Polymetallic complexes part CIV synthesis, characterization and potential antibacterial study of dimeric & tetrameric complexes of Co(II), Ni(II) Cu(II), Zn(II), Cd(II) and Hg(II) with azodye ligands

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Six complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with one tetradentate azodye ligand and six complexes of above metal ions with one octadentate azodye ligand have been synthesized. All the twelve complexes have been characterised by analytical, conductance, magnetic susceptibility, IR, electronic spectra, E.S.R., NMR, thermogravimetric analysis and XRD powder pattern spectra. In addition to this molecular modelling study of the ligands and complexes has been made. The Co(II) and Ni(II) complexes are found to be octahedral, Cu(II) complexes are distorted octahedral and a tetrahedral stereochemistry has been assigned to Zn(II), Cd(II) and Hg(II)complexes. The antibacterial study of the ligands and six complexes is made against gram-positive bacteria *Staphylococcus aureus* and gram-negative bacteria *Escherichia coli.*

Keywords: Polymetallic complexes, Azodye complexes.

INTRODUCTION

The study of polymetallic complexes containing Polydentate(tetra-, hexa- and octadentate) azodye ligands is of recent interest. Besides chemotherapeutic properties[1], azodyes also possess the property of an indicator and hence are used in chemical laboratories. They also find application in dyeing food stuffs and as preservative for food grains[2]. In continuation of our previous work on the study of with the Pharmacological activities of the azodyes and their complexes[3], we report here the preparation of one (bis-bidentate) Fig. 1 and one (bis-tetradentate) Fig. 2 azodye ligands and their twelve dimeric and tetrameric metal complexes.
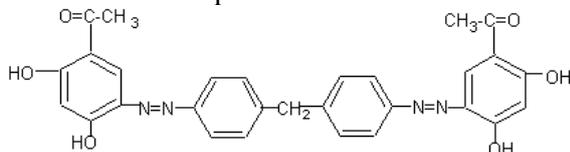
Fig. 1. LH$_2$ (4,4'-bis(2'-hydroxynaptholazo)diphenyl-ether)
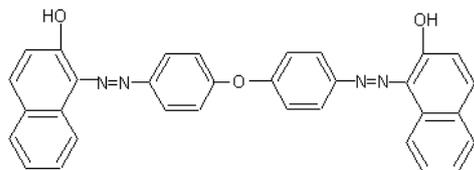
Fig. 2. L'H$_4$ (4,4'-bis(2',4'-dihydroxyacylphenylazo) diphenylmethane)

EXPERIMENTAL

Elemental analysis (C, H, N) were carried out on elemental analyser Perkin Elmer 2400 while metals were determined by EDTA after decomposing the complexes with conc. Nitric acid. All the chemicals were of AR or SRL grade. The chlorine contents were estimated by standard methods. Conductance measurements of the complexes were made using Toshniwal CL 01-06 Conductivity Bridge. The magnetic susceptibility measurements were made at RT by Gouy method using [HgCo(SCN)4] as calibrant. IR spectra (KBr) were recorded using IFS 660 spectrophotometer, electronic spectra (in DMF) using Hilger-Watt Uv-vis peck spectrophotometer, ESR of the Copper complexes were recorded on an EU- spectrometer, NMR on a Jeol GSX 400 with CDCl3 and 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(Cu K α raditions, λ = 154060 Å) and the generation setting of 30 MA and 40KV, the scan axis is Gonio and Start position (2θ) 10.0011. Thermal data was recorded on MRETTLER STARe SW 9.01 and Molecular modelling of the ligands and complexes was done with the help of Arguslab 4.0 software.

The antibacterial activity of two ligands and six complexes has been studied as per cup-plate method [4]. The solutions of the compounds were prepared in dimethylsulfoxide (DMSO) at 500 μgml^{-1}. The bacterial strains are inoculated into 100

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ml of the sterile nutrient broth and incubated at 37 ± 1 °C for 24 hours. The density of the bacterial suspension was standardized by Mc Farland method. Well of uniform diameter (6 mm) were made on agar plates after inoculating them separately with the test organisms aseptically. The standard drug and the test compounds were introduced with the help of micropipette and the plates were placed in the refrigerator at 8-10 °C for proper diffusion of drug into the media. After two hours of cold incubation, the petri-plates were transferred to incubator and maintained at 37± 2 °C for 18-24 hours. Then the petriplates were observed for zone of inhibition by using 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.

