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Original Article

Polymetallic complexes (Part CIII): Tetrameric complexes of Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Hg^{II} with octadentate azodye ligands, and their potential antibacterial activities

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ABSTRACT: Twelve complexes of Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Hg^{II} with two octadentate oxygen–nitrogen donor azodye ligands have been prepared. The complexes were characterized using analytical, conductance, magnetic susceptibility, IR, electronic spectra E.S.R., NMR, thermogravimetric and X-ray diffraction data. The Co^{II} and Ni^{II} complexes are found to be octahedral, Cu^{II} complexes are distorted octahedral and a tetrahedral stereochemistry has been attributed to Zn^{II} , Cd^{II} and Hg^{II} complexes. All the complexes are found to be tetrameric in nature. The antibacterial activities of the ligands and six other complexes with *Escherichia coli*, *Staphylococcus aureus* and *Proteus vulgaris* were investigated.

KEYWORDS: Polymetallic complexes, Tetrameric complexes, Azodye complexes, Antibacterial activities

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INTRODUCTION

There is renewed interest in the study of polymeric complexes containing multidentate azodye ligands. In addition to their potential chemotherapeutic properties, azodyes possess chemical indicator properties and hence are used in chemical laboratories. They also find application in dyeing food stuffs and as preservatives for food grains. In continuation with our previous work (Mahapatra *et al.* 2009; Mahapatra & Sandagi, 2009; Mahapatra & Panda, 2010), this paper reports the preparation of two new octadentate oxygen–nitrogen donor azodye ligands (Figure 1) and twelve tetrameric metal complexes.

MATERIALS AND METHODS

All the chemicals were of BDH or SRL grade. The metal, hydrogen, nitrogen, halogen and sulphur contents were estimated by standard methods. Conductance measurements of the complexes were carried out using Toshniwal CL 01-06 conductivity bridge and the magnetic susceptibility measurements were made at RT by Gouy method. IR spectra (KBr) were recorded using IFS 660 spectrophotometer, electronic spectra (10^{-2} M in DMF) using Hilgen-Watt Uvispeck spectrophotometer, and ESR of the Cu^{II} complexes were recorded on an E4 spectrometer. NMR analysis were performed on a Jeol GSX 400 with CDCl_3 as solvent and TMS

as internal standard, and X-ray diffraction (Powder Pattern) of the complex was recorded on a Phillips PW 1130 diffractometer and the TG, DTG and DTA of the complex is recorded on NETZSCH STA 409 C/CD in nitrogen atmosphere at a heating rate of 10°C per minute.

The antibacterial activities of the two ligands and six complexes were studied using cup-plate method (Miller & Brandt, 1939). The solutions of the compounds were prepared in dimethylsulfoxide (DMSO) at 500 mg/ml. The bacterial strains were inoculated into 100 ml of the sterile nutrient broth and incubated at $37 \pm 1^\circ\text{C}$ for 24 hours. The density of the bacterial suspension was standardized by McFarland method. Wells of uniform diameter (6 mm) were made on agar plates after inoculating them separately with the test organisms under sterile conditions. The standard drug and the test compounds are introduced with the help of micropipette and the plates were placed in the refrigerator at $8-10^\circ\text{C}$ for proper diffusion of the drug into the media. After two hours of cold incubation, the petri-plates were transferred to an incubator and maintained at $37 \pm 2^\circ\text{C}$ for 18-24 hours. The petri plates were observed for zones of inhibition by using a vernier scale. The results are reported by comparing the zone of inhibition shown by the test compounds with the standard drug tetracycline. The results are the mean value of zone of inhibition of three sets measured in millimeter.

