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Природните науки в образованието

Experiments
Учебен експеримент в природните науки

POLYMETALLIC COMPEXES: CV. SYNTHESIS, SPECTRAL, THERMOGRAVIMETRIC, XRD, MOLECULAR MODELLING AND POTENTIAL ANTIBACTERIAL PROPERTIES OF TETRAMERIC COMPLEXES OF Co(II), Ni(II), Cu(II), Zn(II), Cd(II) AND Hg(II) WITH OCTADENTATE AZODYE LIGANDS

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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 characterization of the complexes has been made basing upon analytical, conductance, magnetic susceptibility, IR, electronic spectra ESR, NMR, thermo gravimetric, X-ray diffraction data and molecular modeling. 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 study of the ligands and some complexes against *E.coli* and *S.aureus* has been made.

Keywords: polymetallic complexes, tetrameric complexes, azodye complexes

Introduction

The study of polymeric complexes, containing multidentate azodye ligands with transitional and non-transitional metal ions, is of a great interest today. All azodyes are pharmacologically active (Goodman & Gilman, 1970). They are used as indicators in chemical laboratories and as preservatives and dyeing agents for industries (Isa et al., 1984). In continuation of our previous work (Mahapatra & Patel, 2009; Mahapatra & Sarangi, 2011) this paper reports preparation of two new ocadentate oxygen–nitrogen donor azodye ligands (Figs 1 and 2) and twelve tetrameric metal complexes.

Experimental

All chemicals were of BDH or SRL grade. Elemental analyses (C,H,N) were carried on elemental analyzer Perkin-Elmer- 2400 while the metals were estimated by EDTA

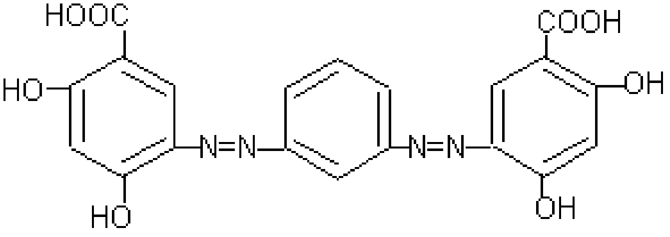

Fig. 1. Structure of ligand-LH_6-1,3-bis(2$^/$,4$^/$-dihydroxy-5$^/$-carboxyphenylazo)benzene

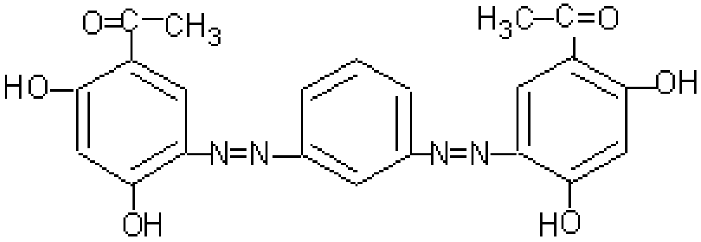

Fig. 2. Structure of ligand-$L^/H_4$-1,3-bis(2$^/$,4$^/$-dihydroxy-5$^/$-acylyphenylazo)benzene

after decomposing with concentrated HNO_3. The chlorine contents were determined by standard method. Conductance measurements of the complexes in DMF (10^{-3}M) were made 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^{-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-Gnio, start-position (2θ-10.004), end-position (2θ-79.9764), anode material-Cu,K-ALPHA1(Å) 1.54060 and generator setting-30mA,40KV. Thermo gravimetric study was made on NETZSCH STA 449F 3 and molecular modeling of the ligand and complex was done with the help of Argus lab software 4.01.

