

Synthesis, Spectral, Magnetic, Thermal Characterization and Antibacterial activity of Co(II) ion with O,O donor ligand of type-6, 8-dicloro-4oxo-4H-chromene-3-carbaldehyde

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Abstract: The Vilsmeier-Haack reaction was used for synthesis of O, O donor ligand 6, 8-dicloro-4oxo-4H-chromene-3-carbaldehyde. This compound was reacted with Co(II) metal ion to form chelate complex. The ligand and their metal complex structure was determined from different technique like elemental analysis, some spectroscopic methods, thermal analysis by thermogravimetrically, magnetic susceptibility measurement like Gouy balance method and microanalytical methods. The octahedral geometry for Co(II) complex has been proposed according to the result obtained from electronic spectra and the magnetic moment. The Ligand and complex, whether these are biologically active or not is determined against different types of bacteria. The agar well diffusion method was used to for determination of the biological activity. The biological activity of ligand goes on decrease with formation of chelate complex with Co(II) metal ion.

Keywords: Cobalt complex; 6, 8-dicloro-4oxo-4H-chromene-3-carbaldehyde; Conductivity, Agar well diffusion.

Introduction:

Chromones are important for the preparation of oxygen heterocyclic compounds of flavonoid¹, xanthenes² etc. The chromones are important heterocyclic component for biological activities like antidepressant³, psychoanaleptic, antimalarial⁴, antiamebic and antifungal⁵, antioxidant, antibacterial. The derivatives of 3-formyl chromone are useful synthetic building blocks in both organic heterocyclic chemistry, drug chemistry and the synthetic bio-inorganic chemistry. The substituted 3-formylchromones have attracted considerable attention as highly reactive compounds, which can form the metal- heterocyclic complexes with useful properties due to the availability of oxygen as a donor center.

The transition metal complexes of 6, 8-dichloro-4-oxo-4H-chromene-3-carbaldehyde has been chosen for the present study due to the reason that it has two carbonyl group for the complexing with Cobalt (II) metal ion. The aim of the work is based on view that plays an important role by the Co(II)- complex of substituted chromone moiety. We are interested to prepare new complex derived from substituted chromone nucleus, which may serve in different fields. The chemistry of the complexes is investigated by all spectral, thermal, magnetic, conductivity techniques. The antimicrobial activity of ligand and its complex was mounted by well diffusion method and the inhibition zone was measured in mm-scale^{6,7}.

2. Experimental

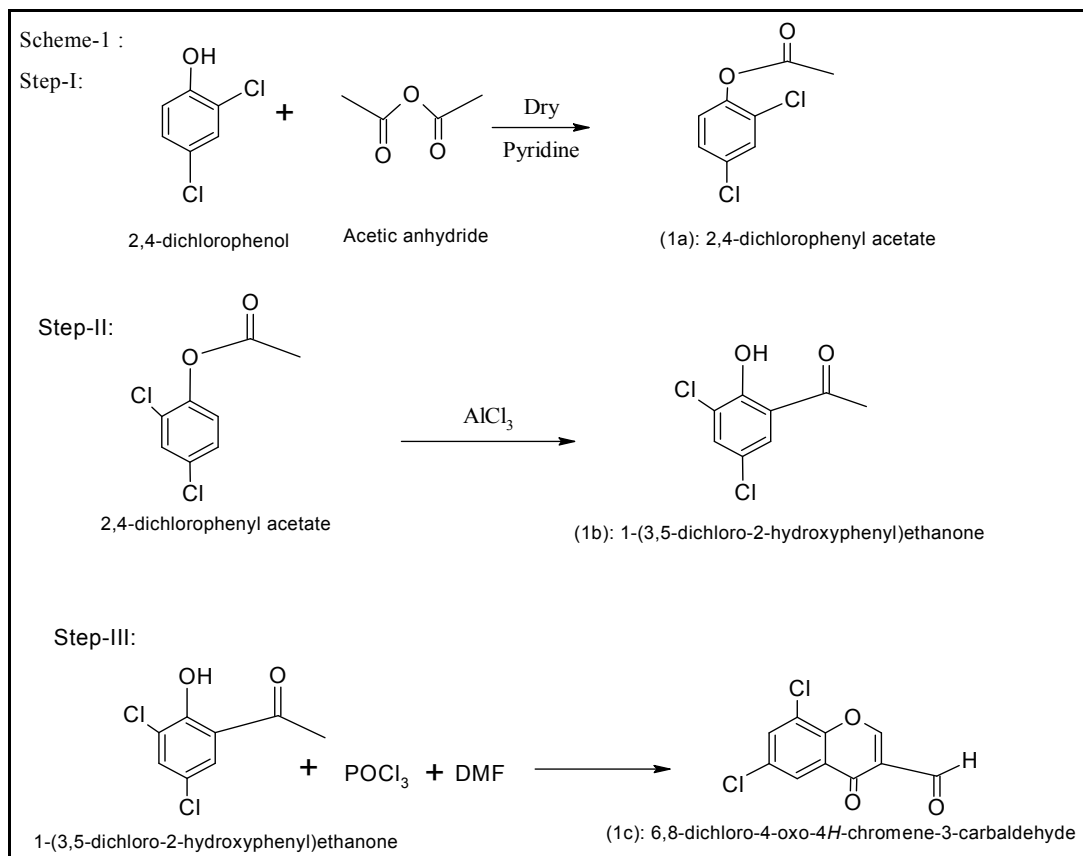
2.1. Chemicals and methods:

