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Research Article

Synthesis, Characterization and Antibacterial Activity of Mixed Cobalt-Transition Metals Compounds.

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ABSTRACT

Solid mixed metal complexes were synthesized by conventional method using bidentated tartrate ligand. When ligand treated with corresponding transition metal salts in a molar proportion it forms metallic complexes in the ratio of $[M_1M_2(T)_3]$ xH_2O, Where M_1 = Cu(II), Zn(II) or Cd(II), M_2 = Co(II), x = no. of H_2O molecules and the ligand T= Tartrate. These metal complexes were characterized by elemental analysis, X-ray diffraction, AAS, IR spectroscopy as well as by TGA. On the basis of these studies, it is proposed that tartrate ion act as a bidentate ligand and co-ordinate to metal through donor oxygen of COO^- group. The ligand as well as metal complexes has been screened for their antimicrobial activity using bacterial strains *Escheriachia Coli, Bacillus Subtillis, Staphylococcus Aureus* etc. and results are discussed.

KEYWORD

Bidentate, tartrate, antimicrobial, bacterial strains etc.

1. INTRODUCTION

Many applications of metal complexes are already well-known for their variety of applications such as, water treatment, electroplating, conduction, dying and other applications [1, 2]. Furthermore, the discovery of many active inorganic compounds has generated a great interest in coordination complexes for their biological activity [1-12].

An increasing resistance of harmful bacteria towards existing drug compounds generates a great necessity to search for new highly active compounds which can kill or inhibit growth of these mutated bacteria [7, 8, 9]. Therefore several researchers focus on to develop new biologically active agents using various metal ions and the ligands [1, 10, 12, 14]. These metal complexes have been tested for their anti-bacterial, antifungal, anticancer, antiviral, anti-inflammatory etc. actions by many authors worldwide [3-18].

In search of such active compounds we extended our work to synthesize and characterize three novel mixed metal complexes and studied their antibacterial activity against some bacterial strains.

2. MATERIALS AND METHODS

All the chemicals used, that is $CoSO_4\,7H_2O$, $CuSO_4\,5H_2O$, $ZnSO_4\,7H_2O$, $CdSO_4$ and $C_4H_8Na_2O_8$ are analytical grade and obtained from Merck, India. The chemicals and solvents were used as received without further purification.

2.1. Preparation of mixed metal-cobalt tartrate complexes

All the complexes were prepared by simple co-precipitation method using water as a solvent medium. The transition metal salts of $CuSO_4\,5H_2O$ is mixed with $CoSO_4\,7H_2O$ salt in equimolar proportion and dissolved in a minimum amount of water. pH of the solution were kept to slight acidic condition. In this solution 10% sodium tartrate solution were added slowly with constant stirring till complete precipitation and the temperature were monitored between 60-70^{o}C. Then equal volume of acetone was added in the reaction mixture and stirring was continued till next 30 minutes. The resultant complex precipitate were filtered, washed with acetone and dried under IR. This complex was preserved in desiccator for further analysis. Similar procedure was repeated with Zn and Cd metal salts to obtain Zn-Co and Cd-Co mixed metal tartrate complexes.

The IR spectra of resultant metal complexes were recorded in the range of 4000 to 400 cm^{-1} at Shimadzu spectrophotometer. The powdered XRD were performed on Bruker D8 advance XRD instrument at wavelength 1.5405A^{o}. The micro analytical technique was used to determine the carbon and hydrogen content. The thermo analytical measurements were obtained with Perkin-Elmer (Delta series-TGA7) instrument.

3. RESULTS AND DISCUSSION

All the synthesized mixed metal complexes show good agreement in calculated and observed values of carbon and hydrogen content. The metals concentration in each complex was checked by atomic absorption spectrophotometer and also shows agreement with calculated values as per molar ratio. The elemental analysis results of synthesized complexes were presented in Table 1.

Based on these results a general molecular formula of synthesized complexes were predicted as $MCo(C_4H_4O_6)_3.xH_2O$, where M = Cu, Zn or Cd and x is number of water molecules in each complex.

Table 1. Elemental Analysis.

