Review Article

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The Antibacterial Activities of Thiazoles, Substituted Thiazoles and Their Metal Complexes- A Review.

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Abstract
Pathogenic bacterial species cause infectious diseases like tetanus, typhoid fever, diphtheria, syphilis, cholera, food borne allergies, leprosy and tuberculosis and therefore they are major cause of human death and disease. Thiazoles, thiazole like compounds and their derivatives are a group of organic species which shows very good antibacterial activities. In the present article an extensive review is done on antibacterial and antifungal activities of thiazole, substituted thiazole and thiazole like compounds and also Schiff bases of thiazole and substituted thiazoles. It is also observed that upon complexation the antibacterial and antifungal property of the Schiff bases increases many folds.

Key Words
Aminothiazoles, substituted thiazoles, antibacterial activity, antifungal activity**.**

Introduction

Pathogenic bacteria are one of the major causes of human death and disease. Pathogenic bacteria cause infectious diseases like tetanus, typhoid fever, diphtheria, syphilis, cholera, food borne allergies, leprosy and tuberculosis [1,2,3]. The use of antibiotics for the control of infectious diseases are among the most potent and successful achievements of modern science and technology. But excess use of antibiotics against bacterial infection increases microbial resistance to antibiotics [4, 5]. Therefore nowadays it is necessary to explore new compounds with potential effects against pathogenic bacteria. There are some organic materials especially heterocyclic compounds which can play an important role in regulating bacterial activities. Among the heterocyclic compounds thiazoles and the derivatives of thiazoles are a group of organic species which shows remarkable antimicrobial activities. This may be due to the fact that they have strong aromaticity in their ring system. As a result of which they have immense *in vivo* stability and also their ring systems are structurally comparable to the imidazolyl moieties of the histidyl present in proteins[6]. The N=C–S moieties present in the thiazole unit has been used in anti-bacterial studies. Therefore thiazole ring is a very important compound in nature. It is present in thiamine coenzyme and tetra hydrothiazole is an important part in the skeleton of penicillin. Hence the thiazole derivatives, particularly the aminothiazoles, have been extensively

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used in pharmaceutical applications due to their wide fungicidal, antimicrobial, anti-TB, anti-cancer and anti-inflammatory activities[7-9]. Patten and coworkers have reviewed the synthesis of a variety of the aminothiazoles and substituted aminothiazoles and evaluated their various biological activities like anti-diabetic, anti-inflammatory and anti fungal activities[10].

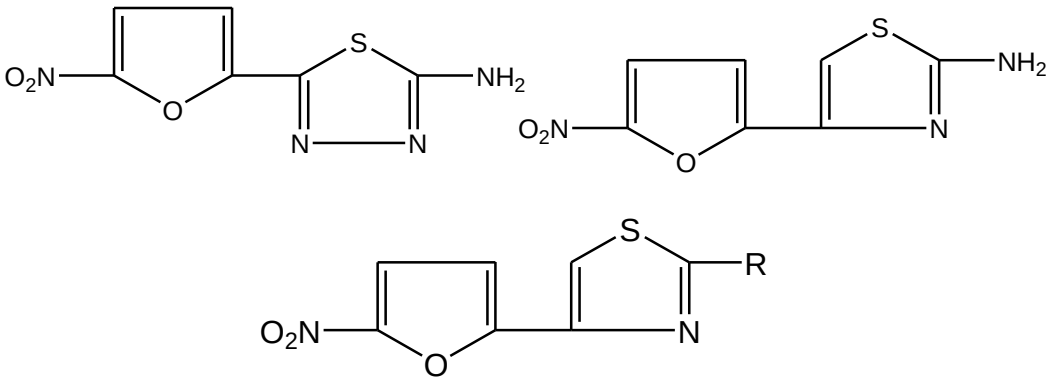
Schiff bases are the important compound because of their versatile nature in chemical permutation and wide range of biological activities and industrial application[11]. They can be also prepared through simple methods by condensing carbonyl compounds with amines. They have been found to posses the pharmacological activities such as antimalarial, anticancer, antibacterial,antifungal,antitubercular, antiinflammetery, antimicrobial, and antiviral etc[12-18]. It can be verified from literature survey that bioinorganic chemistry is developed around coordination compounds present in living systems[19]. Among coordination compounds, transition metal complexes of Schiff bases have attracted wide attention due to their application in catalysis and well known as biological activity furthermore Schiff base complexes have also similarity with the prosthetic part of proteins and enzymes. Pfeiffer and co-workers observed that the properties of Schiff base complexes depend on the nature of the metal ion as well as on the nature of the ligands and also varying the ligands desirable electronic environment can be created around the metal ion[20]. Thus there is a continuing interest in worldwide for the chemistry Schiff bases and their complexes due to their preparative convenience and innumerable applications in catalysis and of many biological systems[21-26]. When Schiff bases are prepared from aminothiazoles, their complex forming property enhanced and their antibacterial property remain intact. It is also a well known fact that upon complexation with metal ions their antibacterial, antiviral and antifungal properties increase many folds[27-31]. Therefore Schiff-bases of amino thiazoles and their transition metal complexes are found to be of great interest in co-ordination chemistry as well as pharmaceuticals chemistry [32-35].

