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Synthesis, Spectral Characterization Powder X-Ray Diffraction and Antifungal Activities of Cr(III), Co(II), Ni(II), Hg(II) and Cd(II) Complexes with Nicotinic Hydrazide and Nitrite Ion as Ligands

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Abstract

The complexes of Cr(III) , Co(II), Ni(II), Hg(II), Cd(II) were synthesized with the ligands NHA and NO_2^- and characterized by using Elemental analysis, Molar conductance measurements, IR, NMR, spectroscopic studies. Many metal complexes generally involved in several catalytic phenomena which are associated with biological and industrial systems. In this present investigation the antimicrobial activity of the metal complexes was assessed by fungal study and the results were compared with the pure ligand NHA. The fungal activity data shows that the metal complexes are potent active then the parent ligand NHA.

Keywords: NHA. Metal complex, antifungal, nitrite

Introduction

Heterocyclic compounds play a significant role in many biological systems, especially N-donor ligand systems being a component of several vitamins and drugs such as NHA [1]. Pyridines derivative are very important in biological activities such as anti tubercular, anthelmintic, fungicidal, antitumor and antibacterial activities.[2-4] NHA act as bidentate ligand sometimes it will act as monodentate ligand and having good ligating character, enhanced biological properties.

Materials and Methods

All the chemicals used for the preparation of the ligands were Alfa Aesar quality and AR grade. Molar conductance of the complexes was measured using a Systronic conductivity bridge at room temperature in DMSO. Conductivity measurements (Ω^{-1} cm^2 mol^{-1}) were carried out in DMSO using a Tacussel conductivity bridge model. Perkin-Elmer PE 938 spectrophotometers were used to record the IR spectra using KBr pellets. Antifungal activities of the complexes were measured by Disc-Diffusion method.

Synthesis of Metal Complexes

The chromium, cobalt, nickel, mercury and cadmium complexes were synthesized by mixing 0.71g, 1.31g, 1.31gand 0.69g and 0.61g of nicotinic Hydrazide (3.79mmol, 6.93mmol, 6.93mmol, 3.64mmol and 3.21mmol) 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, 1g $HgCl_2$ 3.62 mmol1g [$Cd(NO_3)_2.4H_2O$] 3.22 mmol in methanol. The mixture was heated in a microwave oven for about 10 seconds. Then 0.45g, 0.48g, 0.48g, 0.51g and 0.45g of sodium nitrite 6.40mmol, 6.9mmol, 6.9mmol and 7.30mmol and 6.40mmol 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. It is represented in **Table-1.** The ligand (L) is soluble in common organic solvents such as THF, C_2H_5OH, CH_2Cl_2 and DMSO. The octahedral metal complexes are highly soluble in DMSO and DMF and slightly soluble in CH_2Cl_2 and $CHCl_3$

Results and Discussion

The prepared complexes Cr(III) , Co(II), Ni(II), Hg(II), Cd(II) complexes are coloured but the Cadmium complexes are colourless (table-1). All are soluble in DMSO and DMF. The molar conductance values obtained for these complexes at the concentration of 10^{-3} M are in the range of 10-20 Ω^{-1} Mol^{-1} cm^2. These values are too low to account for any dissociation of the complexes in DMF. Hence these complexes can be regarded non-electrolytes[5].

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[6]. The -C=N frequency in pyridine ring of NHA and its complexes are found in 1369-1550 cm^{-1}. In all the complexes the asymmetric stretching frequencies nitrite ion will appears between 1363-1381 cm-1 in all the complexes and the symmetric stretching frequencies of nitrite ion at 1340cm^{-1} .

^{1}H-NMR Spectrum

In the ^{1}HNMR spectrum of NHA the δ value at 7.44 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 3.56 in mercury complex[7]. V_{M-ONO} values are lying in 620-826 cm^{-1} and V_{M-N} values are lying in 820-840 which shows the metal ligating ability[8].

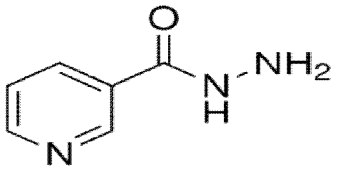

Fig-1. Structure of NHA

Table 1. : Elemental Analysis, Magnetic Moments, Molar Conductance of the Complex.

S No.	Complex	Colour	Conductance (ohm^{-1} cm^2mol^{-1})	Yield %	C %	H %	N %	Metal %
1.	$[Cr_2(NHA)_2(NO_2)_6]$	Magenta	101.7	69.5	28.14 (28.12)	2.73 (2.69)	49.25 (49.21)	13.55 (13.50)
2.	$[Co(NHA)_2(NO_2)_2]$	Orange red	85.2	79.13	40.26 (40.25)	3.35 (3.34)	26.84 (26.83)	14.12 (14.11)
3.	$[Ni_2(NHA)_2(NO_2)_2]$	Pale Blue	95.7	73.18	33.88 (33.86)	3.29 (3.27)	26.35 (26.33)	13.81 (13.80)
4.	$[Hg(NHA)(NO_2)_2]$	Pale yellow	69.9	78.21	24.59 (24.57)	2.39 (2.37)	23.91 (23.89)	21.71 (21.70)
5.	$[Cd(NHA)(NO_2)_2]$	Pale white	79.0	77. 0	21.08 (21.05)	2.04 (2.02)	20.49 (20.47)	32.91 (32.90)