Complex	Formula weight (gm)	C		H		Co		Metal	
		Cal	Obs	Cal	Obs	Cal	Obs	Cal	Obs
$CuCo(C_4H_4O_6)_3H_2O$	584.5	24.59	24.77	2.40	1.93	10.08	11.40	10.87	10.54
$ZnCo(C_4H_4O_6)_34H_2O$	640.3	22.49	23.32	3.12	3.27	9.20	10.17	10.21	10.09
$CdCo(C_4H_4O_6)_33H_2O$	669.3	21.52	20.89	2.69	2.03	8.80	8.73	16.80	17.59

3.1. IR spectral study

IR analysis of metal complexes was performed on Shimadzu spectrophotometer and the graphs are indicated in the figure 1. Also the observed IR frequencies for main signals and their respective assessments of vibrational modes are summarized in table 2. It was observed that the strong intensity band of ligand tartrate from frequency 1750 cm^{-1} shifted to the lower values at ν_{asy} (OCO) 1612 cm^{-1}, 1620 $cm^{-1}$and 1593 cm^{-1} While forν_{sy}(OCO) at 1430 cm^{-1}, 1450 cm^{-1} and 1440 cm^{-1} in the above respective metal complexes. This shift in the frequencies indicate that the tartrate ligand coordinate to metal ion through carboxylate functional group. The frequency band present at 511-525 cm^{-1} specifies to presence of M-O linkage. Also a broad and strong signal of -OH vibration frequency was observed in each metal complex in the range of 3410- 3551 cm^{-1} which shows presence of water as well as secondary alcohol groups hence the complexes are hydrous in nature. From the IR spectral assessment it was confirmed that the ligand tartrate form coordinate bond to metal ions by bidentate linkage through the oxygen donor atoms.

Table 2. IR Spectral Data for the mixed metal complexes.

Sr. No.	Cu-Co	Zn-Co	Cd-Co	Assignment
1	3410	3350.46	3462.34	Vsym -OH
2	1612.54	1620.26	1593.25	Vasy (OCO)
3	1430	1450	1440.87	Vsy (C=O)V(C-C)
4	1383.01	1363.72	1383.01	Vsy C-O (Carboxyl)
5	1317.43	1309.71	1288.49	Vsy C-C
6	1238.34	1228.70	1236.41	Vasy C-O

7	1105.25	1118.75	1114.89	V C-O (alcohol)
8	1047.38	1051.24	1049.31	V C-O (alcohol)
9	929.72	929.72	931.65	Vsy (C-O), δ(O-C=O)
10	831.35	827.49	800.49	Vsy C-H
11	725.26	704.04	715.61	Vsy C-C
12	636.53	632.67	626.89	V -O-H
13	525	551.66	538.16	V (M-O), V(C-C)

