LANTHANUM(III) CHLORIDE COMPLEXES WITH HETEROCYCLIC SCHIFF BASES
Synthesis, spectroscopic characterization and thermal studies

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Condensation of 2-amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzo[b]thiophene with carbonyl compounds such as isatin, *o*-hydroxyacetophenone or benzoin in 1:1 ratio in ethanol medium yielded three distinctly different heterocyclic Schiff bases viz. 2-(N-indole-2-one)amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzo[b]thiophene (ISAT), 2-(N-*o*-hydroxyacetophenone)amino-3-carboxyethyl-4,5,6,7-tetrahydro-benzo[b]thiophene (HAAT) or 2-(N-benzoin)amino-3-carboxyethyl-4,5,6,7-tetrahydro-benzo[b]thiophene (HBAT) respectively. These ligands formed well defined complexes with lanthanum(III) chloride under suitable conditions.

The ligands and the complexes have been characterized on the basis of elemental analyses, molar conductance measurements, UV-visible, IR and proton NMR spectral studies. Kinetics and mechanism of the thermal decomposition of the ligands and the metal complexes have been studied using non-isothermal thermogravimetry. Kinetic parameters were calculated for each step of the decomposition reactions using Coats–Redfern equation. The rate controlling process for all the ligands and complexes is random nucleation with the formation of one nucleus on each particle (Mampel equation). Relative thermal stabilities of the ligands and the metal complexes have been compared.

Keywords: Coats–Redfern equation, lanthanum(III) chloride complexes, Schiff bases, thermal study

Introduction

Schiff bases and related metal complexes, with interesting ligational features, have experienced long standing applications in biological, pharmacological, catalytic, analytical and various other fields [1–5]. Among the prodigious number and variety of Schiff base complexes, those of inner transition metal ions, containing benzothiophene ring system have received only sporadic attention so far [6]. In this communication we describe the synthesis, spectroscopic characterization and thermal decomposition studies of lanthanum(III) chloride complexes of three distinctly different heterocyclic Schiff bases viz. 2-(N-indole-2-one)amino-3-carboxyethyl-4,5,6,7-tetrahydro-benzo[b]thiophene (ISAT), 2-(N-*o*-hydroxyacetophenone)amino-3-carboxyethyl-4,5,6,7-tetrahydro-benzo[b]thiophene (HAAT) or 2-(N-benzoin) amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzo[b]thiophene (HBAT). These Schiff bases have been obtained by condensing 2-amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzo[b]thiophene with isatin, *o*-hydroxyacetophenone or benzoin respectively. During our studies, IR, UV-Vis and proton NMR spectroscopic methods were employed together with analytical data and molar conductivity measurements. However it was amazing how suitable thermal analysis was in the study of our complexes. Apart from providing valuable insight into the thermal stabilities of the ligands and the lanthanum(III) complexes, suitable mechanisms have been also proposed for these thermal decomposition reactions. Kinetic parameters have been also calculated for each step of the decomposition reaction using Coats–Redfern equation.

Experimental

Materials

Lanthanum(III) chloride was prepared by dissolving La_2O_3 in 50% hydrochloric acid followed by crystallization. 2-amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzo[b]thiophene was prepared according to the method suggested by Gewald *et al.* [7].

General method for the preparation of the Schiff bases

The ligands ISAT, HAAT and HBAT were prepared by condensing 2-amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzo[b]thiophene (0.01 mol) with isatin (0.01 mol), *o*-hydroxyacetophenone (0.01 mol) or benzoin (0.01 mol) in ethanol, respectively. The crystals of ISAT, HAAT and HBAT formed were recrystallised from ethanol.

Preparation of the complexes

All the complexes were prepared by a general method. Ethanolic solution of lanthanum(III) chloride was prepared and added to a hot ethanolic solutions of the ligands in 1:1 molar ratio. The solution was refluxed on a water-bath for about 10 h. The pH of the solution was adjusted to 6.5–7.0 and refluxing was continued for about 8 h. The resulting solutions were concentrated and kept overnight. The complex separated was filtered, washed successively with ethanol and ether and dried in vacuum.

