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Synthesis, Spectral Characterization and Antifungal Activities of Cr(III), Co(II), Ni(II) and Hg(II) Complexes With Nicotinic Acid Hydrazide and Azide as Ligands

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Abstract

The mixed Ligand complexes of Cr(III), Co(II), Ni(II) and Hg(II) with nicotinic acid hydrazide(NHA) and azide ion are known as ligands. All the prepared complexes were characterized by elemental analysis, EC measurements, IR, NMR spectral analysis and antifungal studies. From the obtained elemental analysis and spectral data to arrived at the formulae of the complexes. The antifungal activities of complexes compared with those of pure Ligand NHA. All the complexes show less activity against the tested fungus such as A.flavus, A.niger, C.albicance, A.oryzae and A.sojae.

Keywords: Nicotinic acid Hydrazide, antifungal, NHA, azide ion.

Introduction

Heterocyclic containing pyridine ring are very important in anti canvulsunt, anti parkinsonian activity[1]. Pyridine derivatives are very important in biological activities such as anti tubercular, anthelmintic, fungicidal, antitumor and anti bacterial activities[2-4]. It are also used in chemotherapeutic agents[5]. Past few decades the research of nicotinic acid derivatives shows that they are having wide range of therapeutic agent[6]. Introduction of nicotinic acid Hydrazide is an important anti tubercular drug paved new interesting heteroaryl hydrazides and hydrazones.

Material and Methods

The ligands NHA are purchased from Alfa Aesar quality. All the metal nitrates and the solvents such as DMSO, DMF, Ethanol and methanol were used of AR grade.

Instrumental Analysis: The elemental analysis of the complexes was carried out by using (Thermo Finnigan make, Flash EA 1112Series instruments) CNNS (O) analyzer. The molar conductance measurements were conducted in acetonitrile solutions at 10^{-3} M metal complex solution on Eqiptronics EQ 660 Instruments. The IR spectrum of NHA and its complexes were recorder on Perkin Elmer FT IR spectrum 1-RH. The NMR spectrum of NHA and its complexes were recorded in DMSO solution on 300 MHz FT NMR instruments.

Synthesis of Metal Complexes: The chromium, cobalt, nickel and mercury complexes were synthesized by mixing 0.71g, 1.31g, 1.31gand 0.69g of nicotinic hydrazide (3.79mmol, 6.93mmol, 6.93mmol and 3.64mmol) in methanol and the metal nitrates 1g $[Cr(NO_3)_3.9H_2O]$ 2.5 mmol ;1g $[Co(NO_3)_2.6H_2O]$ 3.4 mmol; 1g $[Ni(NO_3)_2.6H_2O]$ 3.4mmol and 1g $HgCl_2$ 3.62 mmol in methanol. The mixture was heated in a microwave oven for about 10 seconds. Then 0.49g, 0.45g, 0.45g and 0.47g of sodium azide 7.53mmol, 6.9mmol, 6.9mmol and 7.23mmol in ethanol was added and the whole mixture was heated in a microwave oven for about 10 seconds. The precipitated complexes were filtered and washed with ethanol and dried. The elemental analysis values are in good agreement with the formulae of the complexes. The electrical conductivity values show the non electrolytic nature of the complexes[7]. It is represented in table-1.

Results and Discussion

IR Spectrum: In IR spectrum the aromatic C-H stretching frequency found at 3408cm^{-1} which gets shifted in 3281-3433cm^{-1} in complexes. The –C=O group frequency in NHA at 1611cm-1 shifted to 1601 to 1643 cm-1 in complexes. The -C=N frequency in pyridine ring of NHA and its complexes are found in 1369-1550 cm^{-1}. In all the complexes the values at 2071 cm^{-1} to 2082 cm^{-1} shows the presence of azide group[8] which is confirmed by the entry of ligand in coordination sphere. The frequency values at below 445cm-1 and above 500cm^{-1} show the M-O and M-N bond respectively[9]. All the values are given in table-2 and represented in figure-2 to 5.

