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(REVIEW ARTICLE)

Microwave assisted Schiff base metal complexes as potential anticancer and antimicrobial agents: A critical review

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Abstract

Schiff bases are organic compounds which contain azomethine group (-C=N-) by reacting primary amines and carbonyl compounds. The presence of an azomethine group in the Schiff base facilitates coordination with transition metal ions. The term Schiff base is normally applied to these compounds when they are being used as ligands to form coordination complexes with metal ions. Such complexes occur naturally, but the majority of Schiff bases are artificial and are used to form many important catalysts. Schiff base metal complexes prepared using microwave irradiation have gained more attention because of their excellent strategy in generating quick and stable products in higher yields by improving the speed of reaction with lesser energy and exhibits various biological activities including antifungal, antibacterial, anti-tubercular, antiviral, antimalarial, anti-diabetic, anticancer, antioxidant, antidiuretic, anti-inflammatory, antipyretic and anti-HIV agents. Apart from biological applications, they are also used as a catalyst in Aldol reactions, polymerization reactions, oxidation reactions and other chemical reactions. Imine-ligand containing transition metal complexes including copper, zinc and cadmium, have proven to be effective starting points for the synthesis of metal or metal chalcogenide nanoparticles. In this review, various metal complexes derived from Schiff bases synthesised using microwave approaches are discussed along with their antibacterial, antifungal and anticancer activities.

Keywords: Green synthesis; Microwave irradiation; Schiff base metal complexes; Organometallic chemistry; Anti-microbial; Anticancer activity

1. Introduction

A German scientist, Hugo Schiff coined the term "Schiff's base" to refer to the products generated while reacting primary amines with carbonyl compounds in 1864. Schiff bases are playing a crucial role as ligands even a decade after their development in coordination chemistry. Schiff bases are the essential group of compounds distinguished by the existence of a double bond connecting carbon and nitrogen atoms (-C=N-), the diversity of these compounds are generated in numerous ways by combining different alkyl or aryl substituents (Figure 1). The essential component in Schiff base is azo-methine in identifying the capability of Schiff bases in complex formation with transition metal ions. The d-block metal ion is coordinated by the electron-donating ligand atom during the complex formation, which modifies the steric and electronic environment of the metal ion. Due to this condition, the sensitivity of the metal ion is stabilised and controlled, which is beneficial for less stable ions at higher oxidation states [1, 2].

The nitrogen atom present in azomethine is responsible for creating a hydrogen bond with the active centres of cell components, which disrupts regular cell functions. Because of their structural similarities to naturally occurring biological compounds, Schiff bases are essential in the biological field. Schiff base metal complexes exhibited various

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biological applications including antibacterial, antifungal, antiviral, anticancer, anti-tuberculosis, antipyretic, anti-inflammatory, antimalarial and anti-HIV agents. Apart from their wide range of pharmacological effects, they have a wide range of applications including chemosensory, electroluminescence effects, optical properties, fluorescence properties, non-linear, cosmetic, material science, agriculture and polymer industries and also used as O_2 detectors. Studies highlighted that the Schiff base metal complexes show greater biological activity than free organic compounds. Transition metal complexes with imine ligands have proven to be an effective precursor for the synthesis of metal or metal chalcogenide nanoparticles [3-6].

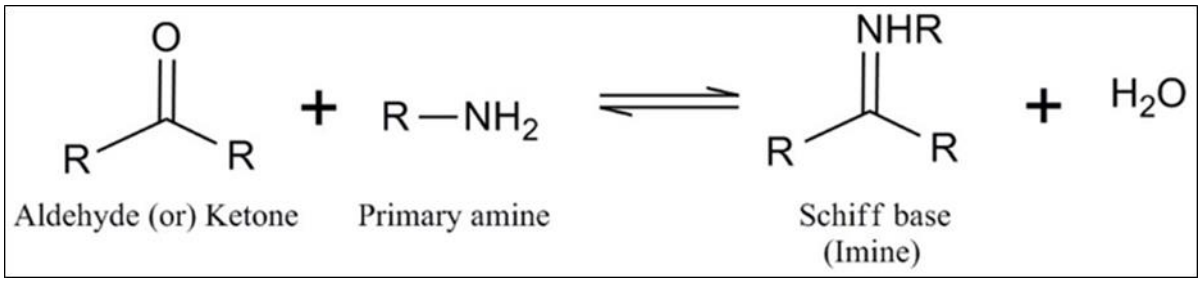

Figure 1 General synthesis for Schiff base

Alfred Werner proposed a hypothesis in 1893 that systematised the field of coordination chemistry, and he was awarded the Nobel Prize in 1913. Schiff bases metal complex are widely utilized in the treatment of multiple viral diseases because of their transition metal complexes and also plays a key role in several areas, including, antibacterial, antifungal, anticancer, and anti-inflammatory, as well as these organometallic materials, used as a catalyst in many reactions such as Aldo reaction, polymerization reaction, oxidation reaction, and others. These metal complexes exert their influence by interacting with intracellular bio-molecules, enhancing lipophilicity, altering cell membrane functions, inhibiting enzymes and arresting the cell cycle. Based on the literature, it is noticed that the therapeutic efficacy is connected with the hydrogen bonding between the active centres of cell components and the imino group of Schiff bases [7-10].

The use of microwave-assisted synthesis of Schiff base metal complexes is regarded as a crucial method for speeding up the process, increasing yield, utilizing less energy, and lowering setup time as compared to conventional synthetic methods. Due to its eco-friendly characteristics, it is regarded as an excellent strategy for sustainable and green chemistry. Due to its quick heating and energy transmission to the reaction medium, microwave heating as an alternative energy source facilitates the use of environmentally friendly solvents or solvent-free conditions and promotes catalytic reactions. The metal complexes synthesised using these techniques are widely used in the treatment of various diseases [11].

In this review, only the literature indexed in ScienceDirect, PubMed, Springer, Google Scholar, ResearchGate and Wiley Online databases were surveyed. The keywords for this survey include green synthesis, microwave irradiation, Schiff base metal complexes, especially, cobalt, copper, manganese, nickel and zinc, biological activity, anti-microbial and cytotoxic activity, both individually and in combination were applied and shortlisted according to the purpose of this study. This review focuses on the Schiff base metal complexes prepared using microwave-assisted synthetic approaches along with their anti-microbial and cytotoxic potential.

2. Microwave assisted Schiff base metal complexes and their biological applications

2.1. Cobalt (Co) complexes

Novel Cobalt (II) aryl thiosemicarbazones complexes namely $[Co(L_1)_2Cl_2]$ **(1)**, $[Co(L_2)_2Cl_2]$ **(2)**, $[Co(L_3)_2Cl_2]$ **(3)** and $[Co(L_4)_2Cl_2]$ **(4)** where L_1= 4-nitroacetophenone thiosemicarbazones (4NAT), L_2 = 3-nitrobenzaldehyde thiosemicarbazones (3NBT), L_3 = 4-hydroxybenzaldehyde thiosemicarbazone (4HBT) and L_4 = 4-aminoacetophenone thiosemicarbazone (4AAT) were prepared by the reaction between thiosemicarbazides with substituted aromatic aldehydes or ketones using microwave irradiation method followed by the complexation with the cobalt complexes. The antibacterial efficacy of the synthesised complexes was screened against *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis.* The results revealed that complexes **(3)** and **(4)** exhibited maximum efficacy against all of these bacterial strains [12].

The transition cobalt metal complex **(5)** was prepared from the Schiff base ligand which was synthesised from o-vanillin and 4-amino azobenzene. Then the Schiff base ligand was reacted with an equimolar amount of hydrated metal salt with a few drops of ethanol and exposed to microwave irradiation for 10 mins at 360 W. The potential cytotoxic activities of the prepared cobalt complex were screened against human colon (HCT-116) and human liver (HepG-2) cancer cell lines and the results revealed the considerable efficacy of the complex against the two cancer cell lines [13].

Bidentate novel Schiff base ligand was prepared by the condensation of 2-amino-5,6-dimethyl benzimidazole with terephthalaldehyde under a solvent free condition in a microwave oven at 750 W for 10 mins periodically resulted in the formation of orange coloured Schiff base ligand namely N-(4-((Z)-(5,6-dimethyl-1H-benzo[d]imidazol-2-ylimino)methyl)benzylidene)-5,6-dimethyl-1H-benzo[d]imidazol-2-amine. Then the synthesised Schiff base ligand was mixed with metal salt (Co $(NO_3)_2.6H_2O$) and exposed to microwave irradiation for 10 mins at 750 W. For the synthesised cobalt complex **(6)**, the antimicrobial activity was screened against *E. coli, S. aureus* and *Salmonella typhi.* The results revealed that the complex exhibited 250, 125 and 100 µg/ml of minimum inhibitory concentration [14].

Schiff bases namely 2-[(5-bromo-2-hydroxybenzylidene)amino]pyridin-3-ol (BSAP) and [5-chloro-2-[((2-hydroxy-1-naphthyl)methylene)amino]phenyl]-phenylmethanone (HNAC) were prepared by treating bromosalicylaldehyde with 2-amino-3-hydroxypyridine and 2-hydroxy-1-naphthaldehyde with 2-amino-5-chlorobenzophenone using 3-4 ml of dry ethanol as solvent and irradiated for 4-5 mins. The synthesised Schiff bases such as BSAP and HNAC were irradiated with Co salts under a microwave oven for 6-10 mins using 3-5 ml of ethanol as a solvent resulting in the formation of Co-BSAP **(7)** complex and Co-HNAC **(8)** complex. The complexes exhibited better anti-microbial potency against *E. coli, S. aureus, Candida albicans* and *Pseudomonas aeruginosa* [15].

