Synthesis, characterization and molecular modeling of Ni(II) & Cu(II) complexes with schiff base derived from *1H*-benzo[d]imidazole-4-amine and 2-hydroxy benzaldehyde

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ABSTRACT

The purpose of this work is synthesis of novel Schiff base ligand, 2-((1H-benzo[d]imidazol-4-ylimino)methyl)phenol and its metal complexes from 1H-benzo[d] imidazole-4-amine and 2-hydroxy benzaldehyde. Nickel and Copper being essential trace elements have given considerable attention for the synthesis of metal complexes. They have been characterized by elemental analysis and spectral techniques like IR, ^{1}HNMR and mass spectrometry. The spectral studies of the complexes reveal that the ligand has coordination through the O and N atoms of the ligand. Cell dimensions a(13.554540 Å), b(9.496137 Å), c(4.471746 Å), α(90.00^0), β(90.00^0) and γ(90.00^0) for Nickel complex and a(22.094890 Å), b(8.983012 Å), c(8.483077 Å), α(90.00^0), β(90.00^0) and γ(90.00^0) for Copper complex are in good agreement with Orthorhombic crystal systems for both. The molecular structure of the complexes has been optimized by MM2 calculation and suggested tetrahedral geometry with sp^3 hybridisation of copper and square planar geometry with dsp^2 hybridization of nickel complex respectively.

Keywords: Schiff base; Benzimidazole; Molecular modeling; MM2; Hybridization

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INTRODUCTION

Coordination chemistry of Schiff bases has attracting considerable attentions of researchers in the field of chemical science as well as in medical science for their immense biological activities and bears a curious history. Such ligands and their complexes due to their biological activities provide a better understanding of metal- protein binding. Thus Schiff bases containing these groups could act as a versatile model of metallic bio-sites. Transition metal complexes of Schiff bases concerning interaction of metal ions with nitrogen and oxygen organic moieties have been of great interest for many years since they are becoming an effective biochemical, analytical and antimicrobial reagents. Many reports have shown that some drugs have greater activity when administered as metal complex as that as free organic compounds [1-3]. Imidazole derivatives of Schiff bases have applications in the field of medical science due to having their high chemoptherapeutic properties [4]. Nitrogen atom of Imidazole moiety bears interesting physical and chemical properties that make different pharmacological activities of the compounds and its derivatives [5]. Literatures revealed that imidazole and its derivatives are reported to have, analgesic and anti-inflammatory activity, cardiovascular activity, anti-neoplastic activity, anti- fungal activity, enzyme inhibition activity, antianthelmintic activity, anti-filarial agent, anti- viral activity and anti- ulcer activity [6-8]. Aniline derivatives of Imidazole, also called benzimidazole are reported to have parasitic and antiviral activities [9], so the Schiff base Ni(II) and Cu(II) complexes of 1H-benzo[d]imidazole-4-amine and salicyldehyde, have been considered as a subject of great interest for the present study, with a hope for future drug with high efficacy. More literature survey regarding the benzimidazole derivatives focuses them as an important drug that selectively inhibits endothelial cell growth and suppresses angiogenesis in vitro and in vivo [10]. 2-hydroxy benzaldehyde is taken as a second organic component

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for the preparation of Schiff base that exhibit varieties of biological activities including antibacterial and antifungal. The aim of present work is to carry out the synthesis, characterization and molecular modeling of Ni(II) & Cu(II) complexes of Schiff bases derived from 1H-benzo[d]imidazole-4-amine and 2-hydroxy benzaldehyde. Nickel and copper have been distinguished as an essential trace element for the life and play a multifunctional role in association with organic molecules in the biological systems [11].

MATERIALS AND METHODS

All the chemicals and solvents used for the synthesis were of analytical grade and purchased from BDH and Merck chemical co. They were used without further purification. The infrared spectra of the ligand and metal complexes were run as KBr discs in the range 4000-400 cm^{-1} on a *Shimadzu* Infrared Spectrophotometer. Elemental analysis (C, H, N) were performed by using a Flash EA 1112 Series elemental analyzer. ^{1}H NMR spectra were determined in DMSO (internal standard TMS) on Bruker spectrometer. $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ salts were used for the synthesis of metal complexes of Schiff base. Mass spectra were carried out, TOF-MS on water KC-455 model in DMSO. The molecular structures of the complexes were optimized by CsChem 3D Utra-11 programme.

