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Thermal decomposition behaviour of some trivalent transition and inner-transition metal complexes of triethanolamine

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Abstract

Thermal decompositions of triethanolamine complexes of Cr(III), Fe(III), Ru(III), Rh(III), La(III), Ce(III) and Nd(III) in dynamic nitrogen and air atmosphere were studied by DTA, TG and DTG. The final solid decomposition products were identified by X-ray powder diffractometry. The thermal stability of the complexes in the solid state was discussed. These complexes exhibit a considerable thermal stability and the stability order was found to be: Nd(III) > La(III) ≅ Ce(III) > Cr(III) > Fe(III) > Ru(III) > Rh(III).

Keywords: DTA; Triethanolamine complex; TG; Trivalent metals; XRPD

1. Introduction

Triethanolamine [$N(CH_2CH_2OH)_3 = NTEH_3$] has been used as a coordinating agent and shown to form air-stable, crystaline complexes with mono-, di- and trivalent transition and representative metal ions [1–4]. Most of the solid metal complexes of $NTEH_3$ are of the high-spin type and have an octahedral geometry in which the molar ratio of the metal ion to ligand is 1 : 2 and the $NTEH_3$ molecule acts a tridendate ligand [5].

We first reported the thermal decomposition of the first row divalent transition metal complexes of $NTEH_3$ and discussed their thermal stability in relation to the chemical

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structure [6]. The present paper describes the thermal behaviour of $NTEH_3$ complexes of some trivalent transition and inner-transition metal ions, Cr(III), Fe(III), Ru(III), Rh (III), La(III), Ce(III) and Nd(III) in flowing nitrogen and air atmosphere.

2. Experimetnal

2.1. Preparation of complexes

According to the procedure described previously [1], 100 ml isopropanol of solution of 0.02 mol $NTEH_3$ and 200 ml warm (60°C) isopropanol solution of 0.01 mol metal salts (MCl_3 or $M(NO_3)_3$) were mixed together and stirred under nitrogen atmosphere for 20 to 30 min. After the formation of the complex crystals, the mixture was filtered off and the crystals were washed with ethanol and acetone respectively and dried in vacuo. The Cr(III) and Fe(III) complexes of $NTEH_3$ were synthesized by Sen and Dotson, previously [1]. The Ru(III), Rh(III), La(III), Ce(III) and Nd(III) complexes were first prepared and the analytical data for these complexes studied are given in Table 1 [7].

2.2. Instrumental

DTA, TG and DTG data were simultaneously obtained using a RIGAKU TG8110 thermal analyser combined with a TAS 100 thermogravimetric analyser. The measurements were carried out in dynamic nitrogen and air atmosphere at a flow rate of 80 ml min^{-1} up to 1000°C. The heating rate was 10 K min^{-1} and sintered α-Al_2O_3 was used as a reference material. The DTG sensitivity was 0.05 mgs^{-1}.

In order to identify the solid decomposition products formed at the final stage of thermal decomposition, large amounts of metal(III) complexes of $NTEH_3$ were heated in a tube furnace at predetermined temperatures under flowing nitrogen and air

Table 1
The analytical data the trivalent metal complexes of $NTEH_3$*

Complex	N%	C%	H%	colour
$[Ru(NTEH_3)_2]Cl_3$	5.08 (5.54)	27.13 (28.47)	6.07 (5.93)	brown
$[Rh(NTEH_3)_2]Cl_3$	5.10 (5.52)	27.54 (28.39)	5.98 (5.91)	orange
$[Ce(NTEH_3)_2](NO_3)_3$	11.08 (11.21)	22.81 (23.06)	4.82 (4.80)	colorless
$[La(NTEH_3)_2](NO_3)_3$	10.25 (11.23)	22.09 (23.10)	4.54 (4.81)	colorless
$[Nd(NTEH_2)](NO_3)_2$	9.41 (10.08)	16.86 (17.28)	3.21 (3.36)	pale blue

* The calculated values are given in parentheses and all the values are given in weight percent.

atmosphere, respectively. The solid decomposition products were identified using a Philips PW 1710 X-ray powder diffractometer with CuK_{α} radiation.

