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Pollymetallic complexes Part-C VI: Synthesis, spectral, thermo gravimetric, computational and antibacterial study of tetrameric Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes with OON-NOO donor hexadentate azodye ligands

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ABSTRACT

The tetrameric complexes of Co(II),Ni(II),cu(II),Zn(II),Cd(II) and Hg(II) with two new symmetrical OON-NOO donor hexadentate azodye ligands, 1,3-bis(2’-hydroxy-3’-formyl-5’-bromophenylazo)benzene and 4,4’-bis(2’-hydroxy-3’-formyl-5’-lazo)diphenylsulphone have been synthesized and characterized by elemental analysis, conductance measurement, magnetic, IR, electronic spectra, ESR, NMR, Thermo gravimetric, XRD(powdered pattern) and molecular modeling studies. The antibacterial study of the ligands and some of the complexes has been made against gram positive bacteria S.aureus and gram negative bacteria E.coli, and this study indicates that some complexes are more potent bactericides than the ligands. The Co(II), Ni(II) complexes are found to be octahedral, Cu(II) complexes distorted octahedral and a tetrahedral stereochemistry has been assigned to Zn(II), Cd(II) and Hg(II) complexes. All the complexes are found to be thermally stable. A triclinic crystal system for Cu(II)complex with the former ligand and orthorhombic crystal system is suggested for the Co(II) complex with the latter ligand. Crystallite size of the complexes were found to be 0.305 nm for Cu(II) complex with LH_2 *and 0.862 nm for Co(II) complex with* $L^{'}H_2$.

Key words: Polymetallic complexes, azodyes, thermogravimetric study, molecular modeling

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INTRODUCTION

Study of the polymetallic complexes with multidentate azodyes ligands has gained a lot of importance in recent years owing to the fact that the azodyes posses a wide range of applications ranging from chemotherapeutics[1] in pharmaceutical industry, indicator in chemical laboratories and as food preservatives and dyeing agents in food industries[2]. In continuation to our earlier works[3], the present study reports the preparation and characterization of some metal complexes of Co(II),Ni(II).Cu(II),Zn(II),Cd(II) and Hg(II) along with their spectral, thermal, molecular modeling and antibacterial studies.

EXPERIMENTAL SECTION

All the chemicals used were of AR grade (merck or BDH). Elemental analysis(C,H,N) were carried out on elemental analysis Perkin Elmer 2400 while metals were determined by EDTA titration method after decomposing the complexes with concentrated HNO_3.The chlorine and Bromine contents were estimated by standard methods.

The molar conductance measurements of the complexes were made using Toschniwal CL-06 conductivity bridge in 10^{-3} M solution in DMF. The magnetic suspectibility measurements of the complexes were made on a GUOY balance at room temperature, using $Hg[Co(SCN)_4]$ as calibrant. IR spectra were recorded on an IFS 660 spectrophotometre, electronic spectra (10^{-3} M in DMF) using Hilger-Watt Uvispeck spectrophotometer, ESR of the Cu(II) complexes on an E4- spectrometer, NMR on a Jeol GSX 400 with DMSO as solvent and TMS as internal standard and X-ray diffraction (Powder Pattern) of the complex was recorded on a Phillips PW 1130 diffractometer with scan axis-Gonio, start position(2θ-10.004), end position(2θ-79.9764), anode material-Cu,K-ALPHA1(Å) **λ**= 1.54060 and generator setting-30mA, 40KV, Thermogravimetric study was made on NETZSCH STA 449F 3 and molecular modelling of the ligand and complex was done with the help of Chem 3D ultra version.

The antibacterial study of the ligands and the complexes has been made using cup-plate method[4],the compounds were tested at the concentration of 500µg/ml in DMSO. A 0.2ml of each was placed in a well made in the nutrient agar medium in which culture of the tested bacteria has been spread to produce uniform growth.The diameter of inhibition zone in mm was measured after 24 hour of incubation at 37 ^oc after comparing with the standard drug Tetracycline.

Preparation of the ligands

The azodyes were prepared by coupling reaction of diazonium chloride obtained from an m- phenylene diamine(0.01mole,1.08 gm) and 4,4'- diaminodiphenylsulphone (0.01 mole , 2.48 gm) with alkaline solution of 5-bromo-salicylaldehde(0.02mol,3.68 gm) each at 0-5 ^0c (Fig-1,Fig-2).

Preparation of the complexes

The metal chlorides in ethanol were mixed separately with ethanolic solution of the ligands LH_2 and $L^{'}H_2$ in 4:1 molar ratio. The resulting solution were heated to 50-60 ^0C for about 1 hour on a heating mantle and the pH was raised to ~7 by adding conc. NH_4OH drop by drop with stirring. The solid metal complexes thus formed were then washed with ethanol and dried in vacuum Fig (3) and Fig (4).