Preparation of the Ligands

The azodyes were prepared by the coupling reaction of the diazonium chlorides obtained from 4,4/-diaminodiphenylether (0.01 mol 2.0 gm) and 4,4/-diaminodiphenyl methane (0.01 mol, 1.98 gm) with alkaline solution of β – naphthol (0.02 mol , 3.36 gm) and 2,4-dihydroxyacetophenone (0.02 mol, 3.96 g.) respectively at 0 to 5 °C.

Preparation of the complexes

The metal chlorides in ethanol were mixed separately with ethanolic solution of the ligands with LH_2 and L/H_4 in 2:1 and 4:1 molar ratio respectively. 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 adding concentrated ammonia drop by drop with stirring. The solid complexes thus formed were then washed with ethanol followed by ether and dried in vacuum (Fig 3 and Fig 4).
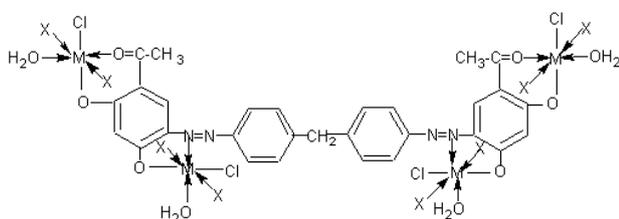
Fig. 3. Proposed Geometry of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with LH_2. . (Where x = H_2O for CO^{II}, Ni^{II}, Cu^{II} ,X= 0 for Zn^{II}, Cd^{II}, Hg^{II})
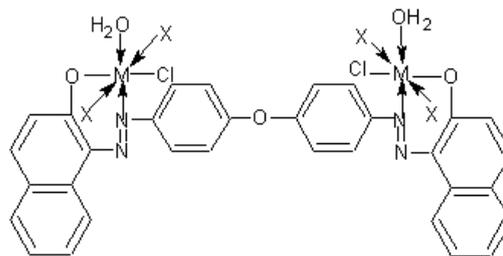
Fig.4. Proposed Geometry of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with L/H_4. (Where x = H_2O for CO^{II}, Ni^{II}, Cu^{II} ,X= 0 for Zn^{II}, Cd^{II}, Hg^{II})

RESULTS AND DISCUSSION

The elemental analysis data agree well with the following compositions of the metal complexes reported (Table 1), have the compositions $[M_2LCl_2(H_2O)_6]$, $[M^1_2LCl_2(H_2O)_2]$, $[M_4L/Cl_4(H_2O)_{12}]$ and $[M^1_4L/Cl_4(H_2O)_4]$ where M = Co(II), Ni(II), Cu(II); M^1 = Zn(II), Cd(II), Hg(II), $LH_2 = C_{32}H_{22}O_3N_4$ and $L/H_4=C_{29}H_{24}O_6N_4$. All the complexes were amorphous in nature, have high melting points and were insoluble in common organic solvents but soluble in dimethylformanide and dimethylsufoxide. The non-electrolytic nature of the complexes were indicated by the low conductance values (3.5 – 4.8 Ω^{-1} cm^2 mol^{-1}) in DMF [5].