3. Results and discussion

3.1. In flowing nitrogen atmosphere

The thermal analysis curves (DTA, TG, DTG) of the complexes in nitrogen atmosphere are illustrated in Figs. 1–7, and the thermoanalytical data such as temperature ranges, weight loss values and the final decomposition products are given in Table 2.

The thermal decomposition of the $NTEH_3$ complexes of Cr(III), Fe(III), Ru(III), Rh(III) and La(III) takes place in several stages while the Ce(III) and Nd(III) complexes of $NTEH_3$ decompose in a single stage. For the former complexes, in the first stage (from approx. 120°C to approx. 220°C), the decomposition and melting of the complexes proceed simultaneously. Some weight loss also occured in this stage. Therefore this stage corresponds the endothermic changes of both melting and decomposition. In the DTA curve of Ru(III) complex (Fig. 3), a sharp exotherm without weight loss at 180°C was observed after the endothermic melting peak at 150°C. This must be due to some form of solid-state transition. The Rh(III) complex showed a sharp exothermic peak at 156°C with a weight loss value 1.97% and this exothermic peak was followed by the melting peak (Fig. 4). The main decompositions of the organic part of these complexes occur at the second and the subsequent stages at

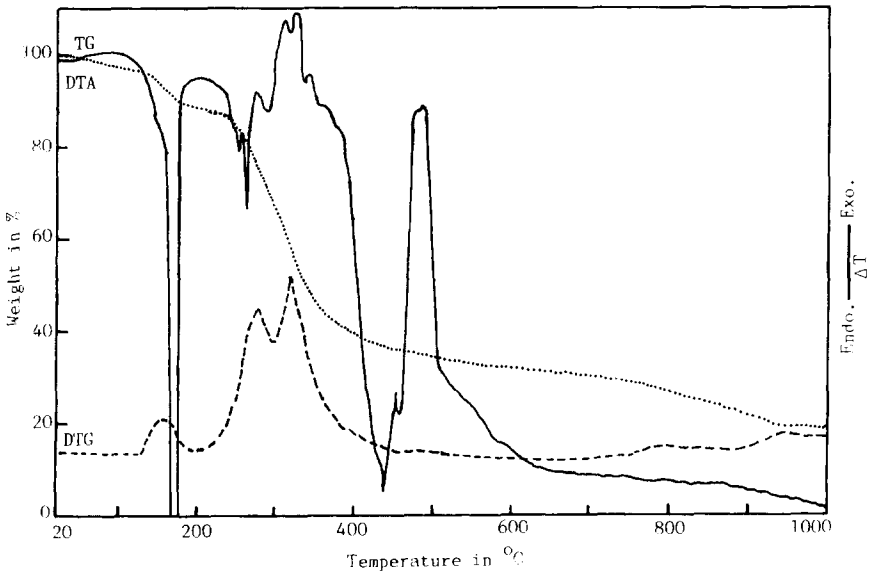

Fig. 1. DTA, TG and DTG curves of $[Cr(NTEH_3)_2]Cl_3$.

