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Intercalation of *p*-Aminobenzylated and Dimethylammoniomethylated Calix[4]areneoctols by Cu(II)–Montmorillonite

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The uptake of two different types of cationic calix[4]areneoctols by Cu(II)–montmorillonite was studied at 25 °C. *p*-Aminobezylated calix[4]areneoctol **1** forms an intercalated phase in which the guest molecules are arranged as a 10.8 Å thick monolayer, with a cone-type conformation and with their cavity axes perpendicular to the inorganic layers. Thermogravimetric and copper(II) release data suggest that the calixareneoctol molecules are taken up in their divalent form and act as a prop to yield a vacant space of 42% in interlayer porosity. The molecules of dimethylammoniomethylated calix[4]areneoctol **2** are also intercalated as a monolayer, but initially in their divalent form and finally in the di- and mono-valent mixed form to fully occupy the interlayer space. The striking contrast between the two calixareneoctols as guest species is substantially due to the difference in bulkiness of their ammonio-substituted groups.

We have developed a new class of organic and inorganic combined host materials, with the expectation that they would act as including agents with high selectivity.[1—4] So far, cyclodextrins have been mainly used as the organic host component to be intercalated in layered parent hosts, such as montmorillonites and zirconium phosphates. Our previous studies have shown a general tendency that cyclodextrin molecules are intercalated as a uni- or bi-molecular layer with their molecular axes parallel or perpendicular to the inorganic layer depending on the electrostatic properties of the cyclodextrins and layered hosts used. In a previous paper,[5] we have first reported the intercalation of a cationic calixarene in Cu(II)-montmorillonite by a mode in which the guest molecules are arranged as a monolayer with their molecular axes perpendicular to the host layer. These observations aroused our interest in a comparative study on the intercalation behavior of a variety of calixarenes. Calixareneoctols are a subclass of calixarenes derived from the acid-catalyzed condensation of resorcinol with aldehyde[6] and act as including agents for neutral organic species[7] or as extracting ones for sugar molecules.[8,9] This paper describes the intercalation behavior of 2,14-bis(*p*-aminophenyl)-8,20-bis-(*p*-ammoniophenyl)calix[4]arene-4,6,10,12,16,18,22,24-octol (**1**), and 2,8,14,20 tetramethyl-5,11,17,23-tetrakis-(dimethylammoniomethyl)calix[4]arene-4,6,10,12,16,18,22,24-octol (**2**) (Fig. 1) towards Cu(II)–montmorillonite.

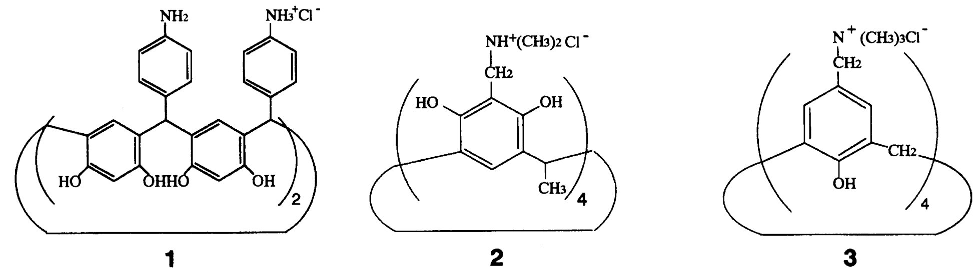
Experimental

The Cu(II)–montmorillonite used as a starting mineral was the same as that used in our preceding studies.[3—5] Calixareneoctol **1** was prepared in a manner similar to that of Aoyama, Tanaka, and Sugahara[8] for several alkylated analogs. *p*-Aminobezaldehyde of commercial grade was in advance mixed with ethanol to use only the dissolved fraction for the sample preparation. Into a solution of *p*-aminobezaldehyde (31.75 g, 0.26 mol) in ethanol (500 ml) were added resorcinol (29.0 g, 0.26 mol) and 12 M hydrochloric acid (40 ml, 1 M=1 mol dm^{-3}) at 0 °C. The mixture was stirred at 70 °C for 10 h and then cooled to room temperature. The resulting solid was separated, washed with ethanol and then with a minimum amount of water, and freeze-dried. The C : H : N ratio evaluated by the elemental analysis agreed well with that calculated by assuming the chemical formula of **1**. The titration curve of **1** with 0.1 M KOH aqueous solution was also in accordance with a value of 1 : 1 for the molar ratio of $-NH_2$ to $-NH_3^+Cl^-$ form. The synthesis of calixareneoctol **2** was described elsewhere.[10] The Cu(II)-clay was soaked in an aqueous solution containing various amounts of **1** or **2** per gram of clay at 25 °C for 10 d, centrifuged, fully washed with water, and freeze-dried. Thermogravimetry (TG) was done for the resulting solids at a heating rate of 10 °C min^{-1}. The amount of copper(II) ions released to solution was measured by atomic absorption analysis. X-Ray diffraction measurements were made using Cu *K*α radiation; 1-tetradecanol having a long *d*-spacing (39.9 Å) was used as an external standard.

Results

Calixareneoctol 1. Figure 2(A) shows X-ray diffraction patterns of the resulting solids obtained at various addition levels. On addition of **1**, a new set of diffraction peaks corresponding to $d\approx 20.3$ Å appeared in place of the diffraction peaks attributable to the host phase. This indicates that at addition levels greater than 0.25 mmol g^{-1} the host phase is fully converted into an intercalated phase with an interlayer spacing of about 20.3 Å. The thickness of the intercalated layer (Δ) was obtained by subtracting 9.5 Å,[2,4] the thickness of the silicate layer, from the observed *d*-spacings. The structural data thus obtained are summarized in Table 1.