IR spectra

In the IR spectra(Table 1)of the ligands, show broad bands were observed at 3445 cm^{-1} (LH_2) and at 3445 cm^{-1} ($L'H_4$) which may be assigned to the stretching vibrations of naptholic and phenolic –OH group. The broadness of these bands may be the O-H…N and O-H…O intramolecular Hydrogen bonding between naptholic/phenolic Hydrogen atom with azo N and Carbonyl O atom. The bands at 1490 cm^{-1} ((LH_2) and 1470 ($L'H_4$) can be attributed to phenolic C – O vibration and in the metal chelates these bands appear at ~ 1465 - 1471 cm^{-1} indicating the bonding of phenolic/naptholic oxygen atoms of the ligands to the metal ions[6]. The sharp bands of the ligands at 1621 cm^{-1} ($L'H_2$) and at 1606 cm^{-1} ($L'H_4$) can be attributed to ν (N=N) vibration and in the metal chelates these bands are shown at 1614 cm^{-1} with the former ligand and at ~1594 - 1599 cm^{-1} with the latter ligand which indicates the coordination of one of the azo nitrogen atoms ions [7]. In the ligand ($L'H_4$) a sharp band appears at 1635 cm^{-1} which can be attributed to ν(>C=O) vibration and in the metal chelates it appears at ~1588 cm^{-1} indicating the bonding of the carbonyl oxygen atom to the metal ions. In the metal complexes, broad bands appear at 3172-3434 cm^{-1} followed by sharp peaks at 825 -

Table 1. Analytical data of the Ligands and the Complexes

Compound	M.P.	Colour	Found/(Calcd.), %				
			C	Cl	H	N	M
LH$_2$	90	Deep red	77.1/(77.4)		3.63/(3.94)	10.01/(10.03)	
L$^/$H$_4$	75	Reddish brown	66.01/(66.41)		4.14/(4.65)	10.65/(10.68)	
[Co$_2$LCl$_2$(H$_2$O)$_6$]	>240	Red	50.24/(50.64)	8.2/(8.3)	3.35/(3.75)	6.4/(6.5)	13.5/(13.8)
[Co$_4$L$^/$Cl$_4$(H$_2$O)$_{12}$]	>240	Brick red	31.1/(31.3)	12.4/(12.7)	3.92/(3.96)	4.7/(5.0)	20.8/(21.1)
[Ni$_2$LCl$_2$(H$_2$O)$_6$]	>240	Coffee	50.64/(50.68)	8.1/(8.3)	3.73/(3.75)	6.3/(6.5)	13.5/(13.7)
[Ni$_4$L$^/$Cl$_4$(H$_2$O)$_{12}$]	>240	Bright red	31.38/(31.12)	12.6/(12.7)	3.93/(3.96)	4.9/(5.0)	20.8/(21.1)
[Cu$_2$LCl$_2$(H$_2$O)$_6$]	>240	Light green	50.09/(50.11)	8.1/(8.3)	3.69/(3.71)	6.3/(6.4)	14.5/(14.7)
[Cu$_4$L$^/$Cl$_4$(H$_2$O)$_{12}$]	>240	Brown	30.55/(30.85)	12.3/(12.5)	3.6/(3.7)	4.7/(4.9)	21.1/(21.4)
[Zn$_2$LCl$_2$(H$_2$O)$_2$]	>240	Darck brown	54.21/(53.93)	6.8/(7.01)	2.93/(3.02)	5.4/(5.53)	25.6/(25.83)
[Zn$_4$L$^/$Cl$_4$(H$_2$O)$_4$]	>240	Light red	34.89/(35.09)	8.7/(8.9)	2.53/(2.82)	5.4/(5.6)	26.1/(26.2)
[Cd$_2$LCl$_2$(H$_2$O)$_2$]	>240	Coffee	48.64/(48.65)	7.7/(7.9)	2.55/(2.70)	6.1/(6.3)	(25.3)
[Cd$_4$L$^/$Cl$_4$(H$_2$O)$_4$]	>240	Brown	28.88/(29.50)	11.7/(11.9)	2.11/(2.37)	4.7/(4.9)	37.5/(37.6)
[Hg$_2$LCl$_2$(H$_2$O)$_2$]	>240	Red	40.64/(40.69)	6.5/(6.6)	2.01/(2.25)	5.1/(5.2)	37.5/(37.6)
[Hg$_4$L$^/$Cl$_4$(H$_2$O)$_4$]	>240	Red	22.67 (22.71)	9.0/(9.2)	1.67/(1.82)	3.5/(3.6)	52.1/(52.2)

844 cm^{-1} and 731 – 749 cm^{-1} assignable OH stretching, rocking and wagging vibrations respectively indicating the presence of coordinated water molecules in the complexes [8]. The conclusive evidence of bonding of the ligands to the metal ions is proved by the appearance of bands at ~ 503 – 518 cm-1 (M-O) and at ~454 - 457 cm^{-1} (M-N) [9].