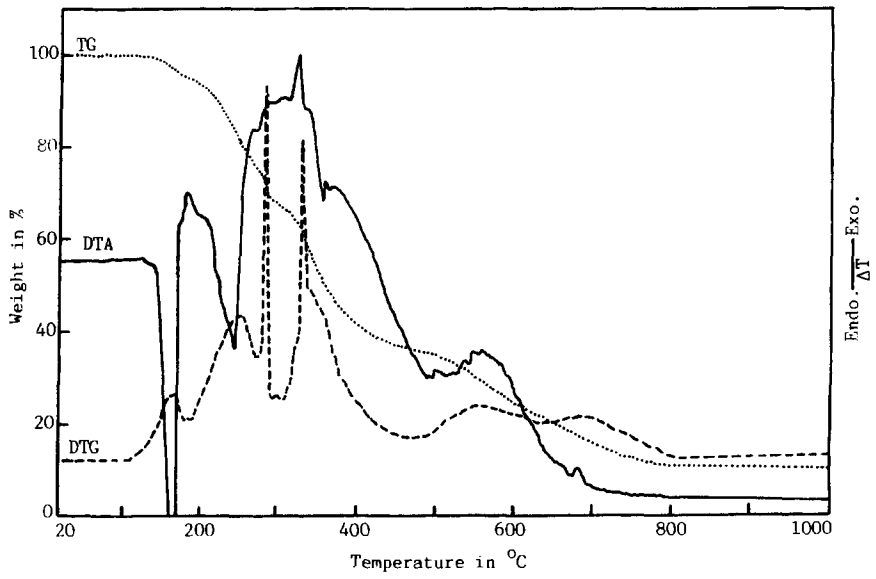

Fig. 2. DTA, TG and DTG curves of $[Fe(NTEH_3)_2]Cl_3$.

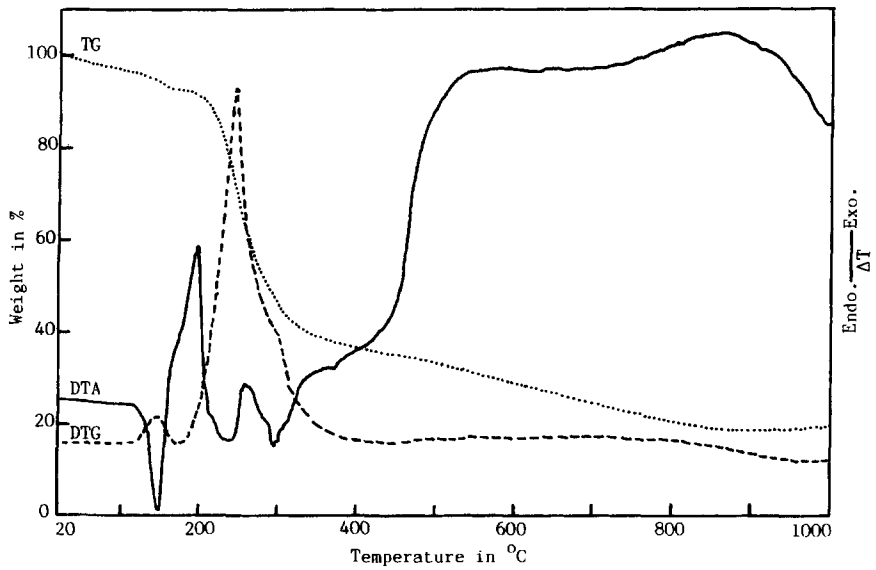

Fig. 3. DTA, TG and DTG curves of $[Ru(NTEH_3)_2]Cl_3$.

higher temperatures. The DTA curves related to these stages exhibit both endothermic and exothermic effects, and indicate that the decomposition process of the ligand is very complicated. The temperature differences between these consecutive decomposition steps are so small that the identification of the solid intermediates is very difficult.

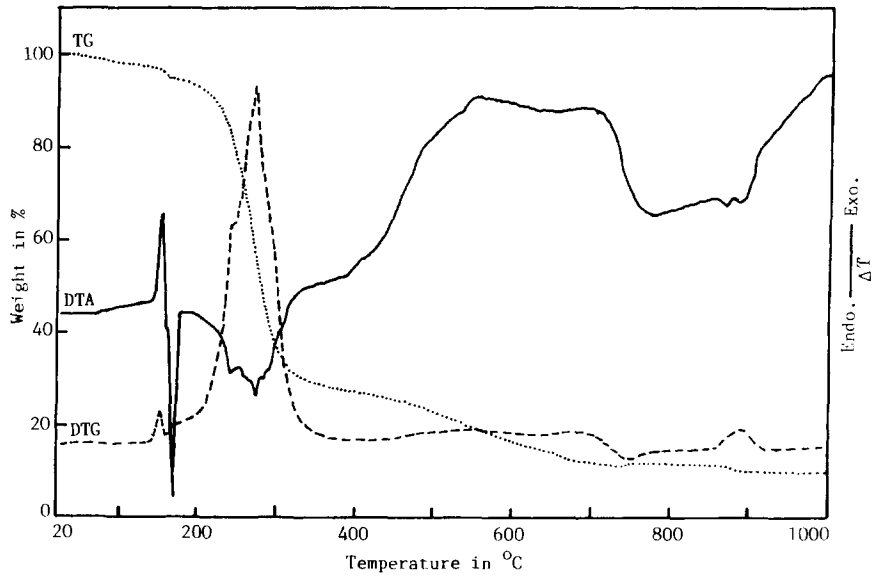

Fig. 4. DTA, TG and DTG curves of $[Rh(NTEH_3)_2]Cl_3$.