The aim of this article is to provide a brief review on the biological activity of Schiff bases and their metal complexes obtained from heterocyclic compounds especially from thiazoles, thiazole like compounds and their derivatives. Also compare their antimicrobial efficiency with simple thiazoles and their derivatives.

Biological Activity of Thiazoles and its Derivatives

Patten et al. prepared several substituted 4- chloro or 4- methoxy 2-amino thiazoles and studied their anti bacterial activity against *Escherichia coli* and *Staphylococcus aureus* and antifungal activity against *Candida albicans* and *Aspergillus niger*[10]. Also compare their antibacterial and antifungal activities against some known chemotherapeutic agent like norfloxacin, grieseofulvin and DMF. It was observed that the substituted

thiazoles have very good antibacterial and antifungal activity against all the tested samples where as chemotherapeutic agents are active against some specific samples. The comparative results are presented in Table-1. Sherman and Dicken[36] have reported a series of 2-amino-4(5-nitro-2-furyl) thiazole and their chloro, hydroxyl and methoxy derivatives (Figures 1). The compounds were tested for the antibacterial activity *in vitro* and found effective in control of experimental infection in mice. Pronounced activities are observed against *Escherichia coli*, *Salmonella* and *Staphylococcus aureus*. 2-Aminothiazole and its acetyl derivative are effective in the control of mouse infection when applied either in the form of oral or intramuscular route. Similarly the antibacterial properties of the compounds of hydroxyaryliminomethyl thiazole, hydroxyl-naphthylthiazol-yl thiazolidene and α-substituted benzylaminothiazole and their derivatives were reported[37-39].



R= -H, -CH_3, -NH_2, -NHC_6H_5, -SCH_3, -SC_2H_5

Fig. 1: Structure of 2-amino-4(5-nitro-2-furyl) thiazoles and their derivatives.

Heterocyclic urea derivatives have a promising affinity against the *Staphylococcus aureus* bacteria. Liebig and coworkers[40] have reported the ureas of 2-aminothiazoles as an active antiviral agent. It was reported by Dumas and coworkers[41] that, the urea derivatives of 5-aminopyrazole or 2-aminothiazoles acted as a potent inhibitor of P-38 Kinease virus. Kane and his research group[42] have prepared a variety of heterocyclic ureas (Figures 2) with *in vitro* activity against *Staphylococcus aureus*. The activity became more pronounced by increasing the solubility of the compounds.

