

Lanthanide-Clay Nanocomposites: Europium(III) Complexes Intercalated in Bentonite

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Abstract. The intercalation of $[\text{Eu}(2,2 \text{ bipyridine})_2]^{3+}$ and $[\text{Eu}(1,10 \text{ phenantroline})_2]^{3+}$ into bentonite results in new nanocomposites which preserve the emission properties of the lanthanide. The exchange of sodium by lanthanide in the bentonite correlates with the host cation exchange capacity as well as with the guest molecular size and the interlaminar volume available in the clay. The intercalated complexes exhibit luminescence indicating an efficient protecting role of the matrix. This in turn points to lanthanide-clay nanocomposite as novel optical materials.

Introduction

The luminescent properties of lanthanide compounds and the improvement of their optical properties have been the focus of numerous fundamental and applied studies[1]. Much attention has been paid to finding new efficient and chemically stable lanthanide-based luminescent substances by anchoring ions and complexes in solid matrices which, in addition to improved emission, are able to protect the lanthanides from degradation by hydrolysis reactions. Results from attempts to overcome this problem by using macrocycles as ligands [2], the inclusion in gels [3] and glasses [4] or by covalent binding to solid matrices[5] are still relatively poor. Natural montmorillonites formed by intrinsically transparent aluminosilicate layers, containing interlaminar sites where exchangeable cations are protected from the environment, may be an adequate matrix to stabilize lanthanide species against reaction with moisture while retaining its optical properties. In this work we describe the synthesis, characterization and luminescence properties of the intercalates of europium(III) complexes with 2,2 bipyridine and 1,10 phenantroline into bentonite.

Experimental

Na-Bentonite. The clay (Sigma) purified by sedimentation techniques was converted to the sodium form by ionic exchange with 1M NaCl. The salt excess was separated by dialysis (Sigma dialysis tubing cellulose membrane). The mean particle size of the product after filtering the suspension through a membrane (Whatman glass micro fiber filters, GF/D) was $>3\mu\text{m}$. The composition of the clay was determined by Plasma Atomic Absorption Spectroscopy (Perkin Elmer ICP-OES OPTIMA 1000DV) and correspond to $\text{Na}_{0.47}(\text{Al}_{1.58}\text{Fe}_{0.17}\text{Mg}_{0.25})(\text{Al}_{0.22}\text{Si}_{3.78}\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$. The sodium content corresponds to a clay cation exchange capacity (*cec*) of 110meq/100g clay. The *cec* of this Bentonite-Na was also determined directly by exchange of sodium with a Cu(II)-ethylenediamine complex [6]. Both *cec* values were comparable within 90 %.

Europium Clay Nanocomposites. The complexes $[\text{Eu}(\text{bpy})_2]\text{Cl}_3$ and $[\text{Eu}(\text{phen})_2]\text{Cl}_3$ were prepared, according to literature procedures [7]. Europium(III)-intercalate were prepared by treating a suspension of 0.50 g (7×10^{-4} mol Na) of the Na-bentonite in deionized water with a solution of water:ethanol (1:1) containing 7×10^{-4} moles of complex, under vigorous stirring during 48 h at 25°C. The products were separated, washed with deionized water: ethanol (1:1), and dried at 50°C for 12 h under vacuum.

Elemental analysis (SISONS ES-1108), %: Found (calculated for $[(\text{Eu}(\text{bpy})_2)_{0.22}(\text{Al}_{1.58}\text{Fe}_{0.17}\text{Mg}_{0.25})(\text{Si}_{3.78}\text{Al}_{0.22}\text{O}_{10})(\text{OH})_2 \cdot 2\text{H}_2\text{O}]$): C: 11.15 (11.08); N:2.37(2.58); H:0.978 (0.929); Eu: 6.90 (7.01) and for Found:(calculated for $[(\text{Eu}(\text{phen})_2)_{0.17}(\text{Al}_{1.58}\text{Fe}_{0.17}\text{Mg}_{0.25})(\text{Si}_{3.78}\text{Al}_{0.22}\text{O}_{10})(\text{OH})_2 \cdot 7\text{H}_2\text{O}]$): C:10.15 (10.40); N:2.32(2.02); H:1.09 (1.08); Eu: 5.6 (5.49).