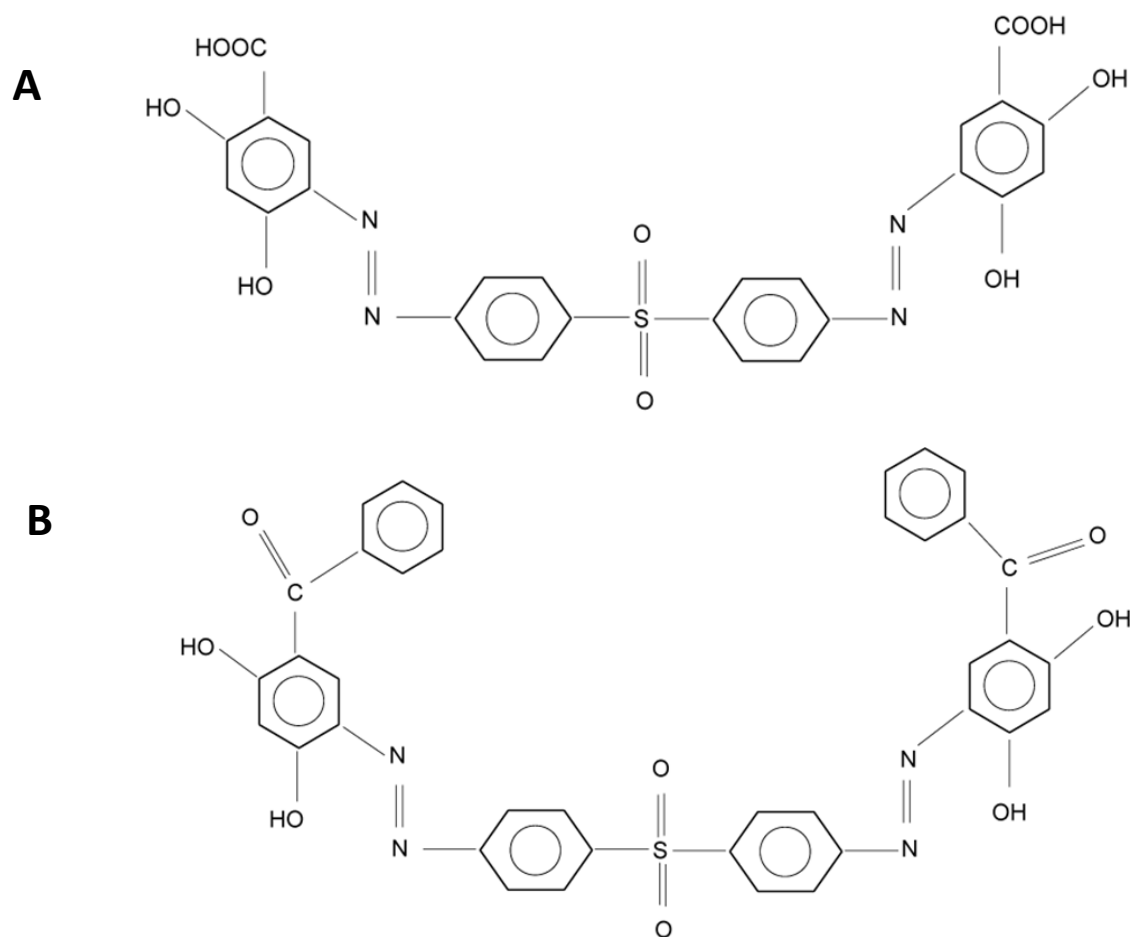


FIGURE 1 Two novel octadentate oxygen–nitrogen donor azodye ligands made in this study

Preparation of the Ligands

The azodyes were prepared by the coupling reaction of the diazonium chlorides obtained from 4,4'-diaminodiphenylsulfone (0.01 mol, 2.48 g) with alkaline solution of 2,4-dihydroxybenzoic acid (0.02 mol, 3.08 g.) and 2,4-dihydroxybenzophenone (0.02 mol, 4.28 g.) respectively at 0-5 °C.

Preparation of complexes

The metal chlorides in ethanol were mixed separately with ethanolic solution of the ligands in 4:1 molar ratio and the resulting solutions were heated to 50-60 °C for about 1 hour on a heating mantle. The solution was then cooled down to room temperature and the pH was raised to - 7 by dropwise addition of concentrated ammonia solution with stirring. The solid complexes thus formed were first washed with ethanol followed by ether, after which they were dried in vacuum.

