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Thermo Gravimetric Analysisof Th (IV) Complexes With Some Nitrogen Donor Ligands

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Abstract
We report here series of new Th (IV) complexes with Schiff base having general composition Th X_4.nL ($X=NO_3$, 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 ligands which coordinate to the central metal atom through azomethine nitrogen.
***Key words**: Schiff base ligand, Th (IV).*

1- INTRODUCATION

Thermal studies of various substances including metal complexes have been of great interest for many workers [1-7]. Thermal decomposition kinetics parameters viz. E*, A and ΔS* have been computed for transition metal complexes [8-12] and for thorium (IV) and dioxouranium (VI) complexes [13-20].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 $Th(NO_3)_4$.4(4CABCA), $Th(NO_3)_4$ .4(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 1-2

(B) Thermal Decomposition Kinetics Studies : Freeman-Carroll (F.C.) [21], Coats-Redfern (C.R.) [22] and Horowitz-Metzger (H.M.)[23],methods were used to evaluate different kinetics parameters from the TGA curves as furnished in Tables 1-2.The corresponding kinetics parameters are given in Tables 3-4.

Table. 1: Thermal decomposition data for -4-NN-bis-2'-cyanoethylaminobenzylidene p-toludine complex with thorium (IV)nitrate.

Complex	Stage of decomposition	Reaction	Peak Temp. in DTG (^{0}C)	Temp. Range in DTG (^{0}C)
$Th(NO_3)_4$. 4 (4CABCA)	I	$Th(NO_3)_4$.4(4CABCA)→$Th(NO_3)_4$. 3.2(4CABCA)	239	221-274
	II	$Th(NO_3)_4$3.6(4CABCA) →$Th(NO_3)_4$. 3(4CABCA)	471	428-498
	III	$Th(NO_3)_4$.3.1(4CABCA) →$Th(NO_3)_4$. 1.50(4CABCA)	560	540-600
	IV	Th $(NO_3)_4$. 1.50(4CABCA) → ThO_2	710	695-720

Table. 2: Thermal decomposition data for 2-Methyl -4-NN-bis-2'-cyanoethylaminobenzylidene p- toludine complex with thorium (IV) nitrate.

Complex	Stage of decomposition	Reaction	Peak Temp. in DTG (^{0}C)	Temp. Range in DTG (^{0}C)
$Th(NO_3)_4$. 4 (2MCABCA)	I	$Th(NO_3)_4$.4(2MCABCA)→$Th(NO_3)_4$. 3.8(2MCABCA)	255	223-270
	II	$Th(NO_3)_4$3.8(2MCABCA) →$Th(NO_3)_4$. 3.1(2MCABCA)	410	428-442
	III	$Th(NO_3)_4$.3.1(2MCABCA) →$Th(NO_3)_4$. 1.66(2MCABCA)	540	533-580
	IV	Th $(NO_3)_4$. 1.66(2MCABCA) → ThO_2	688	670-728

2- Freeman-Carroll (FC) method:

Freeman-Carroll had proposed a method for the evaluation of kinetic parameters using an equation which is represented as

$$\frac{-dx}{dt} = A \exp \{-E^*/RT\}X^n \quad \ldots\ldots(1)$$

Where the symbols have their usual meanings, for the general equation :

$$aA \rightarrow bB + cC$$

Equations (1) have been solved by the authors [21]. The results have been used to study reaction kinetics in the form of:

$$\frac{-E^*/2.303\ R\ (\Delta T^{-1})}{\Delta \log Wr} = -n + \frac{\Delta \log (dw/dt)}{\Delta \log Wr} \quad \ldots\ldots\ldots(2)$$

Where Wr = Wc – W, Wc = weight loss at completion of the reaction and W = weight loss up to time t

Equation (2), suggests that on plotting

$$kl\ \frac{\Delta \log(dw/dt)}{\Delta \log Wr} \quad Vs \quad \frac{(\Delta T^{-1})}{\Delta \log Wr}$$

For the decomposition reaction, order 'n' can be obtained as intercept of the linear graph and E*/2.303 as slope from where E* can be computed.

On applying this equation to the thermal data for representative thorium (IV) and dioxouranium (VI) complexes it was inferred

that the thermal reactions which are mentioned in Tables 1-4 are of order unity. E* values, for each were evaluated from the slopes of the Freeman-Carroll plots which are furnished in Tables 5-8.

