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Thermal Studies Of UO_2 (VI) Complexes With Some Nitrogen Donor Ligands

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Abstract
We report here series of new $U0_2$ (VI) complexes with Schiff base having general composition UO_2X_2.nl (X=CH_3COO,NO_3, n=2), Where L = Schiff base
The complexes were characterized on the basis of analytical conductance, molecular weight and spectral studies. The Schiff base behaves as neutral monodentate ligand which coordinates to the central metal atom through azomethine nitrogen.
***Key words**: Schiff base ligand, UO_2 (VI)*

1- INTRODUCTION

Thermal studies of various substances including metal complexes have been of great interest for many workers [1-4]. Thermal decomposition kinetics parameters viz. E*, A and ΔS* have been computed for transition metal complexes [5-7] and for thorium (IV) and dioxouranium (VI) complexes [8-11].Although it was not possible to study of thermal properties of all the metal complexes due to some unavoidable reasons, the studies were carried out for representative complexes of the series. The complexes studied are $UO_2(NO_3)$. 2(4CABCA), UO_2 $(NO_3)_4$.2(2MCABCA)

(A) Thermal Studies for Complexes: Thermogravimetric analyses (T.G.A.) of the complexes were recorded on thermo-balance Mettler Toledo Star system at the rate 10^0c/min. at Regional Sophisticated Instrumentation. The rate of loss of mass vs temperature (DTG) plots were used as TGA curves. The decomposition data for the complexes are in corporatedTables 1-4.

(B) Thermal Decomposition Kinetics Studies: Freeman-Carroll (F.C.) [12], Coats-Redfern (C.R.) [13] and Horowitz-Metzger (H.M.)[14],methods were used to evaluate different kinetics parameters from the TGA curves as furnished in Tables1-2. The corresponding kinetics parameters are given in Tables 3-4.

Table. 1: Thermal decomposition data for 4-NN-bis-2'- cyanoethylaminobenzylideneo-chloroaniline complex with dioxouranium (VI) nitrate.

Complex	Stage of decom-position	Reaction	Peak Temp. in DTG(^{0}C)	Temp. Range in DTG (^{0}C)
$UO_2(NO_3)_2$.2(4 CABCA)	I	$UO_2(NO_3)_2$.2(4CABCA) →UO_2 $(NO_3)_2$. 1.5(4CABCA)	270	240-285
	II	$UO_2(NO_3)_2$. 1.5(4CABCA) →[UO_3] →U_3O_8	579	545-640

Table. 2: Thermal decomposition data for 2-Methyl -4-NN-bis-2'-cyanoethylaminobenzylideneo-chloroaniline complex with dioxouranium (VI) nitrate.

Complex	Stage of decom-position	Reaction	Peak Temp. in DTG(^{0}C)	Temp. Range in DTG (^{0}C)
$UO_2(NO_3)_2$. 2(2MCABCA)	I	$UO_2(NO_3)_2$.2(2MCABCA) →$UO_2(NO_3)_2$.1.6(2MCABCA)	160	80-180
	II	$UO_2(NO_3)_2$.1.6 (2MCABCA) →[UO_3] →U_3-O_8	520	455-580

Table. 3: Decomposition kinetics parameters of complex UO_2 $(NO_3)_4$. 2(4CABCA) obtained using equations of Freeman Carroll (FC) Coats Red fern (CR) and Horowitz-Metzger (HM)

Complex	Decomposition stage	Equation	Parameters		
			E*(KJMol^{-1})	A(S^{-1})	ΔS*(JK Mol^{-1})
$UO_2.(NO_3)_4$.2(4CABCA)	I	FC CR HM	32.19 35.29 41.66	- 6.86×10^4 7.54×10^4	- -112.85 -112.06
	II	FC CR HM	35.72 37.87 33.68	- 1.22×10^4 1.31×10^4	- -134.17 -133.58

Table.4: Decomposition kinetics parameters of complex $UO_2(NO_3)_2.2(2MCABCA)$ obtained using equations of Freeman Carroll (FC) Coats Red fern (CR) and Horowitz-Metzger (HM)

Complex	Decomposition stage	Equation	Parameters		
			E*(KJMol^{-1})	A(S^{-1})	ΔS*(JK Mol^{-1})
$UO_2(NO_3)_2.2(2MCABCA)$	I	FC CR HM	27.38 25.70 31.44	- 3.09×10^3 3.43×10^3	- -91.96 -91.95
	II	FC CR HM	25.00 32.66 35.50	- 4.79×10^4 5.68×10^4	- -115.93 -114.51
	III	FC CR HM	27.58 24.55 28.40	- 4.93×10^5 9.66×10^5	- -141.64 -136.05
	III	FC CR HM	25.58 24.75 28.56	- 4.93×10^5 9.66×10^5	- -141.64 -136.05

General mechanism for decomposition of the complexes is proposed on the basis of their thermal decomposition data which is given as under.

2- URANYL (VI) COMPLEXES:

Step-I

$$UO_2(L)_n.X_2 \xrightarrow[decomposition]{In\ stage\ of} UO_2(L)_{n-x}.X_2 +_x L$$

($X=^-NO3$) (x=1 to 2) , (n=2,or 4) , (L=2MCABCA , 4CABCA,)

Step-II

$$UO_2(L)_{n-x}.X_2 \xrightarrow[In\ presence\ of\ O_2]{-2x,-(n-x)} [UO_3] \longrightarrow U_3O_8$$

On the basis of aforementioned mechanism the relative bond strength of M-L and M-X bonds is being proposed. It is inferred that M-L Coordination bond is relatively weaker than M-X (metal-anion bond).

This can be understood more clearly by taking an example of Complexes UO_2 (NO3)2.2(2MCABCA. In this case there are three stages of decomposition. In first stage, total weight loss is because of loss of approximate 02 ligand molecules from the complex which is favored by the activation energy value of this stage. Second stage of decomposition involves the loss of rest of the ligands and anion resulting in the formation of oxide U_3O_8 Entropy of activation (ΔS*) in both the stages is negative, it also supports aforementioned decomposition stages.Synthesis and Thermal study of UO_2 (VI) Complexes are reported by Oxana and associates [15].

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