Synthesis and characterization of transition metal complexes derived from microbial active Iminodiacetic acid dihydrazone and dithiodiacetic acid Dihydrazone

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Abstract: *Currently, hydrazone complexes of M(II) were synthesized bearing the formula [ML $(H_2O)_2$](Where M=transition metal ions of 3d series and L= newly synthesized tetravalent ligands). The complexes were analyzed by preliminary lab techniques like repeatable melting point, TLC, recrystallization and molecular weight determination. Auxiliary, the complexes were screened for their Elemental analyses, Conductivity estimation, Metal estimation and Spectroscopic techniques like I.R. Spectra and UV-visible Spectra. As a result, the complexes were found to be stable, high decomposing coloured solids having high purity. The spectral results showed that the complexes are of octahedral structures in which Nitrogen and Oxygen are the donating electrons to central metal ion. In addition, the complexes were antimicrobial screened, E.coli Bacteria and S. alternaria which revealed that the complexes were thrice more active against both types of microbial species than the ligands.*

Key Words: *Antibacterial, Analytical studies, hydrazine.*

1. INTRODUCTION:

Hydrazones are the well known class of biologically active compounds in the field of bioinorganic chemistry. They posses wide range of pharmaceutical activities such like anti tubercular, antimalarial , anti HIV, anti-inflammatory ,anticonvulsant antimicrobial and other pharmacological acitviities[1-12]. In recent years, a large number of biologically active and stable hydrazide–hydrazone was synthesized from many different carbonyl entities. Iminodiacetic acid is a well known tridentet chelating ligand[1, 2]. IDA hydrazides perform comperatatevely better chelating properties as compare to other dicaroxylic acids. Iminodiacetic acid metal complexes have been synthesizes tested and reported[13]. EDTA is broadly used metal complex ants in the chemistry. IDA is the next one which is capable to form metal complexes with many transition metal ions synthesised cobalt and nickel complexes[4].

2. MATERIALS FOR SYNTHESIS:

Cobalt nitrate as a metal salt (Merk), 2,6 -diacetyl pyridine (Sigma-Aldrich) ,iminodiacetic acid (Sigma-Aldrich), hydrazine hydrate (Sisco-chem) , organic solvents methyl alcohol, ethyl alcohol, (DMS) were purified by standard procedures.

2.1 Synthesis of ester

A solution prepared by forerunner method[15]. 1.81 gm of IDA is dissolved in 20 ml of ethanol (99%). Then 0.85 cm3 (0.01M) Homogenous solute Of dimehylsulphide is mixed and the mixture was refluxed at 60 ºC for Twelve hrs. The solution is concentrated. On Cooling solution gets crystallizes. Crystal's filtered, washed by ethyl alcohol, and dried and dried in anhy. $CaCl_2$ desiccator. Pyridine 2, dicarboxyllic acid ester is formed.

2.2 Synthesis of acid dihydrazide

Forerunner method is adopted[15]. For preparing of acid dihydrazide 2.06gm (0.01M) of iminodiacetic acid ester was dissolved in 22 ml. of absolute alcohol and to this clear solution 0.83cm^3 (0.02M) of NH_2-NH_2.H_2O append gradually with constant stirring. The obtaining mixture get refluxed for five hrs. It was distilled and cooled overnight when crystals were obtained . It was filtered under suction then washed with anhy.$CaCl_2$.

2.3 Synthesis of complex-1

[M(II)L1]:M=Co (II), L= (4-Ethyl -2, 6-pyridinediacetyl -N N-imino diacetoyl dihydrazone):- Equimolar quantities of imino diacetic acid dihydrazide (1.80gm, 0.01M), cobalt chloride (2.48 gm , 0.01 M) and 4-ethyl -2, 6 pyridine dicarbonyl dichloride (1.90gm, 0.0IM) were mixed in 10 ml. ethyl alcohol with continuously stirring .The solution obtained and refluxed over a water bath for around eight hours. Subsequently, it was distilled to one third of its main volume. A little amount of sodium tetra fluoroborate was added then the solution was cooled overnight. When, bluish-green crystals separated out, these crystals were filtered then after washed with C_2H_5OH and dried in a vacuum over anhy. $CaC1_2$ in a desiccator.