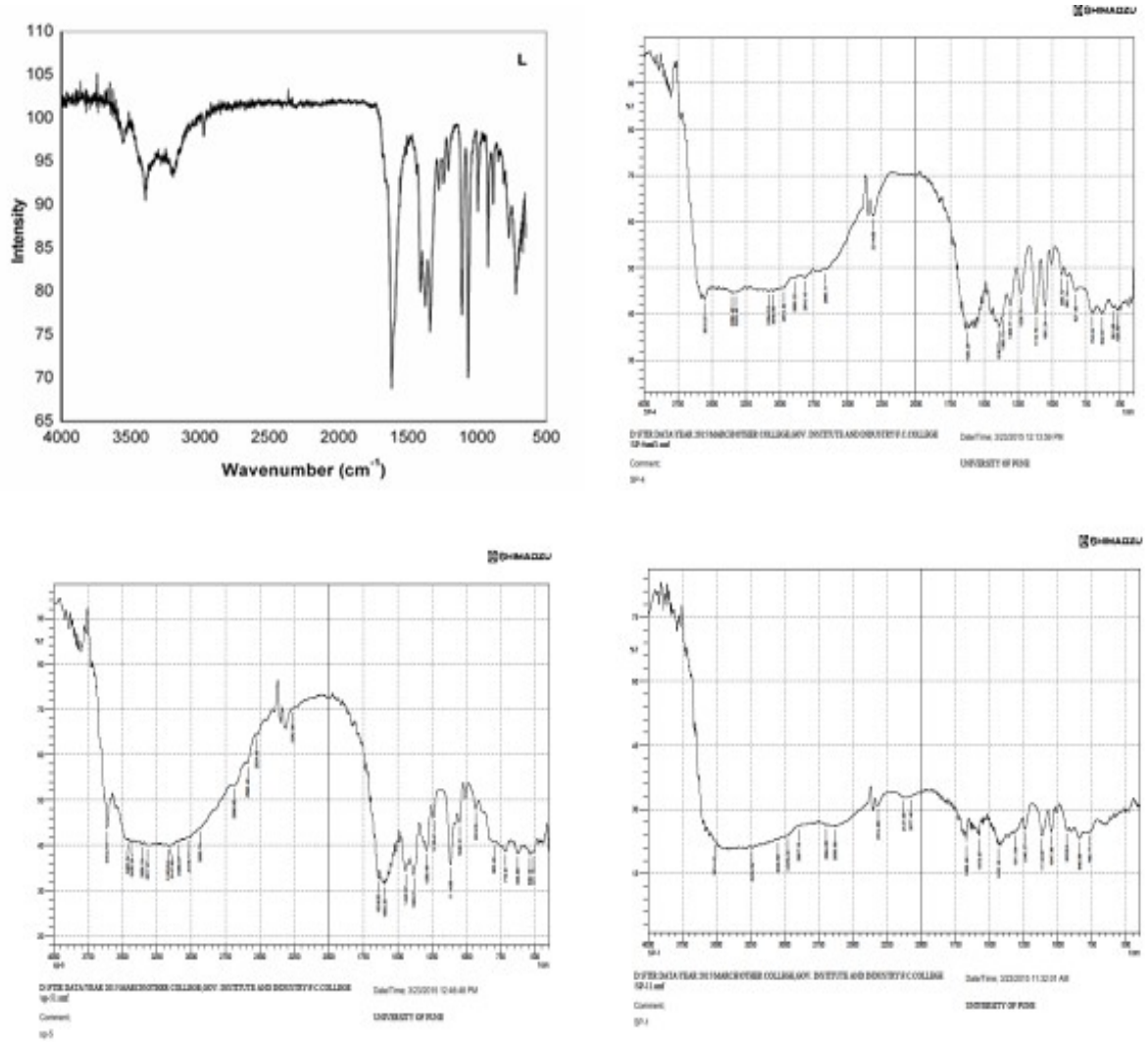

Fig. 1. Infra-Red spectra of a) $CuCo(C_4H_4O_6)_3H_2O$, b) $ZnCo(C_4H_4O_6)_34H_2O$ and c) $CdCo(C_4H_4O_6)_33H_2O$ complexes.

3.2. XRD Study

The X-Ray powder diffraction measurement for the complexes was performed on Bruker D8 advance XRD instrument which are shown in figure 2. The calculated values particle size of compounds using relation D=0.89λ/βCosϴ are summarized in table 3a. Also the observed'd'

spacing values are summarized in table 3b. The nature of the XRD spectra which contains both sharp as well as broad peaks indicates polycrystalline nature of the samples.

Table 3a. Observed Particle Size: (D=0.89λ/βCosθ).

Cu-Co Complex	Zn-Co Complex	Cd-Co Complex
634.85A^o	552.93A^o	571.37A^o

Table 3b. Observed D spacing values (A^o) for the mixed metal complexes.

Cu-Co Complex	Zn-Co Complex	Cd-Co Complex
4.090813	4.166036	4.170547
3.733883	3.863089	3.735694
3.541609	3.746595	3.633491
3.173877	3.477652	3.531866
3.243368	3.320259	3.463579
3.055534	3.218972	3.388913
2.893689	3.126218	3.221665
2.687718	3.00429	3.175185
2.640727	2.85402	3.047073
2.38483	2.719986	2.885019
2.336366	2.5823	2.738358
2.291196	2.458666	2.680237
2.226301	2.396702	2.636208
2.047037	2.293925	2.52144
1.951609	2.256959	2.476849
1.87878	2.168637	2.391493
1.830996	2.077961	2.330006
1.761088	1.983775	2.285757
1.691852	1.909046	2.221806
1.660487	1.785996	2.122039
1.551148	1.688144	2.043236
1.516637	1.61624	1.946677
1.413135	1.554591	1.872842
1.349746		1.821471
		1.75467

