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Review Article

## APPLICATIONS OF METAL – SCHIFF'S BASE COMPLEXES: A REVIEW

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### Abstract

Schiff bases are versatile ligands which are synthesized from the condensation of an amino compound with carbonyl compounds. These compounds and their metal complexes are very important as catalysts in various biological systems, polymers, dyes and medicinal and pharmaceutical fields. Their use in birth control, food packages and as an O<sub>2</sub> detector is also outlined. This review summarizes the applications of Schiff bases and their complexes

**Keywords:** Schiff bases, metal complexes, biological activity, nonlinear optical properties.

### Introduction

Schiff bases derived from an amino and carbonyl compound are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively<sup>1</sup>. In azomethine derivatives, the C=N linkage is essential for biological activity, several azomethines were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities<sup>2</sup>. Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical and biological activities<sup>3</sup>. With the increasing incidence of deep mycosis, there has been increasing emphasis on the screening of new and more effective antimicrobial drugs with low toxicity. Schiff-base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety<sup>4</sup>. A considerable number of Schiff-base complexes have potential biological interest, being used as more or less successful models of biological compounds<sup>5</sup>. Not only have they played a seminal role in the development of modern coordination chemistry, but also they can also be found at key points in the development of inorganic biochemistry, catalysis and optical materials<sup>6</sup>.

### Biological Activities

#### Antimicrobial Activities

Schiff base<sup>7</sup> derived from furyl glyoxal and p-toluidene show antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, and *Proteus vulgaris*. Complexes of thallium (I) with benzothiazolines<sup>8</sup> show antibacterial activity against pathogenic bacteria. Various metal complexes in II<sup>nd</sup> and IV<sup>th</sup> oxidation state derived with aniline<sup>9-13</sup> show different behaviour with different types of bacteria. Metal complexes<sup>14</sup> of Mo (IV) and Mn (II) with ligands hydrazine carboxamide and hydrazine carbothiamide show antibacterial activity against *S. aureus* and *Xanthomonas compestris*. Tridentate Schiff bases<sup>15-18</sup> and their metal complexes show antibacterial activities against *E. coli*, *S. aureus*, *B. subtilis* and *B. pumilus*. Some aldimines<sup>19</sup> (E & Z forms), pyrazine<sup>20</sup>, amino acid derived Schiff bases<sup>21-23</sup> and heterocyclic-ketone derived Schiff bases<sup>24,25</sup> show antibacterial activity. Some heterocyclic<sup>26-28</sup> Schiff bases can act as an antibacterial agent. Isatin derived Schiff bases<sup>29,30</sup> possess anti-HIV activity and antibacterial activity. Schiff bases (benzimidazole<sup>31</sup>, toluidinones<sup>32</sup>, quin-azolinones<sup>33</sup>, furaldehyde<sup>34</sup>, thiazole<sup>35, 36</sup>, pyridine<sup>37</sup> and benzyldithio -

carbazate<sup>38,39</sup>, glucosamine<sup>40</sup>, pyrazolone<sup>41,42</sup>, hydrazide<sup>43</sup>, furfuraldiam-ine<sup>44</sup>, halogenated<sup>45</sup>, thiazolidiones or azetidiones<sup>46</sup>, indole<sup>47</sup>, p-fluorobenzaldehyde<sup>48</sup>, p-anisidiene<sup>49</sup>, thio-semicarbazone<sup>50</sup>, thiadiazolines<sup>51</sup> and imidazolinones<sup>52</sup> show antibacterial activity. Schiff bases, ligands<sup>54</sup> containing cyclo-butane and thiazole rings, show antimicrobial activity.