Lanthanum content of the complexes was determined by the oxalate-oxide method [8].

TG and DTG analyses of the complexes were carried out using Mettler Toledo STAR^e system with a heating rate of 10°C min^{-1} in dynamic air. In all the cases, the compounds were subjected to independent pyrolysis and the observed percentage of mass loss was compared with those from the TG data.

Results and discussion

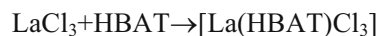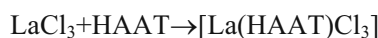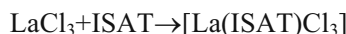The formation of the complexes can be represented by the following equations

$$LaCl_3+ISAT \rightarrow [La(ISAT)Cl_3]$$

$$LaCl_3+HAAT \rightarrow [La(HAAT)Cl_3]$$

$$LaCl_3+HBAT \rightarrow [La(HBAT)Cl_3]$$

Table 1 Analytical data and other details of the ligands

Ligand	Yield/ %	*M.P.*/ °C	Analytical data/%*			
			C	H	N	S
ISAT	78	102	64.36 (64.40)	5.01 (5.08)	7.88 (7.90)	8.98 (9.03)
HAAT	72	105	66.37 (66.40)	6.08 (6.10)	4.01 (4.08)	9.31 (9.33)
HBAT	75	99	71.49 (71.59)	5.83 (5.96)	3.31 (3.34)	7.56 (7.60)

*Calculated values are given in brackets

Attempts to prepare 1:2 complex were not successful presumably due to steric factors. Formulation of these complexes was made on the basis of their elemental analytical data (Tables 1 and 2) and molar conductance values. Molar conductance values (Table 3) in DMSO, DMF and nitrobenzene adequately confirmed the non-electrolytic nature of the complexes. Molecular masses of the complexes were determined by camphor method and the values obtained were close to monomeric values.

Electronic spectra

The electronic spectrum of ISAT in DMSO exhibited two absorption bands at 264 and 300 nm and the electronic spectrum of HBAT in DMSO showed two absorption bands at 266 and 312 nm. These are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively of the azomethine moiety. The electronic spectra of their complexes were dominated by ligand band, with a slight red shift. This shift was attributed to the effect of crystal field upon the interelectronic repulsion between the 4f electrons [9].

The ultraviolet spectrum of HAAT gave a peak at 320 nm characteristic of enol-imine form of the ligand [10, 11]. In the metal complex, the band did not undergo any appreciable change but slightly red shifted indicating that the ligand moiety exists in the complex in the enol-imine form itself.

However in the visible spectra of the complexes there is a weak band ~735 nm due to weak *f–f* transition.

Infrared spectra

The infrared spectrum of ISAT exhibited a strong band at 3170 cm^{-1}, assignable to υ_{N-H} of the indole ring of isatin moiety. This band remained almost unaffected in its lanthanum(III) complex, indicating that the ring nitrogen atom of isatin moiety is not involved in coordination. A strong band at 1730 cm^{-1} in the ligand characteristic of $\upsilon_{C=O}$ of ester has been shifted by 68 cm^{-1} to lower frequency upon complexation indicating coordination of ester carbonyl with lanthanum ion [12].