RESULTS AND DISCUSSION

The metal complexes reported (Table 1) have the compositions $[M_4LCl_2(H_2O)_{14}]$, $[M^I_4LCl_2(H_2O)_6]$, $[M_4L^I Cl_2(H_2O)_{12}]$ and $[M^I_4L^I Cl_4(H_2O)_4]$ where $M = Co^{II}, Ni^{II}, Cu^{II}$, $M^I = Zn^{II}, Cd^{II}, Hg^{II}$, $LH_6 =$

$C_{26}H_{18}O_{10} N_4S$ (Calcd. (%) C, 53.97, H, 3.11, N, 9.6, Found (%) C, 53.47, H, 3.01, N, 9.3), 4,4'-bis(2,4'-dihydroxy, 5' carboxy phenylazo) diphenylsulfone $L^I H_4 = C_{38}H_{26}O_8N_4S$ (calcd. (%) C, 65.32, H, 3.72, N, 8.02, Found (%) C, 64.98, H, 3.42, N, 7.85), 4,4'-bis(2,4'-dihydroxy, 5' benzoyl phenylazo) diphenylsulfone. All the complexes are amorphous in nature, have high melting points and are insoluble in common organic solvents but soluble in dimethylformamide and dimethylsulfoxide. The non-electrolytic nature of the complexes is indicated by the low conductance values ($4.3 - 5.7 \Omega^{-1} cm^2 mol^{-1}$).

In the IR spectra of the ligands, broad bands were observed at $3457 cm^{-1}$ (LH_6) and at $3435 cm^{-1}$ ($L^I H_4$) which 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 in the metal complexes. The band at $1477 cm^{-1}$ (LH_6) and ($L^I H_4$) can be attributed to phenolic C - O vibration and in the metal chelates these bands appear at $1470 cm^{-1}$ indicating the bonding of phenolic oxygen atoms of the ligands to the metal ions (Sathyanarayana, 2004). The sharp bands of the ligands at $1592 cm^{-1}$ (LH_6) and at $1590 cm^{-1}$ ($L^I H_4$) can be attributed to $\nu_{N=N}$ vibration and in the metal chelates these bands are shown at $1590 cm^{-1}$ with the former ligand and at $1582 cm^{-1}$ with the latter ligand which indicates the coordination of one of

TABLE I Analytical data of the ligands and the complexes

Compound	Colour	% Metal Found (Calculated)	% Nitrogen Found (Calculated)	% of Chlorine Found (Calculated)	μ_{eff} BM
LH ₆	Brickred	-	9.4 (9.68)	-	-
L'H ₄	Reddish Brown	-	7.8 (8.0)	-	-
Co ₄ L Cl ₂ (H ₂ O) ₁₄	Reddish Brown	20.6 (20.84)	4.7 (4.952)	6.1 (6.27)	5.0
Co L' Cl ₄ (H ₂ O) ₁₂	Deep Brown	18.1 (18.30)	4.2 (4.34)	10.8 (11.02)	5.1
Ni ₄ L Cl ₂ (H ₂ O) ₁₄	Brown	20.4 (20.77)	4.7 (4.956)	6.1 (6.28)	3.2
Ni ₄ L' Cl ₄ (H ₂ O) ₁₂	Light Red	17.9 (18.24)	4.1 (4.35)	10.8 (11.03)	3.1
Cu ₄ L Cl ₂ (H ₂ O) ₁₄	Light Red	21.8 (22.10)	4.6 (4.87)	5.9 (6.17)	1.8
Cu ₄ L' Cl ₂ (H ₂ O) ₁₂	Brown	19.2 (19.44)	4.1 (4.28)	10.5 (10.87)	1.78
Zn ₄ L Cl ₂ (H ₂ O) ₆	Red	25.6 (25.83)	5.4 (5.53)	6.8 (7.01)	-
Zn ₄ L' Cl ₄ (H ₂ O) ₄	Red	22.1 (22.36)	4.4 (4.78)	11.8 (12.14)	-
Cd ₄ L Cl ₂ (H ₂ O) ₆	Yellow	37.2 (37.45)	4.4 (4.66)	5.7 (5.91)	-
Cd ₄ L' Cl ₄ (H ₂ O) ₄	Coffee	32.8 (33.12)	3.9 (4.12)	10.2 (10.45)	-
Hg ₄ L Cl ₂ (H ₂ O) ₆	Deep Brown	51.5 (51.65)	3.4 (3.60)	5.7 (5.91)	-
Hg ₄ L' Cl ₄ (H ₂ O) ₄	Brown	46.6 (46.91)	3.1 (3.27)	8.1 (8.30)	-