Schiff bases of pyrrolidione, pyridone with o-phenylenediamine and their metal complexes<sup>54</sup> show antibacterial activity. N-5 chloro-salicylidene tauriene Schiff base<sup>55</sup> and its Cu, Ni complexes show antibacterial activities to *Colibacillus* and *Pseudomonas aeruginosa*. Schiff base conjugates of p-amino salicylic acid<sup>56</sup> enhance antimycobacterium activity against *Mycobacterium smegmatis* and *M. lovis BCG*. Schiff<sup>57-59</sup> base with thiophene carboxaldehyde and aminobenzoic acid show antibacterial activity. Lysine based Schiff bases and their complexes<sup>60</sup> with La, Co, Fe, show bacteriostatic activity to *B. subtilis*, *E. coli* and *S. aureus*. Zn (II), Cd (II), Ni (II) and Cu (II) complexes with furfural and semicarbazide<sup>61</sup>, and with furfurylidene diamine<sup>62</sup> Schiff bases show antibacterial activities. Salicylidene derivatives<sup>63</sup>, neutral tetra-dentate ligand and metal-complexes<sup>64</sup> show antibacterial activities against *S. typhi*, *S. aureus*, *Kelbsiella pneumoniae*, *B. subtilis* and *S. flexneri*. Organo-silicon (IV) complexes<sup>65</sup> with bi-dentate Schiff base, and organo-silicon (IV) complexes<sup>66</sup> and organo-lead (IV) complexes<sup>67</sup> with nitrogen donar ligands of sulpha drugs possess antibacterial activities. Using microcalorimetry<sup>68</sup>, antibacterial activities against *E. coli* of Schiff bases and their metal complexes can be studied.

Schiff base derived from indoline-2, 3-dione and 2-aminobenzoic acid and its Tin complex showed antibacterial activity against *Staphylococcus aureus*. The results compared with standard drug (Imipinem) have indicated that compounds were active but activity was lesser than the standard drug. This activity might be due to the presence of a hydroxyl and phenyl group<sup>69</sup>. The increased activity in the organotin complexes may be due to the coordination and polarity of a tin(IV) atom with oxygen of the ligand. The order of increasing activities is ligand < MeSnL < PhSnL < BZ3SnL, the results matched with the previously reported data for the biological activity of organotin complexes<sup>70</sup>.

Complexes of Co(II),Cu(II),Ni(II),Mn(II) and Cr(III) with Schiff bases derived from 2,6-diacetylpyridine and 2-pyridine carboxaldehyde with 4-amino-2,3-dimethyl-1-phenyl- 3-pyrazolin-5-one show antibacterial and antifungal activities against *Escherichia coli*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Mycobacterium Smegmatis*, *Pseudomonas aeruginosa*, *Enterococcus cloacae*, *Bacillus megaterium* and

*Micrococcus leteus*. The results showed that L<sub>1</sub> ligand has a greater effect against *E. coli* than the other bacteria while it has no activity against *S. aureus*. Metal complexes have a greater effect than L<sub>2</sub> against almost all bacteria<sup>71</sup>.

The Schiff base 4-chloro-2-(2-morpholinoethylimino) methylphenolato methanolchloro and its Zn(II) complex were screened for antibacterial activity against two Gram positive bacterial strains (*B. subtilis* and *S. aureus*) and two Gram-negative bacterial strains(*E. coli* and *P. fluorescence*) by the MTT method. The Schiff base showed significant activity against two Gram-negative bacterial strains with MIC of 12.5µg/mL but was inactive against two Gram negative bacterial strains. The Zn complex showed a wide range of bactericidal activities against the Gram positive and Gram negative bacteria, were potent than, or similar with commercial antibiotics (Kanamycin and penicillin)<sup>72</sup>.

Bidentate complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with benzofuran-2-carbohydrazide and benzaldehyde [BPMC] or 3,4-dimethoxybenzaldehyde[BDMcPMC] showed biological activities. Co(II) and Cd(II) complexes of [BPMC] are moderately active toward *E.coli* whereas Cu(II), Zn(II) and Ni(II) complexes of [BPMC] and Cu(II) and Zn(II) complexes of [BDMcOPMC] are more active against *S.aureus* as compared to free ligands. None of the complexes are active against *A.niger*, but in the case of *A.fumigatus*, Cu(II),Co(II), Ni(II) and Cd(II) complexes of [BDMcOPMC] are more active than the parent ligands<sup>73</sup>.

