

Synthesis of New Schiff-Base Complexes and Their Applications



Authors:

¹Dr Navneet Kumar, ²Pratima Sharma*, ³Astha pareek

Address of Correspondence:

¹Assistant Professor, Raj Kumar Goel institute of Technology, Ghaziabad (UP),
^{2,3} Research Scholar, Banasthali University, Rajasthan

Abstract

Schiff bases viz, Salicylaldehyde glycine, DL-2, 3-Diaminopropion-Salicylaldehyde, benzylidene glycine and 4- acetylamido benzylidene aniline were prepared in basic media, using 2M NaOH. The compounds appeared as yellow precipitates. They were then reacted with methanolic solution of copper per chlorate. Application of Schiff bases and their metal complexes as catalysts, in various biological system, polymer and dyes are described. Their use in birth control and food packages. These Schiff bases show the antimicrobial activities, antifungal activities, antiviral activities.

Keywords: Schiff base, Catalysts, Biological activities, Metal complexes

Introduction:

Schiff bases of isatin were reported to possess antibacterial, antifungal, antiviral, anti HIV, antiprotozoal, and anthelmintic activities¹. They also exhibit significant anticonvulsant activity, apart from other pharmacological properties². The study of aromatic substances having a molecular structure with π -bonds in chains is an active research area in the field of conducting substances^{3, 4}, and also metal complexes play an essential role in agriculture, pharmaceutical and industrial chemistry. Ligands a metal surround by a cluster of ions or molecules, is used for preparation of complex compounds named as Schiff bases.⁵ Schiff bases are the compounds containing azimethine group ($-\text{HC}=\text{N}-$). They are condensation products of ketones or aldehydes with primary amines and were first reported by Hugo Schiff in 1864. Formation of Schiff base generally takes place under acid or base catalysis or with heat. The common Schiff bases are crystalline solids, which are feebly basic but at least some form insoluble salts with strong acids. Today,

misspratima29@gmail.com * Corresponding Author Email-Id

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. 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.

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 ions⁶. 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^{7,8}.

Schiff bases are the compounds containing azimethine group (-HC=N-). They are condensation products of ketones or aldehydes with primary amines and were first reported by Hugo Schiff in 1864. Formation of Schiff base generally takes place under acid or base catalysis or with heat. The common Schiff bases are crystalline solids, which are feebly basic but at least some form insoluble salts with strong acids.

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. 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.

Schiff bases have been used extensively as ligands in the field of coordination chemistry, some of the reasons are that the intramolecular hydrogen bonds between the (O) and the (N) atoms which play an important role in the formation of metal complexes and that Schiff base compounds show photochromism and thermochromism in the solid state by proton transfer from the hydroxyl (O) to the imine (N) atoms⁹.

Formation of New Schiff base:-

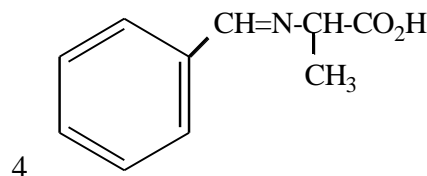
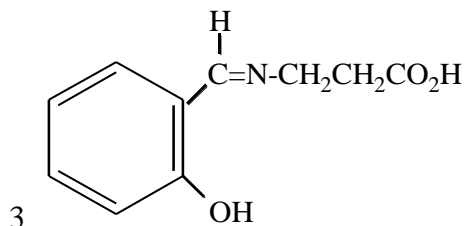
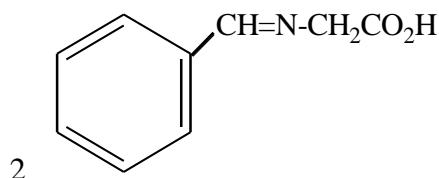
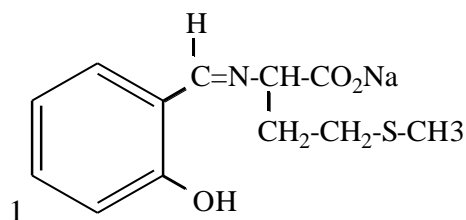