^{1}H-NMR Spectrum: In the ^{1}HNMR spectrum of NHA the δ value at 7.45 to 7.48 corresponds to the aromatic proton which is almost same in mercury complex. The $–NH_2$ value is at 3.56ppm in NHA and 3.44 in mercury complex.

Table- 1
Analytical data of the complexes: found / (calculated) %

Complexes	Colour	Conductance (ohm^{-1} cm^2 mol^{-1})	Yield	C	H	N	Metal
$[Cr_2(NHA)_3(N_3)_6]$	gray	101.7	49.49	28.14 (28.12)	2.73 (2.69)	49.25 (49.24)	13.55 (13.52)
$[Co(NHA)_2(N_3)_2]$	pink	90.1	73.77	34.51 (34.50)	3.35 (3.33)	40.26 (40.24)	14.12 (14.11)
$[Ni(NHA)_2(N_3)_2]$	blue	88.3	42.58	34.53 (34.53)	3.35 (3.33)	40.29 (40.28)	14.07 (14.05)
$[Hg(NHA)(N_3)_2]$	colourless	89.6	8.48	21.58 (21.57)	2.09 (2.05)	37.77 (37.75)	33.70 (33.69)

Table- 2
IR spectral data of the Ligand and its complexes (cm^{-1})

Complexes	C-H Aromatic	C=O	C=N	M-O	M-N	$-N_3$
NHA	3422	1601	1536	-	-	-
$[Cr_2(NHA)_3(N_3)_6]$	3408	1611	1550	569	458	2071
$[Co(NHA)_2(N_3)_2]$	3281	1643	1369	555	445	2067
$[Ni(NHA)_2(N_3)_2]$	3433	1611	1540	524	446	2071
$[Hg(NHA)(N_3)_2]$	3213	1595	1550	496	450	2045

Table-3
^{1}H-NMR spectral data of the Ligand and Mercury complex (ppm)

Complexes	NH_2	Aromatic H	N-H
NHA	3.56	7.45-7.48	2.50
$Hg(NHA)(N_3)_2$	3.44	7.39-7.52	2.50

Table- 4
Antifungal activities of the Ligand and Mercury complexes (mm)

Complexes	A.flavus	A.niger	C.albicance	A.oryzae	A.sojae
NHA	6	5	7	4	7
$[Cr_2(NHA)_3(N_3)_6]$	5	5	4	2	4
$[Co(NHA)_2(N_3)_2]$	2	4	5	5	4
$[Ni(NHA)_2(N_3)_2]$	-	2	-	4	6
$[Hg(NHA)(N_3)_2]$	3	-	2	4	7

