Volume 2 (5), 2014, Page-361-366
e-ISSN: 2348-6465

Pharma Health Sciences

International Journal of Pharma Research and Health Sciences

Available online at www.pharmahealthsciences.net

Original Article

Synthesis, characterization and Biological activity of Copper (II), Cobalt (II), Nickel (II) and Mercury (II) complexes of Schiff base derived from 2-Acetyl-5-chloro thiophene-o-Phenylenediamine

Dr Mohammed Fakruddin Ali Ahamed *,V Mahammad Yunus

Department of chemistry, FIP, Kadapa, Andhra Pradesh, India

ARTICLE INFO

Received: 02 Sept 2014
Accepted: 19 Oct 2014

ABSTRACT

The Metal complexes of Co (II), Ni (II), Cu (II) and Hg (II) with a new Schiff base derivedfrom 2-Acetyl 5-chloro thiophene and o-Phenylenediamine in methanol are reported. The complexeshave been characterized using chemical analysis, (IR, UV-VIS, H^1-NMR),conductometric and magnetic data. According to these data, we propose an octahedral geometry formetal (II) complexes. The invitro antibacterial activities of the investigated complexes were evaluatedagainst few microorganisms by well diffusion technique. It was found that the metal complexes havehigher activity that the standard drugs. Antibacterial activity of the ligand and its complexes werestudied against to gram positive bacteria; *Staphylococcus aureus*and*Bacillus subtilis*andgramnegative bacteria *Salmonella typhi*and*E. coli*.

Key words: Octa-dentate Schiff base, 2-Acetyl 5-chloro thiophene and o-Phenylenediamine, VSM, Biological activity.

www.pharmahealthsciences.net

Quick Response Code

Corresponding author *
Dr Mohammed.Fakruddin Ali Ahmed, Department of chemistry, FIP,Kadapa, Andhra Pradesh, India. E Mail: mfaahamed@gmail.com

1. INTRODUCTION

In view of broad applications of Schiff bases and their metal complexes the research work in the field of coordination chemistry is improved, but still there is a lot of challenging work has been carried out on Schiff base metal complexes along with their different

industrial and chemotherapeutic studies. Schiff base complexes are considered to be among the most important stereo chemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety. [1] However the incorporation of transition metal ions into these compounds have enormous wide applications in the field of the food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical along with biological activities and decrease in the cytotoxicity of both metal ion and Schiff base. [2-3]

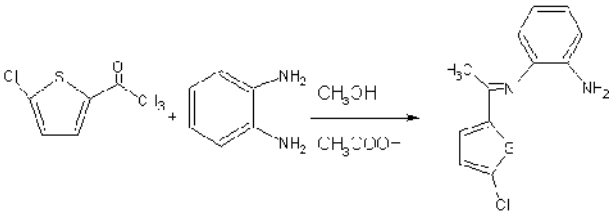
The Schiff base ligands also serve as a cation carrier in potentiometric sensors as they have shown excellent selectivity, sensitivity and stability towards specific metal ions such as Cu(II), Co(II), Ni(II) and Hg(II)[4]. In general ortho-substituted with a hydroxyl group have primarily arouse the researchers' interest, 2-Acetyl 5-chloro thiophene and its Schiff base have shown significant attention with regard to their chelating ability with the transition metal ions[5]. On the other hand Schiff bases derived from o-phenylenediamine and its transition complexes also possess variety of applications including biological, clinical and analytical. In addition to that they have been reported to exhibit photo-luminescence and catalytic activity. [6-7] The o-phenylenediamine acts as a key intermediate used in the production of fungicides, corrosion inhibitors, various pigments, pharmaceuticals compounds. Furthermore it was also used to remove sulfur from ores and coloration by aldehydes in polymeric products. [8]

2. MATERIAL AND METHODS

The entire chemical used was of analytical grade.The solvents were dried and distilled before use according to standard procedures. Melting pointswere determined in a Electro thermal 9200.H^1NMR spectra in $CDCl_3$ and DMSO wererecorded on NMR spectrophotometer. The IR spectra (nujol/KBr) were recorded in the range400-4000 cm-1 by KBr pellet using Perkin-Elmer 457 spectrophotometer. Conductance wasmeasured in DMF at room temperature using aDigitalconductivity bridge. The UV-Visiblespectra in CH_3OH were recorded on a shimadzuUV 1800 spectrophotometer. The metal contentswere determined gravimetrically.