The antibacterial activity of two ligands and six complexes has been studied as per cup-plate method (Miller & Brandt, 1939). The solutions of the compounds are prepared in dimethylsulfoxide (DMSO) at 500 μg/ml. The bacterial strains are inoculated into 100 ml of the sterile nutrient broth and incubated at 37 ± 1°C for 24 hours. The density of the bacterial suspension is standardized by Mc Farland method. Well of uniform diameter (6

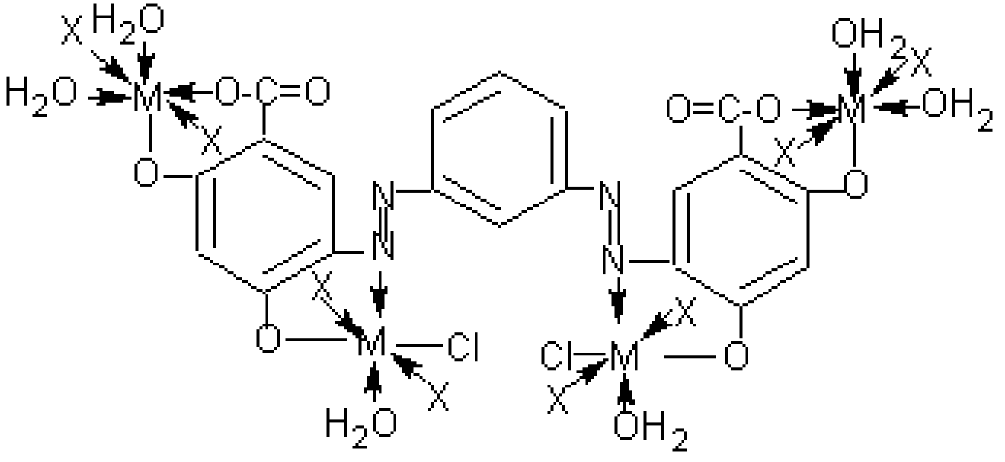

Fig. 3. Structure of metallic complex with ligand LH_6 where $X=H_2O$ for M=Co,Ni,Cu and M=Nil for M=Zn,Cd,Hg

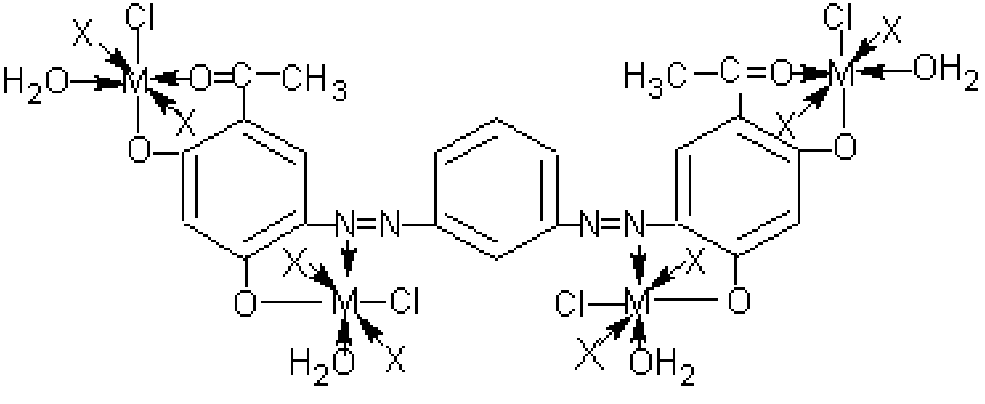

Fig. 4. Structure of metallic complex with ligand $L^/H_4$ where $X=H_2O$ for M=Co,Ni,Cu and M=Nil for M=Zn,Cd,Hg

mm) are made on agar plates after inoculating them separately with the test organisms aseptically. The standard drug and the test compounds are introduced with the help of micropipette and the plates are placed in the refrigerator at 8-10°C for proper diffusion of drug into the media. After two hours of cold incubation, the petriplates are transferred to incubator and maintained at 37± 2°C for 18-24 hours. Then the petriplates are 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 m-phenylenediamine (0.01 mol, 1.08 gm) with alkaline solution of 2,4-dihydroxybenzoic acid (0.02 mol, 3.08 g.) (Fig. 1) and 2,4-dihydroxyacetoophenone (0.02 mol,3.04 g) (Fig.2), respectively at 0-5°C.

Preparation of the 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 adding conc. ammonia drop by drop with stirring. The solid complexes thus formed were then washed with ethanol followed by ether and dried in vacuum (Figs. 3 and 4).

