ORIGINAL ARTICLE

Synthesis, characterisation, XRD, molecular modelling and potential antibacterial studies of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with bidentate azodye ligand

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Abstract   Six monomeric complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with one O N donor bidentate azodye ligand, 3 – (p-tolylazo) – 4 – hydroxyl – 5 – methoxybenzaldehyde (LH) (TAHMB) have been prepared. The complexes have been characterised by analytical, conductance, magnetic susceptibility, IR, electronic spectra, ESR, NMR, X-ray diffraction (Powder pattern) spectra and molecular modelling studies. The Co (II) and Ni (II) complexes are found to be octahedral, Cu(II) complex is distorted octahedral and a tetrahedral stereochemistry has been assigned to Zn(II), Cd(II) and Hg(II) complexes. The energy optimised structures Figs. 3–5 are proposed using the semi empirical ZINDO/1 quantum mechanical calculations. The Ni(II) complex is found to possess an orthorhombic crystal system. The potential antibacterial studies of the ligand and some metal complexes with gram positive and gram negative bacteria have given encouraging results.

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1. Introduction

Synthetic vanillin is used as a flavouring agent in chocolate, icecream, confection, baked goods, beverages and pharmaceu-

ticals (Nicholas et al., 2003). It also contribute to the flavour and aroma of coffee (Semmelroch et al., 1995; Imre et al., 1992), maple syrup (Kermasha et al., 1995) and whole grain products including corn tortillas (Buttery et al., 1995) and oatmeal (Guth and Grosch, 1995). Keeping in view the chemotherapeutic value of vanillin a number of schiff base ligands and their complexes have been reported and their antibacterial activity has been studied (Maurya and Patel, 1999). Azodyes are found to be effective chemotherapeutic agents (Goodman and Gilman, 1970) to be widely used for the cure of bacterial infection. In continuation of our earlier work (Mahapatra and Patel, 2009; Mahapatra and Sarangi, 2011), in the present paper, we have reported the synthesis of one O N donor

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bidentate azodye containing vanillin and its six metal complexes and have studied the antibacterial properties with gram positive and gram negative bacteria besides their structural elucidation by various physical, chemical, spectral and molecular modelling techniques. (See Fig. 1).

2. Experimental

2.1. Materials

The chemicals p-toluidine and 4-hydroxy-5-methoxybenzaldehyde were of E. Merck grade. The chlorides of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) were of S.R.L. grade. All other reagents and solvents were purchased from commercial sources and were of analytical grade.

2.2. Synthesis of the azodye ligand

The bidentate azodye was prepared by the coupling reaction of the diazonium chloride obtained from p-toluidine (0.01 mol, 2.0 g.) with an alkaline solution of 4-hydroxy-5-methoxybenzaldehyde (Vanillin) respectively at 0–5 °C.

2.3. Synthesis of metal complexes

The metal chlorides in ethanol were mixed separately with ethanolic solution of the ligand in 1:2 M ratio and the resulting solutions were heated to 60–70 °C for about one 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 separated were then washed with ethanol followed by ether and dried in vacuum (Fig. 2).

2.4. Physical measurements

The elemental analysis (C, H, N) were carried out on elemental analyser Perkin-Elmer 2400 while metals were determined by
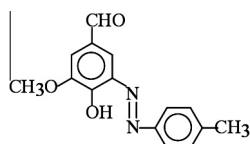

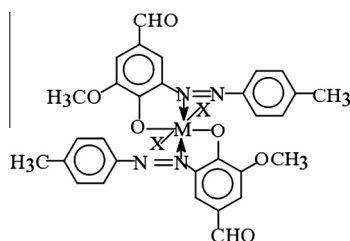**Figure 1** One novel bidentate oxygen–nitrogen donor azodye ligand made in this study (LH).

Figure 2 Proposed geometry of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes where, $M = Co^{II}$, Ni^{II} and Cu^{II}, $X = H_2O$, $M = Zn^{II}$, Cd^{II} and Hg^{II}, $X = $ Nil.

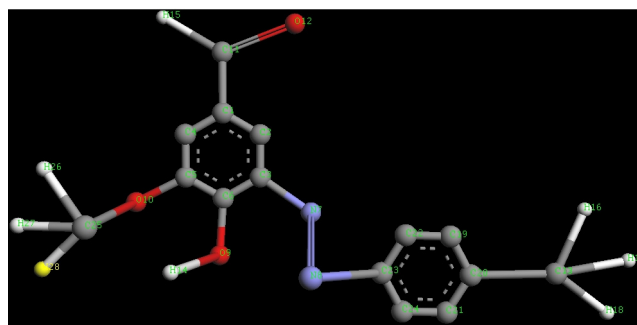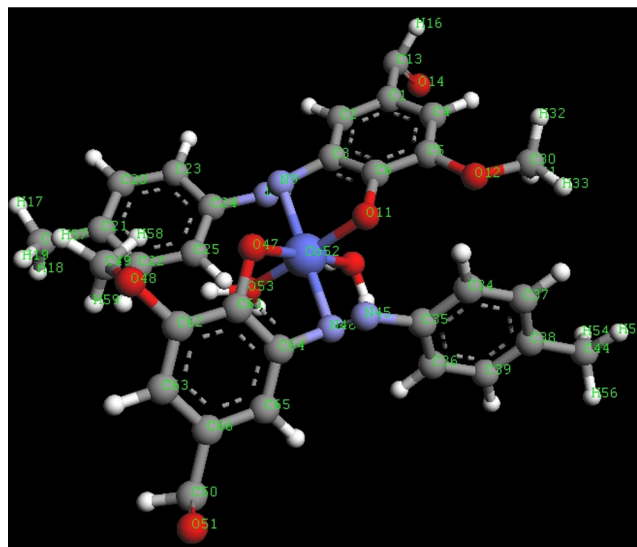**Figure 3** Optimised geometry of ligand (LH).

