IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 7, Issue 5 Ver. II. (May. 2014), PP 26-32
www.iosrjournals.org

"Synthesis, Characterization and Biological Screening of Cu (II)-3-Formylchromone Derivative Complex"

Nitin.H.Kolhe, Shridhar.S.Jadhav*, Sushma.J.Takate, Anil .E.Athare and Supriya.P.Salve

P.G.Department of Chemistry, New Arts, commerce and Science College, Lal-taki Rd, Ahmednagar-414001, affiliated to University of Pune, Maharashtra, (INDIA).

***Corresponding Author: e-mail ssjadhav1957@gmail.com**

Abstract: *The complex of 3-formyl chromone derivative ligand with the Cu(II) complex was isolated in the solid form. Which have been characterized using FTIR spectrums. The FTIR spectrum shows bands for characteristic frequencies at 1604 cm^{-1} indicates C=O group, belongs to pyrone ring. The frequency at 510 to 596 cm^{-1} and band at 916 to 964 cm^{-1} indicates the M-O and M-O=C- in pyrone ring respectively. The UV-Vis spectroscopy shows that carbonyl of aldehyde group and carbonyl of pyrone ring of chromone of ligand shows n- π*and π—π* transition and complex shows electronic absorption at 369nm due to the $^2B_1g \rightarrow {}^2B_2g$ transition. Thermo Gravimetric Analysis (TGA) of complexes and ligand was carried out to determine the procedural and decomposition temperatures. The temperature range in which decomposition occurs in the range between 209°C to 350°C. The magnetic properties were determined from Gouy balance method. The number of unpaired electron found in complex of Cu(II)-3-formylchromone derivative was one and it has dsp2 hybridization. The complex is soluble in DMSO. The molar conductance of the complex are measured in DMSO at a concentration 10^{-3}M.The ligand and their copper complexes were screened for antimicrobial activities by the agar well diffusion technique using DMSO as solvent. The complexes were checked for their biological activity by using, Escherichia coli, and Bacillus subtilis bacteria.*

Keyword: *Chromone derivative, Copper 3-formylchromone, Biological Screening.*

I. Introduction:

Chromones constitute one of the major classes of naturally occurring compounds. The most of chromones are found to be biologically active agents [1]. Some of the biological activities attributed to chromones derivatives include, neuroprotective, HIV-inhibitory, antimicrobial, antibacterial, antitumor, antifungal, antialergic, antiviral, anti-inflammatory, anticancer activities[2-3].The chromones are synthesized by the cyclodehydration of 1-(O-hydroxyaryl)- 1,3 diketones or by VilsmeierHaack reaction[4].We are interest in the synthesis of 3-formyl chromones derivatives is because of their pharmaceutical and chemical importance They have comfortable precursor in Vilsmeier Haack reaction and it gives good yield[5].They form co-ordination complex with transition metal ion like Cu(II).They form attractive intermediates which may lead to form the complexes [6]. The literature survey show that there is no work found to be done on chromone metal-chelate complexes. Therefore we are interest in the co-ordination complexes of chromones with transition metal ion like Cu(II) ion. The present study has to be done to understand the characteristic nature and application of biological active metal-chromones complexes [7].Characterization of ligand and their metal complexes using spectroscopic methods like FTIR, UV-visible and thermal methods like Thermogravimetric analysis (TGA), Magnetic susceptibility measurement by Gouy balance methods. The percent purity of complex was determined by simple volumetric methods. The some of the metal-chromone complexes show the antimicrobial activity was checked by well diffusion methods and the inhibition zone was measured in mm-scale [8-9].

II. Experimental

2. Materials and Methods:

Metal salts ($CuCl_2.H_2O$), Phenol, Acetic anhydride, Pyridine, Anhydrous Sodium Sulphate, Anhydrous $AlCl_3$, Aryl Acetate, Acetophenone, Dimethylformanide (DMF), $POCl_3$, dimethylsulfoxide (DMSO) and ethanol all were of A. R. grade quality and were from BDH and Merck chemicals.

Infrared spectra were recorded in KBr disc on a IRAffinity -1 FTIR-Spectrophotometer Shimadzu in the range 4000-400 cm^{-1} .The electronic spectra were obtained using UV-1800 Shimadzu Spectrophotometer at 26°C in 10^{-3} concentration DMSO solvent .Elemental analysis was done on C,H,N,O using Perkin Elmer analyzer. Magnetic properties were determined from Gouy balance method using analytical single pan balance and magnetic field was provided by electromagnet (Em-10) auto transformer .The metal percentage in complex was determined using the simple volumetric estimation. The solubility of the prepared complex was checked

using solvent DMSO, acetonitrile, water and ethanol. The conductivity of metal complexes was measured in DMSO medium (0.001M) using Conductivity Bridge, Model Systronics type 304 and a dip type cell which in calibrated with KCl solution. Thermo Gravimetric Analysis (TGA) was recorded on TGA-50, Shimadzu Thermogravimetri analyzer having TGA-50 H thermal analyzer detector.

