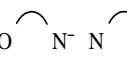


Polymetallic Complexes Part LXXXXV Bis-bidentate Donor Azodye Dimeric Complexes

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Abstract

Twelve dimeric complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with two new bis-bidentate  donor azodye ligands, 4,4'-bis (2'-hydroxy-3',5'-dinitrophenylazo) diphenylsulphone and 4,4'-bis (2'-hydroxy-5'-nitrophenylazo) diphenylsulphone has been synthesized. The structure elucidation of the complexes was made basing upon analytical, conductance, magnetic susceptibility, IR, electronic spectra, ESR, NMR, and X-ray diffraction (powder pattern) data. Antifungal activities of the ligands and a few complexes were also studied. The cobalt (II) and nickel (II) complexes are found to be octahedral, copper (II) complexes are distorted octahedral and a tetrahedral stereochemistry has been suggested to Zn (II), Cd (II) and Hg (II) complexes.

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

Introduction

The azodyes are found to possess chemotherapeutic properties (Gaind and Khanna, 1964; Gulati and Gaind, 1966; Goodman and Gilman; 1970)). In addition they are also used for dyeing food stuffs, for preserving food grains and as indicator in chemical laboratories (Dessouki *et al.*, 1984). We have been trying to synthesize multidentate azodyes and their polymeric metal chelates to study their molecular structure and antimicrobial activities (Mahapatra *et al.*, 2002, 2003, 2004, 2007)

Materials and Methods

All the chemicals were of B. D. H. or E. Merck grade. The metal, carbon, hydrogen, nitrogen, sulphur and chlorine were estimated by standard methods (Vogel 1962). Conductivity measurements of the complexes were made using Toshniwal CL 01-06 Conductivity Bridge. The magnetic moment was measured at room temperature by Gouy method. IR Spectra (KBr) were recorded using IFS 66U spectrophotometer, electronic spectra (10^{-2} M in DMF) using Hilger-Watt uvispeck spectrophotometer, ESR spectra of copper (II) complexes on a E_4 spectrometer and NMR spectra on a Jeol GSX 400 with $CDCl_3$ as solvent and TMS as internal standard and X-ray diffraction (powder pattern) of the complexes $[Co_2LCl_2(H_2O)_6]$ and $[Co_2L'Cl_2(H_2O)_6]$ were recorded on a Phillip PW 1130/00 diffractometer.

Preparation of the ligands

Both the azodye ligands were synthesized by the coupling reaction of the diazonium chlorides obtained from 4,4'-diammoniumdiphenylsulphone (0.01 mol, 2.48 g) separately with alkaline solution of 2,4-dinitrophenol (0.02 mol, 3.68 g) and 4-nitrophenol (0.02 mol, 2.78 g) at 0 to 5°C.

Preparation of the complexes

The metal chlorides in ethanol were mixed separately with ethanolic solution of the ligands in 2 : 1 molar ratio and the resulting solutions were then heated at 50 to 60°C for about 1hr on a heating mantle. On cooling, pH of the solution was raised to ~ 7 by adding concentrated ammonia drop by drop with stirring. The solid complexes, thus separated were then washed with ethanol followed by ether and dried in vacuum.

The antifungal activity of the ligands and some of the complexes were measured (Gilman, 1967; Martin, 1950). The compounds were screened against one strain of fungi, *Aspergillus niger* (Van tieghem). A 1 mg/ml solution in DMF was used. The diameter of zone of inhibition in mm was measured after 72 hours of incubation at 25°C. Streptomycin was used as a reference for this test.