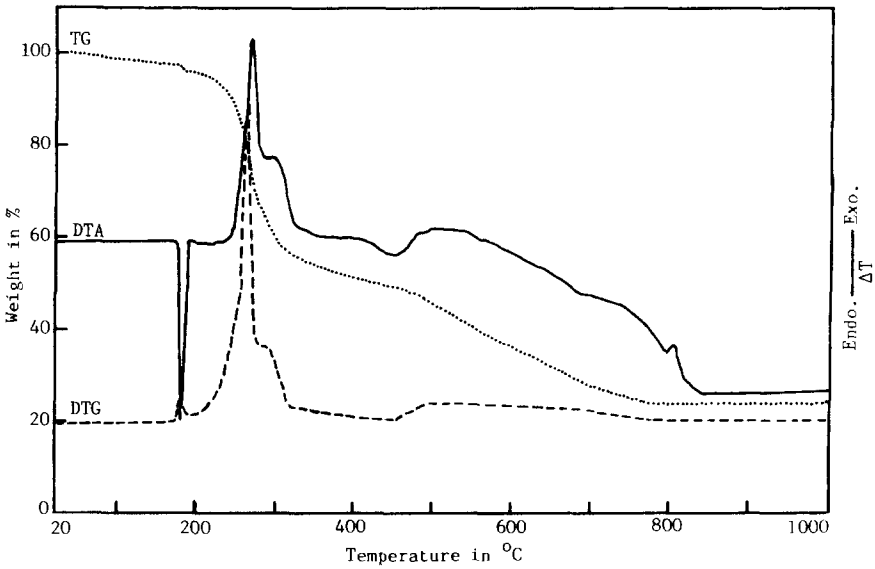

Fig. 5. DTA, TG and DTG curves of $[La(NTEH_3)_2](NO_3)_3$.

However, due to increasing of temperature, these intermediates undergo further decomposition and result in the formation of the stable solid decomposition products. The decompositions of the complexes were completed at around 900°C for Cr(III) and Ru(III) complexes, and at about 800°C for Fe(III) and Rh(III) complexes. The X-ray

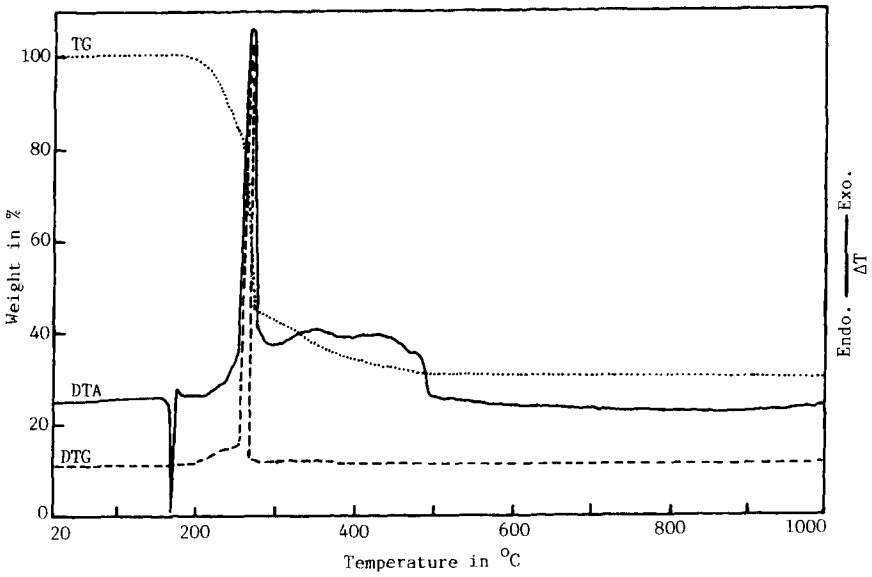

Fig. 6. DTA, TG and DTG curves of $[Ce(NTEH_3)_2](NO_3)_3$.