Table- Physical data for Schiff bases:

S.No	Name	M.p & B.p (°C)	Color	IR bands cm ⁻¹		
				OH	C=O	C=N
1	Salicylidene glycine	180	Yellow	3443.62(b)	-	1618
2	Salicylidene β-alanine	120	Faint yellow	3424.33(b)	1637.89 (s)	1612.17(s)
3	Benzylidene glycine	195	Milky	3423.82(b)	16644.75(s)	1597.43(s)
4	Benzylidene DL-alanine	110	Faint orange	3393.22(b)	1745.51 (m)	1594.01(s)

Synthesis of Schiff bases:-

Synthesis of salicylidene glycine (1) and salicylidene β-alanine (2):-

In a 50 ml conical flask, prepare a separate 10⁻² mole solutions by dissolving (1.2g) of salicylaldehyde, (0.75g) of glycine, (0.89g) of DL- alanine, (0.89g) of β-alanine, and (0.4g) of sodium hydroxide, in 15 ml of ethanol. To prepare any Schiff bases stated, mix the salicylaldehyde solution with the proper amino acid solution and the mixture is stirred. By gradual addition, adds the sodium hydroxide solution to each mixture during a period of 30 minutes. The final mixture is left for about 15 minutes, filtered, washed with cold ethanol and dried. Pure products have m.p's of 180C° , 195C° (decomp.) and 120C° for Schiff bases 1-3 respectively .

Synthesis of benzylidene glycine (3) and benzylidene DL-alanine (4):- In 50 ml round bottom flask attached with a reflux condenser, mix 1.06 g of benzaldehyde, (0.75g) of glycine or (0.89g) of DL- alanine and (0.4g) of sodium hydroxide. Add 20 ml of ethanol to each mixture and the final mixture is refluxed for 3 hours for benzylidene glycine or 2 hours for benzylidene DL- alanine. The mixture is cooled and filtered. Products are washed with cold ethanol and dried. Pure products have a melting points of 195C° (decomp.) and 110C° for Schiff bases (3) and (4) respectively.

Instrumental: - The melting points of solid Schiff bases are measured by electro thermal m.p apparatus model BÜCHI 510. The IR spectra for liquid or solids Schiff bases are measured by a computerized FTIR, Bruker model Tensor 27.

Catalyst: Aromatic Schiff bases or their metal complexes catalyze reactions on oxygenation^{10,11} hydrolysis¹², electro-reduction¹³ and decomposition¹⁴. Some copper complexes, Derived with amino acids, enhance (10-50mints times) hydrolysis rate¹², more than simple copper (II) ion. Synthetic iron (II) Schiff base complexes exhibits catalytic activity towards electron-reduction of oxygen¹⁵.

Biological Activities of Schiff Bases:-

Antimicrobial activities: Schiff base derived from furylgloxyl and p-toludine show antibacterial activity against *E. coli*. Some heterocyclic Schiff base¹⁶⁻¹⁸ can act as a antibacterial agent. Isatin derived Schiff base^{19, 20} posses anti-HIV activity and anti-bacterial activity. Schiff bases (banzimidazole²¹, toluidinones²², quin-azolinones²³, furaldehyde²⁴, thiazole^{25, 26} pyrimidine²⁷, indole²⁸, show antibacterial activity.

Schiff base²⁹⁻³¹ with thiophene carboxaldehyde and aminobenzoic acid show anti-bacterial activity. Lysine based Schiff bases and their complexes³² 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 semicarbazide³³, and with furfurylidene diamine³⁴ Schiff bases show antibacterial activities. Organo-silicon (IV) complexes³⁵ with bidentate Schiff bases, organo-lead (IV) complexes³⁶ with nitrogen donar legands of sulpha drugs posses antibacterial activities.

Antifungal activities:

Benzothiazole Schiff bases³⁷ posses effective antifungal activity. Schiff bases and their metal complexes³⁸ formed between furan or furylglycoxal with various amines show antifunagal activity against *Helminthosporium gramineum* (causing stripe disease in barely) *Syncephalostrum racemosus* (causing fruit rot in tomato).

