

Polynuclear Complexes of Fumaric Acid Dihydrazide with Cu (II), Ni (II) and Co (II)

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Abstract. Metal chloride and metal sulphate complexes of fumaric acid dihydrazide (FZ) of the type $MX_2.FZ.H_2O$, [$M = Cu(II), Ni(II)$, and $X = Cl_2$ and $1/2 SO_4$] and $NiX_3.FZ.2H_2O$ have been prepared. Coordination occurs through oxygen of the $>C=O$ and nitrogen of the $-NH_2$ of the hydrazide group. A polymeric octahedral structure for MCl_2 complexes and sulphate bridged quadricoordinate structure for MSO_4 complexes has been proposed. TGA and DTA results are also reported.

1. Introduction

Hydrazide group $-C(=O)NH.NH_2$ coordinates to metal centre both through $>C=O$ and $-NH$ groups keeping secondary amino group undisturbed¹⁻³, forming the Metal-Oxygen and Metal-Nitrogen bonds simultaneously. Since fumaric acid exists in trans-form, its dihydrazide may also possess a trans-structure as shown in Fig. 1.

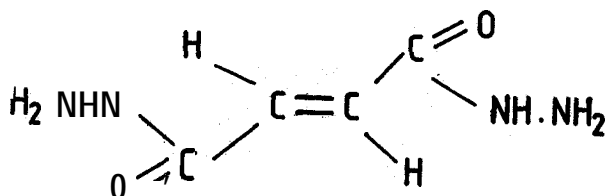


Figure 1. Structure of fumaric acid dihydrazide.

Being a bifunctional ligand, fumaric acid dihydrazide (FZ) is expected to form polynuclear complexes, coordinating through different $-C(=O)NH.NH_2$ groups to different

metal centres, similar to the metal complexes of oxalic, malonic, tere and **iso-phthalic** acids reported by us^{4,5}. In this paper, synthesis and characterization of some complexes of fumaric acid dihydrazide with chlorides and sulphates of bivalent copper, nickel and cobalt is reported. Thermogravimetric studies of these complexes have also been carried out.

2. Experimental

Fumaric acid dihydrazide was synthesised after **Fan**⁶ by reacting diethyl fumaric with hydrazine hydrate (M. P. 125°C (obs) **125-128°C** (lit)). Diethyl fumarate was prepared as described in the literature'. Metal complexes were prepared by adding warm alkaline aqueous solution of dihydrazide to alcoholic solutions of respective metal salts in the molar ratio 1 : 1. The **coloured** precipitates, which formed immediately, were suction filtered, washed with alcohol ether and air dried.

IR spectra in nujol mull were recorded on **Perkin Elmer** spectrophotometer Model 457 using **KBr** plates in the frequency range 4000 – 400 **cm⁻¹**. Electronic spectra in solid state were obtained using nujol mull on Systronics Spectrocolorimeter 103. Magnetic susceptibility measurements were carried out at room temperature by Gouy method using **Hg Co (CNS)₄** as calibrant. Diamagnetic corrections were applied by a method outlined by Mabbs and **Machin**⁸. Thermogravimetric study was carried out using Mom-Budapest Model by heating the samples at a rate of 10°C per minute.

3. Results and Discussion

3.1 *Physical Properties of Complexes* :

Elemental analysis and physical properties of the complexes are given in Table 1. These complexes are quite stable in air and are insoluble in water and common organic solvents. However, they decompose in mineral acids and are sparingly soluble in pyridine and DMF. Molecular weights of these complexes could not be determined owing to their insolubility in suitable solvents. The insolubility of these complexes may be due to their polymeric **nature**^{9,10}. Elemental analysis leads to the stoichiometry ***MX₂.FZ.H₂O*** (*M* = Cu (II), **Ni** (II) and X = **Cl**, 1/2 **SO₄**) and ***NiX₂.FZ₂.2H₂O*** for the complexes. The presence of one water molecule with **Cu** (II) and Co (II) complexes and two with **Ni** (II) complexes is confirmed from thermogravimetric data.

3.2 *Spectral and Magnetic Moment Studies* :

All the complexes showed a broad band around 3400 **cm⁻¹** due to **v-OH** which is absent in the spectrum of the parent ligand. Further, this band disappears from the spectra of dehydrated complexes. Weight loss equivalent to one water molecules for Cu (II)

Table 1. Analytical data and physical properties of complexes.