the azo nitrogen atoms to the metal ions. In the ligand (LH₆) ν_{as} (Coo⁻) and ν_{s} (Coo⁻) bands appear at 1650 and 1430 cm⁻¹ and these bands appear in the complexes at -1634 cm⁻¹ at -1384 cm⁻¹ with a difference ($\Delta\nu$) of -250 cm⁻¹ which supports the monodentate nature of the carboxylate group. In the ligand (L'H₄) a sharp band appears at 1627 cm⁻¹ which can be attributed to ν (>C=O) vibration and in the metal chelates it appears at -1605 cm⁻¹ indicating the bonding of the carbonyl oxygen atom to the metal ions. In the metal complexes, broad bands appear at -3418 - 3448 cm⁻¹ followed by sharp peaks at 833 - 858 cm⁻¹ and -707 - 724 cm⁻¹ assignable to OH stretching, rocking and wagging vibrations respectively indicating the presence of coordinated water molecules in the complexes (Nakamoto, 1986). The conclusive evidence of bonding of the ligands to the metal ions is proved by the appearance of bands at -513 cm⁻¹ (M-O) and at -494 cm⁻¹ (M-N) (Ferraro, 1971).

The magnetic moments of Co^{II}, Ni^{II} and Cu^{II} complexes were found to be around 5.0, 3.2 and 1.8 B.M. respectively indicating octahedral configuration of the complexes (Huheey *et al.*, 2003).

The ESR spectra of the complexes [Cu₄LCu₂(H₂O)₁₄] and [Cu₄ L'Cl₄(H₂O)₁₂] have been recorded at X-band at room temperature. The 'g_{av}' values of the complexes are found to be 2.10655 and 2.07579 respectively by applying Kneubuhl's method (Kneubuhl, 1960). This type of spectrum might be due to dynamic or pseudo rotational type of Jahn-Teller distortion.

In the electronic spectra of Ni^{II} complexes, four ligand field bands were observed at 10170(10210), 17225(17340), 24940(25115) and 32560(32775) cm⁻¹ assignable to ³A_{2g}(F) → ³T_{2g}(F) (ν_1), → ³T_{1g}(F) (ν_2), → ³T_{1g}(P) (ν_3) and CT transitions respectively in an octahedral geometry. The ligand field parameters like Dq = 1017 (1021) cm⁻¹, B=777 (788.3) cm⁻¹, B₃₅ = 0.743(0.757) cm⁻¹ V₂/V₁ = 1.693(1.698) and σ =34.04(32.10) confirm the octahedral configuration for the complexes (Lever, 1984). In the electronic spectra of Co^{II} complexes four bands appear at 8620 (8570^o), 17340(17255), 20410(20395) and 32440(32390) cm⁻¹. The first three bands can be assigned to ⁴T_{1g}(F) → ⁴T_{2g}(F)(ν_1), → ⁴T_{2g}(F)(ν_2), → ⁴T_{1g}(P)(ν_3) transitions respectively and the fourth band is assigned to a CT band. The ligand field parameters like Dq = 872 (860.5) cm⁻¹,

