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SPECTRAL, ANTIBACTERIAL AND ANTIFUNGAL ACTIVITIES OF CO (II), CD (II) AND HG (II) COMPLEXES WITH SODIUM BENZOATE ION

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Abstract

The antibacterial and antifungal activities of Co (II), Cd (II) and Hg (II) complexes with sodium benzoate ion have been complexed and applied to biological activity. The compound were characterized by Estimation of Metal ion, Electronic Spectra, IR-Spectra like FTIR studies and UV-visible transmittance studies andBiological Activities

Keywords:**sodium benzoate ion ; Estimation; FTIR; UVBiological Activities.**

INTRODUCTION

1.1. Nicotinic acid as ligands[11-12]

Although nicotinic acid present in food. The majority of Niacin is produced synthetically by chemical oxidation.

The synthesis and characterization of nicotinic acid ligand containing nitrogen donor site has extended great interest in recent times. Pyridine derivatives are associated with important biological activities such as fungicidal, antitumor and anti-bacterial etc., nicotinic acid is found to be pharmacologically and physiologically active.

Preparation and structural elucidation of a few nicotinic acid complex by spectroscopic methods were deduced.While Niacin is pharmacologically and physiologically active e.g. it is a major compound of important co-enzyme used in DNA repair and cell signaling as confirmed by various research studies.

Chemical Name	Pyridine 3-carboxylic acid
Molecular Weight	123.118
Molecular formula	$C_6H_5NO_2$

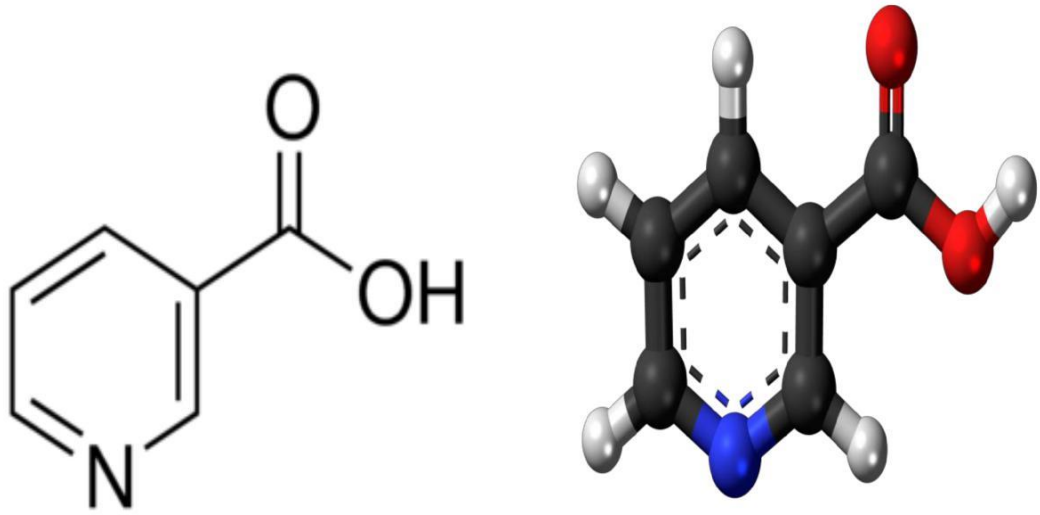

Figure -1 Structure of Niacin

1.2.BENZOATE ION AS LIGANDS [13-15]

Properties

Molecular formula	C_7H_5ONa
Molecular Weight	144.11g
Melting point	300^0C
pH	7.5 (log / liter)
solubility	Soluble in water

Sodium benzoate is produced by the neutralization of benzoic acid with sodium hydroxide. Worldwide Sodium benzoate production in 1997 can be estimated at about 55000-60000 tones. The largest producers the Nederland's, Estonia, the USA and China.

Uses

i. Sodium benzoate is also used in pharmaceuticals for preservation purposes and for therapeutic regimens in the treatment of patients with urea cycle enzymopathies.

ii. A major market for Sodium benzoate is as a preservative in the soft drink industry, as a result of the demand for high-fructose corn syrup in carbonated beverages.

iii. Benzoic acid and Sodium benzoate are use as antimicrobial agent in edible coatings.

iv. A new use is the formulation of sodium benzoate in to plastic such as polypropylene, to improve strength and clarity

v. Sodium benzoate is used as a stabilizer in photographic baths/processing.