Schiff base ligands were prepared by mixing 5-bromosalicylaldehyde with 2-chloro-4-nitroaniline and 2-amino-5-chlorobenzophenone in a grinder and the reaction mixture was irradiated with 3-4 ml of dry ethanol as solvent under microwave oven for 3-4 mins. The resulted Schiff bases were mixed with $CoCl_2.6H_2O$ in a grinder and irradiated under a microwave oven with 3-4 ml of dry ethanol for 4-5 mins resulting in the formation of the complex **(9)** and **(10).** The antibacterial activity of the Co complexes was determined against *S. aureus* and *E. coli* and the antifungal activity of the Co complexes was determined against *A. niger* and *C. albicans.* The synthesised Schiff bases and their Co complexes exhibited significant antimicrobial potential against the respective micro-organisms [16].

Monofunctional bidentate Schiff base ligand was prepared by the condensation of o-vanillin and p-chloroaniline through a conventional microwave oven for 2 mins. The Co complex **(11)** was prepared by reacting the Schiff base and metal salt dissolved in ethanol and double distilled water in presence of benzene for 5-8 mins under a microwave oven. The antibacterial and antifungal efficacy of the Co complex was evaluated against *E. coli, S. aureus, A. niger* and *Fusarium oxysporum.* The complex showed considerable efficacy as compared with the standard drugs such as Streptomycin and Fluconazole [17].

2-aminobenzimidazole and 4,4-dibromo benzyl were reacted under solvent free condition through the microwave oven for 30 mins and the final product was recrystallized with ethanol resulted in the formation of a pale yellow coloured Schiff base ligand. The synthesised Schiff base ligand was mixed with a metal salt and irradiated under microwave irradiation for 30-150 sec resulting in the formation of a stable Co complex **(12)**. The antibacterial efficacy of the Co complex was determined against *E. coli, S. aureus* and *S. typhi* and was found to be 100, 125 and 100 µg/ml of minimum inhibitory concentration [18].

1-(4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)phenyl)-N-(1H-1,2,4-triazole-3-yl)methenamine triazole Schiff base was prepared by thoroughly combining 3-amino-1,2,4-triazole with 4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)benzaldehyde in a mortar and it was irradiated with 3-4 ml of ethanol at 90 W for 90 sec resulted in the formation of orange coloured product. The synthesised Schiff base was mixed with $Co(AcO)_2.4H_2O$ dissolved in 4 ml of ethanol and irradiated under microwave oven resulting in blue-coloured complex **(13)** formation with more yield and less time. The antibacterial potential of the Co complex was evaluated against *E. coli, S. aureus, B. subtilis* and *P. aeruginosa* and was found to be 12, 8, 12 and 14 mm of zone of inhibition and the antifungal activity of the complex was evaluated against *A. niger* and *C. albicans* and was found to be 9 and 6 mm of zone of inhibition. The cytotoxic potential of the complex was determined as 43.90 µM of IC_{50} value against the human colorectal (HCT 116) cancer cell line [19].

Hexadentate Schiff base 6,6'-((*1E,1'E*)-(1,3-phenylenebis(azanylylidene)) bis(methanylylidene))bis-(2-methoxyphenol) was synthesized via condensation of *o*-vanillin and *m*-phenylenediamine under reflux for 1 h resulted in the formation of orange crystalline Schiff base. Then the Schiff base was mixed with metal acetate salt with few drops of triethylamine and the reaction mixture was placed in microwave oven and stirred at 1000 rpm for 10 mins resulting in the formation of the brown coloured complex **(14)**. The cytotoxic potential of the complex was evaluated as 34.73 ±

2.64 μM of IC_{50} value against the human colorectal (HCT 116) cancer cell line [20]. The structures of the cobalt complexes are given in Figures 2 and 3.