2.1 Preparation of ACTPD

The reaction mixture containing 2-acetyl-5-chlorothiophene, (2g, 0.01229mol in 20ml of methanol) phenylenediamine (1.32g,0.01229 mol in 20ml of methanol dissolved in hot condition) wastaken in 250-ml round bottom flask and refluxed for 8h. On coolingthe reaction mixture, dark yellow coloured product was formed. Itwas collected by filtration and washed with hot water and 50 % cold methanol. This compound was recrystallisedfromethanol and dried in vacuo, yield 2.8. g ; m .p . 37°C.



Scheme 1: Synthetic route for the preparation of ligand-ACTPD

2.2 Synthesis of metal complexes

To a methanolic solution of the Schiff base, equal moles of metal salts dissolved in the methanol was added followed by 1 ml of 1M NaOAc was added. This reaction mixture was stirred constantly with magnetic stirrer for 20 minutes. Coloured products were formed after allowing to stand for one hour. The solids were collected and washed with n-Hexane and dried.

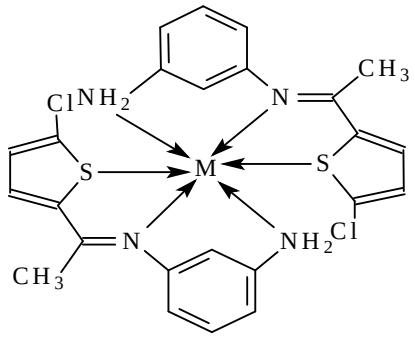


Fig 1: Proposed Structure of Ligand –Metal complexes M=Cu^{2+},Co^{2+},Ni^{2+},Mn^{2+}

3. RESULTS AND DISCUSSION

The analytical data for all the complexes are given in Table- 1. The molar conductivity data of the complexes are consistent with the non-electrolytic nature[9,10]of the complexes. The ligand and complexes were characterized by elemental analysis to determine percentage of C, N, S and H. The observed and calculated percentages of the elements are in good agreement and support one ligand to a metal ion. The number of coordinated ligands to metal determined by Job's continuous method and Mole ratio method established 1: 2 metal to ligand ratio.

3.1 Characterisation of ACTPD

The reagents have been characterized by IR and ^{1}H-NMR spectral data. Infrared spectrum of ACTPD shows bands at [3432(s) 3386(S), 3286(m),3176(m),2979(m);1630(m); 1591(s),1435(s);1362(s); 1248(m) 1174(m), 1297(m); 871(δ), 730(δ); cm^{-1} respectively corresponding to υNH-symmetric, υNH-asymmetric, υ (C-H) aromatic stretch, υ (C=S) stretching, υC=N symmetric, υ (C-C) aromatic ring, δ(C-H) of Thiophene ring, (ACTPD) and δ (C-H)-oop bend (aromatic) and δ (C-C)-oop bend aromatic ring vibrations. ^{1}H-NMR spectra of ACTPD ($CDCl_3$ + DMSO-d_6) showed signals at 2.54 (3H,S)due to -CH_3 ,3.4,(2H,s); 6.6(2H),7.7 (4H,m);due to aromatic ring, 7.4 (2H,s) due to NH_2, C_4H_2S (Thiophene).