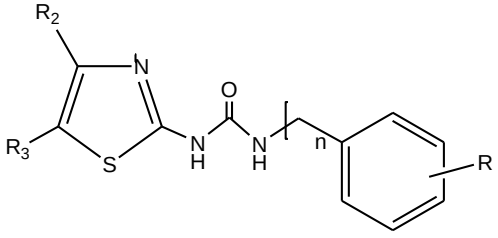


Fig. 2: Structure of aminothiazole ureas.

Vukovic and coworkers[43] have prepared aminothiazoles and coumarin derivatives. The coumarin compounds showed biological activities[44-51]. Vukovic and coworkers have reported the synthesis of a series of 2-aminothiazole derivatives of 4-hydroxyl-chromene-2-one (Figures 3) and tested the antibacterial and antifungal activities. All the compounds showed moderate antibacterial properties. *Echerichia coli* were the least sensitive towards all the compounds. But all the compounds were active against *Pseudomonal glycinea*. On the contrary, the synthesized compounds exhibited better antifungal behavior.

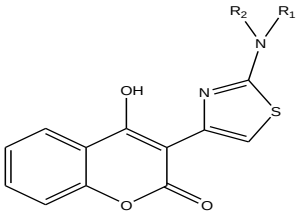
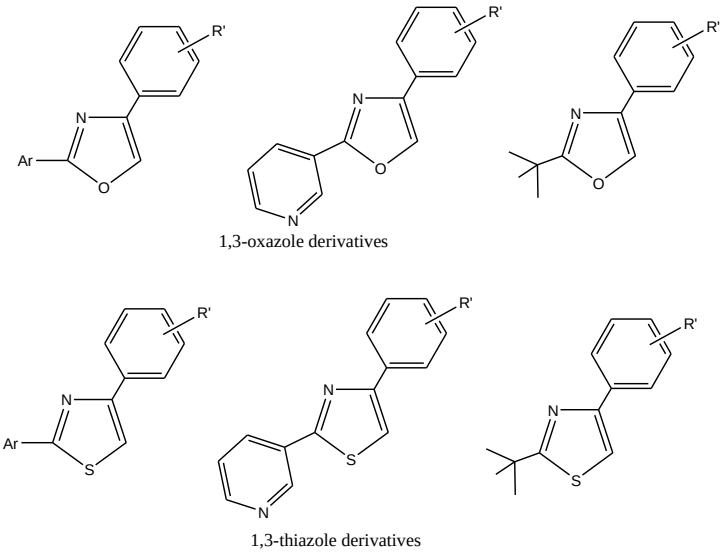


Fig. 3: Structure of 2-aminothiazole derivatives of 4-hydroxy-chromene-2-one.

Kaspady[52] and group synthesized 2-substituted aryl, heteroaryl and alkyl, 4-substituted aryl 1,3-oxazoles and thiazoles and tested their in-vitro antibacterial properties against two gram-positive and two gramnegative strains of cultured organisms such as *Bacillus subtilis, Staphylococcus aureus, Escherichia coli, Klebsiella pneumoniae.* They observed that thethiazole analogs have shown comparatively good antibacterial activity in comparison to their bioisostere counterpart oxazole analogs.



Ar= p-$COOCH_3$-C_6H_4 or m-OCH_3 p-NH_2-C_6H_3 or m-Cl p-NO_2-C_6H_3 or p-NH_2-C_6H_4

R'= Br or Cl

Fig. 4: Structure of substituted 1, 3-oxazole and 1,3-thiazole derivatives.

