

# Mixed Ligand Complexes Derived from Semicarbazone Schiff Base and Heterocyclic Ligands: Structure and Antimicrobial Activity<sup>1</sup>

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**Abstract**—A series of M(II) ternary complexes [M(L)Phen] and [M(L)Oxine], where M = Co(II), Ni(II), Cu(II), and Zn(II), L = ((2-hydroxynaphthalen-1-yl)methylene)-4-nitrobenzohydrazide, Phen = 1,10-phenanthroline and Oxine = 8-hydroxy chloroquinoline, were synthesized and characterized by UV-Vis, ESR, IR, mass spectra, and TG-DTA data. Morphology and crystallinity of the complex [Ni(L)Phen] were studied by scanning electron microscopy. The crystal systems of Cu(II) complexes were determined by powder X-ray diffraction. Biological activity of the ligand and its metal complexes has been screened against four bacterial strains.

**Keywords:** ternary metal(II) complex, powder XRD, docking, fluorescence, antimicrobial

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## INTRODUCTION

Transition metal complexes of Schiff bases are among the most adaptable and thoroughly studied systems up to date due to their numerous clinical, analytical and industrial applications [1]. The Schiff base ligand family of hydrazide and hydrazones is of certain interest due to chelating ability, structural flexibility, interesting electrical and magnetic properties of their complexes with transition metals [2,3]. Such complexes demonstrate some potential in treatment of cancer, tuberculosis [4], leprosy, and mental disorders [5]. 1,10-phenanthroline (phen) molecule, which contains nitrogen as a hetero atom, and its derivatives exhibited antiviral and antifungal activities [6]. The stable phenanthroline complexes inhibited DNA or RNA polymerase and induced strand scission of DNA in the presence of reducing agents [7, 8]. Derivatives of 8-hydroxyquinoline (oxine) and their metal complexes have been used as antibacterial and antifungal agents. One of the oxine derivatives, clioquinol (5-chloro-7-iodo-8-hydroxyquinoline), and its copper complex were used as antifungal, antiprotozoal, antialzheimer, and anticancer drugs [9].

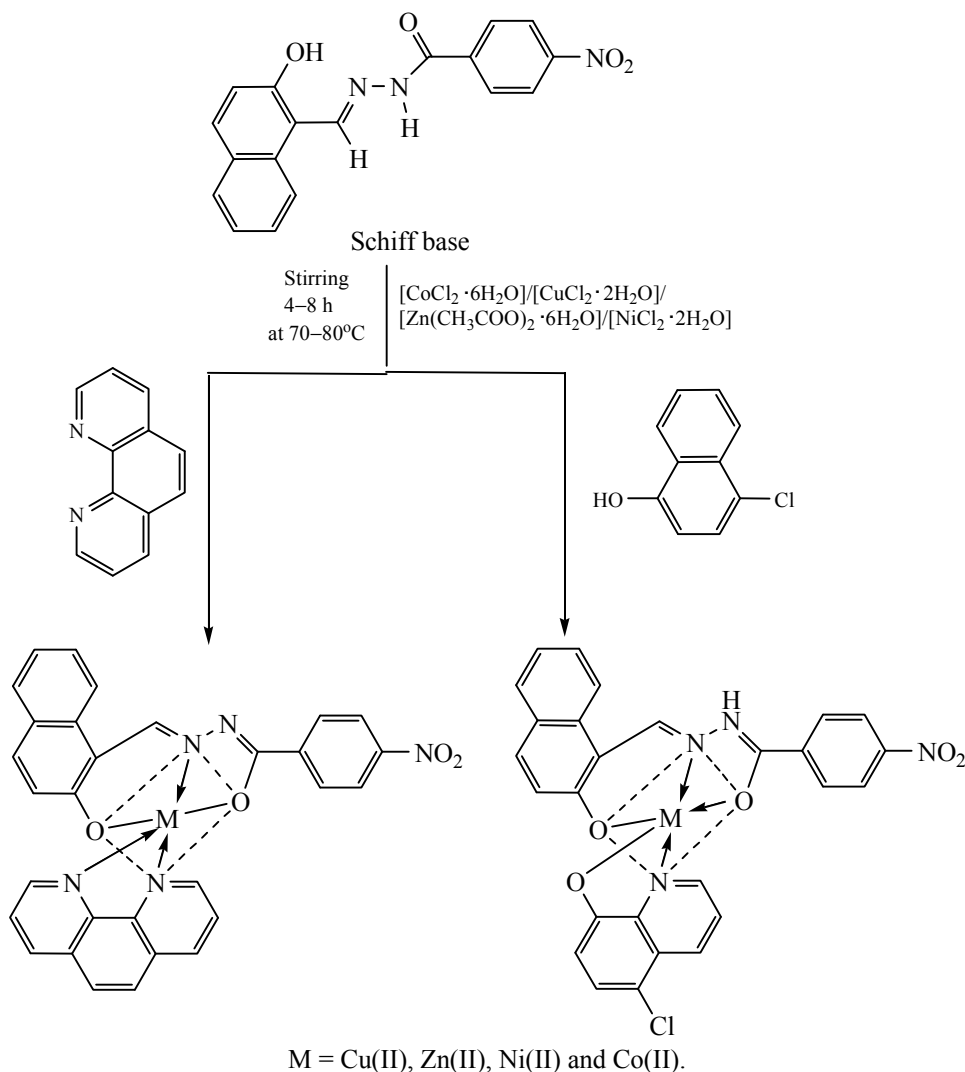
Based on these observations and considering the pharmacological significance of metal complexes of hydrazones and hetero cyclic ligands (1,10-phenanthroline and 5-chloro-8-hydroxy quinoline), here we report synthesis, characterization and antimicrobial studies of some transition metal(II) ternary complexes containing hydrazone and heterocyclic ligands [10]. Our attention was directed to the study of crystal and complex structures.