The infrared spectra of ACTPD show bands at 1697 cm^{-1} for VC=N; 722 for VC-S; 743 for VC-CO; indicating the Schiff base formation. The lowering of VC=N of azomethine group to the extent of 30-50 cm^{-1} in all the complexes suggests the participation[11-13] of azomethine nitrogen in complexation. On coordination, this band is shifted to lower frequency suggests that the ligand is coordinated to metal ion via azomethine nitrogen in all complexes. This change in shift is due to the drift of the lone pair density of azomethine nitrogen towards metal atom[14]. In the far IR spectral region, additional medium to strong bands at 405-420 and 325-355 cm^{-1} are assigned to VM-N and VM-S modes[15, 16] respectively.

The magnetic moment value of Cu-ACTPD was 2.11 BM indicates one electron paramagnetism. This value is higher than the spin-only value of 1.73 BM for one unpaired electron. The higher value of the magnetic moment indicates that complexes are monomeric in nature and there is no metal-metal interaction along the axial position in the complex and have distorted octahedral environment[17-19]. The magnetic moment of Co-ACTPD was found to lie in 2.24 BM which is typically observed for low spin d^7 system of the present type suggest its tetrahedral geometry. Monomeric cobalt complexes have lower magnetic moment values than would be expected for pure tetrahedral complexes suggesting flattening towards planar arrangement. [20-24]

The magnetic moments of Pb (II) complex was observed at 2.63 BM. This value is in the range reported earlier for octahedral complexes[25] but slightly higher than the spin only value of 2.63 BM probably due to slight distortion from the pure octahedral to D_4h symmetry. [26]

3.2 Antibacterial activity results of the ligands and complexes

The antibacterial activity of bidentated aromatic Schiff base ligands and their metal (II) complexeswere tested

against microorganism. Themicroorganisms used in the present investigationsinclude bacteria: *Staphylococcus aureus,Bacillussubtilis, Salmonella typhi*and *E. coli*.Minimum Inhibitory Concentrations (MICs)method was used to determine the antibacterial activity of the synthesized compounds.Thediffusion method is simple and routinely used inhospital laboratories; it requires commercial disks,the medium used is Mueller-Hinton agar with 2%of glucose and the diameter of inhibition zone isvisually read at 24 hr after incubation at 37°C.The antibacterial activity was estimated on thebasis of the size of the inhibition zone formedaround the paper disks on the seeded agar plates.Streptomycin was used as a standard .The resultsare presentated in Table 5.

Percent inhibition values are relative to the inhibition zone (22 mm) of the most active compound with 100% inhibition. The Schiff base and the complexes exhibited varying degrees of inhibitory effects on the growth of the tested bacteria species. The values reveal that the Schiff base become more effective when coordinated to the metal ions. The biological activity of thecomplexes follows the order: Co (II) > Ni (II)≈ Cu (II) ≈Hg (II).Furthermore, the data show that E. coli was inhibited to a greater degree by the Co (II) and Cu (II) complexes. In conclusion the complexes prepared with the new Schiff base could reasonable are used for the treatment of somecommon diseases caused by *E.Coli*. The abovestudy shows that all the complexes haveoctahedral geometry.

4. CONCLUSION

Co(II), Ni(II), Cu(II), and Hg(II)complexes of the Schiff base derived from 2-Acetyl 5-chloro thiophineand Phenylenediaminewere prepared and characterized. The structuralcharacterization of synthesized compound weremade by using the elemental analysis,spectroscopic methods, magnetic andconductance etc.The study reveal that[27] complexes are non-electrolytes[28] Schiff basebehaves as a neutral Bidentate ligand and iscoordinated to the central metal ion through theazomethine N[29]. The metal (II) complexes haveoctahedral geometry.[30] The biological activityof all the complexes is higher that of the free Schiffbase ligand and follows the order: Co (II) > Ni(II)≈Cu (II) ≈Hg (II).This means that metal chelation significantlyaffects the antimicrobial behavior of the organicligand. All the synthesized Schiff base metalcomplexes may prove useful as bactericidal, asfungicidal, as anticancer, antituberculosis. Theinformation obtained from this study will contributesignificantly in the development of new drugs orelse may prove way for using combined therapythat could circumvent resistance problem and thushelp in the improvement of health particularly in the poor section of the community.