Figure 4 Optimised geometry of $[CoL_2 (H_2O)_2]$ complex.

EDTA after decomposing the complexes with conc. HNO_3. Conductance measurements of the complexes were made using Toshniwal CL 01–06 Conductivity Bridge. The magnetic susceptibility was made at RT by Gouy method using Hg $[Co(CN)_4]$ as calibrant. IR Spectra (KBr pellet) were recorded using IFS 66U spectrophotometer, electronic spectra of the Co^{II}, Ni^{II} and Cu^{II} complexes in DMF were recorded on a Hilger–Watt uvispeck spectrophotometer, ESR spectra of Cu^{II} complex was recorded on a E_4-spectrometer and NMR spectra on a Jeol GSX 400 with d6-DMSO as solvent and TMS as internal standard. X-ray diffraction (powder pattern) of the Ni^{II} complex was recorded on a Phillips PW 1130/00 diffractometer.

2.5. Molecular modelling

In addition to the experimental works, the computational work like Molecular modelling of the ligand and complexes has been carried out using molecular mechanics and Hartree–Fock (HF) Quantum methods to ascertain some of the physical parameters of the new compounds. All semi empirical calculations were made using UFF of Gaussain 98 Programme Package of Argus Lab 4.0.1 with 10^{-10} kcl/mol convergence RHF (closed shell) (Thompson and Zerner, 1991; Rappe' et al., 1993; Rappe and Goddard, 1991; Casewit et al., 1992).
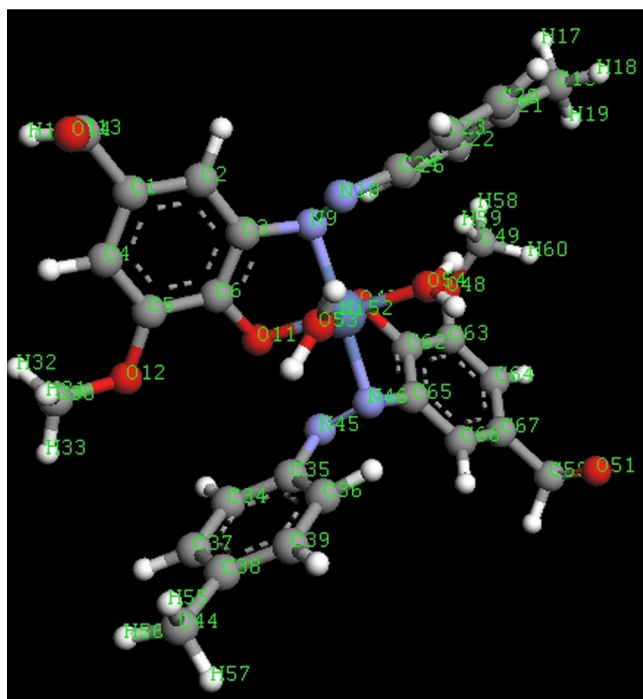
Figure 5 Optimised geometry of [NiL$_2$ (H$_2$O)$_2$] complex.

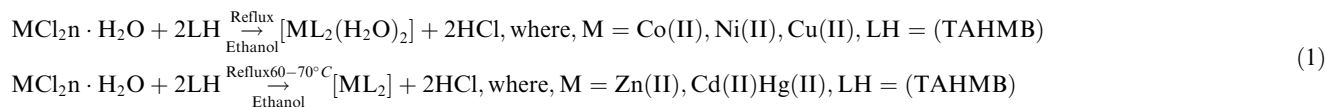**Table 2** Infrared spectra of the ligand and the complexes in cm^{-1}.

Compounds	ν (C–O)	ν (N=N)	ν (M–O)	ν (M–N)
LH	1501	1595	–	–
[CoL$_2$(H$_2$O)$_2$]	1483	1546	515	489
[NiL$_2$(H$_2$O)$_2$]	1482	1545	512	485
[CuL$_2$(H$_2$O)$_2$]	1485	1547	514	487
[ZnL$_2$]	1482	1545	515	489
[CdL$_2$]	1482	1546	513	486
[HgL$_2$]	1485	1545	515	489

ulating 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 h. 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 standard drug Tetracycline. The results are the mean value of zone of inhibition of three sets measured in millimetre.

