



Polymeric chains, hydrogen bonds and magnetism in Nd(III) adipates

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Abstract

An AC susceptibility study of $[\text{Nd}_2(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2)_3(\text{H}_2\text{O})_2]$ (**1**) obtained from a solution at ambient conditions was performed in the range 14–320 K. An ordering transition, $T_C = 280(2)$ K, not related to a structural phase transition, a ferromagnetic like Curie–Weiss behavior above T_C , an antiferromagnetic like dependence of χ'^{-1} at the lowest temperatures and a non-linear thermal dependence of χ'^{-1} in the in-between region have been observed. Samples prepared by hydration of **1** during different periods showed enhancement of the observed features. Links between water content, crystal structure and magnetic response are discussed.

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1. Introduction

The increased activity in the field of metal dicarboxylates (see e.g. [1]) is primarily due to the

wide variety of structures that can be built taking advantage of the versatility of these ligands, of formula: $-\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2-$, which allow to obtain materials with unique properties, especially in magnetism, luminescence and catalysis. Many recent reports have focused on the synthesis and characterization of transition metal and rare earth compounds using dicarboxylates of different length as blocking and bridging ligands [2–6].

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These anions work as multifunctional ligands, not only due to their various coordination modes (several chelating bidentate and/or different bridging, which can coexist) but also because of their ability to act as hydrogen bond acceptors and donors to generate supramolecular assemblies of varied dimensions. Regarding magnetic characteristics, the carboxylate bridge has evidenced to be an efficient pathway to couple paramagnetic or magnetic centers either ferro- or antiferromagnetically [7–10], the coupling constant being influenced by the conformation of the bridge or the geometry of the magnetic center environment. We have recently synthesized from solutions, under ambient conditions, and solved $[\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ and $[\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (Adip: $\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2$) frame structures [5]. Their AC susceptibility showed a rather complex temperature (T) dependence, which seemed to be correlated with the degree of hydration. The current results were yielded by experiments especially designed to clarify this point.

2. Experimental

Reagents of analytical grade, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) and Adipic acid (Sigma), were used in the synthesis without further purification. The synthesis proceeds by dissolving 0.5 mmol of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) (in a 50 mL aqueous solution containing 0.75 mmol of Adipic acid under stirring. The final pH 4.5 was reached by the addition of NaOH solution. The solution was left to evaporate slowly at room temperature (r.t.). The reaction product was filtered, washed with distilled water and dried under P_4O_{10} . The obtained powder ($\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_2$, **1**) was soaked in distilled water for successive periods of 16 h under intermittent stirring conditions, filtered and dried at r.t. to get compounds **2** and **3**. Magnetic measurements were carried out with a LakeShore 7130 AC Susceptometer, with an alternating field of 1 Oe and 825 Hz, in stabilized temperature mode with a step of 3 K per point. A Shimadzu series 50 set of equipments were employed to obtain DTA data, from r.t. to 473 K at 10 K/min, with a nitrogen flux of

50 mL/min, and DSC data from about 173 to 393 K, in a helium atmosphere with a flux of 40 mL/min. X-ray powder diffraction patterns (XRD) were obtained with a Rigaku D-MAX-IIIC diffractometer using CuK_α radiation (Ni-filter) and NaCl and quartz as external calibration standards.

3. Results

XRD data of **1**, Fig. 1, are coincident with the product obtained after the first step of dehydration of $[\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ [5,11], XRD data of **3** are consistent with the single crystal structure of $[\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ [5]. DTA data, Fig. 2, are coherent with the XRD [11]. The curve corresponding to **3** shows two peaks, one at ≈ 356 K caused by the loss of two coordination and all hydration waters, and the other at ≈ 456 K caused by the removal of the remaining two coordination waters; **1** only shows one peak due to the coordination waters' loss [11]. Comparison of all data allows inferring that compound **2** is a partial hydration of **1**. The analysis of χ'^{-1} vs. T curves for the three compounds, Fig. 3, lets us identify three zones with different temperature dependence. Starting from 320 K, as T decreases a change of χ'^{-1} slope at $T_C = 280(2)$ K is observed. This, along with the maximum found at that

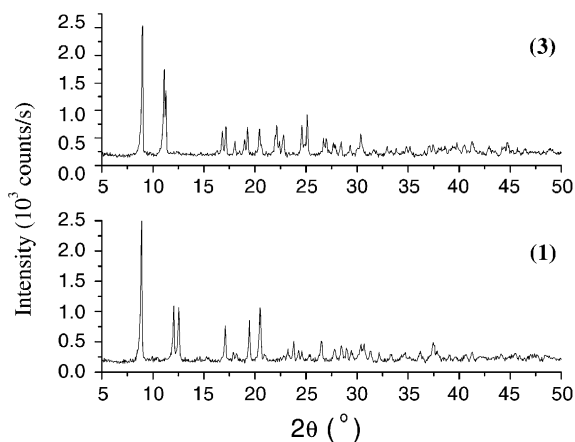


Fig. 1. XRD patterns for (1): $\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_2$ and (3): $[\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$.