Table 2 Analytical data of lanthanum(III) chloride complexes

Complex	Analytical data/%*					
	Metal	C	H	N	S	Cl
[La(ISAT)Cl$_3$]	23.08 (23.18)	37.97 (38.03)	3.63 (3.67)	4.61 (4.67)	5.28 (5.33)	17.89 (17.76)
[La(HAAT)Cl$_3$]	23.43 (23.60)	38.61 (38.74)	3.43 (3.57)	2.21 (2.38)	5.36 (5.44)	17.90 (18.10)
[La(HBAT)Cl$_3$]	20.83 (20.91)	45.01 (45.15)	3.74 (3.76)	2.08 (2.11)	4.71 (4.82)	15.91 (16.03)

*Calculated values are given in brackets

Complex	Molar conductance/Ω^{-1} cm^2 mol^{-1}		
	DMSO	DMF	Nitrobenzene
[La(ISAT)Cl$_3$]	6.5	12.5	3.6
[La(HAAT)Cl$_3$]	9.5	15.4	6.1
[La(HBAT)Cl$_3$]	6.3	12.4	3.4

A strong band observed at 1650 cm^{-1}, corresponding to $\upsilon_{C=O}$ of isatin moiety has been shifted downward by 41 cm^{-1} indicating the coordination of carbonyl oxygen with lanthanum ion. A medium intensity band at 1596 cm^{-1} in the ligand due to $\upsilon_{C=N}$ of azomethine has been shifted to lower frequencies by 24 cm^{-1} upon coordination with lanthanum ion [13].

The IR spectrum of the ligand HAAT showed a broad υ_{O-H} band in the region 3400–3100 and centered at 3256 cm^{-1}, characteristic of internally hydrogen bonded OH group. A strong band at 1645 cm^{-1} assignable to internally hydrogen bonded ester carbonyl group and a medium band observed at 1587 cm^{-1} has been characteristic of internally hydrogen bonded azomethine group. Thus a bifunctional hydrogen bonding was observed in the case of HAAT. In the metal complex, the phenolic O–H band became less broad showing a peak centered at 3300 cm^{-1}. The strong band at 1285 cm^{-1} can be attributed to the phenolic υ_{C-O} of the ligand. But in the complex υ_{C-O} was only slightly shifted towards higher frequency by 15 cm^{-1} indicating that the OH group is coordinated to the metal ion without deprotonation. The band at 1645 cm^{-1} of $\upsilon_{C=O}$ in the free ligand showed negatively shift by 48 cm^{-1} indicating coordination of ester carbonyl with lanthanum(III) ion. A medium intensity band at 1565 cm^{-1} in the complex has been due to $\upsilon_{C=N}$. The negative shift of this band is a clear indication of coordination of azomethine group with lanthanum ion [14, 15].

The IR spectrum of HBAT showed a broad band in the range 3406–3296 and centered at 3264 cm^{-1}, assignable to be hydrogen bonded OH group. This was shifted to 3380 cm^{-1} and became less broad, indicating that the hydrogen bond got weakened and the oxygen atom coordinated to the metal ion without deprotonation [16, 17]. The most informative and intense band due to the internally hydrogen bonded ester carbonyl group was recorded at 1674 cm^{-1} in the ligand and this band shifted to lower frequency at 1647 cm^{-1} in the complex, which demonstrated the coordination of ester carbonyl oxygen to lanthanum(III) ion [18]. Coordination of the hydroxyl oxygen without deprotonation has been apparent from the observation that the strong band at 1350 cm^{-1} due to

υ_{C-O} in the spectrum of the ligand has shown a slight positive shift in the spectrum of the metal complex by 18 cm^{-1}. A medium intensity band at 1589 cm^{-1} in the ligand due to $\upsilon_{C=N}$ of azomethine was shifted to lower frequency at 1566 cm^{-1} upon complexation of azomethine nitrogen with lanthanum(III) ion.

In all cases the substituted thiophene ring vibrations occurring in the ligand at 1525, 1410 and 1370 cm^{-1} did not show any appreciable change in the metal chelates. This gave adequate evidence to the non-participation of ring sulphur atom in coordination [19].

Far infrared spectra of the metal complexes showed several absorption bands which were not observed in the ligand spectrum. The non-ligand bands of medium intensity appearing at 430, 360 and 324 cm^{-1} could be assigned to υ_{Ln-N}, υ_{Ln-O} and υ_{Ln-Cl} modes respectively. Absence of υ_{M-S} band gave added support to the non-participation of ring sulphur atom in coordination.