3. Results and discussion

The metal complexes were prepared according to the following reaction scheme:

$$MCl_2 n \cdot H_2O + 2LH \xrightarrow[Ethanol]{Reflux} [ML_2(H_2O)_2] + 2HCl, \text{where, } M = Co(II), Ni(II), Cu(II), LH = (TAHMB)$$

$$MCl_2 n \cdot H_2O + 2LH \xrightarrow[Ethanol]{Reflux 60-70°C} [ML_2] + 2HCl, \text{where, } M = Zn(II), Cd(II) Hg(II), LH = (TAHMB)$$

(1)

2.6. Antibacterial activity

The antibacterial activity of the azodye ligand and Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes was studied as per the cup-plate method (Brandt Rose and Miller, 1939) using three strains of bacteria like *Staphylococcus aureus*, *Proteus vulgaris* and *Escherichia coli*. The solutions of the test compounds are prepared in dimethylsulphoxide (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 h. The density of the bacterial suspension is standardised by McFarland method. A well of uniform diameter (6 mm) is made on agar plates, after inoc-

The elemental analysis data agree well with the following composition of the metal complexes reported (Table 1), [ML$_2$(H$_2$O)$_2$], [M′ L$_2$] where M = Co^{II}, Ni^{II}, Cu^{II}; $M′$ = Zn^{II}, Cd^{II}, Hg^{II}; LH = 3 – (p-tolylazo) – 4 – hydroxyl – 5 – methoxy benzaldehyde , C$_{15}$H$_{14}$N$_2$O$_3$ (Calcd. (%) C, 66.66; H, 5.22; N, 10.36; Found (%) C, 58.3; H, 3.3; N, 10.3). All the complexes are amorphous in nature and have high melting points. The complexes are insoluble in common organic solvents like methanol, ethanol and benzene but soluble in dimethylformamide and dimethylsulphoxide. The complexes are non-electrolytic in nature as evident from the low conductance values (3.8–5.5 Ω^{-1} cm^2 mol^{-1}) in DMF.

Table 1 Analytical and physical data of the ligand and its complexes.

Sl. No.	Compounds	Melting point (°C)	Colour	% Metal found (calculated)	% Nitrogen found (calculated)	μeff B.M.
1	LH	65	Yellowish Brown	–	10.16 (10.36)	–
2	[CoL$_2$(H$_2$O)$_2$]	> 230	Grey	9.25 (9.30)	8.64 (8.84)	5.1
3	[NiL$_2$(H$_2$O)$_2$]	> 230	Red	9.07 (9.27)	8.65 (8.85)	3.1
4	[CuL$_2$(H$_2$O)$_2$]	> 230	Brown	9.76 (9.96)	8.58 (8.78)	1.8
5	[ZnL$_2$]	> 230	Brown	10.69 (10.79)	9.10 (9.25)	–
6	[CdL$_2$]	> 230	Brown	17.01 (17.21)	8.35 (8.58)	–
7	[HgL$_2$]	> 230	Brown	26.95 (27.06)	7.15 (7.56)	–

LH$_2$ = 3- (p-tolylazo) -4- hydroxyl-5- methoxy-benzaldehyde.

3.1. IR spectra

The IR spectrum of the azodye ligand (Table 2), shows a broad band at 3434 cm^{-1} which may be assigned to a stretching vibration of the phenolic hydroxyl group (Mishra and Keshari, 1981). The broadness of this band may be attributed to O–H...N intramolecular hydrogen bonding. The bands at 1501 cm^{-1} in the ligand may be assigned to phenolic C–O vibration and in the metal complexes this band is observed at $\sim1483 \text{ cm}^{-1}$ indicating bonding of the phenolic oxygen atoms to the metal atoms. The sharp band for the ligand appears at 1595 cm^{-1} can be attributed to $\nu_{(-N=N-)}$ vibration and in the metal complexes this band appears at $\sim1546 \text{ cm}^{-1}$, which indicates the coordination of one of the azo nitrogen atoms to the metal ions (King and Bisnette, 1966). In the Co^{II}, Ni^{II} and Cu^{II} complexes broad bands appear at ~2920–3549 cm^{-1} followed by a sharp peaks at $\sim820 \text{ cm}^{-1}$ and at $\sim725 \text{ cm}^{-1}$ assignable to –OH stretching, rocking and wagging vibrations respectively indicating the presence of co-ordinated water molecules in the complexes (Nakamoto, 1978). The bonding of the ligand to the metal ions is confirmed by the appearance of bands at $\sim515 \text{ cm}^{-1}$ ν (M–O) and $\sim489 \text{ cm}^{-1}$ ν (M–N) (Ferraro, 1971).

3.2. Electronic spectra and magnetic measurements

In the electronic spectrum of Co^{II} complex, four ligand field bands are observed at 8100, 16325, 20275 and 32210 cm^{-1}. The first three bands can be attributed to $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)(\nu_1) \rightarrow ^4A_{2g}(F)(\nu_2)$ and $^4T_{1g}(P)(\nu_3)$ transitions respectively and the fourth band is assigned to a CT band. The ligand field parameters like $D_q = 822.5 \text{ cm}^{-1}$, $B = 821.3 \text{ cm}^{-1}$, $\beta_{35} = 0.845 \text{ cm}^{-1}$, $\nu_2/\nu_1 = 2.015$ and $\sigma = 18.34 \%$ suggest an octahedral stereochemistry for the Co^{II} complexes (Lever, 1968; Magee & Gordan, 1963). In the electronic spectrum of Ni^{II} complex, four ligand field bands are observed at 10200, 17620, 25150 and 32575 cm^{-1} 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 transition respectively in an octahedral geometry. The ligand field parameters like $D_q = 1020 \text{ cm}^{-1}$, $B = 808 \text{ cm}^{-1}$, $\beta_{35} = 0.766 \text{ cm}^{-1}$, $\nu_2/\nu_1 = 1.727$ and $\sigma = 28.86\%$ also confirm an octahedral symmetry for the complex. The electronic spectrum of the copper (II) complex exhibits one broad band at 13300–14470 cm^{-1} with maxima at 13550 cm^{-1} assignable to $^2Eg \rightarrow ^2T_{2g}$ transition in support of an distorted-octahedral configuration of the copper (II) complex. (Yamada, 1966; Proctor et al., 1968). The observed magnetic moment values of the Co^{II}, Ni^{II} and Cu^{II} complexes are found to be 5.1, 3.1 and 1.8 B.M. respectively indicating

Table 3a Selected bond lengths and bond energies of the ligand (LH).

