SYNTHESIS AND SPECTRAL CHARACTERIZATION OF SCHIFF BASE COMPLEXES DERIVED FROM HETEROCYCLIC COMPOUND 4- ACETYL PYRIDINE AND EDA WITH DIVALENT METAL CHLORIDE AND ACETATE BY USING ULTRASOUND METHOD.

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Abstract: Schiff base were derived from 4- acetyl pyridine and ethylene di-amine by using innovative ultrasound method. This method is a time saving and also provided the good yield of product. These Schiff base were used to synthesized metal complexes by using Cu (II) And Co(II) acetate and chloride salt. Schiff base and metal complexes are characterized and studied by FTIR, ^{1}H NMR,SEM with EDS ,TEM,TGA,XRD.
The synthesized Schiff base and metal complexes were used for antimicrobial screening.

***Key words*- Ultrasound method, Schiff base, Metal complexes, Characterization, particle size, antimicrobial activity.**

1. INTRODUCTION:

In the present research work, Schiff base and metal complexes derived from **4**- acetyl pyridine, ethylene di-amine and Cu (II) and Co (II) acetate and chloride salt [1-3]. As we know that the Schiff base and metal complexes have been playing an important role in the varies field like physics, chemistry, nanoscience and medical science. Schiff base are widely used for industrial purposes and also exhibits a broad range of biological activities [4-5] .Schiff bases used as pigments, dyes and polymer stabilizers [4-6]. The Schiff base ligands metal complexes have been studied extensively due to their attractive chemical and physical properties and their wide range of applications in numerous scientific areas [19]. The particle size of metal complexes also provide varies applications in the field of electronics for preparing nanotube, nanowires etc. In the present work we are tried to synthesized Schiff base and complexes by using ultrasound method [8-10]. Sonochemical energy delivery has been used as an excellent alternative to thermal energy in promoting organic reactions [7]. The used of ultra sound methods improve the rate of reaction and yield of the product also increases. This method is useful for saving tremendous amount of energy and time required for synthesis. Now a day's different techniques are used for characterization like SEM, TEM, Powder XRD etc [13-16]. Which are very important to determine the particle size and morphology of crystals Antibacterial and antifungal activity is also studied.

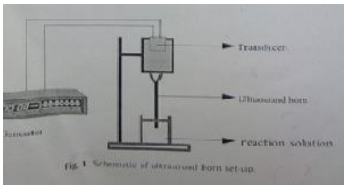
2. EXPERIMENTAL WORK:

2.1. Material-

In this work all the solvents and different chemical like -ethylene di amines and carbonyl compound like 4-acetyi pyridine were used analytical grade and used after the purification. The reaction is performed by ultrasound method [9].The reaction completion were monitored by TLC by using 0.25mm E-Merck Silica gel 60 percolated plates which were visualized with UV light. The solvents like DMSO, DMF, Ethanol and Acetone were used for recrystallization of product and Preparation of sample. The physical constant was taken by melting point apparatus and by open capillary method.

2.2 Method -(Ultrasound set-up) -

Ultrasound for sonochemical Synthesis is generated with the help of ultrasonic instrument set-up (horn type/probe type) the specification and details used during the experiments [8]-
Make:ACE,USA
Operating Frequency: 22LKHz
Rated output Power: 750W
Diameter of stainless steel tip probe: 1.3 x 10^{-2} m [9]



2.3. Preparation of Schiff base by using Ultrasound -

The 4-acetyl pyridine and EDA chemical were used as 2:1 ratio in a 50 ml. beaker with 20 ml alcohols. The reaction mixture were taken and placed under the sonicator probe [8-10], the probe insert ted in the beaker and time set for ultrasound was 3s per interval. The purification of the reactant 4AP was check by silica coated plate and reaction also monitored by TLC are shown in **Fig-1** first TLC for Schiff base purification test and Second for Reaction completion. The physical properties and observations like color, M.P, time of reaction, solvents, yield etc. are noted in Fig-2- table no.1.