## RESULTS AND DISCUSSION

The ligand was synthesized according to the earlier reported method. Synthetic approach to ternary metal(II) complexes is presented in Scheme 1 and Table 1. Structures of the complexes were established by IR, UV-Vis, ESR, and Mass spectra, TG-DTA, powder X-ray diffraction, and scanning electron microscopy (SEM) analysis. All the complexes were colored, non-hygroscopic and stable at room temperature, insoluble in water and alcohol, but soluble in DMF and DMSO.

**IR spectra.** IR bands recorded at 3418, 3214, 1245, 1625, and 1580 cm<sup>-1</sup> for the free ligand were attributed to  $\nu(\text{OH})$ ,  $\nu(\text{N-H})$ ,  $\nu(\text{C-O})$ ,  $\nu(\text{C=O})$ , and  $\nu(\text{C=N})$ , respectively [11]. The band attributed to the azo-

<sup>1</sup> The text was submitted by the authors in English.

**Scheme 1.** Synthetic route to Cu(II), Zn(II), Ni(II), and Co(II) ternary complexes.

methine group of the free ligand was shifted in complexes to  $1572\text{--}1624\text{ cm}^{-1}$  which confirmed binding of azomethine nitrogen to the metal ion [12]. In the spectra of  $[\text{M}(\text{L})\text{Phen}]$  complexes bands of free phenolic–enolic hydroxide were not recorded due to deprotonation, and the  $\nu(\text{C}=\text{O})$  stretching band was shifted to the range of  $1193\text{--}1244\text{ cm}^{-1}$ , indicating coordination of oxygen to the metal ion. The IR spectrum of free 1,10-phenanthroline exhibited the intense bands at  $738$  and  $853\text{ cm}^{-1}$  attributed to aromatic ring vibrations and the band at  $1421\text{ cm}^{-1}$  of the pyridyl vibrations [13]. The above bands were shifted to  $720\text{--}834$  and  $1061\text{--}1108\text{ cm}^{-1}$ , respectively, in their metal complexes spectra [14].

In the spectrum of  $[\text{M}(\text{L})\text{Oxine}]$  complexes the band recorded in the range of  $2924\text{--}3217\text{ cm}^{-1}$  was

assigned to the shift of  $\nu(\text{N}=\text{H})$  band typical for the free ligand. Repositioning of the  $\nu(\text{C}=\text{O})$  band to the range of  $1616\text{--}1651\text{ cm}^{-1}$  was the result of coordination between oxygen atom of the amide carbonyl and the metal ion [13]. The band  $\nu(\text{C}=\text{N})$  of pyridine ring recorded at  $1580\text{ cm}^{-1}$  was shifted to the lower frequency region  $1462\text{--}1497\text{ cm}^{-1}$  in the spectra of its metal complexes. The  $\nu(\text{C}=\text{O})$  band of free oxine,  $1120\text{ cm}^{-1}$ , was observed in the range of  $962\text{--}1088\text{ cm}^{-1}$  in the spectra of its metal complexes [15]. The new bands recorded in the range of  $513\text{--}581$  and  $448\text{--}484\text{ cm}^{-1}$  for the oxine complex spectrum indicated coordination between the metal and oxygen, and the metal and nitrogen atoms, respectively [15].