Electronic spectra and Magnetic measurements

In the electronic spectra (Table 2) of Co(II) complexes, four bands appear at 8150(8182) cm^{-1}, 16350(16550) cm^{-1} and 19765(19950) cm^{-1} and 31550(32460) cm^{-1} . The first three band assigned to 4T1g(F) → 4T2g(F)(ν1), 4T1g(F) → 4A2g(F)(ν2), 4T1g(F) → 4T1g(P)(ν3) respectively and 4th band is CT band. The ligand field parameters like

Dq = 820 (836.8) cm^{-1}, B =777.6 (796.9) cm^{-1}, β35 = 0.743(0.757) cm^{-1} ν2/ν1 = 2.006(2.02) and σ=25(21.95) suggest the octahedral configuration for the complexes [10]. In the electronic spectra of Ni(II) complexes four bands appear at 10120 (10135) cm^{-1}, 16920(17150) cm^{-1}, 24820(24995) cm^{-1} and 31340(32160) cm^{-1}. The first three bands can be assigned to 3A2g(F) → 3T2g(F)(ν1), 3A2g(F) → 3T1g(F)(ν2), 3A2g(F) → 3T1g(P)(ν3) transitions respectively and the fourth band is assigned to a CT band. The ligand field parameters like Dq =1012 (1013.5) cm-1, B=758.6 (782.6) cm-1, β35=0.728 (0.751) cm-1, ν2/ν1 = 1.67 (1.69) and σ=37.3(31.1) suggest an octahedral geometry for the complexes.

Table 2. IR spectral Data of the ligands and the complexes, ν/cm^{-1}

Compound	ν/cm^{-1}				
	(C-O)	(-N=N-)	(C=O)	(M-O)	(M-N)
LH$_2$	1490	1621	-	-	-
L'H$_4$	1470	1606	1635	-	-
[Co$_2$LCl$_2$(H$_2$O)$_6$]	1489	1613	-	518	457
[Co$_4$L'Cl$_4$(H$_2$O)$_{12}$]	1465	1544	1586	503	455
[Ni$_2$LCl$_2$(H$_2$O)$_6$]	1471	1614	-	517	457
Ni$_4$L'Cl$_4$(H$_2$O)$_{12}$] [	1467	1595	1588	505	454
[Cu$_2$LCl$_2$(H$_2$O)$_2$]	1468	1614	-	515	455
[Cu$_4$L'Cl$_4$(H$_2$O)$_{12}$]	1465	1598	1585	510	454
[Zn $_2$LCl$_2$(H$_2$O)$_2$]	1470	1613	-	510	456
[Zn $_4$L'Cl$_4$(H$_2$O)$_4$]	1467	1599	1586	505	455
[Cd$_2$LCl$_2$(H$_2$O)$_2$]	1468	1613	-	512	457
[Cd$_4$L'Cl$_4$(H$_2$O)$_4$]	1467	1595	1585	510	455
[Hg$_2$LCl$_2$(H$_2$O)$_2$]	1470	1614	-	515	455
[Hg$_4$L'Cl$_4$(H$_2$O)$_4$]	1465	1594	1587	510	454

Table 3. Magnetic and Electronic absorption data of the compounds

Compound	μ_{eff}/μ	ν/cm^{-1}	Band assignment	Geometry
[Co$_2$LCl$_2$(H$_2$O)$_6$]	5.01	8150	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	octahedral
		16350	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
		19765	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
		31550	INCT[a]	
[Co$_4$L/Cl$_4$(H$_2$O)$_{12}$]	5.0	16550	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	octahedral
		19950	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
		32460	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
			INCT[a]	
[Ni$_2$LCl$_2$(H$_2$O)$_6$]	3.0	10120	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	octahedral
		16920	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
		24820	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
		31340	INCT[a]	
[Ni$_4$L/Cl$_4$(H$_2$O)$_{12}$]	3.1	1013	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	octahedral
		17150	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
		24995	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
[Cu$_2$ L Cl$_2$ (H$_2$O)$_2$]	1.8	13350	$^2E_g \rightarrow {}^2T_{2g}$	Distorted octahedral
[Cu$_4$ L/Cl$_4$ (H$_2$O)$_{12}$]	1.7	1335	$^2E_g \rightarrow {}^2T_{2g}$	Distorted octahedral

