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Synthesis of Two Types of Intercalation Compounds of $K_4Nb_6O_{17}$ with Tris(2,2′-bipyridyl) Metal Complex Ions

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$K_4Nb_6O_{17}$ is a layered material with two different types of interlayer spaces, interlayer I and interlayer II. It was found that two types of intercalation compounds of $K_4Nb_6O_{17}$ with alkylammonium ions were formed, one in which alkylammonium ions were present in interlayer I only, and the other in which they were present in both the interlayers. Intercalation of $[M(bpy)_3]^{2+}$ (M: Fe, Ru, Ni) into $K_4Nb_6O_{17}$ was carried out using these two types of alkylammonium-intercalated $K_4Nb_6O_{17}$ as the intermediates. Ion exchange reactions of the interlayer alkylammonium ions for the complex ions were conducted, and the formation of two types of products, one in which $[M(bpy)_3]^{2+}$ ions were present in interlayer I only and the other in which they were present in both the interlayers, was confirmed from powder X-ray diffraction patterns and the compositions of the products.

Potassium niobate $K_4Nb_6O_{17} \cdot nH_2O$ is a layered oxide consisting of $[Nb_6O_{17}]^{4-}$ layers and interlayer K^+ ions. $K_4Nb_6O_{17}$ intercalates various inorganic and organic cations by ion exchange,[1-3] and acts as a photocatalyst for water splitting because of its semiconducting property.[4] $K_4Nb_6O_{17}$ is structurally distinguished from other related layered niobates or titanates. It has two different types of interlayer spaces (interlayers I and II) alternately between $[Nb_6O_{17}]^{4-}$ layers (Fig. 1).[5] Interlayer I contains potassium ions with water molecules, while interlayer II contains unhydrated potassium ions under ambient conditions. The peculiar layered structure enables $K_4Nb_6O_{17}$ to have unusual properties in both intercalation chemistry and photocatalysis.

The two types of interlayers exhibit different intercalating capabilities. Kinomura et al. carried out ion exchange reactions of the interlayer potassium ions for various metal ions.[1] They concluded that monovalent cations were intercalated into both the interlayers, and di- and trivalent cations were exchanged with the potassium ions in interlayer I only. Other reports on intercalation into $K_4Nb_6O_{17}$ have not disagreed with these results so far; alkylammonium ions seem to be intercalated into both the interlayers,[2] while methylviologen dication is taken up into interlayer I only.[3]

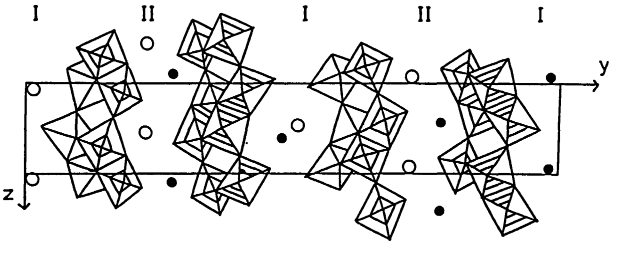

Fig. 1. The structure of $K_4Nb_6O_{17} \cdot 3H_2O$ showing the two interlayer regions.[5]
Squares represent $[NbO_6]$ octahedra at
x=1/4 (☒), x=1/2 (▩), x=3/4 (▦).
Circles represent K^+ at
x=1/4 (○) : x=3/4 (●).

This unusual layered structure and the intercalating property also contribute to the photochemistry of $K_4Nb_6O_{17}$ and its intercalation compounds. Domen et al. reported that the layered structure of $K_4Nb_6O_{17}$ plays a vital role in the photocatalytic water decomposition over $K_4Nb_6O_{17}$.[4] The efficiency of water splitting is significantly improved by loading Ni on $K_4Nb_6O_{17}$, and the presence of nickel in interlayer I but not in interlayer II is the key factor for the high efficiency. We synthesized the methylviologen–$K_xNb_6O_{17}$ intercalation compound and investigated its photochemical behavior.[3] In this intercalation compound, methylviologen dications were intercalated only into interlayer I, and the photochemical behavior differed from that of intercalation compounds of other related layered niobates and titanates with methylviologen because of the specific distribution of the guest.

These observations in both intercalation chemistry and photochemistry prompted us to synthesize two types of intercalation compounds of $K_4Nb_6O_{17}$; one contains the guest species only in interlayer I and the other has them in both the interlayers. If we construct novel photofunctional materials from $K_4Nb_6O_{17}$ through intercalation, such controllability of the guest distribution should be important in optimizing the photochemical properties. In the present study, we used tris(2,2′-bipyridyl) metal complexes ($[M(bpy)_3]^{2+}$) as the guest of the intercalation compounds. Since $[Ru(bpy)_3]^{2+}$ is used as a photochemical probe,[6] intercalation compounds with $[M(bpy)_3]^{2+}$, in particular $[Ru(bpy)_3]^{2+}$, can provide some information on the environment of the probe ions and prove useful for investigating the nature of $K_4Nb_6O_{17}$.