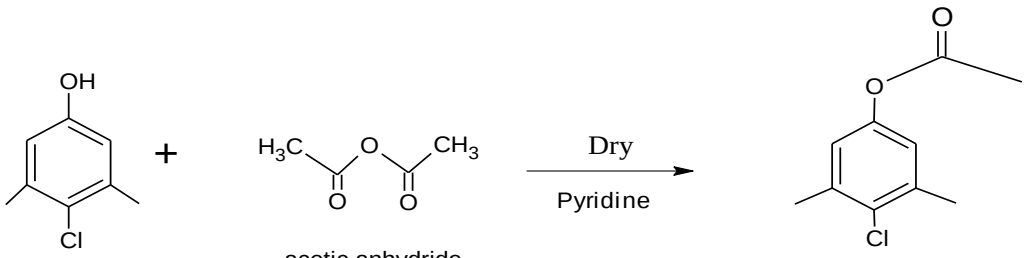
2.1. Synthesis of Ligand: 6-chloro 5, 7 dimethyl-4oxo-4H-chromene-3-carbaldehyde:

The ligand 3-formyl chromone was synthesized by the vilsmeir –Haack reaction [10-11].The synthesis of 3-formylchromone derivative was perform by three steps. The first step is the synthesis of 4-chloro-3, 5, dimethylphenyl acetate from 1mole of 4-chloro-3, 5 dimethylphenol by reacting with 1.15 mole acetic anhydride in presence of 5ml dry pyridine. (scheme.1a) by reported method [12-13].

The second step is preparation of acetophenone derivative that is 1(3-chloro-6-hydroxy-2,4 dimethylphenyl) ethanone (1b.) from 4-chloro-3, 5, dimethyl phenyl acetate (1a.) by using 1.25 mole of anhydrous $AlCl_3$ in large one neck round bottom flask attach with air condenser. Then in it adding the 1 mole of aryl acetate rapidly .The exothermic reaction was occurs with evolution of HCl gas .After complete evolution of HCl gas the whole reaction mixture kept in oil bath and reflux it at temperature in between 140 ºC -150 ºC for 2 hours. Then the reaction mixture allowed to standing over-night. The complex thus formed was breaked by adding ice cold water in round bottom flask. The separated product was filtered and recrystallised from aqueous alcohol. These is a Fries reaction (scheme.1b) by literature method [13-14].The last step is the synthesis of 3-formyl chromones derivative by taking the 25ml dimethylformide in 250 ml round bottom flask with magnetic needle .which was kept in ice bath then adding 15ml $POCl_3$ drop wise. The temperature was maintained below 20°C.The whole reaction mixture was stirred on magnetic stirrer for about 1hr to get pink formylating complex [15]. Then 0.05 mole 1(3-chloro-6-hydroxy-2,4 dimethylphenyl) ethanone (Scheme.1b.) dissolved in minimum amount of DMF. Then it was added (1b.) in to the pink formylating complex maintaining temperature of the mixture below 20°C. Then reaction mixture was stirred for 2 hrs. Then the reaction mixture was allowed to stand at room temperature for overnight .The reaction mixture was poured in to the crushed ice with vigorous stirring.The product was precipitated as yellow solid of 6-chloro5,7dimethyl-4-oxo-4H-chromene-3-carbaldehyde , filtered and recrystallized from acetic acid: ethanol having 1:1ratio. (Scheme.1c).

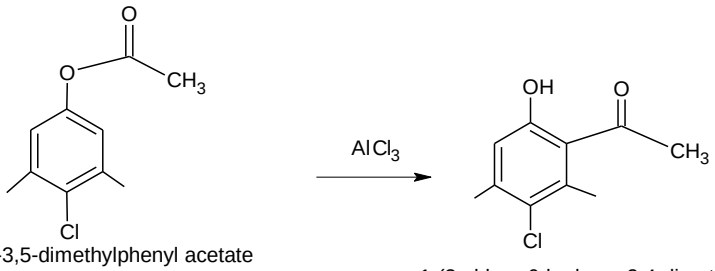
Scheme-1:

Step-I:



4-chloro-3,5-dimethylphenol — acetic anhydride — 1a. 4-chloro-3,5-dimethylphenyl acetate

Step-II:



4-chloro-3,5-dimethylphenyl acetate — 1b. 1-(3-chloro-6-hydroxy-2,4-dimethylphenyl)ethanone

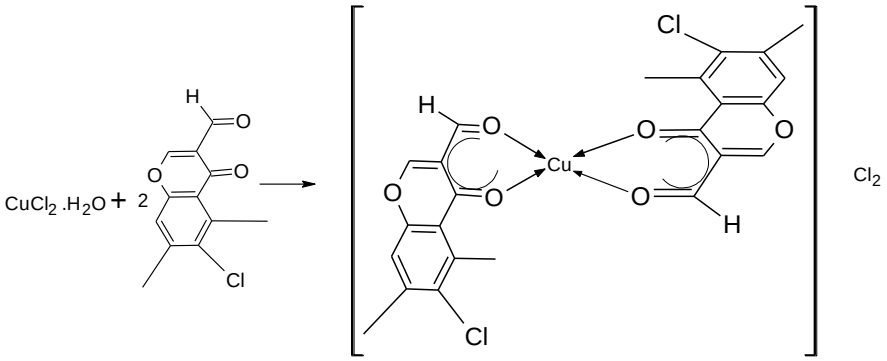
Step-III:

1-(3-chloro-6-hydroxy-2,4-dimethylphenyl)ethanone — 6-chloro-5,7-dimethyl-4-oxo-4*H*-chromene-3-carbaldehyde

2.3. Synthesis of Cu (II) -6-chloro 5, 7 dimethyl-4-oxo-4H-chromene-3-carbaldehyde complex:

The ligand 0.225 gm. of 6-chloro-5,7 dimethyl-3-formyl-chromones was dissolved in 25 ml acetic acid: ethanol(1:1) and reflux .To this reflux ligand solution an 25ml ethanolic solution of appropriate Cu(II) salt solution (2.02 gm) added drop by drop with continuous stirring and the resulting reaction mixture was further refluxed for 3 hrs and allow to stand for overnight . The dark olive green solid was separate out, and it was filtered, washed with ethanol. The complex was dried at room temperature in vacuum (Scheme-2).

Scheme-2:



2a.Bis(6-chloro-5,7-dimethyl-4oxo-4H-chromene-3-carbaldehyde)Cu(II) chloride complex

2.4 Antimicrobial Activity:

The strains of bacteria used were *Escherichia coli* and *B. subtilis*. The identity of all the strains was confirmed. A bacterial suspension was prepared and added to the sterilized medium before solidification. The media with bacteria was poured into sterilized Petri dishes under aseptic condition. The weight 100ug/ml of ligand and copper complexes in DMSO solvent were placed on the surface of the culture and incubated at 37^0C for 24 hours [16-17]. The zones of inhibition was formed by these complexes was recorded in mm by scale.

III. Result And Discussion:

The analytical data along with some physical properties of the ligand and its Cu (II) complex are summarized in Table1.The complex is stable at room temperature. The complex show Metal: ligand ratio 1:2 stiochiometry.

Table-1: The physical properties and analytical data of the ligand and their metal complex

Sr. No	***Compound***	***Color***	***Melting Point ^{0}C***	***Yield %***	***C, H, N Analysis found (Calc. %)***				***Molar Conductivity*** **$cm^2\ \Omega^{-1}\ mol^{-1}$**
					C	H	O	M	
1	(1a.) $[C_{10}H_{11}O_2Cl]$	White	68°C	88.80	60.46(60 .45)	5.58 (5.52)	16.11 (16.09)	--------	-------
2	(1b.) $[C_9H_8ClO]$	White	66°C	57.51	64.49 (64.41)	4.81 (4.81)	9.55 (9.34)		-------
3	(1c.)Ligand $[C_{12}H_9O_3Cl]$	Yellow	162°C	73.46	60.90 (60.84)	3.83 (3.81)	9.55 (9.50)	-------	-------
4	$[Cu(C_{12}H_{18}O_3Cl)_2]Cl_2$	Dark Olive green	194 d*	68.23	45.40 (45.10)	3.17 (3.13)	25.20 (24.98)	10.01 (10.00)	76.4

d*=Decomposition

3.1. Infrared Spectra:

In order to study the bonding mode of ligand to metal in the complex, IR spectrum of the free ligand was compared with the spectra of the metal complex (fig.1) .The free ligand exhibits IR band at, $\nu_{C=O}$ (1703 cm^{-1}) belong to aldehyde group of pyrone ring [18] .The frequency 1648 cm^{-1}indicate $\nu_{C=O}$ belong to cyclic carbonyl group which are present to pyrone ring that is cyclic ketone [19]. The frequency 916-946 cm^{-1}indicate enone system in resonance with aldehyde and conjugated double bond In the IR –spectra of complex (fig.1b.) the band of $\nu_{C=O}$ was shifted from 1703 $cm^{-1}$to 1718 $cm^{-1}$by two unit indicate bonding toward metal [20-21] .The another