1012 (1013.5) cm^{-1}, B=758.6 (782.6) cm^{-1}, β35=0.728 (0.751) cm^{-1}, $\nu2/\nu1$ = 1.67 (1.69) and σ=37.3(31.1) suggest an octahedral geometry for the complexes [11]. The electronic spectra of Cu(II) complexes exhibit one broad band at ~ 13350 – 14520 cm^{-1} with maxima at ~13760 cm^{-1} assignable to 2Eg → 2T2g transition supporting a distorted octahedral configuration for the complexes [12].The effective magnetic moments of Co(II), Ni(II) and Cu(II) complexes were recorded at room temperature and corrected for diamagnetic contribution using pascal's constant. These are around 5.1, 3.1 and 1.8 B.M. respectively which indicating that they have octahedral configuration around the metal ions [13].

ESR spectra

The ESR spectra of the complexes [Cu$_2$LCl$_2$(H$_2$O)$_6$] and [Cu$_4$L/Cl$_4$(H$_2$O)$_{12}$] have been recorded at X-band at room temperature. The gav values of the complexes are found to be 2.0074 and 2.10655 respectively by applying kneubuhl's method [14].This type of spectrum might be due to dynamic or pseudo rotational type of Jahn – Teller distortion. The spin orbit coupling constant λ can be determined from the equation gav=2(1 – λ / 10Dq). The values of λ for the complexes are found to be -25.456 cm^{-1} and -365.999 cm^{-1}. The lowering of λ values of the complexes from the free ion value (-830 cm^{-1}) indicates overlapping metal-ligand orbitals.

1H-NMR spectra

The ^{1}H NMR spectra of the free ligands LH$_2$ and L/H$_4$ were recorded in CDCl$_3$ of DMSO-d$_6$ respectively and showed the following signals at δ (ppm): 7.004-8.862 (20H,m,napthyl), 15.943 (2H,s,naptholic OH). The spectra of L/H4 in DMSO showed the following peaks: 6.250-8.883 (12H, m, phenyl), 12.609 (4H,s, phenolic OH), 2.502-2.664 (2H,m,-CH2-), 2.347 (6H,s,O=C-CH3). The 1H NMR spectrum of the Zinc complex was recorded in the solvent DMSO. The complex multiplet is observed at δ 6.839 – 8.676 ppm which corresponds to 20 napthyl protons [15]. The sharp peak obtained at δ 15.943 ppm (-OH) in the ligand

is found to be absent in the complex indicating deprotonation of the naphtholic proton thereby confirming the bonding of naphtholic oxygen atom to the Zinc ion (Table - 4).

Table 4. ^{1}H NMR Spectroscopic data, δ/ppm

Compound	δ/ppm			
	Ar–H	-CH$_2$-	OH	CH$_3$
LH$_2$[a]	7.004-8.682	-	15.943	-
L'H$_2$[b]	6.250-8.333	2.502-2.664	12.609	3.374
[Zn$_2$LCl$_2$(H$_2$O)][b]	6.839-8.676	-	-	-

[a]=CDCL$_3$ [b]=DMSO-d$_6$

Thermal analysis and kinetic calculation

The thermal decomposition behavior of the complex [Cu$_4$LCl$_4$(H$_2$O)$_{12}$] was studied (Table-5) by using TG and DTA techniques in an atmosphere of nitrogen at a heating rate of 10 oC per minute. The experimental data shows that the decomposition occurs in multiple stages. The thermo gram of the complex shows a mass loss within 120 oC which indicates removal of lattice held H2O molecules, supported by an exothermic peak at 110 oC[18].1Thereafter the compound, loses 11.36% of mass (Calcd, 11.013%) which corresponds to loss of seven coordinated H2O molecules, supported by an exothermic peak at 290 oC. Thereafter, a gradual mass loss of 29.28%