3- Coats –Redfern (CR) method: For the study the kinetics of thermal decomposition reactions, another method, was proposed by Coats and Redfern [22]. These author had given some relations among α the fraction of compound at time‘t’ and some other parameters to study the kinetics. The relations are:

$$\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log\left\{\frac{AR}{aE} * 1-2RtE*-E*2.3RT\right.$$

and $$\log\left\{\frac{-\log(1-\alpha)}{T^2}\right\} = \log\left\{\frac{AR}{aE} * \left(\frac{1-2Rt}{E^*}\right) - E*2.3RT\right.$$

Where α is fraction of the compound at time ‘t’ and it is equal to $(W_0\text{-}W)/(W_0\text{-}W_f)$

Where W_0, W and W_f are initial weight, weight at time ‘t’ and the final weight of the sample respectively and ‘a’ is the rate of heating.Other symbols have usual meanings.

These equations were applied to the decomposition reaction of the selected complexes and it was observed that the plots of

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] \text{ Vs } 1/T$$

are straight lines. This justifies that these reactions may have order unity (i.e.n=1) as observed on the basis of Freeman-Carroll method. E*values for these are obtained from the slopes of Coats-Redfern plots as (-E*/2.3R) and ‘A’ from the intercepts of the plots

for n = 1 …..(4)

ΔS^* values for the reactions are obtained from the following equation

$$\Delta S^* = R \ln \{Ah/kTs\} \quad \text{…..(6)}$$

for n = 1 …..(5)

Results for Coats-Redfern method for the complexes are given in

Tables 5-8

4- Horowitz-Metzger (H.M.) method:

Horowitz-Metzger method is an illustrative of approximate method. The authors derived a relation for first order thermal reactions which may be written as:

$$\log\{\log W\alpha / Wr\} = \frac{F*\theta}{2.3RT_s^2} - \log 2.3 \quad \text{……(7)}$$

Where θ=T-T_s and T_s is the peak temperature and dw/dt is maximum in the DTG curve.

In the present study the approximation method was tried to the representative complexes.

It was observed that the plots of log {log (Wα/Wr)} vs θ are straight lines. E* for these thermal decomposition reactions are calculated from the slopes of these plots and A is calculated using the following equation

$$\frac{E*}{RT_s^2} = \frac{A}{a\exp\{-E*/RT_s\}} \quad \text{……(8)}$$

The results of kinetics parameters are incorporated in Tables 3-4.

In the concluded that the values of E*, A and ΔS^* are appreciable and E* values are sufficiently high while ΔS^* have negative values. The values are comparable with previous observations.

Horowitz-Metzger method gives [23] reasonably good results but it is mathematically less accurate than the integral methods. Coats- Redfern method

seems to be more accurate but considerably time consuming.

Table. 3: Decomposition kinetics parameters of complex $Th(NO_3)_4.4(4CABCA)$ 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$^{-1)}$
$Th(NO_3)_4.4(4CABCA)$	I	FC CR HM	35.15 37.11 42.82	- 7.37×10^4 6.38×10^4	- -52.67 -43.36
	II	FC CR HM	21.18 30.31 31.13	- 1.91×10^4 1.78×10^4	- -66.64 -58.46
	III	FC CR HM	26.28 25.12 35.23	- 9.81×10^5 8.91×10^5	- -125.60 -130.06
	IV	FC CR HM	34.84 36.45 45.82	- 3.30×10^4 3.19×10^4	- -137.61 -111.16

Table. 4 : Decomposition kinetics parameters of complex $Th(NO_3)_4.4(2MCABCA)$ 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})
$Th(NO_3)_4.4(2MCABCA)$	I	FC CR HM	35.11 39.41 45.92	- 7.37×10^4 6.38×10^4	- -54.68 -45.36
	II	FC CR HM	22.13 26.31 38.13	- 1.91×10^4 1.78×10^4	- -63.64 -59.46
	III	FC CR HM	28.22 29.12 30.21	- 9.81×10^5 8.91×10^5	- -135.60 -140.06
	IV	FC CR HM	36.84 39.48 40.14	- 3.30×10^4 3.19×10^4	- -127.61 -121.16

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

5- Thorium(IV) Complexes:

Step-I

$$Th\ (L)_n.X_4 \xrightarrow[decomposition]{In\ stage\ of} Th(L)_{n-x}.X_4 + {}_xL$$

