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MICROWAVE ASSISTED SYNTHESIS, SPECTRAL, ANTIBACTERIAL AND ANTIFUNGAL ACTIVITIES OF Cu(II) COMPLEX WITH 4-AMINOANTIPYRINE AND OXALATE ION

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ABSTRACT

In the background of green chemistry, microwave irradiation provides an alternative to the conventional methods, for providing heating energy to a system. Microwave assisted reactions are fast, clean, economic and eco-friendly and this technique has been proposed as the "Technology of Tomorrow". The Cu(II) complex of 4-aminoantipyrine (AAP) and oxalate ion was prepared by microwave irradiation. The composition of complex $[MXL_2]$ (where M= Cu(II), L=AAP& $X=C_2O_4^{2-}$) was arrived from the elemental analysis, metal estimation, molar conductivity measurements, magnetic moment, UV-Visible, IR and Far-IR spectral studies, tetragonally distorted octahedral geometry is proposed for the complex. The antibacterial and antifungal activities of the AAP and Cu(II) complex were tested against *E.coli streptococcei* and *C.albicance* (fungus) by disc diffusion method. The minimum inhibitory concentration (MIC) values were measured; the results show that the complex is more potent than the free AAP.

KEY WORDS: Copper complex, 4-Aminoantipyrine, Oxalate ion, Antibacterial, Antifungal.

INTRODUCTION

Pyrazole is a five-membered lactam ring containing two nitrogen and ketone in the same molecule. It is active moiety as a pharmaceutical ingredient especially in the class of non-steroidal anti-inflammatory agents. 4-aminoantipyrine is one of the pyrazole derivatives. It is very important in the field of Medicinal and Agricultural chemistry.[1] It is also used as a hemolytic inhibitors, polorographic titration, conductometric and potentiometric determination of lanthanides.[2-3] 4-aminoantipyrine have large scale of applications in biological, clinical, analgesics, antifungal, antibacterial, anticancereous and pharmacological areas.[4-7] The present studies aims at the microwave assisted synthesis, spectral and biological characterization of Cu(II) with AAP and oxalate ion.

MATERIALS AND METHOD

All the chemicals (Copper nitrate, DMSO, DMF, ethanol, methanol and sodium oxalate) used were of AnalaR grade. 4-aminoantipyrine was purchased from Alfa Aesar Company.

Instruments: The elemental analysis of the complex was carried out by using (Thermo Finnigan make, Flash EA1112 Series Instrument) CHNS (O) analyzer. The molar conductance measurements were conducted using 10^{-3} solutions of the metal complexes in acetonitrile with Systronic Conductivity Bridge 304 at 30°C. The UV-Visible spectrum of Cu(II) complex were recorded on Varian, Cary 5000 model UV Spectrophotometer. The IR spectra of the complexes were recorded on a Shimadzu FT IR spectrometer in 4000-400cm^{-1} range with KBr pellet technique. The Far-IR Spectrum of the complexes was recorded by Bruker 3000, FT IR Spectrometer. The antimicrobial and antifungal studies of 4-aminoantipyrine and the complexes were done by disc diffusion method.

Preparation of Cu(II) complex: The complex was prepared by the addition of required mole ratios of 4-aminoantipyrine in methanol and sodium oxalate in ethanol to the copper nitrate solution in methanol followed by the microwave irradiation for a few seconds after each addition by using a microwave oven (IFB-25 PG 1S Model). Dark green colour complex was precipitated with 74.3% yield.

RESULTS AND DISCUSSION

1. Analytical data

The analytical data of the complex correspond to the formula $[Cu(C_2O_4)(AAP)_2]$. The formula is based on the molar conductivity, metal estimation and elemental analysis. The

elemental analytical data were in good agreement with the molecular formula arrived. The molar conductance value of the complex in CH_3CN is 60.34 $ohm^{-1}cm^2mol^{-1}$ which is quite lower than the expected value for an electrolyte and reveals their non-electrolytic nature (1:0 type).[8]

2. UV-Visible spectrum

The UV-visible spectral data is used to study the probable geometry of the synthesized complex. Based on the UV-visible spectrum recorded in room temperature by diffused reflectance spectra (DRS) method, the complex is shown to have tetragonally distorted. The UV-visible spectrum of Cu(II) complex shows three peaks at 205 nm, 305 nm and 699 nm respectively. The peak at 305 nm corresponding to $^2B_{2g} \leftarrow ^2B_{1g}$ and at 699 nm corresponds to $^2A_{1g} \leftarrow ^2B_{1g}$ transitions respectively the peak at 205 nm is obscured by C-T band. The magnetic moment value is 1.80BM for Cu(II) complex these facts indicating the tetragonally distorted octahedral geometry around the Cu(II) ion.[9]

