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Intercalation of a Triethylenetetramine-Substituted Cyclodextrin by Co(II)- and Ni(II)-Montmorillonites

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Synopsis. The intercalation of mono[6-[(8-amino-3,6-diazaoctyl)amino]-6-deoxy]-β-cyclodextrin (CDtrien) by Co(II)- and Ni(II)-montmorillonites was examined at 25 °C. At low uptakes, the CDtrien molecules in both minerals form a monolayer, 13—14 Å thick, with their cavity axes perpendicular to the silicate layers. At higher loadings, guest molecules with the same orientation form a bilayer in Co- (21.8 Å thick) and Ni-montmorillonites (17.6 Å). Their thicknesses are larger than those for the Cu-and Zn-analogues, 16.1 Å, i.e. twice the molecular thickness.

New porous solids have been required for the platforms of immobilized enzymes, for improved columns in adsorption and ion-exchange chromatography, and for effecting gas separations.[1] Our attention has been focused on developing microporous inclusion compounds having novel characteristics. An organic and inorganic double host material is an example which can be obtained by the intercalation of host molecules such as cyclodextrins in inorganic hosts.[2-4] We recently studied the intercalation of mono[6-[(8-amino-3,6-diazoctyl)amino]-6-deoxy]-β-cyclodextrin(CDtrien) by Na-, Ca-, Cu-, and Zn-montmorillonites, and revealed the mechanism of the CDtrien intercalation and the arrangement of the guest molecules in the host cavities.[5] This paper reports on the intercalation of CDtrien by Co(II) and Ni(II)-montmorillonites.

In a previous paper,[5] the mode of intercalation by Ca-montmorillonite was explained by the formation of CDtrien$(H_2O)_2$–Ca complexes. However, after this paper was published, it was found by analytical scanning electron microscopy that the uptake of CDtrien by Ca-montmorillonite is accompanied by a remarkable release of Ca, which forms a second phase. A reexamination by X-ray diffraction suggested that the second phase is calcium carbonate. Thus, the previous explanation must be modified as follows: the intercalation by Ca-montmorillonite proceeds by an ion exchange of interlayer Ca^{2+} ions with the divalent cationic forms of CDtrien, as in the case of Na-montmorillonite.

Experimental

The CDtrien and the Na-montmorillonite used as starting minerals were the same as those used in a preceding study.[5] The Co(II)- and Ni(II)- exchanged minerals were prepared by placing the Na-montmorillonite in a 1.25 mol dm^{-3} solution of $CoCl_2$ and $NiCl_2$ at 25°C for 10d, respectively. The exchanged products were fully washed with water, centrifuged, and lyophilized. The Co(II)- and Ni(II)-clays were soaked in an aqueous solution containing 0.25, 1, 1.5, and 3.0 mmol of CDtrien per gram of clay at 25 °C for 10 d, centrifuged, fully washed with water, and air-dried at 40 °C. The CDtrien and water contents in the resulting solids were determined by thermogravimetric analysis. An X-ray diffraction measurement was made using Fe-*K*α radiation, and 1-tetradecanol having a long *d*-spacing (39.90 Å) was used as an external standard.

Results and Discussion

The uptakes of CDtrien for Co(II)- and Ni(II)-montmorillonites are plotted against the amount of CDtrien added (Fig. 1). The interlayer spacings of the resulting solids were determined from 001 reflections in the X-ray diffraction patterns. Figure 2 shows the variation of Δ, the thickness of the intercalated layer obtained by subtracting 9.5 Å, the thickness of the silicate layer, from the observed d-spacings. When 0.25 mmol of CDtrien was added per gram of each clay, a phase with a Δ value of 12.9—14.1 Å appeared and coexisted with its parent host phase. With a further addition of CDtrien the solids were converted into a single phase with a Δ value of 21.8 (Co-intercalate) or 17.6 Å (Ni-intercalate). The uptake curves of both intercalates showed saturation. The CDtrien uptakes were accompanied by the release of interlayer metal ions, as shown in Fig. 1.

