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Syntheses of complexes of nickel (II) and manganese (II) nitrate with furancarbamide, benzoic acid hydrazide and its acetone hydrazone derivative

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ABSTRACT

Chelate of furancarbamide (FUR), benzoic acid hydrazide (BAH) and its acetone hydrazone (ABH) with nickel (II) and manganese (II) nitrate have been prepared. The complexes and ligands were characterized by Fourier transform infrared spectra analysis, electronic spectra analyses, conductivity, melting point, and solubility. The FTIR analysis indicated that the ligand (FUR) coordinated with the metal ions through the carbonyl oxygen, the azomethine nitrogen and amine nitrogen, while (ABH) coordinated through the carbonyl oxygen and azomethine nitrogen. The BAH ligand coordinated through carbonyl oxygen and the primary amine nitrogen. This is an indication that the ligands acted as tridentate and bidentate donors to the metal ions. The electronic spectra showed the complexes of Ni with ABH and BAH as octahedral geometry. The conductivity data showed the complexes as non electrolytes. Elemental analysis indicate that the complexes of BAH and ABH formed an $M:L_2$. X type with Ni and Mn formed an ML_1 type with ABH. The FUR complex formed with Mn is an ML_1X type complex and ML_3 type for Ni.

Key Word: benzoic acid hydrazide acetonebenzoic acid hydrazone, furancarbamide, metal ion, complex, ligand.

INTRODUCTION

We have previously reported the synthesis and characterization of copper II complexes obtained from furancarbamide (FUR), benzoic acid hydrazide (BAH) and its acetone hydrazone derivatives (ABH). The coordinating properties of various carbazone semicarbazones, hydrazones and Schiff base ligands have been reported (1-8). These compounds have been known for their intriguing chelating properties with transition metals. They have found application in pharmacology, electrochemistry, agrochemicals etc. In this paper we present the synthesis and characterization of FUR, BAH and ABH complexes with nickel II and manganese II nitrate using infrared spectroscopy, electronic spectra, conductivity and other physicochemical properties of the complexes with the aim of studying the nature of the chelating characteristics of the ligands with the transition metals and their possible applications.

MATERIALS AND METHODS

Reagents

All the reagents used for this study are of analytical grade and were obtained from Sigma Aldrich Company and BDH. They were used without further purification.

Preparation of ligands and metal complexes

The methods of preparation of ligands and metal complexes have been reported previously by Emmanuel et al. The weight of Ni and Mn salts and ligands varied according to the stoichiometric calculation shown in the scheme of synthesis of the metal complexes [14].

Synthesis of ligands

Synthesis of furancarbamide ligand by Cherkasov et al, (1970) method as in [8] 40ml of analar grade furfuraldehyde was measured and poured into a 250 ml flat bottom flask, 40g of urea added, followed by 9ml of distilled water. The mixture was heated on a water bath until a temperature of 60°C was reached, 1ml of 20% NaOH solution was then added and heating continued for another 20 minutes. The mixture was cooled on an ice bath and the precipitate filtered and washed with cold water (10-15°C) and then it was dried at a temperature between 40- 50°C. The dried powder obtained was washed with n-Hexane and recrystallized twice from methanol- water solution (30/70%v/v) and dried.

The ligand benzoic acid hydrazide and acetonebenzoic acid hydrazone were synthesized as described by Nwabueze 1996 [10].

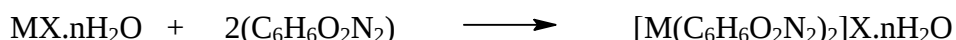
7ml (7.07g) of hydrazine hydrate was added in slight excess to 31.6ml ethylbenzoate in a 500ml round bottom flask, 100ml ethanol was then added and the mixture refluxed for 6 hours at 80°C. It was poured into a beaker and covered with a watch glass and left to crystallize. The crystals were filtered using a suction pump and recrystallized in ethanol, and dried in a desiccators over calcium chloride.

7.8g of hydrazide was dissolved in 100ml ethanol 4.14ml (3.3g) added and heated under reflux for 4 hours. The mixture was poured into a beaker, concentrated and left to crystallize. The crystal was filtered and recrystallized in methanol. The pure crystals were dried in a desiccators.

