Intercalation of Tris(2,2′-bipyridine)ruthenium(II) into a Layered Silicate, Magadiite, with the Aid of a Crown Ether

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Intercalation of the tris(2,2′-bipyridine)ruthenium(II) complex cation into a layered silicate (magadiite; the ideal formula is $Na_2Si_{14}O_{29} \cdot nH_2O$) was investigated. Since the complex cation did not intercalate by a direct ion exchange reaction with the interlayer sodium ions in an aqueous medium, a crown ether, 15-crown-5, was added in the reactant to promote the ion-exchange reaction. Two possible reaction mechanisms were proposed for the present ion-exchange reaction: One is a two-step reaction, where 15-crown-5 was first intercalated into the interlayer space of Na−magadiite and exchanged with tris(2,2′-bipyridine)ruthenium(II) complex cation subsequently. The other is a one-step reaction, where 15-crown-5 forms complex ions with sodium ions deintercalated from the interlayer space and the tris(2,2′-bipyridine)ruthenium(II) complex cation is intercalated into the interlayer space to compensate the charge balance. The present success opens up new opportunities to introduce organic cations into the interlayer space of various layered solids.

Introduction

Intercalation of organic guest species into layered inorganic solids is a way to construct an ordered inorganic−organic assembly with unique microstructures controlled by host−guest and guest−guest interactions.[1] Magadiite (the ideal formula is $Na_2Si_{14}O_{29} \cdot nH_2O$) is a layered silicate,[2] which is capable of incorporating guest species in the interlayer space to form intercalation compounds.[3] The intercalation of organoammonium ions[4] and polar molecules[5] and the preparation of the organosilane grafted[6−10] and the pillared[11] derivatives have been reported previously.

Compared with smectite, which is a group of layered clay minerals studied most extensively in organizing organic guest species,[12] magadiite possesses some unique properties for organizing guest species. (1) The density of the cation-exchange sites on the layer surface is expected to be higher than that of smectite. (2) It can be conveniently prepared in laboratory by hydrothermal synthesis. However, the intercalation of guest species is not so easy if compared with that into smectite, so that the studies on the preparation of intercalation compounds from magadiite have been limited. To introduce bulky organic species, organoammonium-exchanged forms, which have been prepared by conventional ion-exchange reactions in aqueous media, were used as the intermediates. By utilizing the intermediate route, bulky organosilyl groups such as diphenylsilyl, octylsilyl, octadecylsilyl, and perfluoroalkylsilyl groups have successfully been intercalated into the interlayer space of magadiite.[9,10] The silica-pillared magadiites[11] and the polymer−magadiite nanocomposites[13] have also been prepared from the organoammonium−magadiites. The hexadecylpyridinium-exchanged magadiite was proposed to be a possible candidate of the adsorbent for environmental purification.[14]

In this paper, we report a novel way to introduce organic cations into magadiite, where a crown ether (15-crown-5) was

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added to promote the ion-exchange reaction between Na−magadiite and organic cations. It is well-known that crown ethers and relating macrocyclic compounds selectively and strongly bind cations to form stable complexes.[15] The interactions between 15-crown-5 and interlayer exchangeable sodium ions are expected to affect the reactions. Tris(2,2′-bipyridine)-ruthenium(II) (abbreviated as $Ru(bpy)_3^{2+}$)[16] was used as the guest species because of its unique combination of chemical stability, luminescence, and so on. Intercalation of photoactive species such as organic dyes into layered solids has been investigated so far to understand the nature of host−guest systems as well as to prepare novel photofunctional supramolecular systems,[17] since the characteristics of the photoprocesses are sensitive to the environment where photoactive species are adsorbed.[18] Accordingly, photoprocesses of $Ru(bpy)_3^{2+}$ adsorbed on the various inorganic solids have extensively been investigated.[19] The present success in the ion-exchange reaction of a layered silicate in the presence of a crown ether can be applied for the introduction of various cationic guest species, which do not intercalate into the interlayer space of layered solids by conventional ion-exchange methods.