band of frequency 1648 cm^{-1} was found to decrease by 44cm^{-1} unit to word 1604 cm^{-1} .That was attributed to donation of electron from $\nu_{C=O}$ group of cyclic ketone .The frequency was decreased by 60-81 cm^{-1}unit to word 877cm-1 to 857cm^{-1}. The infrared of prepared complexes have shown weak bands in the range of 510-593cm^{-1} [22-23]. This was attributed to the $\nu_{M-O.}$

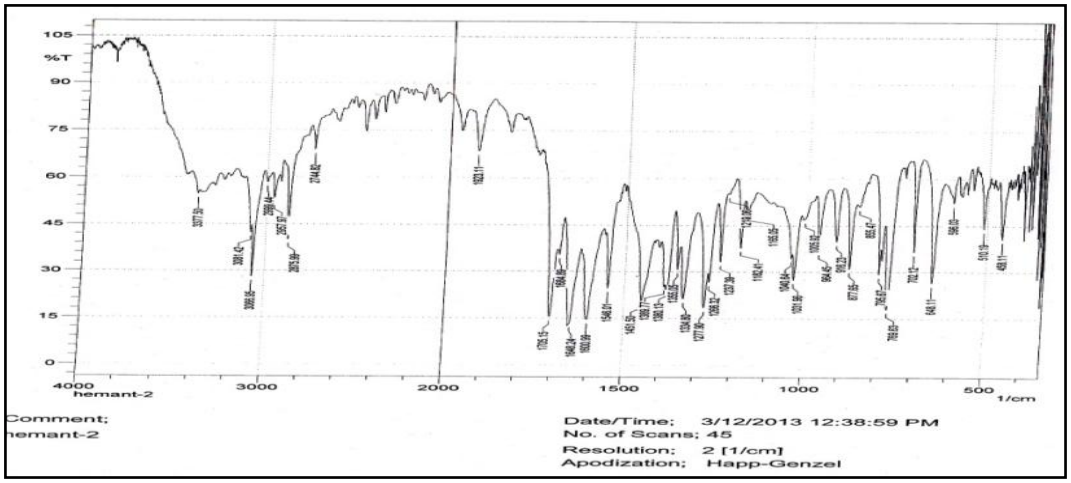


Fig.1.IR-Spectra of Cu(II)-Ligand (Scheme.2)

3.2. Electronic Spectra:

The electronic spectrum (fig.2.) of the complex was measured at 26°C in 10^{-3} concentration DMSO solvent. The electronic spectral data of Cu (II)-3-formyl chromones derivative showed in the range at 369 nm due to the $^2B_1g \rightarrow {}^2B_2g$ transition. Which is compatible with this complex having square planer geometry [24] .This is supported by Magnetic moment value of complex. The electronic spectra of ligand was shown the 381nm-284 nm indicate n–π* and π–π* transition [25-26].