2.4. Preparation of Metal complexes by using Ultrasound -

The synthesized Schiff base were recrystalised and dried under IR lamp the dried product were used for characterization of FTIR and ^{1}H NMR technique after confirmation of Molecular structural peak we were prepared o.o1 mole solution of Schiff base and also prepared 0.01 mole solution of copper acetate and cobalt chloride. The Schiff base solution was prepared in alcohol .10 ml alcoholic solution of Schiff base were added drop wise in the 10 ml solution of metal salts .The reaction mixture containing beaker was placed under the probe of sonicator for sonication by setting the time interval of 3 sec. Up to 20 min. After sonication the reaction mixture beaker was removed and placed for cooling in room temperature. Fine colorful particles were collected at the bottom of beaker. The observations related to complexes are noted in **Fig-2- table no.1.** The proposed mechanism of formation of Schiff base and metal complexes may be represented by **Fig-3-scheme-1.**

The physical properties and observations are given as fallows.

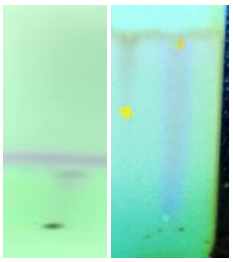
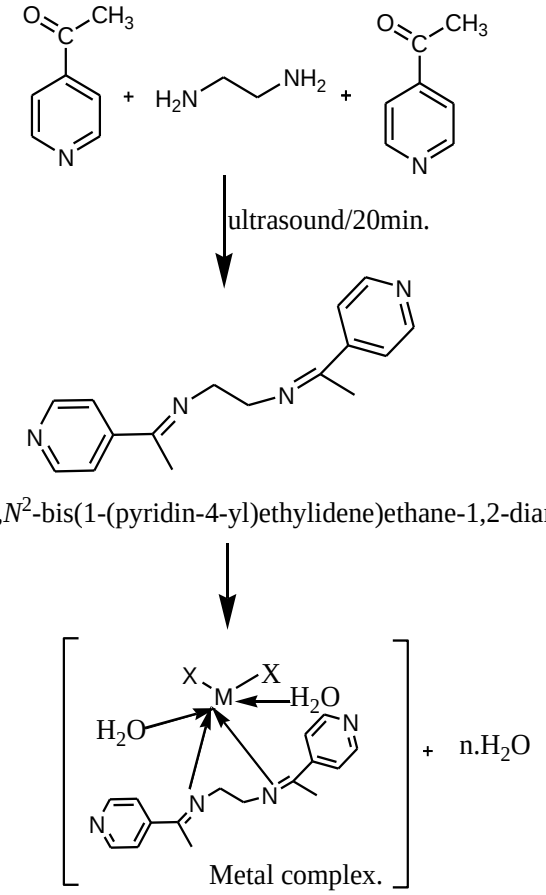


Fig-1-a. Purification of 4AP b. Completion of reaction

Fig-2- Table No.1

S.B and MC.	US				
	Solvent (20 ml)	Color	M.P ^{o}C	Yield %	Time
SB- L	Ethanol	Shiny yellow crystal	110-112	68	20min. Keep overnight
$[COL(Cl)_2(H_2o)_2]$	Methanol	Dark green	>280	70	30 min.
$[CuL(COOCH_3)_2(H_2O)_2]$	Methanol	Faint green	>300	75	30 min.



X= CH_3COOH or Cl and M=Cu,Co

Fig-3-Scheme-I- Proposed mechanism of Schiff base and metal complexes.

3. RESULTS AND DISCUSSION

3.1. IR Spectra-

In the Schiff base ligand which is prepared from4-AP+EDA which are characterized by IR.The most important IR Band compared with metal complexes which is prepared from synthesized Schiff base. IR observed wave no. (cm^{-1}) of Schiff base (L) and Metal Complexes[COL(Cl_2)(H_2o)]and [CuL($COOCH_3)_2(H_2O)_2$.

