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A novel three-dimensional polymeric structure of crystalline neodymium malonate hydrate

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Abstract

The malonate complex of $Nd_2mal_3.6H_2O$ was prepared and its crystal structure determined by X-ray diffraction method. It crystallises in the monoclinic space group $C2/c$ with cell parameters a=17.2240(1) Å, b=12.3690(7) Å, c=11.2070(7) Å, β=127.532(4)° Z=4 and V=1893.4(2) Å^3. The compound forms a layer-type polymeric structure. The layers are formed by neodymium and one independent malonate group, giving a three-dimensional framework structure. The extensive network of hydrogen bonds and bridge bonds observed in this structure enhances the structural stability. The thermal dehydration of the compound was investigated by TGA measurements. The structure model is consistent with the vibrational behavior and the three different temperatures observed in the dehydration process.

Keywords: Malonate hydrates; FT-IR; TGA; Crystal structure

1. Introduction

Many interesting and peculiar properties exhibited by rare earths and related compounds make them of increasing interest in a growing number of highly important areas of materials science and technology [1–7]. Valuable work on such compounds is scattered throughout the literature of chemistry, physics, metallurgy, crystallography, and mining. However, only few reports are available on the malonates of rare earth elements. Malonates are salts of malonic acid, an organic acid which is the next higher homologue of oxalic acid. An interesting feature of malonate ligand is that it exhibits a rather flexible stereochemistry and variable mode of binding with metal ions in the crystalline state [8–16]. In addition, the malonate ligand is characterized by an active methylene group ($-CH_2$) between the two carboxylate groups.

Advanced crystal engineering by selecting malonate ligand and the coordination geometry of neodymium metal centers as a building block can give a series of versatile frameworks with an interesting mode of crystal packing motifs. The flexible coordination ability of neodymium has been discussed, and adopted different modes of bonding, i.e., ranging from monodentate, chelating, and bridging. Various observed bonding schemes are depicted in Fig. 1.

Crystals of this compound was grown by the gel technique [17] and subjected to X-ray analysis, and thus understanding of the coordination geometry around the rare earth ions is vital for our studies. Analysis was also done using the conventional probes of investigation such

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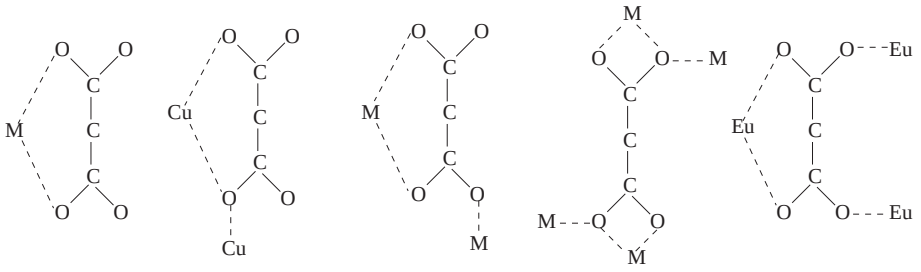

Fig. 1. Bonding schemes.

as Fourier transform infrared (FT-IR) absorption spectroscopy and thermogravimetric (TG) studies.

2. Experimental

Crystals of the title compound were produced in small glass tubes by the controlled diffusion of neodymium ions through inert silica gel in which malonic acid (99.99%) was incorporated. Malonic acid (1 M) was carefully added to sodium metasilicate solution of density 1.03 g cm^{-3} to make its pH value 6. After 3 days, neodymium chloride (99.999%) solution (0.2 M) was carefully poured over the set gel. Pink coloured crystals of the compound used for the investigations were obtained in 4 or 5 weeks. The chemical reaction leading to the formation of the solid product is:

$$2NdCl_3 \cdot 6H_2O + 3CH_2(COOH)_2 \rightarrow Nd_2(C_3H_2O_4)_3 \cdot 6H2O + 6HCl$$

Table 1
Crystallographic data of $Nd_2mal_3 \cdot 6H_2O$[#]

Empirical formula	$C_9H_{17}Nd_2O_{18}$
Formula weight	702.71
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal color, habit	Pale Yellow, Prism
Crystal system	Monoclinic
Space group	*C*2/*c*
Cell dimensions	*a*=17.2240(1) Å
	b=12.3690(7) Å
	c=11.2070(7) Å
	β=127.532(4)°
Volume	1893.4(2) $Å^3$
Z	4
Density(calculated)	2.465 Mg/m^3
Absorption coefficient	5.514 mm^{-1}
F_{000}	1344
Crystal size	0.2×0.2×0.2 mm
Theta range for data collection	25.69° to 32.50°
Index ranges	−25≤*h*≤26
	−18≤*k*≤18
	−13≤*l*≤13
Reflections collected	2105
Independent reflections	1216 [*R*(int)=0.0373]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1216/0/127
Goodness-of-fit on F^2	1.091
Final *R* indices [$I>2\sigma(I)$]	*R*1=0.0579, *wR*2=0.1575
R indices (all data)	*R*1=0.0604, *wR*2=0.1611
Largest diff. peak and hole	1.886 and −1.399 e $Å^{-3}$

[#] Full crystallographic details are available at the Cambridge Crystallographic data centre (CCDC) under the reference No. 226716.

FT-IR spectrum of the compound was recorded in the wavenumber region 4000–400 cm^{-1} using a Bruker IFS66 spectrophotometer, by the KBr pellet method. The spectral resolution was better than 4 cm^{-1}. The spectrum presents all the characteristic bands of the compound.

Thermogravimetric analysis of the compound was carried out using a STA 1500 thermal analysis system by heating the compound up to 900 °C, in nitrogen atmosphere. Runs were taken at a heating rate of 10 °C/min.

Single crystal of dimensions 0.2×0.2×0.2 mm was chosen for X-ray diffraction studies. The measurements were made on a DIPLabo Imaging Plate system with graphite monochromated MoK_α radiation. Thirty-six frames of data were collected using oscillation method. Successive frames were scanned in steps of 5°/min with an oscillation range of 5°. Image processing and data reduction were done by using Denzo [19]. The structure was solved and refined using maXus [18–21] program. All the non-hydrogen atoms were revealed in the first map. Full-matrix least-squares refinement based on 1216 observed reflections ($I>2\sigma(I)$) with isotropic temperature factors for all the atoms converged residual to *R*=0.1027. The hydrogen atoms were placed at calculated positions and were not refined. Refinement of non-hydrogen atoms with anisotropic thermal parameters was started at this stage. After ten cycles of refinement the residuals saturated at *R*=0.0579. Table 1 gives the details of crystal data, data collection, and refinement.

3. Results and discussion

3.1. Spectral analysis

The FT-IR spectrum recorded (Fig. 2) reveals the bonding structure of the compound. Internal vibrations of the compound are mainly due to carboxylate group, methylene group and water molecules. The spectrum was