



SYNTHESIS AND ANTI-MICROBIAL ACTIVITIES OF SOME THIOUREA BASED METAL COMPLEXES

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The transition metal (II) complexes were formed by the reaction of Co(II), Ni(II), Zn(II), Fe(II) and Cu(II) nitrates with the Schiff base ligands. The complexes were characterized using infrared (FT-IR), electronic spectral (UV), elemental analysis, melting points and XRD analysis etc. The transition metal(II) complexes were screened for antibacterial and antifungal activities. Antibacterial activity against four bacteria such as *Escherichia coli*, *Salmonella typhi*, *Staphylococcus aureus* and *Bacillus subtilis* bacterial strains by the agar-cup method. Antifungal activity was studied against four bacteria *Aspergillus Niger*, *Penicillium Chrysogenum*, *fusarium moneliforme* and *aspergillus flavus* bacterial strains by the poison plate method. The complexes were found to exhibit higher to moderate activity against some bacterial species.

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INTRODUCTION

The treatment of infectious diseases always remains a significant and serious problem in society, because of increasing number of multidrug resistant microbial pathogens and emerging infectious diseases. The increasing human resistance and antimicrobial agents are being well thought as essential sources in novel drug discoveries for treating a range of fungal and bacterial infections. In present study, we focus on synthesis of metal complexes, and their antibacterial and antifungal activities.

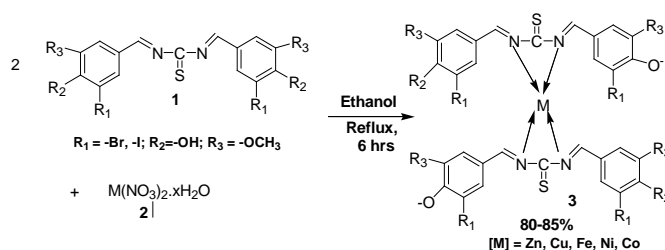
Schiff bases are important precursors in various organic syntheses.¹⁻⁴ The schiff base ligands are immense coordinating compounds. It forms stable complexes with different transition metal ions. The transition metal complexes have been always in the investigation due to their broad applications in wide ranging areas from natural sciences to material science.

Schiff bases have also been exhibits a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties.⁵⁻⁶

The mixed ligand complexes formation was an important aspect in inorganic and analytical chemistry.

The uses of mixed ligand complexes in various fields diverted us to develop novel methodologies with increased atom economy, selectivity and biological applications and environmental approach.⁷ They are also used as catalyst, in medicine like antibiotics and anti-inflammatory agents and antibacterial agents⁸⁻¹⁶ as well as in industry as anticorrosion agents.¹⁷⁻²³

The present investigation reports the synthesis of some substituted novel bis-metal complexes. In this process, Schiff bases and metal nitrate were dissolved in ethanol separately. On addition, the mixture was refluxed for appropriate time (Scheme 1). The separated transition metal(II) complexes were screened for antibacterial and antifungal activities against different bacteria.



Scheme 1. General synthesis route of complexes

RESULTS AND DISCUSSION

Novel metal complexes are synthesized using Schiff bases of thiourea and urea with nitrates of metal Zn(II), Co(II), Fe(II), Cu(II), Ni(II) dissolved in ethanol. Physical parameters were discussed in detail with their colour and melting point and reported in Table 1. Spectral characterization FT-IR and UV-visible spectra of these complexes were scanned and reported.

FT-IR spectrum analysis

Infrared spectra were recorded on a spectrophotometer in wave number region 4000-400 cm^{-1} . The spectra bands of metal complexes at 410-497 cm^{-1} were characterized for metal which indicates that the nitrogen atom of the ligand was coordinated i.e., (M-N) bands frequency. The strong bands at 3200-3640 cm^{-1} assigned as ν O-H group and 1648-1679 cm^{-1} band assigned for ν C=N group. The stretching frequency at 3000-3150 cm^{-1} can be recognized to C-H bond.