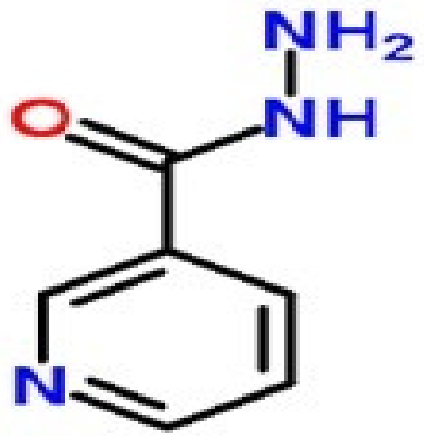

Figure-1
Structure of nicotinic acid Hydrazide

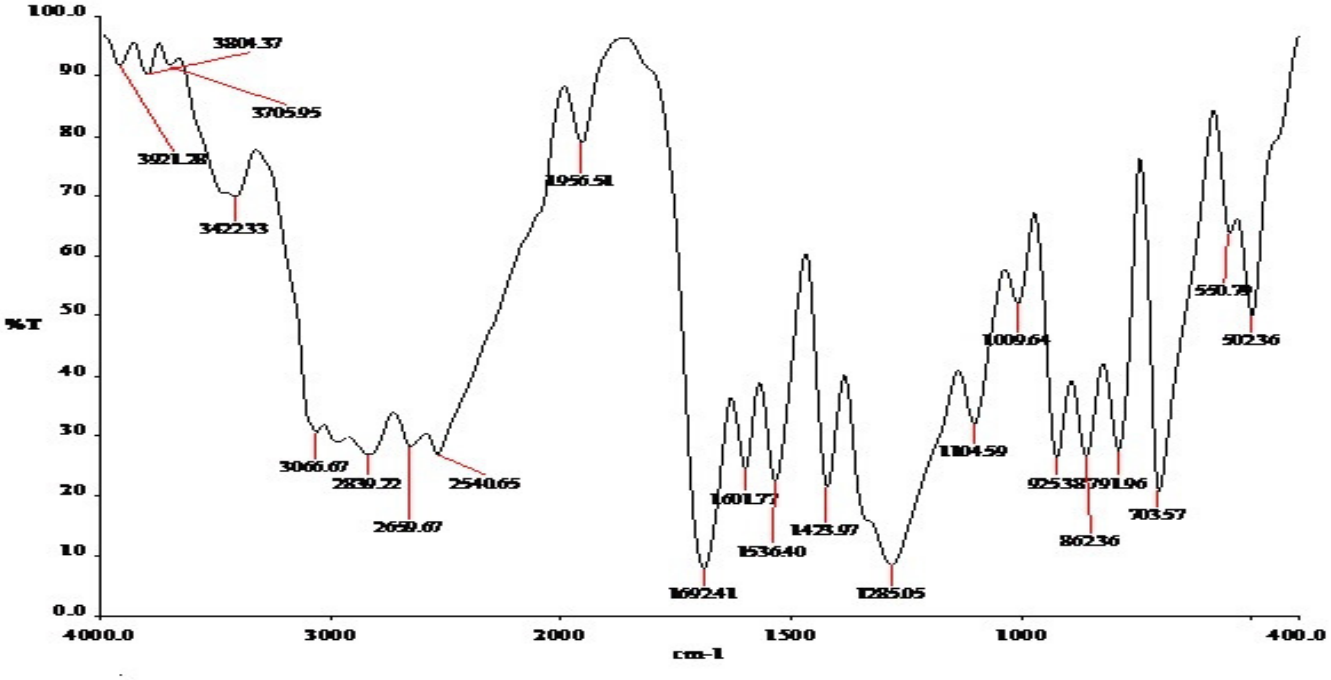

Figure-2
IR spectrum of nicotinic acid Hydrazide

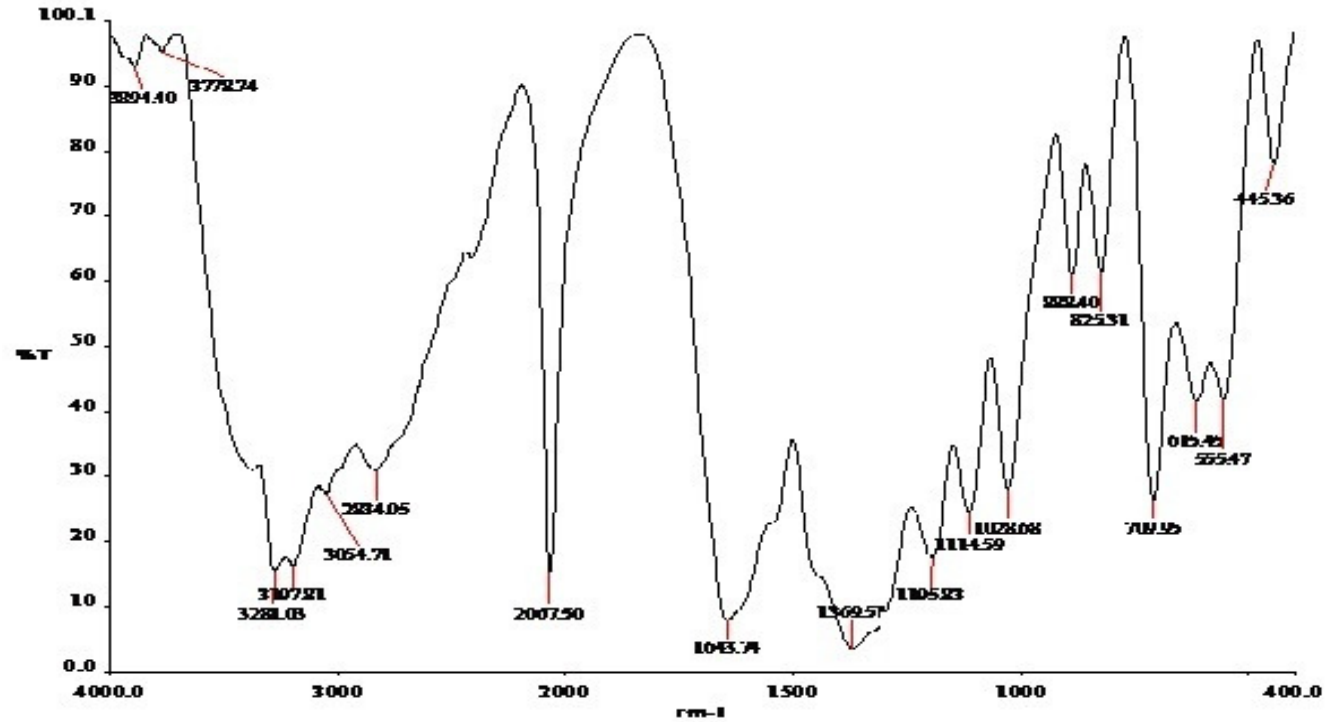

Figure-3
IR spectrum of cobalt complex

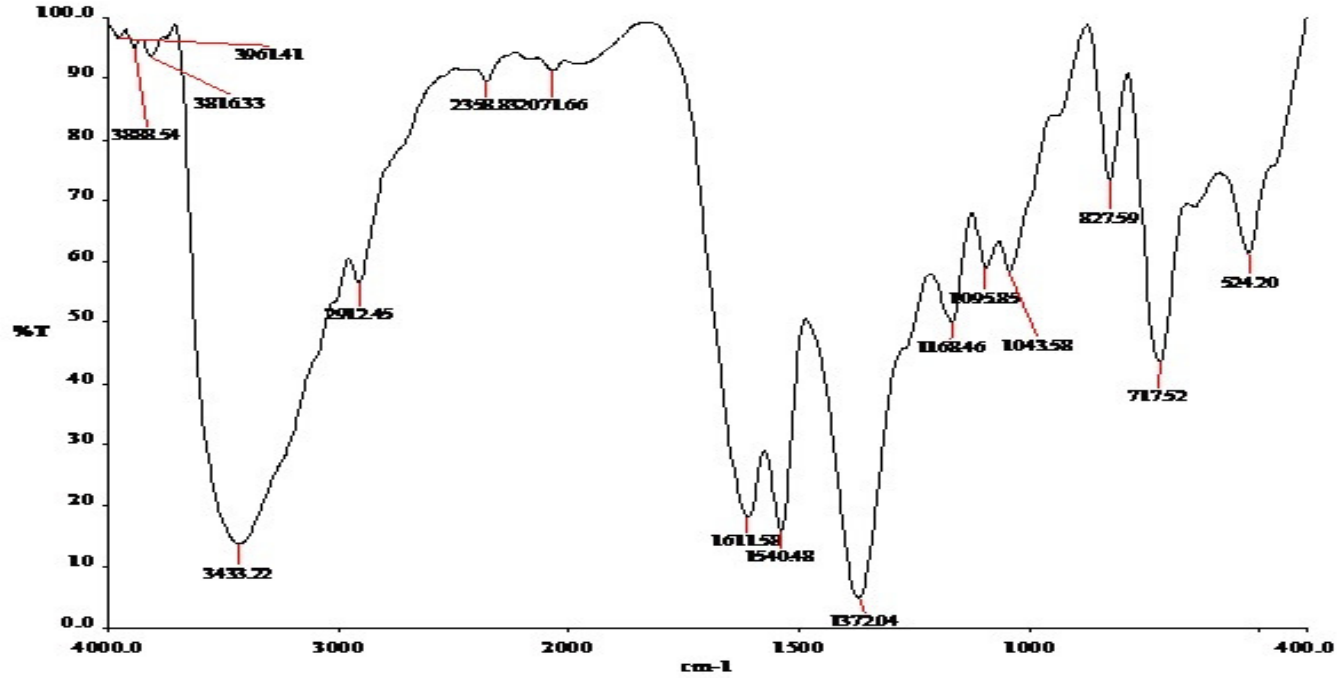

Figure-4
IR spectrum of nickel complex

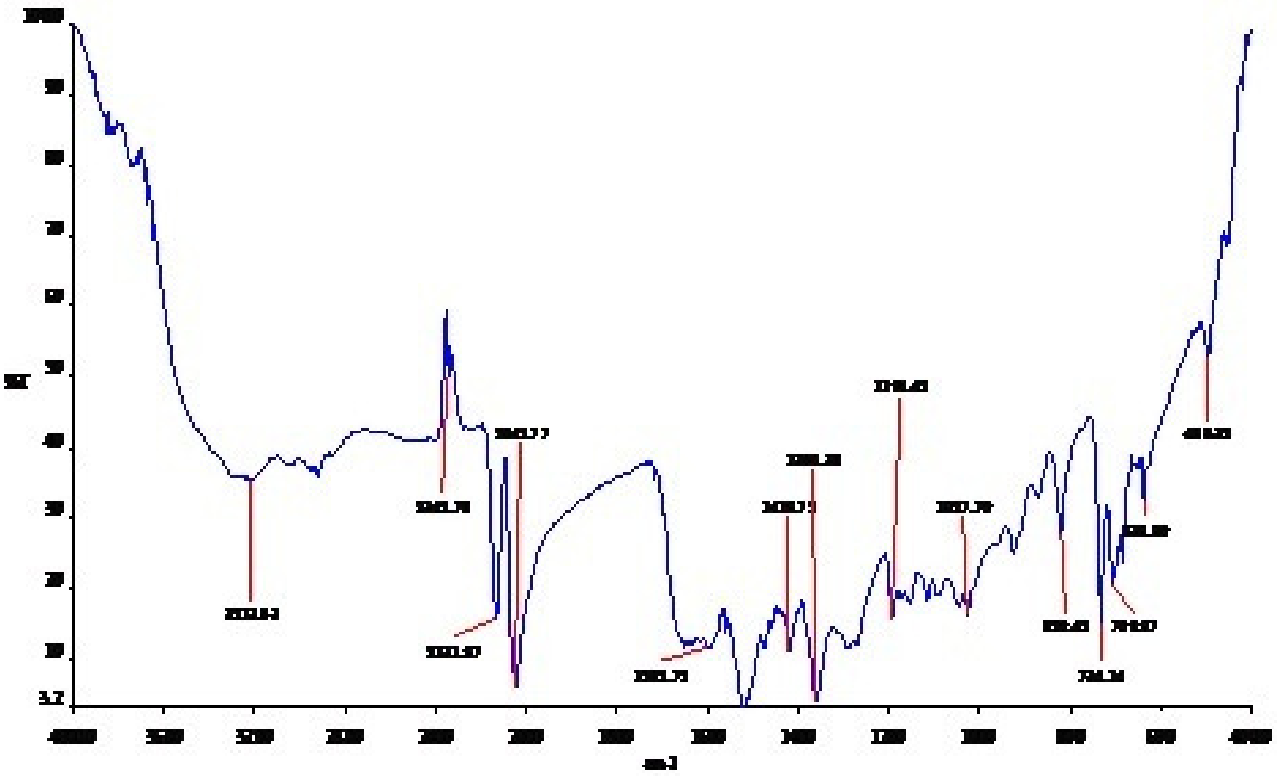

