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Thermal Analysis of Nalidixic Acid Complexes with Cobalt (II), Vanadyl (II), Uranyl (II) and Ruthenium (III)

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Abstract: The thermal decomposition processes for metal complexes of nalidixic acid (NAL) viz: Co (NAL) OH , $VO(NAL)_2(H2O)_3$, UO_2 (NAL) $_2(H_2O)_2$, $Ru(NAL)_2Cl(H_2O)$ has been accomplished on the basis of TG, DTG and DTA studies, and the mechanism conforms to the stoichiometry of the complexes based on elemental analysis.
Keywords: TG, DTG, DTA, nalidixic acid, metal complexes

INTRODUCTION

Quinolones are complexing agents for a variety of metal ions including transition metal ions. The synthesis and characterization of metal complexes with quinolone antibacterial agents are of great importance for understanding the drug-metal ion interaction and for their potential pharmacological use. The activity of quinolones was decreased in the environment of certain metal ions by the formation of sparingly soluble metal complexes. The proposed reason for such maintenance might be the chelate bonding of the quinolone to the metal [1]. Nalidixic acid, $C_{12}H_{12}N_2O_3$ [(1-Ethyl-1, 4-dihydro-7-methyl-4-oxo-1, 8-naphthyridine-3-carboxylic acid), NAL, Fig.1], the first member of the quinolone carboxylic acid family of antimicrobials introduced into clinical practice, was used in the treatment of urinary tract infections [2,3]. Precise dissociation constants as well as stability constants for the binding of the nalidixate anion by several divalent metal ions were reported [4].

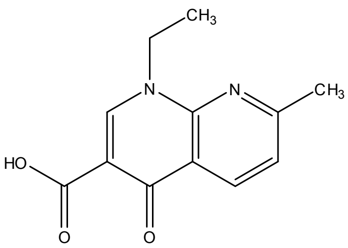


Fig.1. Structure of nalidixix acid

Nakano *et al*[5] reported the ability of quinolone nalidixic acid to form complexes with aluminum, magnesium and calcium ions. Complex formation between nalidixic acid, metal ion and DNA (at guanosine residues) has been suggested [6]. Ruthenium (III) complexes with some quinolone anti-bacteials (oxolinic acid, pipemidic acid, enoxacin and levofloxacin) have been synthesized and characterized by elemental analysis, spectral properties and thermal analysis [7]. Further, the presence of solvent molecules in the coordination sphere of ruthenium can be easily detected using the thermal analysis. We have reported previously the synthesis and characterization of metal complexes of nalidixic acid[8] as well as the complexation equilibria of nalidixic acid with proton and metal ions in aqueous organic mixtures [9].

EXPERIMENTAL

Nalidixic acid, $C_{12}H_{12}N_2O_3$ (1-Ethyl-1, 4-dihydro-7-methyl-4-oxo-1, 8-naphthyridine-3-carboxylic acid, NAL) was procured from Sigma Aldrich. The preparation and characterization of complexes of nalidixic acid has been reported earlier [8]. The thermogravemetric (TG), differential thermogravemetric (DTG) and differential thermal analysis (DTA) studies were carried out on Perkin Elmer (Pyris Diamond) at Institute Instrumentation

Centre, Indian Institute of Technology, Roorke. Al_2O_3 was used as standard. The measurements were made at a heating rate of 10 ° C min $^{-1}$ and a chart sped of 20 cm per hr $^{-1}$ in an atmosphere of nitrogen (flow rate 400 ml $^{-1}$). The representative curve of TG, DTG and DTA for Co (NAL) OH complex is shown in Fig. 2.