Experimental Section

Materials. Sodium−magadiite was synthesized by the method described by Kosuge et al.[20] from colloidal silica, sodium hydroxide, and water at the molar ratio of 1:0.23:18.5 (SiO_2:NaOH:H_2O). The mixture was sealed in a Teflon-lined autoclave at 423 K for 48 h. The product was washed with a dilute aqueous NaOH solution and dried in air. 15-Crown-5 (Tokyo Kasei Industries Co.; abbreviated as 15C5) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (Aldrich) was used as received.

Preparation of the Intercalation Compounds. The introduction of $Ru(bpy)_3^{2+}$ into the interlayer space of Na−magadiite was conducted by two synthetic methods. In method 1, Na−magadiite was allowed to react with an methanol solution
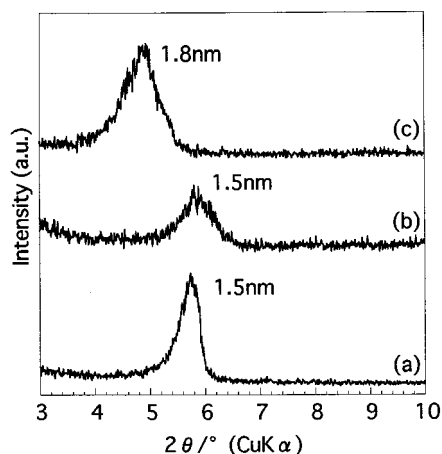
Figure 1. X-ray diffraction patterns of (a) Na−magadiite and (b, c) the reaction products between Na−magadiite and Ru(bpy)$_3^{2+}$ in the absence (b) and presence (c) of 15C5.

containing Ru(bpy)$_3$Cl$_2$ and 15C5 at room temperature. The molar ratio of Ru(bpy)$_3^{2+}$:15C5:Na−magadiite was 10:20:1. In method 2, the 15C5−Na−magadiite intercalation compound was prepared by the reaction between Na−magadiite and a methanol solution of 15C5 and used as the intermediate for the intercalation of Ru(bpy)$_3^{2+}$. The 15C5−Na−magadiite intercalation compound thus obtained was allowed to react with a 0.1 M methanol solution of Ru(bpy)$_3$Cl$_2$; the molar ratio of Ru(bpy)$_3$Cl$_2$:15C5:Na−magadiite was 10:20:1. In both synthetic methods, the resulting solid was corrected by centrifugation, washed with acetone, and dried under a reduced pressure.

For comparison, intercalation of Ru(bpy)$_3^{2+}$ into Na−magadiite was carried out by mixing Na−magadiite and a methanol solution of Ru(bpy)$_3^{2+}$Cl$_2$, and the mixture was allowed to react for several days at room temperature. After centrifugation, the resulting solid was washed with acetone and dried under a reduced pressure.

Characterization. X-ray powder diffraction was performed on a Rigaku RAD IIB diffractometer using monochromatic Cu Kα radiation. Infrared spectra of the KBr disks were recorded on a Shimadzu FTIR-8200PC spectrophotometer for 250 scans with a resolution of 2.0 cm^{-1}. Visible absorption spectra were recorded on a Shimadzu UV-3100PC spectrophotometer. Differential thermal analysis and thermogravimetric analysis were performed on a Rigaku TAS 200 instrument with a heating rate of 10 °C min^{-1} and α-alumina as the standard. The amount of Na in the product was determined by the ICP spectrometry (Japan Jarrel Ash, ICAP575 Mark II). Luminescence spectra were recorded on a Hitachi F-4500 fluorospectrophotometer in the range 500−800 nm with excitation at 450 nm. The bandwidth of the excitation wavelength and emission wavelength was 1.5 nm.

The adsorbed amounts of Ru(bpy)$_3^{2+}$ were determined by the change in the absorbance of the Ru(bpy)$_3^{2+}$ MLCT band at 450 nm between the starting solution and the supernatant. The amount of the adsorbed 15C5 was determined by subtracting the adsorbed amount of Ru(bpy)$_3^{2+}$ from the total organic content determined by the weight loss observed at the temperature range of 100−600 °C of the TG curves.