Bond length in (Å)	Bond energy in kcal/mol
C_1–C_2 (1.379)	462.660
C_6–O_{11} (1.407)	523.501
C_{24}–N_{10} (1.434)	546.821
O_{12}–C_{30} (1.458)	470.728
N_9–N_{10} (1.270)	1047.330
C_5–O_{12} (1.429)	499.417
C_{13}–O_{14} (1.305)	656.228
C_{13}–H_{16} (1.112)	328.226
C_{38}–C_{44} (1.486)	369.948
O_{69}–H_{72} (1.033)	492.252

Table 3b Selected bond angles and bond energies of the ligand (LH).

Bond angle in (Å)	Bond energy in kcal/mol
C_5–C_6–C_3 (120.00)	222.595
C_5–C_6–O_{11} (120.00)	259.618
C_6–C_3–N_9 (120.00)	278.835
C_5–O_{12}–C_{30} (110.00)	243.556
C_3–N_9–N_{10} (106.70)	425.168
N_9–N_{10}–C_{24} (106.70)	425.168
C_2–C_1–C_{13} (120.00)	198.274
C_6–C_5–O_{12} (120.00)	253.419
C_1–C_{13}–O_{14} (109.47)	326.309
C_{62}–O_{48}–C_{49} (104.51)	293.439
O_{14}–C_{13}–H_{16} (109.47)	186.180
O_{12}–C_{30}–H_{31} (109.47)	186.180
C_{24}–C_{15}–H_{17} (109.47)	151.529
C_{24}–C_{25}–H_{29} (120.00)	114.188
C_1–C_{13}–H_{16} (109.47)	121.420
H_{64}–C_{53}–H_{66} (109.47)	74.849

Table 3c Selected bond lengths and bond energies of the $[NiL_2(H_2O)_2]$ complex.

Bond length in (Å)	Bond energy in kcal/mol
O_{11}–Ni_{52} (1.871)	283.008
Ni_{55}–O_{56} (1.846)	294.600
O_{56}–H_{76} (1.009)	528.473
Ni_{55}–N_{48} (1.885)	306.275

Table 3d Selected bond angles and bond energies of the $[NiL_2(H_2O)_2]$ complex.

Bond angle in (Å)	Bond energy in kcal/mol
N_9–N_{10}–Ni_{52} (106.70)	317.313
Ni_{52}–N_9–C_3 (106.70)	213.193
Ni_{52}–O_{11}–C_6 (104.51)	232.748
Ni_{52}–N_{46}–N_{45} (106.700)	317.313
O_{11}–Ni_{52}–O_{53} (90.00)	289.809
O_{11}–Ni_{52}–O_{47} (90.00)	284.114
N_{46}–Ni_{52}–O_{11} (90.00)	310.824
N_{46}–Ni_{52}–O_{53} (90.00)	316.977
N_9–Ni_{52}–N_{46} (90.00)	340.090
Ni_9–O_{52}–H_{46} (120.00)	84.865
H_{76}–O_{56}–H_{77} (120.00)	78.709

Table 3e Selected bond lengths and bond energies of the $[CoL_2(H_2O)_2]$ complex.

Bond length in (Å)	Bond energy in kcal/mol
O_{11}–Co_{52} (1.964)	244.913
Co_{52}–N_9 (1.972)	267.453
Co_{52}–O_{53} (1.939)	254.562

Table 3f Selected bond angles and bond energies of the $[CoL_2(H_2O)_2]$ complex.

Bond angle in (Å)	Bond energy in kcal/mol
Co_{52}–N_{10}–N_9 (106.700)	287.154
Co_{52}–N_9–C_3 (106.700)	194.648
Co_{52}–O_{11}–C_6 (104.510)	210.763
O_{11}–Co_{52}–N_9 (90.00)	270.214
O_{69}–Co_{52}–O_{47} (90.00)	245.869
O_{53}–Co_{52}–O_{47} (90.00)	250.614
N_{46}–Co_{52}–N_9 (90.00)	296.982
N_{46}–Co_{52}–O_{11} (90.00)	270.214
N_9–Co_{52}–O_{53} (90.00)	275.391
Co_{52}–O_{53}–H_{71} (120.00)	75.822

octahedral configuration around the metal ions (Cotton and Wilkinson, 1988). The analytical and physical data of the azodye and the complexes are given in (Table 1).

3.3. ^{1}H-NMR studies

The ^{1}H NMR spectrum of the ligand was recorded in DMSO. The complex multiplet observed at δ 7.381–7.987 ppm corresponds to six phenyl protons. The sharp peak observed at δ 3.346 ppm corresponds to three methyl (–CH$_3$) protons (Cotton and Wilkinson, 1988). The sharp peak appeared at δ 3.950 corresponds to three methoxy (–OCH$_3$) protons. The sharp peak observed at δ 9.912 ppm corresponds to one aldehydic (–CHO) proton (Graph 1).