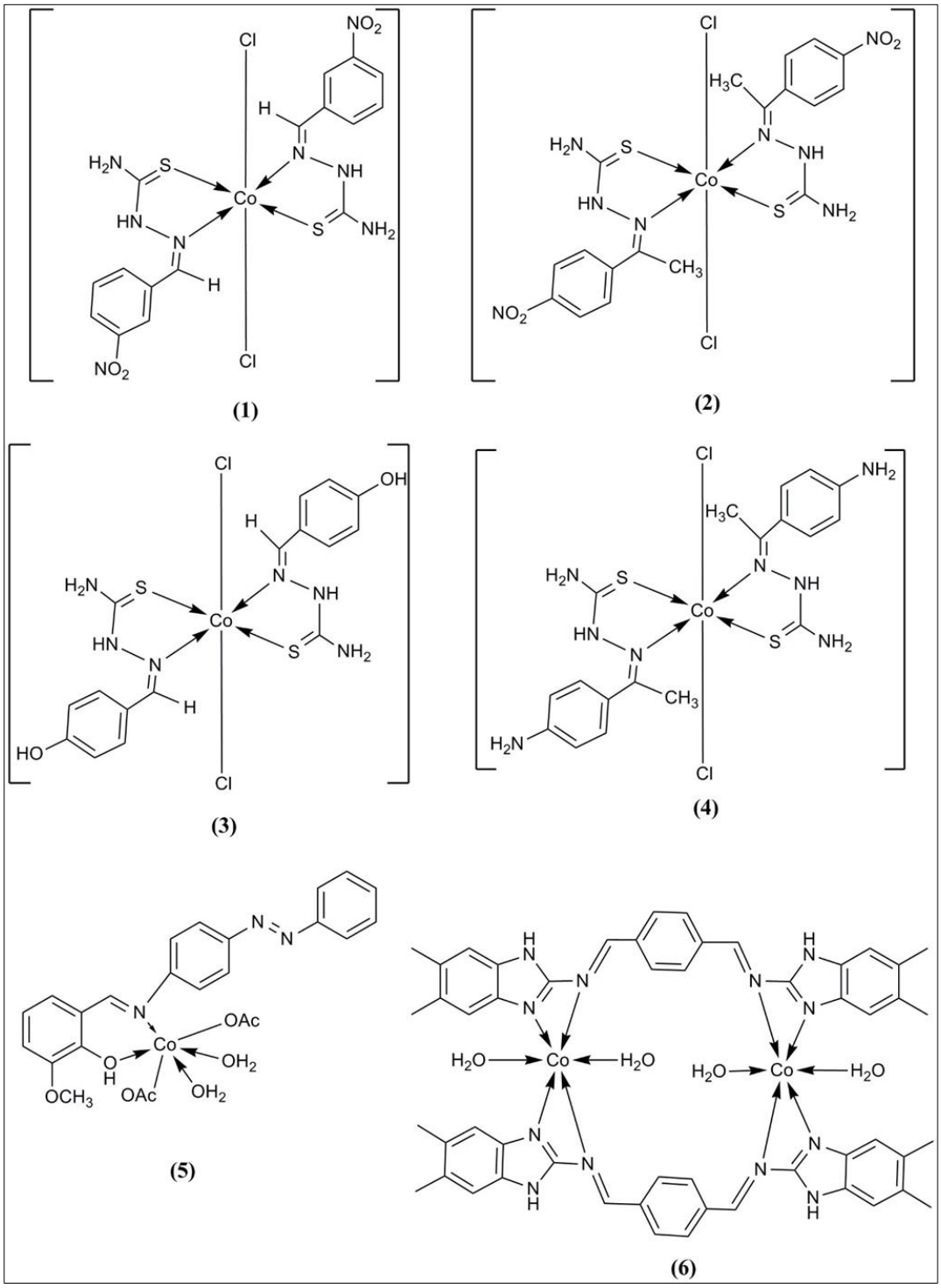

Figure 2 Structures of Cobalt complexes

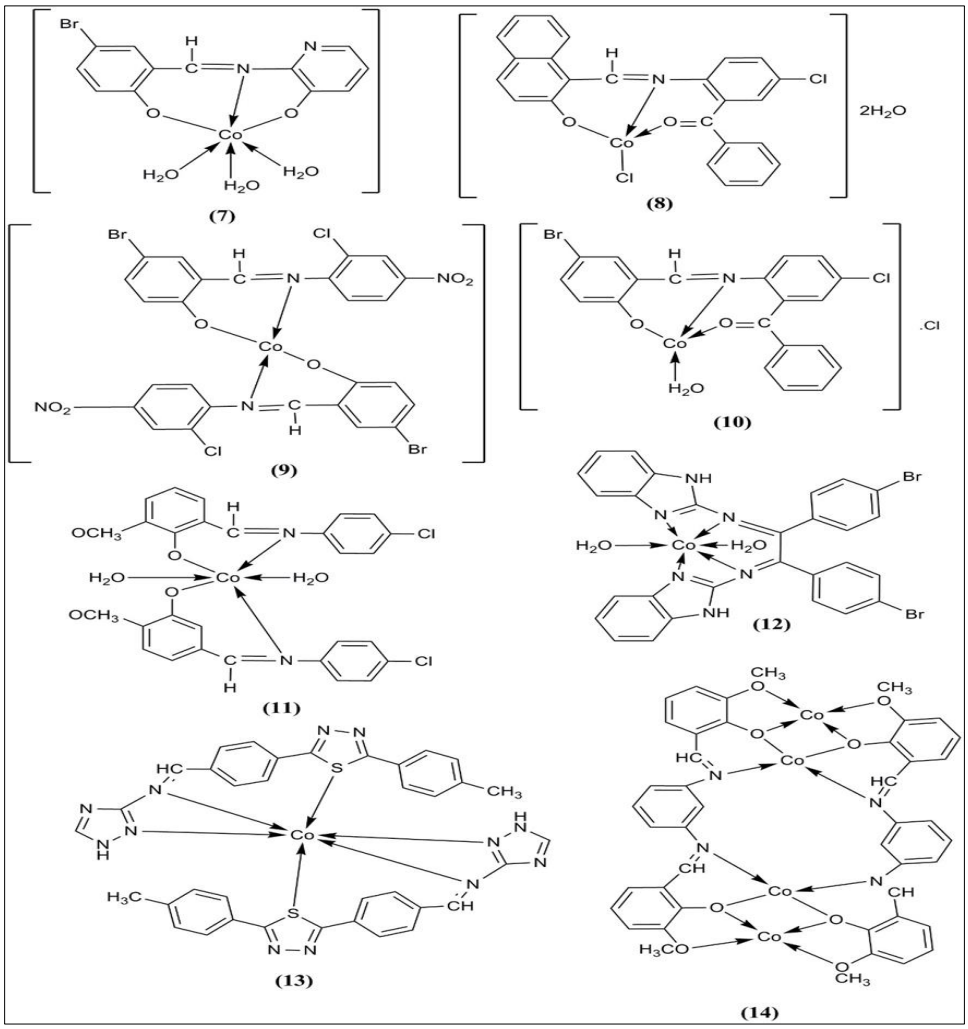

Figure 3 Structures of Cobalt complexes

2.2. Copper (Cu) complexes

Copper (Cu) complex (15) was prepared from the Schiff base ligand which was synthesised from o-vanillin and 4-amino azobenzene. Then the Schiff base ligand was reacted with an equimolar amount of hydrated metal salt with a few drops of ethanol and exposed to microwave irradiation for 10 mins at 360 W. The potential cytotoxic activity of the prepared complex was screened against human colon (HCT-116) and human liver (HepG-2) cancer cell lines and the results revealed that complex exhibited excellent cytotoxic efficacy in the range of 18 and 22 µg/ml of IC_{50} value against HCT-116 and HepG-2 cell lines of the complex against the two cancer cell lines as compared to the Schiff base ligand [13].

Bidentate novel Schiff base ligand was prepared by the condensation of 2- Amino-5, 6-dimethyl benzimidazole with terephthalaldehyde under a solvent free condition in a microwave oven at 750 W for 10 mins periodically resulted in the formation of orange-coloured Schiff base ligand namely N-(4-((Z)-(5,6-dimethyl-1H-benzo[d]imidazol-2-ylimino)methyl)benzylidene)-5,6-dimethyl-1H-benzo[d]imidazol-2-amine. Then the synthesised Schiff base ligand was mixed with metal salt Cu $(NO_3)_2.3H_2O$ and exposed to microwave irradiation for 10 mins at 750 W. The complex (16) showed better antimicrobial potential in the range of 250, 125 and 250 µg/ml of minimum inhibitory concentration against *E. coli, S. aureus* and *S. typhi* [14].

Schiff bases namely 2-[(5-bromo-2-hydroxybenzylidene)amino]pyridin-3-ol (BSAP) and [5-chloro-2-[((2-hydroxy-1-naphthyl)methylene)amino]phenyl]-phenylmethanone (HNAC) were prepared irradiated with metal salt under microwave oven for 6-10 mins using 3-5 ml of ethanol as a solvent resulted in the formation of Cu-BSAP (17) complex and Cu-HNAC (18) complex. The complexes exhibited significant anti-microbial efficacy against *E. coli, S. aureus, C. albicans* and *P. aeruginosa* [15].

Schiff base ligands were prepared by mixing 5-bromosalicylaldehyde with 2-chloro-4-nitroaniline and 2-amino-5-chlorobenzophenone in a grinder and the reaction mixture was irradiated with 3-4 ml of dry ethanol as solvent under microwave oven for 3-4 mins. The resulted Schiff bases were mixed with $CuCl_2.2H_2O$ in a grinder and irradiated under microwave oven with 3-4 ml of dry ethanol for 4-5 mins resulting in the formation of the complexes (19) and (20). The antimicrobial activity of the complexes was determined against *S. aureus*, *E. coli* (bacterial strains), *A. niger* and *C. albicans* (fungal strains). The synthesised Schiff bases and their complexes exhibited significant antimicrobial potential against the respective micro-organisms [16].

Monofunctional bidentate Schiff base ligand was prepared and reacted with metal salt dissolved in ethanol and double distilled water in presence of benzene for 5-8 mins under a microwave oven. The antibacterial and antifungal efficacy of the complex (21) was evaluated against *E. coli, S. aureus, A. niger* and *F. oxysporum.* The complex showed considerable efficacy as compared with the standard drugs such as Streptomycin and Fluconazole [17].

The complex (22) derived from 2-aminobenzimidazole and 4,4-dibromo benzyl Schiff base were reacted under solvent free condition through the microwave oven for 30-150 sec resulting in the formation of a stable complex. The antibacterial efficacy of the Co complex was determined against *E. coli, S. aureus* and *S. typhi* and was found to be 250, 125 and 125 µg/ml of minimum inhibitory concentration [18].

The copper complex (23) obtained from 1-(4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)phenyl)-N-(1H-1,2,4-triazole-3-yl)methenamine triazole Schiff base was prepared by thoroughly combining 3-amino-1,2,4-triazole with 4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)benzaldehyde in a mortar and it was irradiated with 3-4 ml of ethanol at 90 W for 90 sec resulted in the formation of orange coloured product. The synthesised Schiff base was mixed with $Cu(AcO)_2.H_2O$ dissolved in 4 ml of ethanol and irradiated under a microwave oven resulting in brown-coloured complex formation with more yield and less time. The antibacterial of the Cu complex was evaluated against *E. coli, S. aureus, B. subtilis* and *P. aeruginosa* and was found to be 22, 18, 15 and 26 mm of zone of inhibition and the antifungal activity of the complex was evaluated against *A. niger* and *C. albicans* and was found to be 30 and 39 mm of zone of inhibition. The cytotoxic potential of the complex was determined as 128.0 µM of IC_{50} value against the human colorectal (HCT 116) cancer cell line [19].

Schiff base ligand namely 6,6'-((*1E,1'E*)-(1,3-phenylenebis(azanylylidene)) bis(methanylylidene))bis-(2-methoxyphenol) was synthesized via condensation of *o*-vanillin and *m*-phenylenediamine and the resulted Schiff base was mixed with metal salt in the ratio of 2:1. To the reaction mixture, few drops of triethylamine were added and stirred for 10 mins at 1000 rpm using microwave oven resulted in the formation of the brown coloured complex (24). The complex exhibited excellent anti-proliferative activity against the human colorectal (HCT 116) cell line in the range of 6.56 ± 1.26 µM of IC_{50} value [20].

N-salicylidene-4-chloroaniline Schiff base was prepared by mixing the mixture of 2-hydroxybenzaldehyde and 4-chloroaniline thoroughly and irradiated at 160 W for 3 mins under a microwave oven. Then the Schiff base ligand was mixed with copper chloride thoroughly and exposed to microwave irradiation at 160 W for 3 mins resulting in the formation of complex (25). The antimicrobial potential of the Schiff base and copper complex was evaluated against *Bacillus cerus* and *C. albicans.* The results revealed that the Schiff base exhibited moderate activity whereas the complex exhibited excellent activity against the organisms due to chelation [21].

A tridentate Schiff base ligand (E)-1-(2-hydroxy-3-methoxybenzylidene)-3-phenylurea was derived from *o*-vanillin and phenyl urea at 450 W for 15 mins using a microwave oven. The Schiff base ligand was mixed with $Cu(CH_3CO_2)_2.6H_2O$ to form a homogenous mixture and irradiated under a microwave oven for 15 mins at 450 W. The resulting complex (26) showed greater antimicrobial potential against *E. coli, S. aureus, B. subtilis, Salmonella typhimurium, C. albicans* and *Aspergillus fumigatus*. The cytotoxic evaluation of the complex showed 61.1 and 52.7 µg/ml of IC_{50} value against human breast (MCF-7) and human colorectal (HCT 116) cancer cell lines [22].

Salicylideneamoxicillin, salicylidenecephalexin, salicylidenesulphamethoxazole and salicylidenetrimethoprim Schiff bases were prepared by the condensation of the methanolic solution of the drugs including amoxicillin, cephalexin, sulphamethoxazole and trimethoprim with the methanolic solution of salicylaldehyde in presence of an acid catalyst under a microwave irradiation. Then the Schiff base ligands and the metal salt were mixed thoroughly in a 1:2 ratio and the pH was adjusted to 7-8 using 1 % methanolic potassium hydroxide solution and the reaction was completed within 2-3 mins. The resulting metal complexes (27-30) exhibited better antibacterial potential against *E. coli, S. aureus* and *P. aeruginosa* [23].

