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Short communication

Lanthanides–clay nanocomposites: Synthesis, characterization and optical properties

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ABSTRACT

Complexes of Europium(III) and Terbium(III) with 2,2-bipyridine and 1,10-phenanthroline were inserted into Na-bentonite by ion exchange reactions at room temperature. The products display interlaminal distances and stoichiometries in agreement with the ion exchange capacity and the interlayer space available in the clay. The optical properties of the intercalates, being qualitatively similar to those of the free complexes, are additionally improved with respect to exchange processes with the medium, especially in a moist environment. The protection against hydrolysis, together with the intensity of the optical transition ${}^5D_0-{}^5F_2$ observed in the nanocomposite, makes these products promising for the development of novel optical materials.

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1. Introduction

Natural layered clays have been widely studied as conventional materials. However, in the last decade the attention is increasingly focusing in their rich intercalation chemistry, which permits the regulation of their properties thus offering a great potential for the development of smart materials [1,2]. Our approach in this field has been to produce luminescent lanthanide-based nanocomposites in which the lanthanide ions, recognizing determined sites in the clay interlaminal spaces, may be quantitatively embedded in rather inert cavities. In these products the inorganic matrix is expected to play the role of a stabilizer of the lanthanide species against reaction with moisture, while retaining luminescent properties, resulting in an effective protecting effect. It is this effect which makes ours a promising approach to develop improved luminescent materials.

The luminescence efficiency of the forbidden f–f electronic transitions, which are responsible for the sharp and light emission characteristic of lanthanides, strongly depends on the coordination

sphere of the ion. Much attention has been paid to find new efficient and chemically stable lanthanide-based luminescent substances by using ligands which contribute to the absorption of the complex as well as to anchoring the ions in solid matrices. In this way non-radiative relaxation of excited states via high-energy vibrations produced by O–H bonds is avoided. In addition to improved emission, these ligands protect the lanthanides from degradation by hydrolysis reactions [3]. Results from attempts to overcome these problems by using macrocycles as “antenna” ligands [4] occluded in gels [5] or in doped alumina films [6] and porous matrixes as sol–gel materials and zeolites [7,8] are still relatively poor. Natural montmorillonites, which are formed by intrinsically transparent aluminosilicate layers containing interlaminal sites where exchangeable cations are protected from the environment, may be an adequate matrix to stabilize lanthanide species against hydrolysis. In this work we describe the synthesis, characterization and luminescence properties of the intercalates of Europium(III) and Terbium(III) complexes with 2,2-bipyridine and 1,10-phenanthroline into bentonite. The luminescence intensity of the intercalated products is comparable to that of the free complexes, showing that the “antenna” effect of the ligands is maintained while the stability of the complex against hydrolysis is notoriously improved.

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2. Experimental

2.1. Purification and characterization of Na-bentonite

Pristine bentonite obtained from Sigma was first purified by sedimentation techniques and then converted to the sodium form by ionic exchange with 1 M sodium chloride. The salt excess was separated by dialysis (Sigma dialysis tubing cellulose membrane). The mean particle size of the product after filtering the suspension with a membrane (Whatman glass micro-fiber filters, GF/D) was less than 3 μm . The structural formula of our montmorillonite $\text{Na}_{0.47}(\text{Al}_{1.58}\text{Fe}_{0.17}\text{Mg}_{0.25})(\text{Al}_{0.22}\text{Si}_{3.78}\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ was determined by plasma atomic absorption spectroscopy (Perkin Elmer ICP-OES OPTIMA 1000DV). The sodium content corresponds to a cation exchange capacity (cec) of 100 mequiv./100 g of the clay while the determination of the cec by directly exchanging the Na^+ in the bentonite by ethylenediamine complex of Cu(II) [9] is found to be 85 mequiv./100 g.

