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Synthesis and Characterization of Mixed Ligand Complexes of Transition metals with Nicotinic acid and Isonicotinic acid with Hydrazine

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Abstract

Transition metal hydrazine complexes of pyridine–3-carboxylic acid andpyridine–4-carboxylic acid, $[ML_1L_2 (N_2H_4)_2]$ where L_1 = pyridine–3-carboxylic acid, L_2 =pyridine–4-carboxylic acid where M = Co, Ni, Zn and Cd have been preparedand characterized by analytical, IR, UV-Vis, CHNS, TG-DTA, VSM and powder XRD studies. The IR studies show that N-N stretching frequency at 953–969cm^{-1}suggesting abidentate bridging structure of hydrazine molecules to the central metal ion in all the complexes. Thermal decomposition of the compounds are studied from room temperature to 900$^oC$by TG-DTA analysis, which show that all the complexes decompose steadily to yield to metal oxides. VSM measurement shows that all the metal complexes are paramagnetic in nature. Antimicrobial screening was carried out for the synthesized complex against bacteria and fungi. The binding of the complexes with herring sperm DNA was also carried out for the complexes.

Keywords: Hydrazine, (L_1) pyridine–3-carboxylic acid, (L_2) pyridine–4-carboxylic acid, IR spectra, TG-DTA, VSM and DNA binding studies.

Introduction

Hydrazine, dinitrogen tetra hydride (N_2H_4) is a simplest diamine, having an ammonicalodour and is unique in its derivatives [1]. The chemistry of hydrazine is interesting not only because it has potent N-N bond, but due to the presence of two free electron pairs and four replaceable hydrogen atoms, which forms complexes with transition metals. Thermal reactivity of metal hydrazine complexes is of great interest

since the stability of complexes changes dramatically depending upon the anions as well as cations [2]. Hydrazine possesses very good ligating property, the possible coordination modes of hydrazine molecule are monodentate, bidentate, chelating and also bridging. Among these, reports on metal complexes with hydrazine in chelating bidentate fashion are available in the literature [3]. But, a large number of metal complexes in which hydrazine acts as monodentate [4-6], as well as bidentate bridging ligand [7-10] have been synthesized and characterized. In the case of carboxylic acid, the preparation, structure and thermal properties of bis-hydrazine transition metal formate [11], acetate [9, 12] malonate [7, 13] and succinate [13] have also been reported. Hydrazine complex with pyridine n-carboxylic acid with hydrazine ligands namely with picolinic acid and nicotinic acid are reported [14]. Howeverthere is no report the on the transition metal hydrazine complexes containing mixed ligands of pyridine–3-carboxylic acid and pyridine–4-carboxylic acid with hydrazine as coligand. Nicotinic acid is isomer of isonicotinic acid, it contains 2 oxygen donor atom and can strongly to form more metal complexes. Nicotinic acid is a vitamin essential for human and animal health. Isonicotinic acid widely used drug, is a potent inhibitor of the cross linking of fibrin and used for blood coagulation catalyst. Hence an attempt was made to synthesize and characterize the transition metal complexes with mixed ligand namely pyrindine-3- carboxylic acid and pyridine -4- carboxylic acid with hydrazine.

Experimental Section

Mixed ligand complexes of pyridine n-carboxylic acids with hydrazine as coligandwas performed and characterized. Transition metals like Ni, Co, Cd and Zn were used for synthesis.

Preparation of M [$(L_1L_2)_2$ $(N_2H_4)_2$.] (M= Ni, Co, Cd and Zn)

To the known weight of isonicotinic acid (0. 1231g, 0. 001 mol) and nicotinic acid (0. 12311 g, 0. 001mol) was dissolved in double distilled water, to this solution added a known volume of hydrazine (3. 5 ml, 0. 007mol) and stirred the solution well for ten minutes and the pH wasmeasured and found to be 7. A known weight of metal nitrate solution (Ni=0. 2908 g, Co=0. 2910 g, Zn=0. 2970 g, Cd=0. 3084 g, 0. 001mol) was dissolved in water. The ligand solution was poured in to the metal solution slowly with stirring in a magnetic stirrer and the resulting solution was concentrated in a water bath. A polycrystalline substance was obtained immediately was washed with distilled ethyl alcohol, and dried in a desiccators. The hydrazine content in the sample was determined by estimation using KIO_3 as the titrant. The % of metal in the sample was estimated by standard methods given in the VOGEL'S Text book [15].