Table 1: Analytical Data of ACTPD and their metal complex

Compound / complex (colour)	M.Pt.^{0}C Yield %	Mol. Wt.	Elemental Analysis Found (calculated)					
			C %	H%	N%	Cl%	S%	M%
ACTPD(light-yellow colour)	37°	250.7	57.4	4.3	11.1	14.1	12.7	-
		-80%	-45.9	-3.5	-8.9	-11.2	-10.2	-
ACTPD -Co(Light brown colour)	215	309.6	46.5	3.5	9.04	11.4	10.3	19.02
		-75%	-37.2	-2.8	-7.2	-9.1	-8.2	-15.2
ACTPD -Cu(black colour)	210	314.2	45.8	3.4	8.9	11.2	10.2	20.2
		-76%	-36.6	-2.8	-7.1	-9	-8.1	-16.1
ACTPD -Ni (light green colour)	230	309.4	46.5	3.5	9.04	11.4	10.3	18.9
		-80%	-37.2	-2.8	-7.2	-9.1	-8.2	-15.1
ACTPD -Hg(white colour)	220	451.3	31.9	2.4	6.2	7.8	7.1	44.4
		-85%	-25.5	-1.9	-4.9	-6.2	-5.6	-35.5

Table 2: Selected IR bands (cm^{-1}) with tentative assignments

Compound	V̄C=N	V̄C-S	V̄C-Cl	V̄M-N	V̄M-S
ACTPD	1697	722	743	-	-
Cu-ACTPD	1615	650	740	420	355

Co- ACTPD	1608	708	735	415	352
Ni- ACTPD	1610	707	745	412	340
Hg- ACTPD	1623	712	743	405	325

Table 3: Molar conductance data of metal complexes of ACTPD

ACTPD– Complex	Conductance($Ohm^{-1}Cm^2mol^{-1}$)
Cu-ACTPD	26
Co- ACTPD	24
Ni- ACTPD	22
Hg- ACTPD	36

Table 4: Magnetic moment data of metal complexes of ACTPD

ACTPD- Complex	Magnetic Momentum(B.M)
Cu- ACTPD	2.11
Co- ACTPD	2.23
Ni- ACTPD	3.73
Hg- ACTPD	2.11

Table 5: Antibacterial activity results of the ligands and complexes

Compound	*E. coli*	*Salmonella typhi*	*B. subtilis*	*S. aureus*
ACTPD	++	+	+	+
Cu- ACTPD	++++	++	++	++
Co- ACTPD	++++	+++	++	++
Ni- ACTPD	+++	++	++	++
Hg- ACTPD	++	++	++	++