Compound	Colour	M %		Cl/S%		μ eff. B. M.
		cal.	found	cal.	found	
<i>CuCl₂.FZ.H₂O</i>	light green	21.42	21.10	23.92	23.10	2.00
<i>NiCl₂.FZ.2H₂O</i>	light buff	18.96	18.75	22.92	22.80	2.80
<i>CoCl₂.FZ.H₂O</i>	dark brown	17.54	17.40	24.32	24.20	4.38
<i>CuSO₄.FZ.H₂O</i>	faint green	19.75	19.80	9.95	9.80	1.80
<i>NiSO₄.FZ.2H₂O</i>	light green	20.19	20.05	9.56	9.50	3.00
<i>CoSO₄.FZ.H₂O</i>	pink	18.60	18.50	10.10	9.95	4.30

Satisfactory carbon, hydrogen and nitrogen analysis was obtained for ligand.

and Co (II) complexes and two for **Ni** (I I) complexes is evidenced on TG curve in the temperature range 100-1000°C, which is also supported by a corresponding endothermic peaks on DTA curves in the same temperature range indicating the presence of free water molecule.

The bands at 3270 cm^{-1} and 1670 cm^{-1} in the spectrum of ligand are due to $\nu\text{-NH}$ and $\nu > \text{C} = \text{O}$ respectively. For the complexes under investigation, $\nu\text{-NH}$ are lowered by $\approx 70\text{-}140 \text{ cm}^{-1}$ and $\nu > \text{C} = \text{O}$ are shifted to lower region by $40\text{-}50 \text{ cm}^{-1}$. This indicates that both ^{4,5} nitrogen of the amino group and oxygen of carbonyl group are involved in coordination. The coordination through $\text{C} = \text{O}$ group results in the decrease in double bond character and new band in the region 1200 cm^{-1} is assigned to $\nu - \text{C} - \text{O}$. The bands in the region $500\text{-}600 \text{ cm}^{-1}$ and $450\text{-}500 \text{ cm}^{-1}$ are due to $\nu - \text{M} - \text{O}$ and $\nu - \text{M} - \text{N}$ following Gowda and Janardhan¹¹.

The electronic spectra of **CuCl₂** complexes show a broad band around 595 nm which is characteristic of Cu (II) in a distorted octahedral environment¹². **NiCl₂** complex exhibits broad bands at 605 nm and 460 nm and **CoCl₂** complexes exhibits bands at 590 nm and 480 nm. **Ni (II)** and **Co (II)** octahedral complexes generally show two bands in the region $700 - 300 \text{ nm}^{13,14}$. The magnetic moment values (Table 1) of the complexes of **CuCl₂** (2.00 B.M.) **NiCl₂** (2.80 B.M.) and **CoCl₂** (4.38 B.M.) show one, two and three unpaired electrons respectively and are well within the range required for octahedral environment around metal centre¹⁵. Thus, in **MCl₂.FZ.nH₂O** complexes [$n = 1$ for Cu (II) and Co (II) and $n = 2$ for **Ni (II)**] the stoichiometry and bidentate nature of the ligand suggest a polymeric structure as shown in Fig 2. This contention is further supported by the insolubility of these compounds in common organic solvents.

The electronic spectra of **CuSO₄** complex exhibit a broad band at 565 cm^{-1} indicating the tetragonally distorted octahedral structure around **Cu** (II) atom. However, magnetic moment value corresponds to the values reported for square planer copper

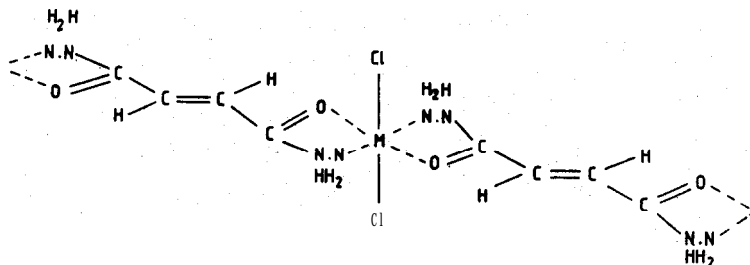


Figure 2. Proposed structure for metal chloride complexes.

complexes¹⁶. The splitting of the strong sulphate bands in the IR spectrum of the complex indicates the presence of bidentate bridged SO_4^{--} ion¹⁷. Hence, we are tempted to suggest a square planer polymeric structure for $CuSO_4.FZ.H_2O$ consisting of a bidentate ligand and bridging sulphate ion as shown in Fig 3.

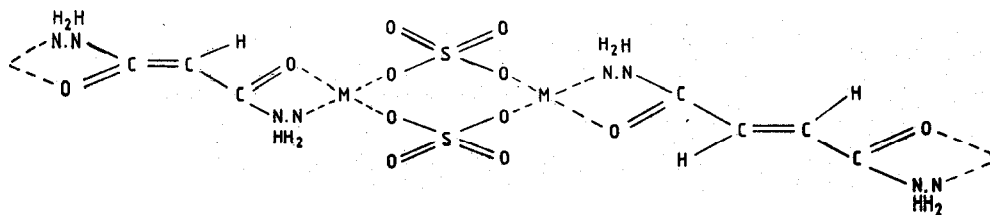


Figure 3. Proposed structure for metal sulphate complexes.