Synthesis of metal complexes

4.83g- 5.25g of furancarbamide was dissolved in 100ml of boiling distilled water in a 250ml beaker. 5.13g -4.72g (0.0189mol) of nickel (II) and Manganese (II) salts was dissolved in 50ml of distilled water respectively and added to the ligand solution and heating continued. It was heated for 10 minutes and then removed from heat and filtered immediately. The filtrate was concentrated and allowed to cool the resulting precipitate was filtered and dried. It gave a 7.5% yield.

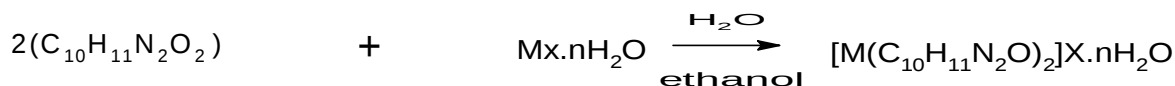
Scheme 1: reaction of preparation of furancarbamide metal complexes



(where M is Ni (II), Mn(II) and X is NO₃, n is 1,2 or 3)

Preparation of the complex of ABH

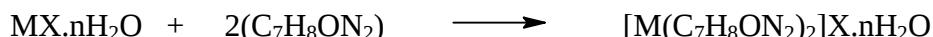
Scheme 2: reaction of preparation of acetone benzoic acid metal complexes



The complex of ABH was synthesized by weighing 0.89g – 0.87 in slight excess of ligand dissolved in 70ml ethanol in a 250ml beaker. Then 0.685g- 0.625g nickel and manganese salt dissolved in water was added to the ligand respectively with stirring. The crystalline precipitate formed were filtered and dried. Yield 69.01-98%

Preparation of benzoic acid hydrazide complex

Scheme 3: reaction of synthesis of benzoic acid hydrazide metal complexes



0.72g-0.78 of BAH was weighed and dissolved in 70ml of ethanol in a 250ml beaker. Then 0.72g (0.01M) of metal salts was weighed and dissolved in 50ml of distilled water respectively. This was then poured gently into the ligand solution with constant stirring. The resulting crystals were filtered and dried in a desiccator. Yield 68.82-28.86%

Physical measurements

Metal ions were determined by gravimetrically after removing the organic residue by digesting with a few drops of concentrated nitric acid. The infra red spectra data of ligand and complexes were recorded on Genesis II FTIR

spectrometer as kbr discs over a range of 4000-500cm⁻¹. The conductivity was determined on Jenway 4330 conductivity and pH meter in DMSO. Electronic spectra were determined on Unicam 9700 series UV/Visible spectrometer over a range of 200-900nm. Melting point analysis was done on Electrothermal melting point apparatus.

RESULTS AND DISCUSSION

The analytical data (Table 1) show the chemical formula and some physical constant of the complexes. The elemental analysis and derived chemical formula showed that the complexes of BAH and ABH for both Ni precipitated with two molecules of the ligands respectively while Mn precipitated with one molecule of ABH and two molecule of BAH. The complexes of FUR precipitated with three molecule of ligand with Ni and one molecule with Mn. The percentage yield of the complexes is in the range 69-100% for the ABH ligand, 28.86-68.89% for BAH ligand and 3.19-60.88% for FUR ligand.

Infrared spectra data for ligands and metal complexes

The relevant infrared spectra data is presented on Table 4. From the data the band due to $\nu(\text{C=O})$ vibration was observed at 1632.80cm⁻¹ for ABH, 1660.77cm⁻¹ for BAH and 1672.03 in the FUR parent ligands. These were lowered in the complexes by ca. -15.46- 34.72cm⁻¹. The lowering of the band due to the coordination of this site to the metal ion; Nakamoto (1997) state that compounds containing weakly coordinating ligand oxygen such as ketones, aldehydes, esters and some nitro compounds upon coordination show a shift in the absorption band of $\nu(\text{C=O})$ either to the lower or higher frequencies [9]. The band corresponding to $\nu(\text{C=N})$ stretching vibration was located in the ligand furancarbamide at 1532.87cm⁻¹, ABH at 1546.9cm⁻¹ it was lower by approximately -84.87 in the [Ni(FUR)] and increased by +48.48 and +3.04 in [Mn(FUR)] and [Mn(ABH)]. The lowering and increase in the vibration band due to $\nu(\text{C=N})$ in the complexes is attributed to the coordination of this site to the metal ion. This band was not observed in the [Ni(FUR)] complex this may indicate a strong coordination of this site to the metal ion [4, 9, 10]. The vibration band due to $\nu(\text{NH})$ was observed at 3199cm⁻¹ was lowered in the complexes of BAH by ca -10.56-29.85cm⁻¹. In the complexes of ABH and Fur it appeared broad and unresolved suggesting the presence of OH of water of crystallization. The presence of M-N was not observed as this was beyond the range of the machine used for this analysis.