Purity as well as the intercalation degree of the products was monitored by powder X-ray diffraction. (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. Emission and excitation luminescence spectra (ISS Co. Multifunctional Fluorometer Model K2), typical λ_{em} and λ_{exc} 610 nm and 360 nm respectively, were recorded at room temperature. The morphology of the products was analyzed by Scanning Electron Microscopy (SEM) (Phillips XL-30 and Hitachi S400 with an EDS system).

Results and discussion

The powder x-ray diffraction pattern reproduced in Fig.1, are characteristic for layered aluminosilicate. The interlaminar distances obtained from the 001 Bragg reflections are 12.2, 18.3 and 19.2 Å for the Na-bentonite, the intercalate with the bipyridine and phenantroline complexes, respectively. The laminar nature of the product is observed in the typical SEM image reproduced in Fig 2. According to the content of guest in the products, determined by chemical analysis of both europium and ligand, the equivalents of intercalated Eu(III) in general exceeds the clay *cec* value. Although the reason for intercalated lanthanide excess is not clear enough, we think it could be due to additional anionic sites provided by surface hydroxyl groups [8].

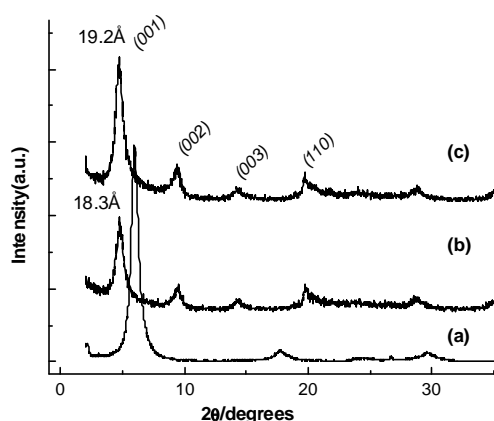


FIGURE 1. X-ray diffraction patterns of (a) Na-bentonite, (b) Bentonite $[\text{Eu}(\text{bpy})_2]_{0.22}$ and (c) Bentonite $[\text{Eu}(\text{phen})_2]_{0.17}$

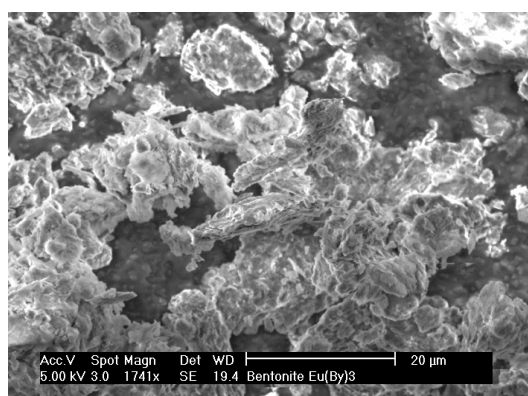


FIGURE 2. Scanning electron micrograph of Bentonite $[\text{Eu}(\text{bpy})_2]_{0.22}$

In order to analyze the observed intercalation ratios, it is interesting to compare the dimensions of molecular models of the isolated complex ions with the volume available in the interlaminar space. Indeed, the molecular van der Waals models of intercalated complexes may be described as

parallelepipeds with dimensions 10.2 Å, 9.8 Å, 7.1 Å and 12.8 Å, 10 Å, 7.6 Å for the $[\text{Eu}(\text{bpy})_2]^{3+}$ and $[\text{Eu}(\text{phen})_2]^{3+}$, respectively, in good agreement with both the observed stoichiometry of the europium intercalated species and the interlamellar distances of the product, as shown schematically 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 mainly determined by both the charge distribution in the host and the molecular dimensions of the guest.

