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Synthesis and characterization of montmorillonite clay intercalated with molecular magnetic compounds

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ABSTRACT

In this work montmorillonite (MMT) clay, whose matrix was modified with an ammonium salt (hexadecyltrimethylammonium bromide – CTAB), was employed as an inorganic host for the intercalation of three different molecular magnetic compounds through ion exchange: a nitronyl nitroxide derivative 2-[4-(*N*-ethyl)-pyridinium]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (*p*-EtRad$^+$) and two binuclear coordination compounds, [Ni(valpn)Ln]$^{3+}$, where H_2valpn stands for 1,3-propanediyl-bis(2-iminomethylene-6-methoxy-phenol), and Ln$=$Gd^{III}; Dy^{III}. The pristine MMT and the intercalated materials were characterized by X-ray powder diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and magnetic measurements. The X-ray diffraction data analysis showed an increase of the interlamellar space of the intercalated MMT, indicating the intercalation of the magnetic compounds. Furthermore, the magnetic properties of the hybrid compounds were investigated, showing similar behavior as the pure magnetic guest species.

1. Introduction

Montmorillonite (MMT) clay is an extensively studied material due to its broad range of applications [1–3]. As a member of the smectite group of minerals, its layered structure consists of one octahedral sheet linked between two tetrahedral sheets through sharing of edge oxygen atoms. The octahedral sites are occupied mainly by Al^{III} ions, partially substituted by lower valence cations like Mg^{II} or Fe^{II}, and the tetrahedral ones are occupied by Si^{IV} with some Al^{III} substitution. This unbalanced substitution generates a negative charge in the layer, which is neutralized by exchangeable hydrated ions, like Na$^+$ or Ca^{2+}, located in the interlamellar space [4,5].

The ability of some layered materials to incorporate guest species in their lattice is of great interest for materials science. Through ionic exchange it is possible to obtain hybrid materials in which the species with the desired properties are arranged between the layers of the host. Usually, the guest's behavior within an array is different from their one in solid or solution states due to constrained environment provided by the layered matrix. Theoretically, the bulk properties of this hybrid material would rely on the guest–guest and guest–host interactions, and could be modulated by changing guest's or/and host's composition [6].

Molecular compounds that display slow magnetic relaxation phenomenon such as Single Molecule Magnets (SMMs) or one-dimensional compounds, called Single Chain Magnets (SCMs), have attracted much attention of the scientific community [7–10]. The interest on these compounds relies not only on this unusual phenomenon but also on their potential applications as high-density storage devices [11,12]. Several strategies can be employed to synthesize this kind of compounds. The use of lanthanides is one of the most promising, since 4*f* metal ions bring large and, in some cases, highly anisotropic magnetic moments [13–15]. In addition, nitroxide and nitronyl nitroxide radicals have been used in molecular magnetism almost since the beginning of the area, being a very useful strategy to obtain interesting compounds [16,17].

Inorganic–organic hybrid compounds involving magnetic species are an attractive class of materials exhibiting a range of unusual optical and magnetic properties [18]. Immobilization of

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the radical species, for example, can modify the spin orientations relative to the position in the molecular crystals, resulting in altered magnetic properties. For instance, Caneschi et al. have reported the magnetic properties of nitronil nitroxide derivative intercalated into layered double hydroxide and zirconium phosphate hosts [6].

Based on this scenario, we found it interesting to investigate the behavior of some molecular magnetic compounds within an ordered matrix, and the montmorillonite's layers were considered appropriate for our interest. In the present work, we have made the intercalation of MMT with three magnetic compounds, namely: one nitronyl nitroxide organic radical and two binuclear coordination compounds containing Ni^{II} and lanthanide ions (Gd^{III} or Dy^{III}) coordinated to the organic ligands. The $[Ni^{II}Dy^{III}]$ binuclear complex shows Single Molecule Magnet (SMM) behavior due to the large magnetic moment and strong magnetic anisotropy of Dy^{III} ion [19]. The pristine MMT and the intercalated ones were characterized by X-ray powder diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The magnetic properties of the hybrid materials were studied.

2. Materials and methods

2.1. General

Sodium fluoride (NaF), magnesium acetate tetrahydrate ($Mg(CH_3COO)_2 \cdot 4H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), silicon dioxide (SiO_2), hexadecyltrimethylammonium bromide (CTAB), iodoethane, gadolinium(III) nitrate hexahydrate ($Gd(NO_3)_3 \cdot 6H_2O$) and dysprosium(III) nitrate trihydrate ($Dy(NO_3)_3 \cdot 3H_2O$) were purchased from Sigma-Aldrich. The solvents THF and acetonitrile were purchased from Tedia Brazil and used without further purification.

2.2. Synthesis of montmorillonite and intercalation with hexadecyltrimethylammonium

The MMT clay was synthesized with the purpose of obtaining a highly pure host. Since the natural clay can have iron in its structure, our synthesized matrix guarantees that the magnetic response will be exclusively due to the intercalate compound.