2.2. Complexes

Ln-ligand organic (lanthanide (Ln): europium and terbium) (ligand organic (L)): 2,2-Bipyridine and 1,10-phenanthroline intercalate. The precursor complexes $[\text{Ln}(\text{L})_2]\text{Cl}_3$ were prepared, according to reported procedures in the literature [10], by keeping a 2,2-bipyridine or 1,10-phenanthroline (Aldrich Co.) in ethanol solution (Merck Co.) with the aqueous europium or terbium chloride solution (Aldrich Co.) during 24 h at room temperature. The product was characterized by both powder X-ray diffraction and elemental analysis.

2.3. Composites

Lanthanide-clay. Eu(III)- and Tb(III)-intercalates were prepared by treating an aqueous suspension of 0.50 g (7×10^{-4} mol Na) of the Na-bentonite in deionized water with a solution containing 7×10^{-4} moles of $[\text{Ln}(\text{L})_2]\text{Cl}_3$, i.e., a 1:3 equivalent ratio, under vigorous stirring during 48 h at 25 $^\circ\text{C}$. The products were separated and washed several times with deionized water. The samples were dried at 50 $^\circ\text{C}$ for 12 h under vacuum.

Elemental analysis (SISONS ES-1108):

Anal. Calcd for Bentonite[Eu(bpy)₂]_{0.22}·4H₂O: C, 10.90; H, 1.09; N, 2.54; Ln 6.90. Found: C, 11.15; H, 0.98; N, 2.37; Ln 6.90.

Anal. Calcd for Bentonite[Tb(bpy)₂]_{0.28}·5H₂O: C, 12.73; H, 1.33; N, 2.97; Ln 8.44. Found: C, 12.42; H, 1.37; N, 3.33; Ln 8.40.

Anal. Calcd for Bentonite[Eu(phen)₂]_{0.16}·4H₂O: C, 10.17; H, 0.84; N, 1.98; Ln 5.37. Found: C, 10.11; H, 0.84; N, 1.97; Ln 5.34.

Anal. Calcd for Bentonite[Tb(phen)₂]_{0.29}·4H₂O: C, 15.38; H, 1.32; N, 2.99; Ln 8.49. Found: C, 15.85; H, 1.34; N, 2.73; Ln 8.66.

The amount of water was calculated from the excess hydrogen found in the analysis.

Clay-lanthanide intercalation products were characterized by X-ray diffraction analysis (Siemens D-5000, Cu K α radiation). FT-IR spectra (Bruker Vector 22 infrared Fourier transform spectrometer) were recorded in the range 4000–250 cm^{-1} using the KBr pellet and excitation and luminescence spectra were measured in compacted solid samples at room temperature using an ISS Co. Multifunctional Fluorometer Model K2 (typical λ_{em} and λ_{exc} were 610 and 360 nm, respectively). The morphology of the products was analyzed by scanning electron microscopy (SEM) (Phillips XL-30).

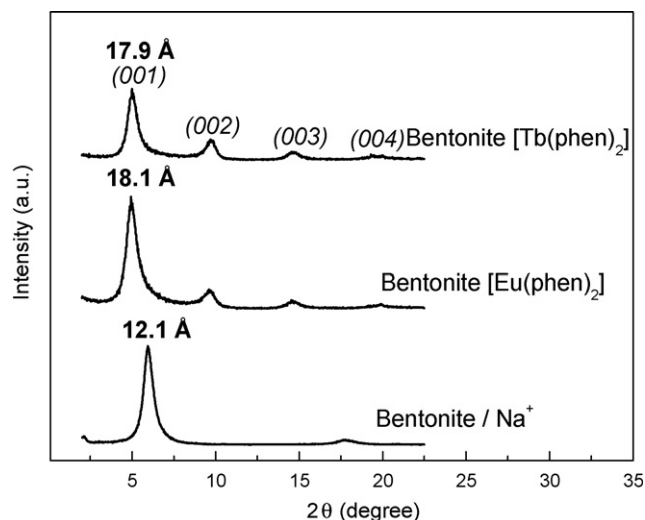


Fig. 1. X-ray diffraction patterns of bentonite- Na^+ and Bentonite[Ln(phen)₂] (Ln: Eu and Tb).