RESULTS AND DISCUSSION

The physical characteristics, micro analytical and molar conductance data of the ligands and the metal complexes are given in table 1. The analytical data of the complexes revealed 4:1 molar ratio (metal:ligand) and corresponds well with the general formula $[M_4L/L^{'}Cl_6(H_2O)_{10}]$ and $[M^{'}L/L^{'}Cl_6(H_2O)_2]$ where M=Co(II),Ni(II),Cu(II) and M'=Zn(II), Cd(II), Hg(II),LH_2=$C_{20}H_{12}N_4O_4Br_2$ (calculated(%)C,45.11 H,2.25, N,10.52, S,4.76, Br, 30.07 found (%) C, 44.85, H,2.08, N,10.3, S,4.46, Br,30.02, $L^{/}H2$=$C_{26}N_4SO_6H_{16}Br_2$ (calculated(%)C,46.42 H,2.38 N,8.3 S,4.76 Br, 23.80 found (%) C, 46.12, H, 2.08, N, 7.9, S,4.26, Br,23.52. All the complexes are amorphous in nature have high melting points and are insoluble in common organic solvents but soluble in Dimethylformamide and Dimethylsulphoxide. Non electrolytic nature of the complexes is indicated from low conductance values (4.5-5.8Ωcm^2mol^{-1}) in 10^{-3}M solution in DMF [5].

IR Spectra

In the IR spectra of the ligands, broad-bands are observed at 3432 cm^{-1}(LH_2) and 3488 cm^{-1}($L^{'}H_2$) respectively which may be attributed to intra molecular O—H…N hydrogen bonding. The absence of this band in the spectra of the metal complexes indicates deprotonation of the phenolic OH group and bonding of phenolic oxygen to the metal ion [6]. This is further supported by the shift of the band at 1476cm^{-1} (LH_2) and ($L^{'}H_2$) to ~1450-1455cm^{-1} and ~1444-1441 cm^{-1} respectively in the metal complexes. The sharp band of the ligands at the 1585cm^{-1} (LH_2) and ($L^{/}H_2$) can be attributed to ν(N=N) vibration and in the metal chelates these bands are shown at 1518-1519cm^{-1} and ~1530-1531 cm^{-1} respectively which indicate the coordination of one the azo nitrogen atoms to the metal ions[7]. In the ligands, a sharp band appears at 1653 cm^{-1} (LH_2) and at 1658 cm^{-1}($L^{'}H_2$) which can be assigned to carbonyl ν(c=0) vibration[8] and in the metal complexes it appears at ~1617-1621cm^{-1} and at 1622cm^{-1} indicating the coordinate of carbonyl oxygen atom to the metal ions[9] .In the metal complexes broad band appears at 3308-

3302cm^{-1} followed by sharp peaks at 824-839 cm^{-1} and at 730-743 cm^{-1} assignable to OH stretching, rocking and wagging vibrations respectively indicating the pressure of coordinate water molecules in the complexes[10]. The conclusive evident of bonding of the ligands to the metal ions is proved by the appearance of bands at ~510-624cm^{-1} (M-O)[11] and at ~459-463 cm^{-1}(M-N) [12] (table 2).

Electronic absorption spectra and magnetic measurement

In the electronic spectra of Ni(II) complexes, four ligand field bands are observed at 10225 (10245), 17370 (17410), 24980 (24995) and 32640 (32680) cm^{-1} respectively assignable to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $\rightarrow {}^3T_{1g}(F)$(ν_2), $\rightarrow {}^3T_{1g}(P)$ (ν_3) and CT transitions respectively in an octahedral geometry. The ligand field parameters like Dq=1022.5(1024.5)cm^{-1},B=778(804)cm^{-1},β_{35}=0.747(0.772)cm^{-1},ν_2/ν_1=1.64(1.70) and σ=33.5(29.53) confirm the octahedral configuration for the complexes[13].The electronic spectra of Co(II) complexes four bands appear at 8260 (8275),16685 (16522),20330 (20445) and 32440 (32390) cm^{-1}. The first three bands can be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, $\rightarrow {}^4A_{2g}(F)$(ν_2), $\rightarrow {}^4T_{1g}(P)$(ν_3) transitions respectively and the fourth band is assigned to a CT band. The ligand field parameters like Dq = 836 (833.8) cm^{-1}, B=788.3 (790.6) cm^{-1}, β_{35}=0.811 (0.814) cm^{-1}, ν_2/ν_1 = 2.01 (1.99) and σ=19.04 (20.04) suggest an octahedral geometry for the complexes [14]. The electronic spectra of Cu(II) complexes exhibit one broad band at ~ 13350 – 14480 cm^{-1} with maxima at ~14372 cm^{-1} assignable to $^2E_g \rightarrow {}^2T_{2g}$ transition in support of a distorted octahedral configuration for the complexes [15]. The sub-normal magnetic moment of Co(II),Ni(II) and Cu(II) complexes(Table-1) could be attributed to metal-metal interaction due to super exchange phenomenon[16] of the phenolic oxygen atoms in a dimeric structure(M-O-M).