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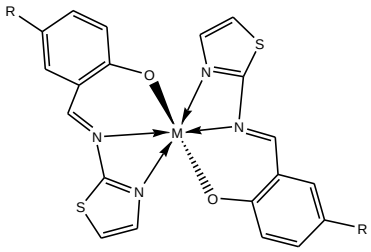
The Schiff-bases and their transition metal complexes are found to be of great interest in coordination chemistry as well as pharmaceutical chemistry[32-35]. The effects of Schiff bases and metal complexes have been extensively studied. A number of reviewers also appeared describing the coordination chemistry of the Schiff bases complexes[53-55]. But the pharmaceutical properties of these metal complexes are not discussed widely. Due to the presence of the active binding sites, they show the properties of complexation with diverse metal ions. Many reports have been based on the biological roles of the compounds when complexed with Cu (II), Ni (II), and Co (II), Zn (II) ions[56-62]. Several research groups have reported the enhancement of the biological activities of the thiazole and substituted thiazoles upon complexation[63-66]. The connected metal centers in such biologically active molecules involve in different functions such as oxygen transport, DNA inhibitor, enzymatic activity, and electron transfer processes[67-71]. The metal complexes are used as therapeutic tools for antibacterial, antiviral and anticancer drugs[72-73]. It has been reported by Kirschner and coworker[74-75] that the interaction between the metal ions from the ligand with cancer associated virus is an important route to use the metal complexes as the tools for anticancer therapy. The pharmaceutical properties of the ring system enhanced many fold, when functional groups which interact with biological receptor are attached to them[76]. A number of thiazole derivatives have been synthesized by Chohan from the condensation reaction between 2-aminothiazole with substituted salicylaldehyde (R = -H, -CH_3, -OCH_3, -NO_2 and -Cl) (Figures 4)[30, 77]. The Schiff bases formed metal complexes with Cu (II), Ni (II) and Zn (II). A comparative account of the bacterial activities of Schiff bases and their metal complexes towards *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Klebsiella pneumoniae* have been made. It was reported that, the metal complexes show antibacterial activities many times more than the Schiff bases.

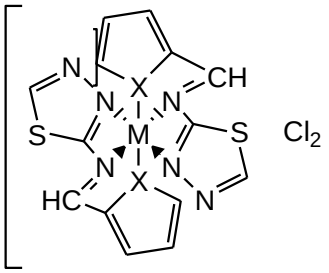


M = Ni(II), Cu(II), Zn(II) R = H, CH3, OCH3, NO2, Cl

Fig. 5: Structure of metal complex of 2-aminothiazole with substituted salicylaldehyde.

Thiazole derivatives complexed with furan, thiophene and pyrrole moieties were prepared by Chohan and Kause (Figures 5) by condensing 2-aminothiazole with furan, thiophene and pyrrole-2-carboxylaldehyde to give tridentate Schiff base ligands[78]. The ligands formed $[M(L)_2]X$ type metal complexes with Co(II), Cu(II), Ni(II) and Zn(II) ions. The

antibacterial activities of the Schiff bases as well as metal complexes were studied. It is observed that, the Schiff base complexes have stronger antibacterial properties in comparison to the corresponding Schiff bases. The above observations are summarized in the table-2 and table-3. It may be concluded that aminothiazole Schiff bases have very good biological properties against various bacterial species and this property increases many folds upon complexation with various metal ions.



L^1; X= O
L^2; X= S
L^3; X= NH

M= Cu(II), Ni(II), Co(II), Zn(II)

Fig. 6: Structure of metal complex of compounds of aminothiazole condensed furan, thiophene and pyrrole moieties.

The anions have a great effect against the bacterial activities. Chohan has evaluated the participating role of the anions on the antibacterial properties of the metal complexes of ligand-7 (L_7), ligand-8 (L_8) and ligand-11 (L_{11}) of table-2 against the bacterial species *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* [79-80]. The activity of the anions followed NO_3^- > $C_2O_4^{2-}$ > $CH_3CO_2^-$ > CI^- > SO_4^{2-} sequence. Comparative results of various metal complexes containing the above anions are giving in the Table-4.