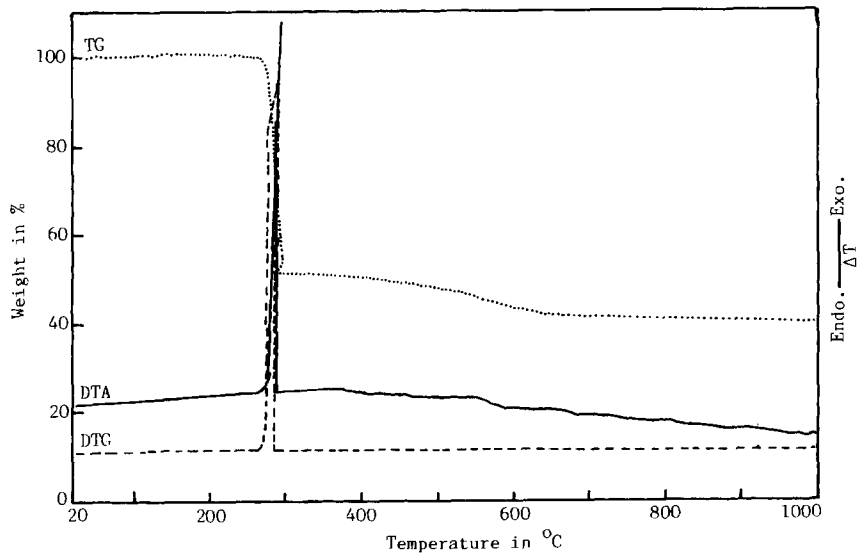

Fig. 7. DTA, TG and DTG curves of $[Nd(NTEH_2)](NO_3)_2$.

diffraction analysis confirmed that the final solid decomposition products formed at about 900°C were Cr_2O_3, Fe, Ru and Rh, for Cr(III), Fe(III), Ru(III) and Rh(III) respectively. X-ray powder diffraction patterns of some of the residues formed at 900°C are illustrated in Fig. 8.

Table 2
Thermoanalytical results (TG, DTG, DTA) for the trivalent metal complexes of $NTEH_3$ in nitrogen atmosphere*

Complex	Melting point in °C	Stage	Temperature range in °C	DTG_{max} in °C	Weight loss in %	Total weight loss in %	Solid decomp. product
$[Cr(NTEH_3)_2Cl_3$	172	1	130–193(endo)	163	7.74		–
		2	195–297(endo)	278	20.46		–
		3	297–980(endo)	320	52.60	80.80(83.35)	Cr_2O_3
$[Fe(NTEH_3)_2]Cl_3$	166	1	126–187(endo)	165	5.10		–
		2	187–273(exo)	251	19.36		–
		3	273–302(exo)	287	7.94		–
		4	305–430(endo)	334	28.31		–
		5	431–636(exo)	565	17.21		–
		6	637–790(endo)	700	9.74	87.66(87.84)	Fe
$[Ru(NTEH_3)_2]Cl_3$	150	1	120–182(endo)	152	3.41		–
		2	184–900(endo)	245	73.68	77.09(80.02)	Ru
$[Rh(NTEH_3)_2]Cl_3$	171	1	133–167(exo)	155	1.97		
		2	167–756(endo)	273	82.02	83.99(79.73)	Rh
$[La(NTEH_3)_2(NO_3)_3$	180	1	168–199(endo)	182	2.00		–
		2	200–283(exo)	263	30.66		–
		3	283–375(exo)	294	12.47		–
		4	375–787(endo)	620	28.37	73.50(72.13)	$La_5O_7NO_3$
$[Ce(NTEH_3)_2](NO_3)_3$	169	1	199–500(exo)	263	70.00	70.00(72.44)	CeO_2
$[Nd(NTEH_2)](NO_3)_2$	–	1	261–600(exo)	285	59.30	59.30(59.60)	Nd_2O_3

* The calculated values are given in parentheses.