3.4. ESR studies

The E.S.R. spectrum of the Cu^{II} Complex No.4 $[CuL_2(H_2O)_2]$ has been recorded at X-band at RT. The 'g_{av}' value of the complex is found to be 2.078169 by applying Kneubuhl's method (Kneubuhl, 1960). This type of spectrum may be due to dynamic or pseudo rotational type of Jahn–Teller distortion (Graph 2). The spin–orbit coupling constant (λ) can be determined from the equation $g_{av} = 2(1–2\lambda/10D_q)$. The value of λ for the complex is found to be -264.767 cm^{-1}. The lowering of the λ value of the complex from the free ion value (-830 cm^{-1}) indicates the overlapping of metal–ligand orbitals.

3.5. Powder XRD studies

The XRD study (powder pattern) of the complex No.3 $[NiL_2(H_2O)_2]$ was made with the help of X-ray diffractometer with Cu as anode material, K – alpha [Å] = 1.54060 and the generator settings 30 mA, 40 kV. The lattice parameters were calculated with the help of a computer programme from LSUCRPC (Visser, 1969). Powder diffraction data 2θ values are shown in (Graph 3). The lattice parameters like a, b, c, α, β, γ and V (volume) are shown in (Table 4) along with miller indices $h\,k\,l$. 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 7.8 as suggested by Woulff (1968). The density (d) 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 and M = molecular weight of the complex. The value of 'n' is found to be 2.0 which agrees well with the suggested structure of the complex. The crystal system of the complex was found to be orthorhombic (Puri et al., 1993). The Scherrer equation in X-ray diffraction and crystallography is
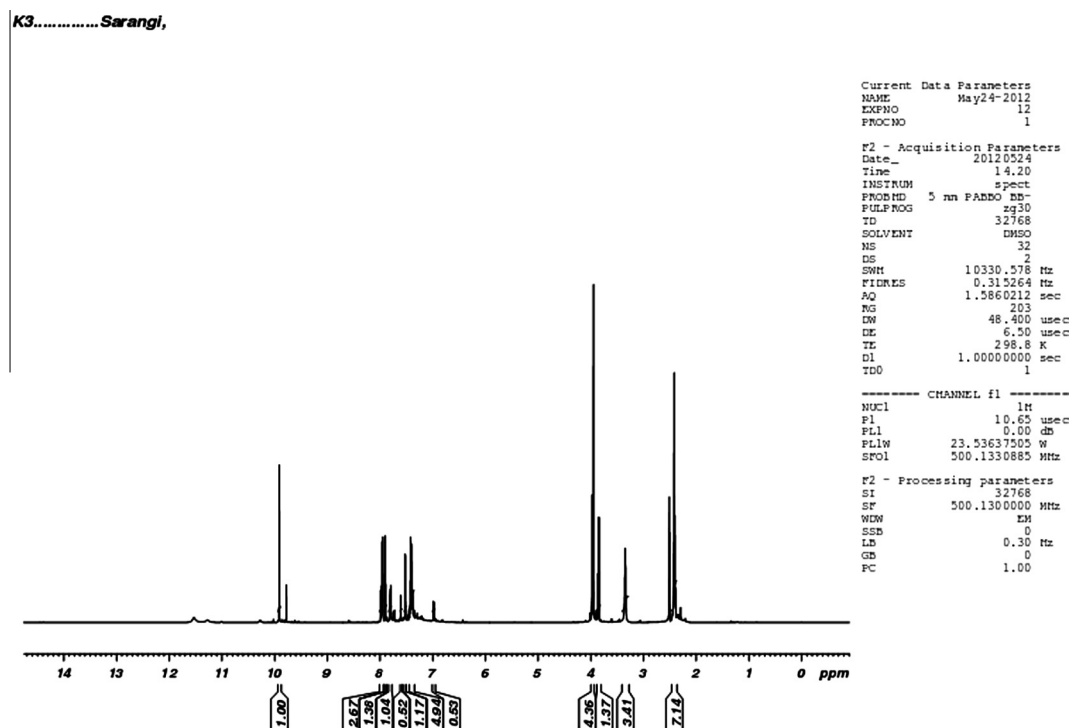
Graph 1 ^{1}H NMR spectra of LH.
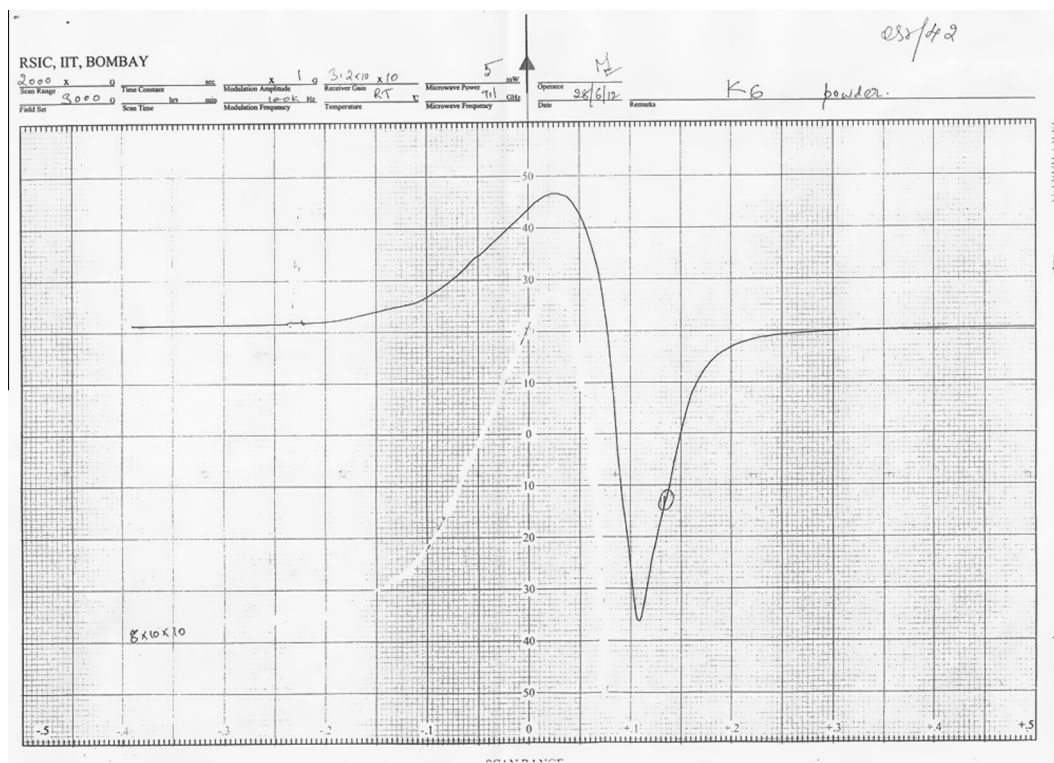
Graph 2   ESR spectra of the [CuL$_2$ (H$_2$O)$_2$] complex.
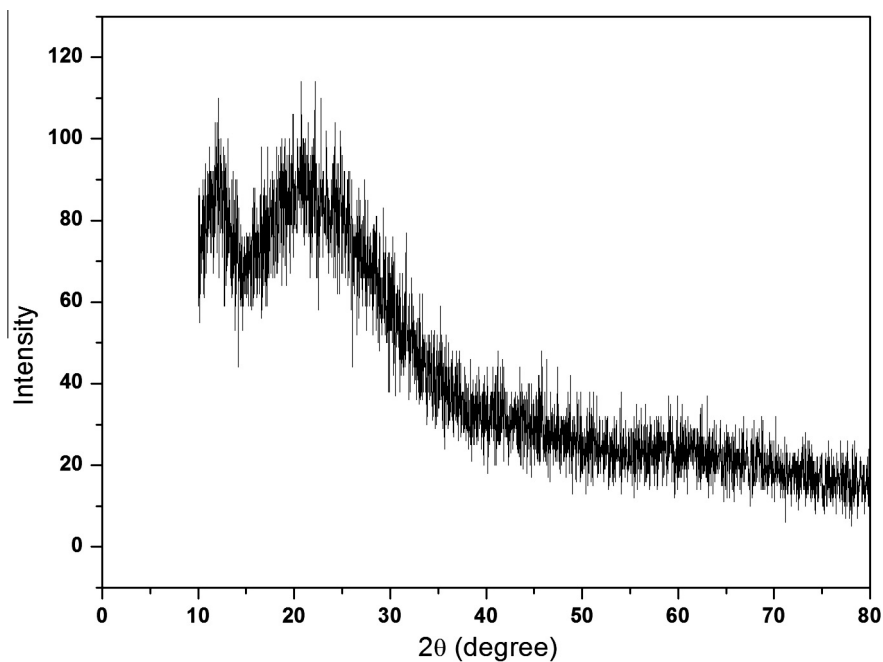
Graph 3   XRD graph for [NiL$_2$ (H$_2$O)$_2$] complex.