Results and Discussion

The X-ray diffraction patterns of products are shown in Figure 1 together with that of Na−magadiite. The X-ray diffraction
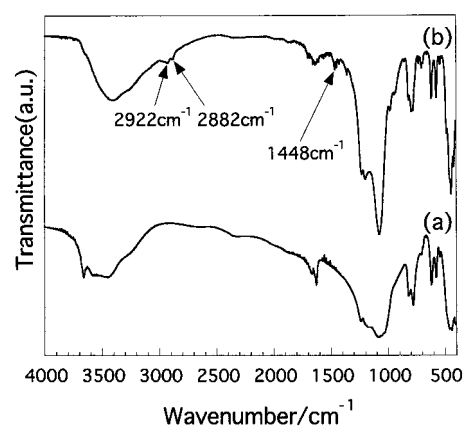

Figure 2. Infrared spectra of (a) Na−magadiite and (b) the Ru-(bpy)$_3^{2+}$−magadiite intercalation compound.

pattern of the product obtained by the reaction between Ru(bpy)$_3^{2+}$ and Na−magadiite in the absence of 15C5 showed the basal spacing of ca. 1.5 nm, indicating that Ru(bpy)$_3^{2+}$ did not intercalate into magadiite. (The basal spacing of the original Na−magadiite is ca. 1.5 nm.) When 15C5 was added to the Ru(bpy)$_3^{2+}$Cl$_2$ solution (method 1), an orange solid was obtained. From the X-ray diffraction pattern (Figure 1c) of the product obtained after the ion exchange reaction for 30 days, the basal spacing increased to 1.8 nm.

Since the thickness of the silicate layer of magadiite is considered to be the same as that (1.1 nm) of dehydrated H−magadiite,[21] the interlayer spacing (gallery height) of the Ru(bpy)$_3^{2+}$−magadiite intercalation compound was estimated to be 0.7 nm by subtracting the thickness of silicate layer (1.1 nm) from the observed basal spacing (1.8 nm). The intercalation of tris(bpy) chelate complex ions into smectites requires the expansion of the interlayer space by ca. 0.8 nm[22] and the intercalated complex ions arranged as a monomolecular coverage with their 3-fold axis perpendicular to the silicate sheet. The basal spacing of the Ru(bpy)$_3^{2+}$−magadiite intercalation compound (1.8 nm) indicates the intercalation of Ru(bpy)$_3^{2+}$ and a monolayer arrangement of the intercalated Ru(bpy)$_3^{2+}$ in the interlayer space of magadiite.

The infrared spectrum of the product is shown in Figure 2. The infrared spectrum showed absorption bands characteristic of 15C5 (such as C−H stretching vibration at 2922 and 2882 cm^{-1}) and Ru(bpy)$_3^{2+}$ (pyridine ring frequency at 1448 cm^{-1}), showing the coadsorption of 15C5 and Ru(bpy)$_3^{2+}$.

In the DTA curve of the Ru(bpy)$_3^{2+}$ intercalated compound, a very sharp exothermic peak appeared at around 350 °C. Since similar very sharp exothermic peaks have been observed in our separate study on the thermal analysis of the Ru(bpy)$_3^{2+}$ complex adsorbed on layered silicates, the exothermic peak observed in the DTA curve was ascribable to the oxidative decomposition of the Ru(bpy)$_3^{2+}$ ions. Broad exothermic peaks, which were ascribable to the oxidative decomposition of the coadsorbed 15C5, were also observed in the DTA curves. The TG curve of the product showed a weight loss of 21% in the temperature range 200−600 °C. The weight loss was ascribed to the decomposition of ligand (bpy) and the coadsorbed 15C5.