**ESR spectra.** ESR spectra of  $[\text{Cu}(\text{L})\text{Phen}]$  and  $[\text{Cu}(\text{L})\text{Oxine}]$  were recorded in DMSO solution at

**Table 1.** Elemental analysis and physical data for metal(II) ternary complexes

Compound	Color	mp, °C	Found, %				Calculated, %			
			C	H	N	M	C	H	N	M
[Cu(L)Phen]	Black	280	62.22	3.66	12.09	10.97	62.44	3.32	12.14	11.01
[Co(L)Phen]	Brown	307	62.90	3.46	12.28	10.12	62.95	3.35	12.23	10.30
[Ni(L)Phen]	Brick red	280	62.75	3.12	12.33	10.22	62.97	3.35	12.24	10.26
[Zn(L)Phen]	Orange	310	62.03	3.64	12.06	11.22	62.24	3.31	12.10	11.30
[Cu(L)Oxine]	Light green	340	56.29	2.29	9.72	11.30	56.26	2.27	9.72	11.02
[Co(L)Oxine]	Black	382	56.75	3.12	9.85	10.35	56.71	3.00	9.80	10.31
[Ni(L)Oxine]	Gray	314	56.70	3.31	9.84	10.22	56.73	3.00	9.80	10.27
[Zn(L)Oxine]	Light orange	398	56.08	2.93	9.72	11.31	56.08	2.96	9.69	11.31

room temperature (Table 2). Spectra of Cu(II) complexes demonstrated one intense peak in the high field region. The spectrum of [Cu(L)Phen] demonstrated a typical axial peak with well-defined  $g_{\parallel}$  and  $g_{\perp}$  values at 2.2910 and 2.0832, and [Cu(L)Oxine] complex demonstrated the similar values at 2.2582 and 2.0962 respectively. The geometric parameter  $G$ , which measures the exchange interaction between copper centers in the polycrystalline compound, was calculated using the equation:

$$G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023).$$

The  $G$  values for the complexes [Cu(L)Phen] and [Cu(L)Oxine] were 3.5686 and 2.7252, respectively, which indicated the considerable exchange interaction [11]. In both Cu(II) complexes the values  $g_{\parallel} > g_{\perp} > 2.0023$  indicated the presence of an unpaired electron in  $d_{x^2-y^2}$  orbital [12–16]. The  $g_{\perp}$  values (2.0832 and 2.0962) were almost the same for both Cu(II) complexes indicating the similar bonding nature [17, 18]. The  $g_{\parallel}$  values lower than 2.3 and the  $G$  values for Cu(II) complexes lower than 4 [19–21] indicated that the metal ligand bonding was of significant covalent nature. The order of values  $g_{\parallel} \geq g_{\perp}$  suggested the square pyramidal geometry of five coordinated complexes.

**Electronic spectra.** The electronic spectrum of free Schiff base demonstrated three bands at 265, 320, and

377 nm [10] that indicated the  $\pi-\pi^*$  transition in aromatic benzene ring, the  $\pi-\pi^*$  transition in azo-methine and the  $n-\pi^*$  transition of carbonyl and nitro chromophores [22], accordingly. In the spectra of metal(II) complexes the second and third bands were shifted to a longer wavelength [23] due to donation of electrons lone pairs of nitrogen and oxygen of the Schiff base to the metal ion and the broad band in the range 385–471 nm could be assigned to LMCT. The broad band in the range of 688–723 nm was due to the  $d-d$  transition [24]. The expected weak  $d-d$  transition in the visible region for the paramagnetic nickel complexes could not be detected even for concentrated solutions, probably due to its overlap with the low energy tail of the charge transfer transition [25]. The Zn(II) complexes did not exhibit any  $d-d$  transitions typical for diamagnetic  $d^{10}$  configuration.

**Mass spectra.** Mass spectra data of the complexes supported their compositions and indicated that the complexes were monomeric with the metal to ligand ratio 1 : 1 : 1.

**Thermal analysis.** The complex [Ni(L)Phen] exhibited thermal stability up to 200°C which confirmed that the complex was free from coordinated water molecules. Decomposition proceeded in three steps. In the first step the nitro group of the Schiff base ligand was given up at the range of 200–300°C. In the second step the observed fulminant loss of coordinated phenanthroline ring took place in the range of 400–600°C. In third step the Schiff base ligand gradual decomposition was observed at 600–1000°C, and the leftover non-volatile component was metal oxide [24]. The entire decomposition process of the complex [Ni(L)Phen] was endothermic.

**Table 2.** ESR data for Cu(II) ternary complexes

Complex	$g_{\parallel}$	$g_{\perp}$	$G$
[Cu(L)Phen]	2.2910	2.0832	3.5686
[Cu(L)Oxine]	2.2582	2.0962	2.7252