a formula which relates the size of the crystallites in a solid to the broadening of a peak in a diffraction pattern. The Debye–Scherrer equation is $B = k\lambda/s \cdot \cos\theta$; where s = Crystallite size, λ = wavelength of X-ray radiation (Cu Kα = 1.54060 Å),

k = constant taken as 0.94, θ = diffraction angle (21.3°), B = Full width at half maximum height (0.946 Å). The crystallite size of the complex No.3 [NiL$_2$ (H$_2$O)$_2$] is found to be (1.607 Å). (Patterson, 1939).

Table 4 X-ray diffraction data of the [NiL$_2$(H$_2$O)$_2$]complex.

Observed 2θ	Calculated 2θ	d spacing	h	k	L	Difference 2θ
11.77	11.72	7.545	1	0	1	0.05
11.93	11.90	7.433	1	1	−1	0.03
12.11	12.10	7.307	1	1	1	0.01
13.11	13.11	6.746	1	4	0	0.00
15.77	15.71	5.636	2	2	−1	0.06
16.91	16.84	5.260	1	4	1	0.07
18.17	18.12	4.892	0	6	0	0.05
19.07	19.01	4.665	1	5	−1	0.06
20.75	20.71	4.285	4	0	0	0.04
20.93	20.93	4.240	4	1	0	0.00
21.43	21.41	4.146	1	0	−2	0.02
22.17	22.14	4.012	3	4	−1	0.03
23.35	23.33	3.809	2	1	−2	0.02
24.81	24.80	3.588	1	8	0	0.01
25.79	25.76	3.456	2	7	−1	0.03
27.35	27.33	3.261	0	9	0	0.02
28.95	28.93	3.084	5	2	1	0.02
29.93	29.92	2.984	0	7	2	0.01

$a = 13.215$ Å $\alpha = 90°$, Volume (V) = 2671.48 Å^3, Figure of merit = 7.8.
$b = 18.973$ Å $\beta = 90°$, Density (d) = 0.789 g cm^{-3}, Bravais lattice = p.
$c = 10.655$ Å $\gamma = 90°$, Number of unit Cell (n) = 2.
Probable Crystal system = Orthorhombic.