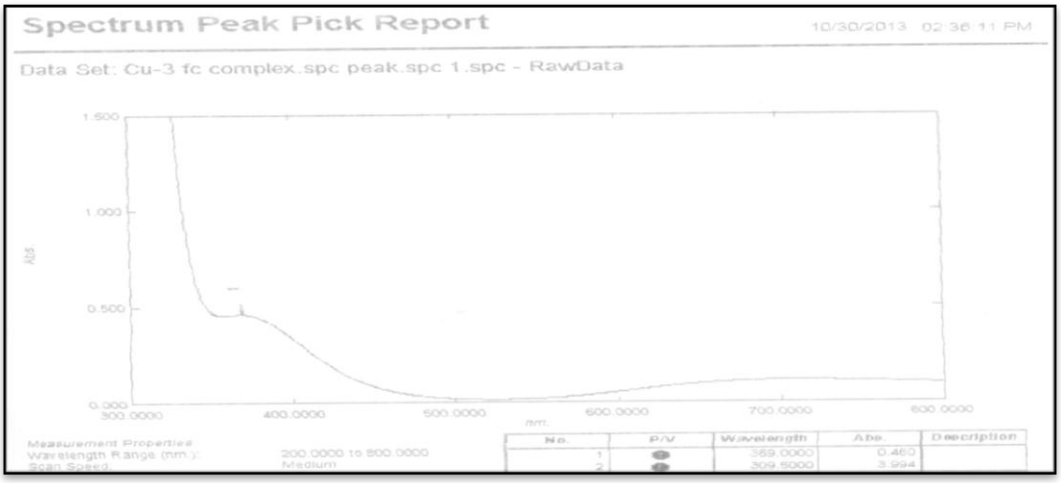


Fig.2.Electronic spectra of Cu (II) –Ligand complex

3.3. Thermogravimetric Analysis (TGA):

The thermogravimetric data was used to determine the decomposition temperature. The TG curves for Cu (II)-3-formyl chromones derivatives shown in Fig.3.During this period of non-isothermal heating rate 5°C / min up to the 1000°C. The sample undergoes some changes in air atmosphere [27]. The thermo gram of Metal-chelates shows decomposition occurs in to two steps .Fig.3a.The metal –ligand complex stable up to 190 °C. The first step was loss of % weight loss 65.884% is attributed with calculated % weight loss 67.68% indicate that two molecules of $[C_8H_8ClO]$ and 2 CO was loss from ligand in metal-ligand complex at 190 °C – 209 °C. In second step the % Wt. loss was 9.632% was attributed with calculated % Wt. loss 10.28 % indicate the loss of $2[C_3H_4O]$ molecules at 288.19°C -329.45°C .The final decomposition product was CuO residue [28,29-30]. The CuO residue stable up to the 1000°C shown in fig.3.

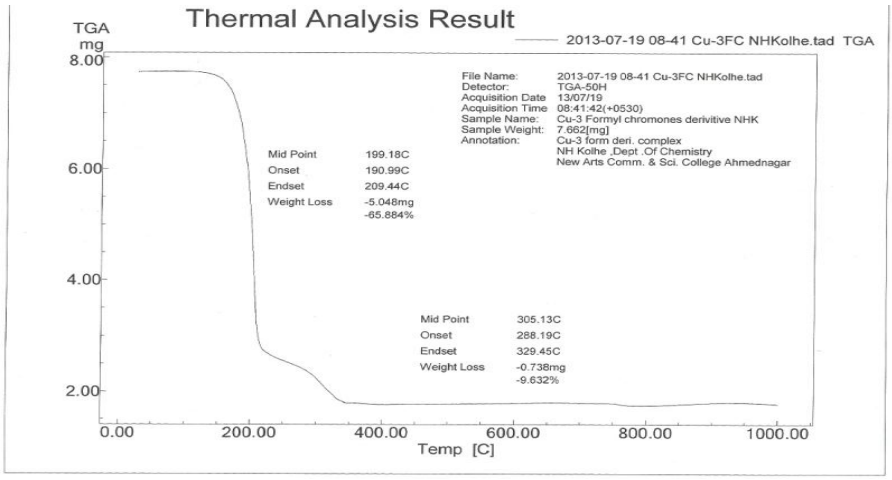


Fig.3.Thermogram of Cu (II)-3-formyl chromones derivatives complex

3.4. Magnetic properties:

The magnetic susceptibility is the ratio of the intensity of magnetism induced in a substance to the magnetizing force of intensity of field to which it is subjected .It provides important electronic structural information of the transition metal complexes [31]. The magnetic susceptibility measurements of the complex in the solid state were determined by Gouy balance using Hg [Co $(SCN)_4$] as a calibrant. The magnetic moment of Cu (II)-3-formyl chromones derivatives has been found to be μeff 1.86 BM., indicative of one unpaired electron of Cu(II) ion and suggesting that the square-planar geometry of the complex [32-33] .The complex shows paramagnetic in nature due to one unpaired electron .The suggested structure from the all collected data is shown in fig.4.

3.5. Molar Conductance:

Molar conductance of the complexes are measured in DMSO at a Concentration 0.001M (10^{-3}M).The observed conductance values 76.4 cm^2 Ω^{-1} mol^{-1}.This indicate the Cu(II)-6-choro-5,7dimethyl-4oxo-4H-chromene-3-carbaldehyde is 1 : 2 electrolytic behavior . [34-35].