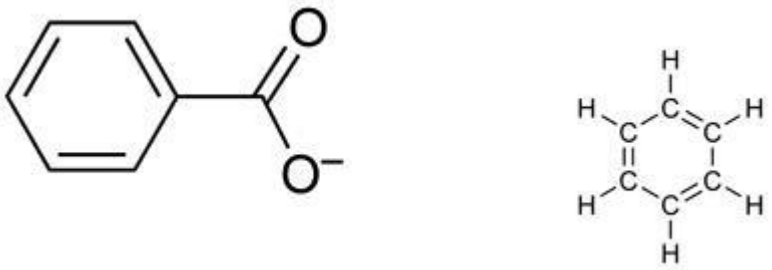

Figure-2 Structure of Benzoate

1.3. Application of Coordination Compounds[16-18]

Metal Complexes in Analytical Chemistry

Inorganic Qualitive Analysis: Several principles of coordinationchemistry are used in inorganic qualitative analysis. The formation ofmetal complexes is employed in the separation and identification ofsome of the metals.

Identification of metals: Complex formation is used to identify several metal in qualitative analysis.The bright colours of the metal complexes render die process of identifying some metals easy and unequivocal in some cases.The colouredcompixes are insoluble in water,in some other cases.they dissolve in water and produce coloured solutions.

Complexometric Titrations: Certain metal ions react stoichiometrically(quantitatively) with certain ligand solutions and form stable metal complexes.

Complexes in Colourimetry: Some of die metals can be colourimetrically estimated by forming their colouredcomplexespeciesin soloution.For adopting this method,the following conditions have to be satisfied:

i. The metal ion should form a water-soluble coloured complex.
ii. The complex species should have sufficient stability to impart a stable colour shade during the estimation.
iii. The complex in solution should the Beer-Lambert law over a sufficient range of its concentration.especially for visual colourimetry.

1.4. Biological Activities[19-23]

Antibacterial and Antifungal Activities

Determination of MIC of the complexes

The Prepared complexes are subjected to microbiological testing by using standard strains of Bacillus subtilis, Staphylococcus aureus, Escherichia coli Pseudomonas aeruginonosa and Proteus vulgaris. Their activities are compared with the parent compounds. The efficacy is determine by the MIC values.

Procedure

- The sample (O.1g) is dissolved in the trypic soy broth (10cm1) in a test tube and then shaken vigorously with the help of gyro mixer in front of a laminar flow cabinet (Preparation of A).
- From preparation A, 1 cm3of the mixture is transformer into 9 cm3trypic soy broth(TSB) test tube in triplicate and thoroughly in front of a laminar flow cabinet (preparation of B).
- The above procedure is repeated for serial dilution to obtain the preparation.
- The drug dilution prepared are as follows: All drug concentrations obtained by the serial dilution method are inoculated with pre-incubated culture. All drug dilutions are inoculated with 1 full loop of the appropriate.

- At the same positive and negative control are also run. The positive and negative controls are free from drug. Only the positive control test tube is inoculated with 1 full loop of the

Broth culture

After inoculation the dilution are incubated at 37° C for 24 hours. Positive and negative controls are also incubated at 37° C for 24 hours. simultaneously.

broth culture After incubation the turbidity (growth) is checked in the test tubes and in the control tubes.

The last tube in serial dilution which showed no turbidity is taken as the MIC of die compound.

- The test tube showing no turbidity and the tubes showing turbidity bactericidal concentration or bacteriostatic concentration. In that case with the help of a loop each tryptic soy broth tube is cultured on preincubatedtryptic soy agar (7100) plates then these plates are incubated at 37°C for 24 hours.
- The plates showing growth represented the bacteriostatic concentration and the plates showing no growth represented the bactericidal concentrations.
- The determination is repeated in order to obtain die exact MIC of a compound.

Test Organisms[24-29]

The microorganisms used as lest organisms are bacteria isolated from clinical sample. Two Gram positive bacteria and three Gram negative bacteria are used test organisms.