Molecular formula: - Co $[C_7H_{10}O_2N_9Cl_2]$ $(BF_4)_2$, Melting point:- 268°C ,Yield:- 5.8gm

2.4 Synthesis of complex-2

The synthesized new hydrazone ligand 4,4-(dimethyl amino) benzaldehyde thiodipropionicaciddihydrazone [DMABTDPDH]and metal salt ($CoCl_2.6H_2O$) are taken in equimolar quantities (1:1) were added to 20 ml of methyl alcohol with continuous stirring. The resulting solution is refluxed over water bath around five hours. The solution thus obtained was refluxed over a water bath for around eight hours. Subsequently, it was concentrated to one third of its original volume. Then the solution was cooled overnight when, light - pink crystals separated out. These crystals were filtered, washed with ether and then dried in vacuum over anhydrous $CaC1_2$ in a desiccator.

Molecular formula: - [Co (II) $C_{24}H_{32}$ O_2 N_6], Melting point: - 280°C, Yield:- 61%

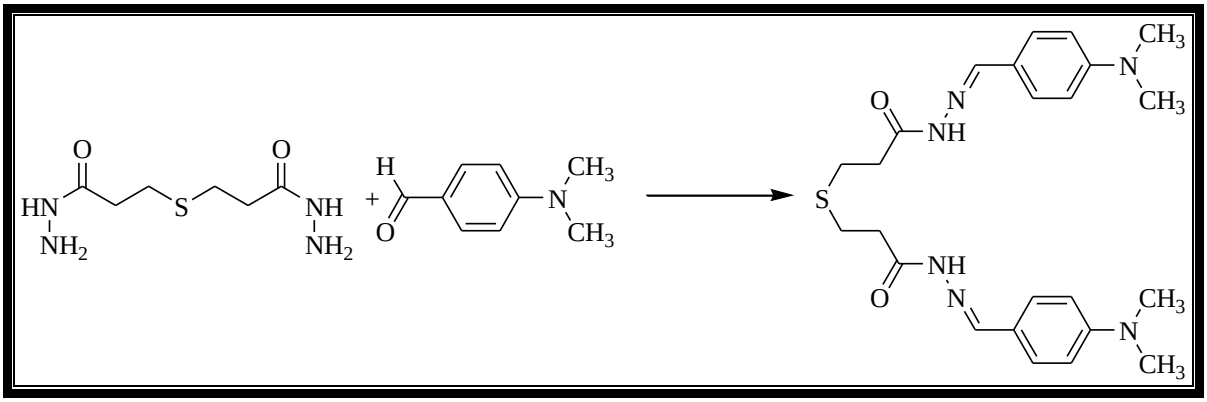

Figure-1 Synthesis of L_2 for second complex

3. Physical measurements:

Reaction progress is noticed by TLC (thin layer chromatography). Open capillary method followed to determine the melting point of metal complex. Carbon, hydrogen and nitrogen elemental analysis performed from CDRI lucknow UP.For getting Infra red Spectra (PerkinElmer 237) spectrometer is used. On Perkin's Elmer (237) spectrometer IR spectra is taken while for 1HNMR, Bruker Advance DPZ400 MHZ spectrometer, $CDCl_6$ as solvent and tetra methylsilen as an internal slandered.

4. Spectra of ^{1}H NMR :

Spectra of H^1 NMR of acid hydrazide ligand exhibits multiple singlet at tau velues 11.09 for (N-H) .8.2 tau value for(C-H). In metal complex the downfield shifting of signal exhibit the bonding between cobalt (II) ion and nitrogen of legend. $CDCl_6$ is used as solvent and tetra methylsilen as a internal slandered.

5. Electronic Spectra :

Elecronic spectra are very much helpful to investigate the geometry of complex and stereochemistry of synthesized metal complexes. d- Electron transition exhibits the actual geometry of compound. In present cobalt complex the one broad band is appear on 16540 cm^{-1} (E_g - T_{2g}) that's conform the octahedral geometry of the compound.

6. Proposed structure:

On the basis of characterization data we can predict the following octahedral geometry of the cobalt (II) metal complex linking with bidentate ligand.

