

SYNTHESIS, CHARACTERISATION AND SPECTRAL STUDIES OF SOME BI & TRIVALENT METAL IONS WITH PYRIDINE-4-CARBOXYLIC ACID HYDRAZIDE

ANIL KUMAR SINGH

Deptt. of Chemistry, H. D. Jain College (VKSU), Ara – 802301 (INDIA)

BIRENDRA KUMAR

Deptt. of Chemistry, Maharaja College (VKSU), Ara – 802301 (INDIA)

AND

ASHOK KUMAR GUPTA, SALINI PRIYA

Deptt. of Chemistry, Sri Arvind Mahila College (MU, Bodh Gaya), Patna – 800004 (INDIA)

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The synthetic, thermal, magnetic and spectral studies on complexes of pyridine-4-carboxylic acid hydrazide or isonicotinic acid hydrazide (INH) with nitrates of Fe(II), Co(II), Ni(II), Cu(II), Zn(II) & Al(III) were carried out in aqueous-ethanolic solutions. The structure of the prepared complexes have been suggested on the basis of their analytical datas, molar conductance, magnetic moments, infrared and electronic spectral studies. Thermogravimetric studies have been done to ascertain the nature of hydrated complexes and also their stoichiometry.

INTRODUCTION

A number of acid hydrazides and their derivatives have been reported [1-13] to display important role in various micro-organism and hence are of pharmacological importance. The therapeutic use of pyridine-4-carboxylic acid hydrazide or isonicotinic acid hydrazide (INH) interested us to study their complexing behaviour with nitrates of bi- and trivalent metals. In order to find out the existence of different types of a metal nitrate-INZ complexes in solution, conductometric titrations of the ligand solution with metal nitrate solutions were carried out. Attempts were then made to isolate the different possible complexes in solid state. For studying the behaviour of INZ-metal complexes on non-isothermal pyrolysis and to help in deciding whether the water molecule present in hydrated complexes are coordinated or present as interstitial molecules, thermogravimetric analysis were carried out. However, due to explosive nature and inflammability of nitrate-INZ complexes, the TGA studies were carried out on Co(III), Ni(II), Cu(II) and Fe(II) sulphate – INZ complexes. The metal nitrate-INZ complexes were characterised on the basis of analytical datas, conductance, magnetic measurements, i.r. and uv-visible spectral studies.

MATERIALS AND METHODS

Nitrates of Al(III), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) etc. used were of AnalaR grade. The nitrate of Fe(III) was prepared in the laboratory from freshly precipitated and well washed ferric hydroxide.

0.005 mole of metal nitrate was taken in a beaker and 5 ml water was added with stirring. About 30-40 ml of 90% ethanol was added and warmed on a steam bath to ensure complete dissolution of the salt. Now, 0.012 mole of isoniazide was dissolved in 50-60 ml of hot 95% ethanol. The hot metal nitrate solution was added slowly with stirring into the hot isoniazide solution. Characteristic coloured precipitate of complex compounds obtained immediately in case of Ni(II) & Cu(II). While in case of Zn(II), the solid complexes separated after 30-40 minutes of warming at 60-70°C and subsequent cooling. In case of Fe(II), Co(II) & Al(III), the reaction mixture was refluxed on water bath for 45 minutes and then the excess of the solvent was removed by distillation under reduced pressure. On cooling the concentrated solution, solid complexes were separated. The precipitate was filtered, washed first with small quantity of warm water, then with ethanol and finally with ether. The precipitate was dried first in vacuum desiccator over silica gel and then in an electric oven at 60-70°C.