Results and discussion

The analytical data of the complexes are compatible with proposed composition for the complexes and are tabulated intable (1).

Table 1 Analytical Data

Complexes	Colour	Hydrazine %		Metal %		Meltingpoint (°C)
		Found	Calculated	Found	Calculated	
Ni [(L_1L_2) $(N_2H_4)_2$]	Light violet	17. 60	17. 43	15. 30	15. 99	340
Co [(L_1L_2) $(N_2H_4)_2$]	Pink	17. 20	17. 41	15. 98	16. 04	342
Zn [(L_1L_2) $(N_2H_4)_2$]	Pale yellow	17. 10	17. 12	17. 40	17. 49	355
Cd [(L_1L_2) $(N_2H_4)_2$]	Pale yellow	15. 13	15. 21	26. 30	26. 71	360

Infrared Spectral Data

The infrared spectra were recorded on IR-Affinity-1 CE-Shimadzu model spectrometer. The important infrared spectral data of all the complexes with their band assignments are summarized in the table (2). All the complexes exhibit N-H stretching. The bands for N-H stretching lie in the rangeof 3051-3306 cm^{-1}. The asymmetric and symmetric stretching frequencies of carboxylate ions are shown at 1613-1598 cm^{-1} and 1522-1545 $cm^{-1.}$ The N-N stretching frequencies of the complexes seen at 910-969 cm^{-1} [16-18] which indicate the bidentatebridging nature of neutral hydrazinemolecule. IR data are shown in the table (2) IR spectra are presented in figure I, II, III and IV.

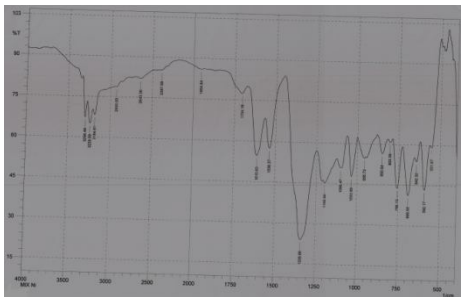


Figure I

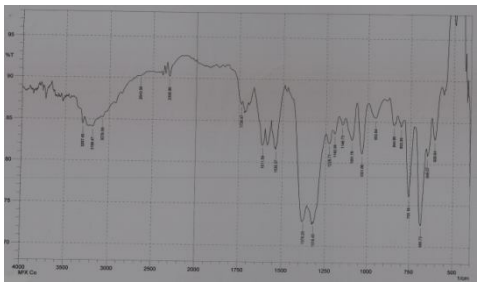


Figure II

IR spectra of Nickel complexIR spectra of Cobalt complex

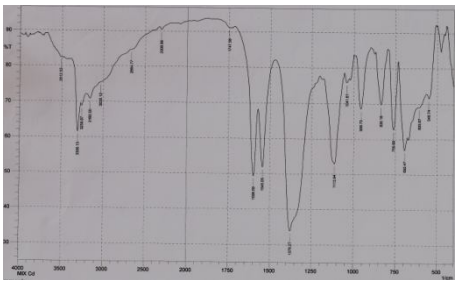


Figure III

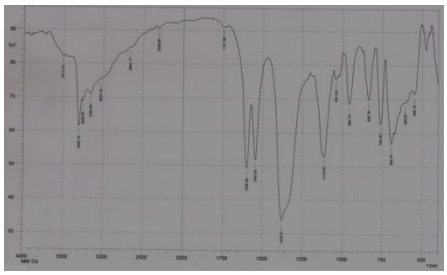


Figure IV

IR spectra of Zinc complexIR spectra of Cadmium complex

Table 2 Infrared Spectral data (cm^{-1})

Complexes	ν (O-H)	ν (N-H)	ν asym (COO^-)	ν sym (COO^-)	ν (N-N)
Ni [(L_1L_2) $(N_2H_4)_2$]	-	3296	1610	1536	956
Co [(L_1L_2) $(N_2H_4)_2$]	-	3297	1611	1536	953
Zn [(L_1L_2) $(N_2H_4)_2$]	-	3296	1613	1522	969
Cd [(L_1L_2) $(N_2H_4)_2$]	-	3306	1598	1545	956

UV Spectroscopy

The electronic spectra of the complexes were recorded in $CHCl_3$ in the 190-800 nm bands appear at 219 nm and 263 nm which are presented at $A_{2g}{}^3$ (F) – $^3T_{1g\ (P)}$ transition, which confirmed octahedral geometry of metal ions. UV spectrum of the Ni complex shown in the figure V