Montmorillonite has been synthesized by different routes using hydrothermal technique from soft to extreme conditions of pressure and temperature, and using diferent precursors [20]. In the present work the hydrothermal synthesis was performed using fluoride medium as mineralizing agent. In this case, fluoride can substitute structural hydroxyl groups, since they have similar charge and size. Such replacement creates defects in the structure, thus increasing the thermal stability of smectite [21,22].

The hydrogel was prepared, in a 20 ml Teflon bottle, fixing the quantity of water in 40% at the total volume using as a source of fluoride, magnesium, aluminum and silicon, NaF, $Mg(CH_3COO)_2 \cdot 4H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and SiO_2, respectively, in a stoichiometric proportion to the nominal formula $Na_{1.6}(Al_{2.4}Mg_{1.6})Si_8O_{20}(OH)_4$. The molar ratios F/Si and H_2O/Si were fixed at 0.05 and 96, respectively. The initial pH was adjusted to a range of 5–6, with sodium hydroxide solution and the obtained hydrogel was left 2 h at room temperature. The Teflon bottle was heated at 230 °C in an autoclave, with a heating rate of 110 °C h^{-1}, and maintained under autogenous water pressure for a period of 3–4 days. At the end of reaction, the autoclave was cooled to room temperature in a rate of 40 °C h^{-1}. The product was filtrated, washed with distilled water and then dried over night at 70 °C. (Yield=75%)

In order to facilitate the intercalation process, the original clay was modified with a quaternary ammonium salt resulting in an enhancement of the interlamellar space making it more hydrophobic, thus facilitating the entrance of the guests of interest [23]. The ion exchange was performed in a suspension at 10 % w/v of clay in a saturated solution of hexadecyltrimethylammonium bromide (CTAB) in deionized water. The dispersion was refluxed at 80 °C under stirring for one day. This procedure was repeated twice, ensuring efficient cation exchange. Afterwards, the suspension was washed with distilled water until the test for bromide in the supernatant was negative. The organic clay (MMT-Org) was dried at 70 °C.

2.3. Synthesis of p-EtRadI

The radical 2-[4-(N-ethyl)-pyridinium]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide Iodide (*p*-EtRadI) was synthesized as described previously [24]. IR ν_{max}/cm^{-1} 1637, 1409, 1370, 1171, 1137, 841.

2.4. Synthesis of $[Ni(valpn)Ln(NO_3)_3] \cdot x(solvent)$

The $[Ni(valpn)Ln(NO_3)_3] \cdot x$(solvent), valpn=1,3-propanediyl-bis(2-iminomethylene-6-methoxy-phenol), Ln=Gd^{III} or Dy^{III} compounds were prepared following reported procedures [25]. IR $[Ni(valpn)Gd(NO_3)_3]$ ν_{max}/cm^{-1} 1620, 1470, 1310, 1300, 1220, 738. IR $[Ni(valpn)Dy(NO_3)_3]$ ν_{max}/cm^{-1} 1625, 1470, 1313, 1297, 1225, 1070, 741.

2.5. Intercalation of magnetic compounds

The intercalation process was based on montmorillonite's average cation exchange capacity (CEC): 100 meq/100 g [23]. The organic clay was intercalated with the three magnetic compounds described above following similar procedures. The method is based on the dispersion of the organic clay in a solution of the molecular magnetic compound of 10 % w/v in acetonitrile, under reflux and stirring. After one day the product (MMT derivatives) was extensively washed with acetonitrile by centrifugation. The pale green solid obtained was dried at room temperature.

2.6. Characterization

FTIR spectroscopy of the MMT derivatives was performed on a Perkin-Elmer 1000 spectrometer and of the pure magnetic compounds and pristine MMT on a Bruker ALPHA spectrometer. Thermogravimetric (TGA) experiments were performed on a thermogravimetric analyzer (Q500 TA Instruments) under air atmosphere, at a flow rate of 20 ml min^{-1}. Samples in platinum pans were scanned from room temperature to 1000 °C at a heating rate of 10 °C min^{-1}. Scanning electron microscopy (SEM) images of pristine MMT were taken with a Zeiss DSM 940 microscope and with a JEOL 6510 microscope for MMT derivatives. All samples were dispersed over a carbon tape and coated with an ultrathin gold layer. X-ray powder diffraction (XRD) measurements were used for evaluation of the basal distance before and after the intercalation. X-ray powder diffraction (XRD) was performed on a Bruker D8 Advanced diffractometer using Cu Kα (λ=1.5405 Å) radiation, Ni filter, Si(Li) detector with scanning from $2\Theta=3°$ to 70°, step of 0.05° and measurement time of 0.2 s. The corresponding "*d*" interplanar basal spacing of the MMT was computed from Bragg's diffraction equation, $2\,d\,sin\theta = n\lambda$, "*n*" (=1) being the order of reflection and "θ" the angle of diffraction.

DC magnetic measurements were performed on a Cryogenic S600 SQUID magnetometer in the temperature range 2–280 K. The sample was placed in a gelatin capsule. The magnetic data were corrected taking into account the contribution of the sample holder and the temperature independent susceptibility, assuming that the paramagnetic part follows the Curie law above 200 K.