Table 5. Thermal data of the Cu(II) complex with the ligand L/H$_4$

Decomposition temp(oC)	Mass loss(obs)	Mass loss(calcd)	Assignment
310	11.36%	11.01%	7 Coord.H$_2$O
550	29.28%	29.15%	5 Coord.H$_2$O, parts of ligand
930	47.70%	47.80%	4 chlorine atoms, rest of ligand

(Calcd 29.15%) is observed due to removal of rest of coordinated H2O molecules and parts of the ligand. Then the compound shows loss of 47.70% (Calcd 47.80%) due to removal of four chlorine atoms and rest of the ligand moiety with the rise of temperature with the formation of CuO at 930 oC supported by an exothermic peak in the DTA curve. The kinetic parameters such as order of reaction, activation energy for the thermal decomposition of [Cu4LCl4(H2O)12] have been determined by Freeman-caroll method [19]. In this method, the equation used is –dw/dt = Rt = Z/RH e-E/RT Wn where RH= rate of heating, w= weight fraction of reacting material, E=activation energy, n=order of reaction, and z=frequency. This equation in the difference form will be Δ log RT = n Δ log w − (E/2.303R) Δ (1/T), when Δ (1/T) is kept constant, a plot at Δ log RT verses Δ log W gave a linear relationship whose slope and intercept provides the value of n and E respectively. The order of the decomposition reaction and the activation energy are found to be1.40 and 5.91J mole-1 respectively. The calculated value of the activation energy is found be low due to the autocatalytic effect the metal ion on the thermal decomposition of the complex [20,21]. The correlation coefficient (r) of the thermal decomposition is 0.96 which fits well with the experimental finding.

Powder X-ray diffraction analysis

The XRD study (powder pattern) of the complex [Ni4L/ Cl4 (H2O)12] has been studied the help of X-ray diffractometer. The prominent peaks of the X-ray diffraction pattern have been indexed out analysed by using computer programme LSUCRPC[16].The lattice parameters (a,b,c, α, β, γ), volume of the unit cell and the miller indices (h,k,l) have been mentioned in Table-6. The indexing is confirmed by comparing between observed and calculated (2θ) values. It is observed that, the peaks of the XRD powder pattern have been successfully indexed as figure of merit (M) is found to be 8.5 as suggested by De Wolff [17]. 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= Avogadronumber, V= volme of the unit cell, M = Formula weight of the complex. The value of 'n' is found to be 2.0 that agree well with the triclinic crystal structure of the complex. The crystallite size of the same complex was calculated from the diffraction line width using the Debye scherrer relation D=kλ/βcosθ where D=particle size, k=dimensionless shape factor, λ=X-ray wavelength, β=line broadening at half the maximum intensity, θ=diffraction angle. This equation relates the size of the particles in a solid in the broadening of a peak in a diffraction pattern. The particle size of the same complex was found to be 0.64 nm.

Molecular modelling

Molecular modelling of the Ligand LH2, L/H4 and metal complexes of Co(II), Zn(II) with LH2, Ni(II) complex with L/H4 have been carried out using molecular mechanics and Hartree-Fock (HF) Quantum methods. The standard 6-31 G basis set

was used in conjugation with the H-F method. All calculations are made using Gaussian 98 programme package [22, 23, 24, 25].

The metal complexes were built and optimization of their geometry was done at mm/H-F/6-31G level of theory Fig.5, Fig.6, Fig.7, Fig.8, and Fig.9.