We employed a guest exchange method in order to synthesize the two types of intercalation compounds because intercalation compounds of $K_4Nb_6O_{17}$ with $[M(bpy)_3]^{2+}$ could not be prepared by a direct reaction. Alkylammonium–$K_xNb_6O_{17}$ intercalation compounds were used as the intermediates. Although the two types of the alkylammonium–$K_xNb_6O_{17}$ intercalation compounds have not been reported to form, we succeeded in preparing two types of alkylammonium-intercalates by varying the reaction conditions. Since the intercalation of $[M(bpy)_3]^{2+}$ to $K_4Nb_6O_{17}$ occurs through ion exchange with intercalated alkylammonium ions, two types of $[M(bpy)_3]^{2+}$–$K_xNb_6O_{17}$ intercalation compounds were synthesized by using the two types of alkylammonium–$K_xNb_6O_{17}$ intercalation compounds.

Experimental

Synthesis of Starting Materials. Tris(2,2′-bipyridyl) complexes of iron and nickel were synthesized as the chlorides $[Fe(bpy)_3]Cl_2 \cdot 7H_2O$ and $[Ni(bpy)_3]Cl_2 \cdot 7H_2O$, following the method of Inskeep.[7] They were confirmed by their infrared (IR) and ultraviolet-visible (UV-vis.) absorption spectra, by the composition using inductively-coupled plasma emission spectroscopy (ICP), and by elemental analyses. $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ was purchased from Aldrich & Co., and was recrystallized twice before use. Alkylammonium chlorides were purchased from Tokyo Kasei & Co. and were used without further purification. $K_4Nb_6O_{17} \cdot 3H_2O$ was synthesized by heating a 2.1 : 3.0 molar mixture of K_2CO_3 and Nb_2O_5 at 1100 °C for 10 h, following the method of Nassau et al.,[8] and confirmed by the powder X-ray diffraction pattern (XRD) and by the composition using ICP.

Intercalation of Alkylammonium Ions. The intercalation of alkylammonium ions into $K_4Nb_6O_{17}$ was carried out by treating $K_4Nb_6O_{17} \cdot 3H_2O$ with an aqueous solution of excess alkylammonium chloride. Lagaly et al. carried out the reaction at elevated temperatures (65—100 °C) and reported that the exchange reached a maximum within three weeks.[2] In our study, similar experimental conditions of 60 °C and three weeks were used in order to obtain a product in which alkylammonium ions existed in both the interlayers. To obtain a product in which alkylammonium ions exist in interlayer I only, on the other hand, the reaction was carried out under much milder conditions; the reaction temperature was not elevated from room temperature and a short reaction time of 30 min was used. The products were then washed with water and dried under ambient conditions.

Intercalation of Tris(2,2′-bipyridyl) Complex Ions. The intercalation of $[M(bpy)_3]^{2+}$ was carried out by treating alkylammonium-intercalated $K_4Nb_6O_{17}$ with an aqueous solution of excess $[M(bpy)_3]Cl_2 \cdot nH_2O$ in a glass ampoule at 80 °C. After ten days, the supernatant solution was removed and the reaction was repeated with a fresh $[M(bpy)_3]^{2+}$ solution for an additional ten days. The products were then washed extensively with methanol and dried under ambient conditions.

Analyses. The products were characterized by powder X-ray diffraction using a Rigaku RADI-B diffractometer (Cu $K\alpha$ radiation, Ni filter). Infrared absorption spectra were recorded on a Perkin–Elmer FTIR-1640 spectrometer using KBr discs. Ultraviolet-visible absorption and diffuse reflectance spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. The compositions of the products were obtained by ICP using a Nippon Jarrell Ash ICAP-575-II spectrometer for Nb, K, and M (Fe, Ru, or Ni) contents and by elemental analyses.

Results and Discussion

The Basal Spacings of $K_4Nb_6O_{17}$ and Its Intercalation Compounds.

