Thiazole Containing Schiffs Bases and Their Transition Metal Complexes

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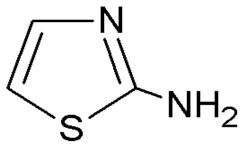
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ABSTRACT: 2-aminothiazole is one of privileged structure which finds applications in number of pharmaceuticals like antiviral, antibacterial, antifungal, antituberculous, antibody and antifungal agents. The 2-aminothiazole nucleus is a recurring scaffold in compounds of pharmaceutical interest. Complexes of Schiff bases derived from 2-aminothiazole have been studied vastly. The complexes were characterized by elemental (C, H, N and metal) and spectral (UV-visible and IR) analysis, magnetic susceptibility and conductivity measurements and evaluation of biological activities. The complexes possess specific geometry. Various ligand field parameters of complexes can be studied. The Schiff bases derived from aminothiazoles and their transition metal complexes are expected to be biologically active compounds.

KEYWORDS: 2-aminothiazole, biological activity, Schiffs base, Metal complexes,

I. INTRODUCTION

Coordination chemistry is prime branch of inorganic chemistry. A number of reviews are published in literature, which throws light on research and development of made in the field of coordination chemistry [1]. It is one of the rare research topics where material scientists, biological scientists and coordination chemists work together. The coordination compounds of ligands containing nitrogen, oxygen and sulphur as the donor atoms exhibit a wide spectrum of biological activities.



Structure of 2-aminothiazole

Presence of exocyclic nitrogen, cyclic sulphur & nitrogen & π electrons in the ring gives coordination ability to 2-aminothiazole Among these ligands Schiff bases attract the attention of researchers mainly due to their facile syntheses, easily availability, electronic properties and good solubility in common solvents. Azomethine compounds or Schiff bases are typically formed by condensation of a primary amine and aldehydes or ketones and first reported by Schiff [2]. Schiff bases were used as starting material for the synthesis of various bioactive heterocyclic compounds [3]. Among the Schiff bases, thiazole containing Schiff bases are important due to their wide applications as antimicrobial, anti-inflammatory, anti-degenerative and anti-HIV agents, drugs [4-5]. Thiazoles and their derivatives form a part of vitamin B₁ and coenzyme carboxylase. Metal complexes with these ligands are becoming increasingly important as biochemical, analytical and antimicrobial reagents in the design of molecular models and material chemistry [6-8]. The use of microwaves in organic synthesis has recently gained in importance [9]. Microwave irradiated reactions under solvent free or less solvent conditions are used for carrying out chemical transformations, which are pollution free, eco-friendly, low cost and offer high yields together with simplicity in processing and handling [10-12]. Microwave systems provide the opportunity to complete complex reactions in minutes. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in yields [13-16]. Microwave assisted synthesis is presented as a very useful tool in coordination chemistry. The synthesis assisted by microwave radiation has

proven to be an excellent tool for the achievement of new structural types of polynuclear transition metal complexes [17].

II. RELATED WORK & IMPORTANCE

Schiff base metal complexes are well studied in past. In the present work microwave assisted synthesis, characterization and applications of thiazole containing Schiff base transition metal complexes is discussed. Kablka et. al. [18] synthesized 2-aminothiazoles by condensation of α -bromo-ketones with thiourea through microwave assisted approach. They found that condensation of α -bromo-ketones with thiourea gives desired product within five minutes under microwave irradiation in absence of catalysts. Meshram et. al. [19] reported 2-aminothiazole derivatives by N-methylimidazole catalyzed cyclization of α-halo ketone carbonyls with ammonium thiocyanate in water-alcoholic media. Schiff base from 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5one with 2-amino-4-phenyl thiazole was synthesized and characterized by elemental analysis, mass spectra, ¹H NMR spectra, ¹³C NMR spectra and F.T.IR spectra by K.S. Pandya et. al. [20]. Ali et. al. [21] have been synthesized two series of l,n-alkylene glycol di[4{N(2-thiazoIylazo- methinyl)}2-methoxy] phenyl ether and l,nalkylene glycol di[4{N(2-benzo-thiazolylazomethinyl)} 2-methoxy]phenyl ether, via reactions 2-aminothiazole and 2-aminobenzothiazole with dialdehyde (which are synthesized from reaction vanillin with l, n-dibromo or chloro alkane in the basic media). The new compounds were characterized by elemental analysis, physical and spectral data. All the Schiff-bases were found to be antibacterial and antifungal. Jordan et. al. [22] have been studied thermal decomposition of 2-aminothiazole (2-amt) complexes of general formula $M(2-amt)_2X_2$, [M = Co(II) and Cu(II) and $Ni(Z-amt)_4X_2$, [X = Cl and Br] in air and argon by TG and DTG as well as by DTA in nitrogen; end products from the decompositions in air have been characterized by X-ray powder diffraction. Siddiqui et. al. [23] have been synthesized Schiff bases derived from o-formylphenoxyacetic acid and a series of aminothiazoles to form a number of potentially biologically active compounds. The structures of these Schiff bases have been characterized using IR and ¹H and ¹³C-NMR spectroscopy. 2-aminophenylthiazole derivatives were synthesized and characterized by FTIR by Singh and coworkers [24]. All the synthesized 2aminophenylthiazol derivatives were tested for their antibacterial and antifungal activity. Pattan et. al. [25] have been synthesized some substituted thiazoles. These compounds were evaluated for various biological activities like Anti-diabetic, anti-inflammatory and anti-fungal activity. Novel Schiff bases derived from some hetero cyclic β -diketones with 4-phenyl-2-aminothiazole have been synthesized and characterized by Elemental analysis, FT-IR, ¹H NMR, ¹³C NMR, Mass spectra, TGA analysis and UV spectra by Thakar et. al. [26]. Schiff bases and their Co(II), Ni(II) and Cu(II) complexes formed by the condensation of 2-acetonaphthone with 2-Amino-4-chlorophenol (AACP), 2-amino-4- methylbenzothiazole (AABT) and 2-aminothiazole (ACAT) have been synthesized by Mishra et. al. [27]. These compounds have been characterized by elemental analysis, FT-IR, FAB- mass, molar conductance, electronic spectra, ESR and magnetic susceptibility.