Table 6. XRD Data of the Ni(II) Complex

Compound	Bond	Bond Length(Å)	Bond Angle(°)
Ligand-LH$_2$	C(5)-O(7)	1.429	C(5)-C(6)-C(3)-120
	C(2)-N(8)	1.434	C(6)-C(5)-O(7)-120
	C(23)-O(28)	1.407	C(1)-C(2)-N(8)-120
	C(5)-C(6)	1.379	C(2)-N(8)-N(9)-106.7
	N(8)-N(9)	1.270	C(23)-O(38)-H(40)-104.51
[Co$_2$LCl$_2$(H$_2$O)$_6$]	O(36)-Co(40)	1.964	O(38)-Co(40)-O(43)-90
	N(9)-Co(40)	1.972	O(38)-Co(40)-Cl(42)-90
	Cl(42)-Co(40)	2.359	O(38)-Co(40)-N(8)-90
			C(18)-N(8)-Co(40)-106.7
[Zn$_2$LCl$_2$(H$_2$O)$_2$]	O(38)-Zn(40)	1.883	O(38)-Zn(40)-O(41)-109.47
	N(9)-Zn(40)	1.903	O(38)-Zn(40)-N(8)-109.47
	Zn(40)-Cl(42)	2.273	O(38)-Zn(40)-Cl(42)-109.47
			Zn(40)-O(41)-H(47)-104.51
Ligand-L$^/$H$_4$	C(35)-O(11)	1.325	C(5)-C(7)-H(94)-109
	C(26)-O(47)	1.407	C(5)-C(7)-C(35)-109.47
	C(5)-C(7)	1.48	C(43)-C(44)-O(11)120
	C(5)-C(4)	1.379	
NiL$^/$Cl$_4$(H2O)$_{12}$	C(9)-N(25	1.434	O(12)-Ni(13)-O(15)-90
	O(12)-Ni(13)	1.894	O(11)-Ni(13)-O(14)-90
	O(11)-N(13)	1.871	N(9)-Ni(17)-O(10)-90
	N(8)-Ni(17)	1.885	O(10)-Ni(17)-Cl(18)-90
	Ni(17)-Cl(!8)	2.264	N(8)-N(9)-Ni(17)-106.7
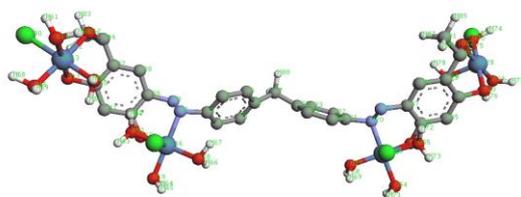
Fig.5. Optimised Geometry of Ligand (LH$_2$)
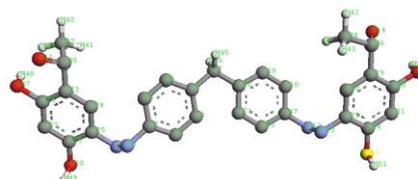
Fig. 6 Optimised Geometry of Ligand(L$^/$H$_4$)
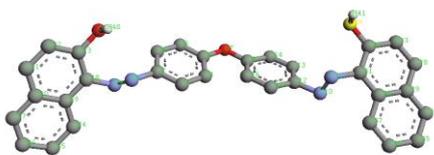
Fig. 7. Optimised Geometry of Co(II) Complex with (LH$_2$)
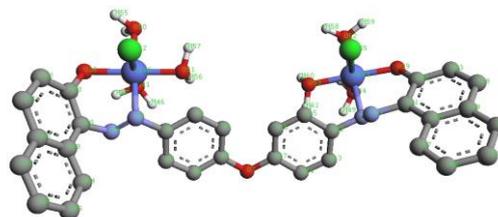
Fig. 8. Optimised Geometry of Zn(II) Complex with (LH$_2$)
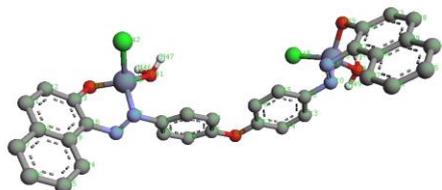
Fig. 9. Optimised Geometry of Ni(II) Complex with L$^/$H$_4$

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Findings of these computed works are in good agreement with the experimental results. The selected band lengths, band the angles of the ligands and complexes are give in Table 7.