Table 1. Synthesis of novel metal complexes

Codes	Complexes (3)	Colour	MP. (°C)
W1	Bis[bis(4-hydroxy-3-methoxybenzylidene)thiourea-]zinc(II)	Yellowish	135 °C
W2	Bis[bis(4-hydroxy-3-methoxybenzylidene)thiourea-]cobalt(II)	Cream	162 °C
W3	Bis[bis(4-hydroxy-3-methoxybenzylidene)thiourea-]iron(II)(II)	Violet	141 °C
W4	Bis[bis(4-hydroxy-3-methoxybenzylidene)thiourea-]copper(II)	Brown	121 °C
W5	Bis[bis(4-hydroxy-3-methoxybenzylidene)thiourea-]nickel(II)	Gray	118 °C
T1	Bis[bis(4-hydroxy-3-iodo-5-methoxybenzylidene)thiourea-]zinc(II)	Pale Brown	160 °C
T2	Bis[bis(4-hydroxy-3-iodo-5-methoxybenzylidene)thiourea-]copper(II)	Gray	230 °C
T3	Bis[bis(4-hydroxy-3-iodo-5-methoxybenzylidene)thiourea-]iron(II)	Faint Brown	150 °C
T4	Bis[bis(4-hydroxy-3-iodo-5-methoxybenzylidene)thiourea-]nickel(II)	Cream	185 °C
T5	Bis[bis(4-hydroxy-3-iodo-5-methoxybenzylidene)thiourea-]cobalt(II)	Purple	159 °C
S1	Bis[bis(3-bromo-4-hydroxy-5-methoxybenzylidene)thiourea-]iron(II)	Gray	161 °C
S2	Bis[bis(3-bromo-4-hydroxy-5-methoxybenzylidene)thiourea-]cobalt(II)	Faint Brown	163 °C
S3	Bis[bis(3-bromo-4-hydroxy-5-methoxybenzylidene)thiourea-]nickel(II)	Brown	162 °C
S4	Bis[bis(3-bromo-4-hydroxy-5-methoxybenzylidene)thiourea-]copper(II)	Faint Brown	142 °C
S5	Bis[bis(3-bromo-4-hydroxy-5-methoxybenzylidene)thiourea-]zinc(II)	Brown	164 °C

The stretching frequencies appear for C-O functional group region are 1268-1385 cm^{-1} . IR stretching frequencies for C=S bond are found to be in the region 1143-1260 cm^{-1} . The medium intensity but relatively shaped (instead of very strong and diffuse) ν_{OH} bands may be the consequence of the fact that only the half of the phenolic hydroxyls are deprotonated to compensate the charges of the central metal cations, and the residual OH groups are located in well defined hydrogen bound network.

Electronic absorption spectrum

DMSO solvent is used for UV-visible spectrum of complexes. The peaks are observed at $\lambda_{\text{max}} = 362 \text{ nm}$ for bis[(4-hydroxy-3-methoxybenzylidene)(4-oxy-3-methoxybenzylidene)thiourea]zinc(II) (W1); $\lambda_{\text{max}} = 363 \text{ nm}$ for bis[(4-hydroxy-3-methoxybenzylidene)(4-oxy-3-methoxybenzylidene)thiourea]cobalt(II) (W2); $\lambda_{\text{max}} = 478 \text{ nm}$ for bis[(4-hydroxy-3-methoxybenzylidene)(4-oxy-3-methoxybenzylidene)thiourea]iron(II) (W3); $\lambda_{\text{max}} = 324 \text{ nm}$ for bis[(4-hydroxy-3-methoxybenzylidene)(4-oxy-3-methoxybenzylidene)thiourea]copper(II) (W4); $\lambda_{\text{max}} = 362 \text{ nm}$ for bis[(4-hydroxy-3-methoxybenzylidene)(4-oxy-3-methoxybenzylidene)thiourea]nickel(II) (W5); $\lambda_{\text{max}} = 325 \text{ nm}$ for bis[(4-hydroxy-3-iodo-5-methoxybenzylidene)(4-oxy-3-iodo-5-methoxybenzylidene)thiourea]zinc(II) (T1); $\lambda_{\text{max}} = 326 \text{ nm}$ for bis[(4-hydroxy-3-iodo-5-methoxybenzylidene)(4-oxy-3-iodo-5-methoxybenzylidene)thiourea]copper(II) (T2); $\lambda_{\text{max}} = 412 \text{ nm}$ for bis[(4-hydroxy-3-iodo-5-methoxybenzylidene)(4-oxy-3-iodo-5-methoxybenzylidene)thiourea]iron(II) (T3); $\lambda_{\text{max}} = 325 \text{ nm}$ for bis[(4-hydroxy-3-iodo-5-methoxybenzylidene)(4-oxy-3-iodo-5-methoxybenzylidene)thiourea]nickel(II) (T4); $\lambda_{\text{max}} = 326 \text{ nm}$ for bis[(4-hydroxy-3-iodo-5-methoxybenzylidene)(4-oxy-3-iodo-5-methoxybenzylidene)thiourea]cobalt(II) (T5); $\lambda_{\text{max}} = 326 \text{ nm}$ for bis[(3-bromo-4-hydroxy-5-methoxybenzylidene)(3-bromo-4-oxy-5-methoxybenzylidene)thiourea]iron(II) (S1); $\lambda_{\text{max}} = 326 \text{ nm}$ for bis[(3-bromo-4-hydroxy-5-methoxybenzylidene)(3-bromo-4-oxy-5-methoxybenzylidene)thiourea]cobalt(II) (S2); $\lambda_{\text{max}} = 325 \text{ nm}$ for bis[(3-bromo-4-hydroxy-5-methoxybenzylidene)(3-bromo-4-oxy-5-methoxybenzylidene)thiourea]nickel(II) (S3); $\lambda_{\text{max}} = 325 \text{ nm}$ for bis[(3-bromo-4-hydroxy-5-methoxybenzylidene)(3-bromo-

