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Thermal and magnetic properties of lanthanide based metal-organic complex: Neodymium tartrate trihydrate

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ABSTRACT

Single crystals of a lanthanide metal organic complex neodymium tartrate trihydrate have been synthesized. Scanning electron microscope reveals the morphology of single crystals as dipyramidal. X-ray crystal structure analyses reveal that the complex has tetragonal structure. The effect of ligand on the magnetic moment of Nd ion was studied. The elemental analyses, infrared spectra and thermogravimetric behaviour of the complex were also studied. The activation energies corresponding to different stages of decomposition were also calculated.

1. Introduction

Metal-organic complexes (MOCs) represent a class of molecule-based materials, which have shown various functionalities or properties due to their hybrid metal-organic nature. MOCs are very important because of their potential applications as luminescent substances [1], as gas storage media [2], most significantly with additional application in catalysis [3], nonlinear optics [4], magnetic materials [5] etc. The association of molecular magnetic materials with design is of great importance, not only to study relevant physical phenomena [6,7] but also to study the correlation between molecular structure and observed magnetic properties, such as spin canting, meta-magnetism and spin–flop transitions [8–11]. Molecule based magnetic materials are continuously studied for their important applications in sensors, magnetic storage, magnetic shielding etc [12]. The basic need of a molecular magnetic material is to incorporate paramagnetic centers (spin carriers) with suitable bridging ligands giving rise to magnetic exchange coupling [13]. Most of the work on magnetic MOCs is concentrated on those MOCs that contain transition metals, because of the good understanding of the magnetic properties of such ions. However, unlike transition metals, the f-electrons in lanthanides make these elements capable of having a larger coordination sphere and connectivity that has recently led to a large number of reports on lanthanide based MOCs. Lanthanide based MOCs benefit from the intrinsic properties of lanthanide metal ions that have unique coordination and electronic properties [14]. One of the main reasons to incorporate Ln^{3+} metal ion into a framework is because Ln^{3+} ions have large J value caused by unquenched orbital contribution. There are reports on the development of metal tartrate complexes [15–24], but most of these articles report the growth of these complexes as spherullites [19–24], not as single crystals. Spherullites are not fully crystalline as they contain some portion of amorphous phase where as single crystals are the true representatives of the behaviour of the material. To the best of our knowledge, there are no reports on the growth, thermal and magnetic behaviour of neodymium tartrate single crystals. In this paper, we report single crystal growth of neodymium tartrate complex, its thermal and magnetic behaviour.

2. Preparation of the metal-organic complex

Single crystals of neodymium tartrate trihydrate (NTT) were prepared by gel diffusion technique at room temperature. The growth of neodymium tartrate crystals is already reported in the literature [24]. They have used an inorganic silica gel and were able to prepare only the spherulites. The present experiments were conducted in an organic agar–agar gel and the single crystals of the material were obtained. The agar–agar gel was prepared by

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dissolving 0.7% w/v of extra pure agar–agar powder in distilled water to which 1 M tartaric acid was added. The solution so prepared was then allowed to set in glass tubes of length 20 cm and diameter 2.5 cm for 2 days. After the gel was properly set, the upper reactant 0.5 M neodymium nitrate hexahydrate [$Nd(NO_3)_3\_6H_2O$] was carefully poured over the set gel. Good quality pink color single crystals of NTT were obtained after leaving the crystallizer undisturbed for about 3 weeks at room temperature. The grown crystals were characterized by different physio–chemical techniques.

3. Results and discussion

3.1. Morphology of the crystals

The external morphological studies were carried out using a scanning electron microscope (HITACHI S-3000H). The SEM micrograph of some single crystals of NTT is shown in Fig. 1 at a magnification of 190×. It is evident that the material has grown in the form of single crystals and have dipyramidal morphology. The growth of other lanthanide tartrate complexes have been reported in the literature [25,26], which also posses the same morphology.

3.2. Elemental composition of the crystals

The contents of carbon and hydrogen in the prepared compound were obtained by using JEOL, JED-2300 energy dispersive spectrometer, attached to a scanning electron microscope JEOL JSM-6390LV. The observed values of weight percentage for C, H and N present in the material are 22.01, 3.02 and 0.01 respectively. On the basis of the experimental quantitative estimation of elements, it is suggested that the chemical formula of the grown crystals is $Nd(C_4H_5O_6)^{-}(C_4H_4O_6)^{2-}\cdot-3H_2O$. The weight percentage values of C, H and N calculated on the basis of this formula are 19.40, 3.05 and 0.00 respectively which are in agreement with the experimental values. The growth of such a metal complex in which tartrate ligand is disordered between a doubly and singly ionized species has been reported in the literature [26]. To further authenticate such a nature of the complex, FTIR analysis was also carried out (Section 3.3).