More et. al. [28] have been reported Co(II) and Zn(II) complexes of Schiff bases derived from 4-(pfluorophenyl)-2-aminothiazole and o-hydroxyaldehydes (substituted salicylaldehyde, o-vanillin and 2-hydroxy-1-naphathaldehyde). The complexes were characterized by elemental (C, H, N and metal), spectral (UV-visible and IR) analyses, magnetic susceptibility, conductivity measurements and evaluation of biological activities. N-(thiophen-2-ylmethylene)benzo[d]thiazol-2-amine Schiff base (L) derived from 2-aminobenzothiazole and 2thiophenecarboxaldehyde was synthesized and characterized using elemental analysis, IR, mass spectra, ¹H NMR and UV-Vis spectra. Complexes are tested for antitumor activity by S. Eldin et. al.[29]. Thakar and coworkers [30] have been synthesized Transition metal complexes of Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) metal ions with the Schiff base derived from the condensation of 2-amino-4(4'-phenyl/methylphenyl)-5methyl-thiazole with 4-acetyl-1(3-chloro phenyl)-3-methyl-2-pyrazoline-5-ones. The complexes were structurally characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements and spectral techniques like IR, UV, ¹H NMR, ¹³C NMR and Mass Spectra. Complexes have been screened for their antifungal and antibacterial activities. Wang et. al. [31] have synthesized cobalt (II) and nickel (II) complexes of 2-aminothiazole with demethylcantharate. These Complexes were characterized by elemental analysis, infrared spectra and thermogravimetric analysis. Synthesis and study of TiO₂ chemically modified by Pd (II) 2-aminothiazole complex for phenol degradation at different pH values were performed by Cristante et. al. [32] Pandya et. al. [33] have studied Schiff bases and their metal complexes derived from some hetero cyclic β-diketones with 4-phenyl-2-aminothiazole. All the synthesized compounds were confirmed for their structure by Elemental analysis, FT-IR, ¹H NMR, ¹³C NMR, Mass spectra, TGA analysis and UV spectra. Metal complexes show moderate antibacterial activity. Metal complexes of Cr(III), Co(II), Ni(II) and Cu(II) with the Schiff bases derived from N- (4-chlorobenzylidene)-5-methyl-1,3-thiazol-2-amine and N-[4-(dimethylamino) benzylidene]-6-nitro-1,3-benzothiazol-2-amine have been synthesized by conventional as well as microwave methods by Jain et. al. [34]. Compounds have been characterized by elemental analysis, FT-IR,

FAB-mass, molar conductance, electronic spectra, ESR, magnetic susceptibility, thermal, electrical conductivity and XRD analysis.

