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Biological Importance and Corrosion Inhibition by Schiff Base Metal Complexes: A Review

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ABSTRACT: Schiff bases are aldehyde or ketone like compounds in which the carbonyl group is replaced by an imine or azomethine group. They are widely used for industrial purposes and also exhibit a broad range of biological activities. Azomethine linkage of Schiff base plays an important role in medical field with so many pharmacological activities such as antimicrobial, antiviral, antitubercular and anticancer activity. The potency of these pharmaceutically useful drugs in treatment of microbial infections and other activities encouraged the development of some more potent and significant compounds and metal complexes. An interesting property of Schiff bases is their use as effective corrosion inhibitors.

KEYWORDS: Schiff base, biological activities, imine, microbial infections, corrosion inhibitors.

I. INTRODUCTION

Azomethine group (-C=N-) containing compounds typically known as Schiff bases have—been synthesized by the condensation of primary amines with active carbonyls. Schiff base ligands have significant importance in chemistry; especially in the development of Schiff base complexes, because Schiff base ligands are potentially capable of forming stable complexes with metal ions [1]. A Schiff base behaves as a flexidentate ligand and commonly coordinates through the O atom of the deprotonated phenolic group and the N atom of azomethine group[2]. Schiff bases form a significant class of compounds in medicinal and pharmaceutical chemistry with several biological applications that include antibacterial, [3] antifungal, [4-6] anticancer,[7-8] anti-oxidant,[9-12] activities. Many Schiff base complexes show excellent catalytic activity in various reactions at high temperature (>100 °C) and in the presence of moisture. Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis, hence the need for a review article highlighting the catalytic activity of Schiff base complexes realized [13]. Today, Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures.

Schiff bases have been previously reported as effective corrosion inhibitors for steel, copper and aluminum in acid medium like hydrochloric acid, sulphuric acid, acetic acid, formic acid etc. This is because the compounds containing functional groups with hetero atoms, which can donate lone pair of electrons, are found to be very efficient as inhibitors against metal corrosion in many environments. Many N-heterocyclic compounds with polar groups and/or π electrons are also acting as efficient corrosion inhibitors in acidic solutions.

II. BIOLOGICAL ACTIVITIES

Antibacterial activities

Resistance to the various antibiotics has increased the mortality rate associated with infectious diseases directly related to bacteria. The lack of effective treatments is the main cause of this problem. The development of new antibacterial



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agents with novel and more efficient mechanisms of action is definitely an urgent medical need. Schiff bases have been pointed to as promising antibacterial agents.

