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Preparation, X-ray crystallography and thermolysis of lanthanide metal nitrate complexes with 2,2′-bipyridine, Part-88

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HIGHLIGHTS

- Lanthanide metal (Ce, Pr, and Nd) nitrate complexes have been prepared.
- Crystal structure for these complexes was confirmed by X-ray crystallography.
- Thermal analysis of these complexes has been done by TG and TG-DTA.
- Kinetics of thermal decomposition has been evaluated by model fitting and iso-conversional methods.

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ABSTRACT

The nitrate complexes of cerium, praseodymium and neodymium with 2,2'-bipyridine of general formulae, $[Ln(bipy)_2(NO_3)_3]$, have been prepared and characterized by X-ray crystallography. Thermal studies were undertaken using thermogravimetry (TG), TG (DTA) differential thermal analysis and ignition delay measurements. The kinetics of thermal decomposition of these complexes was investigated using isothermal TG data by applying model-fitting and iso-conversional methods. The cerium complex decomposes in single step whereas praseodymium and neodymium complexes decompose in three steps.

1. Introduction

Metal complexes of reducing group ligands (e.g. NH_3, ethylenediamine, propylenediamine, etc.) with oxidizing counterions (e.g. ClO_4^-, NO_3^-), exhibit the characteristic of energetic compound. Transition metal complexes with ethylenediamine [1,2], propylenediamine [3,4], 1,4-diaminobutane [5,6], 1,6-diaminohexane [7,8] and hydrogen bonded hexamethylenetetraamine [9,10] have already been investigated. These complexes when raised to higher temperatures, whether by direct heating, friction, impact or shock, undergo exothermic, self-propagative decomposition reactions. On thermolysis, they release the thermal energy and produce corresponding metal oxide which can be utilized as burning rate catalysts [11]. On the other hand, rare-earth oxide thin films can find numerous applications, for example, as luminescent materials, catalysts, buffer and protecting layers and as constituents in oxide superconductors and solid oxide fuel cells [12–14].

Rare earth complexes have been extensively studied owing to their unique structures and their chemical, industrial, biochemical and medicinal applications [15–17]. During the past few decades, there has been a keen interest in the characterization and thermal decomposition of lanthanide metal complexes containing bidentate ligands [18–20]. The important feature of lanthanide is due to relatively steady variation of properties, which results from the 'lanthanide contraction' and thus due to their versatile nature [21,22], lanthanide complexes have achieved much attention in recent years. Out of the various types of bidentates, 2,2′-bipyridine (bipy) is a very common ligand for complexation to lanthanide metal ions [23]. Considerable research have been performed on the lanthanide complexes with 2,2′-bipyridine [24,25]. Recently, we have undertaken thermal studies on transition metal nitrate and perchlorate complexes with 2,2′-bipyridine [26,27]. The metal

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amine nitrate complexes lead to their various application such as in explosives, propellants and pyrotechnics [28,29] and display exothermic decomposition at elevated temperature.

The present investigation deals with the preparation, characterization and thermolysis of lanthanide metal nitrate complexes with 2,2′-bipyridine. These complexes have been characterized by X-ray crystallography. Their thermolysis has been undertaken using (TG) thermogravimetry, (TG-DTA) differential thermal analysis and ignition delay measurements.

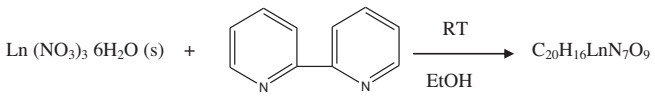
2. Experimental

2.1. Materials

Metal nitrate hexahydrate (CDH and Aldrich), 2,2′-bipyridine (Himedia), ethanol (s.d. fine) were used as received.

2.2. Preparation

The complexes have been prepared by treating the ethanolic solution of corresponding metal nitrate with 2,2′-bipyridine in stoichiometric ratio at room temperature (in absence of nitrogen). These complexes were recrystallized from absolute alcohol, dried over anhydrous calcium chloride and their purity was checked by thin layer chromatography (TLC). The complexes were characterized by X-ray crystallography.



where Ln = Ce, Pr, and Nd.

2.3. Determination of crystal structure

Crystals of the complexes were obtained by recrystallisation from alcoholic solutions. The data collection on the crystals were performed at low temperature (223 K) using a Nonius Kappa CCD diffractometer equipped with a rotating anode generator Nonius FR591.