All chemical were of Analytical reagent grade quality and purity were purchase from Loba chemicals. Metal salt of transition metal ion $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 2,4-dichlorophenol, Anhydrous AlCl_3 , Dimethylformamide, Dimethylsulfoxide, Phosphorylchloride, Ethanoic anhydride, Anhydrous Sodium Sulphate, Aryl Acetate, Pyridine Acetone, and Methanol. All chemical were of Analytical reagent grade quality and purity was purchase from Loba chemicals.

The methods for characterization of ligand as well as its Co(II)-ligands complex were done by different techniques. The Infrared spectra were recorded in KBr disc on a IRAffinity -1 FTIR-Spectrophotometer Shimadzu in the range $4000\text{-}400\text{ cm}^{-1}$. The electronic spectra for products were run on UV-1800 spectrophotometer (Shimadzu) at 27°C in 10^{-3}M concentration in DMSO solvent. The C,H,N,O percentage was determined by Perkin Elmer elemental analyzer. Thermo Gravimetric Analysis (TGA) was recorded on TGA-50, Shimadzu Thermogravimetric analyzer having TGA-50 H thermal analyzer detector. The magnetic property of complex was estimated from Gouy balance method. The solubility of the prepared complex was checked using solvent water, DMSO, CH_3CN , and ethyl alcohol. The molar conductivity of Cobalt-6, 8-dichloro-4-oxo-4H-chromene-3-carbaldehyde complex was measured in DMF 10^{-3}M using Conductometer.

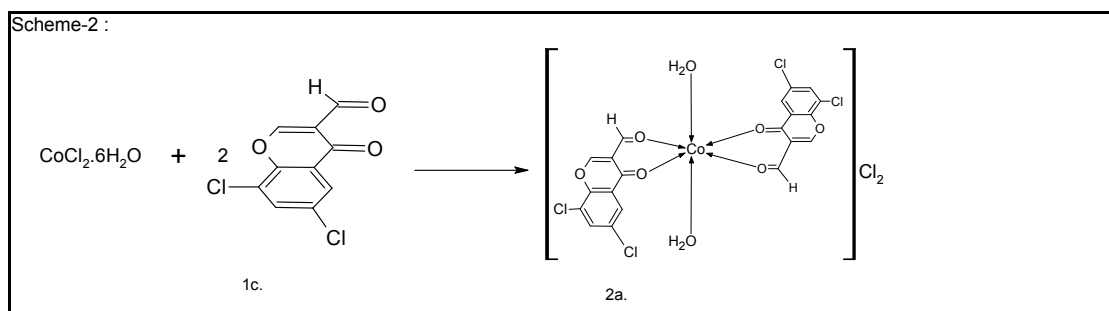
2.2. Synthesis of Ligand:

The ligand 6, 8 dichloro-4oxo-4H-chromene-3-carbaldehyde was synthesized by the Vilsmeier-Haack reaction⁸. The synthesis of substituted 3-formylchromone was done by three steps. The first step is the synthesis of 2, 4 dichlorophenyl acetate from 1mole of 2, 4-dichlorophenol by reacting with 1.15 mole acetic anhydride in presence of 5ml dry pyridine. (Scheme.1a) by reported method⁹. Then the formed product was treated with AlCl_3 . This is a Fries reaction scheme.1-(1b) by reported method¹⁰. The synthesis of 6, 8 dichloro-4oxo-4H-chromene-3-carbaldehyde (ligand) by taking the 25ml dimethylformamide; which was kept in ice bath and then adding 15ml POCl_3 in it drop wise. This is a Vilsmeier-Haack reaction, which were referred¹¹. The product was precipitated as brown solid of 6, 8 dichloro-4oxo-4H-chromene-3-carbaldehyde, which was filtered and recrystallized from acetic acid: ethanol having 1:1ratio. Scheme-1(1c.)



2.3. Synthesis of complex:

The 0.242 gm. (2mole) 6,8 dichloro-4-oxo-4H-chromene-3-carbaldehyde ligand was dissolved in 10 ml hot methanol with two drops of acetic acid. To this hot ligand solution 10ml ethanolic solution of 0.1185gm (1mole) of Co(II) salt solution was added drop by drop with continuous stirring the temperature was maintain at 80°C -90°C for 30 minutes. Then the 2-4 drops of ethanolic ammonia solution were added to maintain the pH. The complex precipitates having green colour. Then the complex was allowed to cool at room temperature the colour of complex was changed from green to yellowish green and finally to yellow. This yellow solid was separated out, filtered and washed with ethanol and product was dried at room temperature



3. Result and Discussion:

3.1. Infrared Spectra:

FTIR spectrum (Figure 1 & 2) of the ligand 6,8-dichloro-4-oxo-4H-chromene-3-carbaldehyde shows absorption band at 1699 cm^{-1} , which is characteristic of the ν (C=O) of γ -pyrone of 3-formylchromone¹². The spectrum of complex, shows absorption band at 1619 cm^{-1} , which has been shifted to lower region by 80 cm^{-1} , indicating the coordination of the ligand through the oxygen atom present in the 4-position of γ -pyrone ring. The FTIR spectrum of ligand shows a band at 1743 cm^{-1} , which is assigned for stretching ν (C=O) of carbonyl of aldehyde group of chromone¹³. The complex IR spectrum shows absorption band at 1720 cm^{-1} . This shift in the band (from 1743 cm^{-1} of ligand to 1720 cm^{-1} of complex) by 23 cm^{-1} , indicates that there is formation of coordination bond with Co(II) metal ion. This is also supported by ν (Co-O) frequency¹⁴, which shows the absorption band at 549 cm^{-1} . In addition to these absorption bands in the FTIR spectrum the band at 935 cm^{-1} to 945 cm^{-1} indicates the presence of pyron ring in ligands as well as in complex. The band at 1566 cm^{-1} -1485 cm^{-1} is assigned to the combination of ν (C=C) of the aromatic ring¹⁵. A high intensity band in the region 1336 cm^{-1} -1350 cm^{-1} is assigned to Oxo ν (C-O) vibration. The complex shows 3070 cm^{-1} due to presence of co-ordinate water molecules. The IR band at 2966 cm^{-1} and 2984 cm^{-1} indicate the presence of -C-H stretch present in the ligand as well as in their complex. The IR spectrum also shows the C-Cl stretch at 843-549 cm^{-1} .