Kelode et. al. [35] has been prepared Schiff base by the condensation of 2 hydroxy-5-chloro-3-nitro acetophenone and thiazole. Metal complexes with Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III), Zr(IV) and UO₂(VI) have been prepared and characterized by elemental analysis, conductance measurements, molecular weight determinations, spectral and thermal studies.New ruthenium carbonyl complexes of N-[(2pyridyl)methylidene]-2-aminothiazole formed by reaction between bidentate Schiff base ligands derived by the condensation of pyridine-2-carboxaldehyde with 2-aminothiazole in a 1:1 mole ratio in acetonitrile and ruthenium carbonyls, $[Ru(CO)_2Cl_2]n/[Ru(CO)_4I_2]$. Complexes having general formula $[Ru(CO)_2(L)X_2]$ (X = Cl (1) and I (2)) (L = N- [(2-pyridyl)methylidene]-2-aminothiazole) have been reported by Mondal et. al. [36]. Catalytic activity of these compounds were investigated to the oxidation of PhCH₂OH to PhCHO, 2-butanol (C₄H₉OH) to 2-butanone, 1-phenylethanol (PhC₂H₄OH) to acetophenone, cyclopentanol (C₅H₉OH) to cyclopentanone, cyclohexanol to cyclohexanone, cycloheptanol to cycloheptanone and cycloctanol to cycloctanone using N-methylmorpholine-N-oxide (NMO) as oxidant. Schiff base metal complexes of Co(II), Ni(II) and Cu(II) derived from 4-chlorobenzylidene-2-aminothiazole and 2- nitrobenzylidene-2-aminothiazole have been synthesized by conventional as well as microwave methods. These compounds have been characterized by Mishra et. al. [37] by using elemental analysis, FT-IR, FAB-mass, molar conductance, electronic spectra, ESR, magnetic susceptibility, thermal, electrical conductivity and XRD analysis.Gupta and coworkers [38] synthesized Schiff base complexes of Cr(III), Co(II), Ni(II) and Cu(II) derived from 5bromosalicylaldehyde with 2-amino-5-nitrothiazole and 4-dimethylaminobenzaldehyde with 2-amino-3hydroxypyridine by conventional as well as microwave methods. These compounds have been characterized by elemental analysis, FT-IR, FAB-mass, molar conductance, electronic spectra, ¹H-NMR, ESR, magnetic susceptibility, thermal, electrical conductivity and XRD analysis. Schiff bases derived from Various substituted acetophenones on treatment with iodine and thiourea yielded 2-amino-4-(substituted-phenyl)-thiazole which on further treatment with various substituted aldehydes gave N-(substitutedbenzylidene)-4-(substitutedphenyl)thiazol-2-amine. All the synthesized compounds were characterized by FTIR, ¹H NMR and Mass data. Synthesized compounds were screened for antibacterial (S. aureus, E. coli, P. aeruginosa) and antifungal (C. albicans, A. flavus, A. fumigatus) activities by Gupta et. al. [39].

III. CONCLUSION

Microbial infections remain the major cause of death over the world. Emergence of multi-drug resistant to different infectious organisms like *M.tuberculosis* made the condition most alarming. Therefore, there is an urgent demand for a new class of antimicrobial agent with a different mode of action and it led medicinal chemists to explore a wide variety of chemical structures. Among the Schiff bases, thiazole containing Schiff bases and their metal complexes are important due to their remarkable antimicrobial activities. Hence it is worthwhile to study the synthesis of Schiff bases and their metal complexes of thiazoles for various applications.