Table 7. Selected bond length and bond angle of the ligands and the complexes

Compound	Concentration/ μgml^{-1}	Zone of Inhibition (mm)	
		E.coli	*S aureus*
LH$_2$	500	14	12
L'H$_4$	500	10	8
Co$_2$LCl$_2$(H$_2$O)$_6$]	500	15	13
[Ni$_2$LCl$_2$(H$_2$O)$_6$]	500	18	14
Zn$_2$LCl$_2$(H$_2$O)$_2$]	500	10	6
Cu$_4$LCl$_4$(H$_2$O)$_{12}$]	500	14	12
Ni$_4$LCl$_4$(H$_2$O)$_{12}$]	500	12	10
Tetracycline	1000	45	30

In the metal complexes, the metal may be coordinated to either N1 or N2 of the azo group. When it is coordinated to N1, it forms a six-member ring and when it is coordinated to N2 it forms a five-member ring. In case of the Co(II) and Zn(II) complexes with LH2,the total energy is found to be 184.744 KcalMole-1 and 111.929 KcalMole-1 respectively when they form five member ring, But energy of the complexes has been reduced to 129.413 KcalMole-1 and 103.27 KcalMole-1 which shows that the metal atoms are bonded to N1 of the azo group. In case of Ni(II) complex with L/H4 the bond energy of the six member ring(378.48 KcalMole-1) is found to be more than the five member ring (321.373 KcalMole-1) which indicates the bonding of Ni atom with the N2 of the azo group.

Antibacterial study

The ligands and metal complexes have been screened for antibacterial activities and the results have been shown in Table-8. The results show that the complexes possess remarkable biological activities against different bacteria. The Co(II)and N(II) complexes with LH2 show more antibacterial activities than and the co(II) and Ni(II) complexes show greater activities than the ligand L/H4. The increase in biological activity of the metal complexes than the ligands may be due to complexation and it can be explained on the basis of chelation theory [26].

The Zn(II), Cd(II) and Hg(II) complexes have tetrahedral geometry based upon analytical conductance and IR spectral data. The azodye (LH2) behaves as bis-bidentate (tetradentate) and the azodye L/H4 behaves as bis-tetradentate (octadentate) ligand forming dimeric and tetrameric complexes respectively

CONCLUSION

Based on physicochemical and spectral data, octahedral geometry for Co(II) and Ni(II) complexes, a distorted octahedral geometry for Cu(II) complexes and a tetrahedral geo metry for Zn(II),Cd(II) andHg(II) complexes are proposed. It is found that the ligand(LH2) behaves as dibasic ON-NO bis-bidentate and the ligand (LH4) behaves as tetrabasic OOON-NOOO bis-tetradentate, coordinating through the phenolic/naptholic oxygen, azo nitrogen and carbonyl oxygen atoms. Thermogravimetry study indicates the complex is thermally stable, the XRD study suggested the triclinic crystal system for the nickel complex. All calculations based on molecular mechanics on the optimized geometries fit well with the experimental findings. The ligands and the complexes are pharmacologically active and the complexes posses enhanced antibacterial activities compared to the free ligands.

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ПОЛИМЕРНИ КОМПЛЕКСИ ЧАСТ CIV СИНТЕЗА, ОХАРАКТЕРИЗИРАНЕ И АНТИБАКТЕРИАЛНО ИЗСЛЕДВАНЕ НА ДИМЕРНИ И ТЕТРАМЕРНИ КОМПЛЕКСИ НА Co(II), Ni(II), Cu(II), Zn(II), Cd(II) И Hg(II) С АЗОБАГРИЛНИ ЛИГАНДИ

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(Резюме)

Бяха синтезирани шест комплекси на Co (II), Ni (II), Си (II), Zn (II), Cd (II) и Hg (II) с един тетрадентатен азобагрилен лиганд и шест комплекси на същите метални йони с един октадентатен азобагрилен лиганд. Всичките дванадесет комплекси са охарактеризирани аналитично, чрез проводимост, магнитна чувствителност, ИЧ, електронен спектри, ЕСР, ЯМР, термогравиметричен анализ и прахова ренгенова дифракция В допълнение към това беше направено изследване на лигандите и комплексите чрез молекулно моделиране. За Co (II) и Ni (II) комплекси се установи, че са осмостенни, Cu (II) комплекси са изкривени осмостенни и четиристенна стереохимия бе присвоена на Zn (II), Cd (II) и Hg (II) комплекси. Антибактериалното проучването на лигандите и шест комплекси беше направено срещу грам-положителни бактерии *Staphylococcus aureus* и грам-отрицателни бактерии *Escherichia coli.*