Synthesis of novel Schiff base ligand
The novel Schiff base ligand was prepared by condensation of 1H-benzo[d]imdazol-4-amine (1.3315 gm; 0.01mol) with 2-hydroxy benzaldehyde (1.2212 gm; 0.01 mol) in 25 ml ethanol and the mixture was refluxed for 3 hrs at 45^{0} C. The resulting solution was allowed to evaporate by slow diffusion process in air for a week. The crystals of novel ligand were collected, washed several times with ethanol and recrystallized from hot ethanol and dried in vacuum desiccators.
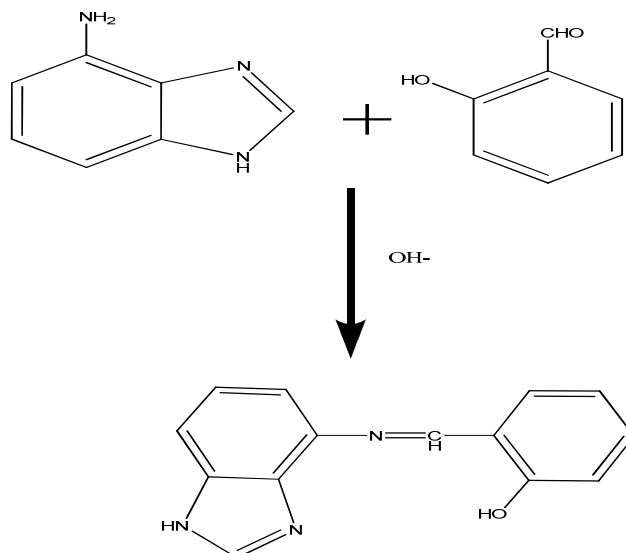

Figure 1. Structure of Novel Ligand [LH]

Synthesis of Metal complexes
The synthesized novel ligand was added to hot ethanolic solution of 0.2 mmol of metal chlorides drop wise and refluxed for 5 hours and dried at room temperature. A good crystalline form of the complexes was obtained. All the complexes were characterized by spectral techniques accordingly.
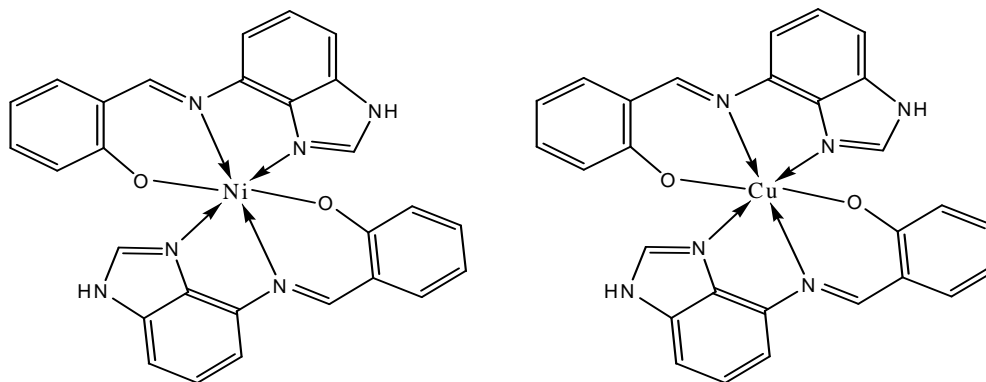

Figure 2. Structure of metal complexes [ML$_2$]

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RESULTS AND DISCUSSION

The synthesized compounds were crystalline, colored, nonhygroscopic, and soluble in water. Composition and identity of the complexes were carried out by elemental analysis. The spectroscopic data for the newly synthesized metal complexes are in good agreement with proposed molecular formula.

Elemental composition analysis

The elemental analysis (CHN) data for the novel ligand, and its metal complexes are summarized in the table below.

Table 1. Elemental analysis data of the complexes

Compound	Empirical Formula	Mol. Wt.	C Found (Calc.)	H Found (Calc.)	N Found (Calc.)	O Found (Calc.)	M Found (Calc.)
Novel Ligand	$C_{14}H_{11}N_3O$	237.26	70.23 70.87	4.92 4.67	17.87 17.71	6.80 6.74	-
Ni(II) Complex	$C_{28}H_{20}N_6NiO_2$	531.19	62.98 63.31	3.81 3.80	15.60 15.82	5.87 6.02	11.12 11.05
Cu(II) Complex	$C_{28}H_{20}CuN_6O_2$	536.04	62.75 62.74	3.76 3.75	15.69 15.68	5.96 5.97	11.81 11.85