Assignments (ν)	SB	[COL(Cl_2)(H_2o)]	[CuL($COOCH_3)_2(H_2O)_2$]
CH	1107	1192	1161
Me	2947	3055	3051
C=C	1620.21	1616	1604
C=N	1577.21	1566	1504
CH3COOH	-	-	651
C-N	1392	1276	1292
M-O	-	501	505
Ring breathing	1165	1192	1161

The above frequencies clearly indicates that the after formation of metal complexes the positive shift of bands in the region of 1500-1600 of C=C and C=N are observed,new bands are also appear in the region of 600-651.some stretching and asymmetric stretching vibrations are also observed. Acetate group were also observed in second complex with sharp peak at 651[16].
The IR Spectra is shown in **Fig.4.**

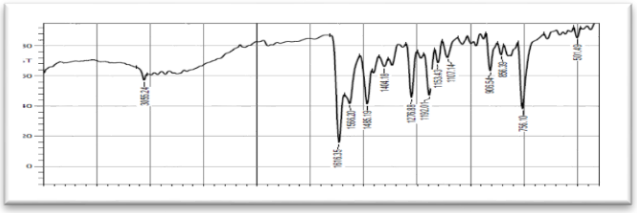


Fig-4-a-SB(L)

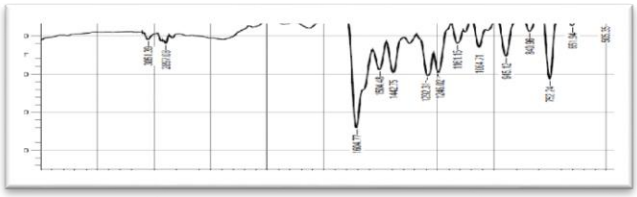


Fig-4-b-COL

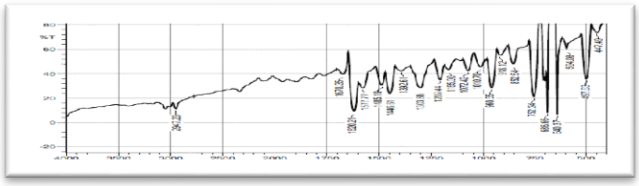


Fig-4-C-CuL

3.2.-^{1}H NMR –

4AP were distillate first and then record there^{1}H NMR spectra after getting proper signals like 3H shows str. Signal at 2.26 , 2H of pyridine shows strong signal at 7.85 δ and 2H shows 8.7 δ. we arereacted 4AP with EDA in presence of ultrasound. Prepared Schiff base characterized by ^{1}H NMR getting signal for 18protons.4H from ethylene molecule shows signal at 3.34 δ,6H from methyl group shows strong signal at 2.25 δ.8 protons from pyridine rings shows two strong signals at 7.85 δ and shows 8.7 δ. 7.85 δ and 2H shows 8.7 δ the prepared SB is symmetrical. The above signal clearly indicates that the reaction is completed.spectra shown in **Fig-5**.

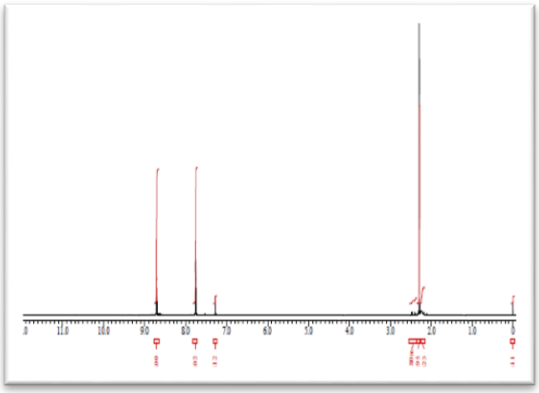


Fig-5-4Ap (reactant)