Shi and coworkers [14] have reported the synthesis of a series of Schiff bases by reacting 5-chloro- salicylaldehyde and primary amines. The compounds were assayed for antibacterial (B. subtilis, E. coli, P. fluorescence and s. coccusaureus) and antifungal (A. niger, C. albicans and T. rubrum) activities. Among the compounds tested, (E)-4chloro-2-((4-fluro- benylimino)-methyl)phenol showed the most favorable antimicrobial activity against B. subtilis, E. coli, P. flurescence, S. aureus and A. niger, respectively. Ispir and coworkers [15] synthesized the 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-phenyl3-pyrozolin-5-one the complexes show antibacterial and antifungal activities against E.coli, S.aureus, K. pneumoniae, M. smegmatis, P.aeruginosa, E.cloacae, B.megaterium and M. leteus. They reported that 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 ligand against almost all bacteria. Lei and coworkers [16] synthesised the Schiff base 4-chloro-2-(2-morphi- olinoethylimino) methylphenolatomethanolchloro and its Zn(II) complex and screened them 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). The Schiff base showed significant activity against two Gram-negative bacterial strains 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 and were potent than or similar with commercial antibiotics (Kanamycin and penicillin). Jain et al. [17] synthesized two novel Schiff's base metal complexes of Co(II) had been from 2-[(5-bromo2-hydroxy benzylidene) amino]pyridin-3-ol,{5-chloro-2-[(2hydroxynaph-thylidene)amino] phenyl}-phenyl methanone. All the synthesized compounds were characterized by various elemental and spectral analyses and also tested against some bacteria. They reported that Schiff base ligand and their Co(II) complexes displayed a good activity against the Gram-positive bacteria; S. aureus and Gram-negative bacteria E. coli. Lekha et al. [18] synthesised the Schiff base ligand 2-[(5-Bromo-2-hydroxy-benzylidene)-amino]-5methyl-pentanoic acid by the condensation of leucine with 5-bromosalicyaldehyde. Cu(II), Co(II) and Ni(II) complexes of the ligand were also synthesised. The synthesized ligand and complexes were structurally characterized by various spectral. The analytical data of the complexes showed the formation of 1:2 metal to ligand ratio with the formula [ML₂]. The ligand and their metal chelates have been screened for their antimicrobial activities. The result showed that the metal complexes have enhanced inhibitory activity than the Schiff base ligand under identical conditions. Sherif and Abdel-Kader [19] synthesized Cu(II) complexes with Schiff's base by the condensation of 1,4-phenylenediamine with 5,7-dihydroxy-6-formyl-2-methyl benzopyran-4-one or 6-formyl-7-hydroxy-5-methoxy-2-methylbenzo-pyran-4-one. The newly synthesized Co(II) complexes were analyzed by different analytical techniques. Both the Co(II) complexes of the two Schiff base ligands had been checked for antibacterial activities by using disk diffusion method against S. capitis and E. coli. The Result confirmed better antibacterial activities of the newly synthesized complexes.

Antifungal Activities

Fungal infections usually are not only limited to the contamination of surface tissues. Recently, there was a considerable increase in the incidence of systemic fungal infections, which are potentially life threatening [20]. Exploration and development of more effective antifungal agents is necessity, and the individual Schiff bases are considered to be promising antifungal medicines [21]. Ruthenium (II) triphenylposphine complex containing bidentate Schiff base derived from condensation of salicyladehyde with aniline o,m, and p-toluidine show antifungal action against fungi *A. flavus* [22].

Gudasi *et al.* [23] investigated the microbial activity of the N-(2-hydroxy-1naphthalidene)- phenylglycine and its transition metal complexes. 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. Cu (II) complexes with Schiff base 3,3'-thiodipropionic acid bis (4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3pyrazoline showed antifungal activity against *A. brassicae*, *A. niger* and *F. oxysporum* and results indicate that the complexes show enhanced activity in comparison to free ligand [24]. Antifungal activities of 2-amino-benzthiazole and 4-aminosalicylic acid Schiff bases were tested against *A. niger* and *C. Corda*. From the result obtained after antifungal activity, it was found that benzthiazole Schiff base are more effective against all tested Fungi than the salicylic Schiff base. The greater activity of these compounds is probably due



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to the presence of benzthiazole moiety [25]. Schiff base ligands derived from sulfonamide and their copper (II) complexes have been tested for their antifungal activity against fungal strains, *T. longifusus*, *C. albicans*, *A. flavus*, *M. canis*, *F. solani and C. glabrata*. The results indicate that complex and ligand show good antifungal activities [26].

Anticancer Activities

Cancer is undoubtedly one of the main health concerns facing our society and one of the primary targets regarding medicinal chemistry. Discovery for new types of anticancer drugs is continuing and the mechanism of interaction of such drugs with DNA is under exploration. Variety of Schiff base metal complexes have been used as drugs and are well known to increase their activity or when administered as metal complexes show higher activity towards specific targets.