FIGURE 2 Spectral properties of the ligands

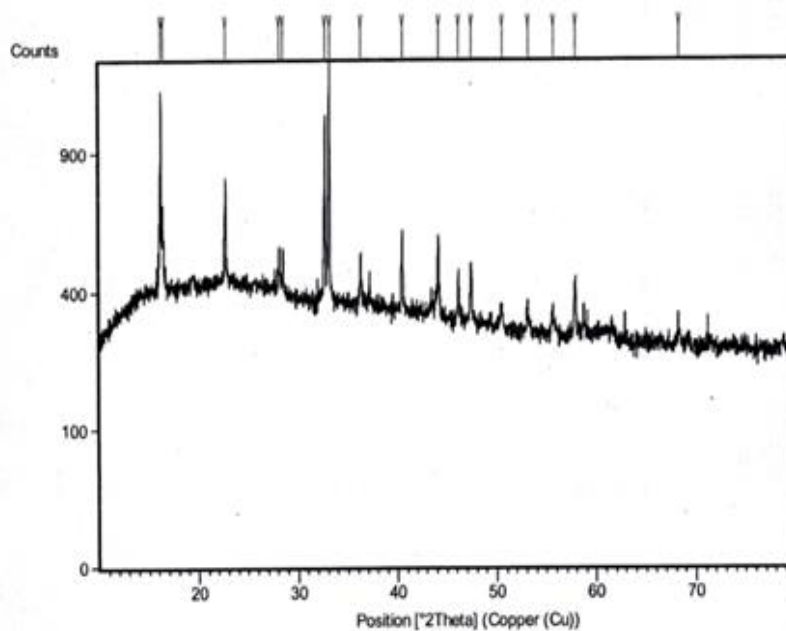


TABLE 2 X-ray diffraction data of the complex

Compound	2 θ value	Unit Cell parameters	Density	n	Possible Geometry
Ni ₄ L' Cl ₄ (H ₂ O) ₁₂	10.9564				
	16.2264				
	16.2434				
	16.4653	A=8.461			
	22.6896	B=8.588			
	28.0792	C=6.293			
	28.4610	α =109.386			
	32.6619	β =110.922			
	33.0784	γ =79.785	2.33	0.5	Triclinic
	36.2108	V=401.99			
	40.3433				
	44.0583				
	46.0977				
	47.3653				
	50.3741				
	53.0464				
	55.5111				
57.7590					
68.0998					
74.4684					
76.8824					