Table 1

Compound	Colour	Decomp. temp. (°C)	Conductivity	Magnetic moment	% Analysis Found/(Calc.)			
					C	H	N	M
[Zn(NO ₃) ₂ .L ₂ .2H ₂ O]	White	190	12.8	Diamag.	28.64 (28.84)	3.51 (3.60)	22.31 (22.43)	12.88 (13.09)
[Fe(NO ₃) ₂ .L ₂ .2H ₂ O]	Deep green	229	38.5	3.20	29.09 (29.40)	3.39 (3.67)	22.93 (22.86)	11.26 (11.40)
[Co(NO ₃) ₂ .L ₂ .2H ₂ O]	Brick red	182	8.6	3.10	28.99 (29.21)	3.53 (3.65)	22.50 (22.72)	11.42 (11.95)
[Ni(NO ₃) ₂ .L ₂ .2H ₂ O]	Bluish grey	280	10.5	2.40	29.02 (29.23)	3.79 (3.83)	17.70 (17.87)	11.82 (11.91)
[Cu(NO ₃) ₂ .L ₂ .2H ₂ O]	Greenish brown	296	9.8	1.62	18.05 (18.16)	3.57 (3.78)	17.00 (17.65)	15.84 (16.02)
[Al(NO ₃) ₃ .L ₂ .2H ₂ O]	Light yellow	260	35.8	Diamag.	27.38 (27.53)	3.34 (3.47)	24.01 (24.10)	5.03 (5.16)

Table 2

Assignments	[Zn(NO ₃) ₂ .L ₂ .2H ₂ O]	[Fe(NO ₃) ₂ .L ₂ .2H ₂ O]	[Co(NO ₃) ₂ .L ₂ .2H ₂ O]	[Ni(NO ₃) ₂ .L ₂ .2H ₂ O]	[Cu(NO ₃) ₂ .L ₂ .2H ₂ O]	[Al(NO ₃) ₃ .L ₂ .2H ₂ O]
ν _{O-H}	3580-3300	3480-3240	3600-3300	3400-3300	3480-3300	3500-3300
ν _{NH-NH2(asym)}	3160	3160, 3110	3150	3260, 3220, 3150	3290, 3120	3210, 3190
ν _{NH-NH2(sym)}	3040, 3000	3100, 3040	3100, 2995	3100, 3080	3060, 3020	3100, 3040
ν _{C=O(asym)}	1640-1630	1602	1630	1660	1660	1650
ν _{NH-NH2(bend)}	1630	--	1610	1630	1635	1630
ν _{C=N(py)}	1440	1400	1400	1405	1405	1405
ν _{C=O(sym)}	1280	1330	1390	1350	1340	1335
ν _{N-N}	1150	1150	1165	1150	1150	1155
Py ring bre	1020	1000	1000	1010	1015	1005
Ring def	760	760	770	760	755	760

RESULTS & DISCUSSION

Some physical properties and analytical datas of the prepared complexes are listed in Table 1. The complexes are generally coloured. They are generally soluble in DMF and DMSO. Fe(II) & Al(III) complexes are more soluble than others.

Thermo Gravimetric Analysis : The TGA studies were originally carried out on metal nitrate-INZ complexes to ascertain the presence of water molecules and their nature (coordinated or uncoordinated). From the % loss in mass and the residue left at the completion of pyrolysis a cross checking of molecular formulae were sought. However, difficulties were faced due to the volatile and explosive nature of the complexes in general and Zn(II) & Al(III) complexes in particular. The non-isothermal decomposition of the biligated complexes $M(NO_3)_2 \cdot x(INZ) \cdot n2H_2O$, where $M = Fe(II), Ni(II), Co(II) \& Cu(II)$ in an atmospheric air was studied with the help of Chevenard and Santon thermo balance in the range of 25-600 °C. One of the two molecules of water was expelled from the complexes in the temperature range of 80 -137.5 °C, while the second one was expelled in the temperature range 137.5 -187.5 °C suggesting thereby that the former may be present as lattice water while the latter as coordinated central metal ions.

Molar conductance : Molar conductance of the complexes were measured in 0.5×10^{-3} M DMF solution at 27°C. Zn(II), Ni(II), Co(II) & Cu(II) complexes show molar conductance values in the range of 8.6 - 12.8 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$, indicate they are non-electrolytes, *i.e.*, both the nitrates ions are present in inner coordination sphere of the metal ions. While Fe(II) and Al(III) complexes show molar conductance values in the range of 35.8 – 38.5 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$, suggesting thereby that these complexes are 1 : 1 electrolytes [14].

Magnetic moment : The magnetic susceptibility measurements suggest the complexes of Zn(II) & Al(III) to be diamagnetic. On the other hand, the complexes of Fe(II), Ni(II), Co(II) & Cu(II) were found to have magnetic moment values 1.62 – 3.20 BM, suggest octahedral geometry of ligands around the metal ion.