A) Gram positive Bacteria

i. Bacillus Subtle
ii. Staphylococcus aureus

B) Gram negative Bacteria

i. Escherichia coli

Materials and methods

Preparation of Co (II). Cd (II), Hg (II) complex using nicotinic acid and sodium benzoate ion

In a Clean beaker 1g metal nitrate or chloride was taken and dissolved in 10ml of methanol to this required mole ration of nicotinic acid in 10ml ethanol was added and mixed well and heated aboul 30 mins on a water bath to this required mole ratios of sodium benzoate in 10ml ethanol was added and the whole mixture was heated on a water bath for about 45 minutes the resulting precipitate was filtered washed with ethanol and dried.

The following reagents and solvents were used for the preparation and characterization of the metal complexes. All the reagents and solvents were used as such without further Purification.

- Nicotinic acid (Alfa Aesar Company)
- Cadmium Nitrate (AnalaR Grade)
- Di Sodium Oxalate (AnalaR Grade)
- Methanol and ethanol (AnalaR Grade)

Characterization

Estimation of Metal ion: In general the metal ions in the complexes prepared were estimated by standard volumetric or colorimetric or gravimetric analysis, after decomposing a known weight of each complex dilHcl or dil $HN0_3$.

Estimation of metal ions in complexes

S.No	Metal Ion	Method	Reagent
1	Cadmium	Volumetric	EDTA
2	Cobalt	Volumetric	EDTA
3	Mercury	Gravimetric	Hgs (precipitate)

Molar Conductance

The molar conductance measurements were recorded by using 10-3m solution of each complex in acetonitrile with Systronic Conductivity Bridge 304at30°C.

Electronic Spectra

The UV- Visible spectra of all the complexes were recorded by using varion make. CARY 5000 model UV-vis-NIR Spectrophotometer between 200 to 800nm.The wavelength accuracy and the limiting resolution of the instruments was ± 0.1 nm and 0.05nm respectively.

IR-Spectra

The IR Spectra of Nicotinic acid and its complexes where recorded on Schimadzu. FTIR 8400 spectrometer in 4000-400cm-1 range using KBr pellet technique.

Biological Activities

Biological Activities

Antibacterial and Antifungal Activities

The antibacterial and antifungal activities of Nicotinic acid and its metal complexes were determined by Kirby - Bauer disc diffusion method. The following procedure was used.An antimicrobial disc was purchased from the suppliers They were packed inspring leaded cartridges containing 25 to 50 disc each.

- Preparation of Muller -Hinton Plate: M-H Plates were Placed at room temperature. The surface of the Plate containing visible liquid and excess of liquid was evaporated. The plates were placed in an incubator at 35°C
- The antimicrobial disc were placed into M-H Plates. Then the Plates were incubator at 35°C
- . The test solution were prepared in DMSO and the proper Standard for each micro and tungus were chosen. Then the test solution were poured into the disc.

- The MIC(Minimum Inhibitory Concentration) values of the zone were measured in milli meter. The microbes E.coli and staphylococcus were tested by using this method. The antibacterial and antifungal activities of the ligand and all the prepared complexes were measured by the above method with amikacin and Ketoconazole as the standards for the bacteria and fungus respectively.
- The MIC(Minimum Inhibitory Concentration) values of the zone were measured in milli meter. The microbes E.coli and staphylococcus were tested by using this method. The antibacterial and antifungal activities of the ligand and all the prepared complexes were measured by the above method with amikacin and Ketoconazole as the standards for the bacteria and fungus respectively.

RESULTS AND DISCUSSION

Metal Estimation

The Co (II) & Cd (II) were estimated by volumemcallywhere as Hg (II) estimated by gravimetrically From the results of metal estimation it is observed that the percentage of metal ion in each complex are in perlect agreement with its formula derived.

Molar Conductance

The molar conductance measurement of all the complexes in water indicates that the complexes are virtually non- electrolytes. There is no anion or calionout side the coordination sphere.

UV- Visible Spectrum of Co(II) Complex

The Co(II) complex exhibited three bands at 530 nm (v_2); 320nm (v_2) and 250 nm (v_3) which are assigned to $^4T_{2g}(F) \leftarrow {}^4T_{1g}$, $^4A_{2g}(F) \leftarrow {}^4T_{1g}$ and $^4T_{1g}(F) \leftarrow {}^4T_{1g}$ transitions, respectively. These transitions suggest distorted octahedral geometry for the complex. The effective magnetic moment ( ) of the Co(II) complex is 3.50 BM which is characteristic for distorted octahedral geometry(Figure-8).

