Intercalation of Europium (III) species into bentonite

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Abstract

It is shown that the intercalation of [Europium(bipyridine)$_2$]$^{3+}$ into bentonite results in a new nanocomposite which preserves the emission properties of Europium (III). The exchange of sodium by europium in bentonite is correlated with the cation exchange capacity and molecular size. The intercalated complex exhibits luminescence where both the 2,2-bipyridine ''antenna'' effect and the intensity maxima are comparable to the free complex suggesting that clay intercalated with rare earths may results in novel optical materials.

1. Introduction

Intercalation chemistry is an essential method to modify and functionalize materials. Natural clays, like many silicates and aluminosilicates, exhibit a rich inclusion chemistry, which is especially attractive because of their large surface area and ion exchange properties. Such characteristics allow clays to be chemically converted into products with new chemical properties while retaining many of their physical characteristics [1,2]. Layered clays may be modified by intercalation thus producing ordered assemblies with structures in which the inorganic oxide layers may be combined at the nanometer level with a variety of chemical species located in the interlaminar spaces. The intercalation of polymers in clays is a chemistry with several material science applications including, for example, to obtain new polymer electrolytes [3,4], to reinforce plastic materials [5] and the encapsulation of metals in layered aluminosilicates as a means to control nanoparticle size [6]. In contrast to transition metal intercalates, where host-guest charge transfer often occurs [7], the aluminosilicate surfaces are more resistant to such interactions. Therefore, clay matrices are promising hosts to encapsulate chemical species protecting the latter from the ambient without altering their characteristic properties.

Lanthanide complexes have gained increasing interest in the development of luminescent materials [8]. They are also particularly suitable as guests in intercalation of clays and among them Europium (III) is particularly well known [9,10]. However, the luminescence efficiency of the f–f electronic transitions, which are responsible for the

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sharp and intensive light emission characteristic of lanthanides, strongly depends on the coordination sphere of the ion. Moreover, while some ligands may have a positive influence, for instance, special organic species give rise to an ''antenna'' effect which increases their luminescence efficiency [11,12], other ligands such as those containing O–H oscillators may act as quenchers. The efficient energy transfer between the resonance level of the ion and the O–H oscillators in the first coordination sphere causes the luminescence intensity to decrease linearly as the number of coordinated water molecules increases [13]. Unfortunately, water incorporated either from the synthesis of the complexes or from ligand exchange reactions with solvent or moisture, is often found coordinated to the lanthanide ions. In order to avoid luminescence quenching, these emission centers must be protected from the deactivating ligands. Among the numerous, successful attempts performed in that direction, some examples of encapsulation by using macrocycles and polymers as ligands [14–17], inclusion in gels and glasses [18–24] or covalent binding to solid matrices [25] may be mentioned. Considering that clays are in general intrinsically transparent to visible and near-UV radiation, in this work, we describe the intercalation of a Eu(III) 2,2-bipyridine complex into bentonite in order to protect the lanthanide center and thus improve its optical properties. We show that the europium complex intercalated commensurately in the clay interlaminar spaces displays an emission spectrum, which while being similar to the free complex, is less sensitive to moisture.

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 microfiber filters, GF/D) was less than 3 μm. The structural formula of our montmorillonite $Na_{0.47}(Al_{1.58}Fe_{0.17}Mg_{0.25}) (Al_{0.22}Si_{3.78}O_{10})(OH)_2 \cdot nH_2O$ was determined by Plasma Atomic Absorption Spectroscopy (Perkin-Elmer ICP-OES OPTIMA 1000DV). The sodium content corresponds to a cation exchange capacity (*cec*) of 110 meq per 100 g of the clay. The *cec* of this Na–bentonite was also determined directly by exchange of sodium with an ethylenediamine complex of Cu(II) [26].

2.2. Europium–sodium ion exchange

A water suspension of 0.50 g (7×10^{-4} mol Na) of the Na–bentonite was treated with aqueous solution containing the equivalent quantity of europium chloride (2.3×10^{-4} mol) during 24 h at room temperature. The product was characterized by powder X-ray diffraction analysis. The Eu content was determined by EDTA titration using xylenol orange as indicator [27]. A virtually complete exchange of Na^+ with Eu^{3+} was observed. Analysis Eu: Found: 5.80%; calculated for $Eu_{0.16} (Al_{1.58}Fe_{0.17}Mg_{0.25}) (Al_{0.22}Si_{3.78}O_{10})(OH)_2 \cdot 9H_2O$: 5.68%.