Amino acid Schiff base derived from 2- hydroxy-5-methylacetophenone and glycine and its transition metal complexes showed bacterial activities. The ligand was bacteriostatic against bacterial strains except *Proteus vulgaris*, *Shigella flexneri*, and *Bacillus coagulans*. All complexes are either resistant or less sensitive against *P.vulgaris*. However compared to the antibacterial activity of the standard antibiotic streptomycin, the activity exhibited by the ligand and metal complexes was lower. The metal complexes showed to exhibited higher activity than the free ligand against the same organism under identical experimental conditions, such increased activity of the metal chelates can be explained on the basis of chelation theory<sup>74</sup>.

Mixed ligand complexes with 2,6-pyridinecarboxaldehydebis(phydroxyphenylamine( L<sub>1</sub>), 2,6-pyridinecarboxaldehydebis (o-hydroxyphenylamine(L<sub>2</sub>) showed anti - bacterial activities. The data obtained reflect that the two Schiff base ligands L<sub>1</sub> and L<sub>2</sub> have moderate activity in comparison with *Staphylococcus aureus*, *Escherichia coli* and less active in comparison with

*Pseudomonas aeruginosa*. L<sub>1</sub> ligand shows a moderate activity towards *Bacillus subtilis* while L<sub>2</sub> ligand is less active. The remarkable activity of the two Schiff base ligands may be arise from the pyridyl-N and the hydroxyl groups which may play an important role in the antibacterial activity[13] as well as the presence of two imine groups which imports in elucidating the mechanism of transformation reaction in biological system<sup>75</sup>. Tetra and hexacoordinate metal chelate complexes of phosphate Schiff base ligands were found to be possess remarkable bacterial properties, it is however interesting that the biological activity gets enhanced on undergoing complexation with the metal ions<sup>76</sup>.

Neutral tetradentate complexes of transition metals with Schiff bases derived from 2-aminophenol/2-aminothiophenol and 1-phenyl-2,3- dimethyl-4(4-iminopentan-2-one)-pyrazol-5-one showed antimicrobial activity against *Staphylococcus aureus*, *Bacillus subtilis*, *Klebsiella pneumoniae*, *Salmonella typhi*, *Pseudomonas aeruginosa*, *Shigella flexineri*, *Aspergillus niger* and *Trichoderma viride*. Most of the complexes have higher activity than the free ligand<sup>77</sup>. Complexes of transition metal with Schiff base derived from 2,3-dihydroquinazolin-4(1H)-one (DHQ) showed antimicrobial activity. Preliminary testing of the ligand and metal complexes for antimicrobial activity on the gram positive *S.aureus* and gram negative *E.coli* shows that the ligand is active only against *S.aureus* and the activity is enhanced by complexation. The metal complexes exhibit more bacteriostatic activity against *E.coli*. The appearance of activity may be due to synergistic mechanism<sup>78</sup>.

A tridentate Schiff base derived from the condensation of Sbenzylthiocarbamate with salicylaldehyde and transition metal complexes showed significant bioactivity against *Pseudomonas aeruginosa* (gram negative) and *Bacillus cereus* (gram positive) while the uranium analogue was effective against *Bacillus cereus* and showed very weak activity against *Candida albicans* fungi<sup>79</sup>.

### Antifungal Activities

Thiazole and benzothiazole Schiff bases<sup>80</sup> possess effective antifungal activity. Presence of methoxy, halogen and naphthyl groups enhance fungicidal activity towards *Curvularia*. Pyrandione Schiff bases<sup>81</sup> show physiological activity against *A. niger*. Some Schiff bases of quinazolinones<sup>82</sup> show antifungal activity against *Candida albicans*, *Trichophyton rubrum*, *T. mentagrophytes*, *A. niger* and *Micosporum gypseum*. Furfurolidene nictoinamide Schiff base<sup>83</sup> shows antifungal activity against *A. niger*, *Alternaria solani* and *Collectotricum capsici*.