5. REFERENCES

1. Keypour H, Rezaeivala M, Valencia L, Lourido PP, Khavasi HR, Synthesis and characterization of some new Co(II) and Cd(II) macroacyclic Schiff-base complexes containing piperazine moiety. Polyhedron 2009; 28(17): 3755-3758.
2. Sonmez M, Berber I, Akbas E, Synthesis, antibacterial and antifungal activity of some new pyridazinone metal complexes. Eur J Med Chem 2006; 41(1): 101–105.
3. Katwal R, Kaur H, Kapur B, Applications of Copper – Schiff's base complexes: A Review. Sci Rev Chem Commun 2013; 3(1): 1-15.
4. Ashraf MA, Wajid A, Mahmood K, Maah MJ, Yusoff I, Spectral Investigation of the Activities of Amino Substituted Bases. Int J Chem Eng Appl 2011; 2(4): 252-255.
5. Raman N, Pitchaikani YR, Kulandaisamy A, Synthesis and characterization of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) Schiff base complexes derived from o-phenylenediamine and acetoacetanilide. Proc Indian Acad Sci (ChemSci) 2001; 113(3): 183–189.
6. Fasina TM, Ogundele O, Ejiah FN, Dueke-Eze CU, Biological activity of Copper(II), Cobalt(II) and Nickel(II) Complexes of Schiff base Derived from o-phenylenediamine and 5-bromosalicylaldehyde. Int J Biol Chem 2012; 6(1): 24-30.
7. Uhlig E. Non-innocent bidentate nitrogen-ligands in electron-rich complexes of 3d-elements. Pure Appl Chem 1988; 60(8) 1235-1240.
8. Geary M J. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. Coord chem Rev 1971; 7: 81-122.
9. Raman N, Raja YP, Kulandaisamy A. Indian Academy of sci., 2001, 113 (3), 183
10. Byeong-Goo J, Chae-Pyong R, Hee-Nam c, Ki-Hyung C, Yohng-Kook C. Korean chem. Soc. 1996; 17(8): 687-693
11. Sarika R et al. Am-Eura J Sci Res 2009; 4 (4): 229-234
12. Sinn E & Morris C M, Coordchem Rev, 4 (1969) 891.
13. Nakagawa L & Shimanonchi T, SpecrochimActa, 20 (1964) 429.
14. Joseph J, Nagashri K, Ajisha Bibin Rani G. Journal of Saudi chemical society 2011
15. Sulekh Chandra, Deepali Jain , Anjana Sarkar and Anupama J. Indian chem soc 2009; 86: 220-224.
16. Zahid H. Chohan, Syed KA. Sherazi Metal based drugs, Islamic university, Bahawalpur, Pakistan Figgis BN & Lewis J, Progs Inorg chem. 6 (1964) 37

17. Hussain Reddy K., Radha Krishna Reddy M., & Lingappa Y., Indian Journal of chem. vol. 35 A, 9 (1996) 775-778
18. Bottcher A., Elias H., E-G. Jager, Langfelderova H., Mazur M., Muller L., Paulus H., Pelikan P., Rudolph M., Valko M., Inorg. Chem... 1993, 32, 4131
19. Huber A., Dr. Ing. Dissertation. Technische Hochschule Darmstadt. 1997
20. Green wood N. N., Earnshaw A., Chemie der Elemente, VCH, Weinheim. 1988
21. Malik, W.U., Bembi, R. and Singh R., Trans Met. Chem.., 8, 321 (1983)
22. Vinod Kumar and Rajesh Dhakarey; Journal of the Indian council of chemistry vol. 20, No.1 2003, pp 46-51
23. Nene YL, Thapliyal PN. 1982, Fungicides in plant diseases control. Oxford and IBH publishing co. pvt. Ltd., New Delhi, pp163
24. Srivastava MK, Mishra B & Nizamuddin M. Pharmacological studies of some 2-methyl-3-(arylthio-carbamido) quinazol-4-ones and 2-methyl-3-(aryliden-carboxamido)quinazol-4-ones. Indian J Chem. 2001; 40B: 342–4.
25. Tweedy BG. Possible mechanism for reduction of elemental sulfur by monilinia fructicola. Phytopathology. 1964; 55: 910–4.
26. Spinu C, Kriza A. Co (II), Ni (II) andCu (II) complexes of bi-dentate schiff bases. ActaChim. Slov 2000; 47(1): 179.
27. Sun B, Chen J, Hu JY, Lix. Synthesisand characterization of some tetra-dentate Schiff base complexes and their heterolepticanalogues. J Chin Chem Lett 2001; 12(II): 1043.
28. Boghaei DM, Mohebi S. Synthesis andcharacterization of some tetra-dentate Schiff base complexes and their heterolepticanalogues, Tetrahedron 2002; 58 (26): 5357.
29. Liu J, Wu B, Zhang B, Liu Y. Synthesisand characterization of some tetra-dentate Schiff base complexes and their heterolepticanalogues. Turk J Chem 2006; 30(1): 41.