2.3. Sodium–bipyridine intercalate

A suspension of 0.50 g (7×10^{-4} mol Na) of Na–bentonite in ethanol–water 1:1 was treated with 5.5×10^{-3} mol 2,2-bipyridine under vigorous stirring during 48 h at room temperature. The product was characterized by powder X-ray diffraction analysis. The bipyridine content was determined by elemental analysis (SISONS ES-1108): found (calculated for $[Na(bpy)_2]_{0.36}[Na(H_2O)_6]_{0.11} (Al_{1.58}Fe_{0.17}Mg_{0.25}) (Al_{0.22}Si_{3.78}O_{10})(OH)_2))$ %: C: 17.4 (17.4); N: 4.07 (4.09); H: 1.46 (1.57).

2.4. Europium–bipyridine intercalate

The precursor complex $[Eu(bpy)_2]Cl_3$ was prepared, according to literature procedures [9,10], by treating a 2,2-bpyridine (bpy) ethanol solution with the aqueous europium chloride solution during 24 h at room temperature. The product was characterized by both powder X-ray diffraction and elemental analysis: Found (calculated for $[Eu(bpy)_2]Cl_3 \cdot 3H_2O$) %: C: 38.7 (38.7); N: 8.77 (9.03); H: 3.32 (3.22); Eu: 26.6 (24.5).

Eu(III)-intercalate was prepared by treating a 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 $[Eu(bpy)_2]Cl_3$, i.e., a 1:3 equivalent ratio, under vigorous stirring during 48 h at 25 °C. The products were separated and washed several times with deionized water. The samples were dried at 50 °C for 12 h. Clay–lanthanide intercalation products were characterized by elemental analysis, X-ray diffraction analysis (Siemens D-5000, Cu Kα radiation), and excitation and luminescence spectra (vide infra). A virtually complete exchange of Na^+ with Eu^{3+} complexes was observed. Analysis: Found: (calculated for $[(Eu(bpy)_2]_{0.22}(Al_{1.58}Fe_{0.17}Mg_{0.25})(Si_{3.78}Al_{0.22}O_{10})(OH)_2 \cdot 4H_2O)$%: C: 11.15 (10.90); N: 2.37 (2.54); H: 0.978 (1.09); Eu: 6.90 (6.90).

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.

3. Results and discussion

3.1. Clay–cation exchange

The purified Na–montmorillonite used in this work was identified as a bentonite with the basic composition $Na_{0.47}(Al, Fe, Mg)_2(Al, Si)_4O_{10}(OH)_2 \cdot nH_2O$, with a *cec* of 110 characteristic for these clays (90–120 meq per 100 g clay) which compares well to other similar clays, for instance, the Na–montmorillonite provided by the Clay Science Society of Japan with a *cec* of 119 meq per 100 g clay [3].

The powder X-ray diffraction pattern in Fig. 1 corresponds to a layered aluminosilicate with an interlaminar distance of 12.2 Å. In the presence of aqueous Eu(III) ions, lanthanide–sodium ion exchange occurs spontaneously, reaching the exchange *cec* value, even without a lanthanide excess. The product has the composition Bentonite$(Eu^{3+} \cdot nH_2O)_{0.16}$ with *n* in the range 6–9, in agreement with a typical lanthanide(III) ion hydration [28]. The interlaminar distance of Eu intercalate is 13 Å according to the hydrated europium ion radius, which is known to be somewhat larger than that of hydrated sodium one. Interestingly, the X-ray diffraction pattern of the product shows a one-dimensional order, which is higher than in the precursor probably arising from both an intercalation effect and the greater contrast in electron density of europium.