ESR Spectra

The ESR spectra of the Cu(II) complexes have been recorded at X-band at RT. The g_{av} [17] values are found to be 2.07577 and 2.08209 respectively by applying kneubuhl's method. This type of spectrum may result due to regular octahedral pseudo rotational type of Jahn Teller distortion.The spin-orbit coupling constant($_\lambda$).can be determined by using the equation

g_{av} = **2(1-2λ/10dq),**

Where = **λ** spin-orbit coupling constant. The values of for the Cu(II) complexes were found to be -542.cm^{-1} and -589.8 cm^{-1} .The lowering of values **λ** of the complexes from the free ion value(-830 cm^{-1} indicates overlapping of metal-ligand orbitals.

^{1}H NMR Spectra

The ^{1}H NMR spectra of the ligands LH_2 and $L'H_2$ were recorded in DMSO. The complex pattern observed at δ 7.028-7.733 ppm and at δ 7.545-8.174 ppm corresponds to 8 and 12 phenyl protons respectively. The sharp peak obtained at δ 10.03 ppm (LH_2) and at δ 10.13 ppm ($L'H_2$) corresponds to phenolic protons [18],aldehydic proton gives peak at δ 9.933 ppm.In the ^{1}H NMR spectrum of Zn(II) complex with $L'H_2$, peak at δ 10.13 ppm is missing which indicates deprotonation of phenolic OH group and bonding of phenolic oxygen with Zn(II) ion.

XRD study

The XRD study (powder pattern) of the complex $[Co_4L'Cl_2(H_2O)_{14}]$ and $[Cu_4LCl_6(H_2O)_{10}]$ were made with the help of X-ray diffractometer. The prominent peaks of the diffraction pattern have been indexed and analyzed by the computer programme LSUCRPC[19]. The lattice parameters(a,b,c,α,β,γ) and volume of the unit cell have been mentioned along with miller indices(h,k,l) in the table-3 and table-4. The indexing is confirmed by comparing between observed and calculated 2θ values which is evident from the figure of merit 6.4 for Co(II) complex and 7 for Cu(II) complex as suggested by De Wolff[20]. The observed and calculated 2θ values of the complex are in good agreement. 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 1 for both the complexes and which agrees well with the suggested structure of the complexes. The crystal system of the complex is found to be triclinic for $[Cu_4LCl_6(H_2O)_{10}]$ and orthorhombic for $[Co_4L'Cl_6(H_2O)_{10}]$.

The mean crystallite size of the complexes were calculated from the diffraction line width using the Debye Scherer relation[21]

$\mathbf{B=K\,\lambda/\beta\cos\theta}$,

Where B=particle size, K=Dimensionless shape factor, λ = X ray wave length, β =Line broadening at half the maximum intensity and θ =Diffraction angle. This equation relates the size of the particles in a solid with the broadening of a peak in a diffraction pattern. The mean particle size of the Cu complex is 0.305 nm and 0.862 nm for Co complex.

Thermal study and determination of kinetic parameter

Thermal analysis of the complex $[Cu_4L^{/}Cl_6(H_2O)_{10}]$ was studied by TG-DTA techniques. The thermal degradation of the complex was recorded at10 ^{o}C per minute in an atmosphere of nitrogen from ambient temperature to 900 ^{o}C. The complex suffers a mass loss of 13.4% which corresponds to loss of all coordinated H_2O molecules within the temperature 200 ^{o}C. Thereafter the complex moiety losses 25% of mass in the temperature range of 200-400 ^{o}C indicating removal of nearly ½ of the ligand supported by an exothermic peak on the DTA curve at 400 ^{o}C. Then the complex moiety suffers a loss of 33.3% of mass corresponding to loss of rest of the ligand moiety in the temperature range of 400-600 ^{o}C. Again the complex moiety losses amass of 43% indicating loss of all six chlorine atoms in the temperature range 600-900 ^{o}C with the formation of CuO as the residue. The kinetic parameters like order of the reation, activation energy for the decomposition reaction of the complex can be calculated by Freeman-caroll method [22]. The equation used for this purpose is

$\mathbf{dw/dt = R_T = Z/R_H\, e^{-Ea/RT}\, W^n}$,

Where R_H = rate of heating, w = weight fraction of the reacting material, E_a = activation energy, n= order of the reaction and Z= frequency factor. This equation in the difference form can be written as

$\mathbf{\Delta \log R_T = n\,\Delta \log w - Ea/2.303R\Delta(1/T)}$

When $\Delta(1/T)$ is kept constant , a plot of $\Delta \log R_T$ verses $\Delta \log W$ gave a linear relationship whose slope and intercept provides the value of n and E_a respectively. The order of the decomposition reaction and the activation energy are found to be 1.08 and 8.34 Jmole^{-1} respectively. The calculated values of the activation energy is found to be low due to autocatalytic effect of the metal ion on the thermal decomposition of the complex. The correlation coefficient(r) of the thermal decomposition is found to be 0 .93 which fits well with the experimental results.