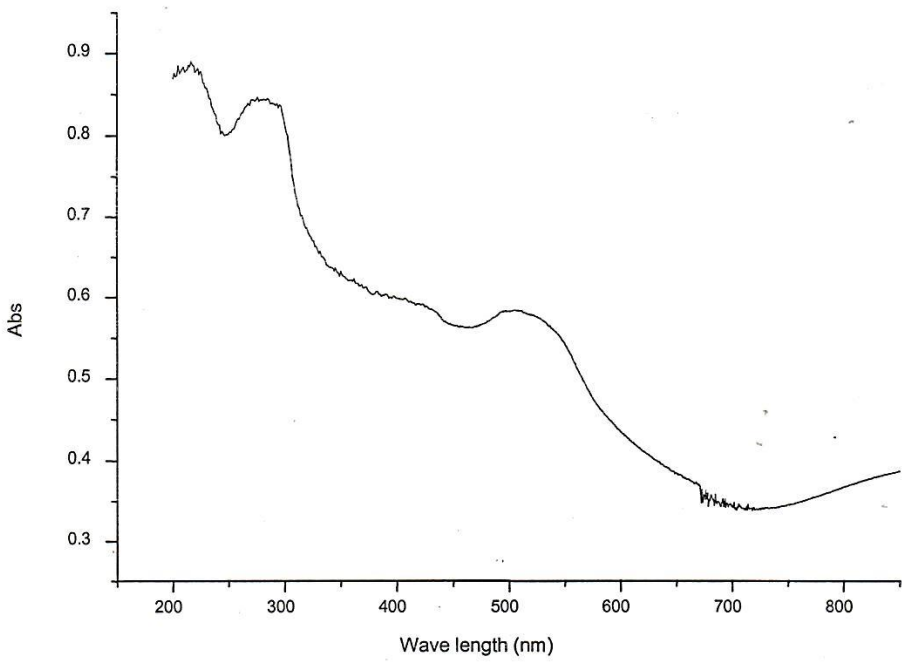

Figure-8

UV-visible spectrum of Co(II) complex

UV -Spectrum of Cd (II) Complex

The electronic configuration of diamagnetic Cd(II) complex is (dia) which confirms the absence of any (d-d) transition. AH the complexes gave only charge transfer transitioas at 269 nm corresponding to CT band confirming the pseudo tetrahedral(Figure-*9).*