Table 1 summarizes the Δ values and compositions of intercalates of Co- and Ni-montmorillonites with

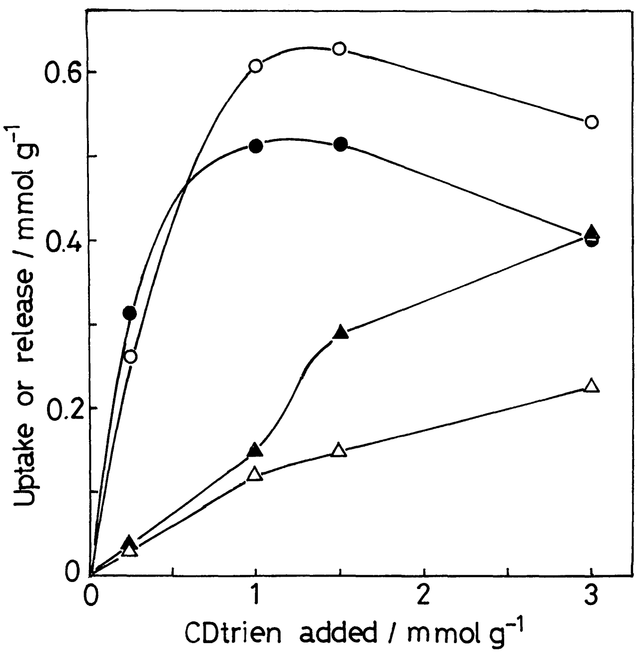

Fig. 1. CDtrien uptake by (○) Co- and (●) Ni-montmorillonites and release of (△) Co^{2+} and (▲) Ni^{2+} ions as a function of CDtrien added.

Table 1. Characterization of Intercalates of Co(II)- and Ni(II)-Monmorillonites with CDtrien at Its Full Loadings

Interlayer metal ion	Δ/Å	Amount of releasable metal ions/mmol g^{-1} clay[a]						Amount of CDtrien/mmol g^{-1} clay[a,d]		
		Initial			Desorbed		Remaining	Total	Neutral form	Divalent cationic form
		Total	Int[b]	Ext[c]	Int[b]	Ext[c]				
Co	21.8	0.63	0.54	0.09	0.06	0.09	0.48	0.63	0.57 (90.5)	0.06 (9.5)
Ni	17.6	0.61	0.54	0.07	0.22	0.07	0.32	0.51	0.29 (56.9)	0.22 (43.1)

a) Anhydrous form of clay. b) The amount of exchangeable cation held as interlayer counter ions for the negatively charged silicate layers. c) The amount of adsorbed cations as any neutralized species on the external surface of crystals. d) Contents in mol% are given in parentheses.

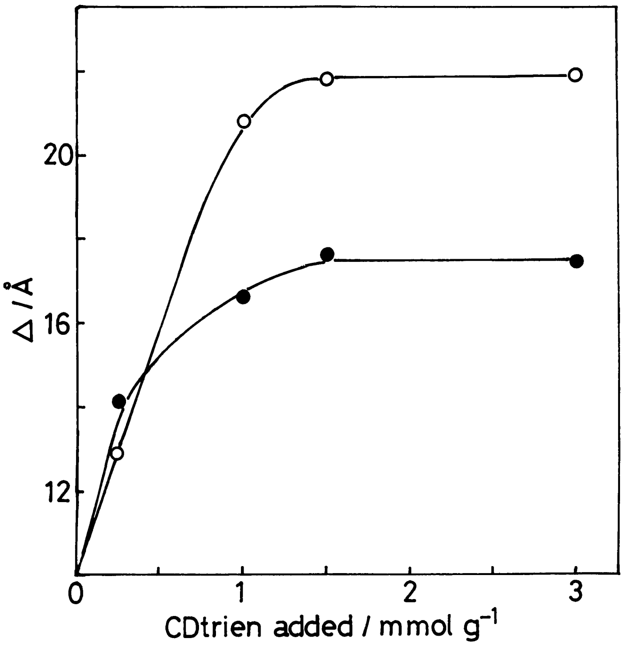

Fig. 2. The thickness of the intercalated layer, Δ (see text), as a function of CDtrien added. Key as in Fig. 1.

CDtrien obtained at an addition level of 1.5 mmol g^{-1}. The initial amounts of the cationic and the neutral forms of interlayer metal ions in Co(II)- and Ni(II)-montmorillonites were evaluated as described previously.[5]

The uptake reaction for Co-and Ni-montmorillonites took place in the pH range of as narrow as 8.3—8.9. Similarly to the previous discussion,[5] the above-mentioned data indicate that the intercalation of CDtrien by Co-and Ni-montmorillonites proceeds by the formation of CDtrien–Co^{2+} or CDtrien–Ni^{2+} complexes at low uptakes and by the combined modes of complexation and an ion exchange of Co^{2+} or Ni^{2+}/CDtrien2H^+ at higher loadings, where CDtrien2H^+ is the divalent form of CDtrien. We can, thus, evaluate the amounts of interlayer metal ions desorbed and those of both neutral and ionized forms of intercalated CDtrien (Table 1). At addition levels of more than 1.5 mmol g^{-1}, the uptake of CDtrien shows a tendency to decrease, in contrast to an increase in the release of interlayer metal ions. This can be explained by assuming that the CDtrien uptake due to ion exchange increases, whereas that due to complexation decreases appreciably, resulting in a decrease in the total uptake of CDtrien.