3. IR and Far-IR spectra

The IR spectrum of free AAP showed peaks of concern at 3431-3325 cm^{-1} (two peaks), 2914 cm^{-1} and 1767 cm^{-1}, attributed to the symmetric, asymmetric stretching frequencies of NH_2, ν(C-H) and ν(C=O) respectively. In Cu(II) complex the symmetric and asymmetric stretching frequencies are broadened to give single band at 3423 cm^{-1} which indicate the nitrogen of amino group is one of the coordinating atom. The oxalate ion frequencies in the complex observed at 804 cm^{-1}, 1597 cm^{-1}, 1417 cm^{-1} can be assigned to ν(O-C=O), ν_a(C=O) and ν_s(C=O) stretching frequencies respectively which confirm the entry of oxalate ion into the coordination sphere.[10]

From the Far-IR spectrum, the bond between the metal and linked atom of the ligand is arrived. The spectrum shows the new bands in the region of 486 cm^{-1} and 454 cm^{-1}, due to the formation of M-O and M-N bonds respectively. Hence, it is concluded that the coordination of metal ion through amino nitrogen atom of AAP and oxygen atom of oxalate ion.[11]

4. Antimicrobial Activities

i) Antibacterial activity

The antibacterial activity of the AAP and Cu(II) complex were tested against the gram positive bacteria *streptococcei* and the gram negative bacteria *E.coli* by Kirby Beaur disc diffusion method using amikacin as standard. A comparative study of the ligand and the

complex indicate that complex exhibit higher antibacterial activity than the free ligand. Such increase of activity is due to the nature of ligand, structure of the complex and non-electrolytic nature of the complex.[12]

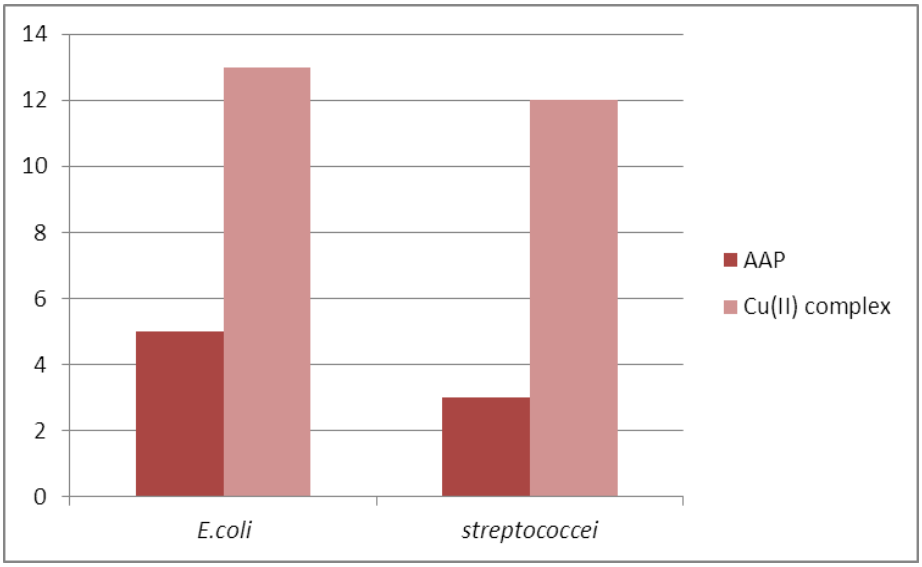

Fig.1 Zone of inhibition for *E. coli* and *streptococcei*

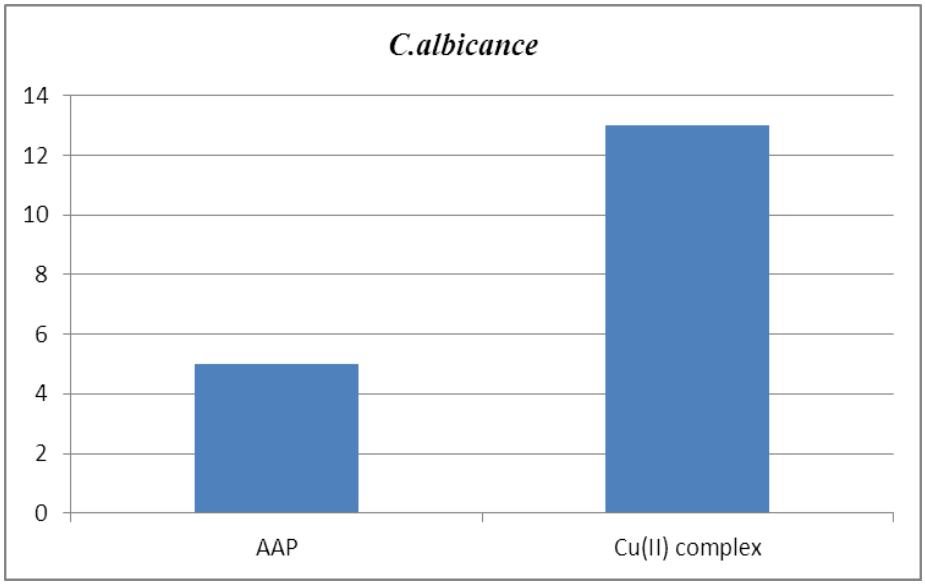

Fig.2 Zone of inhibition for *C.albicance*

ii) Antifungal activity

The antifungal activity of the AAP and Cu(II) complex were tested against *C.albicance* by disc diffusion method using ketokonazole standard. The complex may exhibit higher antifungal activity than the free AAP.[13]