Copper (II) complexes containing Schiff bases derived from S-benzylde thiocarbazate and saccharinate showed anticancer properties. These complexes have been active against the leukemic cell line (HL-60. The activities being higher than the standard anticancer drug Doxorubicin [27]. L-glutamine schiff's base has proteasome inhibitory activity in human breast cancer and leukemia cells. The complex selectively inhibits the proteasomal activity and induces the cell death in cultured breast cancer cells, but not normal, immortalized breast cells [28]. Aniela *et al.* [29] have synthesized and characterized three mononuclear copper(II) complexes with three ligands 2-Methyl-4-nitropyridine N-oxide (L1); 2,6-dimethyl-4-nitropyridine N-oxide (L2); 2,3,6-trimethyl-4-nitropyridine N-oxide (L3). The free ligands and the copper complexes were tested for their *in-vitro* anti-proliferative activity against breast cancer and colon adenocarcinoma. The ligands and the complexes were found to be active against the breast cancer and it was found that increase in the number of methyl groups in the ligand causes a decrease of the activity for both free ligands and the complexes. The results showed that the complexes without or with one methyl group exhibit remarkable cytotoxic activity.

Osowole *et al.* [30] have reported the synthesis and characterization of the Schiff base, 3{[(4,6-dimethoxypyrimidin-2yl)imino]methyl}naphthalen-2-ol and its VO(IV), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) complexes. The anticancer activities of the compounds were analysed against the MCF-7 cell line. From the observations it was concluded that Pd(II) and Cu(II) show the activity within the same order as Cis-platin, whereas the ligand and other metal complexes have been found to be inactive. The high activity of the Pd(II) and Cu(II) complexes may be attributed to their planar structure which has been documented to avoid possible steric hindrance during physiological actions. Thus the coordination enhances the activity of the complexes. El-Aziz *et al.* [31] have synthesized Cu(II), Fe(III), Co(II), Ni(II) and Zn(II) complexes from N-(pyridine-2-ylmethylene)benzo[d]thiazol-2-amine Schiff base and characterized by elemental analysis, electrical conductance, mass spectra, magnetic susceptibility and spectral techniques. *In-vitro* potential cytotoxicity of the Schiff base and its Cu(II), Ni(II) and Zn(II) complexes was tested against human breast carcinoma. The studies reveal that the Cu(II) complex exhibits highly cytotoxic activity towards human breast cancer cell lines. From these studies, it is clearly observed that complexation with metals has a synergistic effect on the antiproliferative activity of these compounds especially against hormone responsive cancers.

Anti-Inflammatory Activities

Vazzana *et al.* [33] synthesized two small sets of aromatic Schiff bases and 2,3-di-iaryl-1,3-thiazolidin-4-one derivatives and tested them for anti-inflammatory and antinociceptive activities. The thiazolidinone derivatives have been obtained from the azomethines through the addition of α -mercaptoacetic acid. Both types of compounds displayed good level of activity against carrageenan induced edema in rat hind paw, while only moderate activity was observed in the writhing test in mice. Anti-inflammatory activity studies of Co (II) complexes of derived from 3,3'-{1,2-phynylene bis (nitrilo (E) methylylidine)} diquinolin-2-ol showed that the metal chelates exhibit a higher inhibitory effect than the free ligand. The anti-inflammatory activity data showed that the metal chelates showed significant anti-inflammatory activity than the free ligand when compared with that of standard diclofenac [34].

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III. CORROSION INHIBITION

An interesting application of Schiff bases is their use as an effective corrosion inhibitor which is based on their ability to spontaneously form a monolayer on the surface to be protected [35]. Schiff bases have been found to posses more inhibitor efficiency than their constituent carbonyls and amines [36].