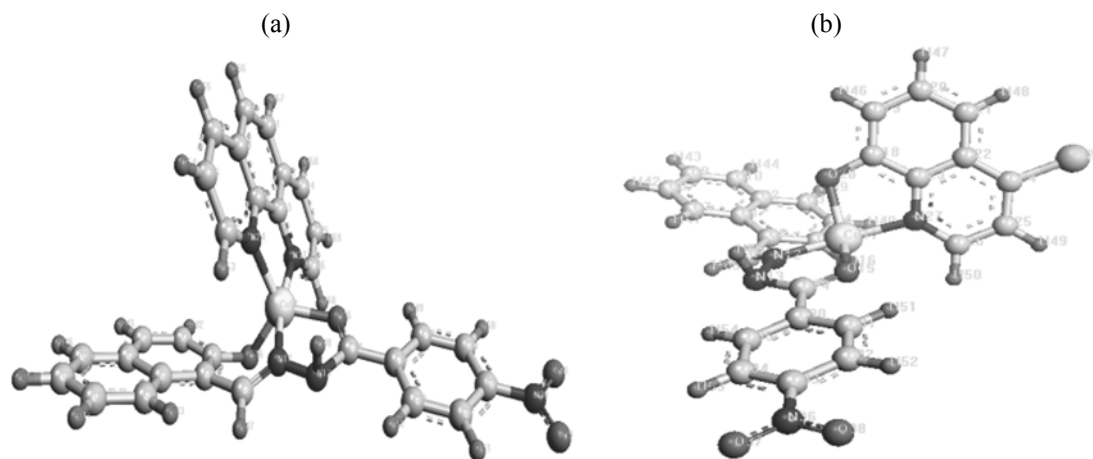


Fig. 1. Optimized geometries of (a) [Cu(L)Phen] and (b) [Cu(L)Oxine].

**X-Ray diffraction.** The powder X-ray diffraction data for the complexes [Cu(L)Phen] and [Cu(L)Oxine] are presented in Table 3. The indexed results [25, 26] yielded the monoclinic unit cell for both complexes. The figures of merit were sufficiently acceptable to support the obtained indexing results  $M(20) = 35.6$  for [Cu(L)Phen] and  $M(20) = 24.8$  for [Cu(L)Oxine]. The best estimated space group was  $P12/m1$  in the monoclinic system for both complexes.

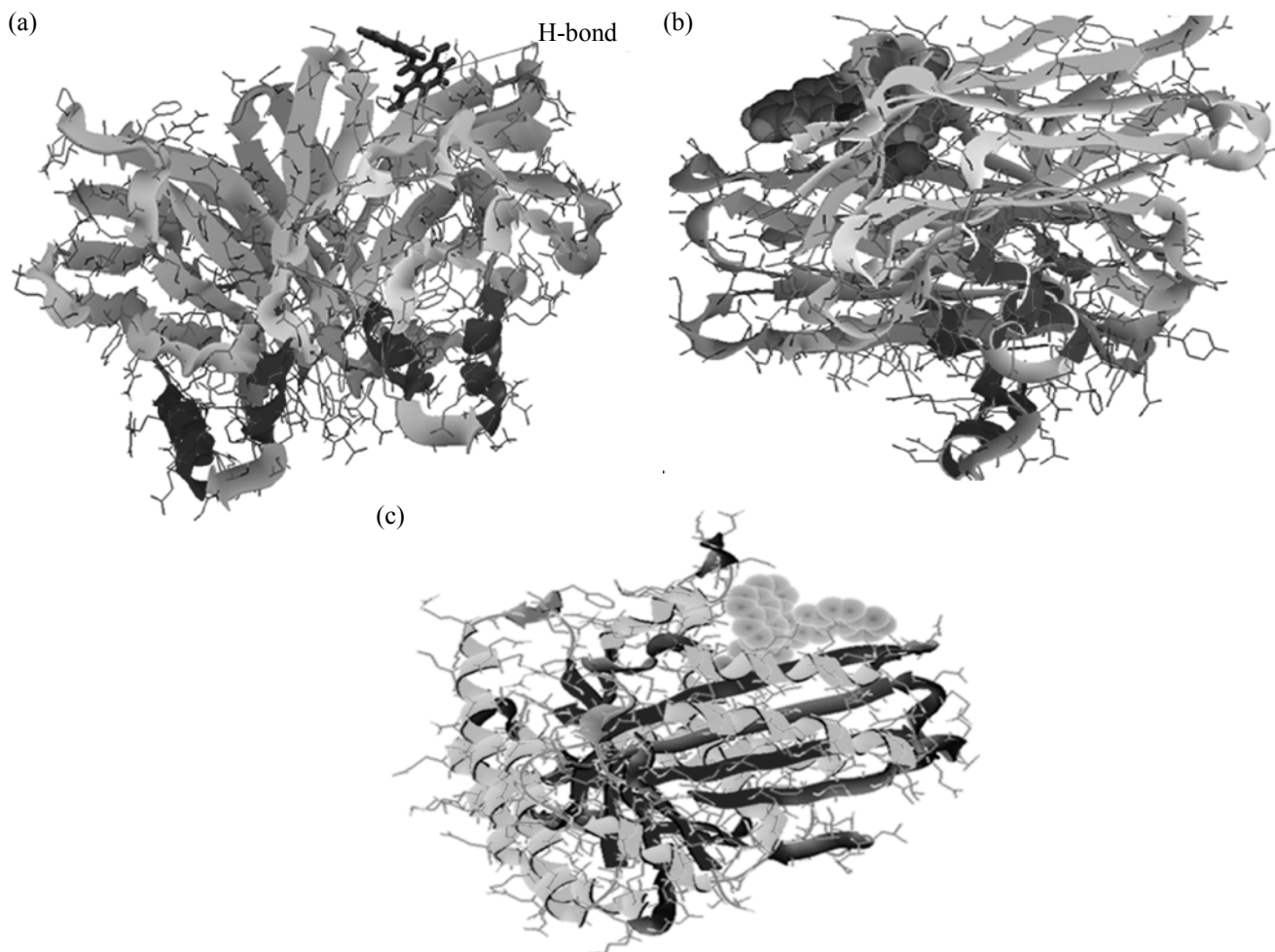
**Morphological analysis (SEM and EDX).** SEM image of the free ligand revealed its powdery and soft morphological nature [10]. Upon chelation of the