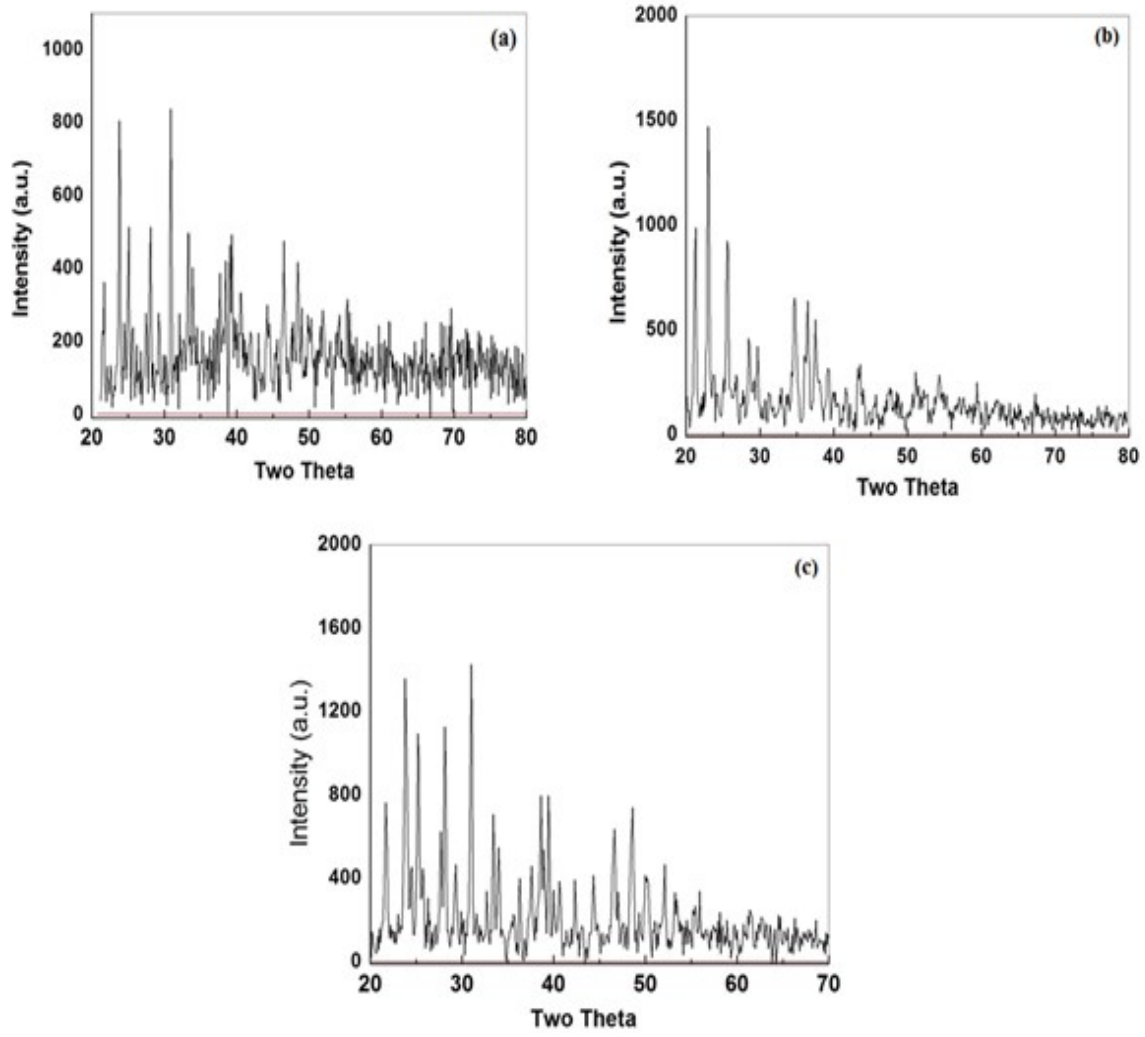

Fig. 2. X-Ray diffraction spectra of a) $CuCo(C_4H_4O_6)_3H_2O$, b) $ZnCo(C_4H_4O_6)_34H_2O$ and c) $CdCo(C_4H_4O_6)_33H_2O$ complexes.

3.3. Thermal Analysis

The thermogravimetric analysis was performed using Perkin-Elmer (Delta series-TGA7) instrument under static air atmosphere with heating rate 10deg min^{-1} upto 600^{o}C. The sample quantity used for analysis was in the range of 30-50 mg. the resultant TGA graph were given in figure 3 and the respective mass loss values are summarized in table 4. Continuous mass decrease in the range of 55-175^{o}C represented loss of water molecules. In each complex have different number of water of crystallization which is very well matches with theoretical values. At the temperature 280-460^{o}C, oxidative decomposition of metal complexes takes place forming a decomposition products $CuCoO_4$, $ZnCoO_4$ and $CdCoO_4$ respectively. Further heating shows a constant weight of these stable metal oxides.