3.6. Optimised geometry studies of the ligand and complexes by molecular modelling method

Molecular modelling of the ligand (LH) and metal complexes of Co(II) and Ni(II) have been carried out using molecular mechanics and Hartree–Fock (HF) Quantum methods. The Universal Force Field (UFF) is used for molecular mechanics calculation with Minimum RMS Gradient: 0.100 in Argus Lab Programme. The ligand was built and optimised. The following physical parameters are obtained.

Boiling point: 912 K, Critical temperature: 877.15 K, Critical pressure: 22.74 Bar, Log P: 4.19, Molar refractivity: 79.24 cm^3/mol, Heat of formation: −262.17 kJ/mol, C log P: 3.89177, CMR: 7.9491, Electronic energy: −21381.1 eV, HOMO energy: −8.86413 eV, LUMO energy: −1.34387 eV, Repulsion energy: 17897.4 eV, Total energy: −3483.78 eV.

The metal complexes were built and optimisation of their geometries was done at mm/H-F/6–31 g level of theory Figs 3–5. Findings of these computed works are in good agreement with the experimental results. The selected bond lengths, bond angles of the ligand, bond angles of the complexes and their bond energies are given in Tables 3a–3f respectively. In the Co(II) and Ni(II) complexes, the metal ion may be bonded to eit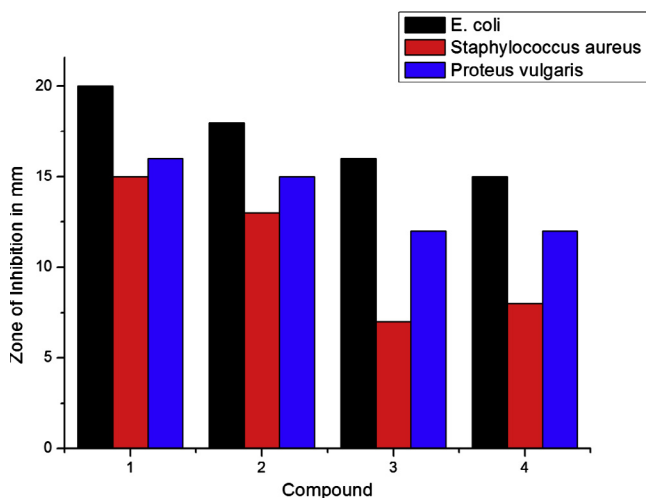her N(9) and N(46) or N(10) and N(45) nitrogen atoms of the azo group. When the metal ions coordinate with N (9) and N(46) of the azo group, they form a five membered ring. But when metal ions coordinate with N(10) and N(45) of the azo group, they form a six membered ring. In case of Co(II) and Ni(II) complexes, the total energies are found to be 106.177 kcal/mol and 109.170 kcal/mol respectively, when they form a five membered ring. The total energies of both the complexes have increased to 151.485 kcal/mol and 121.113 kcal/mol respectively, when they formed a six membered ring. From this energy difference it is concluded that both the metal atoms form a five membered ring with one of the azo nitrogen atoms.

3.7. Antibacterial activity

The ligand and metal complexes have been screened for antibacterial activities and results have been shown in (Table 5). The antibacterial activity of the compounds No.1–5 is examined against three strains of bacteria, one gram positive *S. aureus*, and two gram negative *P. vulgaris* and *E. coli*. The effectiveness of the compounds is classified into three categories, Sensitive, Intermediate and Resistant. If a compound is sensitive to a bacteria then it can be applied to cure the disease caused by the bacteria, while it fails to do so if it is resistant to the bacteria. Accordingly the effectiveness of the compound

Table 5 Antibacterial activities of the ligands and the complexes (Data presented as diameter of zone of inhibition, mm).

Sl. No.	Compound	Concentration	E. coli (MTCC-40)	Staphylococcus aureus (MTCC-87)	Proteus vulgaris (ATCC-29905)
1	LH	500 µg/ml	20	15	16
2	[CoL$_2$(H$_2$O)$_2$]	500 µg/ml	18	13	15
3	[NiL$_2$(H$_2$O)$_2$]	500 µg/ml	16	7	12
4	[CuL$_2$(H$_2$O)$_2$]	500 µg/ml	15	8	12
5	[ZnL$_2$]	500 µg/ml	15	9	17
6	Tetracycline	1 mg/ml	45	30	30

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

can be predicated by knowing the zone of inhibition value in mm. The results (Graph 4) show that the ligand was found to posses more antibacterial activity than the complexes against different bacteria.

The Zn^{II}, Cd^{II} and Hg^{II} complexes have tetrahedral geometry based upon analytical, conductance and IR spectral data.

4. Conclusion

The azodye behaves as an O N donor bidentate ligand and forms octahedral complexes with Co^{II} and Ni^{II} complexes, distorted-octahedral complex with Cu^{II} complex and tetrahedral complexes with Zn^{II}, Cd^{II} and Hg^{II} complexes. The Ni^{II} complex is found to possess an orthorhombic crystal system. All calculations based on molecular mechanics on the optimised geometries of the ligand and the complexes agree with the experimental results obtained from electronic spectral analysis and XRD study. The ligand as well as Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes are found to possess a strong antibacterial activity against both gram positive and gram negative bacteria and hence may be used as chemotherapeutics drugs for the cure of infectious diseases.

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References

Brandt Rose, S., Miller, E.R., 1939. Studies with the Agar cup-plate method: III. The influence of Agar on mercury antiseptics. J. Bacteriol. 38 (5), 525–537.