Infrared spectra : The infrared spectra of the metal nitrate-INZ complexes are very complex, specially in the finger print region of 1700 – 600 cm^{-1} because of nearness and overlapping of several stretching and bending vibrations of the pyridine moiety, carbonyl, primary and secondary amino groups of the acid hydrazide moiety (– CONHNH₂), nitrate group (coordinated or un-coordinated) and water molecules. All the INZ-complexes were found to exhibit a bathochromic shift of ~ 40-100 cm^{-1} along with splitting and lowering of intensity in the $\nu_{\text{NH-NH}_2}$ symmetric and asymmetric stretching bands occurring at ~3300 and 3100 cm^{-1} respectively. This indicates that at least one of the two nitrogen atoms of the hydrazine moiety must be involved in coordination of the organic ligand with central metal ions. The small hypsochromic shift of the $\nu_{\text{N-N}}$ from 995 cm^{-1} by 5-25 cm^{-1} along with a bathochromic shift of 40-20 cm^{-1} , suggests the coordination of the INZ through the terminal hydrazine nitrogen. On the other hand, the bathochromic shifts observed in the $\nu_{\text{C=O}}$ (symmetric stretch) from ~1320 cm^{-1} by about 5-60 cm^{-1} , strongly suggests the coordination of INZ through the carbonyl oxygen atom of the acid hydrazide moiety also. The involvement of the tertiary pyridine ring nitrogen in coordination was ruled out because in all the complexes under study, the band due to $\nu_{\text{C=N}}$ (1450-1390 cm^{-1} in the ligand) either remains

constant or shows blue shift. Presence of non-ligand bands at $\sim 3600-3300\text{ cm}^{-1}$, followed by bands in the region of $\sim 1600\text{ cm}^{-1}$, and $850-750\text{ cm}^{-1}$ in all the complexes suggest the presence of both coordinated and un-coordinated (lattice) water in these complexes.

Electronic spectra : The electronic spectra clearly indicate that Fe(II), Ni(II), Co(II) & Cu(II) complexes have octahedral symmetry while Zn(II) & Al(III) complexes has square planar geometry. However, the magnetic moment values suggest a tetragonally distorted octahedral structure for the Fe(II) & Cu(II) complexes.

Structure & Bonding : On the basis of analytical data, molar conductance, magnetic moment, TGA, infrared and electronic spectral studies, following structures (Fig.1 & 2) are proposed to the complexes :

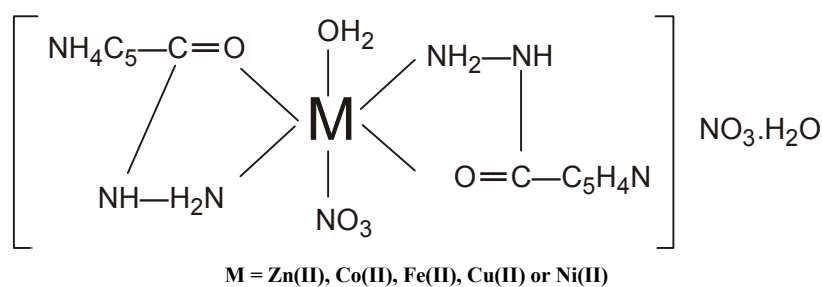


Fig. 1

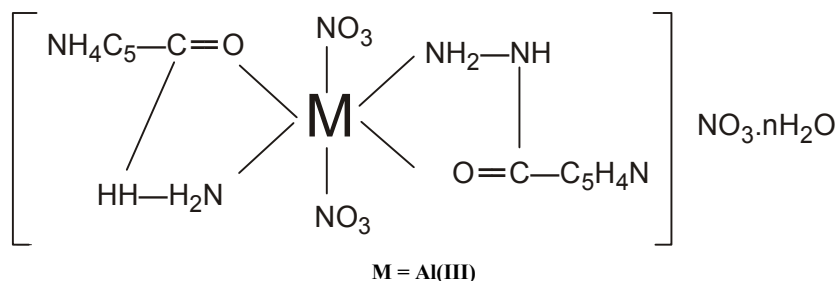


Fig. 2

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