The intercalation of the ligand 2,2′-bipyridine in Na–bentonite was also investigated in order to compare the effects of the intercalation of complexes with different charges on the structure and the stoichiometry of the clay intercalation products. The treatment of the Na–clay with an excess of the bipyridine at room temperature leads to an intercalation product with an interlaminar distance of 17.5 Å in which the interlaminar phase has the composition $[Na(bpy)_2]_{0.36}[Na(H_2O)_6]_{0.11}$ per $(Al, Si)_4O_{10}(OH)_2$ bentonite unit. It is further found that the amount of the resulting intercalated complex partially satisfies the *cec* of the clay, and that remaining sodium ions in the interlaminar spaces are hydrated.
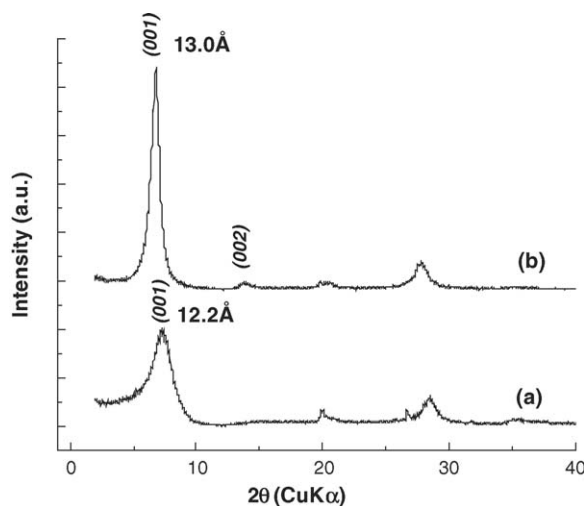

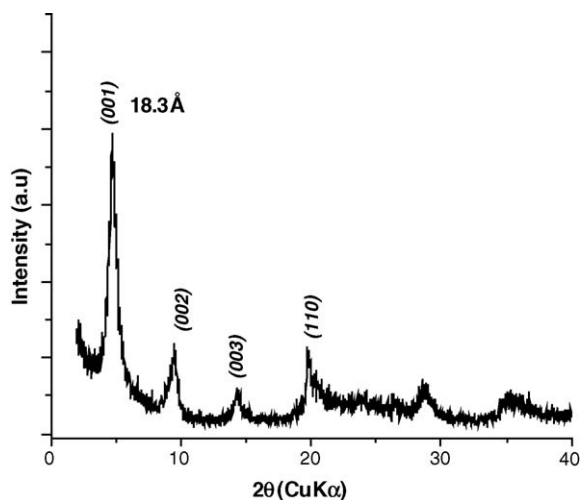Fig. 1. X-ray diffraction patterns of (a) Na–bentonite and (b) Eu–bentonite nanocomposite.

Fig. 2. X-ray diffraction pattern of bentonite[Eu(bpy)$_2$]$^{3+}$.

The exchange of the sodium ion by the Eu(III)–(bpy)$_2$ complex in the bentonite is also achieved under milder conditions. At the end of the reaction, no sodium ions were detected in the product. As observed in Fig. 2, the X-ray diffraction pattern of the intercalate with the bipyridine Eu(III) complex clearly indicates the formation of a lamellar structure with interlaminar distances of about 18.3 Å (see Scheme 1). The laminar nature of the product is also observed in the SEM image reproduced in Fig. 3. According to the amount of the intercalated europium and ligand determined by chemical analysis, all the europium is found as the complex ion [Eu(bpy)$_2$]$^{3+}$. The presence of water, about 4 mol per mol lanthanide, is also detected. According to these data, the stoichiometry of the interlayer phase corresponds to [Eu(bpy)$_2$]$_{0.22}$ per mol bentonite. Apparently, the amount of intercalated Eu(III) exceeds the clay *cec* value. A plausible explanation could be the generation of OH$^-$ ions in the interlayer phase caused by partial hydrolysis of water due to the electric field generated by the trivalent cations. However, the precision of the chemical analysis was not sufficient to distinguish unambiguously OH$^-$ from H$_2$O species in this phase.