REFERENCES

- [1] S. Yamada, Coordination Chemistry Reviews., 190–192 (1999) 537–555.
- [2] H. Schiff, Ann suppli., 3 (1864) 343.
- [3] M.M. Murhekar and R.E. Khadsan, J. Chem. Pharm. Res., 3(6) (2011) 846-849.
- [4] Z.H. Chohan, A. Scozzafava and C. T. Supuran, J. Enzyme Inhib. Med. Chem., 2003, 18(3), 259–263.
- [5] F. Azam, S. Singh, S. L. Khokhra and O. Prakash, J. Zhejiang Univ. Sci. B., 8(6) (2007) 446–452.
- [6] N. Raman, S.J. Raja, J. Joseph and J.D. Raja, J. Chil. Chem. Soc., 52(2) (2007) 1138-1141.
- [7] R.R. Coombs, M.K. Ringer, J.M. Blacquiere, J.C. Smith, J.S. Neilsen, Yoon-Seo Uh, J.B. Gilbert, L.J. Leger, H. Zhang, A.M. Irving, S.L. Wheaton, C.M. Vogles, S.A. Westcott, A. Decken and F.J. Baerlocher, *Trans. Met. Chem.*, 30 (2005) 411-418.
- [8] M. A. Neelakantan, S.S. Marriappan, J. Dharmaraja, T. Jeyakumar and K. Muthukumaran, Spectrochim. Acta part A., 71 (2008) 628-635.
- [9] P. Lidstrom, J. Tierney, B. Wathey and J. Westman, *Tetrahedron.*, 57 (2001) 9225-9283.
- [10] K. Mahajan, N. Fahmi and R.V. Singh, Indian J. Chem. A., 46 (2007) 1221-1225.
- [11] R. Garg, M.K. Saini, N. Fahmi and R.V. Singh, Trans. Met. Chem., 31 (2006) 362-367.
- [12] K. Sharma, R. Singh, N. Fahmi and R.V. Singh, Spectrochim. Acta. part A. 75 (2010) 422-427.
- [13] K. Mahajan, N. Fahmi and R.V. Singh, Indian J. Chem., 46A (2007) 1221-1225.
- [14] K. Mahajan, M. Swami and R.V. Singh, Russ. J. Coord. Chem., 35(3) (2009) 179-185.
- [15] K. Mohanan, S. Kumari and G. Rijulal, J. Rare Earths., 26 (2008) 16-21.
- [16] K. Sharma, R. Singh, N. Fahmi and R.V. Singh, *Spectrochim. Acta part.*, 75A (2010) 422-427.
- [17] Alba Pons-Balague, Maria Jose Heras Ojea, Marisol Ledezma-Gairaud, Daniel Reta Maneru, Simon J. Teat, Jose Sanchez Costa, Guillem Aromi and E. Carolina Sanudo, *Polyhedron.*, (2012) (Article in press).
- [18] G. W. Kabalka and A. R. Mereddy, *Tetrahedron Letters.*, 47 (2006) 5171–5172.
- [19] H. M. Meshram, P. B. Thakur, B. M. Babu and V. M. Bangade, Tetrahedron Letters., 53 (2012) 5265–5269.
- [20] K. T. Joshi, A. M. Pancholi I, K. S. Pandya and A. S. Thakar J. Chem. Pharm. Res., 3(4) (2011) 741-749.
- [21] E.T. Ali, J.H. Tomma and S.S. Mubbrik *ibn J. for Pure and Appl.Sci.*, 21(1) (2008) 73-80.
- [22] B. M. Jordan, Eric S. Raper and James R. Creighton, *Thermochimica Acta.*, 62 (1983) 21-33.
- [23] H. L. Siddiqui, A. Iqbal, S. Ahmad and G. W. Weaver, *Molecules.*, 11 (2006) 206-211.

- [24] D. Singh, M. Srivastava, A. K. Gyananchandran and P.D. Gokulan, *Journal of Current Pharmaceutical Research.*, 04 (2010) 16-19.
- [25] S.R. Pattan, N.S. Dighe, S.A. Nirmal, A.N. Merekar, R.B. Laware, H.V. Shinde and S. Musmade, Asian J. Research Chem., 2(2) (2009) 196-201.
- [26] A. S. Thakar, K. S. Pandya, K. T. Joshi and A. M. Pancholi, *E-Journal of Chemistry.*, 8(4) (2011) 1556-1565.
- [27] A.P. Mishra and D.K. Mishra, International Journal of Pharma and Bio. Sciences., 2 (3) (2011) 430-439.
- [28] A. S. Lawand, P. G. More, A. M. Nalawade and R. B. Bhalvankar, J. Indian Chem., Soc., 88 (2011) 781-787.
- [29] S. Eldin, H. Etaiw, D. M. Abd El-Aziz, E. H. Abd El-Zaher and E. A. Ali, Spectrochimica Acta Part A., 79 (2011) 1331–1337.
- [30] A. Thakar, K. Joshi, K. Pandya and A. Pancholi, *E-Journal of Chemistry.*, 8(4) (2011) 1750-1764.
- [31] N. Wang, Q. Y. Lin, Y. Wen, L. Kong, Shi-Kun Li and F. Zhang, *Inorganica Chimica Acta.*, 384 (2012) 345–351.
- [32] V. M. Cristante, A. G.S. Prado, S. M.A. Jorge, J. P.S. Valente, A. O. Florentino and P. M. Padilha, *Journal of Photochemistry and Photobiology A:Chemistry.*, 195 (2008) 23–29.
- [33] K. S. Pandya, K. T. Joshi, A. M. Pancholi and A. S. Thakar, J. Chem. Pharm. Res., 3(4) (2011) 741-749.
- [34] R. Jain and A. P. Mishra, Jordan Journal of Chemistry., 7(1) (2012) 9-21.
- [35] S. R. Kelode, International Journal of ChemTech Research., 4(4) (2012) 1442-1446.
- [36] T. K. Mondal, S. Kundu, D. Sarkar, M. S. Jana and A. K. Pramanik, S. Jana, Journal of Molecular Structure, 1035 (2013) 277– 284.
- [37] A. P. Mishra and R. K. Jain, J. Chem. Pharm. Res., 2(6) (2010) 51-61.
- [38] S.K. Gupta, A.P. Mishra, H. Purwar and R. K. Jain, *E-Journal of Chemistry.*, 9(4) (2012) 1655-1666.
- [39] R. Gupta, N. K. Fuloria and S. Fuloria, *Indonesian J. Pharm.*, 24(1) (2013) 35 39.