The amount of the adsorbed Ru(bpy)$_3^{2+}$ was determined from the change in the concentration of Ru(bpy)$_3^{2+}$ in the starting solution and the supernatant to be 0.33 mol per a formula unit of magadiite (Si$_{14}$O$_{29}$). The remaining amount of Na ions in the product was determined by ICP to be 0.62 mol per formula unit of magadiite. Hydronium ions were thought to make deficiency of the interlayer positive charge. From the total
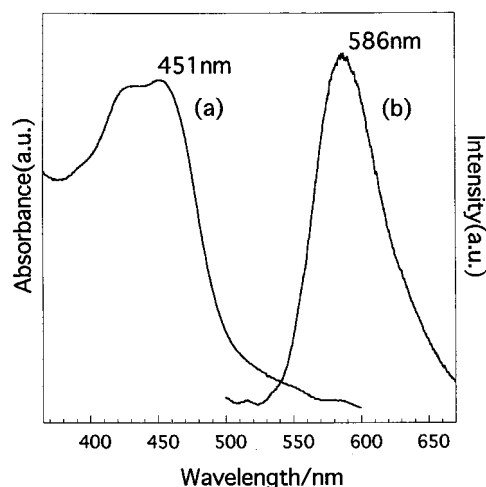
Figure 3. Absorption (a) and luminescence (b) spectra of the Ru(bpy)$_3^{2+}$−magadiite intercalation compound.

amount of adsorbed organic species determined by TG (the observed weight loss was 21%), the amount of coadsorbed 15C5 was estimated to be 0.22 mol per formula unit of magadiite. The CHN analysis (C, 13.7%; N, 2.7%) of the product is consistent with the TG result, supporting the composition {[Ru-(bpy)$_3$]$^{2+}$$_{0.33}Na_{0.62}$(15C5)$_{0.22}$ Si$_{14}$O$_{29}$·nH$_2$O} of the product.

Since the crystal structure of magadiite has not been resolved so far, the detailed arrangement of the intercalated Ru(bpy)$_3^{2+}$ is difficult to elucidate. Therefore, the packing of the Ru(bpy)$_3^{2+}$ is discussed in comparison with Ru(bpy)$_3^{2+}$−smectite systems. The cation-exchange capacity of magadiite was estimated from the ideal formula (Na$_2$Si$_{14}$O$_{29}$) to be ca. 2.2 mmol/g of magadiite. The value is 2 times larger than that (1 mmol/100 g of clay) of conventional smectite. When interlayer exchangeable cations of a smectite have quantitatively exchanged with Ru(bpy)$_3^{2+}$, the intercalated Ru(bpy)$_3^{2+}$ cations form a closely packed monolayer in the interlayer space.[22] The adsorbed amount of Ru(bpy)$_3^{2+}$ (0.33 mol per formula unit of magadiite) corresponds to 0.75 mmol/g of magadiite, which is close to the cation-exchange capacity of smectite. Accordingly, the intercalated Ru(bpy)$_3^{2+}$ cations are thought to form a monolayer with a high packing density in the interlayer space of magadiite.

Figure 3 shows the absorption and the luminescence spectra of the Ru(bpy)$_3^{2+}$−magadiite intercalation compound. The visible spectrum showed the absorption band due to the "metal-to-ligand charge-transfer" transition (MLCT) of Ru(bpy)$_3^{2+}$ around 450 nm. The LMCT luminescence was observed in the luminescence spectrum. The luminescence maximum was observed at around 586 nm, which was blue-shifted from that of an aqueous solution of Ru(bpy)$_3^{2+}$ (608 nm). Wheeler and Thomas observed a luminescence blue shift upon the adsorption of Ru(bpy)$_3^{2+}$ on colloidal silica and explained that the rigid nature of the environment prevented the excited state from fully relaxing to cause the emission shift.[23] When Ru(bpy)$_3^{2+}$ was adsorbed in cellulose, the luminescence spectra changed around the melting point of the cellulose.[24] It was supposed that an increased possibility for relaxation in a more fluid state caused the spectral shift. The blue shifts of the luminescence maxima observed in the present system suggest the rigid nature of the interlayer space of magadiite.