^{1}H NMR spectra

The proton NMR spectral data of the complexes recorded in DMSO-d_6, further substantiate the mode of coordination suggested by IR spectral studies. The ligand ISAT showed signals at 11.0 ppm due to NH proton, which did not show any appreciable change in the complex, confirming non-coordination of NH moiety.

The characteristic signals appearing at 12.96 ppm in the free ligand HAAT and at 12.71 ppm in the complex could be attributed to the phenolic proton and the peak positions indicate that OH coordinates to the metal ion without deprotonation.

The proton NMR spectrum of the ligand, HBAT displayed a signal at 6.09 ppm characteristic of –OH proton which was shifted downfield to about 0.2 ppm, indicative of coordination by the hydroxyl group without deprotonation. The ligands and the complexes also exhibited signals at 1.3–1.8 ppm due to CH$_3$ protons, 2.4–2.6 ppm due to CH$_2$ protons, ~3.4 ppm due to ring of cyclohexane moiety protons and 6.9–7.5 ppm due to aromatic protons.

On the basis of the above spectral data the following structures have been tentatively assigned for the complexes (Figs 1–3).

Thermal decomposition of lanthanum(III) chloride complexes

ISAT and its lanthanum(III) chloride complex

The ligand ISAT was stable upto 150°C and registered decomposition in two stages (Fig. 4). The first stage of decomposition occurred in the temperature range 150 to 250°C with a mass loss of 36.9%. This
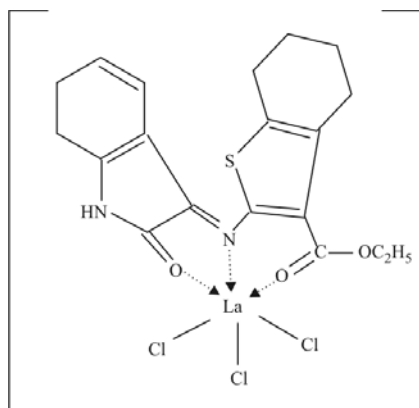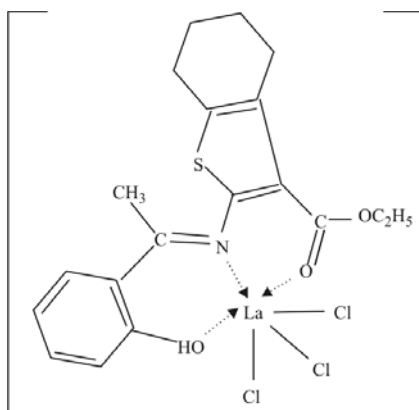
Fig. 1 Structure of [La(ISAT)Cl₃]

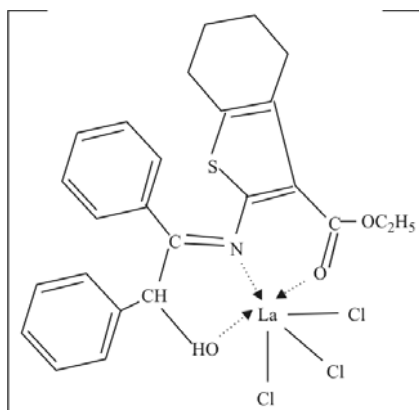
Fig. 2 Structure of [La(HAAT)Cl₃]