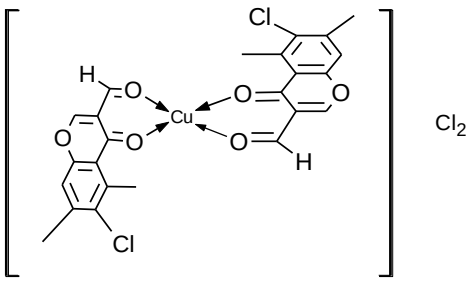
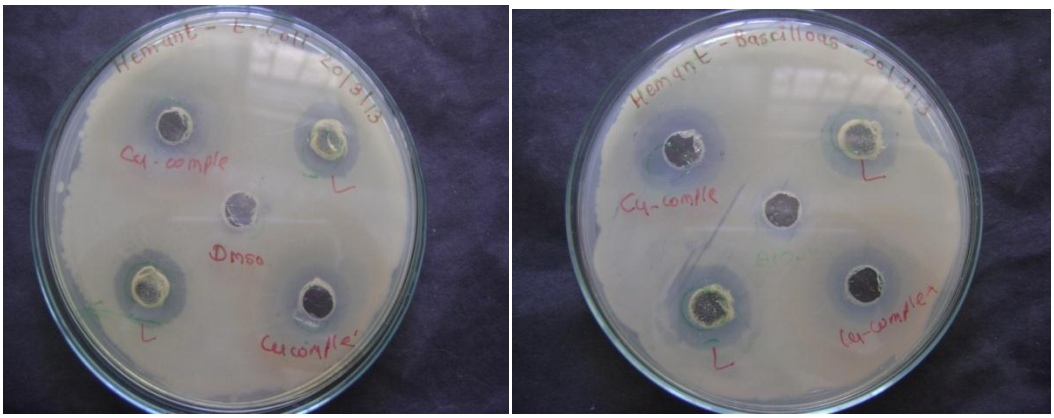


Fig.4.Structure of Bis(6-chloro-5,7-dimethyl-4oxo-4H-chromene-3-carbaldehyde)copper(II) chloride

3.6. Antimicrobial activity:

The antimicrobial activity of synthesized compounds **1c** and 2**a** was determined in vitro against two bacterial strains. For this study, the test cultures of bacterial strains *Escherichia coli*, and *Bacillus subtilis* were maintained in nutrient agar slants at 37°C[36]. The antimicrobial activity of compounds against test bacteria was determined by agar well diffusion method using standard antibiotic ciprofloxacin as positive control and DMSO as negative control [37]. All the experiments were performed in duplicate.

In this study the results of investigation showed that all the compounds have moderate antibacterial activity. Compounds **1c** and **2a** have very good activity against *Bacillus subtilis*. In case of *Escherichia coli* both the complex shows less activity as compared to ligand. (Fig.5).



E.*coli* **B.*subtilis***

Fig: 5- Photograph of Antimicrobial Activity of Ligand & Cu(II)-Ligand complexes.

Table.2-Antimicrobial Activity of ligand and Cu (II)-3-formyl chromones derivatives.

Sr. No.	**Compounds**	**Diameter of Zone of Inhibition (mm)**	
		E.Coli	***B.Subtilis***
1	(1c.) Ligand $[C_{12}H_9O_3Cl_2]$	18 mm	19 mm
2	$[Cu(C_{12}H_{18}O_3Cl_2)_2]Cl_2$	17mm	20mm
3	Ciprofloxacin	40mm	35mm

IV. Conclusion:

The Cu(II) -3-formylchromones derivatives $[Cu(C_{12}H_9O_3Cl)_2]Cl_2$ is found to be totally new and unreported .The FTIR shows the carbonyl oxygen of pyron and aldehyde carbonyl oxygen donate the electron to the metal and form metal-ligand complex . The electronic spectra and magnetic susceptibility was suggested that the square planar geometry and paramagnetic in nature. The thermo gravimetric studies indicate that the decomposition of complex by two stage and final product was CuO. The antimicrobial activity against *E.coli* shown by both the ligand and its metal complex. The antimicrobial activity against *B.Subtilis* was shown by only the ligand and not the metal –ligand complex.

Acknowledgments:

The authors are very grateful to management of Ahmednagar Jilha Maratha Vidya Prasarak Samaj's; Principal Dr.B.H.Zaware, New Arts Commerce and Science College Ahmednagar for providing laboratory facilities.

References:

[1]. N. S. Joshi, B. K. Karale, C. H. Gill,S. B. Bhirud "Synthesis and characterization of new biologically active 2-(1, 3-disubstituted pyrazolyl)chromonesand corresponding pyrimidine, thiopyrimidine, pyrazolyl derivatives," Journal of Heterocyclic Chemistry,2004,41(4):541–548.

[2]. Nathan R. Guz, Frank R. Stermitz, Jeffrey B. Johnson, Teresa D. Beeson, Seth Willen, Jen- Fang Hsiang, and Kim Lewis "Flavonolignan and Flavone Inhibitors of a Staphylococcus aureus Multidrug Resistance Pump: Structure−Activity Relationships," J Med Chem.2001, 44: 261–268.

[3]. Masami Kawase,Toru Tanaka, Hiroyuki Kan, Satoru Tani, Hideki Nakashima and Hiroshi Sakagami, "Biological Activity of 3-Formylchromones and Related Compounds" In Vivo,2007, 21: 829-834.