Schiff base ligand and its metal complex were prepared from 1, 4-butane diamine and salicyldehyde and $Cu(Cl)_2.2H_2O$ under microwave irradiation for 4-5 mins in presence of 20 ml of hot ethanol. The antibacterial potential of the complex

(31) was evaluated against *E. coli* and *S. aureus* in the range of 10 and 8 mm of zone of inhibition as compared to the standard drug, Ciprofloxacin using the agar spread method [24].

The synthesis of novel Schiff base ligand 2-amino 5-nitro thiazole and its copper complex was carried out by mixing 2-amino 5-nitro thiazole and substituted salicyldehyde with a few drops of ethanol and glacial acetic acid. Then, the reaction mixture was taken in Erlen Meyer flask capped with a funnel and it was exposed to microwave irradiation at 450 W for 5-8 mins with 1 min interval. The synthesised ligand was reacted with the metal salt to form the stable metal complex and its antimicrobial activity was determined against the bacterial strains including *S. aureus* and *B. subtilis* and the fungal strains including *C. albicans* and *A. niger* using the disc diffusion method. The results revealed that the complex was more active against *S. aureus, B. subtilis, C. albicans* and *A. niger* in the range of 15, 26.5, 20 and 19 mm of zone of inhibition [25].

Azomethine(1,5-Dimethyl-2-phenyl-[(3,4,5-trimethoxybenzylidene)amino]-1,2-dihydropyrazol-3-one) (DTAD) Schiff base ligand was synthesised by microwave irradiation of 4-aminophenazone with 3,4,5 trimethoxybenzaldehyde using methanol and 2 drops of acetic acid for 1 min at 210 W. Then the chloride and acetate metal salts and the ligand were mixed in a grinder in 1:2 ratio and the reaction mixture was exposed to microwave irradiation for 2-3 mins resulted in higher yields of complexes (32) and (33). The antibacterial activity of the complexes was determined against *E. coli, S. aureus, S. pyogenes* and *S. typhimurium* and the results revealed that the metal chloride complex exhibited better activity as compared to the standard drug chloramphenicol [25]. The structures of the copper complexes are given in Figures 4-6.