Results and discussion

The metal complexes reported (Table 1) have the compositions [$M_4LCl_2(H_2o)_{14}$], [$M^1_4LCl_2(H_2O)_6$], [$M_4\,L^/\,Cl_4(H_2O)_{12}$] and [$M^1_4\,L^/\,Cl_4(H_2O)_{12}$] where M = Co(II), Ni(II), Cu(II); M^1 = Zn(II), Cd(II), Hg(II); $LH_6 = C_{20}H_{14}O_8\,N_4$ (calcd. (%) C, 54.79, H, 3.19, N, 12.78,found(%)C,54.2,H,2.9,N, 12.4), 1,3-bis(2/,4/-dihydroxy-5/-carboxy phenlyazo) benzene, $L^/\,H_4 = C_{22}\,H_{18}\,O_6\,N_4$ (calculated (%) C, 60.82, H, 4.17, N, 12.90, found (% C, 60.42, H, 4.07, N, 12.6), 1,3-bis(2/,4/-dihydroxy-5/-acyllphenlyazo)benzene. All the complexes are amorphous in nature, have high melting points and are insoluble in common organic solvents but soluble in dimethylformanide and dimethylsufoxide. The non-electrolytic nature of the complexes is indicated by the low conductance values of 4.3 – 5.7 Ω^{-1} cm^2 mol^{-1} (Quagliano et al., 1961).

In the IR spectra of the ligands, broad bands are observed at 3430 cm^{-1} (LH_6) and at 3178 cm^{-1} ($L^/H_4$) which may be assigned to stretching vibration of phenolic hydroxyl group. The broadness of these bands may be due to O-H...N hydrogen and O-H...O intramolecular hydrogen bonding. Disappearance of these bands in the metal chelates

Table 1. Analytical data of the ligands and their complexes

Compound	M.P(^{0}C)	Colour	% of Metal Found (calculated)	%of Nitrogen Found (calculated)	% of Chlorine Found (calculated)	μ_{eff} BM
LH_6	85	Brick red		12.4 (12.78)		
$L^{/}H_4$	70	Reddish brown		12.6 (12.9)		
$[Co_4LCl_2(H_2O)_{14}]$	>240	Reddish brown	23.5 (23.79)	5.2 (5.65)	6.9 (7.16)	5.0
$[Co_4L^{/}Cl_4(H_2O)_{12}]$	>240	Deep brown	22.69 (22.99)	5.1 (5.45)	13.62 (13.87)	5.1
$[Ni_4LCl_2(H_2O)_{14}]$	>240	Brown	23.5 (23.71)	5.2 (5.47)	6.9 (7.17)	3.2
$[Ni_4L^{/}Cl_4(H_2O)_{12}]$	>240	light red	22.7 (22.95)	5.2 (5.47)	13.6 (13.88)	3.1
$[Cu_4LCl_2(H_2O)_{14}]$	>240	light red	24.8 (25.17)	5.2 (5.56)	6.8 (7.03)	1.8
$[Cu_4L^{/}Cl_4(H_2O)_{12}]$	>240	brown	24.1 (24.6)	5.07 (5.37)	13.25 (13.62)	1.78
$[Zn_4LCl_2(H2O)_6]$	>240	red	29.5 (29.97)	6.0 (6.41)	7.85 (8.14)	
$[Zn_4L^{/}Cl_4(H2O)_4]$	>240	red	28.7 (28.88)	6.08 (6.18)	15.4 (15.68)	
$[Cd_4LCl_2(H2O)_6]$	>240	yellow	41.89 (42.39)	5.1 (5.27)	6.4 (6.69)	
$[Cd_4L^{/}Cl_4(H2O)_4]$	>240	coffee	40.08 (41.11)	4.8 (5.12)	12.7 (12.98)	
$[Hg_4LCl_2(H2O)_6]$	>240	deep brown	56.4 (56.67)	3.6 (3.96)	4.8 (5.02)	
$[Hg_4L^{/}Cl_4(H2O)_4]$	>240	brown	55.17 (55.47)	3.45 (3.87)	9.7 (9.81)	