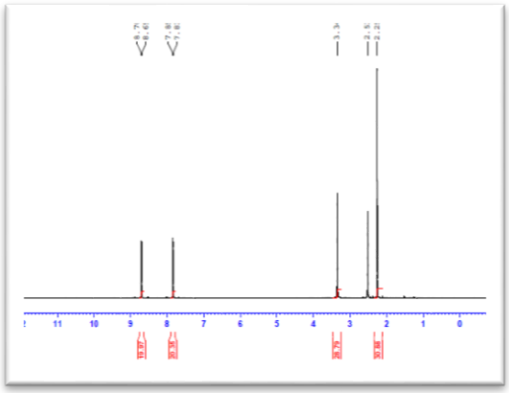


Fig-5-SB

3.3.-Thermal Analysis (TGA and DTA) -

The thermal analyses (TGA and DTA) Curves of the Schiff base and complexes were carried out from 25 ^{0}C to 800 ^{0}C the thermal effect accompanying the Changes in the Solid Complexes [10].The Thermograms which is represents in figures no.6. The Fig- (6a) shows Schiff base decomposition and Fig-(6b,6c) shows metal complexes. In first figure 99.230 % loss are observed which clearly indicates that organic mass of Schiff base were loss completely near coordination. 15%. Of compound loss due to ethylene and Chloride at 250-350 ^{0}C.Above the 400 ^{0}C temperature Pyridine molecule loss At this stage we loss 69% of the compound .32 % remaining about temperature 400 ^{0}C.In [COL(Cl_2)$(H_2O)_2$] complex the different range of temperature are observed in the range of 40-250 ^{0}C loss of water molecule which is used for hydration and compound is clear evidence for Metal Oxide are formed. In [CuL$(COOCH_3)_2(H_2O)_2$] this complex water molecule loss in starting temperature 50-150 ^{0}C.above 250 ^{0}C temperature acetate group is losses. Above 400 ^{0}C loss of Py. molecule.the 88% loss from the total amount remaining 12% is metal oxide. TGA Curves shown in **Fig No.-6**- Schiff base (6a) and Metal comp. (6b, 6c).

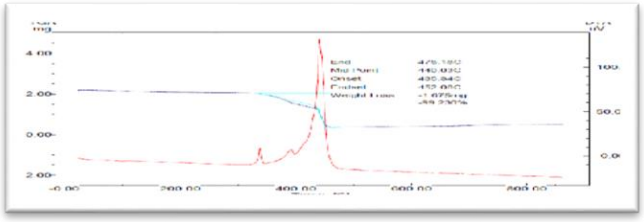


Fig-6a- 99.230% decomposition of SB.

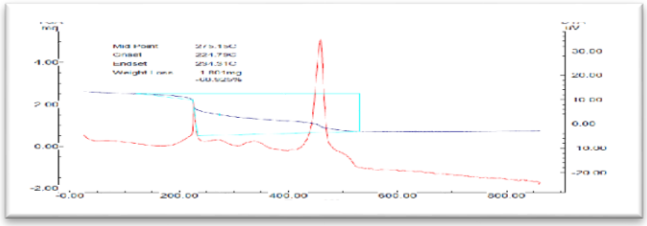


Fig-6b-69% compound decomposed.

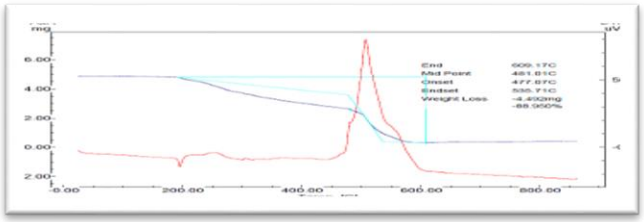


Fig-6c-88% compound are decomposed

3.4- **SEM-EDS And TEM** –

SEM Means scanning electron microscopy and EDS-Electron dispersive Spectrometer these both the systems were used to identify the chemical composition of samples by detecting the characteristic X-rays that are emitted from the materials when they are bombarded with electrons[17]. The SEM image clearly indicates the morphology of the crystals. The Synthesized Schiff base is fine powder like narure its images indicates the particle sizes10µ.the EDS clearly shown that the presence of C,N and Oxygen 65%,15% and 20% respectively. The complex of cobalt that is [COL(Cl_2)(H_20)$_2$] containing elements are indicates by EDS the chloride atom and cobalt's are present in indicative manners. .the morphology of crystal is shown by SEM image, 20 µ particle size is shown by image. In this complex [CuL($COOCH_{3)2}$(H_2O)$_2$] the percentage of oxygen is too much large 45.73% due to acetate and water molecule containing oxygen atom. The SEM Images and EDS graphs for elements are shown in **Figure -No.7-**

(7a-SB,7b- [COL(Cl_2)(H_20)$_2$] , 7c-[CuL($COOCH_{3)2}$(H_2O)$_2$]).