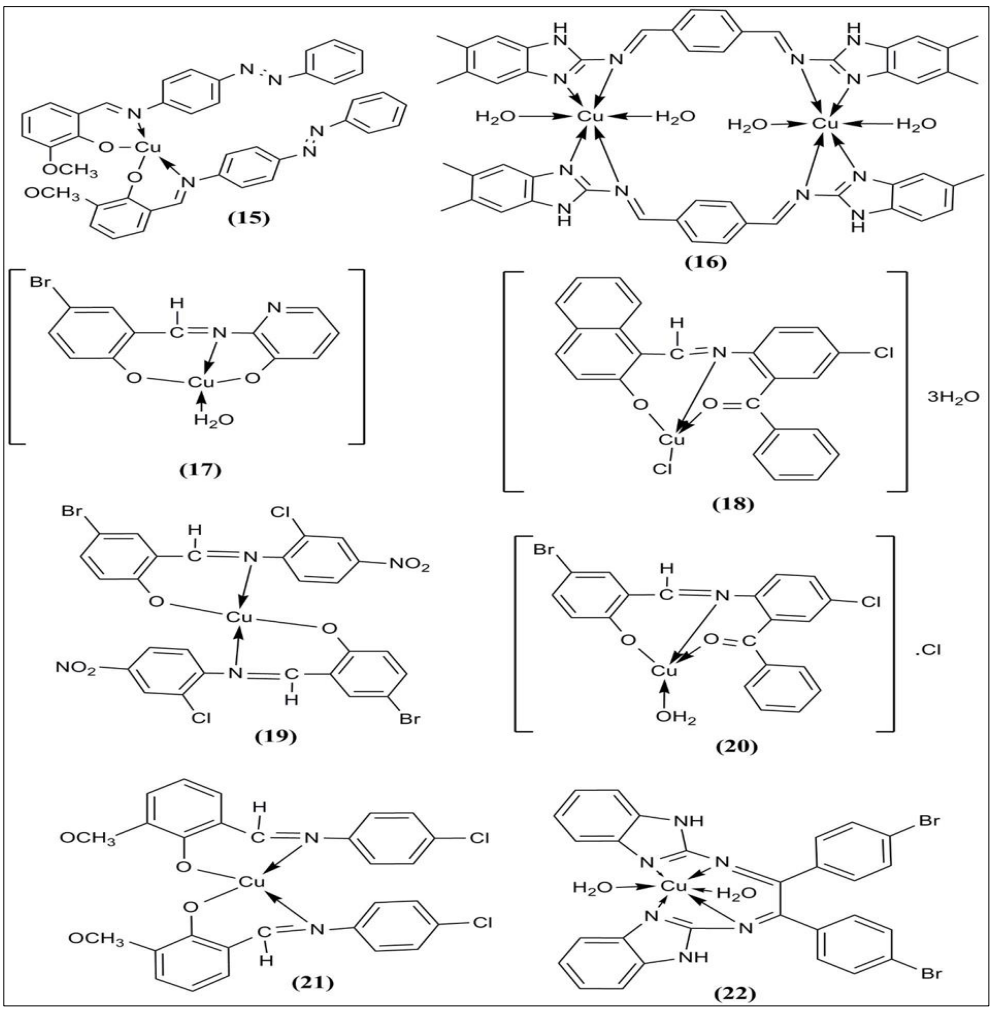

Figure 4 Structures of Copper complexes

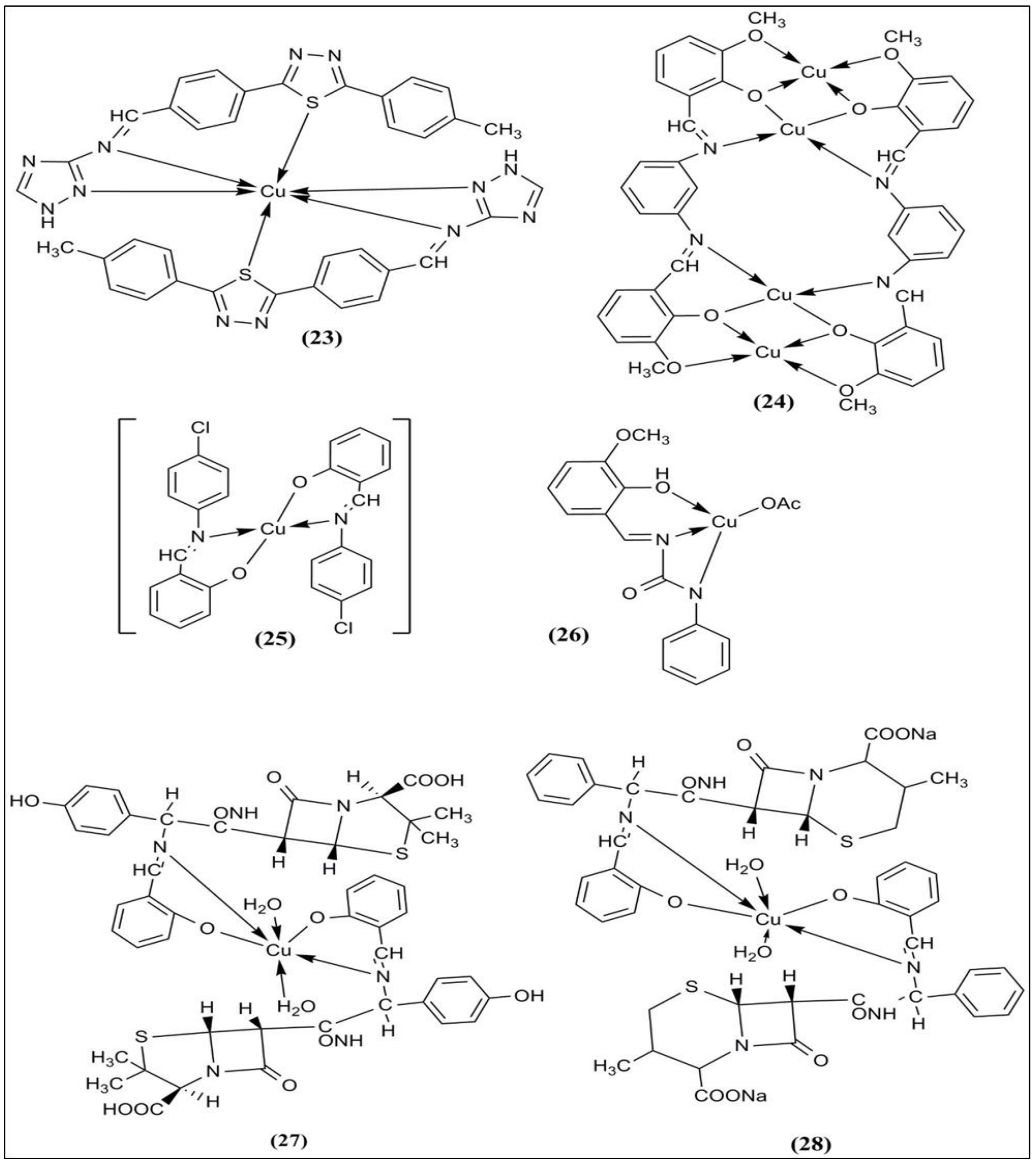

Figure 5 Structures of Copper complexes

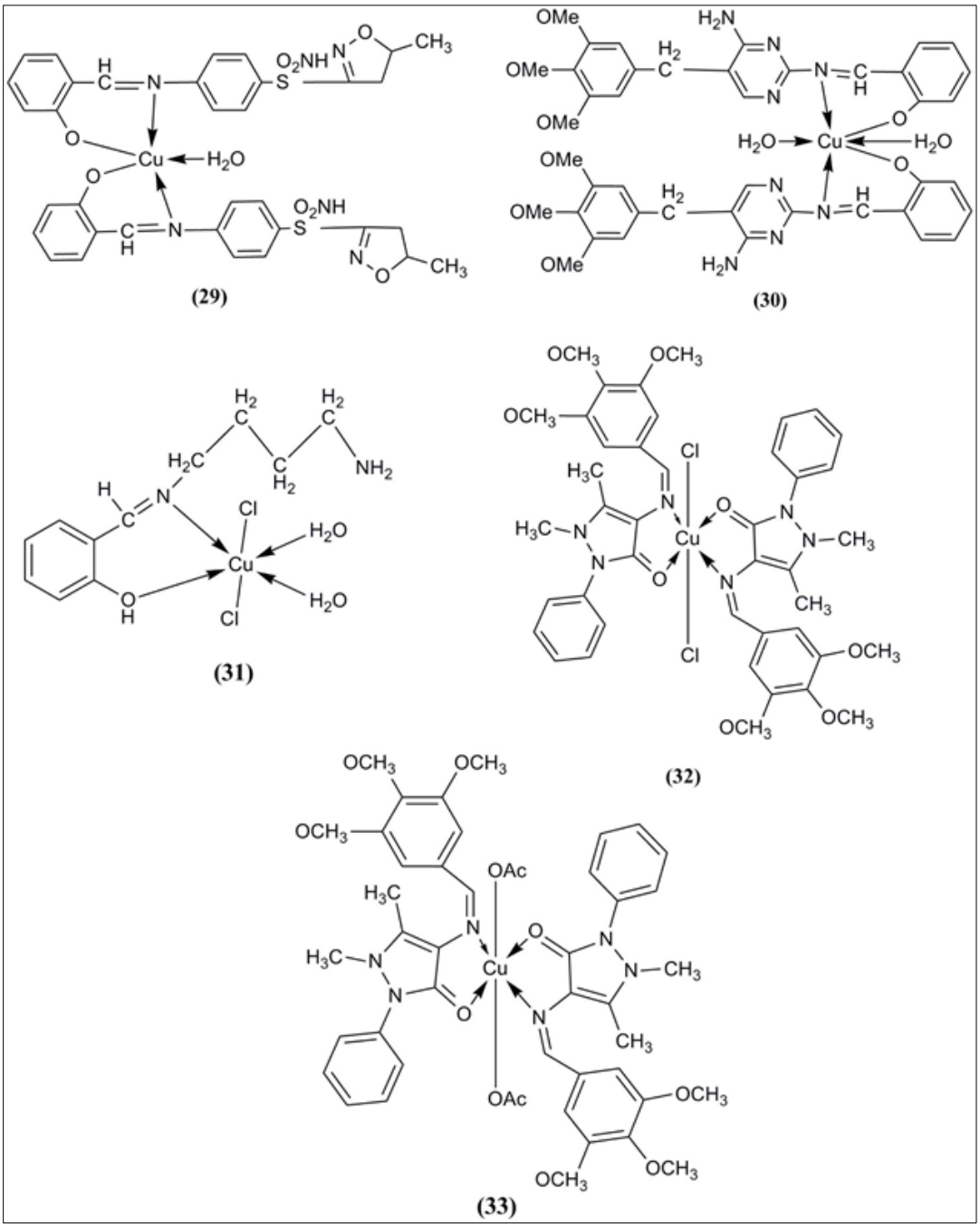

Figure 6 Structures of Copper complexes

2.3. Manganese (Mn) complexes

Manganese (Mn) complex (34) was prepared from the Schiff base ligand which was synthesised from o-vanillin and 4-aminoazobenzene. Then the Schiff base ligand was reacted with an equimolar amount of hydrated metal salt with a few drops of ethanol and exposed to microwave irradiation for 10 mins at 360 W. The antibacterial activity of the complex was found to be significant against *E. coli, S. aureus, B. subtilis* and *S. typhimurium.* The potential cytotoxic activity of the prepared complex was screened against human colon (HCT-116) and human liver (HepG-2) cancer cell lines and the results revealed the complex exhibited excellent cytotoxic efficacy in the range of 20 and 24 µg/ml of IC_{50} value against HCT-116 and HepG-2 cell lines as compared to the Schiff base ligand [13].

A novel Schiff base ligand was prepared by the condensation of 2-amino-5, 6-dimethyl benzimidazole with terephthalaldehyde under a solvent free condition in a microwave oven at 750 W for 10 mins periodically resulted in the formation of orange-coloured Schiff base ligand namely N-(4-((Z)-(5,6-dimethyl-1H-benzo[d]imidazol-2-

ylimino)methyl) benzylidene)-5,6-dimethyl-1H-benzo[d]imidazol-2-amine. Then the synthesised Schiff base ligand was mixed with metal salt $MnCl_2$ and exposed to microwave irradiation for 10 mins at 750 W. The complex (35) showed better antimicrobial potential in the range of 100, 125 and 250 µg/ml of minimum inhibitory concentration against *E. coli, S. aureus* and *Salmonella typhi* [14].

2-aminobenzimidazole and 4,4-dibromo benzyl were reacted under a solvent free condition through the microwave oven for 30 mins and the final product was recrystallized with ethanol resulting in the formation of a pale yellow coloured Schiff base ligand. The synthesised Schiff base ligand was mixed with a metal salt and irradiated under microwave irradiation for 30-150 sec resulting in the formation of a light green-coloured complex (36). The complex exhibited significant antibacterial potential against *E. coli, S. aureus* and *S. typhi* [18].

The manganese complex (37) obtained from 1-(4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)phenyl)-N-(1H-1,2,4-triazole-3-yl)methenamine triazole Schiff base was prepared by thoroughly combining 3-amino-1,2,4-triazole with 4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)benzaldehyde in a mortar and it was irradiated with 3-4 ml of ethanol at 90 W for 90 sec resulting in the formation of orange-coloured product. The synthesised Schiff base was mixed with $Mn(AcO)_2.H_2O$ dissolved in 4 ml of ethanol and irradiated under microwave oven resulting in brown-coloured complex formation with more yield and less time. The antibacterial activity of the complex was evaluated against *E. coli, S. aureus, B. subtilis* and *P. aeruginosa* was found to be 7, 8, 20 and 6 mm of zone of inhibition and the antifungal activity of the complex was evaluated against *A. niger* and *C. albicans* was found to be 20 and 30 mm of zone of inhibition. The cytotoxic potential of the complex was determined as 37.4 µM of IC_{50} value against the human colorectal (HCT 116) cancer cell line [19].

A novel tridentate Schiff base ligand (E)-1-(2-hydroxy-3-methoxybenzylidene)-3-phenylurea was derived from *o*-vanillin and phenyl urea at 450 W for 15 mins using microwave oven. The Schiff base ligand was mixed with $Mn(CH_3CO_2)_2.4H_2O$ to form a homogenous mixture and irradiated under a microwave oven for 15 mins at 450 W. The resulted complex (38) showed greater antimicrobial potential against *E. coli, S. aureus, B. subtilis, S. typhimurium, C. albicans* and *Aspergillus fumigatus*. The cytotoxic evaluation of the complex showed 70.3 and 49.9 µg/ml of IC_{50} value against human breast (MCF-7) and human colorectal (HCT 116) cancer cell lines [20].

3-(1-(2-(1-(2,4-dihydroxyphenyl)ethylideneamino)-cyclohexylimino)-ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one Schiff base was prepared by reacting 1,2-diaminocyclohexane and 2,4-dihydroacetophenone for 4.5 mins at 450 W and after that, the reaction mixture was diluted with ethanol and it was stirred and cooled, resulted in product formation. For the synthesis of the complex, the equivalent quantity of metal salt and Schiff base dissolved in dimethyl formamide and hot ethanol was irradiated at 700 W for 5-8 mins. The antimicrobial potential of the complex was found to be 11, 15, 14, 14 and 13 µg/ml of minimum inhibitory concentration against the micro-organisms including *E. coli, S. aureus*, *P. aeruginosa, C. albicans* and *A. niger* [27].

The Schiff base ligands 1-(2-furanyl) ethanone isonicotinoylhydrazone, 1-(2-thienyl)ethanone isonicotinoylhydrazone, 1-(2- pyridyl)ethanone isonicotinoylhydrazone, 1-(2-naphthyl)ethanone isonicotinoylhydrazone were prepared by the condensation reaction of isonicotinic acid hydrazide with corresponding ethanones in 1:1 molar ratio and the resulted ligands were treated with $MnCl_2.4H_2O$. The antibacterial potential of the Mn complexes was evaluated against *E. coli* and *B. subtilis* was found to be 16-20 mm of inhibition zone and the antifungal potential of the Mn complexes was determined against *C. albicans* and *A. niger* found to be 22-85 mm of inhibition zone [28].