Molecular modeling Study

Molecular modeling of the ligands and the complexes has been carried out using AM1 method of the MOPAC programme present in the Chem 3D ultra 8.0 software. Bond lengths, bond angles ,electron densities, atomic charges ,thermodynamic parameters like heat of formation, total energy, repulsion energy etc were calculated with the help of standard parameters as implemented in the software[23,24]. The structures of ligands LH_2, $L'H_2$ and their Zn(II) and Hg(II) complexes were built by using Chemdraw 2D and their structures were optimized without any symmetry constraint using AM1 method.

The results(Table-6) of the structural calculation have been used to compute the quantitative structure activity relationships properties. For the ligand LH_2 (Fig.10), surface area- 124.69Å^2, volume-36780.70Å^3,Refractivity-126.512cm$^{3/}$/mole and logP-7.2796 and for the ligand $L'H_2$(Fig-11), surface area-126.64 Å^2, volume-45232.94Å^3, Refractivity-160.044 cm3/mole,logP-4.86.

The geometries of the Zn(II) complexes show bond lengths from 2.070-3.560 Å and bond angles are close to 119.5^{o} favoring distorted tetrahedral geometry (Table-7).

The antibacterial activity of the ligands and their metal complexes were tested against *E.coli* and *S.aureus*. Both the ligands and complexes possess antibacterial activities, Ni(II) complexes with both the ligands are found to be more potent than the ligands against *S.aureus*. But Cu(II) complex with $L^{'}H2$ is more active than the same ligand against both the bacteria(Table-8).

Table – I Analytical data of the ligands and complexes

Compound	M.P.	Colour	Found (Calcd.), %					
			Br	C	CL	H	N	M
LH_2	65	Brown	-	45.08	. -	2.21	10.2	. -
				((45.11)	-	10.52	(10.52)	-
$L^{/}H_2$	74	Orange	-	46.12	-	2.34	10.65	-
				(46.42)	-	2.38)	-10.68	-
$[Co_4 L Cl_6 (H_2o)_{10}]$	>240	Reddish Brown	13.78	20.69	18.05	2.55	4.53	20.2
			13.81	(20.71)	(18.38)	(2.59)	(4.83)	(20.34)
$[Co_4 L^{/} Cl_4 (H_2O)_{10}$	>240	Brown	12.29	24.01	16.1	2.59	4.53	20.2
			(12.31)	(24.02)	(16.4)	(2.61)	(4.83)	(20.34)
$[Ni_4 L Cl_6 (H_2O)_{10}]$	>240	Gray	13.79	20.69	18.1	2.55	4.1	19.92
			(13.81)	(20.72)	(18.09)	(2.59)	(4.37)	(20.27)
$[Ni_4 L^{/} Cl_6(H_2O)_{10}]$	>240	Bright Red	12.29	24.01	16.15	2.54	4.05	17.74
			(13.58)	(24.04)	(14.41)	(2.61)	(4.31)	(18.08)
$[Cu_4 L Cl_6 (H_2O)_{10}]$	>240	LightGreen	13.54	20.35	17.9	2.52	4.3	21.16
			(13.58)	(20.39)	(18.09)	(2.54)	(4.75)	(21.580
$[Cu_4 L^{/}Cl_4 (H_2O)_{10}]$	>240	Brick Red	12.11	23.65	15.9	2.55	3.9	18.94
			(12.14)	(23.69)	(16.17)	(2.58)	(4.25)	(19.28)
$[Zn_4 L Cl6(H_2O)_2]$	>240	Light Red	15.54	23.02	20.1	2.84	5.01	24.75
			(15.58)	(23.06)	(20.47)	(2.88)	(5.38)	(25.13)
$[Zn_4 L^{/}Cl_6 (H_2O)_2]$	>240	Red	13.51	26.01	17.8	2.85	4.3	21.92
			(13.55	(26.02)	(18.04)	(2.88)	(4.74)	(22.15)
$[Cd_4 L Cl_6 (H_2O)_2]$	>240	Red	13.04	19.59	17.01	2.41	4.2	32.45
			(13.07)	(19.60)	(17.33)	(2.45)	(4.450	(36.59)
$[Cd_4 L^{/} Cl_6 (H_2O)_2]$	>240	Brown	11.65	22.75	15.2	2.36	3.8	50.53
			(11.69)	(22.79)	(15.56)	(2.40)	(4.09)	(50.73)
$[Hg_4 L Cl_6 (H_2O)_2]$	>240	Red	10.06	15.95	13.15	1.85	3.30	32.65
			(10.11)	(15.97)	(13.46)	(1.89)	(3.54)	(32.85)
$[Hg_4 L^{/} Cl_6(H_2O)_2]$	>240	Red	9.25	17.98	22.67	12.11	3.05	46.25
			(9.29)	(18.12)	(22.71)	(12.37)	(3.25)	(46.61)