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Results and Discussion

The metal complexes synthesized (Table I) have the compositions $[M_2L/L'Cl_2(H_2O)_6]$ and $[M'_2L/L'Cl_2(H_2O)_2]$ where $M = Co(II), Ni(II), Cu(II)$; $M' = Zn(II), Cd(II), Hg(II)$; $LH_2 = C_{24}H_{14}N_8O_{12}S$ (Figure 1) (Calcd, (%): C, 45.10; H, 2.19; N, 17.55; S, 5.01; Found, (%): C, 44; H, 2.1; N, 17.4; S, 4.9);

$L'H_2 = C_{24}H_{16}N_6O_8S$ (Fig. 2) (Calcd, (%): C, 52.55; H, 2.92; N, 15.32; S, 5.83; Found, (%): C, 52.4; H, 2.8; N, 15.2; S, 5.7). All the complexes are amorphous in nature, have high melting points and are insoluble in common organic solvents but sparingly soluble in dimethyl formamide. The non-electrolytic nature of all the complexes is shown from low conductance values ($3.5 - 5.8\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

Table I. Analytical and physical data of the complexes

Compound	Colour	Metal found (calculated)%	Nitrogen found (calculated)%	Sulphur found (calculated)%	Chlorine found (calculated)%	μ_{eff} . BM
LH_2 $C_{24}H_{14}N_8O_{12}S$	Yellow	–	17.1 (17.55)	4.9 (5.01)	–	–
$L'H_2$ $C_{24}H_{16}N_6O_8S$	Reddish brown	–	15.1 (15.32)	5.7 (5.83)	–	–
$[Co_2LCl_2(H_2O)_6]$	Yellow	12.4 (12.63)	11.8 (12.00)	3.2 (3.43)	7.5 (7.61)	5.1
$[Co_2L'C_2(H_2O)_6]$	Deep brown	12.6 (12.79)	9.8 (9.96)	3.6 (3.79)	8.2 (8.42)	5.0
$[Ni_2LCl_2(H_2O)_6]$	Yellow	12.2 (12.58)	11.8 (12.01)	3.2 (3.43)	7.4 (7.61)	3.1
$[Ni_2L'Cl_2(H_2O)_6]$	Deep brown	13.7 (13.93)	9.8 (9.97)	3.6 (3.79)	8.2 (8.42)	3.0
$[Cu_2LCl_2(H_2O)_6]$	Yellow	13.1 (13.49)	11.5 (11.88)	3.1 (3.39)	7.3 (7.53)	1.8
$[Cu_2L'Cl_2(H_2O)_6]$	Brown	14.7 (14.91)	9.7 (9.85)	3.6 (3.75)	8.2 (8.33)	1.8
$[Zn_2LCl_2(H_2O)_2]$	Yellow	14.6 (14.96)	13.1 (13.36)	3.5 (3.82)	8.2 (8.47)	–
$[Zn_2L'Cl_2(H_2O)_2]$	Reddish brown	16.5 (16.68)	10.5 (10.71)	3.9 (4.08)	8.9 (9.05)	–
$[Cd_2LCl_2(H_2O)_2]$	Yellow	23.1 (23.22)	11.2 (11.57)	3.2 (3.30)	7.1 (7.33)	–
$[Cd_2L'Cl_2(H_2O)_2]$	Brown	25.4 (25.61)	9.4 (9.57)	3.5 (3.64)	7.9 (8.08)	–
$[Hg_2LCl_2(H_2O)_2]$	Yellow	34.8 (35.06)	9.5 (9.78)	2.5 (2.79)	6.0 (6.20)	–
$[Hg_2L'Cl_2(H_2O)_2]$	Brown	37.8 (38.05)	7.8 (7.96)	2.9 (3.03)	6.6 (6.73)	–