Table 1

Interlaminar distances obtained from 001 Bragg reflections and stoichiometries of Ln(L)-clay nanocomposites.

Sample	Distance (0 0 1) Å	Δc (Å)
Bentonite- Na^+	12.1	0
Bentonite[Eu(bpy) ₂] _{0.22}	18.3	6.2
Bentonite[Tb(bpy) ₂] _{0.28}	18.5	6.4
Bentonite[Eu(phen) ₂] _{0.16}	18.1	6.0
Bentonite[Tb(phen) ₂] _{0.29}	17.9	5.9

3. Results and discussion

The powder diffraction patterns of the samples lanthanides(phen)-clay nanocomposites shown in Fig. 1 are characteristic for layered aluminosilicates. The interlaminar distances obtained from the 001 Bragg reflections are shown in Table 1. The laminar nature of the product Bentonite[Tb(phen)₂]_{0.29} is observed in the SEM image reproduced in Fig. 2. The amount of guest material in the intercalates, determined by chemical analyses, indicates that the number of

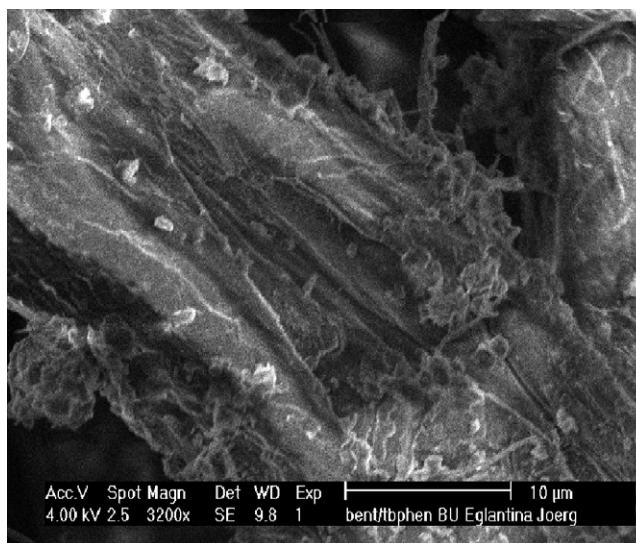


Fig. 2. Scanning electron micrograph of Bentonite[Tb(phen)₂]_{0.29}.

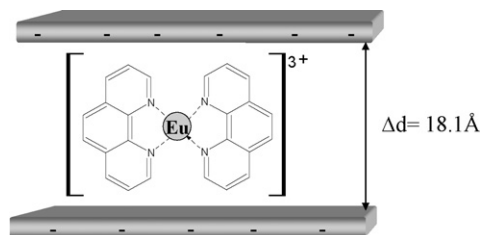


Fig. 3. Scheme of intercalation of Bentonite[Eu(phen)₂]_{0.16} in a lamellar clay.

equivalent of the intercalated Ln(III) in general exceeds the clay cec value, possibly due to additional anionic sites provided by surface hydroxyl groups [11].

In order to analyze the observed intercalation ratios, it is useful to consider the distribution of guest ions in the interlamellar space of the clays determined by the location of the negative charge in the layers. This charge, defined by the sites where silicon atoms are replaced by tetrahedral aluminum, is rather localized. In such case the available surface on the interlamellar space is determined by both quantity (cec) and distribution of the negative charge. If we consider a cec of 0.47 mol charge per Si₄ unit (~26.3 Å²), the mean distance between two negative charges on the plane defined by Si₄ atoms is 5.2 Å, which corresponds to an area of 56 Å² per equivalent of charge [12]. The van der Waals molecular models of intercalated complexes may be in turn described as parallelepipeds with dimensions 10.2, 9.8, 7.1 Å and 12.8, 10, 7.6 Å for the [Ln(bpy)₂]³⁺ and [Ln(phen)₂]³⁺, respectively. These dimensions permit the calculation of the minimum separation between the layers and the area of the layer which the clay needs to accommodate the [Ln(L)]³⁺ cation. A good agreement of these calculations with both the observed stoichiometry of the lanthanides intercalated species and the interlamellar distances of the product is observed in the schematic representation of this geometrical consideration as shown in Fig. 3. From such an analysis it may be concluded that the intercalation of complexes in aluminosilicates with a relatively high cec values like our Na-bentonite is essentially determined by both the charge distribution in the host and the molecular dimensions of the guest.