Fig. 3 Structure of [La(HBAT)Cl₃]

percentage mass loss was assigned to the loss of isatin moiety from the ligand. The DTG curve indicated a peak at 211°C. The second stage of decomposition started at 270 and continued upto 480°C. The mass loss agreed well with the loss of the remaining part of the ligand giving a DTG peak at 382°C in the DTG curve. Lanthanum(III) chloride complex of ISAT decomposed in three stages (Fig.7). The first stage of decomposition started at about 150 and completed at 240°C, corresponding to a mass loss of 21.84% which could be attributed to the loss of isatin moiety of the

ligand. The second stage of decomposition occurred in the range 270–460°C with a mass loss of 37.19% which may be due to loss of the benzothiophene part of the ligand. The third stage of decomposition in the range 560–640°C followed a mass loss of 17.7%, which could be assigned to the loss of chlorine and the oxidation of the metal to La₂O₃ which has been stable above this temperature [20]. The three stages were denoted by the DTG peaks at about 194, 437 and 628°C, respectively. The mass of the residue has been agreed well with that obtained in independent pyrolysis experiment.

HAAT and its lanthanum(III) chloride complex

Quite contrary to the decomposition pattern of ISAT, the decomposition of HAAT was found to be in one stage (Fig.5). The ligand was stable up to 130°C and decomposed completely in the range 130–210°C as indicated by the DTG peak at 181°C. But its lanthanum(III) chloride complex showed two decomposition stages in the temperature ranges 160–260 and 510–600°C (Fig. 8). They were denoted by the DTG peaks at 238 and 575°C. The first stage of decomposition agreed to a mass loss of 58.22% which may be due to the loss of the ligand completely. The second stage indicates a mass loss of 18.26% which may be attributed to the loss of chlorine and oxidation of the metal to a residue of La₂O₃ which was stable above this temperature. The mass loss was in good agreement with the independent pyrolysis experiment.

HBAT and its lanthanum(III) chloride complex

As in the case of the previous ligand, HBAT showed a single stage decomposition (Fig. 6). The ligand was stable up to 150°C and decomposed in the range 150–320°C as indicated by the DTG peak at 236°C.
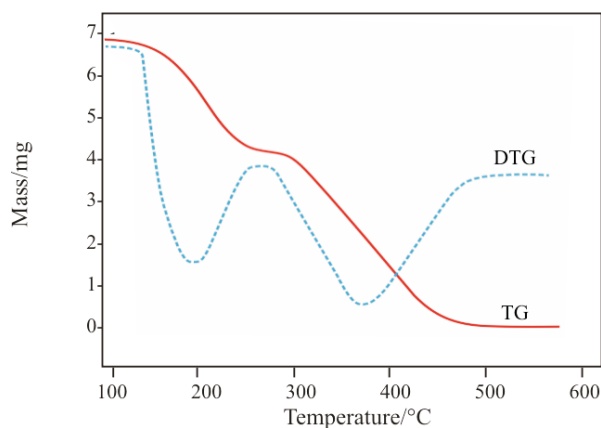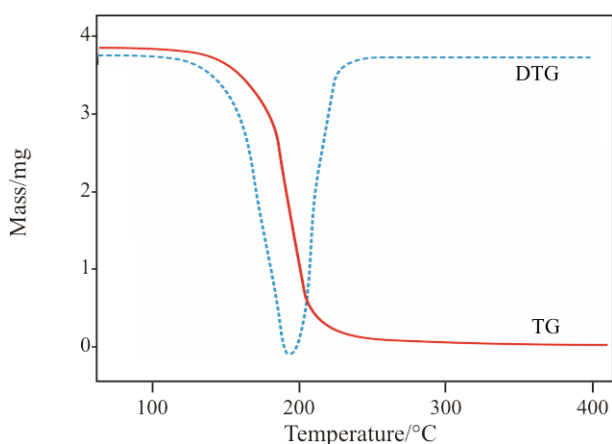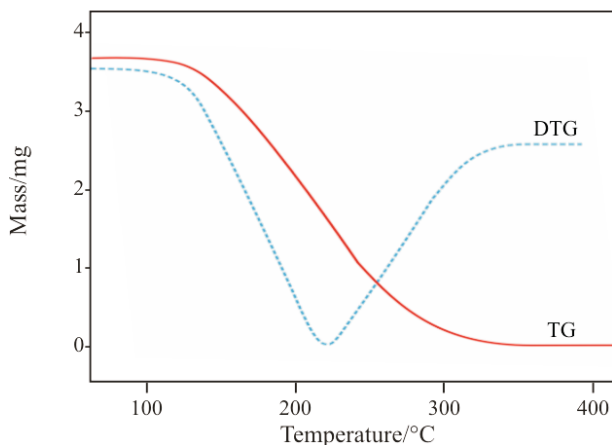

