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Synthesis, characterization and thermolysis of lanthanide metal nitrate complexes with 1, 10-phenanthroline, Part-95

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Abstract: The nitrate complexes of cerium, praseodymium and neodymium with 1,10-phenanthroline (phen) of general formula $[Ln(phen)_2(NO_3)_2(H_2O)_2]\cdot NO_3$ (where, Ln=Ce, Pr and Nd) were prepared and characterized by X-ray crystallography. Thermolysis of these complexes was investigated by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA). Isothermal TG was taken to evaluate the kinetic parameters using model fitting as well as model free isoconversional methods. The thermolytic pathways were also suggested, which involves decomposition followed by ignition. All the three complexes had coordination number ten and showed multistep decompositions. In order to evaluate the response of rapid heating, ignition delay (D_i) measurements were undertaken. The activation energies for ignition were found to decrease in the order: Nd>Pr>Ce.

Keywords: crystal structure; metal nitrate; kinetics; isoconversional; model fitting; ignition delay; rare earths

The study of various lanthanide complexes with multidentate N-donor ligands, have generated a continuously growing interest over the last decades, because of their potential applications as optical materials[1–4], catalysis in polymer synthesis[5–7], organic[8–10], and bioinorganic chemistry[11–13]. The interest in the lanthanide complexes is chiefly ruled by their promising utilization, due to their low toxicity and powerful paramagnetic properties[14–16]. Lanthanide β-diketonate complexes with 1,10-phenanthroline (phen) have been intensively studied as organic light emitting diodes (OLEDs) and in organic electroluminescent (EL) devices[17,18]. Lanthanide ion has high coordination number and can afford enough coordination sites for different ligands, which can lead to the syntheses of lanthanide metal nitrate complexes with unprecedented structures.

Among the different organic candidates, the chelate 1,10-phenanthroline has been subject of special attention. This bidentate aromatic N-donor ligand was usually found in different complexes mostly stabilized with nitrates[19,20]. 1,10-phenanthroline has a rigid structure caused by its central ring resulting in the two N-atoms being held in juxtaposition; this means that phen can coordinate metal ions rapidly, which is an important feature especially in the formation of complexes with lanthanide ions[21]. A phen molecule is planar with its dipole moment is 4.11 D[22]. The high dipole moment, the stiffness, bidentate coordination and the π-π stacking interaction of phenanthroline rings, upon complexation, provide stability to the phen complexes of lanthanide ions. The co-ordination chemistry of the lanthanides is dominated by O-donor ligands[23,24] as expected for oxophilic metal ions[25]. N-donors form stable complexes in non-aqueous solvents and most of the studies have centered upon the bidentate ligands 2,2'-bipyridyl and 1,10-phenanthroline. Considerable amount of work has been done on structure of complexes with phen because of their ability to chelate with metal ions[26,27] but little work has been reported on thermal decomposition of these complexes. Recently, we have undertaken thermal studies on lanthanide metal nitrate with 2,2'-bipyridyl complexes[28]. The metal amine nitrate complexes lead to their various applications such as in explosives, propellants and pyrotechnics[29,30] and display exothermic decomposition at elevated temperature. On thermolysis, they release the thermal energy and produce corresponding metal oxide which can be utilized as burning rate catalysts[31].

The present investigation dealt with the preparation of lanthanide metal nitrate complexes with phen. These complexes were characterized by X-ray crystallography. Their thermolysis was undertaken using thermogravimetry (TG), differential thermal analysis (TG-DTA) and ignition delay measurements.

1 Experimental

1.1 Materials

Metal nitrate hexahydrate (CDH and Aldrich), 1, 10-phenanthroline (s.d.fine) were used as received.

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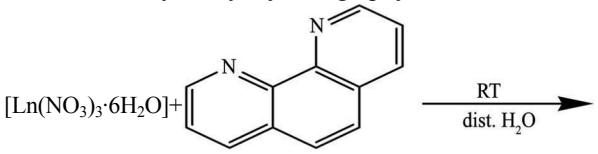
1.2 Preparation

Reaction of $[Ln(NO_3)_3{\cdot}6H_2O]$ (Ln=Ce, Pr and Nd) with phen in a stoichiometric ratio in distilled H_2O, afforded pale yellow crystals of $[Ce(phen)_2(NO_3)_2(H_2O)_2]{\cdot}NO_3$ and $[Pr(Phen)_2(NO_3)_2(H_2O)_2]{\cdot}NO_3$ and colourless crystals of $[Nd(phen)_2(NO_3)_2(H_2O)_2]{\cdot}NO_3$. These crystals were recrystallized from distilled H_2O, dried over anhydrous calcium chloride and their purity was checked by thin layer chromatography (TLC). The complexes were characterized by X-ray crystallography.



$[Ln(phen)_2(NO_3)_2(H_2O)_2]$ (Ln=Ce, Pr and Nd).