[4]. Chandra Kanta Ghosh, Anirban Ray and Amarendra Patra, "Benzopyrans. Part 42. Reactions of 4-Oxo-4H-1-benzopyran-3-carbaldehyde with some active methylene compounds in the presence of ammonia," J. Heterocycl. Chem,2001, 38 :1459.

[5]. Nohara A, Umetani T and Sanno Y studies on antianaphylactic agents –I : A Facil synthesis of 4-oxo-4H-1-benzopyran-3-carboxaldehydes by Vilsmeier reagents" Tetrahedron ,1974,30: 3553.

[6]. Sosnovskikh V Y, Moshkin V S and Kodess M I, "A reinvestigation of the reactions of 3- Substituted chromones with hydroxylamine. Unexpected synthesis of 3-amino-4H- chromeno [3,4-d]isoxazol-4-one and 3-(diaminomethylene)chroman-2,4-dione," Tetrahedron Lett. 2008,49: 6856-6859.

[7]. Cate L.A., Lemke T.L, "Phosphorus—nitrogen compounds XVIII: Hydrazides and thiosemicarbazides," J. Pharm. Sci. 1974,63:1736.

[8]. Subezynski W K, Anholine W E, Hyde J E and Petering O H, "Orientation and mobility of a copper square-planar complex in a lipid bilayer," J Am Chem Soc.1987,46:109.

[9]. Viswanathan M, "Synthesis, Characterization and Antibacterial Studies of Mixed Ligand Complexes of Cobalt(II) and Nickel(II) with Pyrrolidinobenzylurea and Nitrate ion," Asian J Chem.2008,20(8):6090.Akira Nohara, Toshihiro Ishiguro, Yasushi Sanno, Nohara, A., Ishiguto, T., Sanno, Y "A novel conversion reaction of 4-oxo-4H-1-benzopyran-3-