ligand with a metal(II) ion substantial changes in morphology of the compound were observed. From the SEM image of [Ni(L)Phen], sharp nanorod structures with various crystal sizes were observed, whereas agglomeration of [Cu(L)Phen] molecules in nano size poly crystalline particles was determined.

**Molecular modeling.** According to the computation data for [Cu(L)Oxine] complex, bond length and bond energies of  $\text{Cu}^{17}\text{-O}^{28}$  were 2.049 Å and 244.563 kcal/mol, respectively. Those were different from the other Cu–L bond lengths and energies, indicating that oxygen occupied the axial

Table 3. Crystallographic data for complexes [Cu(L)Phen] and [Cu(L)Oxine]

Crystal data	[Cu(L)Phen]	[Cu(L)Oxine]	Crystal data	[Cu(L)Phen]	[Cu(L)Oxine]
Empirical formula	$\text{C}_{30}\text{H}_{19}\text{CuN}_5\text{O}_4$	$\text{C}_{27}\text{H}_{16}\text{ClCuN}_4\text{O}_5$	$\alpha$ , deg	90	90
$M_w$	578.1	576.4	$\beta$ , deg	115.469	124.9
Content of volume	649.16	617.7	$\gamma$ , deg	90	90
Volume per atom	16.917	15.576	$V$ , Å <sup>3</sup>	676.683	591.87
Crystal size, nm	34.33	20.4	$Z$	2	2
Lattice strain	0.0043	0.0082	$2\theta$ range	10–80	10–70
Space group	$P12/m1$	$P12/m1$	$D_{\text{calc}}$ , g/cm <sup>3</sup>	1.419	1.617
Crystal system	Monoclinic	Monoclinic	$\mu(\text{CuK}\alpha)$ , cm <sup>-1</sup>	1.543	1.543
Secific surface area, m <sup>2</sup> /g	12.317	18.18	Number of peaks indexed	16	13
$a$ , Å	22.952	21.347	$\rho_{\text{max}}$	0.17409	0.14021
$b$ , Å	2.5605	2.856	$\rho_{\text{min}}$	0.0032	0
$c$ , Å	12.7538	11.838	$d$ (resolution)	1.19834	1.3353
			Reflection no.	1547	2687



**Fig. 2.** Interaction of (a) Ligand-4YLD (dotted lines represents the H-bond), (b) [Co(L)Phen]- 4YLD, and (c) [Ni(L)Oxine]-2VAM.

position. The remaining Cu–L fragments were planar (Fig. 1a). In case of [Cu(L)Phen] all five Cu–L coordinated bond lengths and bond angles were similar (Fig. 1b).

**Docking studies.** In the present study the target microbial proteins data were obtained from protein data bank (PDB). The possible docking modes between the compounds and the target microbial proteins [*B. subtilis* (PDB: 2VAM) and *S. rolfesii* (PDB: 4YLD)] were studied (Fig. 2). Binding energy and shape based orientation energies for each docking were calculated (Table 4). The energy values of metal complexes were lower than those of ligand against the bacterial protein *B. subtilis*. This indicated that the binding affinity to *B. subtilis* protein was higher for metal complexes, whereas binding affinity to *S. rolfesii* protein lower, except [Co(L)Oxine]. The results of docking matched well the experimental results of antimicrobial activity. The binding modes and geometrical orientations of all the compounds were

almost identical, suggesting that all inhibitors occupied the similar cavity in the receptor but the binding affinities were variable.