The XRD pattern of $K_4Nb_6O_{17}$ is marked with the characteristic series of the $(0\,k\,0)$ diffraction peaks. The XRD pattern reflects the interlayer state, i.e. the difference in electronic distribution between the two interlayers. $K_4Nb_6O_{17} \cdot 3H_2O$, which is the usual hydration state under ambient conditions, has the (0 2 0) diffraction peak at 1.89 nm besides the most intense (0 4 0) peak at 0.95 nm in its XRD pattern (Fig. 2a).[8] The d_{020} value corresponds to the sum of the two interlayer spacings, and it is regarded as the basal spacing because the two interlayers are not the same because of the intercalation of water molecules only into interlayer I. On the other hand, the (0 2 0) peak disappears in the XRD pattern of $K_4Nb_6O_{17}$ (anhyd) whereas the (0 4 0) peak appears at 0.82 nm because the two interlayers are indistinguishable from each other.[8] In this case, the d_{040} value should be considered as the basal spacing. The d_{040} value corresponds to one interlayer spacing when the two interlayers are the same.

Similarly, the basal spacing of the intercalation compounds of $K_4Nb_6O_{17}$ depends on the type of intercalation compounds. The type determines which d-value should be adopted as the basal spacing. When the guest species are intercalated only into interlayer I, the sum of the two interlayer spacings should correspond to the basal spacing. We designate this type of intercalation compounds as A-type intercalation compounds, and the basal spacings as the basal spacing (A). On the other hand, the basal spacing should mean the one interlayer distance when the guest species are intercalated into the both interlayers. In this case, we designate the intercalation compounds as the B-type intercalation compounds, and the basal spacing as the basal spacing (B).

The Intercalation Compound of $K_4Nb_6O_{17}$ with Hexylammonium Ions. The X-ray diffraction pattern of the reaction product of $K_4Nb_6O_{17} \cdot 3H_2O$ with hexylammonium ions obtained by the reaction at 60 °C for three weeks was different from that of $K_4Nb_6O_{17} \cdot 3H_2O$ (Fig. 2b). This pattern was indexed as a single phase. The most intense diffraction peak appeared at 2.07 nm, following higher order peaks. The d-value of 2.07 nm was close to the basal spacing of the hexylammonium–$K_xNb_6O_{17}$ intercalation compound synthesized by Lagaly et al.[2] Thus, the peak at 2.07 nm and the following peaks should be indexed as a $(0\,k\,0)$ series. The presence of these peaks indicated that the interlayer spacings between $[Nb_6O_{17}]^{4-}$ layers were expanded by the reaction with well-ordered stacking. On the other hand, the $[Nb_6O_{17}]^{4-}$ layers themselves were somewhat disordered after the reaction because the diffraction peaks which were concerned with the a and c axes became rather weak and broad.

The type of the product (A or B) is deduced from the XRD results and the composition of the product. If the d-value of 2.07 nm is the basal spacing (A), the Δd value (increase in basal spacing by intercalation) is

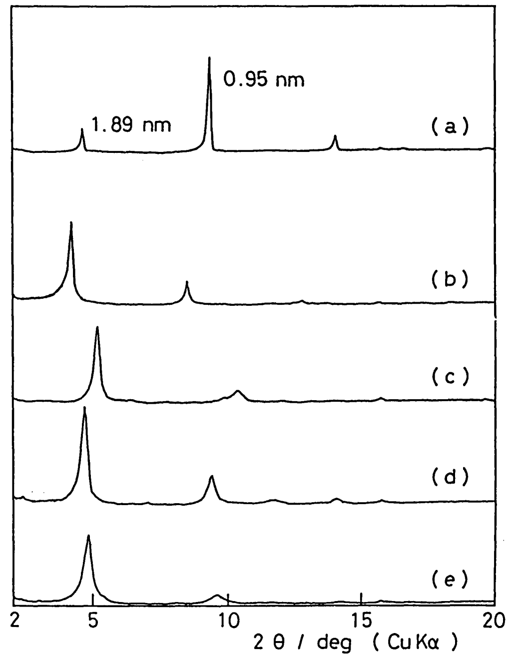

Fig. 2. X-Ray diffraction patterns of (a) $K_4Nb_6O_{17} \cdot 3H_2O$, (b) the reaction product of $K_4Nb_6O_{17}$ with a hexylammonium chloride solution under the conditions of 60 °C and three weeks (the B-type intermediate), (c) the reaction product of the B-type intermediate with $[Fe(bpy)_3]^{2+}$, (d) the reaction product of the B-type intermediate with $[Ru(bpy)_3]^{2+}$, and (e) the reaction product of the B-type intermediate with $[Ni(bpy)_3]^{2+}$.