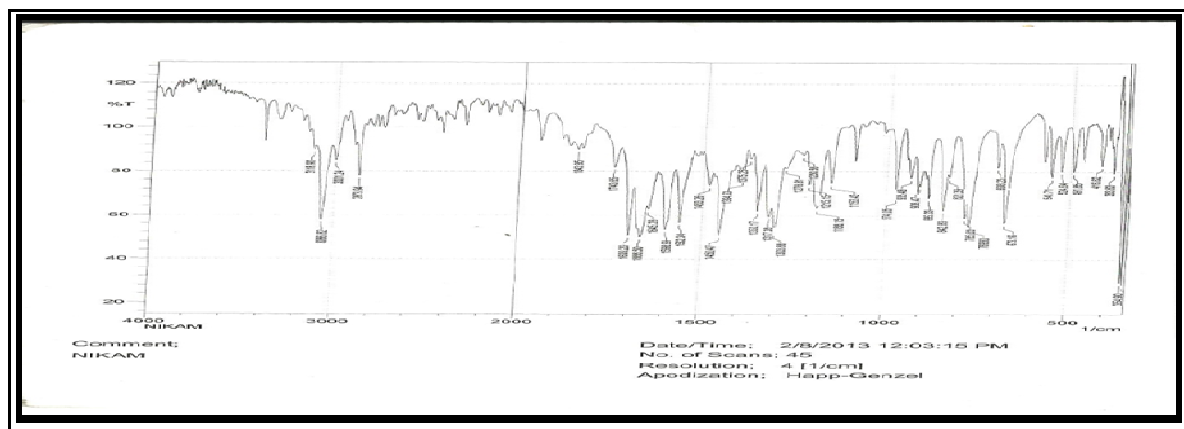


Figure.1. FTIR spectrum of ligand [6,8-dichloro-4-oxo-4H-chromene-3-carbaldehyde]

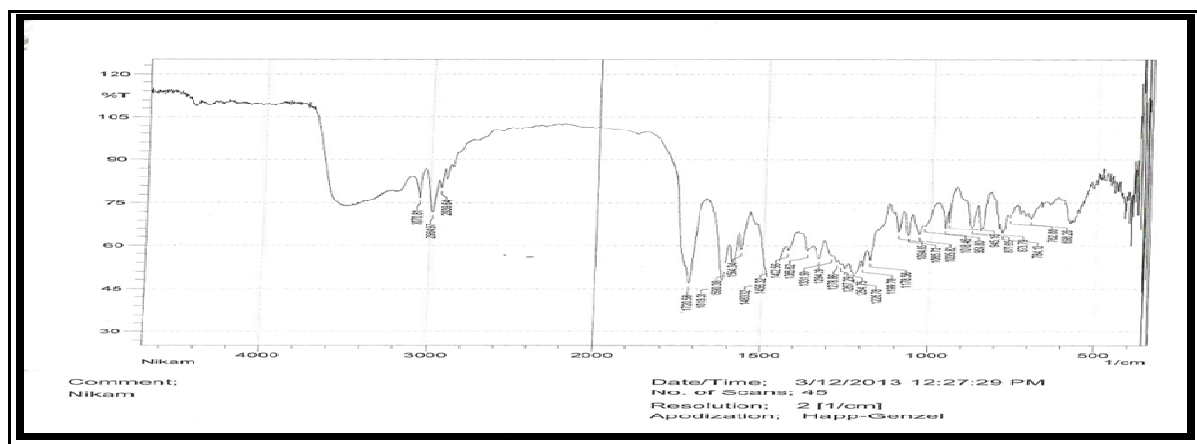


Figure.2.FTIR spectrum of Co(II)-6,8-dichloro-4oxo-4H-chromene-3-carbaldehyde

3.2. UV-Visible Spectra and Magnetic Susceptibility of complex:

The electronic spectrum of Co(II) complex shows three peaks at, 22675.72cm^{-1} , 36900.35cm^{-1} and 41493.00cm^{-1} corresponding to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$, suggesting octahedral geometry¹⁶. The electronic spectra of ligand was shown the 284nm-315 nm indicate $\pi-\pi^*$ and $n-\pi^*$. The magnetic susceptibility measurements of the complexes were performed by Gouy balance method at 25°C temperature by Hg $[\text{Co}(\text{SCN})_4]$ as a calibrate. The magnetic moment of Co(II)-6,8 dichloro-4oxo-4H-chromene-3-carbaldehyde complex has been found to be $\mu_{\text{eff}} = 3.10$ B.M.suggesting that the octahedral geometry of the complex^{17,18}.