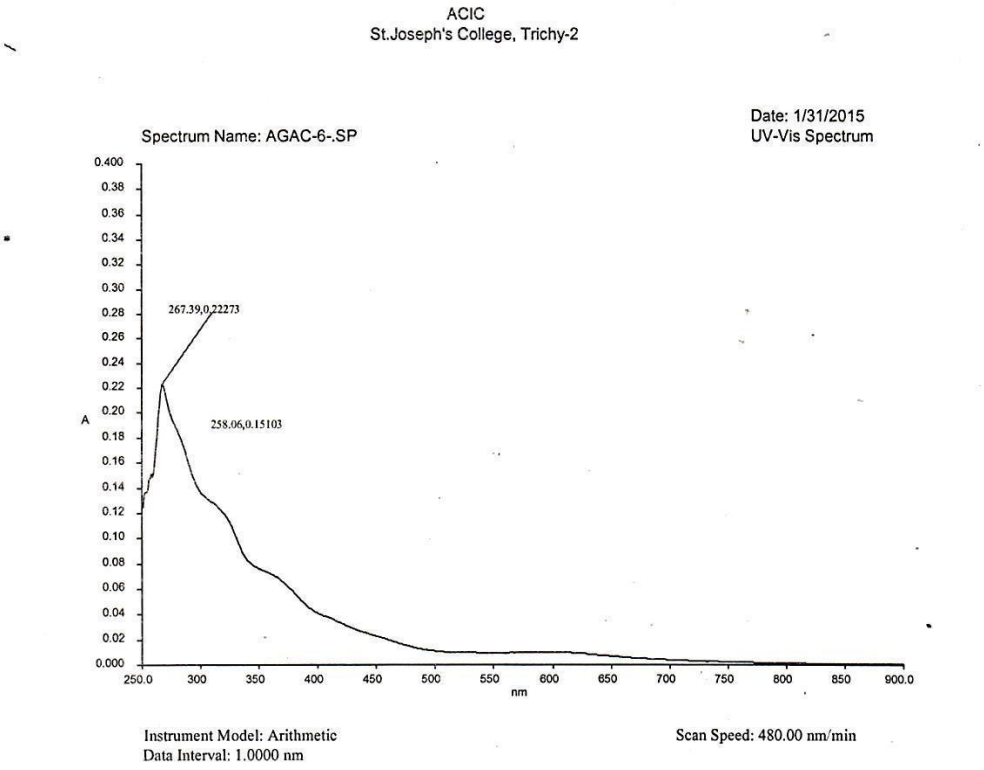

Figure-9

UV-spectrum of Cd(ll) complex

UV-Spectrum of Hg (II) Complex

The electronic configuration of diamagnetic Hg(II) complex is (d10) which confirms the absence of any (d-d) transition. All the complexes gave only charge transfer transitions at 260 nm corresponding to CT band confirming the pseudo tetrahedral(Figure-10).

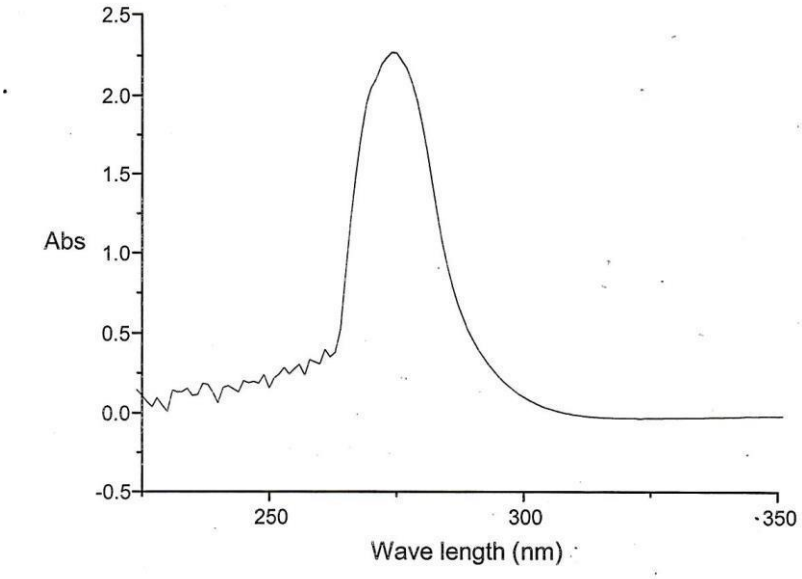

Figure-10 .UV-specrrum of Hg(II) complex

IR-Spectrum

Nicotinic acid, also known as niacin, and though the two are identical in their vitamin functions. Nicotinic acid does not have the same pharmacologic and toxic effects of niacin, which occur incidental to niacin's conversion.The IR spectra of the ligand with its octahedral complexes have been studied in order to characterize their structures. The IR spectra of the free ligand and its metal complexes were carried out in the 4000-400 cm^{-1} range. The IR spectra of all the metal complexes were interpreted by comparing the spectra with those of the free ligand. The relevant peaks alone are considered for discussion