Desai and coworkers [37] carried out the corrosion inhibition testing of Schiff bases derived from benzaldehyde and aliphatic and aromatic primary amines on aluminium alloy 51S in HCl. Schiff bases showed fairly good inhibition efficiency and conversion of an amine into its Schiff base improved its inhibitive action. Desai et al. [38] studied seven Schiff bases as corrosion inhibitors for MS in HCl solutions by weight loss and electrochemical methods. Polarization data indicate that all these compounds act as predominantly cathodic inhibitors. The corrosion inhibition on SS 400 by Schiff base compounds derived from diamines and o-hydroxy, o-methoxy aromatic aldehyde was investigated by weight loss, electrochemical measurements and surface analysis in various aqueous solutions such as tap water, concentrated tap water and HCl solutions by Shokry [39]. It was found that 93% inhibition efficiency was achieved for N,N'-bis(salicyladehyde)1,12-diaminododecane and adsorption obeyed Langmuir isotherm. Quraishi and co-workers [40] investigated the influence of three macrocyclic compounds on corrosion of MS in HCl using weight loss method, potentiodynamic polarization, AC impedance and hydrogen permeation techniques. All the investigated compounds showed significant efficiencies and reduced permeation of hydrogen through MS in HCl. Potentiodynamic polarization results reveal that macrocyclic compounds acted as mixed inhibitors. Rehim et al. [41] have tested 4-amino antipyrine (AAP) for the corrosion inhibition of MS in 2M HCl using weight loss, potentiodynamic polarization and EIS methods. The results showed that AAP is an inhibitor for MS and the inhibition was assumed to take place via adsorption of the inhibitor molecule on the metal surface. Bansiwa et al. [42] conducted weight loss and thermometric methods to study the inhibition of aluminum corrosion in HCl solution by four Schiff bases such as 2-anisalidine-pyridine, 2-anisalidinepyrimidine, 2-salicylidine pyridine, 2-salicylidine-pyrimidine and have shown that they are effective inhibitors for the corrosion of aluminum in HCl. Quraishi et al. [43] have investigated the inhibition efficiency of three Schiff bases 1vanillinthiosemicarbazone, 1-salicyaldehydethiocarbazone, 1-dimethyl-aminobenzaldehydethiosemicarbazone towards MS in aqueous solutions containing 20% formic and 20% acetic acid media by weight loss and potentiodynamic polarization methods. These compounds acted as mixed inhibitors and shown good inhibition efficiency in formic acid solutions. Hosseini et al. [44] have synthesised and studied corrosion inhibition efficiency of Schiff bases N,N'-orthophenylene(salicylaldimine-acetyl acetoneimine) and N,N'-ortho-phenylene(salicylaldimine-2-hydroxy-1napthaldimine) on MS in 0.5M H₂SO₄ using weight loss, polarization and EIS techniques. These compounds achieved 95% efficiency at a concentration of 400 ppm and identified both compounds as good inhibitors. Emregul and Atakol [45] studied the corrosion inhibition efficiency of Schiff base compounds N-(2-hydroxyphenyl)salicyaldimine, N,N'bis-(salicyaldehyde)-1,3-diaminopropane, N,N'-bis-(2-hydroxybenzyl)1,3-diaminopropane on iron in 1M HCl using weight loss, polarization and electrochemical impedance spectroscopy (EIS) techniques. All these Schiff bases act as good inhibitors and among the three compounds N,N'-bis-(2-hydroxybenzyl) 1,3diaminopropane showed maximum inhibition efficiency. Quraishi and Sardar [46] have synthesised organic compounds like 5mercapto-3-butyl-4salicylidine-1,2,4-triazole (MBST), 5-mercapto-3-butyl 4-benzilidineiminio-1,2,4-triazole (MBBT) and 5-mercapto-3butyl-4-cinnam- ylidineimino-1,2,4-triazole(MBCT) and investigated their corrosion inhibition capacity on MS in 1N HCl and 1N H₂SO₄ by weight loss and potentiodynamic polarization techniques. Inhibition efficiency was found to vary with respect to temperature, concentration and immersion time. The adsorption of these compounds on the steel surface for both acids was found to obey Temkin's adsorption isotherm. Emergul and coworkers [47] studied the inhibitor effect of Schiff base compounds N,N'-bis-(salicylidene)-2-hydroxy-1,3propanediamine and N,N'-bis-(2hydroxy acetophenlidene)-2-hydroxy-1,3 propane diimine on MS in 2M HCl medium. The results revealed that the latter Schiff base showed better inhibition property than the former. Sorkhabi et al. [48] have carried out the corrosion inhibition studies on MS in 1M HCl medium using the Schiff bases benzylidine-pyridine-2-ylamine, (4-benzylidene)pyridine-2-yl-amine and (4-chloro-benzidiline) pyridine-2-yl-amine. Results showed that these compounds were excellent inhibitors and inhibition efficiency increased with increase in inhibitor concentration and varied with the type of functional groups substituted on benzene ring. The polarization curves reveal that compounds are mixed type.