Table- 2 IR data of the ligands and complexex

Compound	ν/cm-1				
	(C-O)	(-N=N-)	(C=O)	(M-O)	(M-N)
LH_2	1476	1585	1653	-	-
L/H_4	1476	1585	1658	-	-
$[Co_4LCl_6(H_2O)_{10}]$	1455	1519	1621	510	459
$[Co_4L/Cl_6(H_2O)_{10}]$	1441	1531	1622	624	460
$[Ni_4LCl_6(H_2O)_{10}]$	1451	1518	1617	509	463
$Ni_4L/Cl_4(H_2O)_{10}]$	1442	1530	1622	624	463
$[Cu_4 L Cl_2 (H_2O)_{10}]$	1453	1518	1620	509	460
$[Cu_4 L^{/}Cl_6 (H_2O)_{10}]$	1444	1530	1622	520	462
$[Zn_4 L Cl_6(H_2O)_2]$	1455	1519	1618	510	462
$[Zn_4 L^{/}Cl_6 (H_2O)_2]$	1441	1531	1622	550	460
$[Cd_4 L Cl_6 (H_2O)_2]$	1453	1519	1619	510	460
$[Cd_4 L^{/} Cl_6 (H_2O)_2]$	1441	1531	1622	580	460
$[Hg_4 L Cl_6 (H_2O)_2]$	1454	1518	1621	510	462
$[Hg_4 L^{/} Cl_6(H_2O)_2]$	1442	1530	1622	620	463

Table -3 Electronic absorption and magnetic measurement data of the complexes

Compound	**μ_{eff}/μ_{bm}**	**v/cm^{-1}**	**Band assignment**	**Geometry**
$[Co_4LCl_6(H_2O)_{10}]$	2.7	8260	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	octahedral
		16685	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
		20330	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P$	
		32440	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P$	
$[Co_4L/Cl_6(H_2O)_{10}]$	2.6	8275	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F$	octahedral
		16685	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
		20445	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
		32390	INCT^a	
$[Ni_4LCl_6(H_2O)_{10}]$	2.2	10225	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	octahedral
		17370	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
		24980	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
		32640	INCT^a	
$[Ni_4L/Cl_6(H_2O)_{10}]$	2.3	10245	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	octahedral
		17440	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
		24995	INCT^a	
		32680	INCT^a	
$[Cu_4L/Cl_6(H_2O)_{10}]$	1.4	13370	$^2E_g \rightarrow {}^2T_{2g}$	Distorted octahedral
$[Cu_4L/Cl_6(H_2O)_{10}]$	1.3	13350	$^2E_g \rightarrow {}^2T_{2g}$	Distorted octahedral

Table -4 XRD Data of the$[Cu_4LCl_6(H_2O)_{10}]$ Complex

Observed (2θ)	Calculated (2θ)	D spacing	h k L	Difference (2θ)
10.17	10.19	8.675	1 0 0	.02
11.71	11.71	7.539	1 1 0	.00
12.96	12.98	6.816	1 1 0	.02
13.94	13.96	5.403	0 2 0	.02
14.97	14.98	5.403	0 1 1	.01
16.75	16.78	5.280	-1 2 0	.03
20.60	20.62	4.303	2 0 -1	.02
24.48	24.50	3.361	-2 1 -1	.02
26.37	26.38	3.376	0 1 -2	.01
27.42	27.44	3.248	-2 2 -1	.02
28.20	28.22	3.159	-1 1 2	.02
31.50	31.53	2.835	-2 3 -1	.03
33.30	33.33	2.686	-3 2 1	.03
35.12	35.14	2.552	4 1 0	.02
38.50	38.51	2.336	-1 4 -2	.01
42.20	42.21	2.139	4 3 1	.01
45.15	45.17	2.006	4 4 1	.02
51.50	51.51	1.773	-5 1 2	.01
53.04	53.04	1.773	-4 3 -2	.00

a=10.302 Å	α= 95.947	Volume-963.44 Å3	n=1
b=13.912 Å	β= 97.652	Density-2.02 g cm-3	
c= 6.907 Å	γ = 80.187	Bravais lattice-P	

Table:- 5 XRD Data of the[Cu4LCl6(H2O)10] Complex

Observed (2θ)	Calculated (2θ)	D spacing	h k L	Difference (2θ)
10.93	10.95	8.077	2 0 0	.02
16.66	16.68	5.309	1 0 2	.02
19.41	19.40	4.573	1 1 0	.01
20.40	20.39	4.353	1 1-1	.01
28.88	28.88	3.089	4 0 2	.00
32.75	32.69	2.737	2 1 3	.06
43.57	43.53	2.077	5 1 3	.04
46.60	46.60	1.948	5 1 -5	.00
50.34	50.31	1.812	5 2 -3	.03
53.37	53.34	1.716	8 0 -5	.03
58.35	58.31	1.581	8 0 -6	.04
68.19	68.20	1.314	7 2 -4	.01

a=9.012 Å	α= 90^0	Volume-1049 Å3	n=1
b=16.207 Å	β= 90^0	Density-2.05 g cm-3	
C7.185 Å	γ = 90^0	Bravais lattice-P	

