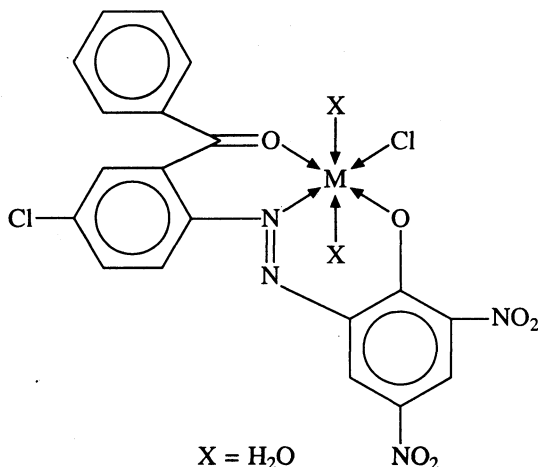


Fig. 1.

EXPERIMENTAL

All the chemicals were BDH make. The ligand (LH) was prepared by the coupling reaction of diazonium chloride obtained from 2-amino-5-chlorobenzophenone with 2,4-dinitrophenol at 0°C.

Preparation of the Complexes: A mixture of ethanolic solutions of the metal chlorides and azo dyes (in 1 : 1 molar ratio) was refluxed for 0.5 h. On cooling conc. ammonium hydroxide was added dropwise. The metal complexes formed were then filtered and washed with ether and dried in vacuum.

Metal contents of the complexes were estimated by standard methods. CHN were analysed by semi-micro combustion method using MLW Microelementary CHN analyser. Conductance was measured in 10^{-3} M DMF solutions of the complexes. Magnetic susceptibility was measured by Gouy method. IR spectra (KBr) were recorded on a Perkin-Elmer 398 spectrophotometer, electronic spectra on a Hilger and Watt Unispeck spectrophotometer, NMR spectra in acetone- D_6 on an EM-390 (90 MHz) NMR spectrophotometer at room temperature, and ESR spectra of the copper complex at room temperature on a Varian E₄ ESR spectrophotometer. X-ray diffraction of the complex has been recorded on PW 1130 model X-ray diffractometer supplied by M/S Phillips, Holland.

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