Table 2. :IR Spectral data of NHA and its metal complexes (Cm^{-1})

Complex	$V_{C=C}$	$V_{C=O}$	$V_{C=N}$	V_{C-N}	V_{M-N}	V_{M-ONO}
NHA	2045	2100	2080	1850	-	-
$[Cr_2(NHA)_2(NO_2)_6]$	2047	2100	2000	1853	832	620
$[Co(NHA)_2(NO_2)_2]$	2043	2102	2020	1862	828	622
$[Ni_2(NHA)_2(NO_2)_2]$	2044	2102	2010	1867	830	826
$[Hg(NHA)(NO_2)_2]$	2043	2100	2100	1060	840	630
$[Cd(NHA)(NO_2)_2]$	2044	2110	2005	1875	835	622

Powder X-ray Analysis:

The XRD (powder pattern) of the complexes $[Co(NHA)(NO_2)_2]$ and $[Ni(NHA)_2(NO)_2]$ were indexed in X-ray difractometer and the unit cell parameters have been calculated with the help of a computer from 2 θ values (Fig.1). The direct constant parameters like A, B, C, q, p, y, nd v (volume) are given in Table-3.[9]

Antimicrobial activity

The biological effects of the coordination complexes have been established by their antitumor, antiviral and antimalarial activities. This characteristic property has been related to the ability of the metal ion to form complexes with ligand containing nitrogen donor atoms. The ligands and their antimicrobial activities of NHA and its metal complexes were tested against the following microorganisms: *A.flavus, A.niger, C.albicance, A.oryazae, A. sojae*.[10]

Table 3. : X-ray powder pattern reports

Compound	2θ			Unit Cell Parameters	Density	N	Possible Geometry
$[Co(NHA)(NO_2)_2]$	13.284	13.936	16.141		(gcc) 0.83	1	Monoclinic
	17.228	18.130	18.264	A = 13.300 Å			
	19.300	21.756	22.659	B = 20.543 Å			
	25.010	25.516	30.914	C = 6.985 Å			
	32.051	39.253	41.659	α = 90.000°			
	42.244	43.849	46.389	β = 102.325°			
	47.308	48.194	49.881	γ = 90.000°			
	50.032	51.419	53.174	V = 1864.37			
	53.541	53.976	54.076	Å^3			
	54.277	55.680	56.148				

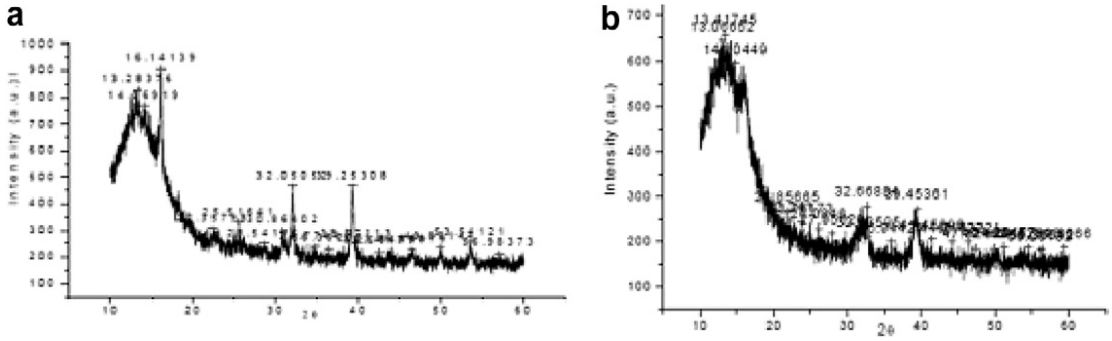

Fig.2 XRD (Powder Pattern) of the complexes (a) [Co (NHA) $(No_2)_2$] and (b) [Ni $(NHA)_2(No)_2$].

Table 4. : Antifungal activities data for the NHA and its metal complex

Complexes	***A.flavus***	***A.niger***	***C.albicance***	***A.oryazae***	***A.Sojae***
NHA	7	7	8	7	8
[Cr_2 (NHA) $(No_2)_6$]	6	8	7	8	8
[Co (NHA) $(No_2)_2$]	6	7	7	8	7
[Ni $(NHA)_2$ $(No_2)_2$]	7	6	8	7	8
[Cu (NHA) $(No_2)_2$]	6	7	7	8	7
[Cd (NHA) $(No_2)_2$]	7	9	8	9	8

Conclusion

The present study deals with the preparation and characterization of transition metal complexes of 3-Pyridine carboxylic acid Hydrazide ion five complexes were prepared with Cr(III) , Co(II), Ni(II), Hg(II), Cd(II). These structures are assigned on the basis of analytical, conductance, magnetic measurement, UV, and IR spectral data. Biological studies of these complexes show better activity compared to their respective ligands.

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