The Nd(III) complex does not have a melting point and begins to decompose at 261°C which is the highest decomposition temperature among these trivalent metal complexes. This may be attributed to the nature of the chemical bonding present in this complex. Some of the bonds in the Nd(III) complex are ionic whereas the bonding in other complexes is mainly covalent [7]. The Nd(III) complex also differs in stoichiometry from the others (Table 1). The complexes containing metal ions other than lanthanides show only endothermic effects but the decomposition of the organic group of La(III) and Ce(III) and Nd(III) complexes are violently exothermic (Figs. 5–7) to give $La_5O_7NO_3$ and CeO_2 and Nd_2O_3, respectively. This violent reaction may presumably attributed to the high oxygen content of the complementary anion (NO_3^-) present in these complexes. This kind of effects were also observed for the complexes containing oxygen-rich anions like perchlorate [8] and nitrate [9,10]. The decomposition of La(III), Ce(III) and Nd(III) complexes ends at approximately 800, 500 and 600°C, respectively.

Among the decomposition products lanthanum oxide nitrate was found to be the most interesting. This compound was first reported by Delgado et al. [11] and thermal

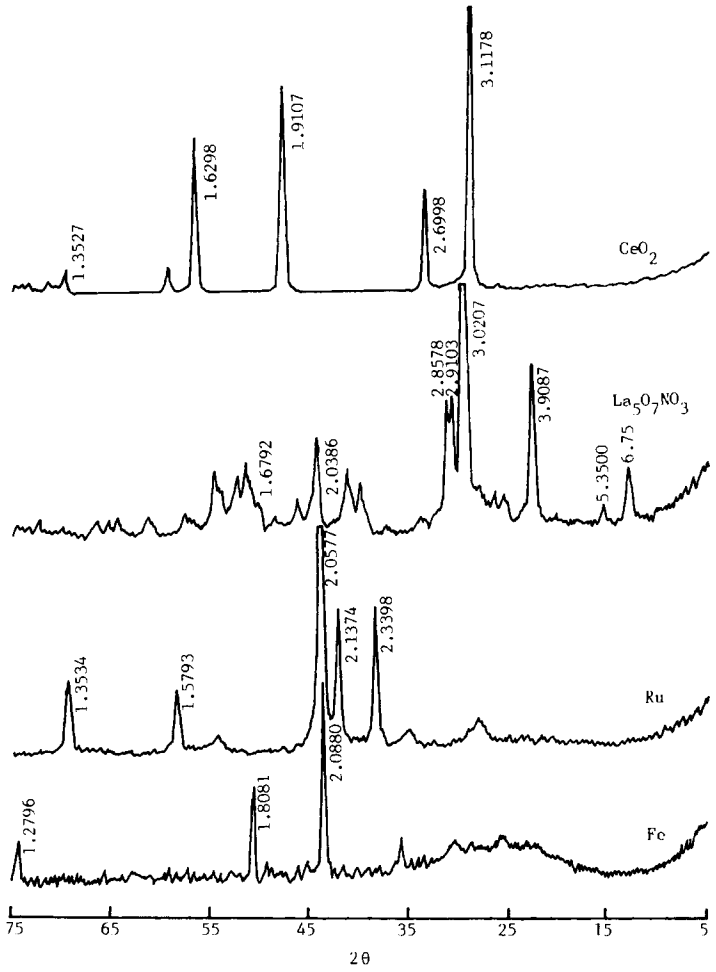

Fig. 8. X-ray diffraction patterns of the solid decomposition products formed at 900°C in nitrogen atmosphere.

decomposition of La(III) complex of $NETH_3$ seems to be another method for the preparation of this compound.

The experimental and calculated values for complete loss are given in Table 2 and found to be in very good agreement with each other. However, the experimental and calculated data for Rh(III) complex was quite different.

3.2. *In flowing air atmosphere*

Thermoanalytical data in air atmosphere are given in Table 3. The decomposition and melting of the complexes an air occur in the same way as observed in nitrogen atmosphere and the initial decomposition temperatures do not change significantly.