Programmes used: data collection collects (Nonius B.V; 1998) data reduction and absorption correction Denzo-SMN [30]. The structure were solved by direct methods (SHELXS-97) [31] and refined by full matrix least square method on all F2 data using SHELXL-97 [32]. Refinement with anisotropic thermal parameters for non-hydrogen atoms led to the *R*-values of 0.0193 (Ce), 0.0242 (Pr) and 0.0240 (Nd). The theta range for data collection lies from 4.22 to 28.25 Å (Ce complex), 4.24 to 28.56 Å (Pr complex) and 4.26 to 28.27 Å (Nd complex). The crystal structure (graphics done with Schakal [33]) of the complexes are shown in Fig. 1. The crystal parameters of the complexes are summarized in Table 1. Bond lengths, bond angles (Table 1, supplementary data) and hydrogen coordinates (Table 2) are also reported.

2.4. Thermal studies

2.4.1. Nonisothermal TG

These studies on complexes (mass 20 mg, 100–200 mesh) were undertaken in static air atmosphere at a heating rate of 10 °C/min using indigenously fabricated TG apparatus [34]. Gold crucible was used as sample holder and data is reported in Fig. 2.

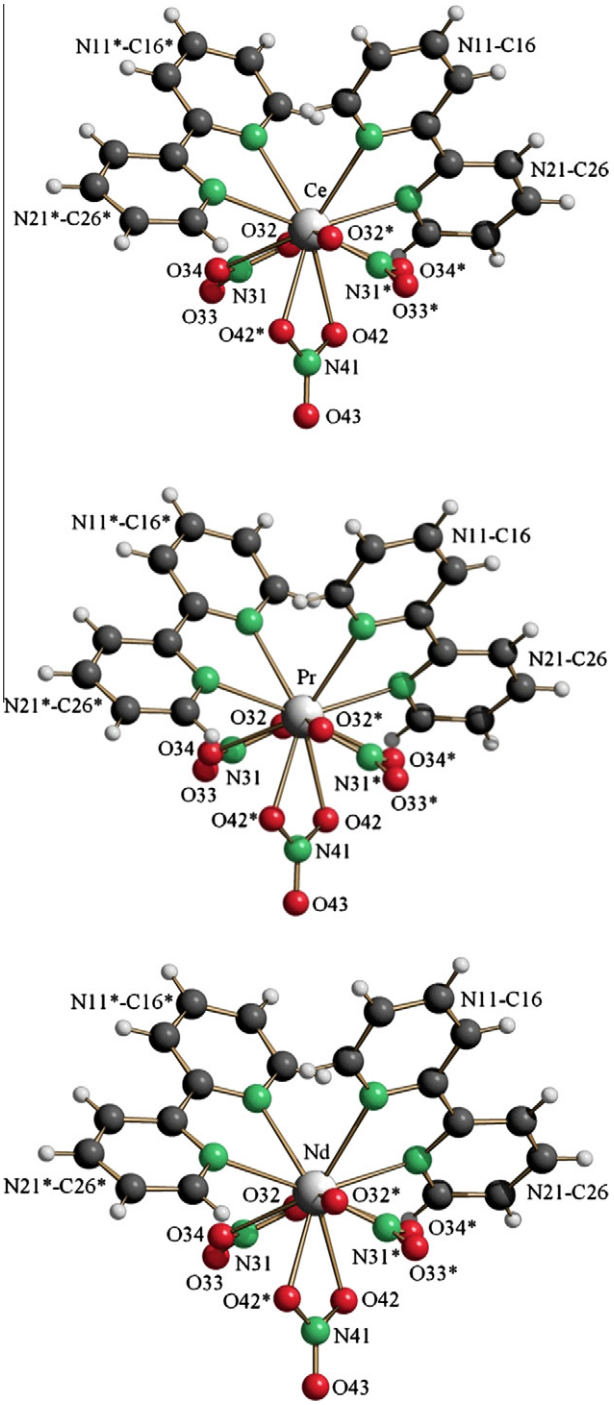


Fig. 1. Crystal structures of Cerium, Praseodymium and Neodymium complexes.

2.4.2. 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 °C/min. The curves are shown in Fig. 3 for cerium, praseodymium and neodymium complexes respectively. The phenomenological data on TG-DTA are summarized in Table 3.

2.4.3. Isothermal TG

The isothermal TG on these complexes (mass 20 mg, 100–200 mesh) were carried out in static air using the above said TG apparatus at appropriate temperatures and data is reported in Fig. 4.