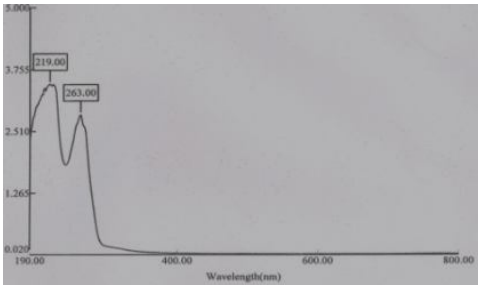


Figure V UV spectrum of Nickel complex

Elemental Analysis

Elemental analysis data of the complexes are listed in table (3). The percentage of CHN in the complexes matched with the found CHN analysis. Elemental analysis was performed on vario EL III CHNS analyser.

Table 3

Complexes	%C		%H		%N	
	Found	Calcd	Found	Calcd	Found	Calcd
Ni [(L_1L_2) $(N_2H_4)_2$]	39. 00	39. 27	4. 3	4. 39	22. 77	22. 90
Co [(L_1L_2) $(N_2H_4)_2$]	39. 10	39. 25	4. 39	4. 39	22. 10	22. 88
Zn [(L_1L_2) $(N_2H_4)_2$]	38. 38	38. 57	4. 44	4. 31	22. 55	22. 49
Cd [(L_1L_2) $(N_2H_4)_2$]	34. 43	34. 25	3. 55	3. 83	19. 50	19. 77

Thermal analysis

The TG-DTA was recorded on perkin-Elmer SII thermal analyzer. The TG-DTA of the complex arepresented in the figure VI. The TG-DTA data of Nickel complex is summarized in table (4).

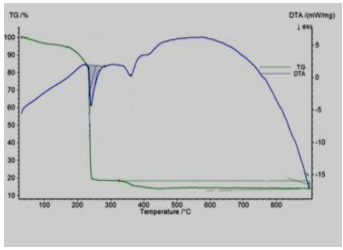


Figure VI TG-DTA data ofNickel complex

Table 4

Complexes	DTA peak Temp (^{O}C)	Thermogravimetry			Nature of decomposition
		Temp Range (^{O}C)	Mass loss (%)		
			Found	Calculated	
Ni [(L_1L_2) $(N_2H_4)_2$]	250 (-) 380 (-)	100-250 250-500	17. 5 80. 00	17. 50 75. 43	Dehydrazination Complete decomposition leading to NiO residue.

(-) exothermic, (+) endothermic

VSM Studies

Among the synthesized complexes theof Nickel and Cobalt complexes were subjected tomagnetic studies by using VSM (vibrational sample magnetometer) in the field of 10000 to 20000 gauss. VSM performed by using John Foxx: Metamatic (Elka Rhapsody). The analysis confirmed the paramagnetic nature of metals in the complexes. Nickel and Cobalt complexesVSM studies shown in the figure (VII, VIII).

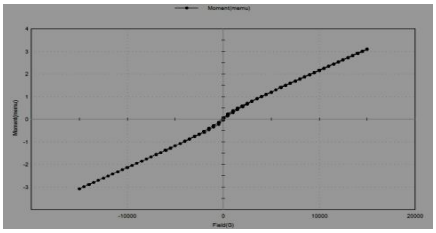


Figure VII

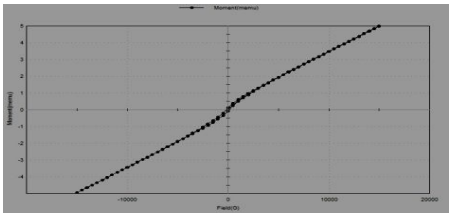


Figure VIII

Magnetic study of Nickel complexMagnetic study of Cobalt complex

X-ray Diffraction studies

Powder XRD pattern was recorded in Bruker Advanced D8 Diffractometer. The XRD patterns of the complexes are presented in the figure (IX). XRD patterns of all complexes show the isostructural nature of complexes.