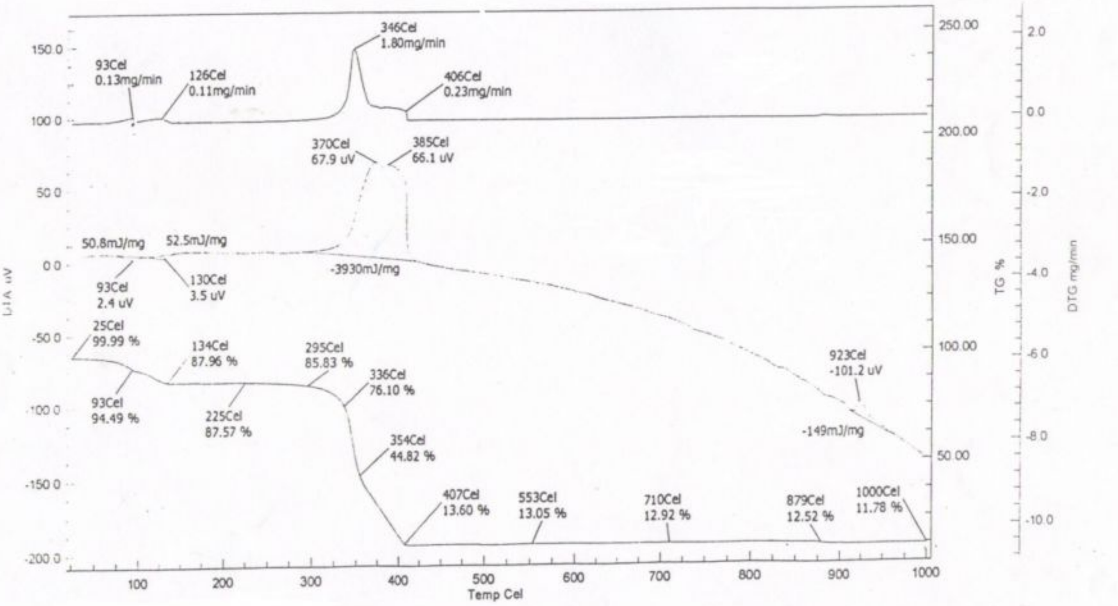
RESULTS AND DISCUSSION

The metal complexes of nalidixic acid (NAL) were studied by thermogravemetric analysis from ambient temperature to 1273 °C in nitrogen atmosphere. The TG curves are shown as % mass loss versus temperature, the DTA curves as the rate of loss of mass versus temperature, and DTG curves as enthalpy changes. The TG, DTG and DTA profiles of NAL are given in Fig. 2. The endothermic peak at 220 °C in the DTA curve is due to melting of the NAL and the heat of fusion is 0.435 J mol $^{-1}$. The parameters of TG curve shows that NAL decomposes in two steps over the temperature range 100 - 332 °C and 333 - 528 °C. The sharp mass losses 94.67 % occur in the temperature range 100 - 332 °C. The DTG profile shows one endothermic peak with maximum at 314°C. DTA curve also showed that heat absorbed corresponding to endothermic decomposition at 314 °C is 0.537 J mol $^{-1}$.

Co (NAL) OH Complex

The TG, DTG and DTA profiles of cobalt (II)-NAL complex are given in Fig. 3. The first mass loss about 12.04 % occurs in temperature ranges 25 - 134 °C. The next exothermic decomposition of the complex occurs in 296 - 407 C with 13.00 % residual mass which change to about 11.78 % in 408 - 1000 °C. The heat evolved in decomposition of complex in temperature range 296 – 407 °C was found to be 6.397 J mol $^{-1}$. The DTG curve showed that two simultaneous decompositions occurred during this stage. The thermal decomposition process can be shown below:

$$\mathbf{Co\ (NAL)OH} \xrightarrow[\mathbf{25\ -\ 134\ °C}]{\mathbf{-\ OH}} \mathbf{Co(NAL)} \xrightarrow[\mathbf{296\ -\ 1000\ °C}]{} \mathbf{Co}$$



TG, DTA and DTG curves of Co(II)-NAL complex

Fig.2

Table 1. The character parameters of TG, DTG and DTA curves of NaL and its metal complexes.