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IV. CONCLUSION

Schiff base ligands and their metal complexes have been investigated to possess potential biological activities in long history of medical application. A great variety of these ligands and their complexes containing hetero atoms show remarkable corrosion inhibition activity which has opened the field of research. However, the biological activity of these Schiff base ligands and their metal complexes deserves further investigation for better result in research field. Although the research on this subject is incipient, a number of reports disclosing the effects of the Schiff bases on the pathogens of clinical interest have recently been increasing. Schiff base compounds have been shown to be promising leads for the design of more efficient biologically active metal complexes.

REFERENCES

- 1. Tariq M., Research report, 24. 2010,
- 2. Archana Singh, K.B.S.Chauhan and P. Singh published in Asian Journal of Chemical and Environmental Research, vol.3(2), 31-33, April 2010.
- 3. Suman Malik, Suparna Ghosh and Liviu Mitu; published in J.Serb.Chem.Soc., 76(10) 1387- 1394, 2011.
- 4. K. Singh, M. S. Barwa, P. Tyagi, Eur. J. Med. Chem., 41, 1, 2006.
- 5. P. Pannerselvam, R. R. Nair, G. Vijayalakshmi, E. H. Subramanian, S. K. Sridhar, Eur. J. Med. Chem., 40, 225, 2005.
- 6. S. K. Sridhar, M. Saravan, A. Ramesh, Eur. J. Med. Chem., 36, 615, 2001.
- 7. S. N.Pandeya, D. Sriram, G. Nath, E. Declercq, Eur. J. Pharmacol., 9, 25, 1999.
- 8. R. Mladenova, M. Ignatova, N.Manolova, T. Petrova, I.Rashkov, Eur. Polym. J., 38, 989,2002.
- 9. O. M. Walsh, M. J. Meegan, R. M. Prendergast, T. A. Nakib, Eur. J. Med. Chem., 31, 989, 1996.
- 10. M. Cacic, M. Molnar, B. Sarkanj, E. Has-Schon and V. Rajkovic, Molecules, 15, 6795-680, 2010.
- 11. S. Dave, N. Bansal, International Journal of Current Pharmaceutical Research, 5 (1), 6-7, 2013.
- 12. A. Nagajothi, A. Kiruthika , S. Chitra And K. Parameswari ,Research Journal of Chemical Sciences, 3 (2), 35-43, 2013.
- 13. Lippard SJ, and Berg JM. Principles of bioinorganic chemistry, University Science Books, 411. 1995.
- 14. L. Shi, H. M. Ge, S. H. Tan, H. Q. Li, Y. C. Song, H. L. Zhu and R. X. Tan, European Journal of Medicinal Chemistry, Vol. 42, No. 4, pp. 558-564. 2007,
- 15. E.Ispir, S.Toroglu, A.Kayraldiz, Transition Met. Chem 33.pp 953. 2008.
- 16. Lei Shi, W-J Mao, Y.Yang, H-L Zhu, J. of Coord. Chem. 62, 3471.2009.
- 17. R. Jain and A. P. Mishra, Journal of Serbian Chemical Society 77, 1.2012.
- 18. LekhaL,Kanmaniraja K, Rajagopal G, Sivakumar D and Easwaramoorthi D.,International Journal of Chemical and Pharmaceutical Sciences,Vol. 4 (2).2013
- 19. O. E. Sherif and N. S. Abdel-Kader, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 117, 519. 2014.