1.3 Determination of crystal structure

Crystals of 0.12 mm×0.08 mm×0.03 mm (Ce), 0.07 mm×0.03 mm×0.02 mm (Pr) and 0.12 mm×0.08 mm×0.03 mm (Nd) were mounted on a Nonius Kappa CCD diffractometer, equipped with a rotating anode generator Nonius FR591 and used for data collection at low temperature 273(2) K. Programmes used: data collection collects (Hoft R. Data collection software, nonius collect, Delft, The Netherlands: Nonius, 1998) data reduction and absorbtion correction Denzo-SMN[32]. The structures were solved by direct methods (SHELXS- 97)[33], and all the non-hydrogen atoms were refined anisotropically using full matrix, least-squares technique on F^2. The theta range for data collection lies from 4.10º to 25.00º (Ce complex), 4.08º to 25.00º (Pr complex) and 4.06º to 25.00º (Nd complex). Refinement with anisotropic thermal parameters for non-hydrogen atoms led to the observed reflection R values of 0.0193, 0.0242 and 0.0240. The crystal structure (graphics done with Schakal[34]) of the complexes are shown in Figs. 1 and 2 with thermal ellipsoidal representation at 50% probability level. The hydrogen atoms of 1,10-phenanthroline were placed in idealized positions and refined with a 'riding model'. Details concerning crystal data and refinement are summarized in Table 1 and selected bond lengths (nm) and bond angles (º) are given in Table 2. Hydrogen coordinates and isotropic displacement parameters (Table 2, supplementary material) are also reported.

2 Thermal studies

2.1 Non-isothermal TG

Non-isothermal TG studies on complexes (mass ~20 mg, 100–200 mesh) were undertaken in static air at the heating rate of 10 ºC/min using an indigenously fabricated TG apparatus[35]. Gold crucible was used as sample holder and data are reported in Fig. 3.

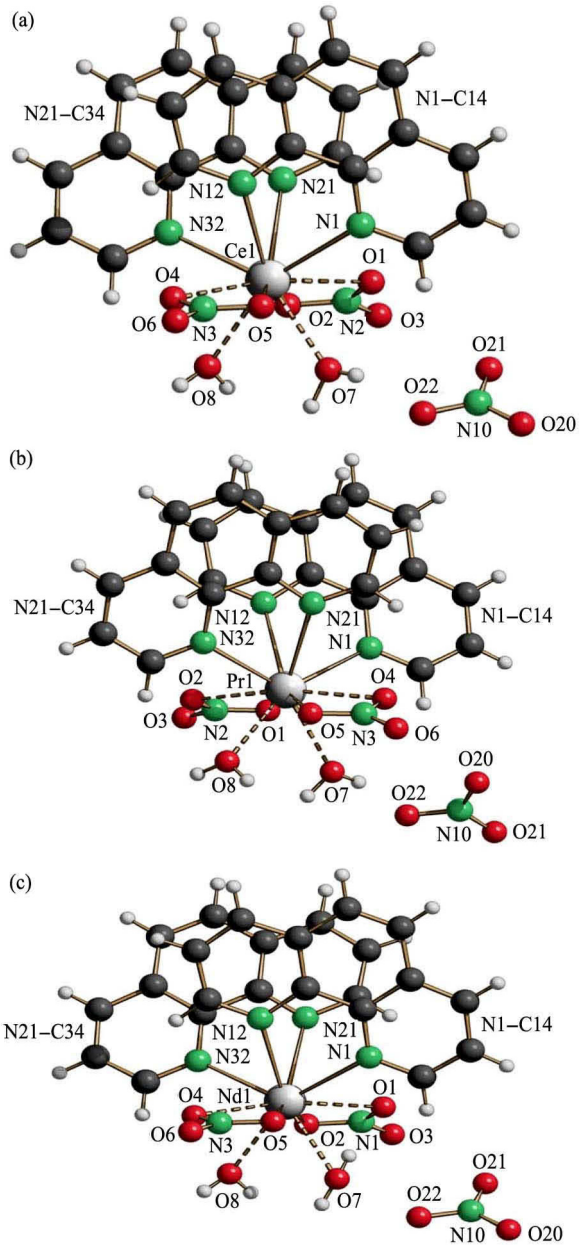


Fig. 1 Crystal structure of lanthanide complexes
(a) Cerium; (b) Praseodymium; (c) Neodymium

2.2 Simultaneous TG-DTA

Simultaneous TG-DTA of the complexes was obtained on Pyris Diamond star system under nitrogen atmosphere at the flow rate of 200 mL/min at a heating rate of 10 ºC/min. The curves are shown in Fig. 4 for the three complexes and the phenomenological data on TG-DTA are summarised in Table 3.

2.3 Isothermal TG

These studies on complexes (mass ~20 mg, 100–200 mesh) were carried out in static air using the above said TG apparatus at appropriate temperatures and data are reported in Fig. 5.

2.4 Kinetic analysis of isothermal TG data

The kinetic analysis using isothermal TG data has