indicates the bonding of the phenolic –OH groups in the metal complexes. The bands observed at 1500 cm^{-1}(LH_6) and 1506 cm^{-1} ($L^{/}H_4$) can be attributed to phenolic C – O vibration and in the metal chelates these bands appear at ~ 1486 cm^{-1} and ~ 1492 cm^{-1} respectively indicating the bonding of phenolic oxygen atoms of the ligands to the metal ions (Mishra & Kesari, 1981). The sharp bands of the ligands at 1555 cm^{-1} (LH_6) and at 1597 cm^{-1} ($L^{/}H_4$) can be attributed to $V_{N=N}$ vibration and in the metal chelates these bands are shown at ~1550 cm^{-1} with the former ligand and at ~1593 cm^{-1} with the latter ligand which indicates the coordination of one of the azo nitrogen atoms to the metal ions (King & Bisnette, 1966). In the ligand (LH_6) $\nu_{as}(Coo^-)$ and ν_s (Coo^-) bands appear at 1610 and 1380 cm^{-1} and these bands appear in the complexes at ~1599 cm^{-1} at ~1373 cm^{-1} with a difference ($\Delta\nu$) of ~226 cm^{-1} which supports the monodentate nature of the carboxylate group (Dean & Phillips, 1980). In the ligand ($L^/H_4$) a sharp band appears at 1622 cm^{-1} which can be attributed to ν (>C=O) vibration and in the metal chelates it appears at ~1565 cm^{-1} indicating the bonding of the carbonyl oxygen atom to the metal ions. In the metal complexes, broad bands appear at ~3249 – 3232 cm^{-1} and~2915-3387 followed by sharp peaks at ~796-799 cm^{-1} and ~785 – 799 cm^{-1} assignable to OH stretching, rocking and wagging vibrations respectively indicating the presence of coordinated 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 ~ 527-538, ~527-529 cm^{-1} (M-O) and at ~494 cm^{-1},~505 cm^{-1} (M-N) (Ferraro, 1971).

The magnetic moments of Co(II), Ni(II) and Cu(II) complexes are recorded at RT and diamagnetic correction was made using Pascal's constants. The observed magnetic moment values for the Cu(II), Co(II), Ni(II) and Cu(II) found to be around 5.0, 3.2 and 1.8 B.M. respectively indicating octahedral configuration of the complexes which is further supported by their electronic spectral data (Cotton & Wilkinson, 1985).

The ESR spectra of the complexes $[Cu_4LCl_2(H_2O)_{14}]$ and $[Cu_4\ L^/Cl_4(H_2O)_{12}]$ have been recorded at X-bond at room temperature. The g_{av} values of the complexes are found to be 2.10609 and 2.06375 respectively by applying Kneubuhl's method (1960). This type of spectrum might be due to dynamic or pseudo rotational type of Jahn – Teller distortion. The spin orbit coupling constant of the copper complex can be determined by using the relation g_{av}=2(1-2ג/10Dq). The values of ג for the complexes are -364.55cm^{-1} and -219.14cm.$^{-1}$ The lowering of ג values of the complexes from the free ion value (-830 cm^{-1}) indicates overlapping of metal ligand orbitals.

In the electronic spectra of Ni(II) complexes (Table 2), four ligand field bands are observed at 10400(10410), 17150(17180), 25300(25370) and 31310(32130) cm^{-1} respectively assignable to $^3A_{2g}(F) \rightarrow {^3T_{2g}}(F)\ (\nu_1), \rightarrow {^3T_{1g}}(F)(\ \nu_2), \rightarrow {^3T_{1g}}(P)\ (\nu_3)$ and CT transitions respectively in an octahedral geometry. The ligand field parameters like Dq = 1015 (1012) cm^{-1}, B=780 (754) cm^{-1}, β_{35} = 0.749(0.724) cm^{-1},ν_2/ν_1=1.64(1.65) and σ=33.5(27.6) confirm the octahedral configuration for the complexes (Lever, 1968). In the electronic spectra of Co" complexes four bands appear at 8140(8202), 16500(16540), 19745(19925) and 32440(32390) cm^{-1}. The first three bands can be assigned to $^4T_{1g}(F) \rightarrow {^4T_{2g}}(F)(\nu_1), \rightarrow {^4T_{1g}}(F)(\ \nu_2), \rightarrow {^4T_{1g}}(P)(\ \nu_3)$ transitions respectively and the fourth band is assigned to a CT band. The ligand field parameters like D_q = 836 (833.8) cm^{-1}, B=788.3 (790.6) cm^{-1}, β_{35}=0.811(0.814) cm^{-1}, ν_2/ν_1 = 2.02 (2.01) and σ=23.3(22.8) suggest an octahedral geometry for the complexes (Devoto et al., 1957). The electronic spectra of Cu(II) complexes exhibit one broad band at ~ 13340 – 14510 cm^{-1} with maxima at ~13750 cm^{-1} assignable to $^2E_g \rightarrow {}^2T_{2g}$ transition in support of a distorted octahedral configuration for the complexes (Yamada, 1966).