Conclusion

Thiazoles and the substituted thiazoles are playing a great role as antibacterial, antifungal, antitumor species. Schiff bases of thiazole and their derivatives have also show very good biological activity against the above microorganisms. Upon complexation, the antibacterial activity of these Schiff bases increases many folds. We have precisely reported the data in tabular form to show the activity of the thiazoles and their derivatives. We have synthesized several aminothiazole resins and used them for purification of water. The studies on antibacterial properties of polymeric resins containing aminothiazole Schiff bases are rare in the literature. Our aim is to study the antibacterial property of those polymeric Schiff bases and their metal complexes. The result of these investigations will be reported in our further communications.

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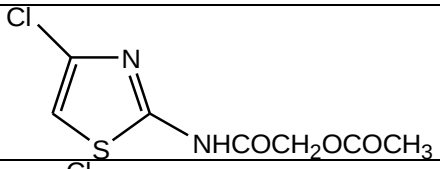
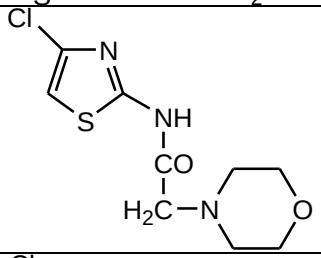
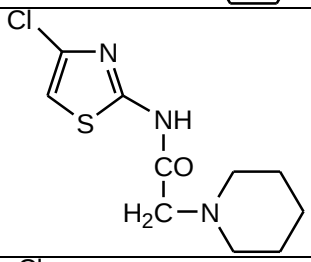
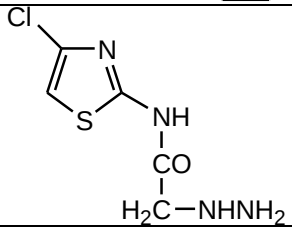
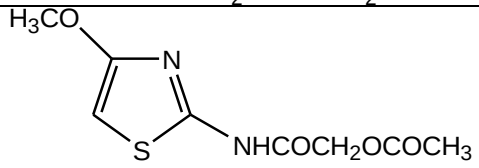
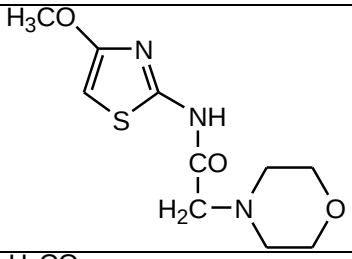
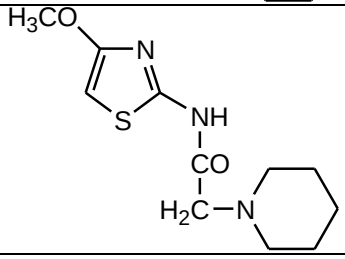
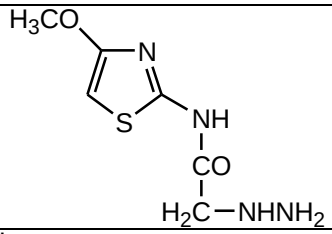
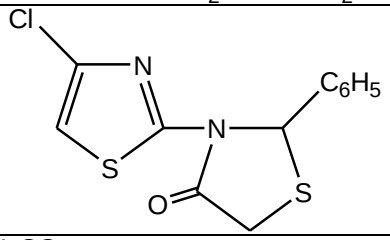
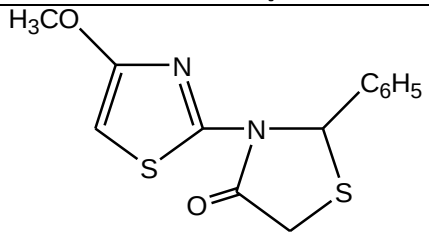
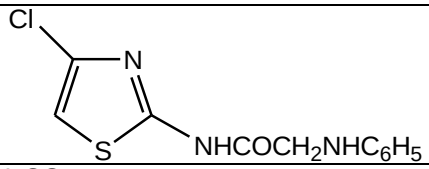
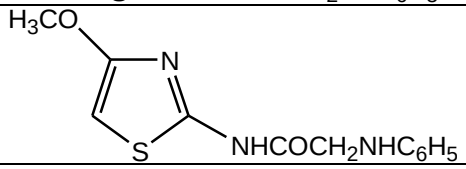
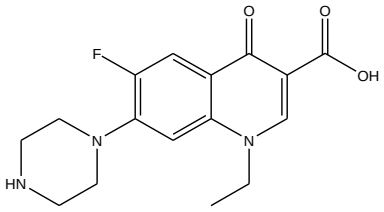
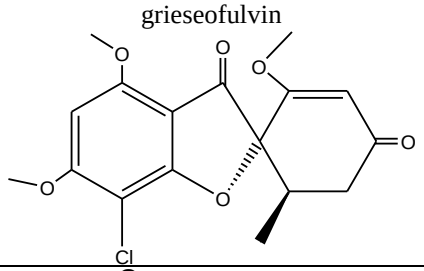
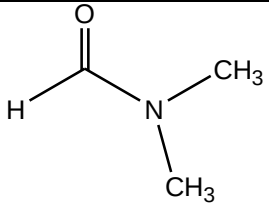
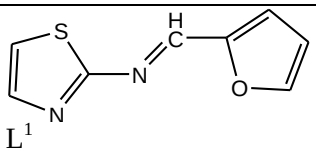
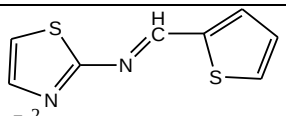
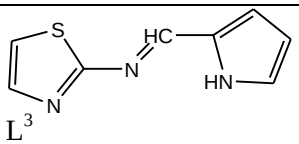
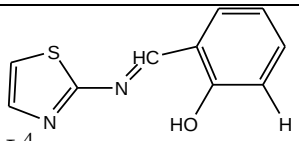
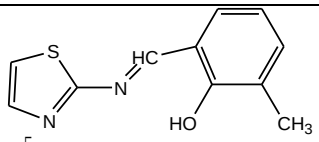
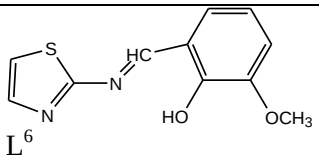
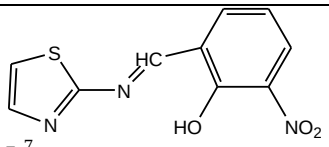
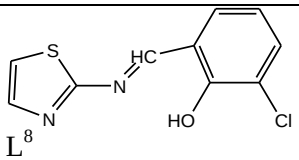
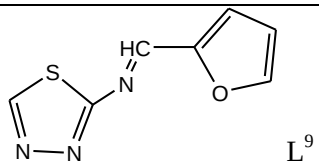
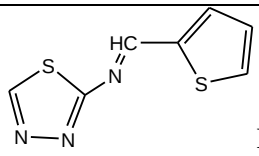
Table 1: Anti-bacterial, anti-fungal screening activity of some substituted aminothiazoles.