Electronic spectra data

The electronic spectra were recorded in DMSO solution and absorption maxima in the UV/visible region are of the complexes is listed on Table 3 along with suggested assignment. The ligands showed absorption at 31,400 and 22,300cm⁻¹

The electronic spectra of Mn with BAH and FUR showed a ligand metal charge transfer (LMCT) transition at λ_{max} approximately 31,056 and 31,786cm⁻¹. Mn (II) with ABH showed a weak absorption around 1659.7cm⁻¹ it is assigned a d-d transition. The transition shown by the complexes is similar to reported transition of Mn [11-12]. Due to the doubly forbidden transition in the d⁵ configuration of manganese the absorption bands of the octahedral geometry are always very weak [11]

The spectra of Ni (II) with ABH and BAH showed absorption bands at 16,077 and 16,355cm⁻¹ respectively. These band are assigned the transition due to $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$. Ni with FUR showed not absorption in the visible region. This may be due to its partial solubility in DMSO, however absorptions were observed in the UV region in the range 52,029 - 38,138cm⁻¹. This may due to the interaction of the ligand with the metal ion. An octahedral geometry is proposed for the complex as shown from the analytical data and the green colour given by the complex [11].

The molar conductance measurements showed that the complexes are non-electrolytes (Table 4). They are insoluble in most organic solvents (Table 5) indicating a polymeric nature of the complexes.

Proposed names for complexes

1. [Ni(FUR)₃](NO₃)₂ ----- trifurancarbamide Nicke(II) nitrate
2. [Mn(FUR)](NO₃)₂ ----- furancarbamide Manganese (II) nitrate
3. [Ni(ABH)₂](NO₃)₂ ----- diacetonebenzoic acid hydrazone Ni (II) nitrate
4. [Ni(BAH)₂](NO₃)₂ ----- dibenzoic acid hydrazide Nickel (II) nitrate
5. [Mn(ABH)](NO₃)₂ ----- acetonebenzoic acid manganese (II) nitrate
6. [Mn(BAH)₂](NO₃)₂ ----- dibenzoic acid hydrazide Manganese (II) nitrate

Table 1: Analytical data of complexes

Compound	Formula	Formula weight	% metal comp	% C	% H	%N	Colour of the complex
[Ni(ABH) ₂](NO ₃) ₂	[Ni(C ₁₀ H ₁₁ N ₂ O ₂) ₂](NO ₃) ₂ . 5H ₂ O	632.0273	9.04(9.40)	38.55	3.55	8.99	Blue
[Ni(BAH) ₂](NO ₃) ₂	[Ni(C ₇ H ₉ N ₂ O ₂) ₂](NO ₃) ₂	565.0828	9.4(10.3)	14.87	1.60	4.95	Blue
[Mn(ABH)](NO ₃) ₂	[Mn(C ₁₀ H ₁₁ N ₂ O ₂)](NO ₃) ₂	354.1616	14.94(15.50)	33.91	3.13	7.90	Light brown
[Mn(BAH) ₂](NO ₃) ₂	[Mn(C ₇ H ₉ N ₂ O ₂) ₂](NO ₃) ₂ .5H ₂ O	406.1119	13.63(13.52)	20.70	4.71	6.89	Light brown
[Ni(FUR) ₃](NO ₃) ₂	[Ni(C ₆ H ₆ N ₂ O ₂) ₃](NO ₃) ₂ . 4H ₂ O	669.0668	8.75(8.17)	32.31	2.11	12.19	Green
[Mn(FUR)](NO ₃) ₂	[Mn(C ₆ H ₆ N ₂ O ₂)](NO ₃) ₂ .2H ₂ O	219.0902	18.60(18.58)	24.76	2.76	9.62	Brown