The ^1H NMR spectra of the ligands LH_6 and $L^/ H_4$ were recorded in DMSO. The sharp peaks observed at δ7.152-7.63 ppm (LH_6) and δ7.354-7.632 ppm ($L^/ H_4$) correspond to 08 protons in each ligand. The peak observed at δ3.65 ppm ($L^/ H_4$) can be assigned to six methyl protons. The sharp peak observed at δ10.473 ppm (LH_6) and δ12.621 ppm ($L^/H_4$) corresponds to 04 phenolic protons in each ligand (Williams & Fleming, 1994). In case of Zn(II) complex with LH_6, there is no peak at δ10.473 ppm indicating deprotonation of phenolic proton and formation of a bond between the Zn(II) ion with oxygen atom of the phenolic group.

The XRD study (powder pattern) of the complex $[Co_4LCl_2(H_2O)_{14}]$ was 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 (Visser, 1969). 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 Table 3. The indexing is confirmed by comparing between observed and calculated 2θ values which are evident from the figure of merit (6.4) as suggested by De Wolff (1969). 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 is the 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 crystal system of the complex is found to be monoclinic. The mean particle size of the same complex can be measured from the Debye-Scherer relation (Patterson, 1939), $D=k\Upsilon/\beta\cos\theta$, where D stands for the particle size, k is a dimensionless shape factor, Υ is a X-ray wavelength, β is a line broadening at half the maximum intensity, θ is a 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 0.67 nm.

The thermal decomposition behavior of the complex $[Co_4LCl_2(H_2O)_{14}]$ was studied by using TG, and DSC techniques in an atmosphere of nitrogen at a heating rate of 10°C per minute and the mass loss of the complex was recorded from ambient temperature to 1400°C. The complex compound starts losing its mass gradually with the rise of temperature and shows a loss of 29.9% of mass up to 300°C which corresponds to loss of coordinated H_2O molecules. The compound suffers a mass loss of 20.51% from 300°C to 600°C indicating loss of 1/5th of the ligand and two chlorine atoms. There after the complex moiety loses of 25.81% in the temperature range of

Table 2. IR Data of the ligands and complexes (ν cm^{-1})

Compound	ν (C-O)	ν(N=N)	ν(COO$^-$)	ν(COO)$_{sys}$	ν(C=O)	ν(M-O)	ν(M-N)
LH_6	1500	1555	1610	1380	-	-	-
$L^{/}H_4$	1506	1597	-	-	1622	-	-
$[Co_4LCl_2(H_2O)_{14}]$	1486	1550	1599	1373	-	527	462
$[Co_4L^{/}Cl_4(H_2O)_{12}]$	1492	1593	-	-	1565	528	505
$[Ni_4LCl_2(H_2O)_{14}]$	1484	1549	1597	1372	-	529	463
$[Ni_4L^{/}Cl_4(H_2O)_{12}]$	1490	1592	-	-	1564	527	504
$[Cu_4LCl_2(H_2O)_{14}]$	1482	1551	1598	1374	-	530	464
$[Cu_4L^{/}Cl_4(H_2O)_{12}]$	1491	1591	-	-	1566	529	504
$[Zn_4LCl_2(H2O)_6]$	1485	1550	1599	1372	-	532	464
$[Zn_4L^{/}Cl_4(H2O)_4]$	1492	1592	-	-	1565	528	503
$[Cd_4LCl_2(H2O)_6]$	1484	1548	1598	1371	-	528	462
$[Cd_4L^{/}Cl_4(H2O)_4]$	1490	1593	-	-	1564	529	504
$[Hg_4LCl_2(H2O)_6]$	1486	1548	1599	1371	-	530	463
$[Hg_4L^{/}Cl_4(H2O)_4]$	1491	1592	-	-	1565	528	505