Infrared spectral analysis

The comparison of IR spectra of novel ligand and metal complexes reveal the binding mode of ligands to metal ions which is confirmed by a negative shift in the positions of absorption peaks. IR spectra of free ligand show a broad band around 3350 cm^{-1} which can be attributed to NH stretching vibration of benzimidazole moiety. One more medium intensity band at the region of 3600-3640 cm^{-1} is assignable to phenolic OH group whose negative shift in metal complexes indicated metal coordination with phenolic oxygen. Medium intensity bands in the range of 1625 cm^{-1} due to ν(C=N) in the novel ligand was shifted hypsochromically about 1025 cm^{-1} which was in the range of 1607 - 1590 cm^{-1} in metal complexes, indicating the imine nitrogen atom involvement in coordination to metal ions [12-14]. This fact is further supported by the appearance of medium intensity band in the region below 500 cm^{-1} assignable to ν_{M-N} vibration. The appearance of one more medium intensity band in the region of 446 - 409 cm^{-1} assignable due to ν_{M-O} vibration, also indicated the metal oxygen binding mode in the complexes [15-16]. Thus from the IR- spectral assignments it is clear that the compounds may be bonded to metal ions through the imine nitrogen.

^{1}H NMR spectral analysis

^{1}H NMR spectral comparison of novel ligand and metal complexes was made to confirm the binding nature of ligand with metal ions viz. Ni (II) & Cu(II). The integral intensities of each signal in the ^{1}H NMR spectra of novel ligand and its metal complexes were found to agree with the number of different types of protons present.
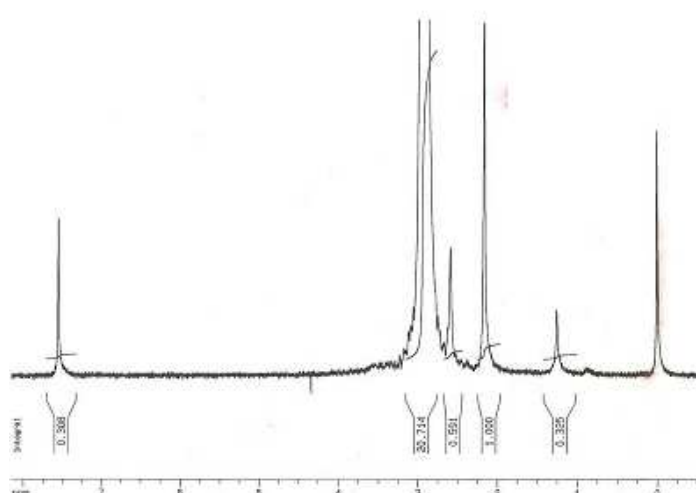

Figure 3. ^{1}HNMR spectra of Cu(II)-complex

Table 2. ^{1}H NMR spectral data

Compounds	δ (ppm)
$C_{14}H_{11}N_3O$ (Ligand)	5.0(s) [OH-Ar & NH imidazole]; 6.76-7.7 [CH-Ar]; 8.39(s) [CH imine]; 8.1(s) [CH imidazol]
Ni-complex	9.00(s) [^{1}H-ArH]; 7.0-7.621 [8 ^{1}H Ar-CH}
Cu-complex	9.00(s) [^{1}H-ArH], 7.0-7.621 [8 ^{1}H Ar-CH}

TOF-Mass spectral analysis
The proposed molecular formula of metal complexes was confirmed by the TOF mass spectral analysis by comparing their formula weight with m/z values. The mass spectra contain molecular ion peak (M^{+}) at m/z 531.19 for Ni(II) complex and 536.09 for Cu (II) complex. These data are in good agreement with the respective molecular formula. Fragmentation of the complex as m/z: 530.10 (100.0%), 532.10 (39.6%), 531.10 (32.6%), 533.10 (13.6%), 534.09 (5.4%), 532.11 (4.5%), 534.10 (2.6%), 535.10 (1.8%), 536.09 (1.4%) for Ni complex and 535.09 (100.0%), 537.09 (45.3%), 536.10 (30.6%), 538.10 (14.3%), 537.10 (4.9%), 536.09 (2.2%), 539.10 (2.2%)