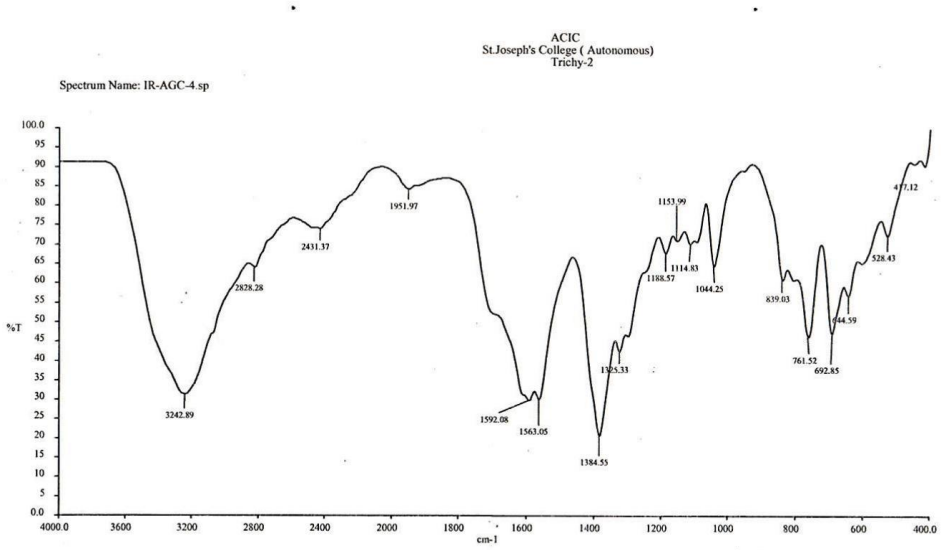

Figure-11

IR SPECTRAM OF Co(II) COMPLEX

The comparison of the band positions of various vibrations are ascertained with good evidence. The presence of v(COOH) asymmetric stretching vibration is confirmed by the hand at 1711 cm-1 and the symmetrical stretching vibration is observed at 1368 cm"1. In the infrared spectrum of metal complexes, the v C-N stretching vibrations were observed flt 1464-1626 cm-1 and were due to coordination of the nitrogen from C-N to the metal, stretching vibration for the nicotinic acid reduced at the complex.

The uncoordinated nicotinic acid showed a strong peak at 1368 cm-1, which is characteristic of the imine v(C-N) group. The aromatic C~C that is djrectly attached with the pyridine nitrogen also affected upon complexation and arc situated at a frequency significantly

different than the free ligands. Coordination of the nicotinic acid ligand to the metal centre through the nitrogen atom is expected toreduce the electron density in the methine link and hence lower the v(C=C) and v(C-N) frequencies.

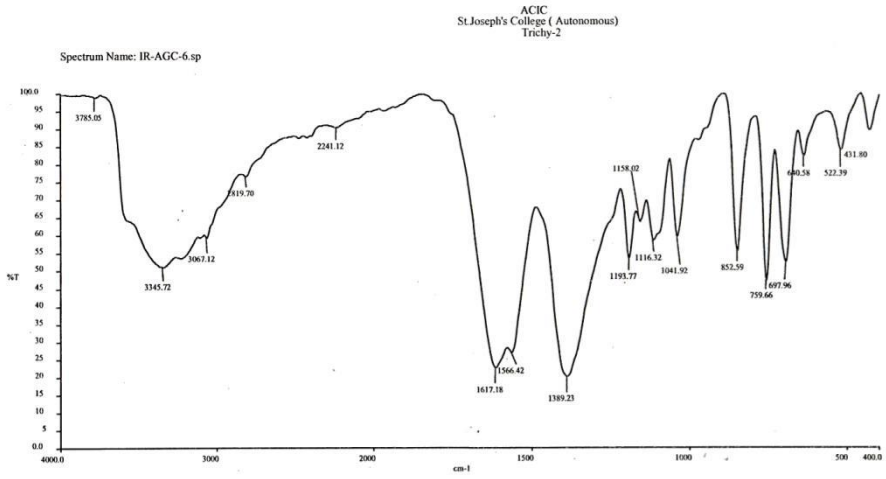

Figure-12

IR SPECTRAM OF Cd(II) COMPLEX

The peak due to v(C=C) is slightly shifted to lower frequencies and appears between 1314-1368 cm"1, indicating the coordination of the imine nitrogen to the metal. The peak at 1626cm-1lcorresponds to the asymmetric C=0 stretching confirms that all the complexes, the ligand do not coordinate with COOH oxygen. The free ligand showed a medium intensity band at 3267 cm"1 assigned to v(CH) vibrations, which has been observed in the 2778- 2939 cm"1 region in the case of the complexes. It can be observed that there is no considerable shift in the v(C-H) vibrations in the case of the complexes compared to the ligands indicating non-involvement of acid groupin the coordination. The low frequency skeletal vibrations due to M-N stretching provide

direct evidence of the complexation and bands are observed in the 479-417 cm-1 region.