Antiviral activities:

Schiff base of gossypol³⁹ show high antiviral activity. Flourination⁴⁰ on aldehyde part of shiff base enhances insectoacracidal activity. Schiff bases (thiadiazole derivatives with salicylaldehyde) and their metal complexes⁴¹ with Mo (IV) show insecticidal activities against bollworm and promote cell survival rate of mung bean spouts.

Applications of Schiff bases:-

Effect of N-salicyladehyde amino glucose (SG) Schiff base complex 120 with Cu (II) and Zn (II) inhibit synthesis of O₂ markedly, inhibitory effect of Cu (SG) was more than that of Zn (SG) . Complexes Cu (SG) and Co (SG) combines with salman sperm DNA. Tetradentate Schiff base and its metal complexes with Mn (II), Ni (II), Cu (II), and Zn (II) show miscellaneous effect on membrane in amylose production.

Some Schiff bases⁴² posses' simple harmonic generation activity. Amino Schiff base forms chelates with Cu (II) and Fe (II) and acts as a thrombin inhibitor⁴³. Carnosine and anserine act as effective trans-glycating agent in decomposition of aldose-derived Schiff basses⁴⁴

Results and Discussion: - Schiff bases show failure synthesis from salicylaldehyde or benzaldehyde with some amino acids, by the usual classical synthetic method,⁴⁵ this is because Schiff base have reversible nature of synthesized Schiff bases reaction. It had previously used a several catalysts^{45, 46-48} to overcome on such problem, but now there is way to use sodium hydroxide catalyst for the first time during synthesis of Schiff bases, which is highly accepted as a catalyst and kinetic⁴⁹ point of view.

References:-

- 1) S. N. Pandeya, P. Yogeeswari, D. Sriram, et al., *Chemotherapy*, **1999**, 45, 192.
- 2) S. K. Sridhar, S. N. Pandeya, J. P. Stables, A. Ramesh, *Eur. J. Pharm. Sci.*, **2002**, 16, 129.
- 3) N. Sari, P. Gürkan, *Trans. Met. Chem.*, **2003**, 28, 687.
- 4) E. Sezer, B. Ustamehmetoğlu and A.S. Saraç, *Int. J. Polym. Anal. Charact*, **1999**, 1-13.
- 5) Dhar D N & Taploo C. L, *Shiff bases and their application*, *J. Science.Ind (Res)* 41 **1982**, 501-506.
- 6) P. Souza, J.A. Garcia-Vazquez and J. R. Masaguer, *Transition Met. Chem.* 10 **1985**, 410.
- 7) H. Naeimi, J. Safari and A. Heidarneshad, *Dyes Pigments* 73 **2007**, 251.
- 8) S. J. Lippard and J.M. Berg, *Principles of bioinorganic chemistry*, University Science Books, California, **1994**.
- 9) Y. Elerman, M. Kabak, A. Elmali, *Z. Naturforsch. B* 57 **2002**, 651.
- 10) Nishinga A, Yamada T, Fujjisawa H & Ishizaki K, *J. Mol. Catal*, 48, **1988**, 249-64.
- 11) Xi Z, Liu W, Cao G, Du w, Huang J, Cai K & Guo H, *Chem Abstr*, **1986**, 357-63.
- 12) Chakraborty H, Paul N & Rahman M L, *Trans Met Chem (Lond)*, 19, **1994**, 524-526.
- 13) Zhao Y D, Pang D W, Zong Z, Cheng J K, Luo Z F, Feng C J, Shen H Y & Zhung X C, *Huaxae Xuebao*, 56, **1998**, 178-183.
- 14) Sreekala R, Yusuff K K & Mohamme, *Chem Abstr*, **1994**, 507-510.
- 15) Mishra V, Saksena D K & Jain M C, *Snth React Inorg Met Org Chem*, 17, **1987**, 987-1002.
- 16) Bhusare S R, Pawar V G, Shinde S B, Pawar R P & Vibhute Y B, *Int J Chem Sci*, 1, **2003**, 31-36.
- 17) Singh K, Barwal M S & Tyagi P, *J. Med. Sci*, 1, **2003**, 31-36.
- 18) Pandeya S N, Sriram D, Nath g & De C E, *Chem Abstr*, 132, **2000**, 22931.
- 19) Kar D M, Sahu S K, Pradhan D, Dash G K & Mishra P K, *Chem Abstr*, 141, **2004**, 23376.
- 20) Song L, Xie Y & Wang H, *Chem Abstr*, 134, **2001**, 222664.
- 21) Patel V K & Jejurkar C R, *Chem Abstr*, 122, **1995**, 44857.
- 22) Misha P, Gupta N P & Shakya K A, *J. Ind chem. Soc*, 69, **1991**, 618-619.
- 23) Casazar J, Morvay J & Herczey O, *Chem Abstr*, 107, **1987**, 7153.
- 24) Pop R D, Donea A, Chioream V & Farcasan V, *Chem Abstr*, 109, **1987**, 85714.
- 25) More P G, Bhalvankar R B & Pattar S C, *J Indian Chem Soc*, 78, **2001**, 474-475.
- 26) Jeewoth T, Bhowon M G, Wah H & Li K, *Trans Met Chem*, 24, **1999**, 445-448.
- 27) Shikkargol R K, Mallikarjuna N N & Angadi S D, *Chem Abstr*, 138, **2003**, 116763.
- 28) Idrean M, Siddique M, Patil S D, Joshi A G & Rut A W, *Chem Abstr*, 135, **2001**, 226842.
- 29) Mohan S & Saravanan J, *Chem Abstr*, 138, **2003**, 170023.
- 30) Mohamed G G, Omar M & Hindy A M M, *Spect Chem Acta, Pent mol Bimol Spect*, 62, **2005**, 1140-1150.
- 31) Ma Y, Fan Y & Wang D Y, *Chem Abstr*, 143, **2005**, 3996.