FIGURE 3 Thermal decomposition behaviour of the complexes

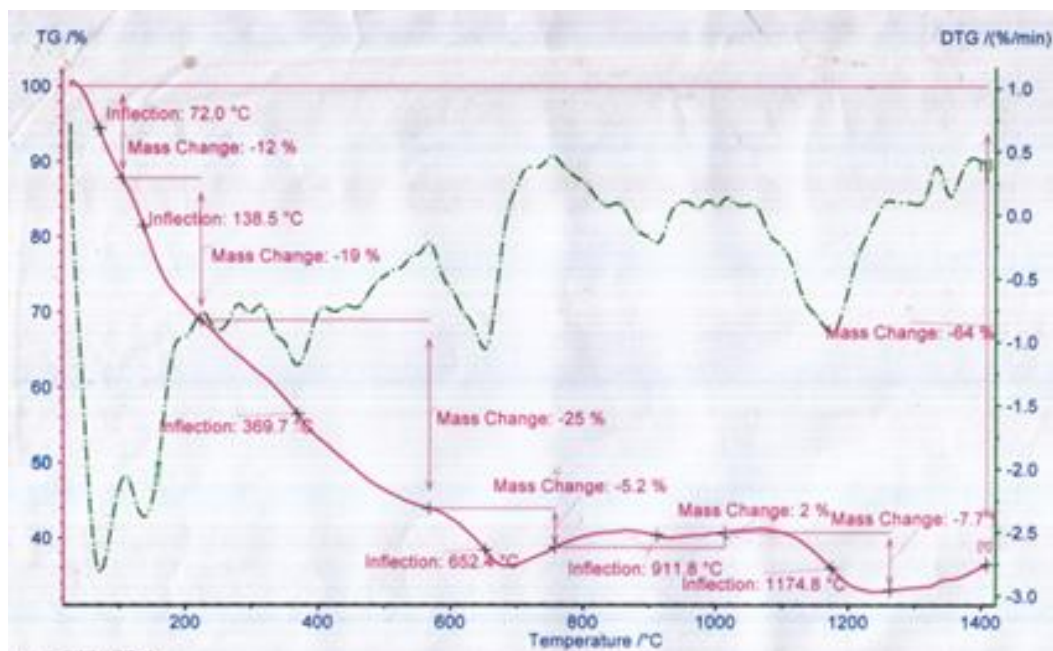
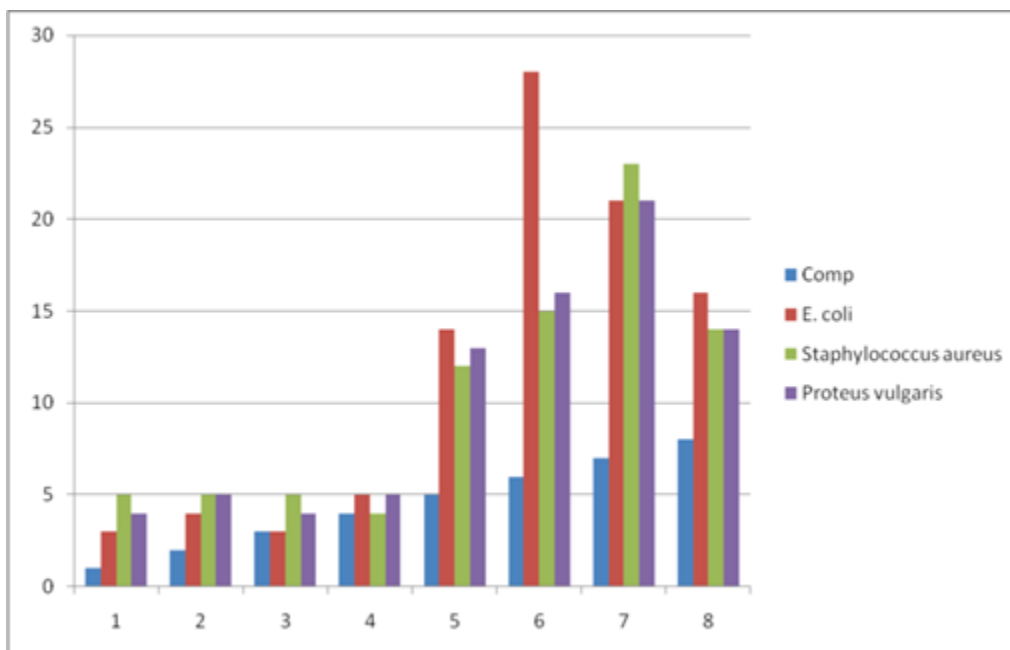


TABLE 3 Antibacterial activities of the ligands and the complexes (data presented as diameter of zone of inhibition, mm)

Comp	<i>E. coli</i>	<i>S. aureus</i>	<i>P. vulgaris</i>
1- LH ₆	3	5	4
2 - L/H ₄	4	5	5
3 - [Cu ₄ L Cl ₂ (H ₂ O) ₁₄]	3	5	4
4 - [Co ₄ L Cl ₂ (H ₂ O) ₁₄]	5	4	5
5 - [Zn ₄ L Cl ₂ (H ₂ O) ₆]	14	12	13
6 - [Cu ₄ L'Cl ₂ (H ₂ O) ₁₂]	28	15	16
7 - [Ni ₄ L'Cl ₄ (H ₂ O) ₁₂]	21	23	21
8 - [Zn ₄ L'Cl ₄ (H ₂ O) ₄]	16	14	14

FIGURE 4 Effect of the complexes on the growth of selected *E. coli*, *S. aureus*, and *P. vulgaris*



$B=792.6$ (794) cm^{-1} , $B_{35}=0.8163$ (0.8177) cm^{-1} , $\nu_2/\nu_1 = 2.011$ (2.009) and $\sigma=22.50$ (22.29) suggest an octahedral geometry for the complexes (Devota *et al.*, 1957). The electronic spectra of Cu^{II} complexes exhibit one broad band at $-13560 - 14480$ cm^{-1} with maxima at -13820 cm^{-1} assignable to ${}^2E_g \rightarrow {}^2T_{2g}$ transition in support of a distorted octahedral configuration for the complexes (Yamada, 1966).