- 20. Rehman W., Baloch M. K., Muhammad B., Badshah A., Khan K. M. Curr. Med. Chem., 13, 11, pp 1321–1335. 2006,
- 21. Characteristic spectral studies and in vitro antifungal activity of some Schiff bases and their organotin (IV) complexes. Chin. Sci. Bull., 49, 2, pp 119–122. 2004.
- 22. Nallaswamy Dharmaraj, P. Viswanathamurthi and K. Natarajan, Transition Metal Chemistry 26: pp 105-109, 2001
- 23. K.B.Gudasi, M.S.Patil, R.S.Vadavi, R.V. Shenoy, S.A.Patil. Transition Metal Chemistry, 31 580.2006.
- 24. S. Chandra, D. Jain, A. K. Sharma and P. Sharma, Molecules, 14, 174 2009.
- 25. Muhammad Aqeel Ashraf, Karamat Mahmood, Abdul Wajid, International Conference on Chemistry and Chemical Process (IPCBEE) vol.10 2011
- 26. H. C. Zahid, A. S. Hazoor and T. S. Claudiu, Labo. di. Chimica. Bioinorg., 27, 58, 2012.
- 27. Y. Xiao, C. Bi, Y. Fan, C. Cui, X. Zhang and Q. Ping Dou, Int. J. Oncogy, 33, 1079, 2012.
- 28. C. Jovanovski, S. Tancera and B. Soptrajanov, Spectrosc. Lett., 28, 1095, 1995.
- 29. Aniela P, Anna K, Marzena P, Joanna W, Maria CG, Julia J, Anna A, Maria K.. J. Inorg. Biochem, 104, pp 153–160. 2010.
- 30. Osowole AA, Akpan EJ. Eur. J. Appl. Sci, 4(1): pp 14-20. 2012.
- 32. El-Aziz DMA, Etaiw SHE, Ali EA J. Mol. Struct, 1048: pp 487-499. 2013.
- 33. A. Vazzana, E. Terranova, F. Mattioli and F. Sparatore, ARKIVOC, Vol. No. 5, pp. 364-374. 2004
- 34.B. H. M. Jayakumarswamy, F. Rahaman, V. K. Revankar and K. Vasantakumar Pai, Int. J. Pharm. Tech. Res., 3, 1864, 2011.
- 35. Quan Z, Chen S, Li Y, Cui X, Corros. Sci.; 44: 703, 2002
- 36. Chitra S, Parameswari K, Int.J. Electrochem. Sci. 2010; 5: 1675-1697; b) Bilgic S, Cabiskan N, J. Appl. Electrochem. 31: 79 2001.
- 37. M. N. Desai, M. M. Pandya, and G. V. Shah, Indian J. Techn., pp 292-294.1981.
- 38. M. N. Desai, M. B. Desai, C. B. Shah and S. M. Desai, Corros. Sci., 26, pp827-837.1986.
- 39. H. Shokry, M. Yuasa, I. Sekine, R. M. Issa, H. Y. El-Baradie and G. K. Gomma, Corros. Sci., 40,pp 2173-2186.1998.
- 40. M. A. Quraishi, J. Rawat and M. Ajmal, Corrosion, 54, pp 996,1998.41. S. S. A. E. Rehim, M. A. M. Ibrahim and K. F. Khaled, J. Appl. Electrochem., 29 pp 593-599, 1999.
- 42. A. Bansiwal, P. Anthony and S. P. Mathur, British Corrosion Journal, 35, pp 301-303.2000.
- 43. M. A. Quraishi, D. Jamal and M. Luqman, Indian J. Chem. Techn., pp 479-483.2002.
- 44.M. Hosseini, S. F. L. Mertens, M. Ghorbani and R. M. Arshadi, Mater. Chem. Phys. 78 pp 800–808 .2003.
- 45. K. C. Emregul and O. Atakol, Mater. Chem. Phys., 83 pp 373–379.2004.
- 46. M. A. Quraishi and R. Sardar, Indian J. Chem. Techn., pp 103-107. 2004.
- 47. K. C. Emregul, A. A. Akay and O.Atakol, Mater. Chem. Phys., 93 pp 325-329 .2005
- 48. H. A. Sorkhabi, B. Shaabani and D. Seifzadeh, Appl. Surf. Sci., 239 pp 154-164 .2005