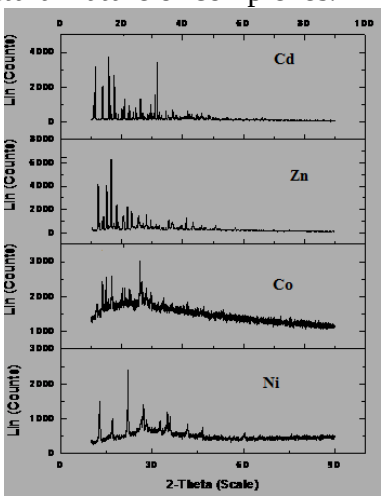


Figure IX X-ray powder diffraction pattern of Cd, Zn, Co and Ni complexes

Antimicrobial Studies

The complexes were subjected to antibacterial studies by disc diffusion method two bacterial species (E. Coli and Staphylococcus aureus) and two fungal species (Candida albicans and Aspergillus fumigates) and the results are measured by the zone of inhibition in mm and tabulated in tables (5 & 6) and figures (X & XI). The antibacterial studies indicates that the Nickel hydrazine complex has more bacterial activity compared to other complexes against E. Coli and Staphylococcus aureus. Overnight culture are grown at 37^0C Kirby- Bauer procedure and diluted to Muller Hinton Broth. This overnight culture was diluted to 10^{-2}. MIC Ni complexes shown in the table (7, 8, 9 & 10).

Antibacterial studydata of the complexes

Table5

S. no	Sample Name	Zone of Inhibition (mm)	
		E. coli	Stapylococcusaureus
	McFarland Standard	30	33
1	Ni [(L_1L_2) $(N_2H_4)_2$]	15	19
2	Co [(L_1L_2) $(N_2H_4)_2$]	08	09
3	Zn [(L_1L_2) $(N_2H_4)_2$]	11	10
4	Cd [(L_1L_2) $(N_2H_4)_2$]	18	14

Antibacterial study

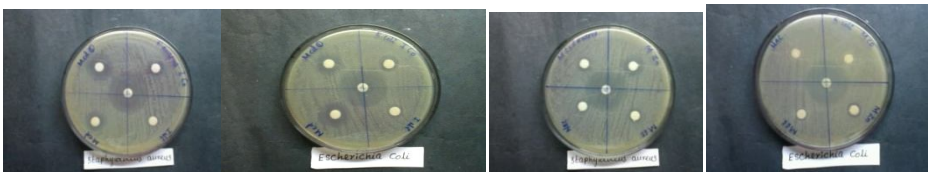


Figure X Ni, Co, Zn and Cd complexes againstStaphylococcusaureus and E. coli

Antifungal activity is tabulated in tabulated in the table (5) and figure (X). The studies exhibit that Nickel hydrazine complex has more fungal activity compared to other complexes against Aspergillus fumigatesand Candidaalbicans. Which are clear from the Zone of inhibition measurement in mm.

Antifungal studydata of the complexes

Table 6

S. no	Complexes	Zone of Inhibition (mm)	
		Candida albicans	Aspergillus fumigates
	McFarlandStandard	13	12
1	Ni [(L_1L_2) $(N_2H_4)_2$]	09	11
2	Co [(L_1L_2) $(N_2H_4)_2$]	10	8
3	Zn [(L_1L_2) $(N_2H_4)_2$]	09	08
4	Cd [(L_1L_2) $(N_2H_4)_2$]	08	09

Antifungal activity

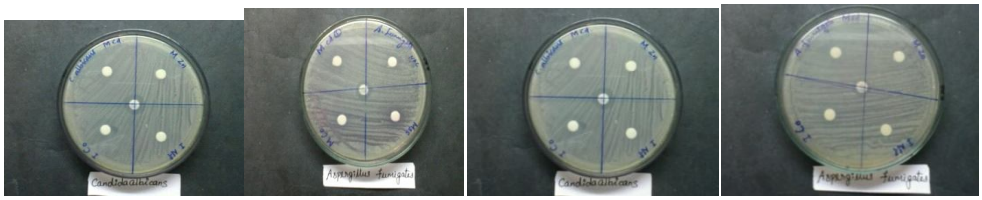


Figure XI Ni, Co, Zn and Cd complexes againstCandida albicans and Aspergillusfumigates

Minimum inhibition concentration of Nickel complex against Staphylococcuaureus bacteria

Table 7

Complex	Organism	1000 µg/ml	500 µg/ml	250 µg/ml	125 µg/ml	62. 5 µg/ml	31. 25 µg/ml	15. 625 µg/ml
Ni [(L_1L_2) $(N_2H_4)_2$]	Staphylococcus aureus	-	-	-	-	-	+	+