calculated to be 2.07—1.64=0.43 nm. The value of 1.64 nm is twice that of the d_{040} value of $K_4Nb_6O_{17}$ (anhyd), corresponding to the "d_{020}" value ($K_4Nb_6O_{17}$ (anhyd) does not have the (020) peak in its XRD pattern as described before). Likewise, the Δd value is calculated to be 2.07—0.82=1.25 nm if the d-value of 2.07 nm is the basal spacing (B). Although the former Δd value is possible for a flat monolayer arrangement of hexylammonium ions, the latter is similar to those in the intercalation compounds of other layered niobates or titanates with hexylammonium ions.[9,10] On the other hand, the composition of the product was determined to be as follows; the molar ratio of $K:(C_6H_{13}NH_3):Nb=0.6:2.5:6.0$. The deficient positive charge is supposed to be supplied by H_3O^+ or H^+ ions, and this phenomenon was observed in other intercalation compounds with alkylammonium ions described later. Since an aqueous solution of hexylammonium chloride is acidic, it is possible that H_3O^+ ions were intercalated competitively with hexylammonium ions. This composition indicated that hexylammonium ions were intercalated into both of the interlayers, i.e. the intercalation compound is the B-type. If the ion exchange occurred only in interlayer I, the molar ratio of K^+/Nb would be more than 2.0/6.0 and the ratio of $C_6H_{13}NH_3^+/Nb$ would be less than 2.0/6.0. Consequently, we concluded that the B-type intercalation compound of $K_4Nb_6O_{17}$ with hexylammonium formed under the reaction conditions of 60 °C for 3 weeks.

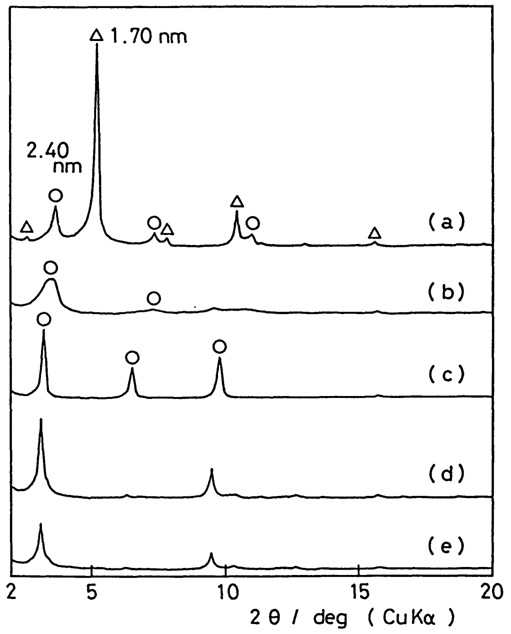

Fig. 3. X-Ray diffraction patterns of (a) the reaction product of $K_4Nb_6O_{17}$ with a butylammonium chloride solution under the conditions of 60 °C and three weeks (○ represents the diffraction peaks of the X phase and △ represents the peaks of the Y phase), (b) the reaction product of $K_4Nb_6O_{17}$ with an n-butylammonium chloride solution under the conditions of room temperature and 30 min (the A-type intermediate), (c) the reaction product of the A-type intermediate with $[Fe(bpy)_3]^{2+}$, (d) the reaction product of the A-type intermediate with $[Ru(bpy)_3]^{2+}$, and (e) the reaction product of the A-type intermediate with $[Ni(bpy)_3]^{2+}$.

Similar results were obtained for the reaction product of dodecylammonium ions with $K_4Nb_6O_{17}$. The basal spacing (B) was 3.15 nm (Δd=2.33 nm). The molar ratio of $K:(C_{12}H_{25}NH_3):Nb$ in the intercalation compound was found to be 0.7:2.8:6.0. This implied the intercalation of dodecylammonium ions into both the interlayers of $K_4Nb_6O_{17}$. However, very weak diffraction peaks which have d-values of (3.15×2) nm and (3.15×2/3) nm also appeared in the XRD pattern. This fact meant that the configurations of dodecylammonium ions in the two interlayers were not completely identical. Namely, the interlayer state of the two interlayers were not the same.

The configuration of alkylammonium ions in the interlayer of $[Nb_6O_{17}]^{4-}$ is not clear. The Δd values lie between the expected values for monolayer and bilayer arrangements of alkylammonium ions with the alkyl chains directed perpendicularly to the niobate sheets.[2] There are two possible explanations. The first possibility is that the alkylammonium ions are arranged as bilayers with inclined alkyl chains to the layer surface as in the case of alkylammonium ions intercalated into other related layered niobates or titanates.[9,10] The second interpretation is that the alkyl chains are oriented in a gauche-block conformation, as suggested by Lagaly et al.[2]

The Intercalation Compound with Butylammonium Ions. The reaction product of butylammonium ions with $K_4Nb_6O_{17}$ under the same experimental conditions contained two phases of butylammonium-intercalate (Fig. 3a). The phase which gave a diffraction peak at 2.40 nm was named the X phase, and the phase which gave a diffraction peak at 1.70 nm was named the Y phase. This result was different from that of the previous report in which only the Y phase of the butylammonium–$K_xNb_6O_{17}$ intercalation compound was reported.[2] Propylammonium ions also gave a double phase product with $K_4Nb_6O_{17}$ under the same reaction conditions.