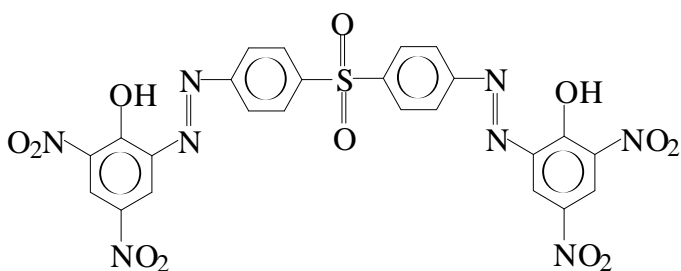


Fig. 1. Structure of LH_2

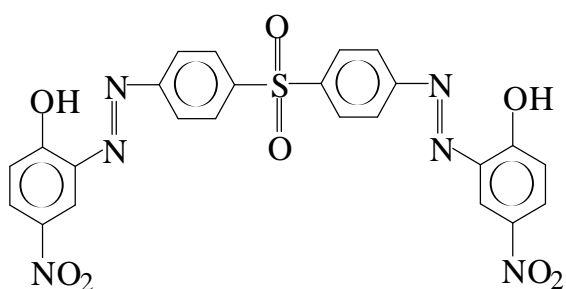


Fig. 2. Structure of $L'H_2$

In IR spectra of the ligands, one broad band appears at 3444 cm^{-1} (LH_2) and at 3435 cm^{-1} ($L'H_2$) and it may be attributed to intramolecular O-H...N hydrogen bonding. Disappearance of these bands in the metal chelates indicates the bonding of the phenolic -OH groups to the metal atoms. The bands at 1536 cm^{-1} (LH_2) and at 1513 cm^{-1} ($L'H_2$) can be attributed to phenolic C-O vibration and in the metal chelates these bands appear at $\sim 1521\text{ cm}^{-1}$ and $\sim 1495\text{ cm}^{-1}$ repetitively indicating the bonding of the ligands to the metal ions through the phenolic oxygen atoms (Mishra and Keshari, 1981). The sharp band in the ligands appear at 1598 cm^{-1} (LH_2) and at 1591 cm^{-1} ($L'H_2$) and it can be assigned to $\nu_{(N=N)}$ vibration and in the metal complexes these bands appear at $\sim 1564\text{ cm}^{-1}$ and $\sim 1582\text{ cm}^{-1}$ which indicate the bonding of one of the azo nitrogen atoms to the metal atoms (King, 1966). In the metal chelates, broad bands appear at $\sim 3420\text{-}3551\text{ cm}^{-1}$ and $\sim 3521\text{-}3544\text{ cm}^{-1}$ followed by sharp peaks at $\sim 845\text{ cm}^{-1}$, $\sim 715\text{ cm}^{-1}$ ($\sim 836\text{ cm}^{-1}$, $\sim 728\text{ cm}^{-1}$) assignable to OH stretching, rocking and wagging vibrations respectively indicating the presence of co-ordinated water molecules in the complexes (Nakamoto, 1978). The conclusive evidence of bonding of the ligands to the metal ions is

proved by the appearance of bands at $\sim 541\text{-}543\text{ cm}^{-1}$ (M-O) and $\sim 465\text{-}467\text{ cm}^{-1}$ (M-N) (Ferraro, 1971).

The Co(II), Ni(II) and Cu(II) complexes exhibit magnetic moments at ~ 5.0 , ~ 3.0 and $\sim 1.8\text{ BM}$ indicating the presence of three, two and one unpaired electrons respectively (Cotton and Wilkinson, 1988).

In the electronic spectra of Co^{II} complexes, four ligand field bands are observed at 8250 (8255) cm^{-1} , 16480 (16520) cm^{-1} , 20267 (20295) cm^{-1} and 32270 (32310) cm^{-1} . The first three bands can be attributed to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(v_1)$, $\rightarrow {}^4A_{2g}(F)(v_2)$ and $\rightarrow {}^4T_{1g}(P)(v_3)$ transitions respectively and the fourth band is assigned to a CT band. The ligand field parameters like $Dq = 823.0$ (826.5) cm^{-1} , $B = 799.8$ (803.33) cm^{-1} , $\beta_{35} = 0.823$ (0.827) cm^{-1} , $v_2/v_1 = 1.997$ (2.001) and