Compound	TG		DTG	DTA	Remarks
	T_{range}/°C	Total mass loss %	Peaks/°C	Peaks/°C	
$C_{12}H_{12}N_2O_3$ (NAL)	100-332 333 - 528	94.67 100	314[b]	220 (endo) 314 (endo)	Melting of NAL Endothermic decomposition
Co (NAL) OH	25-134 134-295 296-336 337-407 408-1000	12.04 14.17 23.90 86.40 88.22	93 126 346 406	93(endo) 130 (endo) 370 (exo) 385 (exo)	Two simultaneous exothermic decomposition of complex occurs in 296-407 °C
$VO(NAL)_2(H2O)_3$	22-162 163-305 306-443 444-578	8.23 83.16 51.32 86.44	165 387 394 456-553[b]	394 (exo) 473-557 (exo)	Loss of three water molecules up to 350°C Three simultaneous exothermic decomposition of complex occurs in 306-578 °C
UO_2 (NAL) $_2(H_2O)_2$	23-350 351-490	4.60 61.47	351-490[b] with peak at 407	454 (exo)	Loss of two water molecules up to 350 °C. Decomposition of the complex occurs in temperature range 350 – 490 °C
$Ru(NAL)_2Cl(H_2O)$	25-100 101-455	2.51 83.31	282[b]	199-455 (exo)	Loss of one water molecules up to 100°C Exothermic decomposition of complex occurs in 199-455 °C

b - broad

$VO(NAL)_2(H_2O)_3$ Complex

The TG, DTG and DTA profiles of the complex are shown in Fig. 4. The first mass loss in temperature range 22 - 162 °C is of the order of 8.23 % (expected value 9.25 %) which corresponds to the removal of three water molecules. The complex decomposes in three stages in the temperature ranges (163 - 305 °C, 306 - 443 °C and 444 - 578 °C) as indicated by TG curve. The residual mass of the order of 13.56 % (expected 14.21 %) is due to formation of VO_2 which remains stable up to 690 °C. DTA profile shows two peaks with maxima at 394 C and 473 - 557 °C.

The thermal decomposition process can be shown below:

$$VO(NAL)_2(H_2O)_3 \xrightarrow[22\text{ - }162\ °C]{-3H_2O} VO(NAL)_2 \xrightarrow[163\text{ - }578\ °C]{} VO_2$$

UO_2 (NAL) $_2(H_2O)_2$ Complex

The TG, DTG and DTA profiles of the complex are shown in Fig. 5. The mass loss 4.6 % corresponds to loss of two water molecules up to 350 °C. The single decomposition of the complex occurs in first step in the temperature range 350 – 490 °C with a mass loss of 61.47 %. The heat liberated during this step was 5.644 J mol $^{-1}$ which corresponds to the exothermic peak with maximum at 454 °C. The broad nature of DTG and DTA curves corresponding to this step indicates that a number of reactions are taking place simultaneously without giving stable intermediate species. The residual mass in the temperature range 490 - 998 °C was found to be 38.53 (expected 37 %) and corresponds to end product U_3O_8. Based on these observations, the thermal decomposition process can be shown below:

$$UO_2(NAL)_2(H_2O)_2 \xrightarrow[23\text{ - }350\ °C]{-2H_2O} UO_2(NAL)_2 \xrightarrow[351\text{ - }998\ °C]{} U_3O_8$$

$Ru(NAL)_2Cl(H_2O)$ Complex

The TG curve (Fig.6) of Ru (III)-NAL complex reveals mass loss of 2.51 % (expected 2.90 %) in the temperature range 25 - 100 °C. The total mass loss calculated from TG curve is about 83.7 % up to 455 °C. DTA curve for this complex shows one broad exothermic peak in the temperature range 200 - 455 °C. Based on these observations, the probable thermal decomposition scheme is given below:

$$Ru(NAL)_2Cl(H_2O) \xrightarrow[25\text{ - }100\ °C]{-H_2O} Ru(NAL)_2Cl \xrightarrow[101\text{ - }455\ °C]{} Ru$$

To summarize, it is concluded that in these complexes, the mass loss as a function of temperature occurs as expected from the molecular formula as deduced from elemental analysis.

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