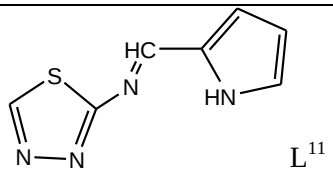
Sr. No.	***Aminothiazoles***	***S. aureus***	***E. coli***	***A. niger***	***C. albicans***
1		++++	+++++	++++++	++++
2		+++++	+++++	++++++	++++++
3		++++	++++	++++++	+++++++
4		++++	++++	+++++++	+++++++
5		++++	++++	++++++	++++++
6		++++	+++++	+++++++	+++++++
7		++++	+++++	+++++++	++++++++

8		+++++	+++++	+++++++	+++++++
9		+++++	+++++	+++++++	++++++++
10		++++	++++	++++++	+++++++
11		++++	+++++	++++++	++++++
12		+++++	++++	+++++++	++++++
13	 norfloxacin	-	+++++	-	-
14	grieseofulvin 	-	-	-	++++++++
15	 DMF	-	-	-	-

Inhibition zone diameter mm: +: 1-4; ++: 4–8; +++: 9-12; ++++: 13-16; +++++: 17-20; ++++++: 21-24; +++++++: 25-28; ++++++++: 29-32.

Table 2: Anti-bacterial, anti-fungal screening activity of some aminothiazole Schiff bases.

Sr. No.	Aminothiazole Schiff bases	*E. coli* (% of inhibition)	*S. aureus* (% of inhibition)	*P. aeruginosa* (% of inhibition)	*K. pneumoniae* (% of inhibition)
1	 L^1	45-64	27-45	27-45	45-64
2	 L^2	45-64	27-45	45-64	27-45
3	 L^3	45-64	27-45	27-45	45-64
4	 L^4	45-64	27-45	27-45	45-64
5	 L^5	27-45	45-64	45-64	27-45
6	 L^6	45-64	27-45	27-45	27-45
7	 L^7	27-45	45-64	27-45	27-45
8	 L^8	45-64	27-45	27-45	45-64
9	 L^9	45-64	45-64	27-45	45-64
10	 L^{10}	45-64	27-45	45-64	27-45

11	 L^{11}	45-64	45-64	64-82	45-64

Percent inhibition values are relative to inhibition zone (22 mm) of the most active compound with 100 % inhibition.

Table 3: Anti-bacterial, Anti-fungal screening activities of some aminothiazoles Schiff base metal complexes.

Sr. No.	**Aminothiazole Schiff base metal complexes**	***E. coli*** **(% of inhibition)**	***S. aureus*** **(% of inhibition)**	***P. aeruginosa*** **(% of inhibition)**	***K. pneumoniae*** **(% of inhibition)**
1	L^1-Co(II)	64-82	45-64	64-82	64-82
2	L^1-Cu(II)	64-82	45-64	45-64	64-82
3	L^1-Ni(II)	82-100	45-64	64-82	64-82
4	L^1-Zn(II)	64-82	64-82	64-82	64-82
5	L^2-Co(II)	64-82	64-82	45-64	45-64
6	L^2-Cu(II)	82-100	64-82	64-82	64-82
7	L^2-Ni(II)	45-64	64-82	27-45	82-100
8	L^2-Zn(II)	64-82	64-82	45-64	64-82
9	L^3-Co(II)	64-82	45-64	64-82	82-100
10	L^3-Cu(II)	64-82	64-82	64-82	45-64
11	L^3-Ni(II)	64-82	64-82	64-82	45-64
12	L^3-Zn(II)	45-64	64-82	64-82	45-64
13	L^4-Ni(II)	64-82	64-82	64-82	64-82
14	L^4-Cu(II)	64-82	64-82	64-82	45-64
15	L^4-Zn(II)	64-82	82-100	45-64	64-82
16	L^5-Ni(II)	64-82	64-82	64-82	64-82
17	L^5-Cu(II)	82-100	64-82	64-82	64-82
18	L^5-Zn(II)	45-64	82-100	64-82	64-82
19	L^6-Ni(II)	64-82	82-100	64-82	45-64
20	L^6-Cu(II)	45-64	64-82	27-45	45-64
21	L^6-Zn(II)	64-82	64-82	64-82	45-64
22	L^7-Ni(II)	64-82	45-64	45-64	45-64
23	L^7-Cu(II)	64-82	64-82	82-100	64-82
24	L^7-Zn(II)	82-100	64-82	45-64	82-100
25	L^8-Ni(II)	82-100	64-82	64-82	64-82
26	L^8-Cu(II)	64-82	64-82	64-82	64-82
27	L^8-Zn(II)	64-82	45-64	45-64	64-82
28	L^9-Co(II)	64-82	82-100	45-64	64-82
29	L^9-Cu(II)	64-82	45-64	64-82	64-82
30	L^9-Ni(II)	82-100	64-82	64-82	64-82
31	L^9-Zn(II)	82-1002	64-82	64-82	64-82
32	L^{10}-Co(II)	64-82	64-82	64-82	64-82
33	L^{10}-Cu(II)	82-100	64-82	64-82	64-82
34	L^{10}-Ni(II)	64-82	64-82	45-64	45-64
35	L^{10}-Zn(II)	64-82	64-82	64-82	45-64
36	L^{11}-Co(II)	64-82	64-82	64-82	64-82
37	L^{11}-Cu(II)	82-100	82-100	64-82	64-82
38	L^{11}-Ni(II)	45-64	64-82	82-100	64-82
39	L^{11}-Zn(II)	64-82	64-82	64-82	64-82