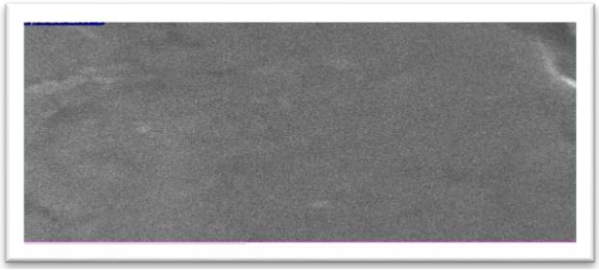
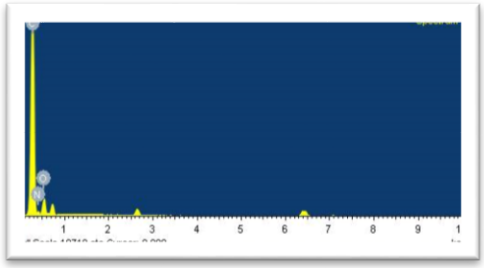


Figure No.- 6a-SB,morphology of SB



EDS-SB

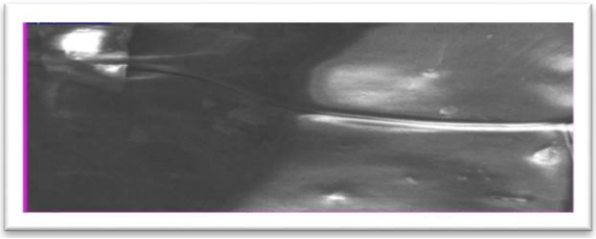
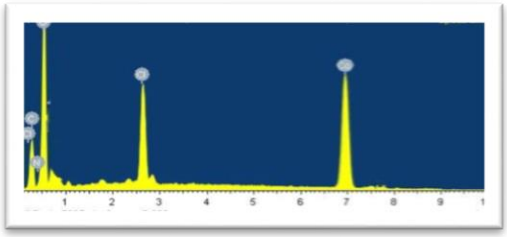
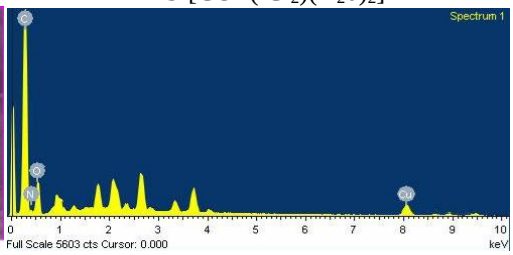


Figure No.- 6a- [COL(Cl_2)(H_20)$_2$]



EDS-[COL(Cl_2)(H_20)$_2$]

Figure No.- 6a- CuL($COOCH_{3)2}$(H_2O)$_2$]



EDS-[CuL($COOCH_{3)2}$(H_2O)$_2$]

TEM imaging is a transmission electron microscope which produced high resolute images. By using this images researcher are able to find out geometry of particles as well as particle size. In the present work TEM images of complexes are provided very useful information for our study. Images are predicted in **Fig-No-7. In 7a**-the [COL(Cl_2)(H_20)$_2$] images are shown the crystal of this complexes are rod likes which are completely crystalline in nature having a particle size from5nm to100nm for a single road like crystals[19]. The second complex is amorphous in nature some images also shows the porous nature of the complex. The particle size of second compound is found 30nm-50nm.The **Fig-7b** shows images of complex.