**Fluorescence emission spectra.** Schiff base exhibited a strong fluorescence emission at 513 nm with excitation at 450 nm. In contrast with fluorescence spectra of the Schiff base, partial fluorescence quenching phenomenon was observed in its metal complexes demonstrating emission peaks at 545, 565, 553, and 544 nm for Co(II), Ni(II), Cu(II), and Zn(II) complexes, respectively. The metal complexes of [M(L)oxine] demonstrated weak fluorescence emission peaks at 513, 531, 546, and 541 nm for Co(II), Ni(II), Cu(II), and Zn(II) complexes, respectively. The fluorescence spectral data indicated that fluorescence emission intensity of Schiff base was decreased dramatically upon its formation of complexes with transition metal ions. The decrease in emission intensity of [M(L)Phen] complexes was in the order of

**Table 4.** Docking data for the ligand and its metal complexes against *Bacillus subtilis* and *Sclerotium rolfisii* proteins

Compound	<i>Bacillus subtilis</i> (PDB: 2VAM)		<i>Sclerotium rolfisii</i> (PDB: 4YLD)	
	$E_{\text{tot}}^a$ , kJ/mol	$E_{\text{shape}}^b$ , kJ/mol	$E_{\text{tot}}^a$ , kJ/mol	$E_{\text{shape}}^b$ , kJ/mol
Ligand (L)	-312.60	-312.60	-326.4	-326.4
[Cu(L)Phen]	-315.82	-315.82	-321.44	-325.66
[Co(L)Phen]	-356.05	-356.05	-311.20	-321.16
[Ni(L)Phen]	-321.88	-321.75	-255.20	-253.16
[Zn(L)Phen]	-318.28	-316.24	-253.89	-253.21
[Cu(L)Oxine]	-338.59	-338.59	-303.89	-295.75
[Co(L)Oxine]	-335.78	-331.41	-335.61	-333.61
[Ni(L)Oxine]	-361.32	-361.32	-319.53	-315.08
[Zn(L)Oxine]	-335.73	-335.73	-268.65	-275.59

<sup>a</sup>Total binding energy (score). <sup>b</sup> Shape based orientation energy.

L > Ni(II) > Zn(II) > Cu(II) > Co(II) and in the case of [M(L)Oxine] complexes it in the order of L > Co(II) > Ni(II) > Cu(II) > Zn(II).

**Antimicrobial activity.** The synthesized Schiff base and its metal complexes were screened for their antimicrobial activity by the well diffusion method (Kirby-Bauer method). The bacterial strains of *E. coli*, *S. aureus*, *B. subtilis* and *P. putida* and fungal strains of *S. rolfisii* and *M. phaseolina* and standard antibacterial and antifungal drugs, streptomycin and endofill, accordingly, were incubated for 24 h at 37°C. Activity of the compounds was tested at different minimum inhibition concentrations (MIC). At the MIC value of 200 µg/mL, the *B. subtilis* and *S. aureus* demonstrated high inhibition, whereas *E. coli* and *P. putida* did not exhibit significant inhibition in the presence of metal complexes (Table 5). Antifungal activity was exhibited by the compounds only at concentration of 1 mg/mL and at lower concentration no activity was detected (Table 6). The metal complexes were more potent than the Schiff base.

## EXPERIMENTAL

Metal salts, [CoCl<sub>2</sub>·6H<sub>2</sub>O], [CuCl<sub>2</sub>·2H<sub>2</sub>O], [Zn(CH<sub>3</sub>COO)<sub>2</sub>·6H<sub>2</sub>O], [NiCl<sub>2</sub>·2H<sub>2</sub>O], and hydrazine hydrochloride were purchased from Merck. Nitro benzoic acid, 2-hydroxy naphthaldehyde, 5-chloro quinolin-8-ol and 1,10-phenanthroline were purchased from Sigma Aldrich. The metal ratio for the complexes was determined on a Perkinelmer-500 atomic absorp-

tion spectrophotometer. Melting points of the compounds were measured on a Polmon instrument (Model no. MP-96). IR spectra were recorded on a Shimadzu FT-IR 8400S spectrophotometer using KBr pellets. UV-Vis spectra were recorded on a Shimadzu UV-Vis 2600 in DMSO at room temperature in the wavelength range of 200–800 nm. Fluorescence study was carried out on a Shimadzu spectrofluorometer at room temperature. ESR spectra were recorded by ESR Spectrometer (JEOL-Japan). CHN Analysis was carried out on a Vario macro elemental analyzer (USA). Powder X-ray diffraction data were collected at room temperature on a Shimadzu diffractometer using monochromatic CuK<sub>α2</sub> radiation ( $\lambda = 1.54060 \text{ \AA}$ ). The patterns were scanned over the angular range 1.64°–70° and 10°–80° for [Cu(L)Oxine] and [Cu(L)Phen], respectively. Indexing of the powder diffraction pattern was carried out with the expo-2014 software program. The pattern was pretreated by calculating and subtracting the back-ground then smoothing before stripping K<sub>α2</sub> radiation by using the Pearson method. Diffraction peaks were searched automatically based on the Cheby-shave method with the number of coefficients 20. Indexing has been carried out using peak positions read from the powder diffraction profiles by DICVOL6 and NTREOR9 methods. Morphology of compounds was studied on a ZEISS SEM-EDX packed scanning elec-tron microscope. Thermal degradation of compound was studied on a Mettler TG-DTA analyzer. Docking study of compounds was carried out by using Hex 8.0 software. ESP mapping was done by Argus Lab 4.0 software.