Schiff bases and their metal complexes<sup>84</sup> formed between furan or furyl glyoxal with various amines show antifungal activity against *Helminthosporium gramineum* (causing stripe disease in barely), *Syncephalostrum racemosus* (causing fruit rot in tomato) and *C. capsici* (causing die back disease in chillies). Moreover, ligand hydrazine and carbothioamide<sup>85</sup> and their metal complexes show antifungal activity against *A. alternata* and *H. graminicum*. Molybdenum and manganese complexes control disease (caused by *A.alternata*) in brinjal crop. Benzothiazole or phenyl-azo-thiazole<sup>27</sup> derived Schiff bases and metal complexes show microbiological activity against *A. niger* and *A. alternata*. Tridentate Schiff base<sup>86</sup> and their metal complexes show biocidal activities. Ruthenium (II) complexes<sup>87</sup> with Schiff base salicylaldimine, thalium(I) complexes<sup>88</sup> with benzothiazolines, copper (II) complexes<sup>89</sup> of benzoylpyridine Schiff base show antifungal activities. Oxovanadium (IV) complexes<sup>90</sup> with triazole shows antifungal activity. As (III), Sb (III), and Bi (III) complexes<sup>91</sup> with o- tolylammonium di-thiocarbamate are antifungal against *A. niger* and *A. alternata*. Some novel cephalixin- derived Schiff bases<sup>92</sup> and their metal complexes show antifungal activities. Schiff bases<sup>93</sup> derived from salicylaldehydes and boronate esters show antifungal activities against *A. niger* and *A. flavus*. Schiff base<sup>94</sup> of salicylaldehyde and O,O-di-methyl thiophosphoramidate and their complexes with Cu(II), Ni(II), and Zn(II) are effective chemicals to kill *Tetranychus bimaculatus*.

The microbial activity of the N-(2-hydroxy-1-naphthalidene) phenylglycine and its transition metal complexes was investigated. From the antifungal screening data it is concluded that the activity of the ligand has increased upon complexation. Cu(II), Ni(II) and Co(II) complexes have shown better antifungal activity compared to the ligand and the corresponding metal salts<sup>95</sup>. Two bidentate Schiff base ligands 2- (2-hydroxy-3, 5-dichloro/dibromo) benzaldehyde-[4- (3-methyl-3-mesitylcyclobutyl)-1, 3-thiazol-2-yl]hydrazone, L<sub>1</sub>H, L<sub>2</sub>H and their metal complexes were tested against a yeast-like fungus *C.albicans*<sup>96</sup>. The fungicidal effect of salicylaldimine containing formaldehyde and piperazine moiety and its metal polychelates were determined against two yeast *Candida albicans*, *Aspergillus*. The Cu(II)-polychelate exhibited high activity against *Candida albicans* and the other show mild activity. The presence of N and O donor groups in the ligand and its metal polychelates inhibited enzyme production because enzymes that require free hydroxyl group for their activity appear to be especially susceptible to deactivation by the metal ion of polychelates. All the metal polychelates are more toxic than the ligand<sup>97</sup>.

Neutral complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases derived from 3-nitrobenzylidene-4-aminoantipyrine and aniline(L<sub>1</sub>)/p-nitroaniline(L<sub>2</sub>)/p-methoxyaniline (L<sub>3</sub>) showed antifungal activity. A comparative study of the MIC values for the ligands and their complexes indicates that the complexes exhibit higher antimicrobial activity. Such increased activity of the complexes can be explained on the basis of overtone's concept and Tweedy's chelation theory<sup>98</sup>. Inhibition is enhanced with the introduction of an electron withdrawing nitro group in the phenyl ring<sup>99</sup>. Semicarbazones and thiosemicarbazones complexes of Ni(II) metal showed antifungal activities against 11 pathogenic fungi. The complexes were moderate active against all pathogenic fungi and much lower than those of standard fungicide Nistatin<sup>100</sup>. Co(II),Ni(II) and Cu(II) complexes with Schiff base 3,3'-thiodipropionic acid bis (4- amino - 5- ethylimino-2,3-dimethyl-1-phenyl- 3-pyrazoline showed antifungal activity against *Alternaria brassicae*, *Aspergillus niger* and *Fusarium oxysprum* and results indicate that the complexes show the enhanced activity in comparison to free ligand<sup>101</sup>.

### Antiviral Activities

Schiff bases of gossypol show high antiviral activity<sup>102</sup>. Silver complexes in oxidation state I showed inhibition against Cucumber mosaic virus; glycine salicylaldehyde Schiff base Ag (I), gave effective results up to 74.7% towards *C. mosaic virus*<sup>103</sup>.

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