The ${}^1\text{H}$ NMR spectra of the ligands LH_6 and $\text{L}'\text{H}_4$ were recorded in CDCl_3 . The sharp peaks observed at $6.66 - 7.76$ δ (LH_6) and $6.48 - 7.76$ δ ($\text{L}'\text{H}_4$) correspond to 12 and 22 phenyl protons respectively. The sharp peak observed at 12.621 ($\text{L}'\text{H}_4$) corresponds to 04 phenolic protons (Silversten & Webster, 2004). The XRD study (powder pattern) of the complex $[\text{Ni}_4 \text{L}'\text{Cl}_4 (\text{H}_2\text{O})_{12}]$ was made with the help of an X-ray diffractometer. The unit cell parameters were calculated from the 2θ values (Figure 2). The direct constants of the lattice like a , b , c , α , β , γ and V (volume) shown in Table 2 suggest (Atkins & Paula, 2002) the probable geometry of the complex to be triclinic. The density of the complex was determined by the floatation method in a saturated solution of KBr , NaCl and benzene separately. The number of formula units per unit cell (n) is calculated from the relation $n = dNV/M$ where d =density of the compound, N =Avogadro's number, V =volume of the unit cell, M =molecular weight of the complex. The value of n is found to be 0.5 which agrees well with the suggested structure of the complex.

The thermal decomposition behavior of the complex $[\text{Ni}_4 \text{L}'\text{Cl}_4 (\text{H}_2\text{O})_{12}]$ was studied by using TG, DTG and DTA techniques in an atmosphere of nitrogen at a heating rate of 10 $^\circ\text{C}$ per minute

(Figure 3). The complex compound starts losing its mass gradually with the rise of temperature and loses all the lattice held water molecules at 72.0 $^\circ\text{C}$. Then the compound starts decomposing and loses 19% of mass at 138.5 $^\circ\text{C}$ with the removal of 12 coordinated H_2O molecules along with one chlorine atom. At 369 $^\circ\text{C}$ the compound loses rest three chlorine atoms along with $1/4^{\text{th}}$ of the ligand molecules which is supported by the exothermic peak in DTA A graph at 358 $^\circ\text{C}$. At 652.4 $^\circ\text{C}$, the compound loses 5.2% of mass indicating removal of $1/12^{\text{th}}$ of the ligand moiety which is supported by the exothermic peak in DTA curve at 660.2 $^\circ\text{C}$. At 1174.8 $^\circ\text{C}$, the compound loses a mass of 7.7% with the removal of $1/9^{\text{th}}$ of the ligand moiety. At 1400 $^\circ\text{C}$, the compound suffers a mass loss of 64% equivalent to loss of rest of the ligand moiety with the formation of NiO as the final product (Jeffery *et al.*, 1989) The Zn^{II} , Cd^{II} and Hg^{II} complexes have tetrahedral geometry based upon analytical conductance and IR spectral data. Both the azodye ligands behave as bis-tetradentate (octadentate) ligands forming tetrameric complexes.

The antibacterial activities of the compounds were examined against three bacteria, *Escherichia coli*, *Staphylococcus aureus* and *Proteus vulgaris*. The effectiveness of the compounds can be predicted by determining the zone of inhibition value. It was observed that both the ligands and the cobalt and the copper complexes with LH_6 had no effect on all the organisms, whereas the zinc complex with LH_6 was found to be inhibitory to the growth of all three bacterial strains. The nickel, copper and zinc complexes with the second ligand ($\text{L}'\text{H}_4$) are found to be very sensitive to *E. coli*, *S. aureus* and *P. vulgaris* as evidenced from higher diameters of zone of inhibition (Table 3; Figure 4).

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