The relative intensities of the X phase and the Y phase in the reaction product with butylammonium ions depended heavily on the reaction temperature and time. When very mild conditions (room temperature, 30 min) were used, the XRD pattern of the reaction product showed the formation of only the X phase (Fig. 3b). The Y phase appeared by an increase in the reaction temperature or the reaction time, and it became the dominating phase finally while the relative intensity of the X phase decreased drastically. However, we could not obtain pure Y phase. The X phase remained even when the reaction temperature was raised to 120 °C or when the reaction time was extended to two months.

The composition of the reaction product which was synthesized at 120 °C (the product was mostly the Y phase) was found to be as follows; the molar ratio of $K:(C_4H_9NH_3):Nb=1.0:2.1:6.0$. The molar ratio of K^+/Nb was much less than $2.0/6.0$ and the ratio of $C_4H_9NH_3^+/Nb$ was over $2.0/6.0$ in this product, as in the reaction product with hexyl- or dodecylammonium ions. This composition suggests that the product of the Y phase contains butylammonium ions in both of the interlayers of $K_4Nb_6O_{17}$. Namely, the Y phase indicates the B-type intercalation compound. Thus, the basal spacing (B) is 1.70 nm, and the Δd value is calculated to be 0.88 nm. The Δd value corresponds with the increase in basal spacings when *n*-butylammonium ions were intercalated into other layered niobates or titanates.[9,10]

On the other hand, the composition of the product which was synthesized under mild conditions (when the product was only the X phase) was found to have a molar ratio of $K:(C_4H_9NH_3):Nb=1.9:1.6:6.0$. This result suggests that K^+ ions in interlayer II are not affected by the reaction. Therefore, we infer that the product of the X phase is the A-type intercalation compound which contains butylammonium ions only in interlayer I. Thus, the *d*-value of 2.40 nm is regarded as the basal spacing (A), and then the Δd value is calculated to be 0.76 nm. This value is different from the Δd value of the B-type butylammonium-intercalate, though the reason for this is not clear. However, there is a possibility that the configuration of butylammonium ions in interlayer I is different from that in interlayer II. In Fig. 3a, there are weak diffraction peaks at 3.40 and 1.13 nm. These peaks should be observed when the two interlayers of the B-type intercalation compound are distinguishable from each other, and suggests that the two interlayers are not identical in this phase.

From such dependence of the appearance of the two phases on the reaction conditions, we concluded that the intercalation of butylammonium ions into $K_4Nb_6O_{17}$ occurred stepwise. First, the guest ions are intercalated into interlayer I only (the A-type intercalation compound), and then intercalated into interlayer II to yield a final product in which both the interlayers contain butylammonium ions (the B-type intercalation compound). This reaction scheme is demonstrated in Fig. 4. The reaction product under the conditions of 60 °C and three weeks was a mixture of the two types of the intercalation compounds, i.e. in this reaction product, butylammonium ions were contained in interlayer I and in some of interlayer II.

This stepwise intercalation was found to proceed not only with butylammonium ions but with other alkylammonium ions. When the experimental conditions of room temperature and 30 min were applied to the reaction with hexylammonium ions, the reaction product contained the A-type intercalation compounds with a basal spacing (A) of 2.9 nm, in addition to the B-type intercalation compound (the 2.07 nm phase, Fig. 2b). In this case, however, we could not obtain a single phase product of the A-type intercalation compound.

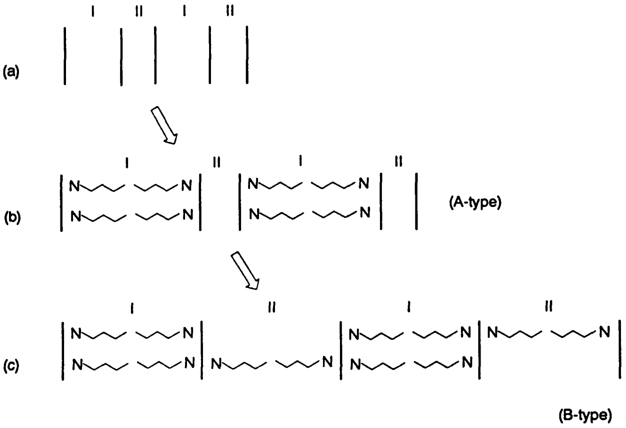

Fig. 4. Schematic diagram showing the stepwise intercalation of alkylammonium ions into the two interlayer regions of $K_4Nb_6O_{17}$. $K_4Nb_6O_{17}\cdot 3H_2O$ is represented here in a simplified form (a). Alkylammonium ions are first intercalated into interlayer I only (b). With extension of reaction time or raising of temperature, intercalation into interlayer II will take place (c). The alkyl chains are depicted in a perpendicular orientation to the layers although they are not really arranged in a perpendicular manner.