Fig. 4 TG and DTG curves of ISAT

Table 4 Thermal decomposition data of ISAT and [La(ISAT)(Cl)$_3$]

Compound	Decomp. stage	Temp. range/°C	Peak temp./°C	Mass loss/%	Cal. mass loss/%	Probable assignment
ISAT	I	150–250	211	36.90	37.00	Loss of isatin moiety
	II	270–480	382	63.10	63.00	Loss of benzothiophene moiety
[La(ISAT)(Cl)$_3$]	I	150–240	194	21.84	21.85	Loss of isatin moiety
	II	270–460	437	37.19	37.20	Loss of benzothiophene moiety
	III	560–640	628	17.70	17.77	Loss of anion and formation of La$_2$O$_3$

Fig. 5 TG and DTG curves of HAAT

Fig. 6 TG and DTG curves of HBAT

The lanthanum(III) chloride complex of the ligand was thermally stable up to 140°C and decomposed in two stages in the temperature ranges 140–240 and 280–600°C which were denoted by the DTG peaks at 179 and 450°C (Fig. 9). The first stage of decomposition followed a mass loss of 29.54% which may be due to the loss of benzoin moiety of the ligand and the second stage showed a mass loss of 49.63% which could assigned to the loss of remaining part of the ligand, loss of chlorine and the oxidation of the metal to La$_2$O$_3$.

Mass of the residue was in agreement with the mass of residue obtained in independent pyrolysis experiment.

Kinetic aspects

The kinetic evaluation of the thermal decomposition of the ligands and the lanthanum(III) chloride complexes was carried out. All stages were selected for the study of the kinetics of decomposition of the complexes. The kinetic parameters, the activation energy E and the pre-exponential factor A were calculated using Coats–Redfern equation. Here, $\lg(\alpha)/T^2$ vs. $1/T \cdot 10^3$ plots gave a straight line whose slope and intercept were used for calculating the kinetic parameters by the least squares method. The goodness of fit was tested by evaluating the correlation coefficient. The entropy of activation ΔS could be calculated using the equation

$$\Delta S = R \ln \frac{Ah}{kT_s}$$

where R=gas constant, A=pre-exponential factor, k=Boltzmann constant, T_s=DTG peak temperature, h=Planck's constant.

Analysis of the data using Coats–Redfern equation revealed that the ligands have fractional order of decomposition but complexes have fractional order of decomposition and unity. There were no regular variations in the values of the kinetic parameters of decomposition as with other common physical constants. The activation energy of the decomposition reactions was in the range 54–334 kJ mol^{-1} which indicated that the metal-ligand bond has been weak [21]. These values were comparable with those reported for similar types of complexes [22, 23]. There was no definite trend in the values of the entropy of activation. But the negative value of the entropy of activation indicated that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal [24–26].