Buttery, Ron, G., Louisa, C., Ling, 1995. Volatile flavor components of corn tortillas and related products. J. Agric. Food Chem. 43 (7), 1878–1882.

Casewit, C.J., Colwell, K.S., Rappe, A.K., 1992. Application of a universal force field to main group compounds. J. Am. Chem. Soc. 114, 10046–10053.

Cotton, F.A., Wilkinson, P.G., 1988. Advanced Inorganic Chemistry, fifth ed. John Wiley & Sons.

Ferraro, J.R., 1971. Low Frequency vibration of inorganic and co-ordination compound. Plenum press, New York.

Goodman, L.S., Gilman, A., 1970. The Pharmacological Basis of Therapeutics, fourth ed. MacMillan, New York.

Guth, Helmut., Grosch, W., 1995. Odorants of extrusion products of oat meal: changes during storage. Zeitschrift für Lebensmittel-Untersuchung und -Forschung A 196 (1), 22–28.

Imre, B., Sen, A., Grosch, W., 1992. Potent odorants of the roasted powder and brew of Arabica coffee. Zeitschrift für Lebensmittel-Untersuchung und -Forschung A 195 (3), 239–245.

Kermasha, S., Goetghebeur, M., Dumont, J., 1995. Determination of phenolic compound profiles in maple products by high-performance liquid chromatography. J. Agric. Food Chem. 43 (3), 708–716.

King, R.B., Bisnette, M.B., 1966. Organonitrogen derivatives of metals carbonyls. II. Arylazo derivatives of molybdenum. Inorg. Chem. 5, 300–306.

Kneubuhl, F.K., 1960. Approximations in calculation of EPR parameters. J. Chem. Phys. 33, 1074–1078.

Lever, A.B.P., 1968. Inorganic Electronic Spectroscopy. Elsevier, Amsterdam, UK.

Magee, R., Gordan, L., 1963. The infrastructure of chelate compounds-III[1]: a study of some tervalent metal chelate compounds of 8-hydroxyquinoline in the region 5000–250 cm^{-1}. Talanta 10, 967–970.

Mahapatra, B.B., Patel, N., 2009. Polymetallic complexes Part LXXXXV bis-bidentate O N–N O donor azodye dimeric complexes. Bangladesh J. Sci. Ind. Res. 44 (4), 445–452.

Mahapatra, B.B., Sarangi, A.K., 2011. Polymetallic complexes Part LXXXXI dimeric and monomeric complexes of CoII, NiII, CuII, ZnII, CdII and HgII with N O–O N and N O donor bis-bidentate and bi-dentate azodye ligands. Bangladesh J. Sci. Ind. Res. 46 (2), 259–264.

Maurya, R.C., Patel, P., 1999. Synthesis, magnetic and special studies of some novel metal complexes of Cu(II), Ni(II), Co(II), Zn[II), Nd(III), Th(IV), and UO2(VI) with schiff bases derived from sulfa drugs, viz., sulfanilamide/sulfamerazine and o-vanillin. Spectrosc. Lett. 32 (2), 213–236.

Mishra, L.K., Keshari, B.N., 1981. Thiohydrazides as complexing agents: Part I- complexes of Ni(II), Co(II & III), Cu(II), Zn(II), Cd(II), Pd(II) & Hg(II) with o-hydroxyphenylthiohydrazide. Indian J. Chem. Sect-A 28, 883–887.

Nakamoto, K., 1978. Infrared and Raman spectra of inorganic and coordination compounds. John Wiley, NY, USA, p. 239.

Nicholas, J.W., Melinda, J., Mayer, M.J., Narbad, A., 2003. Vanillin. Pyhtochemistry 63 (5), 505–515.

Patterson, A., 1939. The Scherrer formula for X-ray particle size determination. Phys. Rev. 56 (10), 978–982.

Procter, I.M., Hathaway, B.J., Nicholls, P., 1968. The electronic properties and stereochemistry of the copper (II) ion. Part I. bis(ethylenediamine)copper(II)complexes. J. Chem. Soc. (A) 1 (1), 1678–1684.

Puri, B.R., Sharma, L.R., Kalia, K.C., 1993. Principle of Inorganic Chemistry. S. Lal Nagin Chand & Co, New Delhi.

Rappe III, A.K., Goddard, W.A., 1991. Charge equilibration for molecular dynamics simulations. J. Phy. Chem. 95, 3358–3363.

Rappe', A.K., Colwell, K.S., Casewit, C.J., 1993. Application of a universal force field to metal complexes. Inorg. Chem. 32, 3438–3450.

Semmelroch, P., Laskawy, G., Blank, I., Grosch, W., 1995. Determination of potent odourants in roasted coffee by stable isotope dilution assays. Flavour Fragrance J. 10 (1), 1–7.

Thompson, M.A., Zerner, M.C., 1991. A theoretical examination of the electronic structure and spectroscopy of the photosynthetic reaction center from Rhodopseudomonas viridis. J. Am. Chem. Soc 113, 8210–8215.

Visser, J.W., 1969. A fully automatic program for finding the unit cell from powder data. J. Appl. Crystal 2, 89–95.

de Woulff, P.M., 1968. A simplified criterion for the reliability of a powder pattern indexing. J. Appl. Crystal 1, 108–113.

Yamada, S., 1966. Recent aspects of the stereochemistry of schiff-base-metal complexes. Coordination Chem. Rev. 1, 415–418.