Figure-5
IR spectrum of mercury complex

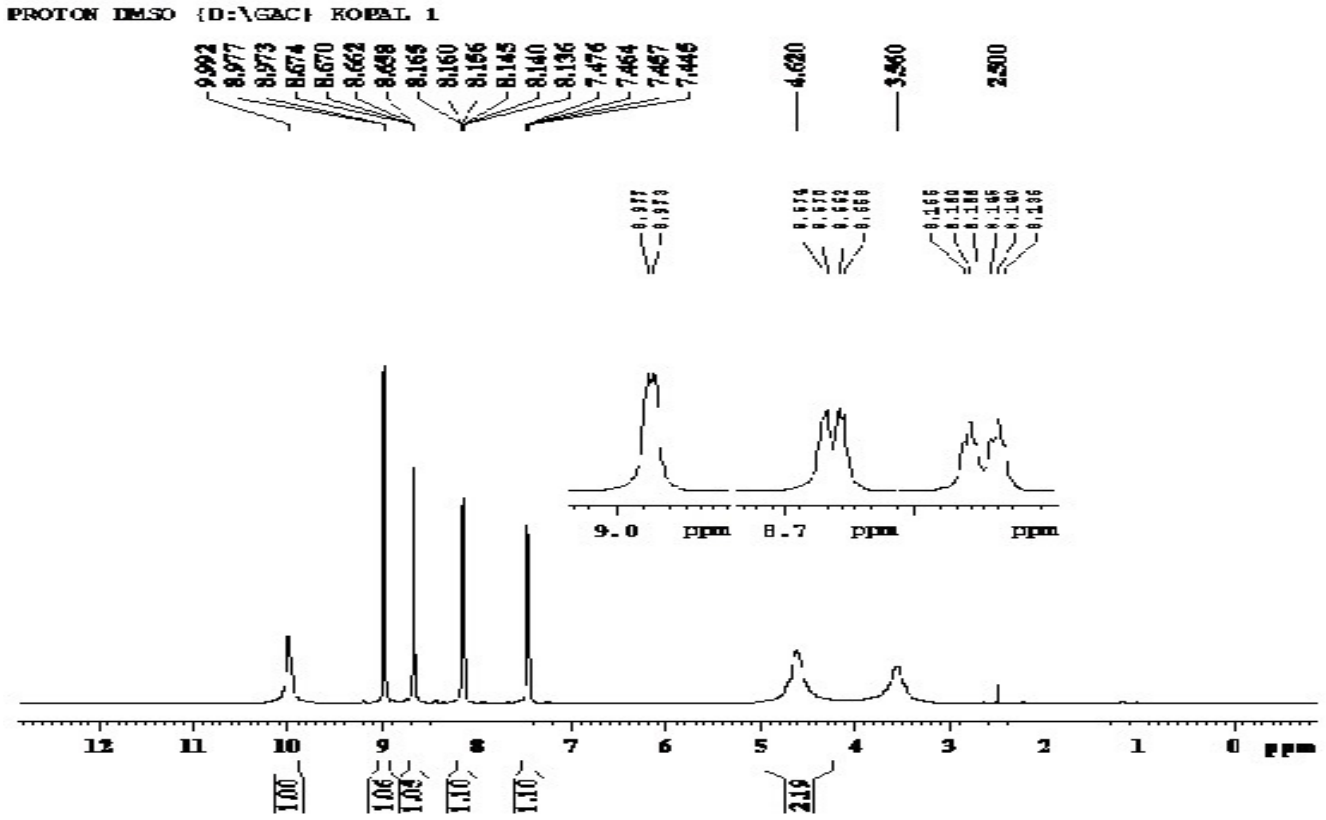

Figure-6
NMR-spectrum of nicotinic acid Hydrazide

Antifungal Activities of the Ligand and its Complexes: The antifungal activities of the ligand NHA and its complexes were done by disc diffusion method[10]. All the test solutions were prepared in DMSO and the Ketokonazole was used as the standard. Among the complexes were tested in antifungal activity only mercury and nickel complexes were moderately active against the *A.sojae* fungi when compared to those of pure Ligand. All other complexes are resistant to the fungus viz., *A.flavus, A.niger, C.albicance, A.oryzae and A.sojae.* The values have been presented in table-3.

Conclusion

From the obtained analytical, IR and NMR spectral data the formulae of the complexes are $[Cr_2(NHA)_3(N_3)_6]$, $[Co(NHA)_2(N_3)_2]$, $[Ni(NHA)_2(N_3)_2]$ and $[Hg(NHA)(N_3)_2]$. The electrical conductivity values of all the complexes revealed that the nonelectrolyte nature antifungal activities of the ligand NHA and its complexes show moderate activity against the tested fungus.

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