X-ray powder diffraction study
X-ray powder diffraction patterns of all ligands and their complexes were recorded between 9 and 80(2θ). The value of (2θ), interplanar spacing d (Å) and the relative intensities (I/I0) of the compounds under study were recorded in table 5.
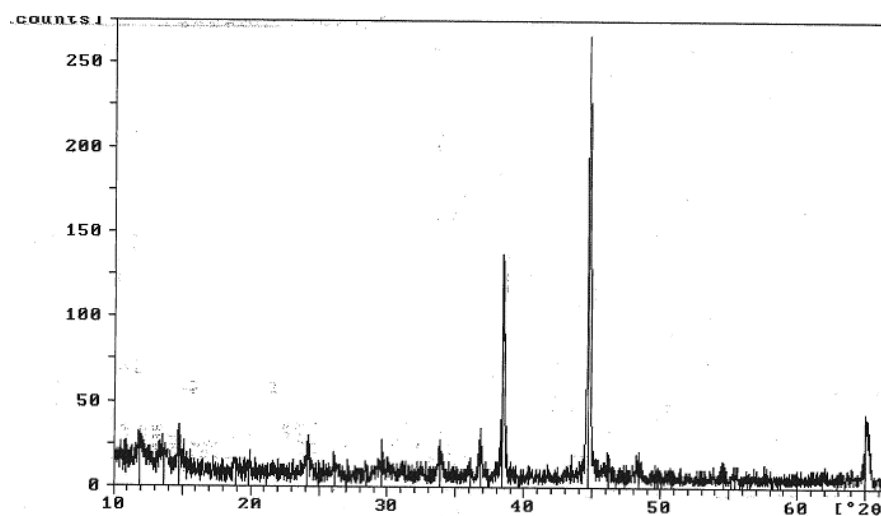

Figure 4. XRD spectra of Copper complex

Table 3. Crystallographic data for complexes

Compounds	Complex 1	Complex 2	Ligand
Formula	$C_{28}H_{20}N_6NiO_2$	$C_{28}H_{20}N_6CuO_2$	$C_{14}H_{11}N_3O$
FW	531.19	535.09	237.26
Temp (K)	293	293	293
Wavelength	1.54056	1.54056	1.54056
Crystal System	Orthorhombic	Orthorhombic	Monoclinic
Space group	P N M A	I M M A	P2/m
Unit cell dimension			
a(Å)	13.554540	22.094890	10.312
b(Å)	9.496137	8.983012	7.7972
c(Å)	4.471746	8.483077	8.9554
α	90.000	90.0000	90.00
β	90.000	90.000	120.00
γ	90.000	90.000	90.00
Volume (A^3)	575.58	1683.71	617.78
θ range (0)	19.0-70.0	7.0-30.0	12-67
Limiting indices	$0 \leq h \leq 8$ $0 \leq k \leq 5$ $0 \leq l \leq 2$	$0 \leq h \leq 7$ $0 \leq k \leq 2$ $0 \leq l \leq 2$	$-1 \leq h \leq 2$ $-4 \leq k \leq 4$ $0 \leq l \leq 7$
Particle size(nm)	49.123	50.341	11.92
Intensity (%)	7.2–100	5.9–100	3.4-100
R indices	0.0000106	0.000131	0.0000362
Density	1.405	1.343	1.151
Z	1	2	1

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Kinetics of thermal decomposition

Recently, there has been increasing interest in determining the rate- dependent parameters of solid-state non-isothermal decomposition reactions by analysis of TG curves Thermogravimetric (TG) and differential thermo gravimetric (DTA) analyses were carried out for different metal complexes in ambient conditions. The thermogravimetric analysis revealed that the complexes of Cu & Ni loses mass between 65°C and 140°C, corresponding to nearly 15 % of the total mass, followed by considerable decomposition up to 600°C, which corresponds to the decomposition of the ligand molecule leaving metal oxide NiO and CuO as residue. On the basis of thermal decomposition, the kinetic analysis parameters such as activation energy (E*), enthalpy of activation (ΔH*), entropy of activation (ΔS*), free energy change of decomposition (ΔG*) were evaluated graphically by employing the Coats – Redfern relation.

$$\text{Log } [-\text{Log } (1- \alpha) /T^2] = \log [AR/ \theta E^*(1-2RT/E^*)]-E^*/2.303RT \qquad \text{....................(1)}$$

Where α is the mass loss up to the temperature T, R is the gas constant, E* is the activation energy in J mole^{-1}, θ is the linear heating rate and the term (1-2RT/E*) ≅ 1. A straight line plot of left hand side of the equation (1) against 1/T gives the value of E* while its intercept corresponds to A (Arrhenius constant). The Coats and Redfern linearization plots, confirms the first order kinetics for the decomposition process. The calculated values of thermodynamic activation parameters for the decomposition steps of the metal complexes are reported in Table 4. According to the kinetic data obtained from the TG curves, the activation energy relates the thermal stability of the metal complexes. Among metal complexes, activation energy increases as complex 1 < complex 2. Same trends happen with thermal stability of metal complexes. Both complexes have negative entropy, which indicates that the complexes are formed spontaneously. The negative value of entropy also indicates a more ordered activated state that may be possible through the chemisorptions of oxygen and other decomposition products. The negative values of the entropies of activation are compensated by the values of the enthalpies of activation, leading to almost the same values for the free energy of activation.