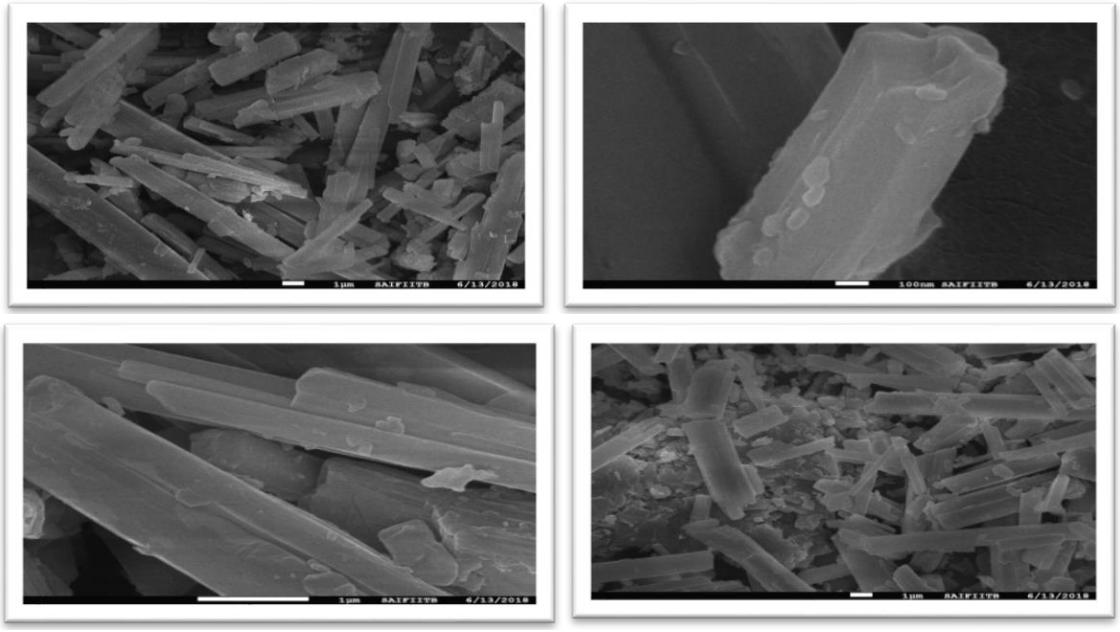


Fig-No-7. In 7a- [COL(Cl_2)(H_20)$_2$]

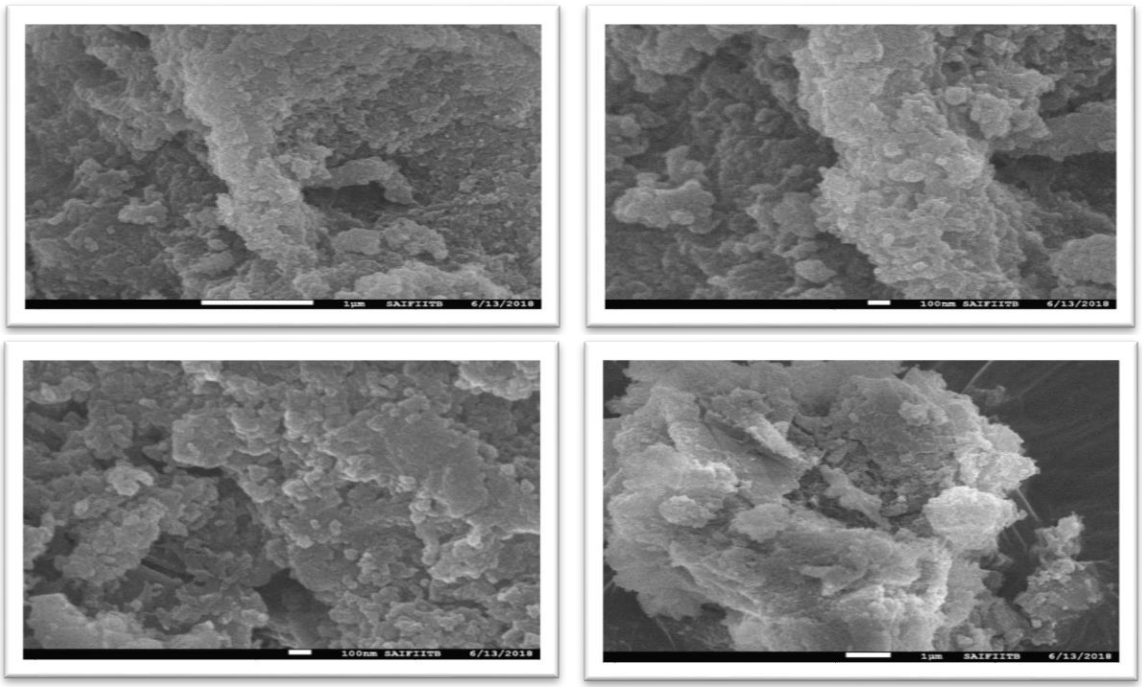


Fig-No-7. In 7b [COL(Cl_2)(H_20)$_2$] complex.