According to the literature,[6] the stability constants for trien–Cu^{2+}, trien–Ni^{2+}, trien–Zn^{2+}, and trien–Co^{2+} complexes in solution are $10^{20.4}$, $10^{14.0}$, $10^{12.1}$, and $10^{11.0}$, respectively. If stability constants of CDtrien–metal ion complexes in the solid state are assumed to be comparable to those in solution, the complexation tendency would be of the order of $Cu^{2+} \gg Ni^{2+} > Zn^{2+} > Co^{2+}$. In contrast, the experimental result is the order $Co^{2}(90.5) \gg Cu^{2+}(65.9) > Ni^{2+}(56.9) \gg Zn^{2+}(23.8)$, where the amounts of the neutral form of intercalated CDtrien in mol% are given in parentheses. The high degree of complexation for Co^{2+} ion could be explained in terms of the extremely high stability of the structure of interlayer CDtrien complexes, as is discussed later. The relatively high degree of complexation for the Ni^{2+} ion can also probably be attributed to a similar structural effect.

The previous observations[5] showed that Cu(II)- and Zn-montmorillonites intercalate CDtrien to form a bilayer at high uptakes: the bilayered molecules are in a close contact with each other at a van der Waals distance of 16.1 Å, with their cavity axes perpendicular to the silicate layers and with the trien groups pointing both upward and downward in the intramolecular-complexing or divalent cationic forms. On the other hand, the Δ values for the Co(II)- and Ni(II)-intercalates are greater by 5.7 and 1.5 Å than those for the Cu- and Zn-analogues, respectively. This fact suggests that the CDtrien molecules in the former two intercalates are also arranged as a bilayer with the same orientation, but with a looser contact of 5.7 or 1.5 Å between the layers.

Upon heating up to 150 °C, the CDtrien layers of the Co(II)-intercalate contracted in thickness from 21.8 to 19.7 Å, due to the release of interlayer water. No interlayer contraction, on the other hand, was observed for the Cu- and Zn-intercalates. These observations suggest that at least a part of the interlayer water molecules participates as a ligand in the formation of the expanded bilayer in the Co-intercalate. It is thus suggested that the CDtrien molecules in Co(II)-montmorillonite form a 1:1 octahedral aqua complex, CDtrien$(H_2O)_2$–Co^{2+}, and that they are dimerized with a tail-to-tail arrangement, as illustrated in Fig. 3. The intercalated CDtrien$(H_2O)_2$–Co^{2+} complex would be highly stabilized by such a dimerization. A similar dimerized structure was observed for the CDen intercalate of Cu-montmorillonite.[2]

The intercalated layers of the Ni(II)-intercalate is also contracted in thickness from 17.6 to 16.2 Å upon heating up to 150 °C. This fact suggests that a slight expansion

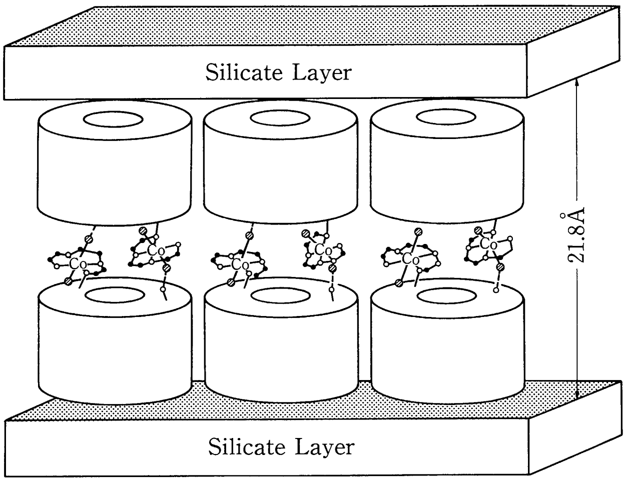

Fig. 3. A tentative model of the arrangement of CDtrien molecules in the interlayer space of Co-montmorillonite. ●, C; ○, N; ◍, water molecule.

of the CDtrien bilayer in the Ni(II)-intercalate also results from the interlayer water molecules and that the anhydrous form of the intercalate may have a structure similar to that of the Cu(II)- and Zn-intercalates. Thus, the CDtrien molecules in Ni(II)-montmorillonite are likely to make an isolated octahedral aqua complex, CDtrien(H$_2$O)$_2$–Ni^{2+}. The slight increase in the thickness of CDtrien(H$_2$O)$_2$–Ni^{2+} complex bilayer can be understood by assuming that they are more rigid and more bulky than the square plannar CDtrien–Cu^{2+} or tetrahedral CDtrien–Zn^{2+} complex.

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