It is not clear at the moment as to why the reaction proceeds further with longer alkylammonium ions. One possible reason is the interlayer gauche-block model reported by Lagaly et al.[2] The gauche-blocks are formed to increase the stability of the interlayer alkylammonium ions,[11] and longer alkylammonium ions form gauche-blocks more readily than shorter alkylammonium ions. Thus, intercalation proceeds further with the longer alkylammonium ions because they can be more stable in the interlayers.

Intercalation of $[M(bpy)_3]^{2+}$ into $K_4Nb_6O_{17}$. The two types of single phase intercalation compounds of $K_4Nb_6O_{17}$ with alkylammonium ions were used as the intermediates in the synthesis of the two types of $[M(bpy)_3]^{2+}$-$K_xNb_6O_{17}$ intercalation compounds. The B-type hexylammonium-$K_xNb_6O_{17}$ intercalation compound formed by the reaction at 60 °C for three weeks (referred to as the "B-type intermediate" hereafter) was used to obtain the B-type of $[M(bpy)_3]^{2+}$-$K_xNb_6O_{17}$ intercalation compounds. The A-type butylammonium-$K_xNb_6O_{17}$ intercalation compound which was formed by the reaction at room temperature for 30 min (referred to as the "A-type intermediate" hereafter) was used in order to prepare the A-type $[M(bpy)_3]^{2+}$-$K_xNb_6O_{17}$ intercalation compounds.

The XRD patterns of the reaction products from the B-type intermediate are shown in Fig. 2c—e. While the whole profile of the pattern of the intermediate was maintained after the reaction, the position of the (0 *k* 0) peaks changed. Therefore, the structure of the intercalation compounds with $[M(bpy)_3]^{2+}$ was basically similar to that of the intermediate, i.e. the guest species were contained in both the interlayers. In addition, we observed weak diffraction peaks at both sides of the most intense peak. This phenomenon was the same as that observed in the B-type butylammonium-$K_xNb_6O_{17}$ intercalation compound (Fig. 3a), and means that $[M(bpy)_3]^{2+}$ is not intercalated identically into the two types of the interlayers.

Table 1. Basal Spacings[a] of the Reaction Products of $K_4Nb_6O_{17}$ with $[M(bpy)_3]^{2+}$

$[M(bpy)_3]^{2+}$	Type[b]	Basal spacing/nm	Δd/nm
$[Fe(bpy)_3]^{2+}$	B	1.69	0.87
$[Ru(bpy)_3]^{2+}$	B	1.88	1.06
$[Ni(bpy)_3]^{2+}$	B	1.83	1.01
$[Fe(bpy)_3]^{2+}$	A	2.69	1.05
$[Ru(bpy)_3]^{2+}$	A	2.79	1.15
$[Ni(bpy)_3]^{2+}$	A	2.80	1.16

a) Basal spacing (B) for the reaction products from the B-type intermediate, and basal spacing (A) for the reaction products from the A-type intermediate. Δd is calculated as the difference between the basal spacings of the products and those of $K_4Nb_6O_{17}$(anhyd), which are 1.64 nm (for the A-type) and 0.82 nm (for the B-type). b) The type of the intercalation compound as well as that of the basal spacing.

Similarly, the XRD patterns of the reaction products of the A-type intermediate with $[M(bpy)_3]^{2+}$ maintained the profile of the diffraction pattern of the intermediate, although the positions of the (0 *k* 0) peaks changed (Fig. 3c—e). Therefore, the basic structure of the intermediate was retained in the formed intercalation compounds, i.e. $[M(bpy)_3]^{2+}$ was contained in interlayer I only.

The basal spacings of the intercalation compounds with $[M(bpy)_3]^{2+}$ are listed in Table 1. When $[Ru(bpy)_3]^{2+}$ was intercalated into other layered inorganic materials, such as clay minerals,[12] zirconium bis(hydrogenphosphate),[13] and $MnPS_3$,[14] the basal spacings were reported to increase by 0.8—0.9 nm, and the octahedral complex was considered to be oriented with its C_3 axis directed perpendicularly to the layers. The Δd values of the $[M(bpy)_3]^{2+}$-$K_xNb_6O_{17}$ intercalation compounds were around 1.0—1.1 nm, indicating that the configurations of $[M(bpy)_3]^{2+}$ were not similar to those in other layered compounds. Two possible explanations can be adopted for these large Δd values. We presume that $[M(bpy)_3]^{2+}$ can be arranged to increase the interlayer spacings by more than 0.9 nm since the real layer surface of $K_4Nb_6O_{17}$ is uneven as shown in Fig. 1. Further, the interlayer space can also be expanded if other cations, such as unremoved alkylammonium ions, are co-intercalated with $[M(bpy)_3]^{2+}$.