CONCLUSION

Cu(II) complex with 4-aminoantipyrine and oxalate ion were synthesized and characterized by various physico-chemical and biological methods. The analyses confirmed the composition and geometry of the complex. The probable geometry of the complex is assigned as tetragonally distorted octahedral. It is a non-electrolyte and shows better activity against the tested microbial species compared to the free AAP.

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REFERENCES

1. Dharmaraj P, Kodimunthiri D, Sheela CD, Shanmuga Priya CS. Synthesis, spectral studies and antibacterial activity of Cu(II), Co(ii) AND Ni(II) complexes of 1(2-hydroxyphenyl)-3-phenyl-2-propen-1-one, N^2 –(3,5-dimethyl-1H-pyrazole-1-yl) methyl]hydrazone. 2009; J. Seb. Chem. Soc, 74(8-9): 927.
2. Anubama B, Padmaja M, Gyana Kumari C. Synthesis, characterization biological activity and DNA binding studies of Metal complexes with 4-aminoantipyrine schiff base ligand. E-journal of Chemistry, 2012; 9(1): 389-400.
3. Harikumaran Nair ML, Sheela A. Synthesis, spectral, thermal and electrochemical studies of oxomolybdenum (V) and dioxomolybdenum (VI) complexes of an azo dye derived from 4-amino-2,3-dimethyl-1-phenylpyrazole-5-one. Indian Journal of Chemistry. 2008; 47A: 1787-1792.
4. Himaja M, Kailash Rai, Anish KV, Ramana MV, Karigar AA. Synthesis and evaluation of anthelmintic and insecticidal activity of 4-aminoantipyrine derivative of amino acid and peptides. Journal of Pharmaceutical and Scientific Innovation, 2012; 1(1): 67-70.
5. Raman N, Kulandaisamy A, Shanmugasundaram A. Synthesis, spectral redox and antimicrobial activities of sciff base complexes derived from 1-phenyl-2,3-dimethyl-4-aminopyrazole-5-one and acetoactanilide. Transition Metal Chemistry, 2001; 26:131-135.
6. El-ajaily MM, El-Ferjani RM, Maihub AA. Preparation and physical investigation of complexes derived from 4-dimethylaminobenzaldehyde and 4-aminoantipyrine sciff base with Ni(II),Cu(II), Rh(III) and Pt(IV) ions. Jordan Journal of Chemistry. 2007; 2: 287.

7. Tudor Rosu, Elena Pahontu, Catalin Maxim, Rodica Georgescu, Nicolae Stanica, Gabriela Laura Almajan, Aurelian Gulea. Synthesis characterizatio and antibacterial activity of some new complexes of Cu(II), Ni(II), Vo(II), Mn(II) with sciff base derived from 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin05-one. Polyhedron, 2010; 29(2): 757-766.
8. Raman N, Johnson Raja S, Joseph J, Dhaveethu raja J. Synthesis, spectral characterization and DNA cleavage study of heterocyclic sciff base metal complexes. J. Chil. Chem. Soc, 2007; 52(2): 1138-1141.
9. Raman N, Mitu L, Sakthivel A, Pandi MSS. Studies on DNA cleavage and antimicrobial careening of transition metal complexes of 4-aminoantipyrine derivatives of N_2O_2 type. J.Iran.Chem.Soc, 2009; 6(4): 738-748.
10. Jeena Pearl A, Abbs Fen Reji TF. Synthesis, characterization, antimicrobial and DNA cleavage studies on some metal complexes incorporating 4-chlorobenzaldehyde and 4-aminoantipyrine. Journal of Chemical and Pharmaceutical Research, 2013; 5(1): 115-122.
11. Mishra AP, Pandey LR. Synthesis, structure and reactivity of oxovanadium(IV) sciff base complexes. Ind. J.Chem, 2005; 44A, 1800-1805.
12. Dharmaraj N, Viswanathamurthi P, Natarajan K. Ruthenium(II) complexes containing bidentate sciff bases and their antifungal activity. Transition Met. Chem, 2001; 26: 105-109.
13. Raman N, Sakthive A, Rajasekaran K. Synthesis and spectral characterization of antifungal sensitive schiff base transition metal complexes. Mycobiology, 2007; 35(3):150-153.