A mononuclear Mn (III) complex was prepared from *N,N'*-1,2-ethylene-bis(3-ethoxysalicylideneimine Schiff base ligand synthesised from 3-ethoxysalicylaldehyde, 1,2-diaminoethane, dicloroacetic acid and metal salt using a microwave irradiation at 200 W for 10 mins. The results revealed that the mode of coordination was found to be octahedral and the complexes were stabilized by hydrogen bonds. The complexes showed potential antibacterial activity against *E. coli, S. aureus, B. subtilis* and *P. aeruginosa* [29]. The structures of the manganese complexes are given in Figure 7.

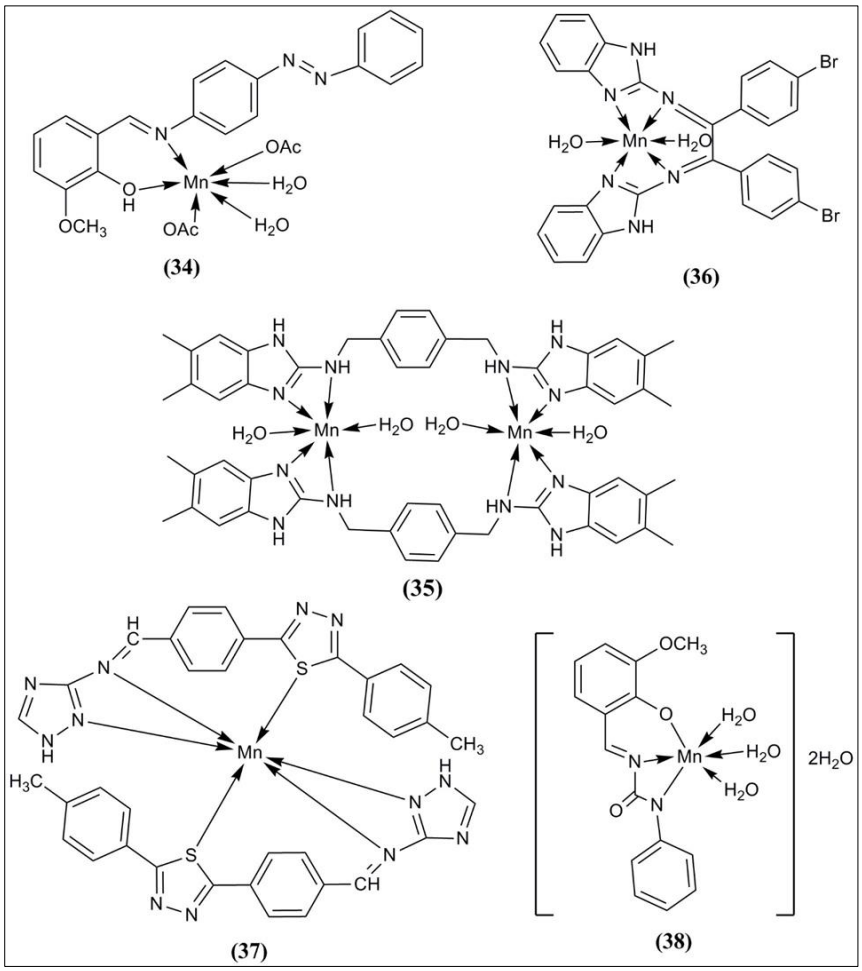

Figure 7 Structures of Manganese complexes

2.4. Nickel (Ni) complexes

A novel Nickel (Ni) complex **(39)** derived from the Schiff base ligand was synthesised from o-vanillin and 4-aminoazobenzene under microwave irradiation in a short time with better yield. Then the Schiff base ligand was reacted with an equimolar amount of hydrated metal salt with a few drops of ethanol and exposed to microwave irradiation for 10 mins at 360 W. The antibacterial activity of the complex was found to be more active against *E. coli, S. aureus, B. subtilis* and *S. typhimurium* in the range of 16, 20, 20 and 18 mm of zone of inhibition. The potential cytotoxic activity of the prepared complex was screened against human colon (HCT-116) and human liver (HepG-2) cancer cell lines and the results revealed the complex exhibited excellent cytotoxic efficacy in the range of 35 and 48 µg/ml of IC_{50} value against HCT-116 and HepG-2 cell lines of the complex against the two cancer cell lines as compared to the Schiff base ligand [13].

Novel metal complex derived from Schiff base ligand was prepared by the condensation of 2- Amino-5, 6-dimethyl benzimidazole with terephthalaldehyde under a solvent-free condition in a microwave oven at 750 W for 10 mins periodically resulted in the formation of orange-coloured Schiff base ligand namely N-(4-((Z)-(5,6-dimethyl-1H-benzo[d]imidazol-2-ylimino)methyl) benzylidene)-5,6-dimethyl-1H-benzo[d]imidazol-2-amine. Then the synthesised Schiff base ligand was mixed with metal salt Ni $(NO_3)_2.6H_2O$ and exposed to microwave irradiation for 10 mins at 750 W resulting in the formation of reddish-brown complex. The complex **(40)** showed better antimicrobial potential in the range of 250, 100 and 250 µg/ml of minimum inhibitory concentration against *E. coli, S. aureus* and *S. typhi* [14].

Novel Nickel complexes **(41)** and **(42)** derived from the Schiff bases namely 2-[(5-bromo-2-hydroxybenzylidene)amino]pyridin-3-ol (BSAP) and [5-chloro-2-[((2-hydroxy-1-naphthyl)methylene)amino]phenyl]-phenylmethanone (HNAC) were prepared by treating bromosalicylaldehyde with 2-amino-3-hydroxypyridine and 2-hydroxy-1-naphthaldehyde with 2-amino-5-chlorobenzophenone using 3-4 ml of dry ethanol as solvent and irradiated for 4-5 mins. The synthesised Schiff bases such as BSAP and HNAC were irradiated with metal salts under a microwave

oven for 6-10 mins using 3-5 ml of ethanol as a solvent resulting in the formation of Ni-BSAP complex **(41)**and Ni-HNAC complex **(42)**. The complexes were found to be more active against *E. coli, S. aureus, C. albicans* and *P. aeruginosa* [15].

The metal complexes **(43)** and **(44)** were synthesised from Schiff base ligands which were prepared by mixing 5-bromosalicylaldehyde with 2-chloro-4-nitroaniline and 2-amino-5-chlorobenzophenone in a grinder and the reaction mixture was irradiated with 3-4 ml of dry ethanol as solvent under microwave oven for 3-4 mins. The resulting Schiff bases were mixed with $NiCl_2.6H_2O$ in a grinder and irradiated under a microwave oven with 3-4 ml of dry ethanol for 4-5 mins resulting in the formation of complexes **(43)** and **(44)**. The antimicrobial activity of the complexes were determined against *S. aureus*, *E. coli, A. niger* and *C. albicans.* The synthesised Schiff bases and their complexes exhibited better antimicrobial potential against the respective micro-organisms [16].

A monofunctional bidentate Schiff base ligand was prepared and reacted with metal salt dissolved in ethanol and double distilled water in presence of benzene for 5-8 mins under a microwave oven. The antibacterial and antifungal efficacy of the complex **(45)** was evaluated against *E. coli, S. aureus, A. niger* and *F. oxysporum.* The complex showed excellent efficacy as compared with the standard drugs such as Streptomycin and Fluconazole [17].

2-aminobenzimidazole and 4,4-dibromo benzyl were reacted under a solvent-free condition through the microwave oven for 30 mins and the final product was recrystallized with ethanol resulted in the formation of a pale yellow coloured Schiff base ligand. The synthesised Schiff base ligand was mixed with a metal salt and irradiated under microwave irradiation for 30-150 sec resulting in the formation of a light green-coloured stable complex **(46)**. The antibacterial efficacy of the complex was determined against *E. coli, S. aureus* and *S. typhi* and was found to be 100, 100 and 250 µg/ml of minimum inhibitory concentration [18].

The 1:2 metal complexes were derived from 1-(4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)phenyl)-N-(1H-1,2,4-triazole-3-yl)methenamine triazole Schiff base was prepared by thoroughly combining 3-amino-1,2,4-triazole with 4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)benzaldehyde in a mortar and it was irradiated with 3-4 ml of ethanol at 90 W for 90 sec resulted in the formation of orange coloured product. The synthesised Schiff base was mixed with $Ni(AcO)_2.4H_2O$ dissolved in 4 ml of ethanol and irradiated under a microwave oven resulting in a pale brown-coloured complex **(47)** formation with more yield and less time. The antibacterial efficiency of the complex was evaluated against *E. coli, S. aureus, B. subtilis* and *P. aeruginosa* and was found to be 15, 12, 15 and 18 mm of zone of inhibition and the antifungal activity of the complex was evaluated against *A. niger* and *C. albicans* and was found to be 29 and 20 mm of zone of inhibition. The cytotoxic potential of the complex was determined as 89.0 µM of IC_{50} value against the human colorectal (HCT 116) cancer cell line [19].