3.3. Identification of functional groups

Fourier transform Infrared (FT-IR) spectroscopy is an effective technique to identify the functional groups and to elucidate the molecular structure of the compound. The FT-IR spectrum was recorded on a Bruker Vector 22 spectrometer using KBr pellet technique in the wave number range of 400–4000 cm^{-1} (Fig. 2). There is a strong and broad peak centered on about 3270 cm^{-1}. The broad peaks, generally, appear because of the overlapping contribution of various units. Here the band is due to the stretching vibrations of hydroxyl, water molecules and C–H groups. This indicates the presence of water of crystallization or water of hydration.

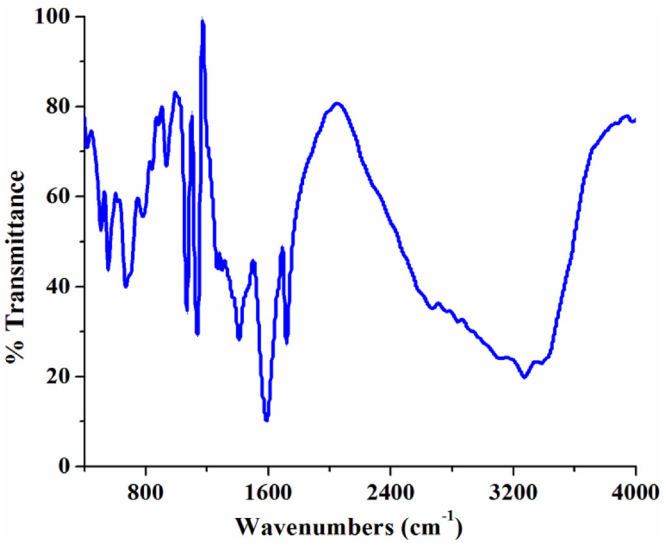

Fig. 2. FTIR spectrum of Neodymium tartrate trihydrate single crystals.

The presence of a strong and narrow peak at 1719 cm^{-1} corresponds to the stretching mode of C=O of unionized COOH group which suggests that one of the tartrate ion is singly ionized. The presence of absorption peaks at 1587 cm^{-1} and 1409 cm^{-1} corresponds to the asymmetric and symmetric modes of carboxylate anion. The presence of other modes such as C–O stretching, νC(OH), δ(C–H) deformation and metal-oxygen stretching have also been detected [27]. The assignments for various absorptions in the FTIR spectra of neodymium tartrate single crystals are shown in Table 1. It is thus clear that the FTIR spectroscopic results of NTT crystals confirm the presence of water of crystallization, tartrate ligands (singly as well as doubly ionized) and metal-oxygen bonding.

3.4. Structural analysis

The single crystals were finely grinded and subjected to powder XRD. X-ray powder diffraction data were collected at room temperature with Bruker AXS D8 Advance powder diffractometer using CuK_α ($\lambda = 1.5406$ °A) radiation. The sample was scanned over the range of $20° \leq \theta \leq 80°$ with a step scan rate of 0.020° per step and a count time of 31.2 s per step. The applied voltage and current are

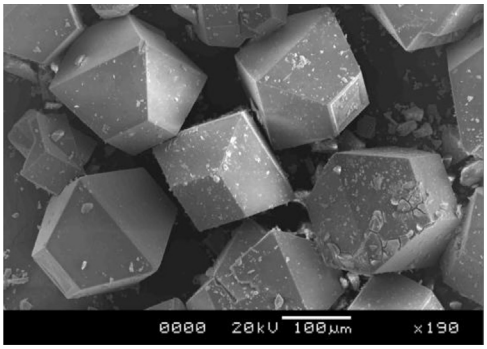

Fig. 1. SEM micrograph of single crystals of neodymium tartrate trihydrate.

Table 1
FTIR peaks and their assignments.

Wave numbers	Assignments
3269.87	ν(O–H) of water and acid
1719.47	ν(C=O) unionized COOH group
1587.32	$\nu_{asy}(COO^-)$
1409.45	$\nu_{sy}(COO^-)$
1266.3	$\rho(CH_2)$
1135.84	νC(OH)
1068.51	δ(C–H)
934.23	ν(C–C)
781.34	δ(O–C=H)+ ν(MO)
669.55	ν(Nd–O)
554.10	Torsion COOH
507.35	$\rho(H_2O)$

ν = stretching, δ = bending deformation, ρ = rocking.