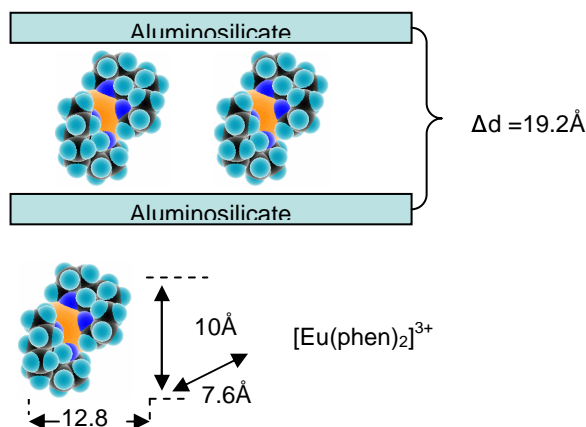
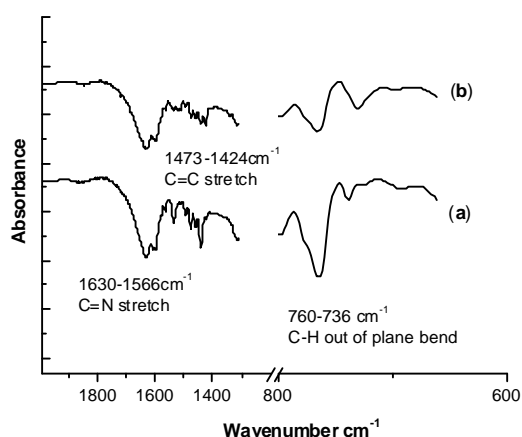


FIGURE 3. Scheme of intercalation $[\text{Eu}(\text{phen})_2]^{3+}$ in a lamellar clay

FTIR spectra of the Eu-Clay nanocomposites are depicted in Fig. 4. They show the typical absorption bands in the region C=C and C=N stretching modes and the C-H out of plane vibration, which are the observed in free ligands. These features indicate that (a) the matrix appears to be chemically inert and (b) the complex cations are practically unaltered in the intercalated state.



suggest to put fig 4 and 5 side by side as fig 1 and fig 2

FIGURE 4. IR absorption spectra of the intercalated structures (a) Bentonite $[\text{Eu}(\text{phen})_2]_{0.17}$ and (b) Bentonite $[\text{Eu}(\text{bpy})_2]_{0.22}$

Room temperature luminescence spectra of these nanocomposites are in general similar to those of the free complexes. In Figure 5 emission and excitation spectra of $\text{Eu}(\text{bpy})_2\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ and Bentonite $[\text{Eu}(\text{bpy})_2]_{0.22}$ are shown. 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. However, contrarily to the original complexes, the luminescence of the nanocomposite samples left exposed to air during 6 month remains practically the same, indicating that the matrix effectively protects the light emitting species.

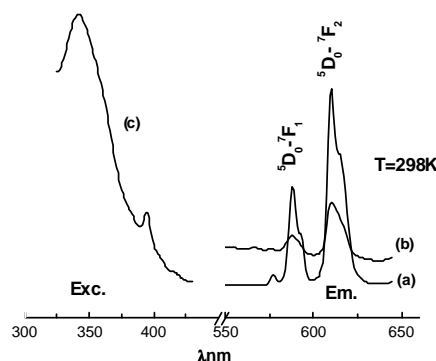


FIGURE 5. Excitation and emission spectra of (a) $\text{Eu}(\text{bpy})_2\text{Cl}_3 \cdot 3\text{H}_2\text{O}$, (b) $\text{Bentonite}[\text{Eu}(\text{bpy})_2]_{0.22}$, and (c) $\text{Eu}(\text{bpy})_2\text{Cl}_3 \cdot 3\text{H}_2\text{O}$. Suggest writing out in full “emission” and “excitation”

Conclusions

The intercalation of the ions $[\text{Eu}(\text{bpy})_2]^{3+}$ and $[\text{Eu}(\text{phen})_2]^{3+}$ into Na-bentonite has been achieved under mid conditions cation exchange. The extent of the exchange of sodium by europium in the bentonite appears to be limited only by both the cation exchange capacity of the clay and the molecular size of the intercalant, agreeing with the *cec* of the clay, molecular dimension of the guest and the volume available in the interlaminal space. The aluminosilicate matrix is practically inert resulting in a luminescent behavior of intercalated complexes similar to those of the free complexes. Moreover, the lanthanide species appear to be better protected again hydrolysis in the confined state. Several questions remain open. For example, it is essential to extend the study of the optical properties. We expect that the protection of the complex by the clay host twill lead to higher quantum efficiencies of optical transitions in the nanocomposite, compared to the free complex, and may lead to novel optical materials.

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