(E)-1-(2-hydroxy-3-methoxybenzylidene)-3-phenylurea Schiff base ligand was derived from *o*-vanillin and phenyl urea at 450 W for 15 mins using a microwave oven. The Schiff base ligand was mixed with $Ni(CH_3CO_2)_2.\ 4H_2O$ to form a homogenous mixture and irradiated under a microwave oven for 15 mins at 450 W. The resulting complex **(48)** showed greater antimicrobial potential against *E. coli, S. aureus, B. subtilis, C. albicans* and *Aspergillus fumigatus* in the range of 16, 10, 18, 23 and 23 mm of zone of inhibition and does not exhibited activity towards *S. typhimurium.* The cytotoxic evaluation of the complex showed 149 and 49.9 µg/ml of IC_{50} value against human breast (MCF-7) and human colorectal (HCT 116) cancer cell lines [22].

Azomethine Schiff base ligand namely (1,5-dimethyl-2-phenyl-[(3,4,5-trimethoxybenzylidene)amino]-1,2-dihydropyrazol-3-one) (DTAD) was synthesised using microwave irradiation of 4-aminophenazone with 3,4,5 trimethoxybenzaldehyde with methanol and 2 drops of acetic acid for 1 min at 210 W. Then the chloride and acetate metal salts and the ligand were mixed in a grinder in 1:2 ratio and the reaction mixture was exposed to microwave irradiation for 2-3 mins resulted in higher yields of complexes (**49)** and (**50)**. The antibacterial activity of the complexes was determined against *E. coli, S. aureus, S. pyogenes* and *S. typhimurium* and the results revealed that the metal chloride complex exhibited better activity as compared to the standard drug chloramphenicol [26].

A mononuclear Nickel complex was derived from the Schiff bases 4-methyl-2-[(4-methylpyridin-2-ylimino)methyl]phenol and 4-methyl-2-[(pyridin-2-ylmethylimino)methyl]phenol with 5-methyl salicylaldehyde and methanol under microwave irradiation for 20 mins at 200 W and the antibacterial activity of the complex was found to be effective against *S. aureus*, *B. subtilis*, *E. coli* and *P. aeruginosa* in the range of 6.3-19.3 mm of zone of inhibition [30]. The structures of the nickel complexes are given in Figures 8 and 9.

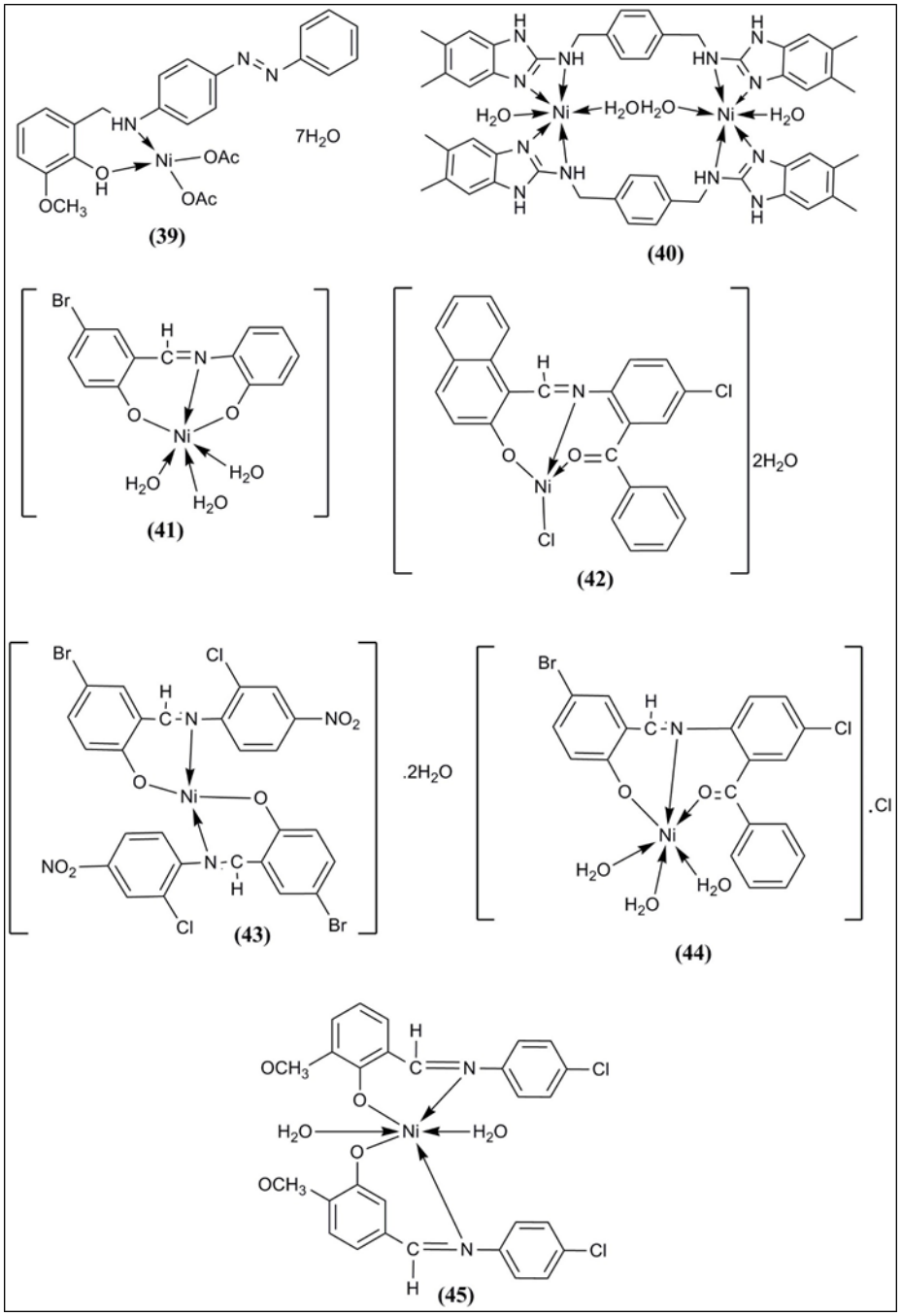

Figure 8 Structures of Nickel complexes

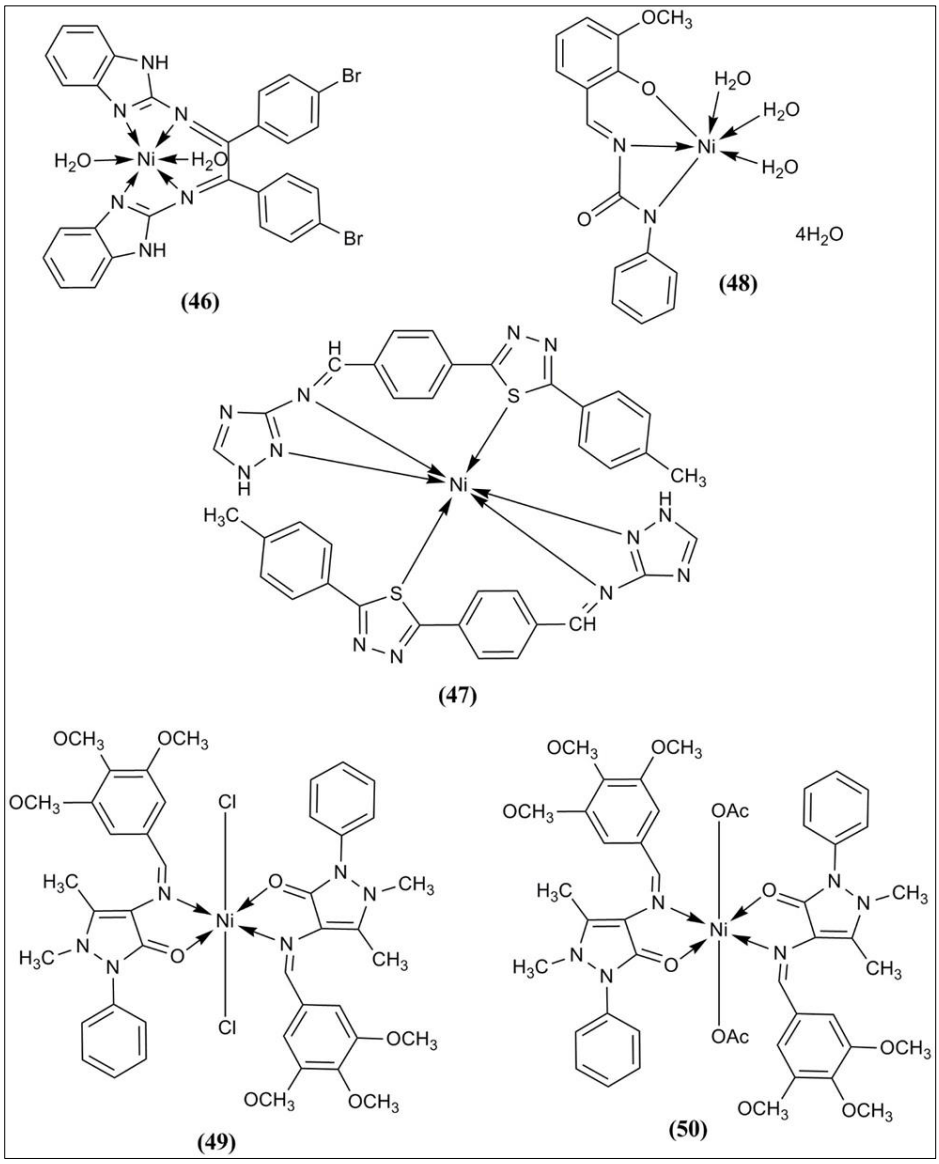

Figure 9 Structures of Nickel complexes

2.5. Zinc (Zn) complexes

A novel Zinc (Zn) complex **(51)** synthesised from the Schiff base ligand was synthesised from o-vanillin and 4-aminoazobenzene under a microwave irradiation in a short time with better yield. Then the Schiff base ligand was reacted with an equimolar amount of hydrated metal salt with a few drops of ethanol and exposed to microwave irradiation for 10 mins at 360 W. The antibacterial activity of the complex was found to be active against *E. coli, S. aureus, B. subtilis* and *S. typhimurium* in the range of 16, 22, 22 and 11 mm of zone of inhibition. The potential cytotoxic activity of the prepared complex was screened against human colon (HCT-116) and human liver (HepG-2) cancer cell lines and the results revealed the complex exhibited considerable cytotoxic efficacy in the range of 8 and 10 µg/ml of IC_{50} value against HCT-116 and HepG-2 cell lines as compared to the Schiff base ligand [13].