3.5-X-ray-diffraction analysis-

Figure 8a and 8b shows the XRD pattern of cobalt and copper metal complexes. The crystalline peak appear in cobalt complex in between the 2θ equal to 2-60 ^{0}C .these peaks in fig-8a shows that purely crystalline nature of compound the crystalline size is calculated by using Debye-Scherrer equation $D = 0.9\ \lambda/B_{1/2} \cos\theta$[10].Where $\lambda = 0.15406$ nm is the wavelength of X-ray. Θ is the maximum peak angle in degrees and $B_{1/2\ \text{is the}}$ FWHM of the peak. The particle size of the above synthesized compounds are in the range of 1 to 25 nm size.The In 8b fig. the compound possess the amorphous nature of the compound [18-19].

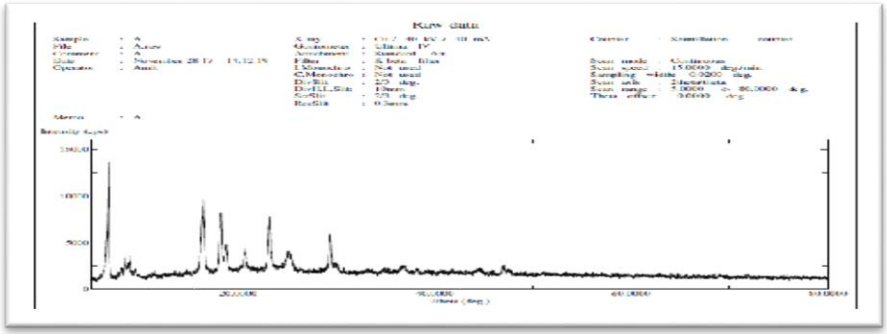


Fig-8a-[COL(Cl_2)(H_20)$_2$]

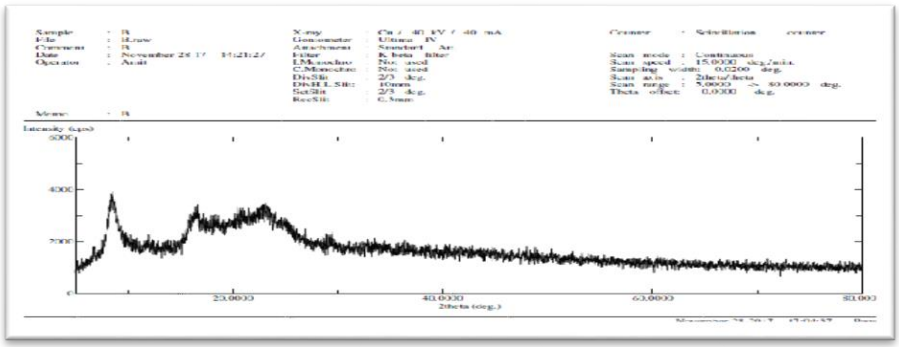


Fig-8c-[COL(Cl_2)(H_20)$_2$] complex.

3.6.Antimicrobial activity-

The synthsised compounds shows antimicrobial activity against *E.Coli*,*Pseudomonas aeruginosa*,*Staphylococcus aureus* and Nystain ,for antifungal *Candida sp* were used..DMSO had no effect on the microorganism in the concentrations studied 2mg/1ml solution in DMSO of Schiff base and metal complexes.

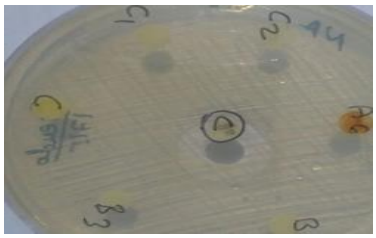


Fig-9.

CONCLUSION:

In the present research work the synthesis of SB and Metal complexes are done by ultrasound method. It is one of the best method to synthesize the compounds it's time saving and also energy saving method.

The particle size of the synthesized compound is measured in between the 5 to 50 nm which is investigated by using XRD analysis. Nowadays nanoparticles are play an important role in electroplating, nanotubes and nanowires and also in chemosensor.

The strong antimicrobial activity of the compound is shows that the synthesized SB and Metal complexes will be very useful for pharmaceutical industries.

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