Table 4. TGA data for the mixed metal complexes.

Complex	% Mass loss		Temp Range ^{O}C
	Observed	Calculated	
	3.47	3.07	55-150
$CuCo(C_4H_4O_6)_3H_2O$	67.79	67.08	200-500
	11.32	11.24	60-170
$ZnCo(C_4H_4O_6)_34H_2O$	66.30	66.86	210-500
	8.36	8.07	60-175
$CdCo(C_4H_4O_6)_33H_2O$	61.12	61.75	200-550

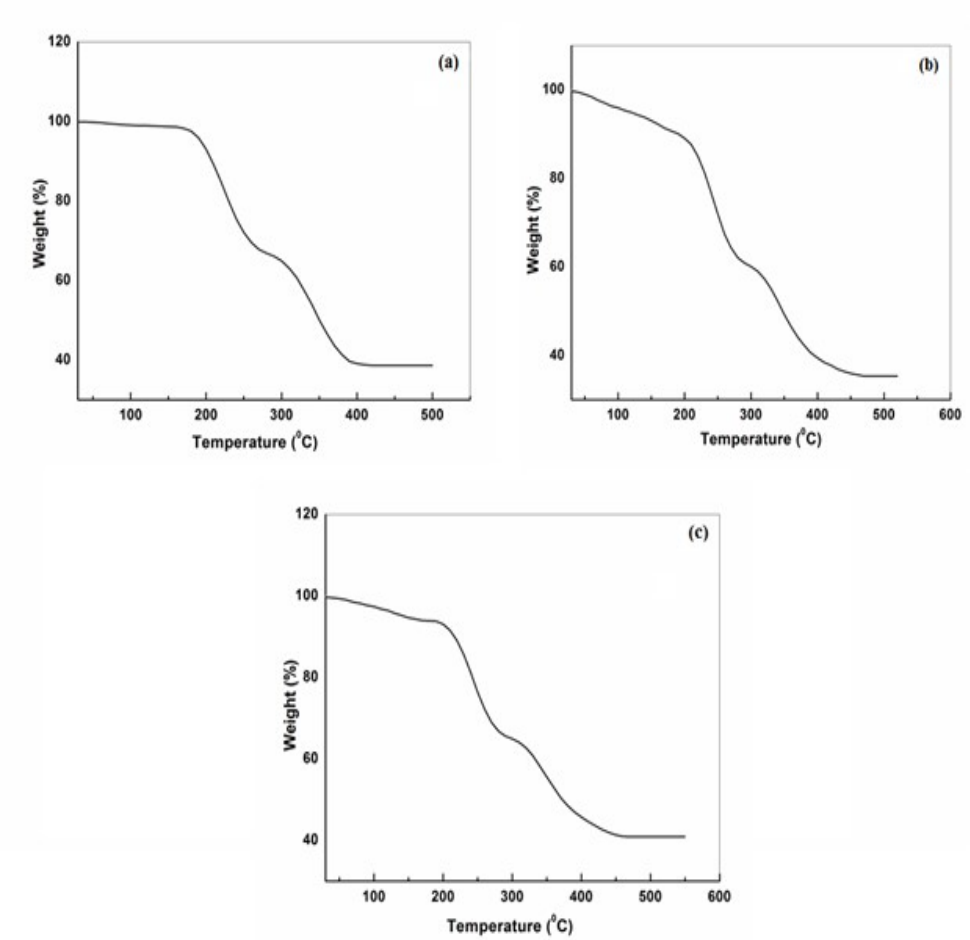

Fig. 3. Thermo gravimetric analysis graphs of a) $CuCo(C_4H_4O_6)_3H_2O$, b) $ZnCo(C_4H_4O_6)_34H_2O$ and c) $CdCo(C_4H_4O_6)_33H_2O$ complexes.

3.4. In vitro screening of antimicrobial activity

All the synthesized complexes as well as ligand were screened for their antimicrobial activity against *Escheriachia Coli* (Gram-negative*), Bacillus Subtillis* (Gram-positive)and *Staphylococcus Aureus* (Gram-positive) bacterial strain. To carry this process well diffusion

method is used in which first microbial strains were inoculated on agar medium in plates. Complexes and ligand solution with concentration 1mg/ml were prepared. Well was prepared on each inoculated plate and filled with test solution. The plates were then incubated at 37°C for next 24 hrs. and zone of inhibition were measured for each compound. Simultaneously analysis of control solvent as well as reference drug ampicillin was carried out similarly. Figure 4 shows and plates with growth inhibition and table 5 represent the zone of inhibition measured in mm.