3.2. Complex intercalation ratios

In order to analyze the difference in the intercalation ratios observed for the Na(I) and Eu(III) derivatives, it is interesting to compare the dimensions of molecular models of the isolated complex ions with those available in the interlaminar space. In these clays, the negative charge in the layers, defined by the sites where silicon atoms are
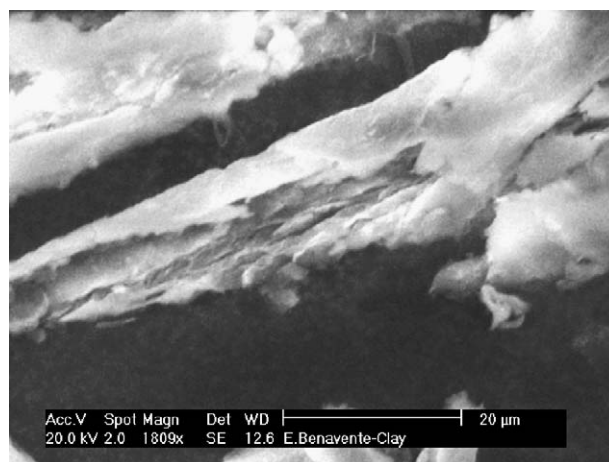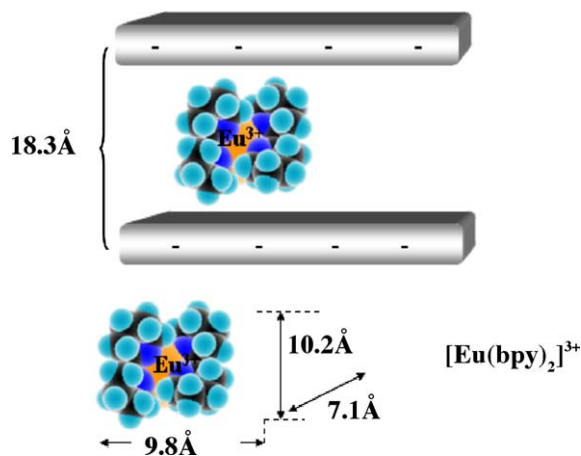

Fig. 3. Scanning electron micrograph of bentonite[Eu(bpy)$_2$]$^{3+}$.

Scheme 1. Intercalation of $[Eu(bpy)_2]^{3+}$ in a lamellar clay.

replaced by tetrahedral aluminum, is rather localized. In such a case, the available surface on the interlaminar space is determined by both quantity (*cec*) and distribution of the negative charge. If we consider a *cec* of 0.47 mol charge per Si_4 unit (~ 26.3 Å^2), the mean distance between two negative charges on the plane defined by Si_4 atoms is 5.2 Å, which corresponds to an area of 56 Å^2 per equivalent of charge. The molecular van der Waals models of intercalated complexes may be described as parallelepipeds with dimensions 9.0, 8.6, 7.0 and 10.2, 9.8, 7.1 Å for the $[Na(bpy)_2]^+$ and $[Eu(bpy)_2]^{3+}$, respectively. One of these dimensions for each ion $[Na(bpy)_2]^+$ and $[Eu(bpy)_2]^{3+}$, accounts for the side length of 9.0 and 10.2 Å, respectively, which agrees well with the corresponding increments of the interlaminar space *d* caused by the intercalation (see Table 1). In this way, we can define the molecular orientation of the confined complexes. Thus, for the ion $[Na(bpy)_2]^+$ a surface of ~ 60 Å^2 per equivalent of charge is obtained, which is slightly higher than the value calculated for the clay surface. Accordingly, the maximum complex intercalation ratio, even assuming a totally homogeneous charge distribution, has to be lower than the *cec*. Surface and charge balance arguments indicate that a part of the Na^+ ion should be found as a less surface-demanding complex with ligands smaller than the bipyridine. In our case, elemental analysis points to the aqueous ion. In contrast, the surface per equivalent of charge for the $[Eu(bpy)_2]^{3+}$ ion complex, 23.2 Å^2, should lead theoretically to an intercalation ratio equivalent to the *cec* of the clay. This agrees well with the observed stoichiometry of the europium intercalation product discussed above. From this analysis, it may be concluded that the intercalation of complexes in aluminosilicates with a relatively high *cec* value like our bentonite is mainly determined by both the charge distribution in the host and the molecular dimensions of the guest.

3.3. Luminescence spectra

Luminescence spectra at room temperature of the Eu(III)–bpy complex pure and intercalated in bentonite are shown in Fig. 4. It is observed that all the main features in the emission spectrum of the free complex are also found in the intercalated one. The homogeneity in the surrounding environment of the Eu^{3+} appears to be similar in both cases. Since both spectra in Fig. 4 are obtained under the same experimental conditions, the relative intensities indicate that