**Table 5.** Antibacterial activity of the ligand and its metal complexes

Compound	MIC concentration, $\mu\text{g/mL}$	Sensitivity				Compound	MIC concentration, $\mu\text{g/mL}$	Sensitivity			
		<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>	<i>Pseudomonas putida</i>			<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>	<i>Pseudomonas putida</i>
Ligand (L)	50	-	-	-	-	[Co(L)Phen]	50	+	+	+	-
	100	+	+	+	+		100	+	+	+	-
	200	+	++	-	-		200	+	++	+	-
[Co(L)Oxine]	50	+	+	-	-	[Ni(L)Phen]	50	-	+	-	-
	100	+++	++	-	-		100	+	++	+	-
	200	+++	++	+	-		200	+	+++	+	-
[Cu(L)Oxine]	50	+	-	-	-	[Zn(L)Phen]	50	+	++	-	-
	100	++	+	+	-		100	++	++	+	-
	200	+++	++	+	-		200	+++	+++	+	-
[Zn(L)Oxine]	50	+	-	-	-	[Cu(L)Phen]	50	-	+	-	-
	100	+++	++	-	-		100	++	++	+	-
	200	++	+++	-	-		200	++	+++	+	-
[Ni(L)Oxine]	50	-	++	+	-	Streptomycin	100	+++	+++	++++	++++
	100	+	+++	+	-						
	200	++	+++	+	-						

**Table 6.** Antifungal activity of the ligand and its metal complexes at 1 mg/mL

Compound	Inhibition zone, mm	
	<i>Sclerotium rolfsii</i>	<i>Macrophomina phaseolina</i>
Ligand (L)	2	-
[Co(L)Oxine]	4	6
[Cu(L)Oxine]	-	3
[Ni(L)Oxine]	3	1
[Zn(L)Oxine]	-	4
[Co(L)Phen]	-	5
[Cu(L)Phen]	1	1
[Ni(L)Phen]	2	-
[Zn(L)Phen]	4	1
Endofill	7	7

Molecular modeling of metal complexes was carried out using the Argus Lab 4.0 software program. Geometry optimization was carried out using the Universal force field (UFF). The selected bond distances, bond angles and bond energies of [Cu(L)Phen] and [Cu(L)Oxine] can be presented by the authors. The Hex 8.0 program was applied for protein docking using spherical polar fourier correlations. Parameters used for docking included: correlation type shape only, FFT mode 3D, grid dimension 0.6, receptor range 180, ligand range 180, twist range 360, distance range 40, and solutions 2000, and search program included: SPF transform, FFT steric scanning, FFT final search, energy refinement, and total docking. Fluorescence emission spectra of the Schiff base (L) and its metal ternary complexes [M(L)Phen] and [M(L)Oxine], concentration 0.03 mM, were recorded in DMSO at room temperature with the measured emission wave length range from 200 to 800 nm.

**Synthesis of ternary metal(II) complexes.** Hot methanol solution of the ligand [(2-Hydroxynaph-

thalene-1-yl)methylene-4-nitrobenzohydrazide] (1.0 mmol), hot methanol solution of a metal salt, [CoCl<sub>2</sub>·6H<sub>2</sub>O], [CuCl<sub>2</sub>·2H<sub>2</sub>O], [Zn(CH<sub>3</sub>COO)<sub>2</sub>·6H<sub>2</sub>O], or [NiCl<sub>2</sub>·2H<sub>2</sub>O] (1.0 mmol), and methanol solution of 1,10-phenanthroline/5-chloro-8-hydroxyquinoline (1.0 mmol) were mixed together upon constant stirring. The mixture was refluxed for 4–8 h. The mixture was cooled down. The precipitate was filtered off, washed, recrystallized, and dried in a desiccators over P<sub>4</sub>O<sub>10</sub>.

**[Cu(L)Phen].** Yield 78%. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1244 (C–O<sub>phen</sub>), 1580 (C=N), 1600 (N=C–O), 1101 (C=N<sub>phen</sub>), 794, 774 (C=C<sub>phen</sub>), 484 (Cu–N), 536 (Cu–O). UV-Vis spectrum,  $\lambda$ , nm: 270, 323, 391, 713. MS:  $m/z$ : 577 [ $M + 1$ ]. C<sub>30</sub>H<sub>19</sub>CuN<sub>5</sub>O<sub>4</sub>.