Table-6 Parameter of the molecular modeling of the ligands

Ligand	Total energy (ev)	Heat of formation (Kcal/mol)	Electronic energy (ev)	Repulsion energy (ev)	Homo (ev)	Lumo (ev)
LH_2	-5537.21	-182.57	-36161.3	30624.1	-9.4228	-1.4913
$L^{/}H_2$	-7193.6	-38.22449	-52646	45452	-9.6299	-1.7766
$[Zn_4LCl_6(H_2O)_2]$	-8522.7	-174.15134	-65785.5	57262.8	-6.8851	-1.5013
$[Hg_4LCl_6(H_2O)_2]$	-8517.93	-293.43316	-67925.9	59407.9	-8.1790	-1.8965

Table- 7 selected bond lengths and bond angles of ligands and complexes

Compound	Bond	Bond Length(Å)	Bond Angle(^{o})
LH_2	N(7)-N(8)	1.223	C(3)-N(7)-N(8)-120
	C(9)-N(8)	1.438	C(9)-N(7)-N(8)-122
	C(26)-Br(28)	1.936	C(11)-C(10)-O(8)-118
	C(6)-O(7)	1.251	-
$[Zn_4LCl_6(H_2O)_2]$	N(7)-N(8)	1.278	C(3)-N(7)-N(8)-122.80
	C(9)-N(8)	1.417	C(9)-N(7)-N(8)-122.28
	O(8)-Zn(33)	2.159	C(11)-C(10)-O(8)-102
	N(7)-Zn(33)	2.070	N(7)-Zn(33)-O(45)-117
	Cl(36)-Zn(33)	2.214	Cl(36)- Zn(33)-O(45)-112
	O(29)-Zn(31)	2.287	-
	Cl(37)-Zn(31)	2.109	-
$L^{/}H_2$	N(16)-N(17)	1.224	C(12)-C(13)-N(16)-112
	C(13)-N(16)	1.436	C(13)-C(14)-N(16)-123
	C(25)-O(26)	1.234	C(12)-N(16)-N(17)-120
	C(19)-O(27)	1.373	
$[Zn_4L^{/}Cl_6(H_2O)_2]$	N(16)-N(17)	1.238	C(12)-C(13)-N(16)-114
	C(13)-N(16)	1.440	C(13)-C(14)-N(16)-125
	C(25)-O(26)	1.252	C(12)-N(16)-N(17)-121
	C(19)-O(27)	1.303	O(38)-Zn(40)-O(39)-105
	O(38)-Zn(40)	3.560	O(38)-Zn(40)-Cl(45)-102
	O(39)-Zn(40)	2.252	O(39)-Zn(40)-O(48)-116
	Cl(45)-Zn(40)	2.260	O(38)-Zn(40)-O(47)-124

Table – 8 Antibacterial screening of ligands and complexes

Compound	**Concentration/µgml^{-1}**	**Zone Inhibition (mm)**	
		E .coli	S . aureus
LH_2	500	13	10
LH_2	500	14	10
$[Cu_4LCl_6(H_2O)_{10}]$	500	10	12
$[Cu_4L/Cl_6(H_2O)_{10}]$	500	15	12
$[Co_4LCl_6(H_2O)_{10}]$	500	12	12
$[Co_4L/Cl_6(H_2O)_{10}]$	500	13	12
$[Ni_4LCl_6(H_2O)_{10}]$	500	15	14
$[Ni_4L/Cl_6(H_2O)_{10}]$	500	12	10
$[Zn_4LCl_6(H_2O)_2]$	500	10	10
Tetracycline	500	45	30