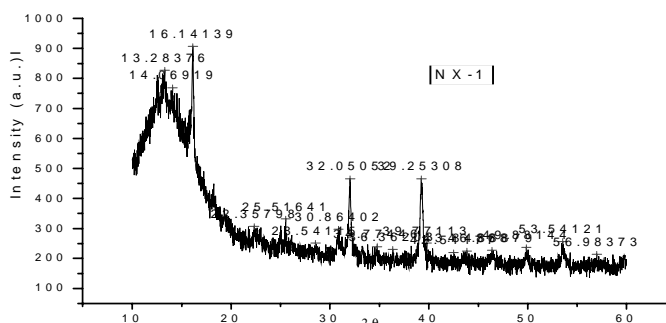


Fig. 3. X-ray diffraction graph of the
Complex: $[Co_2LCl_2(H_2O)_6]$

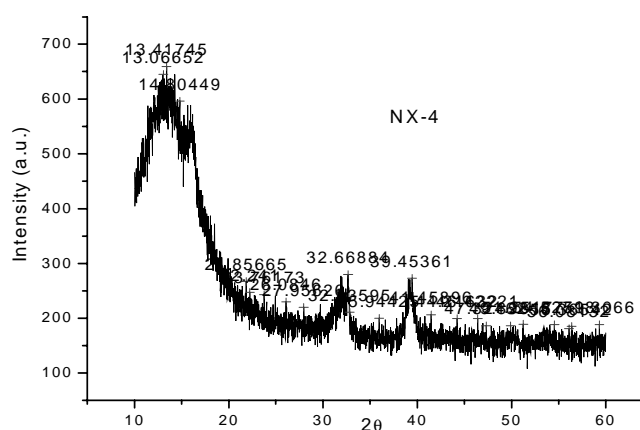


Fig. 4. X-ray diffraction graph of the
Complex: $[Co_2L'Cl_2(H_2O)_6]$

Table II: Powder X-Ray diffraction data of the complexes

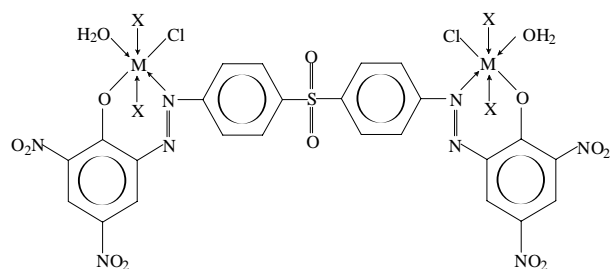
Compound	2 θ values	Unit Cell parameters	Density (g/cc)	n	Possible geometry
[Co ₂ LCl(H ₂ O) ₆]	13.284 13.936 16.141 17.228 18.130 18.264 19.300 21.756 22.659 25.010 25.516 30.914 32.051 39.253 41.659 42.244 43.849 46.389 47.308 48.194 49.881 50.032 51.419 53.174 53.541 53.976 54.076 54.277 55.680 56.148 56.265 56.466 56.766 56.833 56.984 57.184 57.836 58.087 58.621 59.323	A=13.300 Å B=20.543 Å C=6.985 Å $\alpha=90.000^\circ$ $\beta=102.325^\circ$ $\gamma=90.000^\circ$ V=1864.37 Å ³	0.83	1	Monoclinic
[Co ₂ L'Cl ₂ (H ₂ O) ₆]	13.066 13.417 14.804 21.856 22.241 23.761 26.084 27.956 32.668 32.835 35.944 39.453 41.458 44.216 46.422 47.324 49.898 51.251 54.527 56.081 56.365 59.306	A=8.546 Å B=18.487 Å C=7.371 Å $\alpha=90.000^\circ$ $\beta=106.893^\circ$ $\gamma=90.000^\circ$ V=1114.34 Å ³	1.25	1	Monoclinic

$\sigma = 21.506$ (20.918)% suggest an octahedral geometry for the complexes (Lever and Ogden 1967). In the electronic spectra of Ni(II) complexes, four ligand field bands are observed at 10230 (10145) cm⁻¹, 17295 (17335) cm⁻¹, 24990 (24995) cm⁻¹ and 32710 (32780) cm⁻¹ assignable to ³A_{2g}(F) → ³T_{2g}(F)(ν_1), → ³T_{1g}(F)(ν_2) and → ³T_{1g}(P)(ν_3) and CT transition respectively in a distorted octahedral symmetry field. The ligand field parameters like Dq = 1023.0 (1014.5) cm⁻¹, B = 733 (793) cm⁻¹, $\beta_{35} = 0.742$ (0.761) cm⁻¹, $\nu_2/\nu_1 = 1.690$ (1.708) and $\sigma = 34.770$ (31.406)% also confirm the octahedral symmetry for the complexes. The electronic spectra of the Cu (II) complexes show one broad band at ~ 13562-14885 cm⁻¹ with a maxima at ~ 14355 cm⁻¹ which could be attributed to ²E_g → ²T_{2g} transition in support of a distorted octahedral geometry of the complexes (Hathway and Billing 1970).