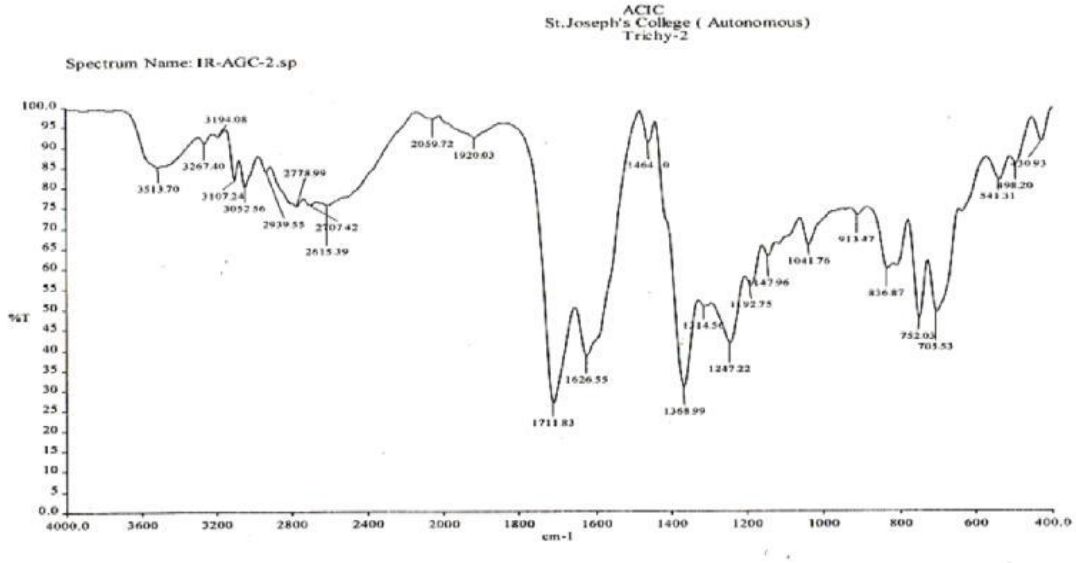

Figure-13

IR SPECTRAM OF Hg(II) COMPLEX

Pyridine ring vibrations of free nicotinic acid at 11464 cm ' shifts to higher frequencies in the spectrum of the metal complexes. The shifts in the spectrum of the complexes may indicate that the pyridine ring is coordinated. The bands due to the asymmetric and symmetric stretching of carboxylate in the metal complexes occur in the range of 1679-1663 cm"1. This shows that the coordination does not takes place through the carboxyl group. The low intensity bands in the region of 456-400 cm-' are attributed to M-N and M-0 Vibration.

BIOLOGICAL ACTIVITIES[74-75]

Antibacterial and Antifungal Activities

The antibacterial and antifungal activities of nicotinic acid metal complex were tested against P.aerugmosa, bacillus subtitles by the disc diffusion method. The test solution was prepared in the DMSO solvent. Amikacin and kctoconazole were used as standards for antibacterial and antifungal activities respectively. The results indicate that the complex are highly active against the tested organisms compared with the free ligand. The antibacterial and antifungal activities of the complexes were carried out by disc diffusion method and compared with the metal complexes. The data of the biological activities indicate the metal complexes have good activity compared to the free NA. This fact confirms from the tweedy chelation theory.

Hg complex are highly active against the tested organisms compared with the free ligand. The antibacterial and antifungal activities of the complexes were carried out by disc diffusion method and compared with the metal complexes. The data of the biological activities indicate the metal complexes have good activity compared to the free NA. This fact confirms from the tweedy chelation theory.

Figure-14

BIOLOGICAL ACTIVITIES SLIDE

SUMMARY AND CONCLUSION

- . The Introduction highlights the importance of ligands, metal ions and common synthetic techniques and general characterization of complexes.
- Next section deals with the objectives of present study.
- The literature survey in which the reports on the works done by other scientists (related to present work) are mentioned.
- Experimental methods used for the preparation of complexes using the above mentioned metal ions and ligands are detailed. The complexes were characterized by following methods.

1. Metal estimation
2. Electrical conductance measurement
3. Electronic spectral study
4. IR-Spectra
5. Biological activities

From metal estimation the molecular formulae of the complexes, were arrived. The molar conductance values of the complexes revealed that the non electrolytic nature.

- The probable geometries of the complexes are distorted octahedral for Co(II) and pseudo tetrahedral for Cd(II) & Hg(II) Complexes.

- IR spectral data of the complexes indicate that Nicotinic acid acts as monodentate ligand and coordinates with nitrogen atom of amine group. The entry of the anionic ligand oxalate into the coordination sphere of the metal was confirmed by comparing the IR spectral data of the prepared complex with the corresponding oxalate complexes reported earlier.

The antimicrobial activities of all the complexes were carried out against the bacterial strains such as E, coli and s. aureus by disc diffusion method. Cadmium complex were found to be more active than the NA. The nature of metal ions and the nature of ligands, the coordination modes and the geometry of the complexes play an important role in deciding the activity of metal complexes.

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