4-oxy-5-methoxybenzylidene)thiourea]copper(II) (S4); $\lambda_{\text{max}} = 362 \text{ nm}$ for bis[(3-bromo-4-hydroxy-5-methoxybenzylidene)(3-bromo-4-oxy-5-methoxybenzylidene)thiourea]zinc(II) (S5) which were assignable to $\pi \rightarrow \pi^*$ transitions.

X-Ray diffraction studies

XRD study of bis[bis(4-hydroxy-3-methoxybenzylidene)thiourea-]nickel(II) were made on RIGAKU miniflex-II with Cu-K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$). The powder XRD patterns were recorded in the 2θ range between 10° and 80° with a step size of 0.02. The X-ray powder diffractogram of nickel(II) complex exhibits crystalline in nature. The X-ray powder diffractogram of Ni(II) complex [(C₃₄H₃₀N₄NiO₈S₂)] is given in (Figure 1). The diffractogram of Ni(II) complex showed eleven reflections with maxima at 2θ (12.88 $^\circ$) corresponding to d value 6.8781 \AA . [from Table 1 (W5)].

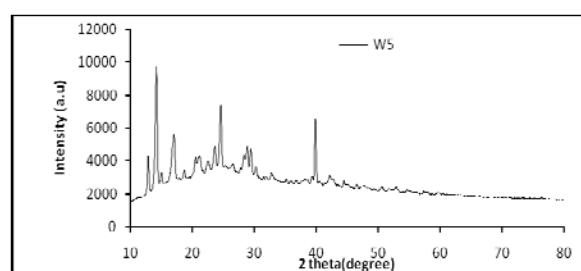


Figure 1. XRD pattern of Bis[bis(4-hydroxy-3-methoxybenzylidene)thiourea]nickel(II) complex (W5)

XRD study of the bis[bis(4-hydroxy-3-iodo-5-methoxybenzylidene)thiourea-]cobalt(II) were made on RIGAKU Miniflex-II with Cu-K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$). The powder XRD patterns were recorded in the 2θ range between 10° and 80° with a step size of 0.02. The X-ray powder diffractogram of cobalt (II) complex exhibits crystalline in nature. The X-ray powder diffractogram of cobalt(II) complex [C₃₄H₂₆CoI₄N₄O₈S₂] is given in (Figure 2). The diffractogram of Co(II) complex showed twenty three reflections with maxima at 2θ (29.5 $^\circ$) corresponding to d value 1.5706 \AA . [from Table 1 (T5)].

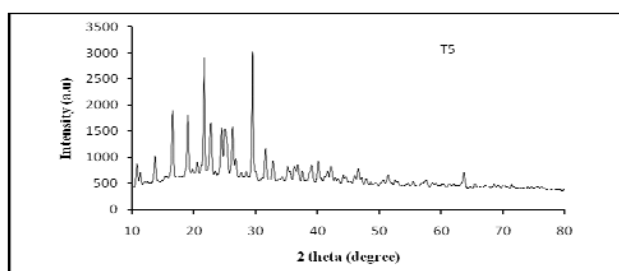


Figure 2. XRD pattern of bis[bis(4-hydroxy-3-iodo-5-methoxybenzylidene)thiourea-]cobalt(II) (T5)

XRD study of the bis[bis(3-bromo-4-hydroxy-5-methoxybenzylidene)thiourea-]iron(II) were made on RIGAKU miniflex-II with Cu-K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$). The powder XRD patterns were recorded in the 2θ range between 10° and 80° with a step size of 0.02° . The X-ray powder diffractogram of iron(II) complex exhibits crystalline in nature. The X-ray powder diffractogram of Fe(II) complex $[\text{C}_{34}\text{H}_{26}\text{Br}_4\text{FeN}_4\text{O}_8\text{S}_2]$ is given in (Figure 3). The diffractogram of Fe(II) complex showed twenty one reflections with maxima at 2θ (26.49°) corresponding to d value 2.9292 \AA . [Figure 3, Table 1 (S1)].