Table 4. Thermodynamic activation parameters of the metal complexes

Complex	Order/n	Steps	E*/Jmol^{-1}	A/sec^{-1}	ΔS*/ JK^{-1}mol^{-1}	ΔH*/ Jmol^{-1}	ΔG*/ kJmol^{-1}	k×10^2 s^{-1}
$C_{28}H_{20}N_6NiO_2$	1	I	57.66	1.125×10^5	-92.49	112.745	61.228	1.72
		II	65.804	1.256×10^5	-110.175	96.114	89.18	1.02
$C_{28}H_{20}CuN_6O_2$	1	I	59.066	6.27×10^5	-85.136	74.10	55.29	3.27
		II	7.178	1.16×10^5	-109.603	125.89	93.104	1.79

Molecular Modeling

3D molecular modeling of the proposed structure of the complexes was performed using CsChem3D Ulta -11 program package. The correct stereochemistry was assured through the manipulation and modification of the molecular coordinates to obtain reasonable low energy molecular geometries. The optimized structures of the complexes were performed by MM2 programme contained CS chem. Office programme. The potential energy of the molecule was the sum of the following terms: E = E$_{str}$ + E$_{ang}$ + E$_{tor}$ + E$_{vdw}$ + E$_{oop}$ + E$_{ele}$. Where all E's represent the energy values corresponding to the given types of interaction. The subscripts str, ang, tor, vdw, oop and ele denote bond stretching, angle bonding, torsion deformation, van der waals interactions, out of plain bending and electronic interaction, respectively. Molecular modeling showed square planar geometry for Ni(II) complex and tetrahedral geometry for Cu(II) complex.
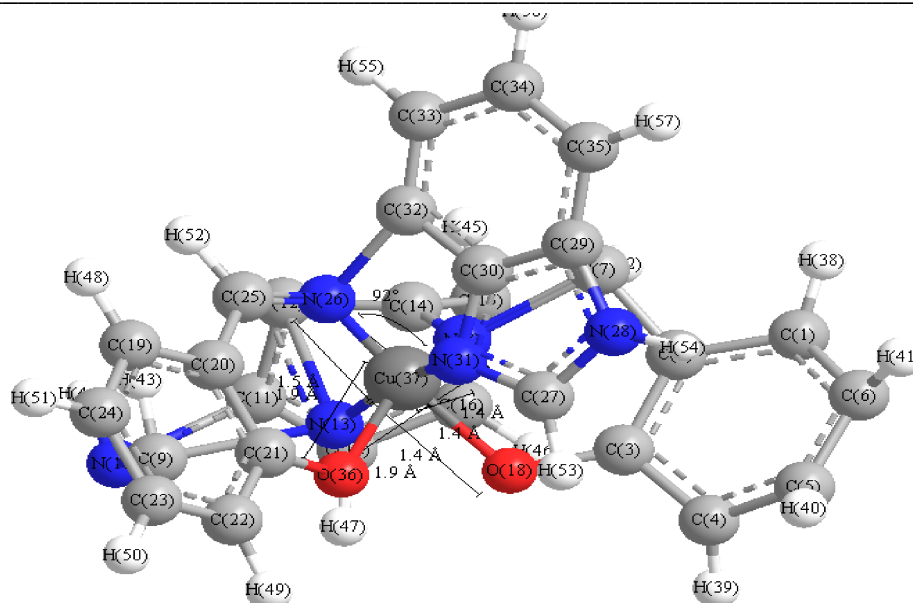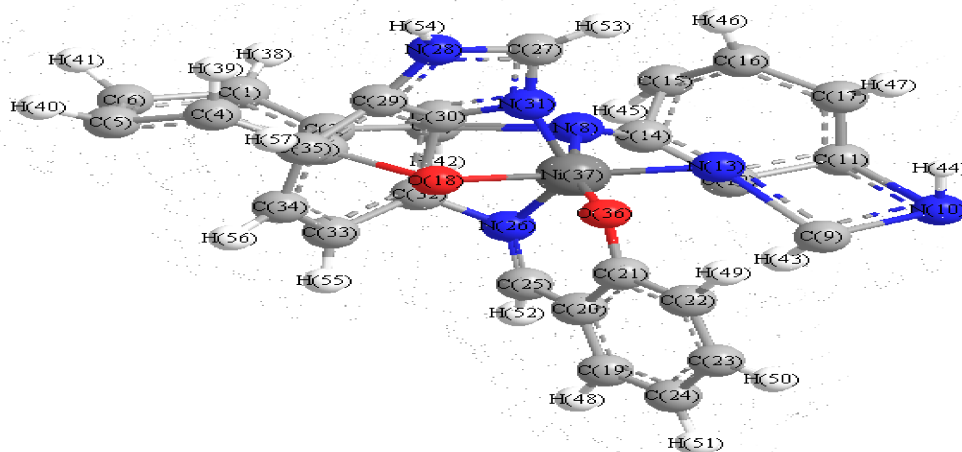
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Figure 5. Optimized structure of Nickel complex