From these observations, the successful introduction of Ru(bpy)$_3^{2+}$ into the interlayer space of magadiite with the aid of 15C5 was confirmed. There are two possible reaction mechanisms for the successful ion exchange in the presence of 15C5 as schematically shown in Figure 4. (1) 15C5 molecules
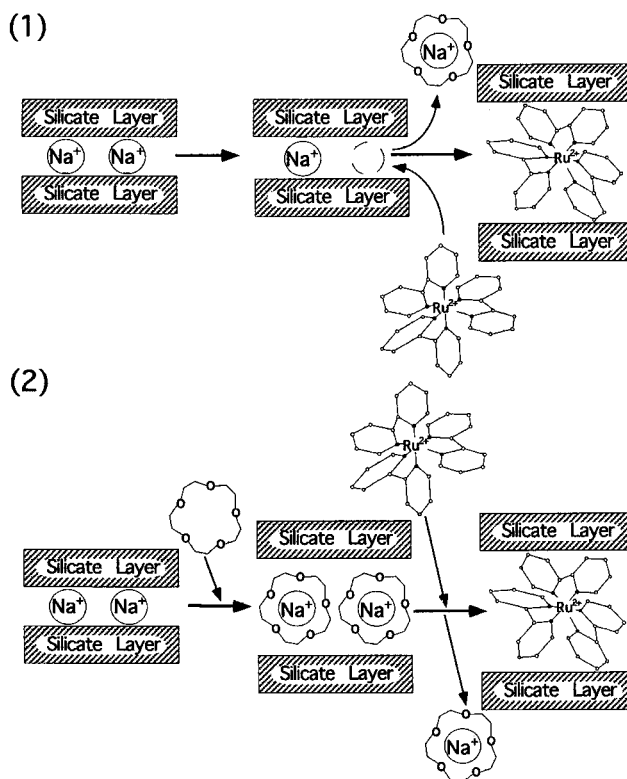

Figure 4. Proposed schematic drawing of the cation-exchange reaction in the presence of 15C5.
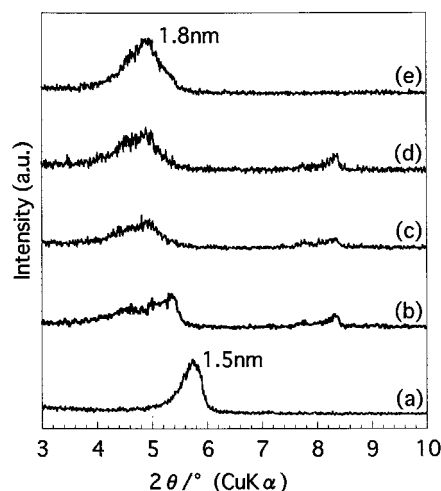

Figure 5. X-ray diffraction patterns of (a) Na−magadiite and (b−e) the reaction products by the reaction between Ru(bpy)$_3^{2+}$ and magadiite in the presence of 15C5 for (b) 14, (c) 20, and (d) 30 days. Trace (e) showed the XRD pattern of the washed (d).

form complex ions with sodium ions deintercalated from the interlayer space, and Ru(bpy)$_3^{2+}$ cations are intercalated into the interlayer space to compensate for the charge balance. (2) 15C5 molecules are first intercalated into the interlayer space of Na−magadiite, and the complex ions formed in the interlayer space are exchanged with Ru(bpy)$_3^{2+}$ cations subsequently.

The change in the X-ray diffraction pattern is shown in Figure 5. After the reaction for 14 days, the diffraction peak due to the Na−magadiite disappeared, and two peaks with the basal spacings of 1.65 and 1.9 nm appeared. The peak of 1.65 nm decreased after the reaction for 30 days, while the peak of 1.8 nm intensified. Since the minimum expansion of the interlayer space to accommodate Ru(bpy)$_3^{2+}$ cations is 0.7−0.8 nm, the basal spacing of 1.65 nm cannot be ascribed to the phase where

Ru(bpy)$_3^{2+}$ was intercalated. Therefore, the peak of 1.65 nm was ascribed to an intermediate phase where 15C5 molecules were intercalated. This observation suggests that the Ru-(bpy)$_3^{2+}$−magadiite intercalation compound formed through mechanism 2.