The ESR spectra of the copper complexes [Cu₂LCl₂(H₂O)₆] and [Cu₂L'Cl₂(H₂O)₆] were recorded at X-band at room temperature. The 'g_{av}' value of the first complex is found to be 2.08170 by applying Kneubuhl's method (Kneubuhl,

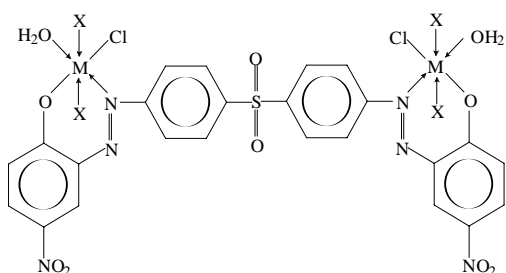
1960). This type of spectrum may be due to dynamic or pseudorotational type of Jahn-Teller distortion. In the second complex computation made by Piesach and Blumberg's method (Peisach and Blumberg, 1969) suggests the presence of two 'g' values. The geometry around the copper ions in the unit cell is elongated octahedral with g_⊥ = 2.0555 and g_{||} = 2.23495. The axial symmetry parameter "G" for the complex is found to be 4.23 which suggest (Hathway *et al.*, 1968; Hathway and Tomlinson, 1968) the absence of exchange interaction among magnetically equivalent Cu^{II} ions in the unit cell. The g_{||} is a function for representing covalency. The g_{||} is found to be less than 2.3, indicating covalent nature of the complex, g_{||} > g_⊥ > g_e (2.0023) indicates that the unpaired electron is localised in d_{x²-y²} orbital.

The ¹H NMR spectra of the ligands LH₂ and L'H₂ were recorded in CDCl₃. The complex pattern observed at δ 7.602-8.946 (LH₂) and at δ 6.636-8.377 (L'H₂) correspond to



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

Fig. 5



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

Fig. 6

12 and 14 number of phenyl protons respectively. The phenolic protons could not be detected as it is out of the range of the instrument used.

The XRD (Powder Pattern) of the complexes [Co₂LCl₂(H₂O)₆] and [Co₂L'Cl₂(H₂O)₆] were indexed in X-ray diffractometer and the unit cell parameters have been calculated with the help of a computer from 2θ values (Fig. 3 and 4 respectively). The direct constant parameters like A, B, C, α, β, γ, V (volume) are given in Table II.

The density of the complexes has been determined by the floatation technique in a saturated solution of NaCl, KBr and benzene separately. The number of formula units per unit cell (n) was 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 complex. The value of 'n' is found to be 1.0 for both complexes which agree well with the suggested monoclinic structure of the complexes (Puri *et al.*, 1993).

The Zn(II), Cd(II) and Hg(II) complexes are suggested to be four co-ordinated having a tetrahedral geometry basing upon analytical, conductance and IR spectral data. Hence both the azodyes behave as bis-bidentate (tetradentate) ligands and form dimeric complexes with the divalent metal ions as shown in Fig. 5 and 6 respectively.