Figure 6. Optimized structure of Copper complex

Table 5. Data for selected bond lengths and bond angles of Metal complexes

Nickel Complex		Copper Complex	
Bond length (Å)		Bond length (Å)	
N(26)-Cu(37)	1.4563	N(26)-Ni(37)	1.8134
N(31)-Cu(37)	1.4345	N(31)-Ni(37)	1.8016
N(13)-Cu(37)	1.4271	N(13)-Ni(37)	1.8327
N(8)-Cu(37)	1.4256	N(8)-Ni(37)	1.8553
O(36)-Cu(37)	1.8541	O(36)-Ni(37)	1.8030
O(18)-Cu(37)	1.8556	O(18)-Ni(37)	1.8963
Bond angles		Bond angles	
N(26)-Cu(37)-N(31)	92.3729	O(36)-Ni(37)-N(31)	101.0901
N(26)-Cu(37)-N(13)	95.3199	O(36)-Ni(37)-N(26)	108.6758
N(26)-Cu(37)-N(8)	95.6571	O(36)-Ni(37)-O(18)	78.9103
N(26)-Cu(37)-O(36)	105.8350	O(36)-Ni(37)-N(13)	84.5957
N(26)-Cu(37)-O(18)	174.3786	O(36)-Ni(37)-N(8)	165.0912
N(31)-Cu(37)-N(13)	159.0813	N(31)-Ni(37)-N(26)	130.4218
N(31)-Cu(37)-N(8)	112.0650	N(31)-Ni(37)-O(18)	67.9248
N(31)-Cu(37)-O(36)	80.8239	N(31)-Ni(37)-N(13)	104.9507
N(31)-Cu(37)-O(18)	86.5939	N(31)-Ni(37)-N(8)	79.0999
N(13)-Cu(37)-N(8)	86.5239	N(26)-Ni(37)-O(18)	79.8496
N(13)-Cu(37)-O(36)	78.3685	N(26)-Ni(37)-N(13)	116.3274
N(13)-Cu(37)-O(18)	87.5232	N(26)-Ni(37)-N(8)	81.3886
N(8)-Cu(37)-O(36)	154.6463	O(18)-Ni(37)-N(13)	160.1087
N(8)-Cu(37)-O(18)	79.6484	O(18)-Ni(37)-N(8)	114.3666
O(36)-Cu(37)-O(18)	79.4686	N(13)-Ni(37)-N(8)	80.9984
Cu(37)-O(36)-C(21)	118.2774		

CONCLUSION

Bio-active benzimidazole moiety of the novel ligand has been studied extensively and is an entity which has interesting physical and chemical behaviors. The present article focuses on synthesis, characterization and molecular modeling of the complexes, which showed the coordination of metal ions through nitrogen of 1H-benzo[d]imidazole-4-amine group and oxygen atom of 2-hydroxy benzaldehyde group. In spite of this, there is also involvement of nitrogen of imine group for coordination. The synthesized complexes were characterized by elemental analysis, MS, IR, ^{1}HNMR and the structure was optimized by Chem Office Ultra-11 programme package. The negative entropy values indicated the spontaneous formation of complexes. X-ray powder diffraction data indicated orthorhombic crystal system for both metal complexes. The complex was found to possess metal to ligand ratio of 1:1. It has been observed that complexation between metal ions and ligand takes place above pH 7. The Solubility of the complexes in water was found to be more than that of ligand.

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