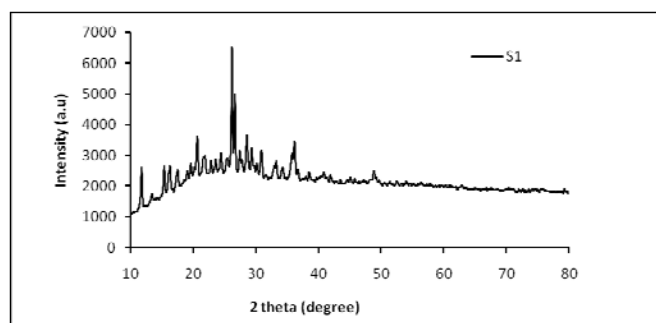


Figure 3. XRD pattern of Bis[bis(3-bromo-4-hydroxy-5-methoxybenzylidene)thiourea-]iron(II) (S1)

The complexes are probably polymers with octahedral coordination with chelate structure involving the phenolate groups but the complete elucidation of their structure requires further spectroscopical and single crystal X-ray diffraction studies.

Biological screening

The biological screening of synthesized compounds was discussed in two sections i.e. antibacterial activity, antifungal Activity.

Antibacterial activity

In this research work the antibacterial activity was studied, but the standardization of all the parameters of ligands and calculation of MLD for individual organism is necessary. The antibacterial activities of 15 complexes with bacterium *E. coli* were studied using agar cup method and compared with standard antibiotic penicillin. It was found that 3 complexes (T3, S5 and W4) showed considerable antibacterial activity. But complexes S5 showed significant antibacterial activity because the zone of inhibition showed by standard antibiotic penicillin was 21 mm while the complexes S5 26 mm zone of inhibition.

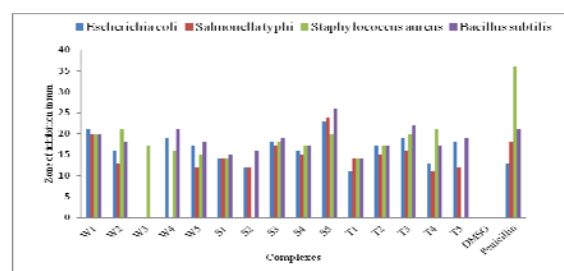


Figure 1. Antibacterial activity of novel metal complexes

Antibacterial activity of 15 complexes with bacterium *Salmonella typhi* were studied by agar cup method and compared with standard antibiotic penicillin. It was found that 2 complexes (W1 and S5) showed considerable antibacterial activity. But complexes S5 showed significant antibacterial activity. The zone of inhibition showed by standard antibiotic penicillin was 18mm while the complexes S5 24 mm zone of inhibition

The antibacterial activity of 15 complexes with bacterium *Staphylococcus aureus* were studied by agar cup method and compared with standard antibiotic penicillin. It was found that *staphylococcus aureus* was resistant to all the 15 complexes because the zone of inhibition obtained by standard penicillin was higher as compared to complexes.

Table 2. Antibacterial activity of novel metal complexes

Label	<i>Escherichia coli</i>	<i>Salmonella typhi</i>	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>
W1	21 mm	20 mm	20 mm	20 mm
W2	16 mm	13 mm	21 mm	18 mm
W3	0 mm	0 mm	17 mm	0 mm
W5	17 mm	12 mm	15 mm	18 mm
S1	14 mm	14 mm	14 mm	15 mm
S2	12 mm	12 mm	0 mm	16 mm
S3	18 mm	17 mm	18 mm	19 mm
S4	16 mm	15 mm	17 mm	17 mm
S5	23 mm	24 mm	20 mm	26 mm
T1	11 mm	14 mm	14 mm	14 mm
T2	17 mm	15 mm	17 mm	17 mm
T3	19 mm	16 mm	20 mm	22 mm
T4	13 mm	11 mm	21 mm	17 mm
T5	18 mm	12 mm	0 mm	19 mm
DmsO	0 mm	0 mm	0 mm	0 mm
Penicillin	13 mm	18 mm	36 mm	21 mm

The antibacterial activity of 15 complexes with bacterium *Bacillus subtilis* were studied by agar cup method and compared with standard antibiotic penicillin. It was found that 3 complexes (W4, T3 and S5) showed considerable antibacterial activity. But complexes S5 showed significant antibacterial activity because the zone of inhibition showed by standard antibiotic penicillin was 18 mm while the complexes S5 26 mm zone of inhibition.