A novel bidentate Schiff base ligand was prepared by the condensation of 2-amino-5, 6-dimethyl benzimidazole with terephthalaldehyde under a solvent-free condition in the microwave oven at 750 W for 10 mins periodically resulting in the formation of orange-coloured Schiff base ligand namely N-(4-((Z)-(5,6-dimethyl-1H-benzo[d]imidazol-2-ylimino)methyl)benzylidene)-5,6-dimethyl-1H-benzo[d]imidazol-2-amine. Then the synthesised Schiff base ligand was mixed with metal salt $Zn(NO_3)_2.6H_2O$ and exposed to microwave irradiation for 10 mins at 750 W. The complex **(52)** showed better antimicrobial potential in the range of 250, 125 and 500 µg/ml of minimum inhibitory concentration against *E. coli, S. aureus* and *S. typhi* [14].

A novel Zn complex derived from Schiff base was prepared from 2-aminobenzimidazole and 4,4-dibromo benzyl were reacted under a solvent-free condition through the microwave oven for 30 mins and the final product was recrystallized with ethanol resulting in the formation of a pale yellow-coloured Schiff base ligand. The synthesised Schiff base ligand was mixed with a metal salt and irradiated under microwave irradiation for 30-150 sec resulting in the formation of a greenish-yellow coloured complex **(53)**. The complex exhibited better antibacterial potential against *E. coli, S. aureus* and *S. typhi* in the range of 500, 100 and 500 µg/ml of minimum inhibitory concentration [18].

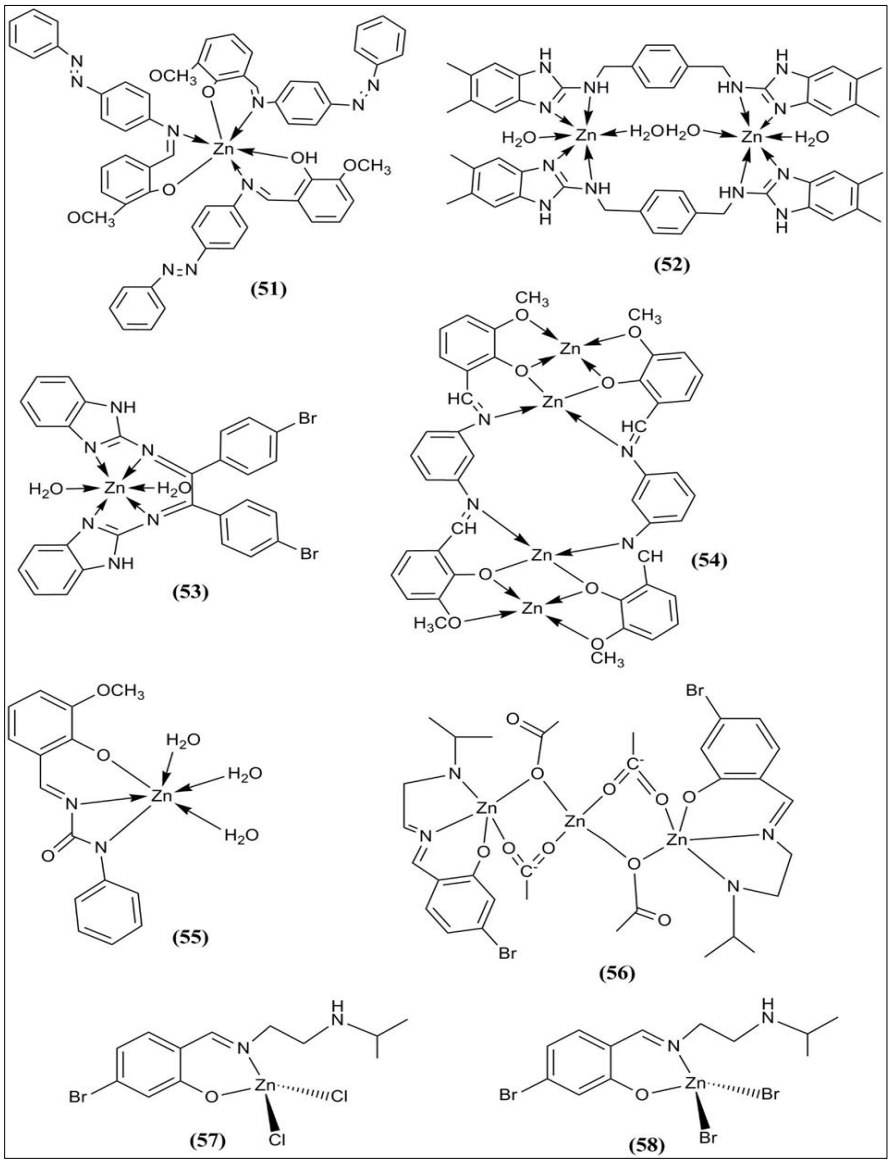

Figure 10 Structures of Zinc complexes

Hexadentate Zn Schiff base metal complex derived from the Schiff base 6,6'-((*1E,1'E*)-(1,3-phenylenebis(azanylylidene)) bis(methanylylidene))bis-(2-methoxyphenol) was synthesized via condensation of *o*-vanillin and *m*-phenylenediamine under reflux for 1 h resulted in the formation of orange crystalline Schiff base. Then the Schiff base was mixed with metal acetate salt with a few drops of triethylamine and the reaction mixture was placed in microwave oven and stirred at 1000 rpm for 10 mins resulting in the formation of the yellow coloured complex **(54)**. The cytotoxic potential of complex was evaluated as 20.08 ± 1.32 µM of IC_{50} value against the human colorectal (HCT 116) cancer cell line [20].

A novel tridentate Schiff base ligand (E)-1-(2-hydroxy-3-methoxybenzylidene)-3-phenylurea was derived from *o*-vanillin and phenyl urea at 450 W for 15 mins using a microwave oven. The Schiff base ligand was mixed with $Zn(CH3CO_2)_2$. $2H_2O$ and irradiated under a microwave oven for 15 mins at 450 W. The resulted complex showed greater antimicrobial potential against *E. coli, S. aureus, B. subtilis, Salmonella typhimurium, C. albicans* and *Aspergillus fumigatus*.

The cytotoxic evaluation of complex **(55)** showed 61.3 and 51.9 µg/ml of IC_{50} value against human breast (MCF-7) and human colorectal (HCT 116) cancer cell lines [22].

A mononuclear zinc complex derived from the Schiff bases 4-methyl-2-[(4-methylpyridin-2-ylimino) methyl]phenol and 4-methyl-2-[(pyridin-2-ylmethylimino)methyl]phenol with 5-methyl salicylaldehyde and methanol under microwave irradiation for 20 mins at 200 W and the antibacterial activity of the complex was found to be effective against *S. aureus*, *B. subtilis*, *E. coli*, and *P. aeruginosa* in the range of 6.3-16.1 µm of zone of inhibition [30].

Zinc Complexes Derived from the Schiff base 5-bromo-2-(((2-isopropylamino)ethyl) imino)methyl)phenol was prepared from the condensation of 4-bromosalicylaldehyde, *N*-isopropylethane-1,2-diamine and zinc acetate dehydrate/zinc chloride/zinc bromide under microwave irradiation at 200 W for 10 mins resulting in the formation of complexes **(56-58).** The antibacterial potential of the complexes was determined against *E. coli, S. aureus, B. subtilis* and *S. typhi* and the results revealed that the complexes exhibited greater activity against *E. coli* and *S. aureus* [31]. The structures of the zinc complexes are given in Figure 10.

3. Conclusion

In coordination and organometallic chemistry, microwave systems have become more effective in producing novel transformations in inorganic synthesis. Because of the more efficient heating, it improves the rate of reactions. Microwave-assisted synthesis Schiff base metal complexes have attracted more attention because of their eco-friendliness, safety, potency and efficacy in a short time than the conventional synthetic chemistry. In this review, various metal complexes derived from the potent Schiff bases were summarized along with their anti-proliferative and anti-microbial efficacy against various microorganisms and cancer cell lines. The various metal complexes showed promising cytotoxic activity with effective IC_{50} values. Hence it would be beneficial to consider using Microwave irradiation while designing a novel inorganic synthesis.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare no potential conflicts of interest with respect to research, authorship and/or publication of this article.

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