$NiSO_4$ and $CoSO_4$ complexes show a broad band at 590 nm and 595 nm respectively which is characteristic of four coordinated environment around the metal centre. Magnetic moment of $NiSO_4$ complex (3.00 B.M.) is within the range required for tetrahedral Ni (II) atom. The possibility of square planer or pseudo tetrahedral structure is eliminated because square planer Ni (II) complexes are diamagnetic¹⁸, and according to Sacconi¹⁹, pseudo tetrahedral complexes possess the magnetic moment in the range 3.2-3.3 B.M. Magnetic moment value 4.30 B.M. for $CoSO_4$ complex is comparable with values observed for tetrahedral Co (II) complexes. Besides, square planer Co (II) complex have the magnetic moment in the range 2.2-2.3 B.M.¹⁹ Thus, a tetrahedral symmetry around Co (II) is confirmed. The IR spectra of both $NiSO_4.FZ.2H_2O$ and $CoSO_4.FZ.H_2O$ indicate that sulphate group acts as a bridging bidentate ion. Hence, a quadricoordinate tetrahedral structure is suggested for $NiSO_4.FZ.2H_2O$ and $CoSO_4.FZ.H_2O$ as shown in Fig 3.

3.3 Thermogravimetric Analysis :

The DTA peaks for all the complexes are given in Table 2. All MCl, complexes decompose almost in imislar fashion. The endothermic peaks at 105-110°C complexes

Table 2. Thermal decomposition data MCl, and **MSO₄** complexes

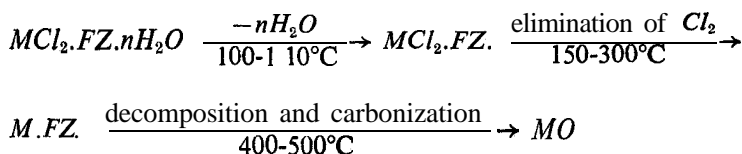
Compound	DTA peak temperatures (°C)				
CuCl₂.FZ.H₂O	105 (-)	195 (+)	310(+)	460(+)	
NiCl₂.FZ.2H₂O	100 (-)	310(+)	360(+)	410 (+)	
CoCl₂.FZ.H₂O	100 (-)	260 (+)	410 (+)	490 (+)	320 (+)
CuSO₄.FZ.H₂O	110 (-)	260(+)	390(+)	730(-)	
NiSO₄.FZ.2H₂O	100 (-)	350(+)	410(+)	500 (+)	710 (-)
CoSO₄.FZ.H₂O	100 (-)	225(+)	400(+)	700 (-)	

(-) and (+) signs after temperatures represent endotherm and exotherm respectively.

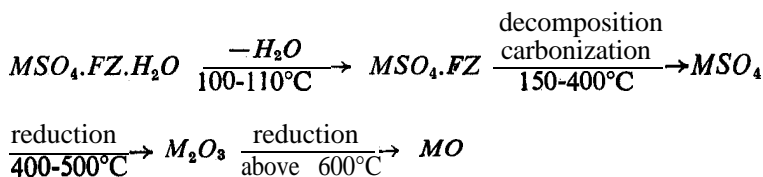
on DTA curve are due to loss of respective water molecules. The chlorine molecules are lost in the temperature range 150-300°C after which amine groups are eliminated in the temperature range 300-400°C followed by the decomposition and **carbonization** of the ligand which spreads over the temperature range 400-500°C. The formation of respective metal oxides occurs in the temperature range 500-600°C. The thermal stability of these complexes decreases in order of **CoCl₂.FZ.H₂O** > **NiCl₂.FZ.2H₂O** > **CuCl₂.FZ.H₂O**.

Thermal decomposition of metal sulphate complexes follow a similar pattern until respective anhydrous metal sulphates are formed after elimination of respective water molecules and decomposition of ligand molecule. Anhydrous **CuSO₄** and **CoSO₄** are first reduced to **MO₂** and then converted to respective metal oxides. **NiSO₄** decomposes in a slightly different manner. It is first reduced to **M₂O₃** around 490°C which is then converted to MO, in the temperature range 500-550°C which remains constant upto 700°C. Then, it begins to decompose at 720°C and finally gets converted to nickel oxide at 790°C. The endothermic peak at 790°C on DTA curve confirms the elimination of oxygen from MO. The mode of thermal decomposition of the complexes can be represented as follows :

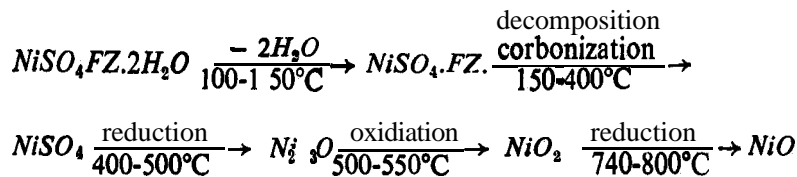
(i) **MCl₂.FZ.nH₂O** complexes



(ii) **MSO₄.FZ.H₂O** complexes **M = Cu (II), Co (II)**



(iii) $NiSO_4.FZ.2H_2O$ complexes



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