In this study all the 15 complexes were tested. Complex S5 showed significant activity against three test cultures i.e. *E. coli*, *Salmonella typhi* and *Bacillus subtilis*, but no complex active against *Staphylococcus aureus* (Table 2).

Table 2. Antibacterial activity of novel metal complexes

Sr.No.	Label	<i>Escherichia coli</i>	<i>Salmonella typhi</i>	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>
1	W1	21 mm	20 mm	20 mm	20 mm
2	W2	16 mm	13 mm	21 mm	18 mm
3	W3	00 mm	00 mm	17 mm	00 mm
4	W4	19 mm	00 mm	16 mm	21 mm
5	W5	17 mm	12 mm	15 mm	18 mm
6	S1	14 mm	14 mm	14 mm	15 mm
7	S2	12 mm	12 mm	00 mm	16 mm
8	S3	18 mm	17 mm	18 mm	19 mm
9	S4	16 mm	15 mm	17 mm	17 mm
10	S5	23 mm	24 mm	20 mm	26 mm
11	T1	11 mm	14 mm	14 mm	14 mm
12	T2	17 mm	15 mm	17 mm	17 mm
13	T3	19 mm	16 mm	20 mm	22 mm
14	T4	13 mm	11 mm	21 mm	17 mm
15	T5	18 mm	12 mm	00 mm	19 mm
16	DMSO	00 mm	00 mm	00 mm	00 mm
17	Penicillin	13 mm	18 mm	36 mm	21 mm

Table 3. Antifungal activities of novel metal complex derivatives

Sr. No.	Compounds	<i>Aspergillus niger</i>	<i>Penicillium chrysogenum</i>	<i>Fusarium moneliforme</i>	<i>Aspergillus flavus</i>
1	W1	RG	-ve	-ve	-ve
2	W2	+ve	-ve	-ve	RG
3	W3	RG	-ve	-ve	RG
4	W4	RG	-ve	-ve	-ve
5	W5	RG	-ve	+ve	RG
6	S1	-ve	-ve	-ve	-ve
7	S2	-ve	-ve	-ve	RG
8	S3	-ve	-ve	-ve	-ve
9	S4	-ve	-ve	-ve	-ve
10	S5	-ve	-ve	-ve	-ve
11	T1	RG	-ve	-ve	RG
12	T2	RG	-ve	-ve	-ve
13	T3	-ve	-ve	-ve	-ve
14	T4	RG	-ve	-ve	RG
15	T5	RG	-ve	-ve	RG
16	Grysofulvin	-ve	-ve	-ve	-ve
17	Blank	+ve	+ve	+ve	+ve

+ve – Growth (no antifungal activity); ve – No growth (antifungal activity observed); RG – reduced growth

Antifungal Activity

Antifungal activity of 15 metal complexes was tested for antifungal activity of four test fungal cultures by using poison plate technique. Complexes (S1, S2, S3, S4 S5 and T3) showed antifungal activity, Eight complexes (W1, W3, W4 W5, T1, T2 T4 and T5) reduces the growth while remaining one complexes W2 support the growth of fungal culture that mean serve as nutrient for *Aspergillus flavus*.

Penicillium chrysogenum and *Fusarium moneliforme* are more susceptible than the other two test fungal culture *Aspergillus niger* and *Aspergillus flavus*. *Aspergillus flavus* was susceptible for complexes (W1, W4, S1, S3, S4, S5, T2 and T3) while reaming reduces the growth.

In this study found that complexes S1, S2, S3, S4 and S5 shows significant antifungal activity against all the four tested fungal culture (Table 3).

EXPERIMENTAL SECTION

Preparation of bis(bis(4-hydroxy-3-methoxybenzylidene)thiourea-H)cobalt(II) (W2)

A mixture of Schiff base (1E,3E)-1,3-bis(4-hydroxy-3-methoxybenzylidene)thiourea 6.88 g, 2 mmol) and cobalt nitrate (1.82 g, 1 mmol) dissolved in ethanol (5 ml) was refluxed for 6 hours. The pH of solution was adjusted to 7-8

using alcoholic ammonia solution. The progress of reaction mixture is monitored by thin layer chromatography (TLC) using petroleum ether: ethyl acetate (7:3 ml) elute. The coloured products were isolated after reduction of volume by evaporation. It was filtered of washed with ethanol, dried under vacuum and recrystallized in ethanol. Spectral data for synthesized complexes

Bis[(4-hydroxy-3-methoxybenzylidene)(4-oxy-3-methoxybenzylidene)thiourea]zinc(II) (W1): FTIR (KBr, cm^{-1}): 3640 (Ar-OH), 3150 (Ar-C-H), 2970 (C-H), 1649 (C=N), 1238 (C-O phenolic), 1165 (C=S), 434 (Zn-N) cm^{-1} ; UV-Vis: $\lambda_{\text{max}} = 362 \text{ nm}$.