Table 3. XRD data of the complex $[Co_4l\ Cl_2\ (H_2O)_{14}]$

Observed 2θ	Calculated 2θ	D spacing	h k l	Difference in 2θ
10.22	10.22	8.645	1 0 0	.00
15.93	15.91	5.576	0 2 0	.02
22.85	22.84	3.890	2 1 -1	.01
26.88	26.86	3.316	2 1 1	.02
32.29	32.33	2.767	2 3-1	.04
35.94	35.94	2.497	0 1 3	.01
39.49	39.54	2.280	1 1 3	.01
46.67	46.66\	1.945	4 2 -2	.01
46.86	46.85	1.863	4 2 1	.01
50.58	50.57	1.803	0 6 1	.01
53.98	53.99	1.697	2 3 -4	.01
56.21	56.21	1.635	2 0 4	.000
57.28	57.26	1.608	2 6 -2	.02
58.62	58.64	1.573	4 3 2	.02
59.16	59.18	1.560	3 6 0	.02
65.71	65.69	1.420	0 3 5	.02

a=8.836 Å α=90° n=1 Bravais lattice= p
b=11.31 Å β=101.91° d=2.52gm.cm^{-3} Figure of merit=6.4
c=7.856 Å γ=90° volume=756.01 Crystal system=monoclinic

600-900°C corresponding to loss of nearly ½ of the ligand moiety. Again the complex moiety suffers a mass loss of 37.79% in the temperature range of 900-1400 °C indicating loss of rest of ligand molecules with the formation of CoO as the residue. The kinetic parameters like of the reaction, activation energy for the decomposition reaction of the complex can be calculated by Freeman-Carroll method (1958). The equation used for this purpose is $-dw/dt=R_T=Z/R_H\, e^{-Ea/RT}w^n$, 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 $\Delta \log R_T=n\Delta \log w-Ea/2.303R\Delta(1/T)$. When $\Delta(1/T)$ is kept constant, a plot of $\Delta \log R_T$ verses $\Delta \log w$ gives 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 1.5 and 7.36 J/mole respectively. The calculated values of the activation energy are found to be low due to autocatalytic effect of the metal ion on the thermal decomposition of the complex. The correlation(r) of the thermal decomposition is 0.94 which fits well with the experimental results.

Molecular modeling of the ligand and the complex has been carried out using molecular mechanics and Hartree –Fock (HF) quantum mechanics. The standard 6-31G basis set was used in conjugation with H-F method. All calculations are made using Gaussian 98 programme (Rappe & Goddard, 1991; Rappe et al., 1993).

The ligand LH_6 (Fig 5) and its Co(II) complex (Fig 6) are built and their geometries are optimized at MM/H-F/6-31G level of theory. Findings of these computed works are in good agreement with the experimental results. In the metal complex, the metal may be coordinated to either N(1) or N(2) of the azo group. When it is coordinated to N (1), it forms a six member ring and it forms a five member ring when coordinated to (N2). In the case of Co(II) complex with LH_6 the total energy is found to be183.744 KcalMole^{-1} when it forms five member ring and when it forms six member ring, the total energy is194.426 KcalMole^{-1} which clearly proves that the metal atom is bonded to N(2) of the azo group. The formation of a five member ring in place of a six member ring is preferred because it posses less energy and it might be correct from the stereo chemical view point

The antibacterial activities of the compounds are examined against two bacteria, *E. coli, S. aureus*. The effectiveness of the compound can be predicted by knowing the zone of inhibition value in mm. It is observed that both the ligands and their complexes posses remarkable biological activities against both the bacteria. Co(II), Ni(II), Cu(II) and Zn(II) are more active than the ligands. The enhanced activity is due to complexation and it can be explained on the basis of chelation theory.