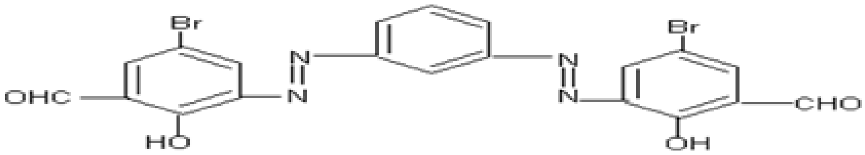

Fig-1 Proposed Geometry of LH_2

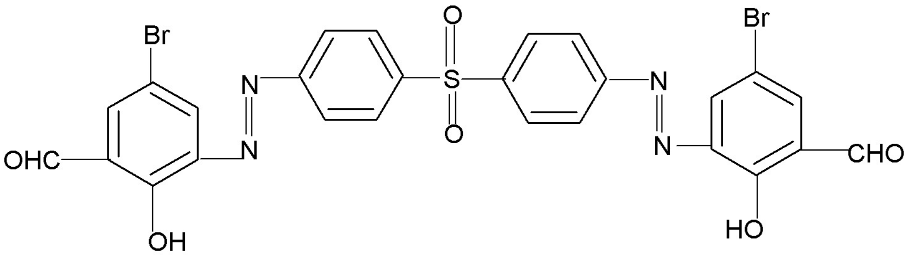

Fig-2 Proposed Geometry of L/H$_2$

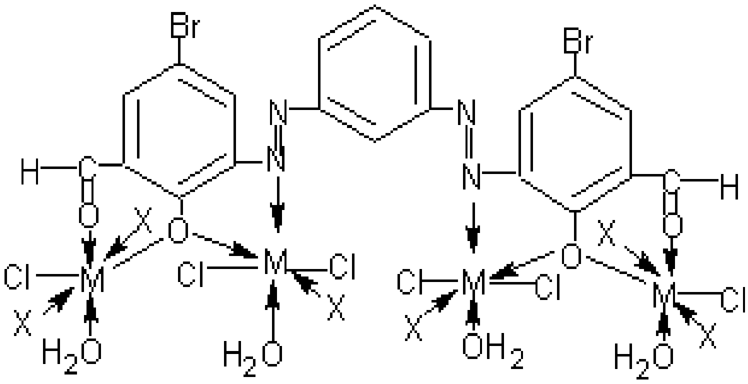

Fig-3 Proposed Geometry of the complexes with LH2, X= H$_2$O for M=Co(II),Ni(II),Cu(II) and X=NIL for M=Zn(II),Cd(II),Hg(II).

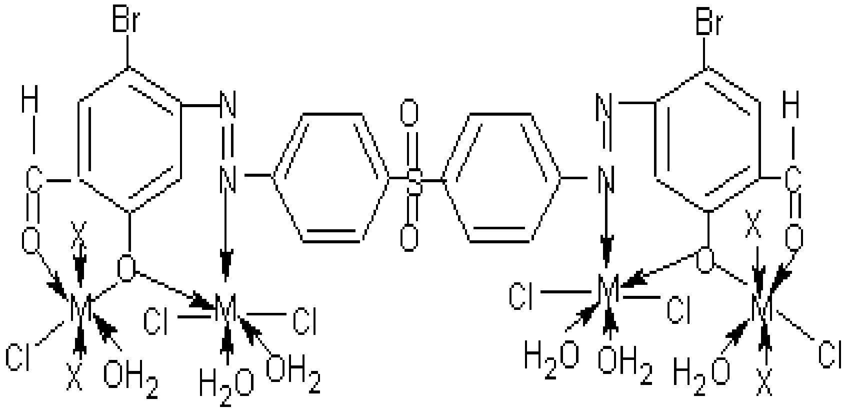

Fig-4 Proposed Geometry of the complexes with L$'$H2, X= H$_2$O for M=Co(II),Ni(II),Cu(II) and X=NIL for M=Zn(II),Cd(II),Hg(II).