Table 4: Anti-bacterial, Anti-fungal screening activities of some aminothiazoles Schiff base metal complexes with various anions.

Sl. No.	**Aminothiazole Schiff base metal complexes**	***E. coli*** **(% of inhibition)**	***S. aureus*** **(% of inhibition)**	***P. aeruginosa*** **(% of inhibition)**
1	$Ni(L_7)_2(NO_3)_2$	64-82	64-82	64-82
2	$Ni(L_7)_2(SO_4)$	64-82	64-82	64-82
3	$Ni(L_7)_2(C_2O_4)$	64-82	82-100	64-82
4	$Ni(L_7)_2(CH_3CO_2)_2$	64-82	45-64	45-64
5	$Ni(L_8)_2(NO_3)_2$	82-100	64-82	64-82
6	$Ni(L_8)_2(SO_4)$	64-82	64-82	64-82
7	$Ni(L_8)_2(C_2O_4)$	82-100	64-82	64-82
8	$Ni(L_8)_2(CH_3CO_2)_2$	45-64	64-82	27-45
9	$Cu(L_7)_2(NO_3)_2$	64-82	64-82	82-100
10	$Cu(L_7)_2(SO_4)$	64-82	64-82	64-82
11	$Cu(L_7)_2(C_2O_4)$	64-82	82-100	45-64
12	$Cu(L_7)_2(CH_3CO_2)_2$	45-64	82-100	64-82
13	$Cu(L_8)_2(NO_3)_2$	64-82	64-82	64-82
14	$Cu(L_8)_2(SO_4)$	64-82	64-82	64-82
15	$Cu(L_8)_2(C_2O_4)$	64-82	82-100	64-82
16	$Cu(L_8)_2(CH_3CO_2)_2$	64-82	45-64	45-64
17	$Zn(L_7)_2(NO_3)_2$	82-100	64-82	64-82
18	$Zn(L_7)_2(SO_4)$	64-82	64-82	64-82
19	$Zn(L_7)_2(C_2O_4)$	82-100	64-82	64-82
20	$Zn\ (L_7)_2(CH_3CO_2)_2$	45-64	64-82	27-45
21	$Zn(L_8)_2(NO_3)_2$	64-82	64-82	82-100
22	$Zn(L_8)_2(SO_4)$	64-82	64-82	64-82
23	$Zn(L_8)_2(C_2O_4)$	64-82	82-100	45-64
24	$Zn(L_8)_2(CH_3CO_2)_2$	45-64	82-100	64-82
25	$Cu(L_{11})_2(SO_4)$	64-82	45-64	45-64
26	$Cu(L_{11})_2(NO_3)_2$	64-82	82-100	64-82
27	$Cu(L_{11})_2(C_2O_4)$	64-82	64-82	64-82
28	$Cu(L_{11})_2(CH_3CO_2)_2$	82-100	64-82	64-82
29	$Zn(L_{11})_2(SO_4)$	82-100	82-100	45-64
30	$Zn(L_{11})_2(NO_3)_2$	82-100	64-82	64-82
31	$Zn(L_{11})_2(C_2O_4)$	64-82	82-100	64-82
32	$Zn(L_{11})_2(CH_3CO_2)_2$	64-82	82-100	64-82

Conflict of Interest: Not Declared

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