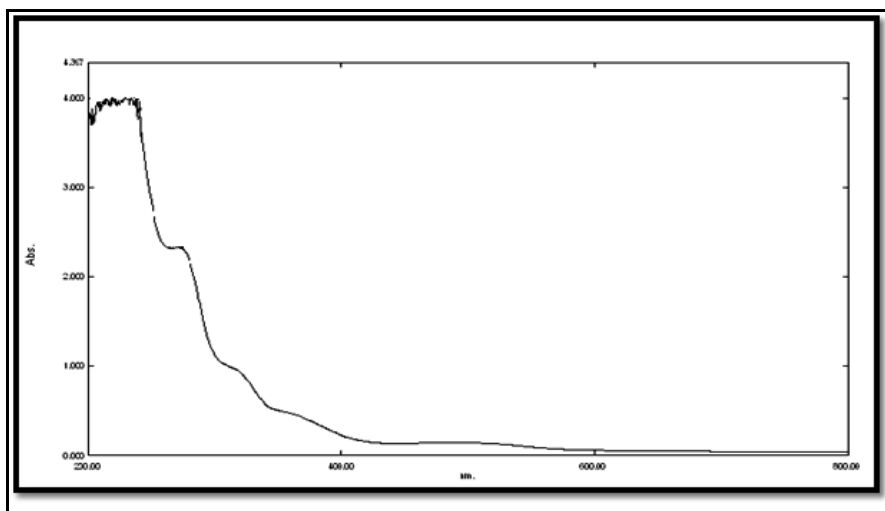


Figure.3.Uv-Vis spectra of Co (II) 6,8-dichloro-4oxo-4H-chromene-3-carbaldehyde

3.3. Molar Conductance and some physicochemical properties:

Molar conductance of the complex is measured in DMF at a concentration of 10^{-3} M. The observed conductance value for cobalt complex is $173.14\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$, indicates that the complex is 1:2 electrolytes¹⁹. The analytical data along with some physical properties of the ligand and its Co(II) complex are summarized in Table1.

Table-1: The Analytical data of the ligand and their metal complex

Sr. No.	Compound/ Complex	M.W.	Color	% Yield	M.P °C	C,H,OAnalysis Found (Cal.%)				Molar Conductivity $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
						C	H	O	M	
1	1c.[C ₁₀ H ₄ C ₁₂ O ₃]	243.04	Brown	65.35 %	173	48.40 (49.42)	1.66 (1.66)	19.45 (19.75)	-----	-----
4	2a.[C ₂₀ H ₁₄ Cl ₄ CoO ₈]Cl ₂	651.95	Yellow	73.45 %	64.21d *	36.18 (36.85)	1.86 (1.86)	19.18 (19.63)	9.01 (9.04)	173.14

M.W= Molecular weight, M.P. = Melting Point, d*=Decomposition

3.4. Thermal analysis:

Thermo-gravimetric analysis (TGA) and DTGA of 1c. Ligand [C₁₀H₄C₁₂O₃] suggests that the decomposition occurs in one step. The observed mass loss was found to be 60.32%, which is attributed to calculated % mass loss 61.02 %. The calculated and observed % mass loss is in good agreement, which indicate the loss of C₅H₄OCl₂ group in temperature range 147.39 °C - 399.02 °C. The compound further breaks to form the carbon residue (Figure.4).

TG and DTGA curve of Co(II) complex (Fig.5) was carried out in inert (N₂) atmosphere with flow rate 50ml/min. and the heating rate was 5 °Cmin⁻¹. The thermogram shows single decomposition step. The thermogram indicate the decomposition of complex was fast and continue up the temperature 521.12 °C. The decomposition start from temperature range 64.21 °C to 147.41 °C with % mass loss was 5.43% which was attributed to calculate mass loss is 5.52%. The % mass loss was good agreement to loss of two co-ordinate water molecules from the complex. The further decomposition is continuing by loss of two C₅H₄OCl₂ molecules from the temperature 147 °C to the temperature 521 °C. This was attributed to % mass loss was found 74.22 %, which was attributed to calculated weight loss 76.23%. The calculated and observed % mass loss was differs by 2.5% due to the carbon black residue was deposited on the sample holder. Then at temperature more than 730 °C the horizontal curve was observed it indicate that the formation of final residue of CoO²⁰⁻²¹.