(n=4) (x= 4)

(L=4CABCA, 2MCABCA)

($X=NO_3^-$)

Step-II

$$Th\ (L)_{n-x}.X_4 \xrightarrow[In\ presence\ of\ O_2]{-4x,-(n-x)L} ThO_2$$

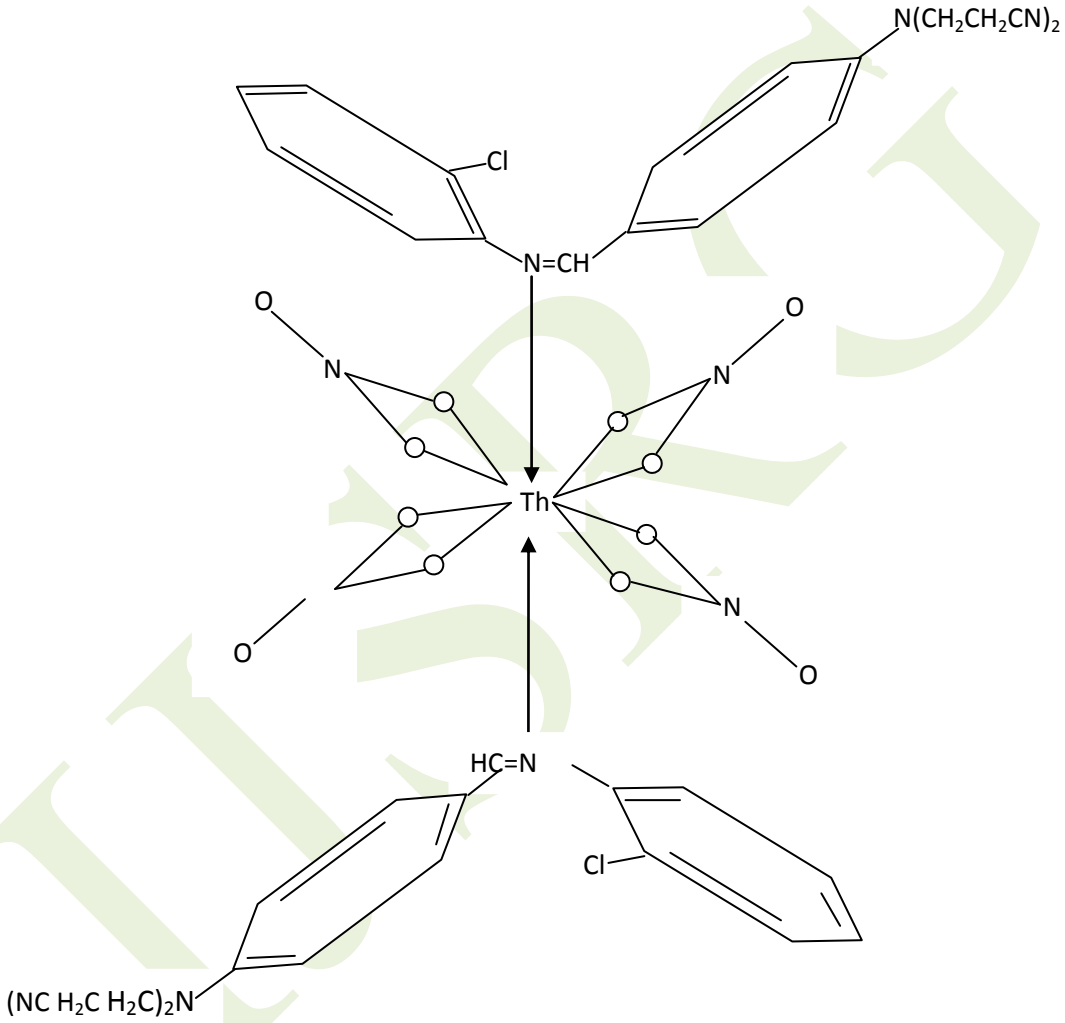
On the basis of aforementioned mechanism the relative bond strength of M-L and M-X bonds is being proposed. It is inferred that M-L Coordination bond is relatively weaker than M-X (metal-anion bond).

This can be understood more clearly by taking of examples of Complexes . In this case there are four stages of decomposition. In first stage, total weight loss is because of loss of approximate 04 ligand molecules from the complex (Refer Table 1) 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 ThO_2. Entropy of activation (ΔS^*) in both the stages is negative, it also supports aforementioned decomposition stages.Synthesis and Thermal study of Th(IV) Complexes are reported by Oxana and associates[24].