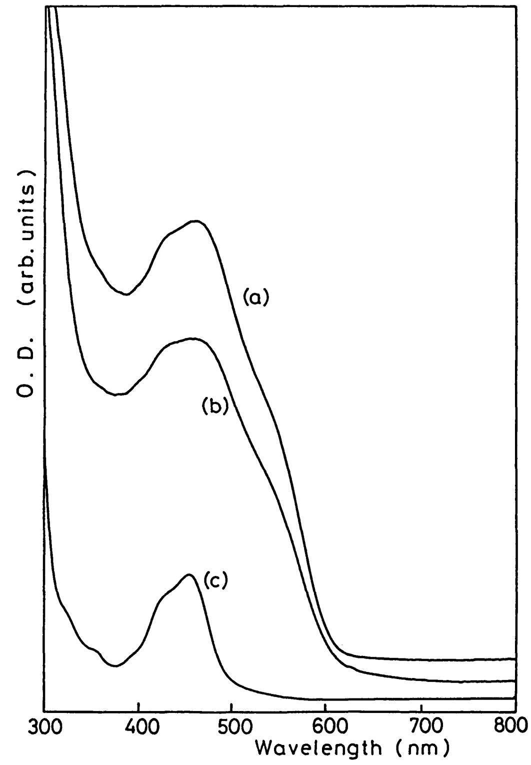

Fig. 5. Diffuse reflectance spectra of the reaction products of $K_4Nb_6O_{17}$ with $[Ru(bpy)_3]^{2+}$: (a) synthesized from the B-type intermediate, (b) synthesized from the A-type intermediate, (c) transmission spectrum of $[Ru(bpy)_3]^{2+}$ (in aqueous solution).

On the other hand, the Δd values differed with the type of the intercalation compounds. This fact suggests slightly different configurations of the guest species in the two interlayers.

The presence of the tris(2,2′-bipyridyl) complex ions in the products was also confirmed by diffuse reflectance spectra. The spectra of the reaction products with $[Ru(bpy)_3]^{2+}$ are shown in Fig. 5. All the spectra of the products exactly resembled those of the guest tris(2,2′-bipyridyl) complexes in aqueous solutions. However, the MLCT bands of the complexes appeared at slightly red-shifted positions in the reaction products compared to those in aqueous solutions.[15] For example, the MLCT band of $[Ru(bpy)_3]^{2+}$ appeared at 456 and at 462 nm in the A-type and the B-type intercalation compounds, respectively, while it was observed at 452 nm in an aqueous solution. Similarly, the MLCT band of $[Fe(bpy)_3]^{2+}$, which is observed at 522 nm in an aqueous solution, shifted to 532 nm in the reaction products. These red-shifts have also been observed in most of other intercalation compounds of $[M(bpy)_3]^{2+}$, and are attributed to a somewhat strained configuration of the complex ions in the interlayers,[13,14] However, we could not differentiate spectrally between the products from the A-type intermediate and those from the B-type intermediate.

Additional evidence for the presence of the complex ions in the products was provided by their IR spectra. Despite thorough washing, the products exhibited many bands due to ring vibrations of the 2,2′-bipyridyl ligand in the region of 1300 to 1700 cm^{-1}. These bands appeared at slightly shifted positions from that of $[M(bpy)_3]Cl_2$, reflecting a weak interaction between the 2,2′-bipyridyl ring and the host lattice. However, it was not possible to differentiate between the products from the A-type and those from the B-type intermediate. Moreover, bands due to alkylammonium ions were observed (2800—3000 cm^{-1}; ν_{C-H}, for example) in addition to those due to the 2,2′-bipyridyl ring in all the samples except the B-type $[Fe(bpy)_3]^{2+}$-$K_xNb_6O_{17}$ intercalation compound, implying that the ion exchange of alkylammonium ions for $[M(bpy)_3]^{2+}$ did not proceed completely under the given reaction conditions.