Bis[(4-hydroxy-3-methoxybenzylidene)(4-oxy-3-methoxybenzylidene)thiourea]cobalt(II) (W2): FTIR (KBr, cm^{-1}): 3216 (Ar-OH), 3050 (Ar-C-H), 2978 (C-H), 1648 (C=N), 1236 (C-O phenolic), 1162 (C=S), 429 (Co-N) cm^{-1} ; Anal. Calc. for $\text{C}_{34}\text{H}_{30}\text{CoN}_4\text{O}_8\text{S}_2$: C: 54.76, H: 4.06, N: 7.51, Found: C: 54.57, H: 3.74, N: 7.55; UV-Vis: $\lambda_{\text{max}} = 363 \text{ nm}$.

Bis[(4-hydroxy-3-methoxybenzylidene)(4-oxy-3-methoxybenzylidene)thiourea]iron(II) (W3): FTIR (KBr, cm^{-1}): 3206 (Ar-OH), 3010 (Ar-C-H), 2839 (C-H), 1672 (C=N), 1272 (C-O phenolic), 1143 (C=S), 475 (Fe-N) cm^{-1} ; UV-Vis: $\lambda_{\text{max}} = 478 \text{ nm}$.

Bis[(4-hydroxy-3-methoxybenzylidene)(4-oxy-3-methoxybenzylidene)thiourea]copper(II) (W4): FTIR (KBr, cm^{-1}): 3233 (Ar-OH), 3140 (Ar-C-H), 2839 (C-H), 1679 (C=N), 1385 (C-O phenolic), 1207 (C=S), 411 (Cu-N) cm^{-1} ; UV-Vis: $\lambda_{\text{max}} = 324 \text{ nm}$.

Bis[(4-hydroxy-3-methoxybenzylidene)(4-oxy-3-methoxybenzylidene)thiourea]nickel(II) (W5): FTIR (KBr, cm^{-1}): 3205 (Ar-OH), 3045 (Ar-C-H), 2940 (C-H), 1648 (C=N), 1343 (C-O phenolic), 1274 (C=S), 430 (Ni-N) cm^{-1} ; Anal. Calc. for $\text{C}_{34}\text{H}_{30}\text{NiO}_8\text{S}_2$: C: 54.78, H: 4.06, N: 7.51, Found: C: 54.60, H: 4.54, N: 7.49; UV-Vis: $\lambda_{\text{max}} = 362 \text{ nm}$.

Bis[(4-hydroxy-3-iodo-5-methoxybenzylidene)(4-oxy-3-iodo-5-methoxybenzylidene)thiourea]zinc(II) (T1): FTIR (KBr, cm^{-1}): 3200 (Ar-OH), 3050 (Ar-C-H), 2942 (C-H), 1665 (C=N), 1295 (C-O phenolic), 1257 (C=S), 670 (C-I), 435 (Zn-N) cm^{-1} ; Anal. Calc. for $\text{C}_{34}\text{H}_{26}\text{ZnI}_4\text{O}_8\text{N}_4\text{S}_2$: C: 32.52, H: 2.09, N: 4.46, Found: C: 32.57, H: 2.54, N: 4.35; UV-Vis: $\lambda_{\text{max}} = 325 \text{ nm}$.

Bis[(4-hydroxy-3-iodo-5-methoxybenzylidene)(4-oxy-3-iodo-5-methoxybenzylidene)thiourea]copper(II) (T2): FTIR (KBr, cm^{-1}): 3499 (Ar-OH), 3105 (Ar-C-H), 2846 (C-H), 1666 (C=N), 1293 (C-O phenolic), 1258 (C=S), 672 (C-I), 410 (Cu-N) cm^{-1} ; UV-Vis: $\lambda_{\text{max}} = 326 \text{ nm}$.

Bis[(4-hydroxy-3-iodo-5-methoxybenzylidene)(4-oxy-3-iodo-5-methoxybenzylidene)thiourea]iron(II) (T3): FTIR (KBr, cm^{-1}): 3485 (Ar-OH), 3150 (Ar-C-H), 2915 (C-H), 1667 (C=N), 1268 (C-O phenolic), 1237 (C=S), 672 (C-I), 497 (Fe-N) cm^{-1} ; UV-Vis: $\lambda_{\text{max}} = 412 \text{ nm}$.