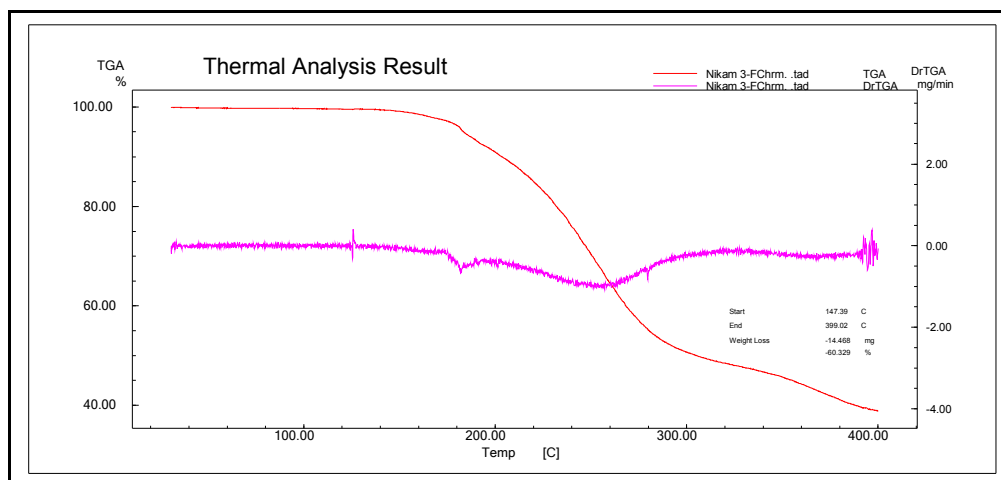


Figure.4. TGA and Dr.TGA of ligand [6-8dichlorol-4oxo-4H-chromene-3-carbaldehyde]

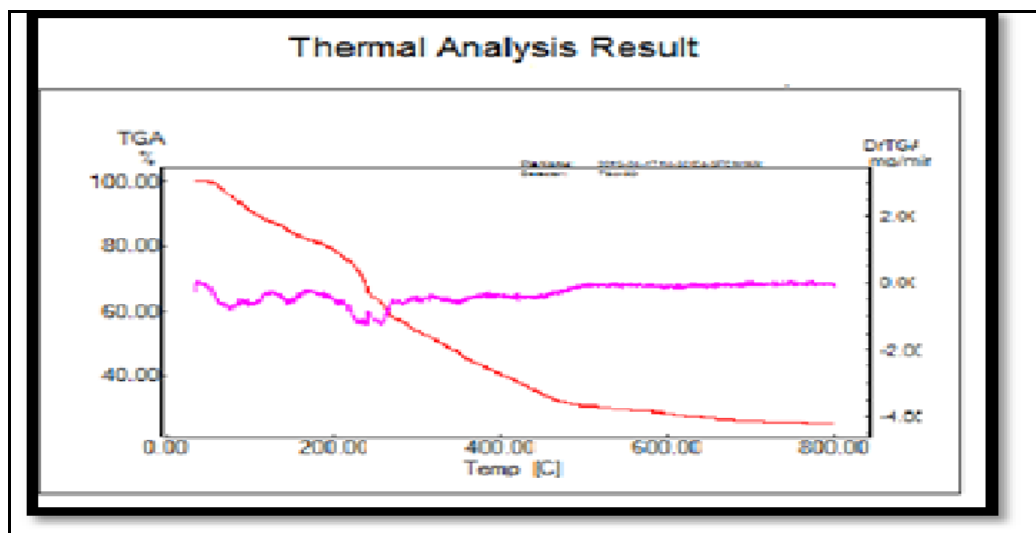
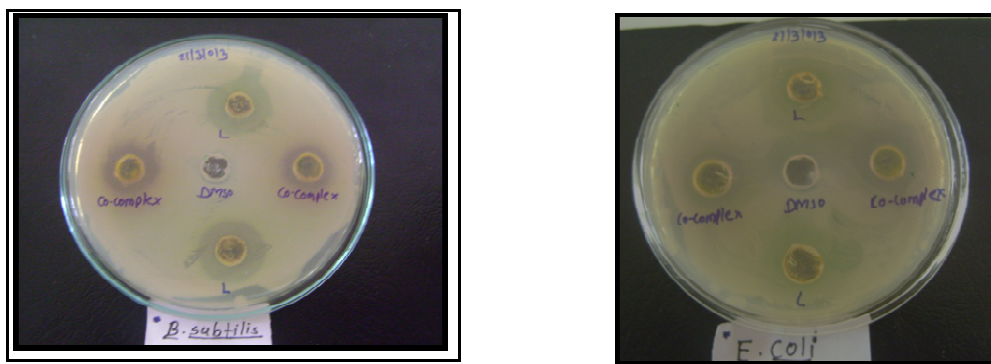