[10]. carboxaldehydes to 3-substituted-5- (2-hydroxybenzoyl)-2(1H)-pyridones" Tetrahedron Lett.1974, 13:1183.
[11]. Anton Vilsmeier; Haack, "The Vilsmeier–Haack reaction," A. Ber., 1927,60: 119.
[12]. Meth-Cohn, O.; Stanforth, S. P. Comp. Org. Syn.,1991, 2: 777–79.
[13]. K. Fries and G. Finck, "Über Homologe des Cumaranons und ihre Abkömmlinge, Chemische Berichte ,1908,41 (3): 4271–4284.
[14]. Fries, K.; Pfaffendorf, W. "Über ein Kondensationsprodukt des Cumaranons und seine Umwandlung in Oxindirubin," Chemische Berichte ,1910,43 (1): 212–219.
[15]. Archer, W. L "Formylation of dimethylaniline. Campaigne,"Organic Syntheses, 1953,4:331.
[16]. D. F. Millikan and E. E. Pickett, "Biochemical Patterns in Leaf Tissue from Virus-Infected and Disease-Free Apple : II. Some Cation Effects" Phytopathology, 1964,55: 89-91.
[17]. S. C. Nayak, P. K. Das, and K. K. Sahoo," Synthesis and Characterization of Some Cobalt (III) Complexes Containing Heterocyclic Nitrogen Donor Ligands" Chem. Pap., 2003,57(2) : 91-96.
[18]. P. Tharmaraj, D. Kodimunthiri, C.D. Sheela & C.S. Shanmuga Priya, "Synthesis, spectral Characterization, and antimicrobial activity of copper(II), cobalt(II), and nickel(II) complexes of 3-formylchromoniminopropylsilatrane", J coord chem., 2009,62: 2220- 2228.
[19]. N.G Kozlov,F.S.Gusak,K.N.Koroleva,E.V.Tereshko,A.B.Lokot, I. P "6,6- Heptamethylenetetrahydropyran-2,4-dione in the Synthesis of Benzopyrano[3,4]quinolines and Pyrano [4,3]phenanthrolines." Russian Journal of OrganicChemistry, 2004,40(4):555-559.
[20]. Jairo Quiroga, Diana Mejía, Braulio Insuasty, Rodrigo Abonía, Manuel Nogueras, Adolfo Sánchez, JustoCobo and J. N. Low, J.; "Synthesis of 6-(2-hydroxybenzoyl)pyrazolo[1,5-] Pyrimidines by reaction of 5-amino-1h-pyrazoles and 3-formylchromone" J. Heterocyclic Chem.,2002,35: 51–54.
[21]. Mükerrem Kurtoglu, Esin İspir, Nurcan Kurtoğlu, Sevil Toroğlu, "Activity, "Transition Met. Chem.,2005, 30(6): 765-770.
[22]. M. S. Ameerunisha Begum, Sounik Saha, Akhtar Hussain & Akhil R Chakravarty, "Synthesis, crystal strycture and DNA cleavage activity of aquo- bis(dipyridophenazine)copper(II) complex," Indian Journal of Chemistry, 2009, 48:9-14.
[23]. A. Maihub, S.S. Hudere, M.M. El-ajaily, "Complexation behavior of Schiff base toward transition metal ions" American Micro chemical J.,2005, 81:191-194.
[24]. Pritha Talukdera , Amitabha Dattaa, Samiran Mitraa, and Georgina Rosairb, "Square Planar Complexes of Cu(II) with an N2O Donor Set of a New Schiff Base Ligand: Synthesis and Structural Aspects Z. Naturforsch.,2004, 59b: 655 - 660.
[25]. B. N. Ghose & K. M. Lasisi "Schiff Base Complexes of Titanium: Reaction of Titanium (IV) Tetrachloride with Dibasic Tetradentate Schiff Bases",. Synth React Inorg Met-Org Chem, 1986,16, 1121.
[26]. B. K. Ganguly,P. Bagchi"Studies on the Ultraviolet Absorption Spectra of Coumarins and Chromones. Part I J.org.chemistry,1956, 21 (12):1415–1419.
[27]. Sherif, Omyma E. Abdel-Fattah, HusseinM. El-Ajily, Marie M. "Characterization of transition metal ion chelates with 8-(arylazo chromones using thermal and spectral techniques" Journal of Thermal Analysis & Calorimetry,2003,74(1):181-200.
[28]. N. Deb, S.D.Baruah, N.S. Sarma and N.N. Dass "Synthesis, characterization and thermal investigation of M[M(C2O4)3]·xH2O (x=4 for M=Cr(III); x=2 for M=Sb(III) and x=9 for M=La(III), Thermochim Acta. ,1994,320: 53-67.
[29]. Dziewulska-Kułaczkowska, "Manganese (II), cobalt (II), nickel (II), copper (II) and zinc(II) complexes with 4-oxo-4H-1 benzopyran-3-carboxaldehyde, Journal of Thermal Analysis & Calorimetry" 2010,101 (3):1019-1026.
[30]. R.C.Aggarwal, N.K. ingh and R.P.Singh,"Magnetic and Spectroscopic Studies on Salicylaldoxime and o-Hydhoxynaphthaldoxime Complexes of Some Divalent 3d Metal Ions Synth. React. Inorg. Met.-Org.Chem, 1984,14 (5):637-650.
[31]. R.C.Felicio, da silva , L.F. Ceriorio, E.R. Dockal., "Tetradentate Schiff Base Copper(II complexes"Synth. React. Inorg. Met-org.chemi., 1999,29 (2): 171-192.
[32]. M. Cato, H. B. Jonassen and J. C. Fanning, "Copper(II) Complexes with Subnormal Magnetic Moments, Chem. Rev,1964,64:99.
[33]. E. F. Hasty, L" J. Wi1son and D. N. Hendrickson, "Structural studies of precursor and Partially oxidized conducting complexes. A neutron diffraction and x-ray diffuse Scattering study of the dimerized platinum chain in rubidium tetracyanoplatinate chloride (2:1:0.3) trihydrate, Inorg. Chem., 1978, 17:834.
[34]. Sulekh Chandra, Lokesh Kumar Gupta, Deepali Jain, "Spectroscopic studies on Mn(II), Co(II), Ni(II) and Cu(II) complexes with tetradentate (N_4) macrocyclic ligand derived from ethylcinnamate moiety",Spectrochim Acta,2004,60(10): 2189
[35]. W.C.Vosburg and G. R.Cooper., "Complex Ions. I. The Identification of Complex Ions in Solution by Spectrophotometric Measurements Warren C. Vosburgh, Gerald R. Cooper , J.Am. Chem. Soc., 1941,63: 437.
[36]. Z. H. Chohan, M.S. Iqbal, S. K. Aftab Design, synthesis, characterization and antibacterial properties of copper(II) complexes with chromone-derived Compounds. Journal of Applied Science, 2009,24(1):47-56.
[37]. N. Raman, V. Muthuraj, S. Ravichandran, A. Kulandaisamy" Synthesis, characterisation and electrochemical behaviour of Cu(II), Co(II), Ni(II) and Zn(II) complexes derived from acetylacetone andp-anisidine and their antimicrobial activity" Journal of Chemical Sciences, 2012,115(3):161-167.