Table 3
Thermoanalytical results (TG, DTG, DTA) for the trivalent metal complexes of $NTEH_3$ in air atmosphere*

Complex	Melting point in °C	Stage	Temperature range in °C	DTG_{max} in °C	Weight loss in %	Total weight loss in %	Solid decomp. product
$[Cr(NTEH_3)_2]Cl_3$	172	1	140–191 (endo)	170	4.56		–
		2	201–335 (exo)	310	36.25		–
		3	336–465 (exo)	361	42.98	83.79 (83.35)	Cr_2O_3
$[Fe(NTEH_3)_2]Cl_3$	166	1	124–184 (endo)	164	9.18		–
		2	185–260 (exo)	230	14.78		–
		3	260–303 (exo)	270	7.72		–
		4	304–347 (exo)	334	9.93		–
		5	348–397 (exo)	357	8.62		–
		6	404–530 (exo)	468	33.19	83.42 (82.66)	Fe_2O_3
$[Ru(NTEH_3)_2]Cl_3$	150	1	120–175 (endo)	141	3.72		–
		2	177–324 (exo)	246	48.11		–
		3	325–378 (exo)	365	27.47	79.30 (73.69)	RuO_2
$[Rh(NTEH_3)_2]Cl_3$	171	1	133–200 (exo)	178	4.88		–
		2	201–360 (exo)	253	56.36		–
		3	365–408 (exo)	395	25.65	86.89 (75.00)	Rh_2O_3
$[La(NTEH_3)_2](NO_3)_3$	180	1	168–192 (endo)	179	2.54		–
		2	198–290 (exo)	264	31.80		–
		3	291–360 (exo)	302	9.93		–
		4	360–414 (exo)	400	5.74		–
		5	412–535 (exo)	469	23.29	73.30 (73.86)	La_2O_3
$[Ce(NTEH_3)_2](NO_3)_3$	169	1	195–367 (exo)	285	71.07	71.07 (72.44)	CeO_2
$[Nd(NTEH_2)](NO_3)_2$	–	1	255–285 (exo)	268	60.95	60.95 (59.60)	Nd_2O_3

* The calculated values are given in parentheses

The number of the decomposition stages is nearly identical, but the nature of the decomposition is quite different. In contrast to the nitrogen atmosphere, the decomposition reaction of the ligand of the complexes is extremely violently exothermic. This is due to the combustion of the organic part present in the complexes. The decomposition reaction proceeds rapidly within the temperature range approx. 180–500 °C with exothermic effects. The final decomposition products formed were found to be the respective metal oxides of the complexes as identified by X-ray powder diffractometry.

The calculated weight loss values are also consistent with the experimental values except for Ru(III) and Rh(III) complexes. As observed in nitrogen atmosphere the Rh(III) complex yields much higher weight loss (86.89%) in air atmosphere. The weight loss calculations based on the final decomposition product (Rh_2O_3) give a much less weight loss value (75.00%). The reason of this variation could not be understood, but may be explained by the formation of volatile products. Thus some of the Rh may escape in this way. The same effect was also observed for the Ru(III) complex in air atmosphere.

3.3. Thermal stability of the complexes

The relative stability of the complexes may be discussed in two ways such as kinetic stability usually expressed as the activation energy values of decomposition reactions or thermal stability given as the temperature values at which decomposition begins. In this study, since the decomposition and melting processes overlapped each other, the kinetic calculations like energy of activation and order of decomposition reaction could not be carried out. Nevertheless the main decomposition temperatures were used to determine the relative stability and the thermal stability of the $NTEH_3$ complexes in the solid state increased in the order: Nd(III) > La(III) ≅ Ce(III) > Cr(III) > Fe(III) > Ru(III) > Rh(III). The present results indicate that the complexes with the inner-transition metals have grater stability than those with the transition metals. When compared in the same transition period, trivalent complexes of $NTEH_3$ are thermally less stable than the divalent complexes. For example, the main decomposition temperatures of the $NTEH_3$ complexes containing Cr(III) and Fe(III) are 195° and 187°, respectively while Mn(II), Fe(II) and Ni(II) complexes begin to decompose at 225°, 210° and 203°C, respectively [6]. As exaplained above the Nd(III) complex includes some ionic bonds and hence its thermal stability was found to be the highest among these complexes. The other complexes contain covalent bonds and their thermal stability must be related to the strength of the bonds between the metal ions and the ligand.

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