The frequencies observed in Fourier transform infrared (FTIR) spectra of the lanthanide–clay nanocomposites and lanthanide complexes are listed in Table 2. They show the typical absorption bands in the region C=C and C=N stretching modes and the C–H out of plane vibrations, which are observed in free ligands. These features indicate that the matrix appears to be chemically inert and the cation complexes are practically unaltered in the intercalated state as shown in Fig. 4 of FTIR spectra of the complex Tb(bpy)₂Cl₃ and nanocomposite Clay[Tb(bpy)₂]_{0.28}.

Room temperature luminescence spectra of these nanocomposites are in general similar to those of the free complexes. Independent of the lanthanide and the ligand the shape and relative intensity in excitation and emission spectra are similar to

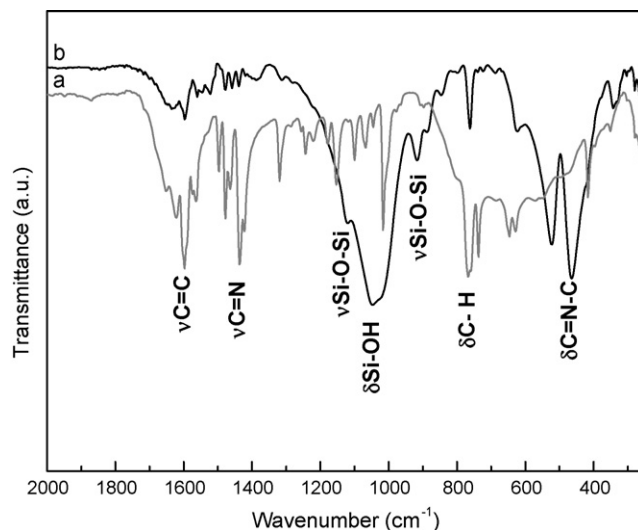


Fig. 4. FTIR spectra of the (a) complex Tb(bpy)₂Cl₃ and (b) nanocomposite Clay[Tb(bpy)₂]_{0.28}.

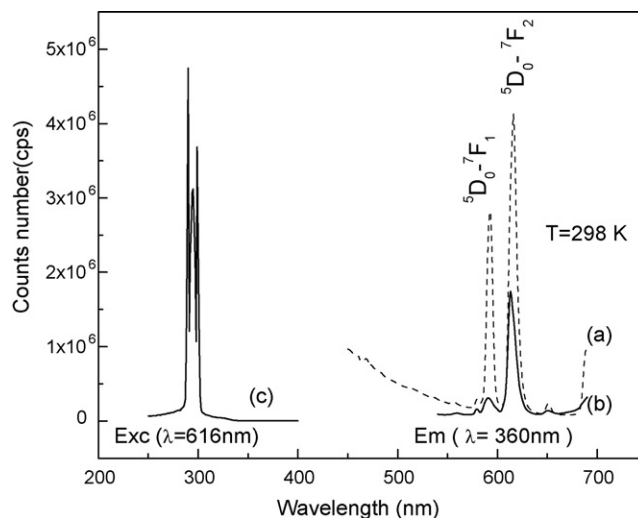


Fig. 5. Room temperature emission spectra of (a) Eu(phen)₂Cl₃·H₂O and (b) Bentonite[Eu(phen)₂]_{0.16} and (c) excitation spectrum of Eu(phen)₂Cl₃·H₂O.