Figure.5. TGA and Dr.TGA of complex $[C_{20}H_{14}Cl_4CoO_8]Cl_2$

3.5. Antimicrobial activity

For the study of antimicrobial activity the bacterial cultures selected were, gram negative culture *Escherichia coli* and gram positive culture *Bacillus subtilis* were maintained in nutrient agar slants at 37°C. The *in vitro* antibacterial activity was measured by agar well diffusion method at 100 µg/mL concentration²². The standard antibiotic ciprofloxacin used as positive control and DMSO as negative control. All the experiments were performed in duplicate. The results were recorded by measuring the zone of inhibition in millimeter (mm). The 6-8 dichloro-4-oxo-4H-chromene-3-carbaldehyde as ligand and their Co(II) complexes were evaluated for anti-bacterial activity with different strains of bacteria. Results were shown in table-2.

The ligand obtained greater activity against *E. coli* and *B. subtilis* compared with Co(II) complex. The antimicrobial activity of ligand and their complex was shown clearly against the gram positive bacteria while it was less clear against the gram negative strain for complex and not for 6-8 dichloro-4-oxo-4H-chromene-3-carbaldehyde.



L : Ligand (6, 8 dichloro-4-oxo-4H-chromene-3-carbaldehyde)
Co-complex : $[C_{20}H_{14}Cl_4CoO_8]Cl_2$ Complex
DMSO : Dimethylsulphoxide.

Figure 6: Photograph of Antimicrobial activity of ligand and Co(II) complex (2a.)

Table-2: Zone of Inhibition of L and their complex

Compounds	B.Subtilis		E.Coli.	
	L	19mm	20mm	18mm
$[C_{20}H_{14}Cl_4CoO_8]Cl_2$	15mm	14mm	11mm	13mm

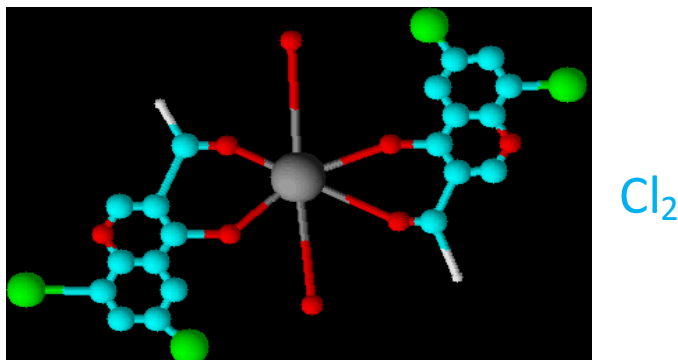


Fig.7.Suggested 3D structure of Complex

Conclusion:

The chromone O, O donor ligand acts as a good chelating agent as well as precipitant agents for Co(II) metal ion. The Co(II) complex was synthesized and well characterized by spectral, Thermal, Magnetic susceptibility methods. The vitro antimicrobial activity of complex is less response against gram negative strain. While ligand 6-8 dichlorol-4oxo-4H-chromene-3-carbaldehyde shows well antimicrobial activity against gram positive as well as gram negative bacteria. The molar conductance measurement shows it has electrolytic in nature. The electronic spectra and magnetic susceptibility was suggested that the octahedral geometry. The thermo gravimetric studies indicate that the decomposition of complex was continue up to the temperature 722.05 °C by loss of co-ordinate water and organic compounds and CoO as final residue was obtained.

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