Table III. Antimicrobial activities of the compounds with their inhibition zones in (mm)

Compound	<i>Aspergillus niger</i> Van Tieghem
LH ₂ C ₂₄ H ₁₄ N ₈ O ₁₂ S	+++
L'H ₂ C ₂₄ H ₁₆ N ₆ O ₈ S	+++
[Co ₂ LCl ₂ (H ₂ O) ₆]	+
[Co ₂ L'Cl ₂ (H ₂ O) ₆]	-
[Ni ₂ LCl ₂ (H ₂ O) ₆]	-
[Ni ₂ L'Cl ₂ (H ₂ O) ₆]	-
[Cu ₂ LCl ₂ (H ₂ O) ₆]	-
[Cu ₂ L'Cl ₂ (H ₂ O) ₆]	+++
[Zn ₂ LCl ₂ (H ₂ O) ₂]	++
[Zn ₂ L'Cl ₂ (H ₂ O) ₂]	-

Diameters of the zone of inhibition:

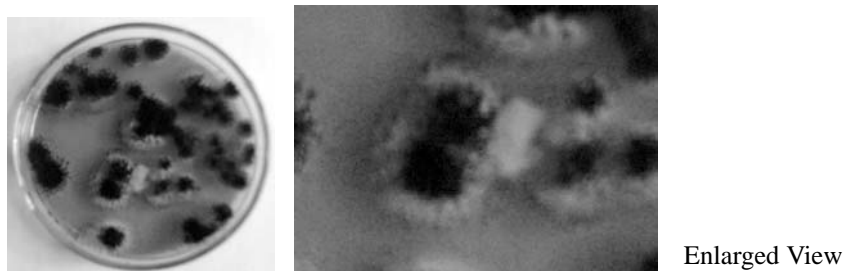
- (-) Resistant (14mm or less)
- (+) Less active (15-16mm)
- (++) Moderate active (16-17mm)
- (+++) High active (> 17mm)

The solvent used was DMF.

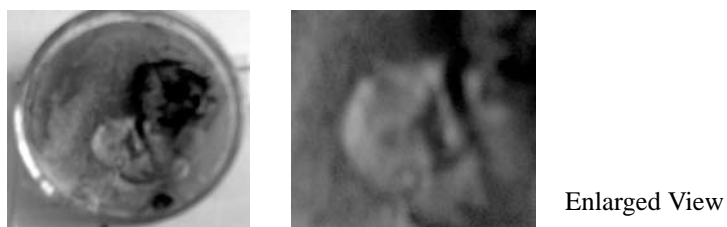
The antifungal activities of the ligands and some of their metal complexes were studied and the results were shown in Table III. These data show that some of the compounds are highly active, moderately active, less active and not active (resistant). A few photographs showing the antifungal activity of the compounds have been given in Fig. 7.



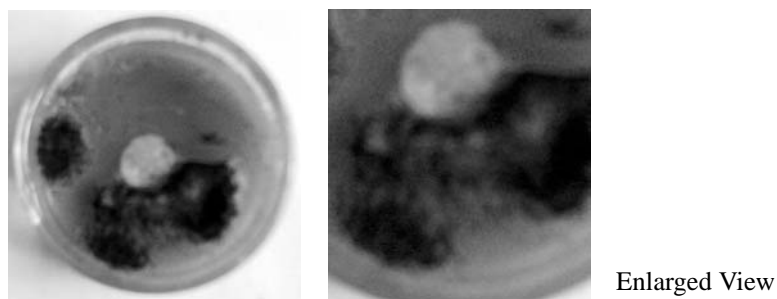
Photographs taken under the compound microscope of conidial heads for *Aspergillus niger*



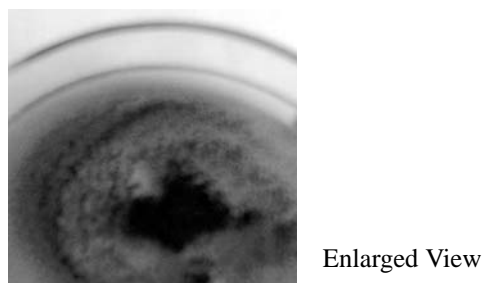
LH₂ (+++) High active (> 17mm)



L'H₂ (+++) High active (> 17mm)



[Cu₂L'Cl₂(H₂O)₆] (+++) High active (> 17mm)




[Zn₂LCl₂(H₂O)₂] (++) Moderate active (16-17mm)

Fig. 5. Few photographs showing the antifungal activity

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