To support the idea mentioned above, the intercalation of 15C5 into the interlayer space of Na−magadiite was attempted. The intercalation of crown ethers and cryptands into the interlayer spaces of smectites has been reported.[25] Additionally, we have successfully introduced 18-crown-6 into the interlayer space of a layered polysilicate, K−kenyaite, which shows a relatively low intercalating capability if compared with those of smectites.[26] By the reaction between Na−magadiite and an methanol solution of 15C5 (molar ratio of 15C5/Na was 10) at 80 °C, an intercalation compound with the basal spacing of 1.8 nm was obtained. The infrared spectrum of the product showed absorption bands characteristic of 15C5 (such as C−H stretching vibration at 2922 and 2882 cm^{-1}). Considering the TG result (22.5% weight loss), the formation of the Na−magadiite−15C5 intercalation compound with the composition of {(15C5)$_{1.2}$·Na$_2$-Si$_{14}$O$_{29}$·nH$_2$O} was confirmed. Taking the molecular structure of the 15C5 into consideration, the intercalated 15C5 molecules are thought to form a bilayer in the interlayer space with their molecular planes parallel to the silicate sheet or a monolayer with their molecular planes inclined to the silicate sheet.

The Na−magadiite−15C5 intercalation compound thus obtained was used as the intermediate for the cation-exchange reaction with Ru(bpy)$_3^{2+}$ (method 2). After the reaction of the Na−magadiite−15C5 intercalation compound with a methanol solution of Ru(bpy)$_3$Cl$_2$, an orange solid was obtained. The basal spacing gradually increased with increased reaction periods and became 1.9 nm after the reaction for 20 days. The basal spacing is similar to that observed for the product prepared by the cation-exchange reaction between Na−magadiite and Ru(bpy)$_3$Cl$_2$ in the presence of 15C5. The absorption and luminescence spectra of the product are similar to those observed for the product prepared by method 1. The amounts of the adsorbed Ru(bpy)$_3^{2+}$ and the remained 15C5 were determined considering the TG (15.7% weight loss) and the UV results to be 0.3 and 0.03 mol per formula unit of magadiite, respectively. The amount of the intercalated Ru(bpy)$_3^{2+}$ was almost same for the product prepared by method 1. These observations indicate the successful formation of a Ru(bpy)$_3^{2+}$−magadiite intercalation compound by mechanism 2.

The intercalated amounts of Ru(bpy)$_3^{2+}$ were similar irrespective of the synthetic methods, confirming the amount of Ru(bpy)$_3^{2+}$ cations to be intercalated was limited by their packing in the interlayer space. The reason for the larger basal spacing (1.9 nm) of the intercalation compound prepared by method 2 than that (1.8 nm) of the intercalation compound prepared by method 1 is not clear at present. The location of the coadsorbed 15C5 and the amounts of coadsorbing water molecules may be concerned.

In our separate paper, we have reported the introduction of alkylammonium ions into potassium−tetratitanate (K$_2$Ti$_4$O$_9$·nH$_2$O) with the aid of a cryptand, [2.2.2]-cryptand.[27] In that case, the preparation of the [2.2.2]-cryptand−potassium−tetratitanate intercalation compound was unsuccessful, showing that the ion exchange proceeded by mechanism 1 (Figure 4). In the present Ru(bpy)$_3^{2+}$−magadiite systems, mechanism 2 is thought to be dominant to introduce Ru(bpy)$_3^{2+}$ cations into the interlayer space of magadiite although both reaction paths are possible. Since the intercalation of organic guest species into layered inorganic solids is an important way to construct

functional inorganic/organic supramolecular systems, the present success in the one-pot synthesis of Ru(bpy)$_3^{2+}$−magadiite intercalation compound opens up new opportunities to the preparation of various intercalation compounds with controlled microstructures and properties.

Conclusion

The interactions between sodium ions and a macrocyclic compound, 15-crown-5-ether, promoted the ion-exchange reaction between a layered silicate, magadiite, and a Ru(bpy)$_3^{2+}$ complex cation to give the novel Ru(bpy)$_3^{2+}$−magadiite intercalation compound. The application of the present method to the preparation of a wide variety of inorganic−organic supramolecular systems is promising, since macrocyclic ligands with variable guest binding selectivities and layered solids with a wide variety of structures and properties are known. There are also advantages in using an organic solvent as many organic cations will be soluble in the organic solvent and insoluble in water. The present one-pot synthesis is applicable to prepare various host−guest inclusion compounds.

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