**[Co(L)Phen].** Yield 76%. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1222 (C–O<sub>phen</sub>), 1596 (N=C–O), 1586 (C=N), 1106 (C=N<sub>phen</sub>), 773 (C=C<sub>phen</sub>), 473 (Co–N), 513 (Co–O). UV-Vis spectrum,  $\lambda$ , nm: 275, 358, 471, 688. MS:  $m/z$ : 572 [ $M + 1$ ]. C<sub>30</sub>H<sub>19</sub>CoN<sub>5</sub>O<sub>4</sub>.

**[Ni(L)Phen].** Yield 80%. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1220 (C–O<sub>phen</sub>), 1596 (N=C–O), 1586 (C=N), 1108 (C=N<sub>phen</sub>), 775, 834 (C=C<sub>phen</sub>), 470 (Ni–N), 581 (Ni–O). UV-Vis spectrum,  $\lambda$ , nm: 264, 323, 377, 458. MS:  $m/z$ : 572 [ $M + 1$ ]. C<sub>30</sub>H<sub>19</sub>NiN<sub>5</sub>O<sub>4</sub>.

**[Zn(L)Phen].** Yield 84%. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1193 (C–O<sub>phen</sub>), 1607 (N=C–O), 1619 (C=N), 1061 (C=N<sub>phen</sub>), 720, 788 (C=C<sub>phen</sub>), 477 (Zn–N), 571 (Zn–O). UV-Vis spectrum,  $\lambda$ , nm: 272, 325, 385. MS:  $m/z$ : 578 [ $M + 1$ ]. C<sub>30</sub>H<sub>19</sub>ZnN<sub>5</sub>O<sub>4</sub>.

**[Cu(L)Oxine].** Yield 75%. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3217 (N–H), 1243 (C–O<sub>phen</sub>), 1651 (C=O), 1624 (C=N), 1462 (C=N<sub>oxine</sub>), 1088, 748 (C=C<sub>phen</sub>), 448 (Cu–N), 552 (Cu–O). UV-Vis spectrum,  $\lambda$ , nm: 265, 325, 439, 723. MS:  $m/z$ : 577 [ $M + 1$ ]. C<sub>27</sub>H<sub>17</sub>ClCuN<sub>4</sub>O<sub>5</sub>.

**[Co(L)Oxine].** Yield 88%. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2924 (N–H), 1277 (C–O<sub>phen</sub>), 1623 (C=O), 1572 (C=N), 1497 (C=N<sub>oxine</sub>), 1088, 833 (C=C<sub>phen</sub>), 485 (Co–N), 552 (Co–O). UV-Vis,  $\lambda$ , nm: 236, 263, 336, 414, 695. MS:  $m/z$ : 569.7 ( $M - 1$ ). C<sub>27</sub>H<sub>17</sub>ClCoN<sub>4</sub>O<sub>5</sub>.

**[Ni(L)Oxine].** Yield 74%. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2926 (N–H), 1239 (C–O<sub>phen</sub>), 1616 (C=O), 1578 (C=N), 1464 (C=N<sub>oxine</sub>), 1084, 712 (C=C<sub>phen</sub>), 481 (Ni–N), 530 (Ni–O). UV-Vis spectrum,  $\lambda$ , nm: 281, 328, 408. MS:  $m/z$ : 569 ( $M - 1$ ). C<sub>27</sub>H<sub>17</sub>ClNiN<sub>4</sub>O<sub>5</sub>.

**[Zn(L)Oxine].** Yield 78%. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2926 (N–H), 1242 (C–O<sub>phen</sub>), 1618 (C=O), 1577 (C=N), 1496 (C=N<sub>oxine</sub>), 962, 711 (C=C<sub>phen</sub>), 451

(Zn–N), 542 (Zn–O). UV-Vis spectrum,  $\lambda$ , nm: 275, 332, 439. MS:  $m/z$ : 578 ( $M + 2$ ). C<sub>27</sub>H<sub>17</sub>ClZnN<sub>4</sub>O<sub>5</sub>.

## CONCLUSIONS

A number of bivalent ternary metal complexes has been synthesized and characterized by IR, ESR, UV-Vis, and Mass spectrometry. The experimental results matched the theoretical molecular modeling. The latter supported the square pyramidal geometry of the metal complexes. Powder X-ray crystallography revealed the monoclinic crystal structure for [Cu(L)Oxine] and [Cu(L)Phen] complexes. The morphological study of [Ni(L)Phen] and [Cu(L)Phen] supported the polycrystalline nature of the products. According to antimicrobial tests the complexes demonstrated clear antibacterial activity.

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