Table 8

Complex	Organism	MIC value
Ni [(L_1L_2) $(N_2H_4)_2$]	Staphylococcus aureus	62. 5µg/ml

Minimum inhibition concentration of Nickel complex against Aspergillus fumigates

Table 9

Complex	Organism	1000 µg/ml	500 µg/ml	250 µg/ml	125 µg/ml	62. 5 µg/ml	31. 25 µg/ml	15. 625 µg/ml
Ni [(L_1L_2) $(N_2H_4)_2$]	Aspergillusfumigates	-	-	-	-	+	+	+

Table 10

Complex	Organism	MIC value
Ni [(L_1L_2) $(N_2H_4)_2$]	Aspergillus fumigates	125µg/ml

+ → Presence of Growth
- → Absence of Growth

Based on anti microbial activity study the entire complexes possess antimicrobial activity. Among the synthesized complex Ni complex were found to be more active again Staphylococcus aureus bacteria andAspergillus fumigates fungi. Minimum inhibitory concentrationsstudy thesynthesized complex Ni having greatest value 62. 55 µg /ml in antibacterial activity and 125 µg /ml in antifungal activity.

DNA binding study

Protocol

The extracted cough thymus DNA of 10 µl was added with metal solution each 10 µl and incubated at 37°C for 3 hours and pH was maintained at 8. The control was DNA and distilled water. It was then run on horizontal agarose gel electrophoresis in 0. 8 % agarose slab gel in 1X Tris- Acetate EDTA (TAE) buffer at room temperature. The 6X gel loading dye was added to the DNA-metal mixture and control which in turn was loaded on the gel 15 µl and the electrophoresis unit was run at 50 V with an appropriate DNA marker till the dye migrated to a sufficient distance in the gel and visualized using a UV trans illuminator.

UV-visible spectrophotometricstudies

To the 10 mg of Deoxyribonucleic acid, 1 ml of sterile distilled water and 50 µl of each cobalt and nickel solution was added and incubated at room temperature for an hour. The controlled was maintained without adding the metals. The samples were measured at 370 nm in UV-vis spectrophotometer and readings were measured. The metals compounds were mixed with calf thymus DNA and incubated for 3 hrs in Room temperature and run on 0. 8% Agarose gel and the results were viewed under gel documentation and documented. The presence of DNA bands denoted the binding of the compounds with the test DNA [19]. DNA binding studies shown in figure (XII).

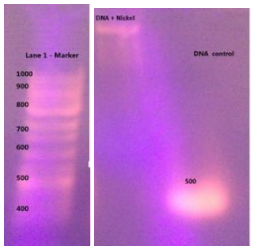
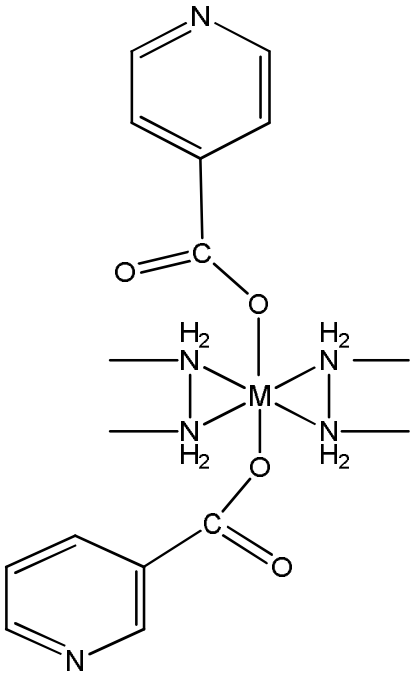


Figure XII DNA binding study of Nickel complex

Conclusion

The mixed ligand complexes oftransition metals like Nickel, Cobalt, Zinc and Cadmium with hydrazine are synthesized. Pyridine-3-carboxylic acid and pyridine-4-carboxylic acid yields neutral hydrazine mixed ligand complexes at pH 7. Octahedral geometry is suggested for all the complexes with six coordination. Based on the evidences drawn from IR, UV, TG-DTA, CHNS, Powder XRD and magnetic studies and also on the complex. Where hydrazine acts as bidentate bridging ligand and Pyridine-3-carboxylic acid and pyridine-4-carboxylic acid acts asmonodentate ligands to the metal via Carboxylate ion coordination. The following structure was assigned for the complexes. The new complexes seems to posses antibacterial and antifungal activity. They also posses DNA binding abilities.



M= Ni, Co, Zn and Cd

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