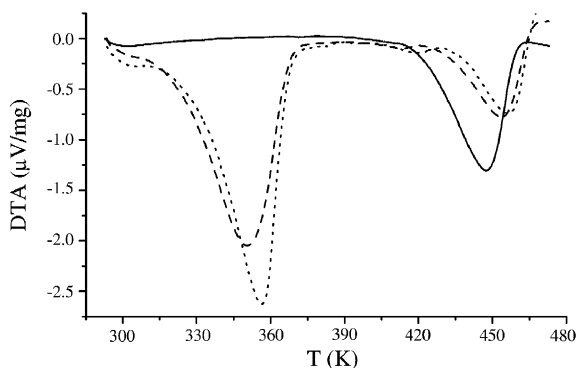


Fig. 2. DTA curves for: $\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_2$ (**1**) (solid), **1** partially hydrated (**2**) (dash), and $[\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (**3**) (dots).

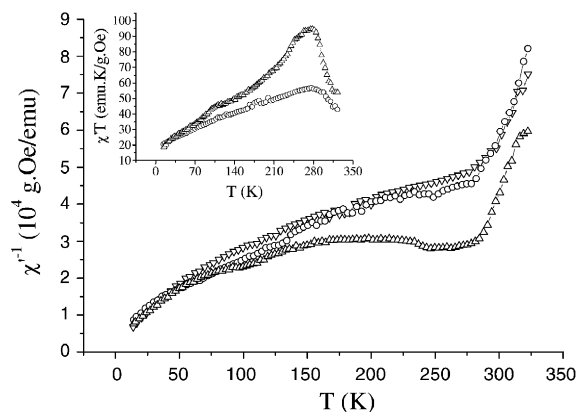


Fig. 3. χ^{-1} vs. T for: $\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_2$ (**1**) (\circ), **1** partially hydrated (**2**) (∇), and $[\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (**3**) (\triangle). The internal layout shows the χT product for compounds **1** (\circ) and **3** (\triangle).

temperature in $\chi' T$ indicates a magnetic transition, which is congruent with DSC curves in the range 275–285 K. Peaks in DSC data are found at 278.2(3) K and 279.6(3) K for **1** and **3**, respectively in Fig. 4. All χ' curves above T_C can be fitted with a Curie–Weiss law and a Curie constant value of about 1.2(1) emu K/g Oe. Below T_C , χ' vs. T shows additional slope changes, in all the compounds, but no other neat transition T can be observed. At the lowest T values, curves slope (similar for the three compounds) would indicate an antiferromagnetic (AF) order, though no maximum in χ' is

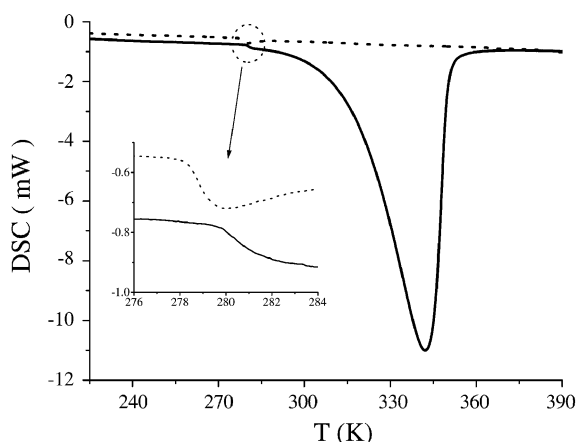


Fig. 4. DSC data, for $\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_2$ (dot) and $[\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (solid). Reduced layout shows the thermal transition related to the magnetic order temperature.

reached in the measured range. The three curves in the medium T value's range display noticeable differences suggesting diversity of magnetic orders (likely co-existing).

4. Discussion

As described in Ref. [5], Nd(III) ions in **3** are nine, coordinated by two O atoms of water molecules and seven from Adip. Two alternating bridges help the Nd to build infinite polymeric chains, which are linked by a three-dimensional HB network comprising hydration waters and some of the Adip O atoms. The Nd(III) ions in $[\text{Nd}_2(\text{Adip})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ [**5**], **4** are also nine, coordinated with only one water in the coordination sphere [5], polymeric chains and a HB network are also observed. Kiritsis et al. [12] study on $[\text{La}_2(\text{Adip})_3(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (isostructural with **3**) and on its dehydration products, would indicate that **1** is not porous. Therefore, chain formations (probably similar to the ones in **4**) and no HB network may be expected in **1**. From the previous analysis it seems feasible that the T_C value and the magnetic behavior above it in the three samples were related with the polymeric chains, while magnetic behavior in the in-between T region and the differences observed in χ'^{-1} as function of

the degree of hydration were associated with modifications in the super exchange paths produced by the HB network changes as function of T [5,11]. To confirm or discharge an AF order at the lowest T , new susceptibility measurements at temperatures below 14 K are crucial.

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