The results obtained shown that all the complexes and ligand exhibit moderate antimicrobial activity. The reference drug used for study show better activity and the control solvent used for dilutions show zero activity against all bacterial strains. Complex $ZnCo(C_4H_4O_6)_3 4H_2O$ exhibit better activity than other compound with *Escheriachia Coli, Bacillus Subtillis* and *Staphylococcus Aureus* but less than the reference drug ampicillin. The inhibition power of each complex can give as $ZnCo_2(C_4H_4O_6)_3 4H_2O$ > $CuCo_2(C_4H_4O_6)_3 0.5H_2O$ > $CdCo_2(C_4H_4O_6)_3 2.5H_2O$. Free ligand shows less activity compare to all the synthesized complexes. The enhanced activity of the complexes may be due to metal chelate ring formation which imparts lipophilicity of compounds.

Table 5. Zone of Inhibition in mm.

Compound	***Escheriachia Coli***	***Bacillus Subtillis***	***Staphylococcus Aureus***
Cu-Co Complex	19	16	12
Zn-Co Complex	20	24	21
Cd-Co Complex	13	15	11
Ligand (L)	12	07	09
Reference (A)	36	30	28
Solvent (C)	00	00	00

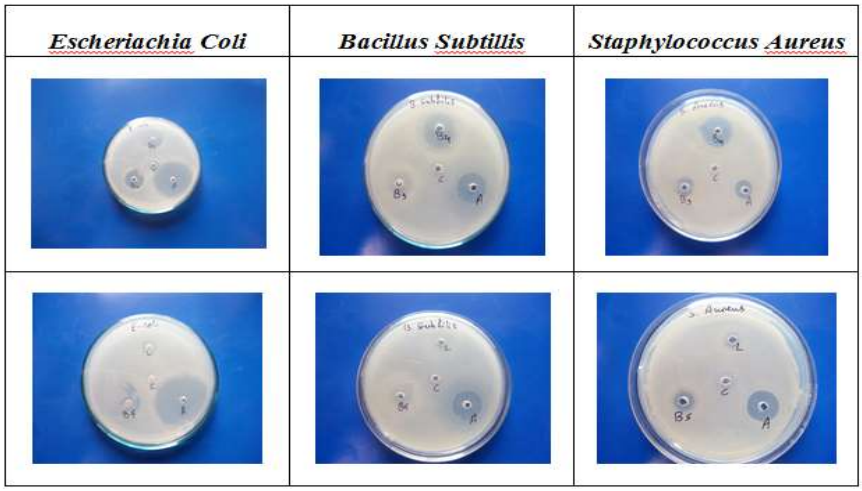

Fig. 4. Antimicrobial activity of Mixed Metal Complexes.

4. CONCLUSION

Three novel mixed metal complexes using Cu(II), Zn(II) and Cd(II) metal ions along with Co(II) were synthesized successfully by co-precipitation method. The observed metal content as well as C, H data is very well match with the calculated one. Form the IR spectroscopic data propose that the coordination of tartrate ligand with metal ions are through bidentated linkage of two oxygen donor sites and form a stable metal chelate complex with the polymeric network. The IR data also suggest presence of hydrous nature of the complexes (broad peak at 3410-3551 cm^{-1}) which was later confirmed by thermal analysis. The XRD analysis of these complexes suggests polycrystalline nature of the compounds. Thermal analysis confirms the presence of water molecules in the crystal structure. Also it proposes oxidative decomposition of metal complexes at higher temperature to give stable metal oxides. From the above analysis data the molecular composition of the complexes proposed as $CuCo(C_4H_4O_6)_3H_2O$, $ZnCo(C_4H_4O_6)_34H_2O$ and $CdCo(C_4H_4O_6)_33H_2O$ respectively.The complexes possesses good antibacterial spectrum against gram positive as well as gram negative bacteria. All the mixed metal complexes shows enhanced biological activity than the ligand. Between all synthesized complexes $ZnCo(C_4H_4O_6)_34H_2O$ shows increased inhibition activity against all tested bacterial strains.

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