The Zn(II), Cd(II) and Hg(II) complexes have tetrahedral geometry based upon analytical conductance and IR spectral data. Both the azodyes behave as bis-tetradentate (octadentate) ligands forming tetrameric complexes.

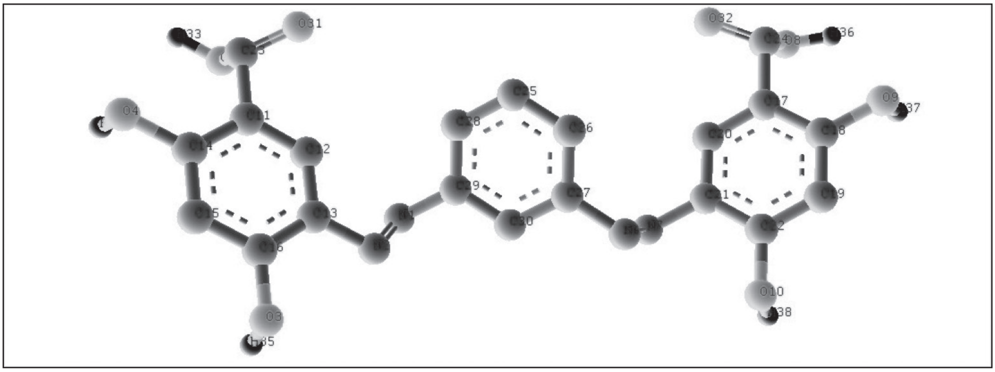

Fig. 5. Optimized geometry of the ligand LH_6

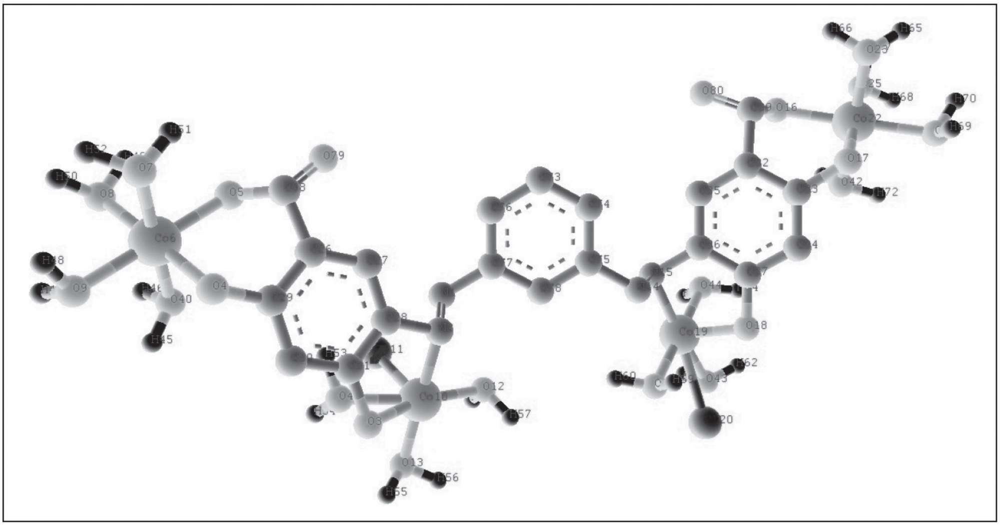

Fig. 6. Optimized of the Co(II) complex with the ligand LH_6

Conclusion

An octahedral geometry for Co(II) and Ni(II),a distorted octahedral geometry for Cu(II) complex and a tetrahedral geometry for Zn(II), Cd(II) and Hg(II) complexes are proposed on the basis of physicochemical and spectral data. The ligand LH_6 behaves as hexabasic octadentate and the ligand $L^/H_4$ behaves as tetrabasic octadentate coordinating through carboxyl/phenolic oxygen, azo nitrogen and carbonyl oxygen atoms. All the complexes are found to be thermally stable. A monoclinic crystal system is suggested from the study of XRD powder pattern for the Co (II) complex. All the calculations based on molecular mechanics on the optimized geometries of the ligand LH_6 and its Co(II) complex agree with the experimental results. Both the ligands and complexes are pharmacologically active and the complexes have more antibacterial power than the free ligands.

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