Table 1
Interlaminar distances in bentonite nanocomposites

Compound	Δd (0 0 1) (Å)
Bentonite $[Na \cdot 6H_2O]^+_{0.47}$	12.2
Bentonita$[Eu \cdot 9H_2O]^{3+}_{0.16}$	13.0
Bentonita$[Na(bpy)_2]^+_{0.36}$	17.5
Bentonite$[Eu(bpy)_3]^{3+}_{0.15}$	18.3
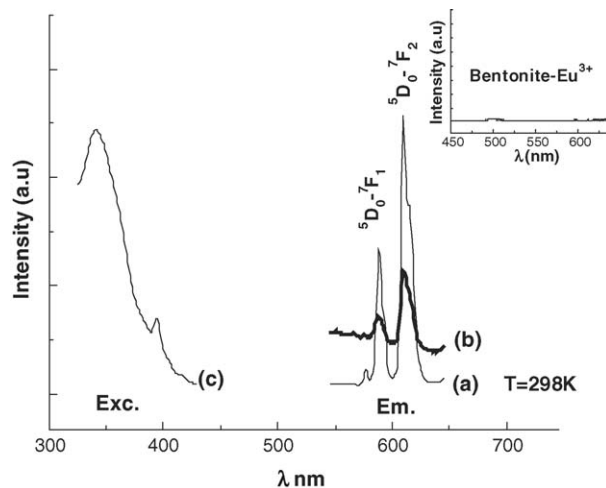
Fig. 4. Room temperature emission spectra of (a) Eu(bpy)$_2$Cl$_3$·3H$_2$O and (b) bentonite[Eu(bpy)$_2$]$^{3+}$, and excitation spectrum of (c) Eu(bpy)$_2$Cl$_3$·3H$_2$O. The inset shows the emission spectra of bentonite[Eu]$^{3+}$.

quantum yield in the intercalated species is at least comparable to the free one, when the concentration difference of 6.9 and 26.5% Eu in the intercalated and in the free complex, respectively, are taken in account. There are, however, some changes in the emission spectrum of the lanthanide complex, which could be assigned to clay–matrix effects. In general lanthanide narrow bands similar to those of the gaseous ion would be expected, but in many cases effects due to the environment are observed. Changes in the homogeneity of the environment around the chelated lanthanide ions are known to alter the emission behavior. In our case, the most important impact is a red shift of the emission bands. Direct orbital interactions inducing neuphelauxetic effects [29,30] or insertion in solid phases [31] induce shift in the emission peak. Moreover, a change in the monochromacity degree of the products is also apparent. Thus the intensity ratio [$^5D_0 \rightarrow ^5F_2$/$^5D_0 \rightarrow ^5F_1$] changes, from approximately 2.5 in the free complex to 3.9 in the bentonite, suggesting a lower symmetry around the Eu(III) in the confined complex [32,33].

In contrast, the spectra of both Na–bentonite and aqueous Eu–bentonite intercalates do not show any detectable luminescence bands in this range (see inset to Fig. 4). Since spectra are recorded under similar conditions ($\lambda_{exc} = 360$ nm) the intensities of the signals observed in Fig. 4 indicate that in the intercalated state the "antenna" effect of the ligand is conserved. Moreover, the protecting effect of the matrix against moisture has been also demonstrated. Thus, although the free complex was rather liable to hydrolysis, the luminescence intensity and spectral range of the intercalated sample were maintained even after exposure to atmosphere for about 6 months.

4. Conclusions

We intercalated [Eu(bpy)$_2$]$^{3+}$ into natural aluminosilicate bentonite. We found that bentonite is a suitable matrix to intercalate [Eu(bpy)$_2$]$^{3+}$. The exchange of sodium by europium in bentonite appears to be limited only by the cation exchange capacity of the clay and the molecular size of the intercalant. Measured interlaminar distances and stoichiometries for the intercalation of [Eu(bpy)$_2$]$^{3+}$ and [Na(bpy)$_2$]$^{3+}$ agree well with the available clay interlaminar volume. The intercalated complex exhibits luminescence where both the 2,2-bipyridine "antenna" effect and the intensity maxima are comparable to the free complex. Nevertheless, several questions remain open. For example, it is essential to extend the study of the optical properties of these nanocomposites to the dynamic domain to determine the life times of the observed transitions. An extension of this study to other rare earths may show whether this is a general phenomenon. We expect that the protection of the complex by the host clay together with the observed higher quantum efficiencies of optical transitions in the nanocomposite, here $^5D_0 \rightarrow ^5F_2$, compared to the free complex, may lead to novel optical materials.

Acknowledgments

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