those shown in Fig. 5. A comparison of the emission peak intensities of the intercalate with those of the pristine-free complexes shows that the characteristic “antenna” effect of the ligands remains practically unaltered and the ⁵D₀–⁵F₂ optical transition is clearly observed. This is not surprising considering the actual concentration of the lanthanide, which in the intercalate is approximately one-fifth (20%) from that in the complex. However,

Table 2
Selected absorption frequencies from FTIR spectra of the lanthanide–clay nanocomposites.

Sample	Assignments						
	δC=N–C (cm ⁻¹)	δC–H (cm ⁻¹)	νSi–O–Si (cm ⁻¹)	δSi–OH (cm ⁻¹)	νSi–O–Si (cm ⁻¹)	νC=N (cm ⁻¹)	νC=C (cm ⁻¹)
[Eu(bpy) ₂]	514	764				1434	1597
Clay[Eu(bpy) ₂]	552	758	916	1046	1119	1438	1596
[Eu(phen) ₂]	636	731				1421	1621
Clay[Eu(phen) ₂]	624	731	916	1046	1110	1423	1625
[Tb(bpy) ₂]	628	767				1436	1597
Clay[Tb(bpy) ₂]	623	758	916	1047	1119	1438	1596
[Tb(phen) ₂]	636	731				1422	1623
Clay[Tb(phen) ₂]	623	731	916	1045	1125	1423	1625

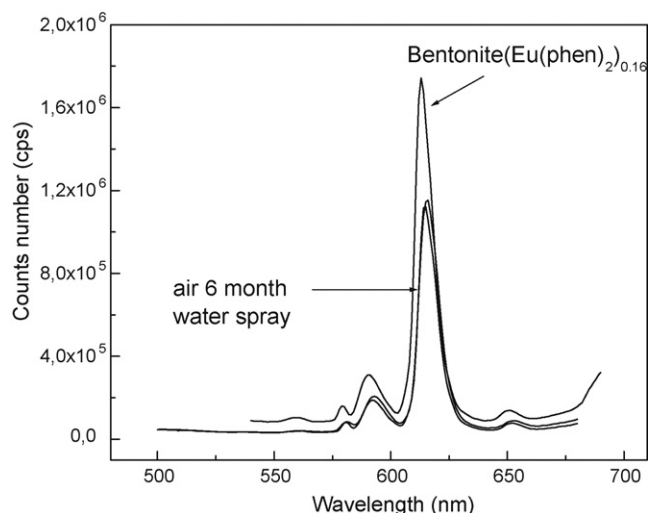


Fig. 6. The luminescence spectrum of the Bentonite[Eu(phen)₂]_{0.16} nanocomposite left exposed to air and moisture during 6 months and dry after being sprayed with water.

contrarily to the original complexes, the luminescence of the nanocomposite samples either left exposed to air and moisture during 6 months or dried after spraying with water remains practically the same, as shown in Fig. 6, thus indicating that the matrix effectively protects the light emitting species.

4. Conclusions

The intercalation of [Ln(2,2-bipyridine)₂]³⁺ and [Ln(1,10-phenanthroline)₂]³⁺ (Ln: Eu and Tb) into bentonite results in new laminar nanocomposites which exhibit luminescence under relatively drastic humidity conditions indicating that the clay

matrix plays an efficient protecting role. The exchange of sodium by lanthanide complexes in bentonite appears to be limited only by the cation exchange capacity of the clay and the molecular size of the intercalated guest. Experimental interlaminar distances and stoichiometries observed in the intercalation of the complexes agree well with the molecular size of the guests and the available clay interlayer space. The protection of the complex by the host clay, together with the intensity of the optical transition ⁵D₀-⁵F₂, observed in the nanocomposites, leads to novel optical materials.

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