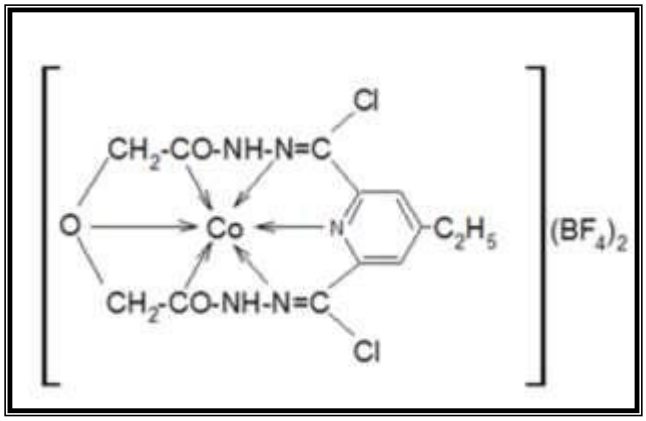

Fig.2 [Co (II) (EPCCIDAH)]BF_4

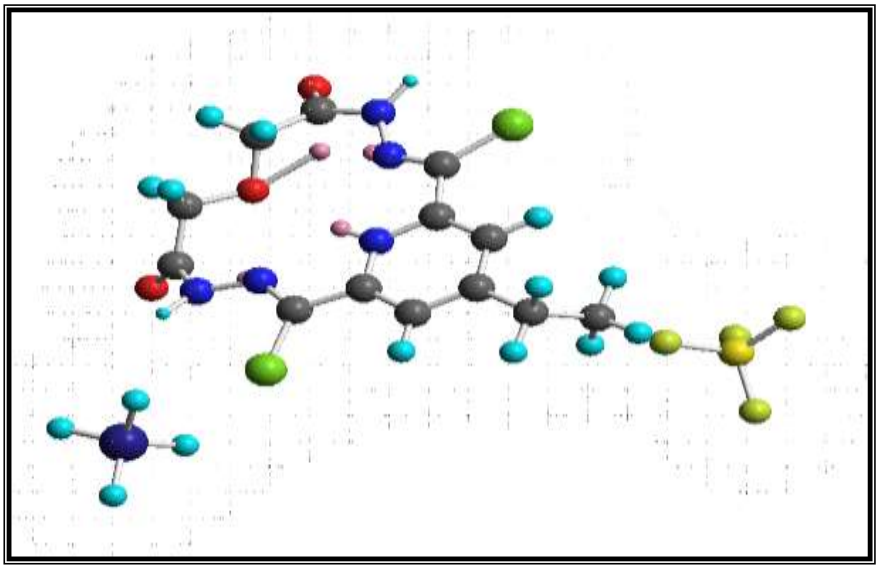

Figure-3 Molecular modeling of structure of ML1

6.1 Proposed structure of second complex ML2

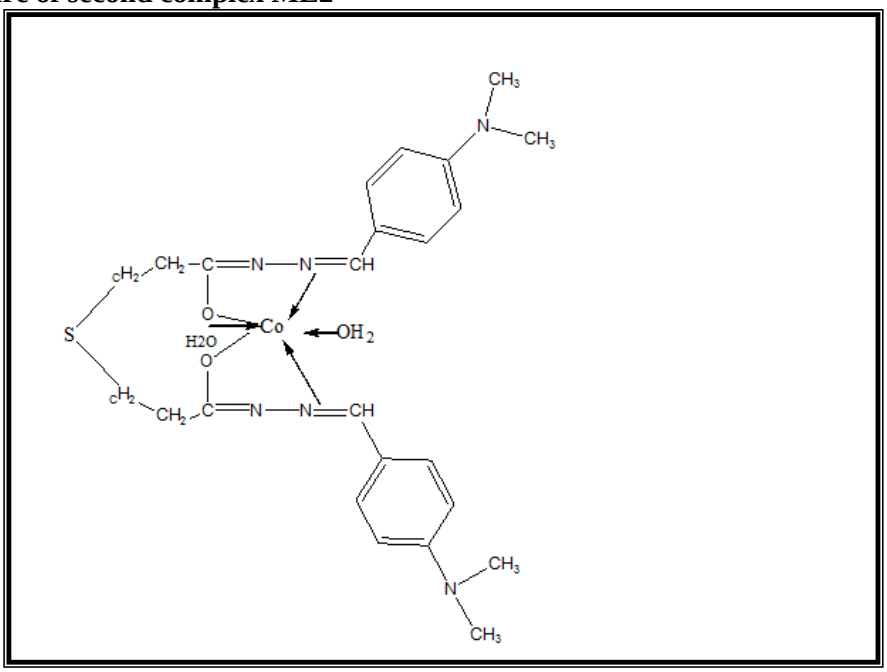

Figure-4 proposed structure of ML2

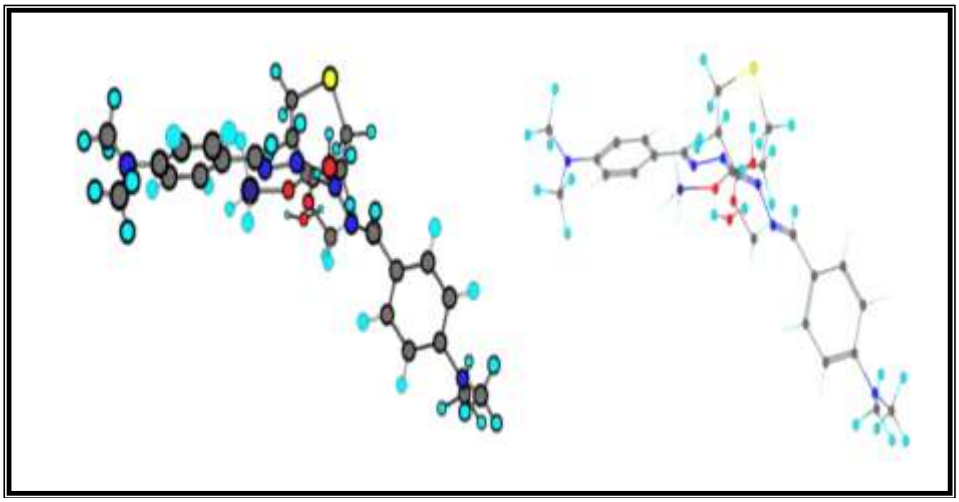

Figure-5 Molecular modeling of structure (solid and chain structures)ML2

IR Spectra

IR spectra of the complex exhibit the mode of bonding in between metal ion and lingand. In complex one IDA dihydrazone is used as dicarboxilic acid while in complex second oxidiacetic acid di hydrazone ligand is used.

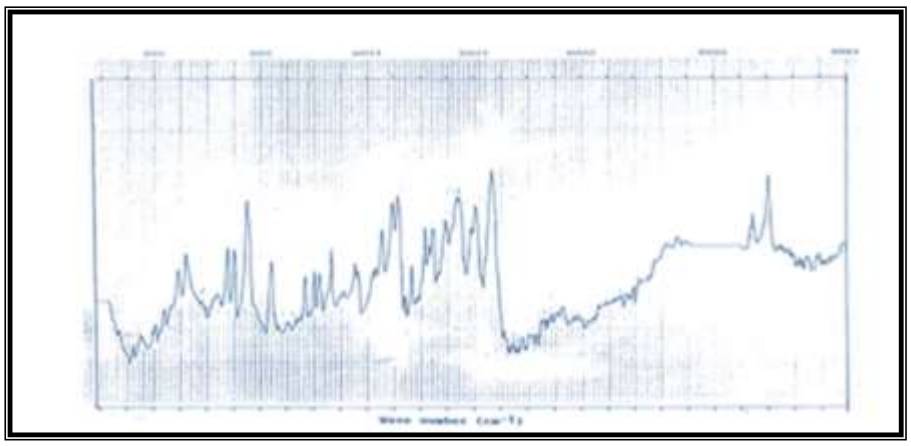

Figure-5 IR of ML1

Table- 1: Absorption Frequencies (in cm^{-1}) data for Infrared Spectra of Ligand as well as the Complexes of Hydrazone:

Sr.	Functional Group	Absorption Bands of Ligand	Complex I	Complex II
1	-CH2	2990	2940	2950
2	NH Bending	3410	3340	3350
3	NH Stretching	1330	1280	1260
4	NH2 Stretching	1470	-	-
5	Aromatic Stretching	1100	1650	1070
6	-C-O	1730	1660	1620
7	-C-N	-	1680	1580
8	M-N	-	320	500
9	M-O	-	420	400

7. Antibacterial Activity

Hydrazones and their transition metal complexes exibit good activities against bacteria. Anti bacterial properties of synthesized acid hydrazone and its metal complex is screened against B. subtilis and E. coli microbes.

8. Antifungal Activity

Thousands of hysrazone complexes have been teasted against fungi[13].For screening the antifungal nature of the synthesized compound towards Penicillium marneffei and Aspergillus fumigatus agar diffusion method is adopted[19,20]. For comparing the Fungal activity of synthesized cobalt(II) compound Greseofulvin is used as a standard drug. The observations show that Co (II) complexes exhibited excellent action.

9. Results and Discussion

Physical, analytical facts or information's suggests that the given metal complex of general composition [Co (II) (EPCCIDAH) (BF_4)]:(4-ethyl-2,6-pyridine dicarbonyldichloride-N, N'-oxydiacetoyl dihydrazone) with octahedral structure. The metal complex is coloured (light pink),solid and stable

10. CONCLUSION:

The present work show the biological activities of hydrazone derivatives, such as analgesic, anti-inflammatory, antihypertensive, vasodilator, anticonvulsant activities, antioxidant, antiviral, antitumor, antimycobacterial, antimicrobial, antimalarial and antidepressant activities. Therefore, the out com of this work suggests to synthesis of series of biologically active hydrazones and their complexes. The metal complexes of hydrazones are much more efficient against bacteria and fungi as their corresponding ligands.

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