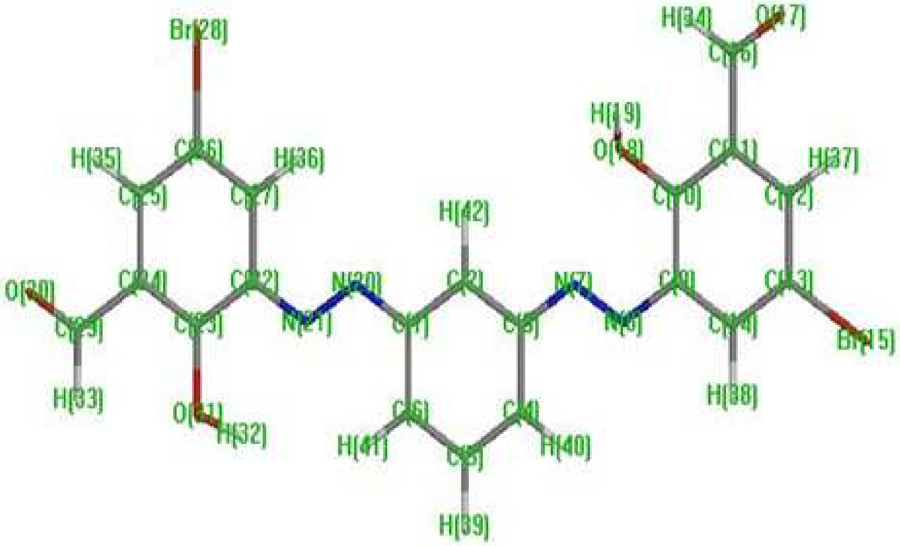

Fig-5 Optimized Geometry of LH_2

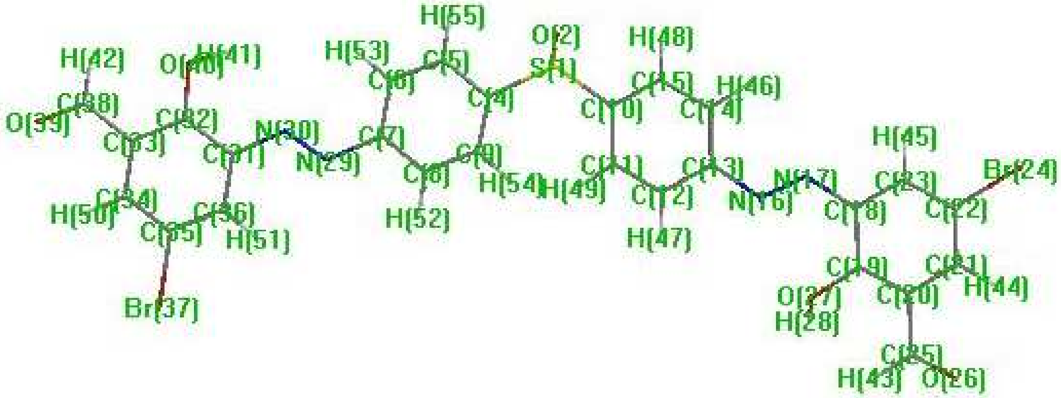

Fig-6 Optimized Geometry of $L^{'}H_2$

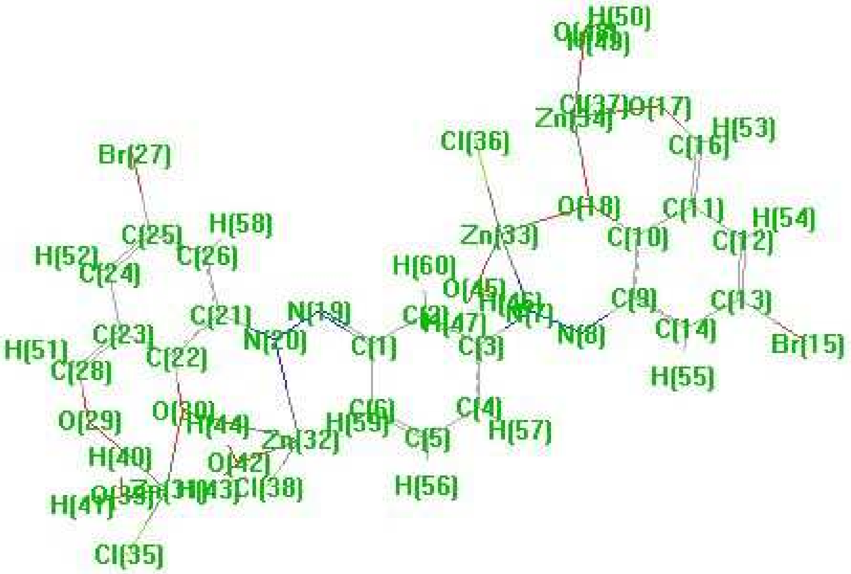

Fig-7 Optimised Geometry Zn(II) complex of LH_2

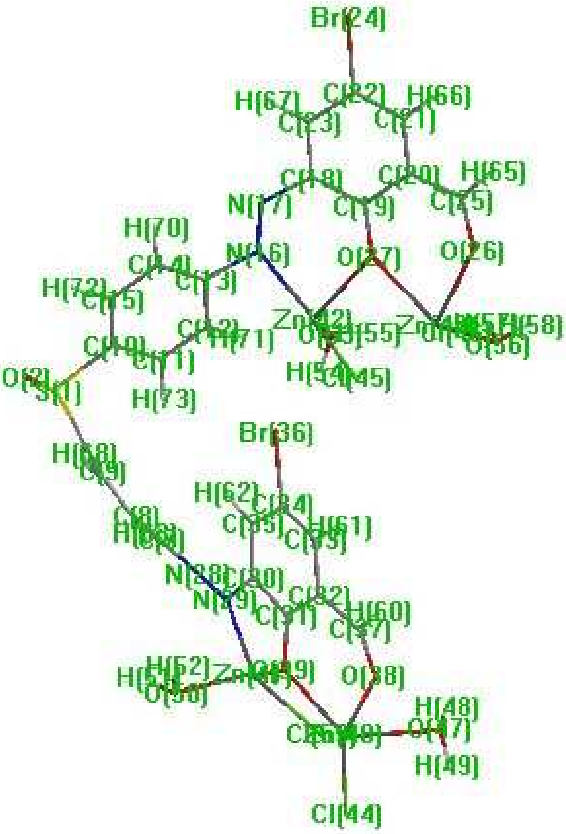

Fig-8 Optimized Geometry Zn(II) complex of L'H_2

CONCLUSION

The Co(II) ,Ni(II) complexes posses octahedral geometry, Cu(II) complexes distorted octahedral geometry and a tetrahedral geometry is suggested for Zn(II) ,Cd(II),Hg(II) complexes. It is found that both the azodyes behave a dibasic hexadentate azodye ligands coordinating through phenolic oxygen, azo nitrogen and carbonyl oxygen atoms. The ligands form tetrameric complexes with the metal ions. The XRD study suggests orthorhombic for $[Co_4L^{'}Cl_4(H_2O)_{10}]$ and triclinic for $[Cu_4LCl_4(H_2O)_{10}]$ respectively. Thermogravimetric study indicates thermal stability of the complexes. All the calculations based on the molecular mechanism on the optimized geometries fit well with the experiment findings. Both the ligands and their complexes posses' antibacterial activities against gram positive and gram negative bacteria.

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