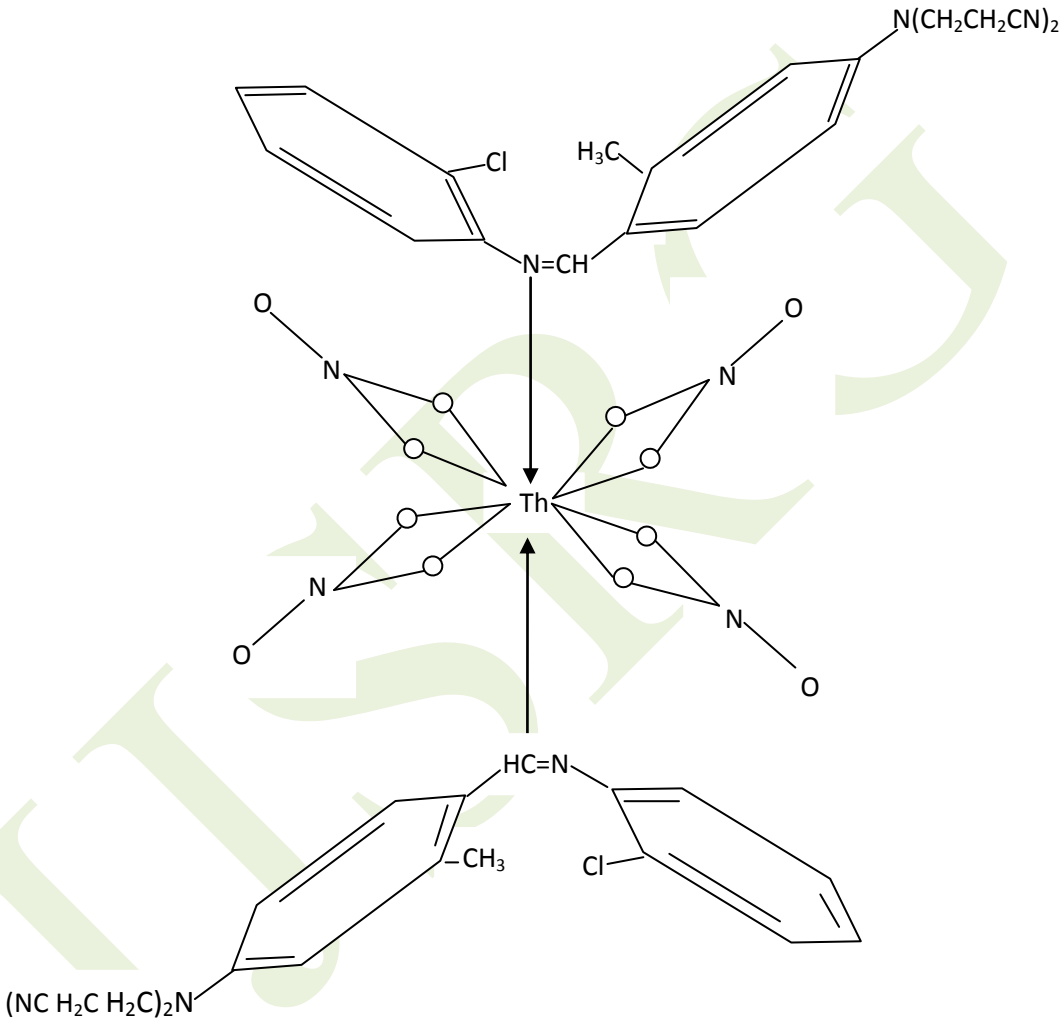
6- Suggested Structures of Complexes :Thorium (IV) Complexes :

The preferred coordination number for Th (IV) is either 6, 8 or 10 in thorium (IV) complexes . In case of nitrato complexes, the nitrato groups are present inside the coordination sphere and are bidentate in nature as discussed in chapter – 5 in the IR studies portion, therefore the coordination number 10 is suggested for central Th (IV) metal atom. It has been observed from a single crystal X-ray structure determination of $Th(NO_3)_4.5H_2O$ that the nitrato groups are linked to the thorium through two oxygen atoms.

1. $Th(NO_3)_4.4(4CABCA$



2 $Th(NO_3)_4.4(2MCABCA)$



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