Table 5 Thermal decomposition data of HAAT and [La(HAAT)(Cl)$_3$]

Compound	Decomp. stage	Temp. range/°C	Peak temp./°C	Mass loss/%	Cal. mass loss/%	Probable assignment
HAAT	I	130–210	181	100	100	Loss of the compound completely
[La(HAAT)(Cl)$_3$]	I	160–260	238	58.22	58.28	Loss of the ligand completely
	II	510–600	575	18.26	18.10	Loss of anion and formation of La$_2$O$_3$

Table 6 Thermal decomposition data of HBAT and [La(HBAT)(Cl)$_3$]

Compound	Decomp. stage	Temp. range/°C	Peak temp./°C	Mass loss/%	Cal. mass loss/%	Probable assignment
HBAT	I	150–320	236	100	100	Decomposition/oxidation of the compound completely
[La(HAAT)(Cl)$_3$]	I	140–240	179	29.54	29.50	Loss of benzoin moiety
	II	280–600	450	49.63	49.52	Loss of anion and formation of La$_2$O$_3$
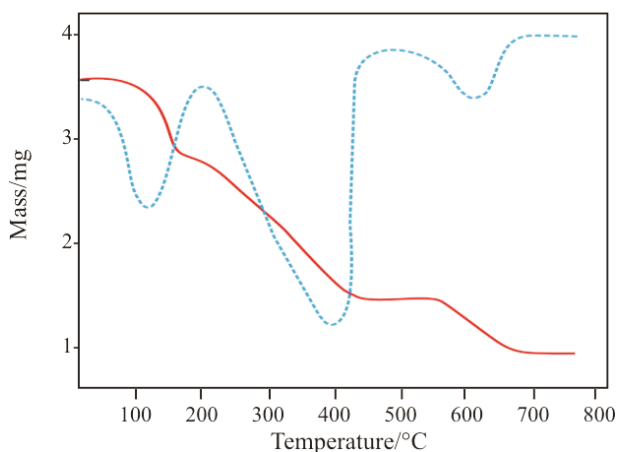
Fig. 7 TG and DTG curves of [La(ISAT)Cl$_3$]
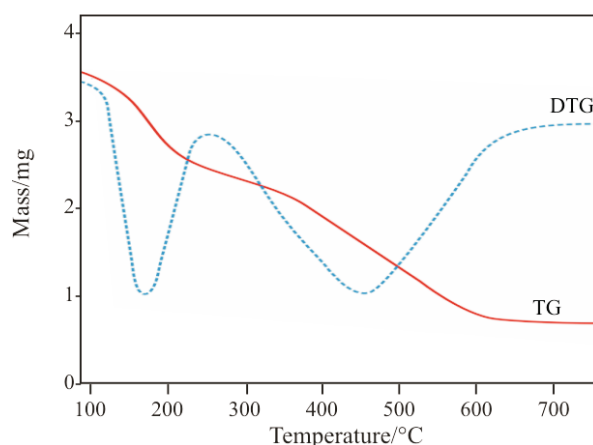
Fig. 9 TG and DTG curves of [La(HBAT)Cl$_3$]
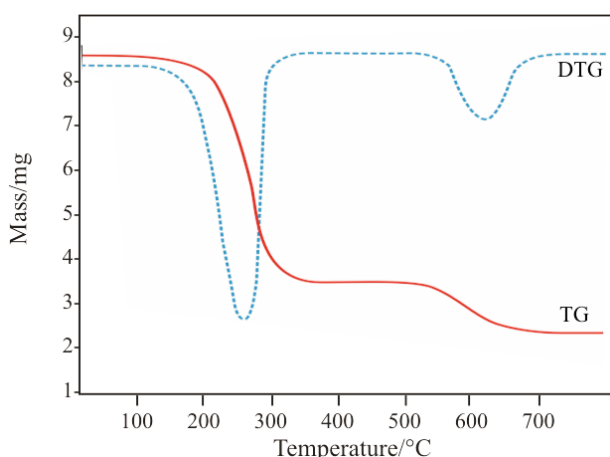
Fig. 8 TG and DTG curves of [La(HAAT)Cl$_3$]

Mechanism

Elucidation of the mechanism for the solid-state thermal decomposition reaction is difficult. All the heterogeneous processes can be classified into three categories – nucleation and growth, diffusion and phase boundary reactions. Several kinetic equations have been derived corresponding to the above three possible rate-determining steps. The kinetic equations which govern the reaction mechanism are based on the assumption that the form of $g(\alpha)$ depends on the reaction mechanism. In the present investigation nine forms of $g(\alpha)$ have been used. The form of $g(\alpha)$ best representing the experimental data was considered as the mechanism of the reaction. In all the compounds and in different stages, the highest value of the correlation coefficient is for $g(\alpha)=-\ln(1-\alpha)$, which the random nucleation mechanism with one nucleus on each particle. This represents the 'Mampel model'.