Value in brackets are the theoretical % metal composition

Table 2: Relevant Infrared spectra data

Compound	$\nu(\text{NH})(\text{OH})$ cm ⁻¹	$\nu(\text{C}=\text{O})$ cm ⁻¹	$\nu(\text{C}=\text{N})$ cm ⁻¹	$\Delta\nu(\text{C}=\text{O})$ cm ⁻¹	$\Delta\nu(\text{NH})$ cm ⁻¹	$\Delta\nu(\text{C}=\text{N})$ cm ⁻¹
FUR	3323	1672.03	1532.87	-	-	-
ABH	3218.34; 3024.48	1632.80	1546.96	-	-	-
BAH	3199	1660.77	-	-	-	-
[Ni(FUR) ₃](NO ₃) ₂	3349.5	1638.54	1448.00	-33.49	-	-84.87
[Mn(FUR)](NO ₃) ₂	3349.76	1625.70	1581.38	-46.	-	+48.48
[Ni(ABH) ₂](NO ₃) ₂	3386.15,3731.8	1601.93	-	-30.08	-	-
[Ni(BAH) ₂](NO ₃) ₂	3169.15	1626.06	-	-34.72	-29.85	-
[Mn(ABH)](NO ₃) ₂	3088.14	1617.34	1550.00	-15.46	-	+3.04
[Mn(BAH) ₂](NO ₃) ₂	3188.44	1638.59	-	-20.64	-10.56	-

Table 3: Electronic spectra data of metal complexes

Compounds	λ_{max} cm ⁻¹	Assignments
[Ni(FUR) ₃](NO ₃) ₂	33,138	LMCT
[Mn(FUR)](NO ₃) ₂	31,786	LMCT
[Ni(ABH) ₂](NO ₃) ₂	16,077	³ A ₂ g -> ³ T ₁ g(F)
[Ni(BAH) ₂](NO ₃) ₂	16,355	³ A ₂ g -> ³ T ₁ g(F)
[Mn(ABH)](NO ₃) ₂	16,597	d-d
[Mn(BAH) ₂](NO ₃) ₂	31,056	LMCT

Table 4: Conductivity and melting point data of metal complexes

Compounds	Conductivity	Melting point/decomposition temp
[Ni(FUR) ₃](NO ₃) ₂	0.044	214 ^D
[Mn(FUR)](NO ₃) ₂	0.022	41.2-52.6 ^M
[Ni(ABH) ₂](NO ₃) ₂	0.537	238-247 ^M
[Ni(BAH) ₂](NO ₃) ₂	0.556	231-250 ^D
[Mn(ABH)](NO ₃) ₂	1.850	85-87 ^M
[Mn(BAH) ₂](NO ₃) ₂	0.712	159-162 ^M

D ---- decomposed

M ---- melt

Table 6: Solubility study of complexes in some solvents

Compound	Hex	Ac	MeOH	Eoth	DMSO	H ₂ O
[Ni(FUR) ₃](NO ₃) ₂	PS	PS	INS	PS	S	INS
[Mn(FUR)](NO ₃) ₂	S	PS	PS	PS	PS	PS
[Ni(ABH) ₂](NO ₃) ₂	INS	INS	INS	INS	S	INS
[Ni(BAH) ₂](NO ₃) ₂	INS	INS	INS	INS	S	INS
[Mn(ABH)](NO ₃) ₂	INS	S	S	S	S	S
[Mn(BAH) ₂](NO ₃) ₂	INS	S	PS	PS	S	S on heating

CONCLUSION

We reported here the syntheses and characterization of new complexes of Ni (II) and Mn (II) with furancarboxamide (FUR), benzoic acid hydrazide (BAH) and its acetone hydrazone derivative ABH. The syntheses gave a bidentate function of the ligands. Ni (II) with FUR gave a chelate of the type ML₃ while BAH and ABH gave an ML₂ type. Mn (II) gave ML₁ type with FUR and ABH while BAH gave an ML₂ type complexes. An octahedral geometry is proposed for the complex compounds using the present experimental data.

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