Table 2 lists the composition of the $[M(bpy)_3]^{2+}$-$K_xNb_6O_{17}$ intercalation compounds. The amount of 2,2′-bipyridyl was calculated on the basis of the amount of the central metal ions, and the amount of alkylammonium ions was obtained by subtraction of the 2,2′-bipyridyl contents from the total organic contents determined by elemental analyses. Although the reason is not clear, alkylammonium ions were removed completely only in the B-type $[Fe(bpy)_3]^{2+}$-$K_xNb_6O_{17}$ intercalation compound. This result explains the small Δd value of the intercalation compound, and the larger Δd value of the other intercalation compounds are presumed to be attributed to co-intercalation of alkylammonium ions. On the other hand, the amount of K^+ ions was reduced by the reaction in the A-type intercalation compounds. The amount of K^+ ions in the A-type $[M(bpy)_3]^{2+}$ intercalation compounds suggests that ion exchange of K^+ for H_3O^+ or H^+ occurred in interlayer II. Since H_3O^+ and H^+ are monovalent cations, they can exchange with K^+ directly in interlayer II. In addition, it is possible that such removal of K^+ ions occurred in the formation of the A-type butylammonium-$K_xNb_6O_{17}$ intercalation compound. Although we presumed that K^+ ions in interlayer II were not affected by the reaction for the composition $(K_{1.9}(C_4H_9NH_3)_{1.6}Nb_6O_{17})$, we can not deny the possibility that some of the K^+ ions in interlayer II were removed.

As to the amounts of $[M(bpy)_3]^{2+}$ ions, they were smaller than those of the removed alkylammonium ions. We assume competitive ion exchange of H_3O^+ (or H^+) as presumed in the reaction of alkylammonium ions with $K_4Nb_6O_{17}\cdot 3H_2O$; $[M(bpy)_3]^{2+}$ ions might be intercalated competitively with H_3O^+ (or H^+) ions. Moreover, the amounts of $[M(bpy)_3]^{2+}$ were also smaller than the maximum amount which was defined by the charge density of the host and the bulkiness of the guest. The charge density of the $[Nb_6O_{17}]^{4-}$ layer was 0.126 nm^2 per charge,[8] while the area occupied by one $[M(bpy)_3]^{2+}$ ion was calculated to be 0.92 nm^2 from the results of Rillema and Jones.[16] Therefore, if they were intercalated in a monolayer configuration, the maximum amount of $[M(bpy)_3]^{2+}$ per $[Nb_6O_{17}]^{4-}$ was 0.55 for the B-type intercalation compounds and 0.27 for the A-type intercalation compounds (i.e. only 27% of the

Table 2. Composition of the Intercalation Compounds of $K_4Nb_6O_{17}$ with $[M(bpy)_3]^{2+}$ [a)]

Guest	Type	$[M(bpy)_3]^{2+}$	Alkylammonium[b)]	K	Nb
$[Fe(bpy)_3]^{2+}$	B	0.3	0	0.6	6.0
$[Ru(bpy)_3]^{2+}$	B	0.3	0.3	0.5	6.0
$[Ni(bpy)_3]^{2+}$	B	0.3	0.7	0.5	6.0
$[Fe(bpy)_3]^{2+}$	A	0.1	0.8	1.1	6.0
$[Ru(bpy)_3]^{2+}$	A	0.2	0.6	1.4	6.0
$[Ni(bpy)_3]^{2+}$	A	0.2	0.4	1.4	6.0

a) The amount of each component is expressed in molar ratios. b) Hexylammonium for the B-type intercalation compounds, and butylammonium for the A-type intercalation compounds.

original K^+ sites could be occupied). Hence, the results in Table 2 imply that about 50% of the available interlayer area was occupied by $[M(bpy)_3]^{2+}$. Namely, $[M(bpy)_3]^{2+}$ was not packed so densely in the interlayer of $K_4Nb_6O_{17}$, although the reason for this is not clear.

Conclusions

Two types of intercalation compounds of $K_4Nb_6O_{17}$ with $[M(bpy)_3]^{2+}$, in which the complex ions existed either in interlayer I only or in both the interlayers, were synthesized. We clarified that the guest exchange method using alkylammonium-$K_xNb_6O_{17}$ intercalation compounds as the intermediates is valuable for intercalation chemistry of $K_4Nb_6O_{17}$. It was found that the intercalation of alkylammonium ions into $K_4Nb_6O_{17}$ could take place either in interlayer I only or in both the interlayers, and the two types of intercalation compounds with $[M(bpy)_3]^{2+}$ were obtained through ion exchange of the interlayer alkylammonium ions with $[M(bpy)_3]^{2+}$. Since this ion exchange is expected to occur with other cations besides $[M(bpy)_3]^{2+}$, the use of these intermediates should lead to a possibility of synthesizing the two types of intercalation compounds of $K_4Nb_6O_{17}$ with a variety of other guest species, and may contribute to further developments in the fields of intercalation chemistry and photochemistry of $K_4Nb_6O_{17}$.

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