Bis[(4-hydroxy-3-iodo-5-methoxybenzylidene)(4-oxy-3-iodo-5-methoxybenzylidene)thiourea]nickel(II) (T4): FTIR (KBr, cm^{-1}): 3498 (Ar-OH), 3000 (Ar-C-H), 2845 (C-H), 1666 (C=N), 1295 (C-O phenolic), 1257 (C=S), 670 (C-I), 434 (Ni-N) cm^{-1} ; UV-Vis: $\lambda_{\text{max}} = 325 \text{ nm}$.

Bis[(4-hydroxy-3-iodo-5-methoxybenzylidene)(4-oxy-3-iodo-5-methoxybenzylidene)thiourea]copper(II) (T5): FTIR (KBr, cm^{-1}): 3207 (Ar-OH), 3050 (Ar-C-H), 2845 (C-H), 1665 (C=N), 1295 (C-O phenolic), 1257 (C=S), 671 (C-I), 433 (Co-N) cm^{-1} ; Anal. Calc. for $\text{C}_{34}\text{H}_{26}\text{CuI}_4\text{N}_4\text{O}_8\text{S}_2$: C: 32.52, H: 2.09, N: 4.46, Found: C: 32.69, H: 2.24, N: 4.35; UV-Vis: $\lambda_{\text{max}} = 326 \text{ nm}$.

Bis[(3-bromo-4-hydroxy-5-methoxybenzylidene)(3-bromo-4-oxy-5-methoxybenzylidene)thiourea]iron(II) (S1): FTIR (KBr, cm^{-1}): 3302 (Ar-OH), 3055 (Ar-C-H), 2852 (C-H), 1676 (C=N), 1292 (C-O phenolic), 1200 (C=S), 680 (C-Br), 458 (Fe-N) cm^{-1} ; Anal. Calc. for $\text{C}_{34}\text{H}_{26}\text{Br}_4\text{FeN}_4\text{O}_8\text{S}_2$: C: 38.59, H: 2.48, N: 5.29; Found: C: 38.60, H: 2.54, N: 5.69; UV-Vis: $\lambda_{\text{max}} = 326 \text{ nm}$.

Bis[(3-bromo-4-hydroxy-5-methoxybenzylidene)(3-bromo-4-oxy-5-methoxybenzylidene)thiourea]cobalt(II) (S2): FTIR (KBr, cm^{-1}): 3323 (Ar-OH), 3060 (Ar-C-H), 2931 (C-H), 1674 (C=N), 1290 (C-O phenolic), 1170 (C=S), 680 (C-Br), 412 (Co-N) cm^{-1} ; Anal. Calc. for $\text{C}_{34}\text{H}_{26}\text{Br}_4\text{CoN}_4\text{O}_8\text{S}_2$: C: 38.48, H: 2.47, N: 5.29, Found: C: 38.57, H: 2.54, N: 5.35; UV-Vis: $\lambda_{\text{max}} = 326 \text{ nm}$.

Bis[(3-bromo-4-hydroxy-5-methoxybenzylidene)(3-bromo-4-oxy-5-methoxybenzylidene)thiourea]nickel(II) (S3): FTIR (KBr, cm^{-1}): 3298 (Ar-OH), 3100 (Ar-C-H), 2850 (C-H), 1674 (C=N), 1290 (C-O phenolic), 1155 (C=S), 678 (C-Br), 441 (Ni-N) cm^{-1} ; UV-Vis: $\lambda_{\text{max}} = 325 \text{ nm}$.

Bis[(3-bromo-4-hydroxy-5-methoxybenzylidene)(3-bromo-4-oxy-5-methoxybenzylidene)thiourea]copper(II) (S4): FTIR (KBr, cm^{-1}): 3274 (Ar-OH), 3102 (Ar-C-H), 2982 (C-H), 1675 (C=N), 1291 (C-O phenolic), 1159 (C=S), 680 (C-Br), 436 (Cu-N) cm^{-1} ; UV-Vis: $\lambda_{\text{max}} = 325 \text{ nm}$.

Bis[(3-bromo-4-hydroxy-5-methoxybenzylidene)(3-bromo-4-oxy-5-methoxybenzylidene)thiourea]zinc(II) (S5): FTIR (KBr, cm^{-1}): 3410 (Ar-OH), 3140 (Ar-C-H), 2924 (C-H), 1676 (C=N), 1290 (C-O phenolic), 1159 (C=S), 680 (C-Br), 418 (Zn-N) cm^{-1} ; UV-Vis: $\lambda_{\text{max}} = 362 \text{ nm}$.