Table 7 Kinetic parameters for the thermal decomposition of ISAT and [La(ISAT)Cl$_3$]

Compound	Decomp. stage	Peak temp./°C	Order/ n	Correl. coeff.	Energy of activation, E/kJ mol^{-1}	Arrhenius factor, A/s^{-1}	Entropy of activation, ΔS/J K^{-1} mol^{-1}	Probable mechanism
ISAT	I	211	2.2	0.9930	101.36	$1.2869\cdot10^5$	−144.22	Random nucleation – one nucleus on each particle
	II	382	1.9	0.9903	129.72	$1.2062\cdot10^8$	−92.26	Random nucleation – one nucleus on each particle
[La(ISAT)Cl$_3$]	I	194	1	0.9968	97.23	$2.1654\cdot10^8$	−81.77	Random nucleation – one nucleus on each particle
	II	437	1	0.9947	64.65	$1.83\cdot10^6$	−36.74	Random nucleation-one nucleus on each particle
	III	628	2.5	0.9964	334.29	$6.7191\cdot10^{17}$	90.17	Random nucleation-one nucleus on each particle

Table 8 Kinetic parameters for the thermal decomposition of HAAT and [La(HAAT)Cl$_3$]

Compound	Decomp. stage	Peak temp./°C	Order/ n	Correl. coeff.	Energy of activation, E/kJ mol^{-1}	Arrhenius factor, A/s^{-1}	Entropy of activation, ΔS/J K^{-1} mol^{-1}	Probable mechanism
HAAT	I	181	1.5	0.9992	131.29	$2.3106\cdot10^{13}$	15.07	Random nucleation – one nucleus on each particle
[La(HAAT)Cl$_3$]	I	238	1	0.9976	99.85	$1.4578\cdot10^8$	−86.75	Random nucleation – one nucleus on each particle
	II	575	1	0.9919	274.02	$1.6509\cdot10^{15}$	40.95	Random nucleation – one nucleus on each particle

Table 9 Kinetic parameters for the thermal decomposition of HBAT and [La(HBAT)Cl$_3$]

Compound	Decomp. stage	Peak temp./°C	Order/ n	Correl. coeff.	Energy of activation, E/kJ mol^{-1}	Arrhenius factor, A/s^{-1}	Entropy of activation, ΔS/J K^{-1} mol^{-1}	Probable mechanism
HBAT	I	236	1.8	0.9943	74.84	$3.7175\cdot10^5$	−136.33	Random nucleation – one nucleus on each particle
[La(HBAT)Cl$_3$]	I	179	2	0.9886	99.48	$12.4888\cdot10^9$	−60.79	Random nucleation – one nucleus on each particle
	II	450	1	0.9856	54.32	$1.3170\cdot10^3$	−188.61	Random nucleation – one nucleus on each particle

Conclusions

From the thermal decomposition studies of ISAT, HAAT, HBAT and their lanthanum(III) chloride complexes, it could be concluded that the nature of decomposition and stability changes with the nature of the ligand. All the complexes give a stable residue of La_2O_3 around 600°C. The initial decomposition temperature is frequently used to define the relative stabilities of metal complexes [27]. On the basis of this, the relative thermal stabilities of the ligands can be represented as: HBAT>ISAT>HAAT. However, the stabilities of the complexes is in the order: $[La(HAAT)Cl_3]>[La(ISAT)Cl_3]>[La(HBAT)Cl_3]$.

Acknowledgements

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