- 32) Shlyakhov E N, Tomnalik L E, Burdenko T A, Chaika T S, Taspkov V I, & Samus N M, Chem abstr, 110, **1989**.
- 33) Kumar M, Chem Abstr, 140, **2004**, 267419.
- 34) Jain M & Singh R V, Chem Abstr, 140, **2004**, 280760.
- 35) Gupta M K, Sharma p, Varshney S & Varshney A K , Chem Abstr, 140, **2004**, 16774.
- 36) Dash B, Mahapatra P K, Panda D & Patnaik J M , J Indian Chem Soc, 61, **1984**, 1061-1064.
- 37) Dhakrey R, and Saxena G, J Indian Chem Soc, 64, **1987**, 1150-1158.
- 38) Mirzabdullaev A B, Aslanova D Kh, & Ershov F I, Chem Abstr, 99, **1984**, 22191.
- 39) Kozlov N S, Korotyshova G P, Rozhkova N G & Andreeva E I, Chem Abstr, 106, **1987**, 155955.
- 40) Zhu L, Chen N, Li H, Song F & Zhu X, Chem Abstr, 141, **2004**, 374026.
- 41) Liu X, Wang J, Le Z, Feng C, Shen H & Zang X, Chem Abstr, 127, **1997**, 3433028.
- 42) Chen X, Qi N & Chen L, Chem Abstr, 122, **1995**, 9623.
- 43) Toyota E, Sekizaki H, Takahashi Y, Kunihiro & Tanizawa K, Chem Abstr, 143, **2005**, 37905.
- 44) Szwer G & Benjamin S, Biochem Biophys Res Comm, 336, **2005**, 36-41.
- 45) Ed. S. Patai, John Wiley and Sons, New York, 1970, 61-146.
- 46) J. H. Billman and K. M. Tai, J.Org. Chem., **1958**, 23, 535.
- 47) M. E. Taylor and T. J. Fletcher, J.Org. Chem., **1961**, 26, 940.
- 48) D.Y.Curtin and J.W.Hausser, J. Amer. Chem. Soc., **1961**, 83, 3474.
- 49) D.Y.Curtin and J.W.Hausser, J. Amer. Chem. Soc., **1961**, 83, 3474.