CONCLUSION

In conclusion, series of novel metal complex derivatives using thiourea schiff bases has been synthesized and screened for antibacterial and antifungal activities. Some of them metal complexes exhibits moderate to excellent antibacterial and antifungal activities. Synthesized compounds are characterized using infrared (FT-IR), electronic spectral (UV), elemental analysis, melting points and XRD analysis etc.

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REFERENCES

- Tupare, S. D., Bhagat, D. V., Dake, S. A., Pawar, R. P., *Int. J. Chem. Sci.*, **2012**, 10(4), 1-7.
- Pawar, R. P., Andurkar, N. M., Vibhute, Y. B., *J. Indian Chem. Soc.*, **1999**, 76, 271-272.
- More, S. V., Dongarkhadekar, D. V., Chavan, R. N., Jadhav, W. N., Bhusare, S. R., Pawar, R. P., *J. Indian Chem. Soc.*, **2002**, 79, 768-769.
- Kendrekar, P. S., Siddiqui, R. F., Patil, P. S., Bhusare, S. R., Pawar, R. P., *Indian J. Pharm. Sci.*, **2003**, 65, 313-315.

- ⁵Dhar, D. N.; Taploo, C. L., *J. Sci. Ind. Res.*, **1982**, *41*, 501-506.
- ⁶Przybylski, P., Huczyński, A., Pyta, K., Brzezinski, B., Bartl, F., *Curr. Org. Chem.*, **2009**, *13*, 124-148.
- ⁷Casassas, E., Izquierdo-ridora, A., Tauler, R., *J. Chem. Soc., Dalton Trans.*, **1990**, 2341-2345.
- ⁸De, B., Marbaniang, E. M., Kalita, R., Debnath, M., Das, M. C., Kalita, U., Lalfukmawia, S., Gupta, J. K., *J. Inst. Chemists (India)*, **2005**, *77*, 20-22.
- ⁹Brousse, B. N., Massa, R., Monglioni, A. G., Alho, M. M., D'Accorso, N., Gutkind, G., Moltrasio, G. Y., *J. Chilean Chem. Soc.*, **2004**, *49*, 45-49.
- ¹⁰Raman, M., Muthural, V., Ravichandran, S., Kulandaisamy, A., *Proc. Indian Acad. Sci. (Chem. Sci.)*, **2003**, *115(3)*, 161-167.
- ¹¹Mulwad, V. V., Shriodkar, J. M., *Indian J. Heterocycl. Chem.*, **2002**, *11*, 199-202.
- ¹²Chohan, Z. H., Farooq, M. A., Scoozafava, A., Supuran, C. T., *J. Enzym Inhib. Med. Chem.*, **2002**, *17*, 1-7.
- ¹³Shikkargol, R. K., Malikarjuna, N. N., Angadi, S. D., *Natl. Acad. Sci. Lett.*, **2001**, *24*, 39-43.
- ¹⁴More, P. G., Bhalvankar, R. B., Pattar, S. C., *J. Indian Chem. Soc.*, **2001**, *78*, 474-475.
- ¹⁵Bi, S., Li, G., *Synth. React. Inorg. Met.-Org. Chem.*, **1999**, *29*, 1829-1841.
- ¹⁶Desai, J. M., Desai, K. K., *Asian J. Chem.*, **1999**, *11*, 1071-1073.
- ¹⁷Sun, B., Chen, J., Hu, J. Y., Lix, J., *Chin. Chem. Lett.*, **2001**, *12*, 1043.
- ¹⁸Boghaei, D. M., Mohebi, S., *Tetrahedron*, **2002**, *58*, 5357.
- ¹⁹Liu, J., Wu, B., Zhang, B., Liu, Y., *Turk. J. Chem.*, **2006**, *30*, 41.
- ²⁰Britovsek, G. J. P., Gibson, V. V., Mastroianni, S., Oakes, D. C. H., Red, S. C., Solan, G. A., White, A. J. P., Williams, D. J., *Eur. J. Inorg. Chem.*, **2000**, *2*, 431.
- ²¹Budakoti, A., Abid, M., Azam, A., *Eur. J. Med. Chem.*, **2006**, *41*, 63.
- ²²Jin, V. X., Tan, S. I., Ranford, J. D., *Inorg. Chim. Acta.*, **2005**, *358*, 677-686.
- ²³Mehta, N. K., Agarwala, V. S., *Int. Corros. Cong. Proc.*, **1996**, *13*, 1.

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