The calixareneoctol contents in the intercalated solids were evaluated with the combined use of TG and Cu^{2+} release data in the manner previously described.[5] Figure 3 shows the TG curves for the intercalated solids with **1** in which the weight loss at temperatures above 250 °C is due to the desorption of intercalant species and condensation of hydroxyl groups in the host phase. The total amount of Cu^{2+} ions desorbed from the solids



1 **2** **3**

Fig. 1. *p*-Aminobenzylated and dimethylammoniomethylated calix[4]areneoctols (**1** and **2**) and trimethylammoniomethylated calix[4]arenetetrol (**3**).

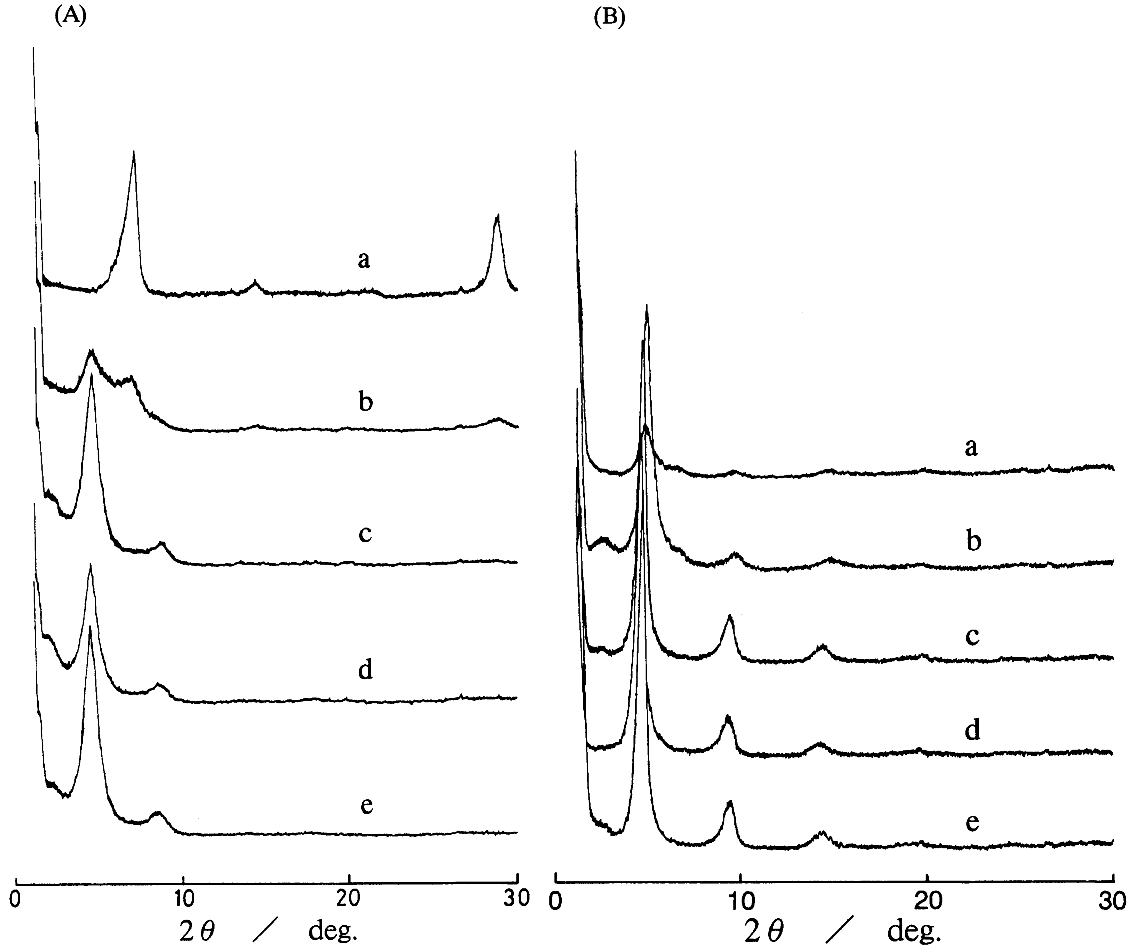


Fig. 2. X-Ray diffraction patterns of Cu(II)–montmorillonite and its intercalates with calixareneoctols **1** (A) and **2** (B) (Cu $K\alpha$ radiation). Calixareneoctol addition levels (mmol g^{-1}): (A) 0 (a), 0.25 (b), 0.5 (c), 0.75 (d), and 1.0 (e); (B) 0.20 (a), 0.25 (b), 0.5 (c), 0.75 (d), and 1.0 (e).

Table 1. Characterization of Intercalates of Cu–Montmorillonite with **1** at Various Loadings

Amount of **1** added	Interlayer spaceing	Δ	Amount of **1**	Amount of releasable Cu^{2+}ion/mmol g^{-1} clay					Cu^{2+} ion /**1** ratio
				Initial			Desorbed	Remaining	
mmol g^{-1} clay	Å	Å	mmol g^{-1} clay	Total	Int.	Ext.			
0.25	20.0	10.5	0.17	0.63	0.54	0.09	0.12	0.51	3.0
0.5	20.1	10.6	0.26	0.63	0.54	0.09	0.25	0.38	1.5
0.75	20.3	10.8	0.23	0.63	0.54	0.09	0.25	0.38	1.7
1.0	20.3	10.8	0.26	0.63	0.54	0.09	0.23	0.40	1.5

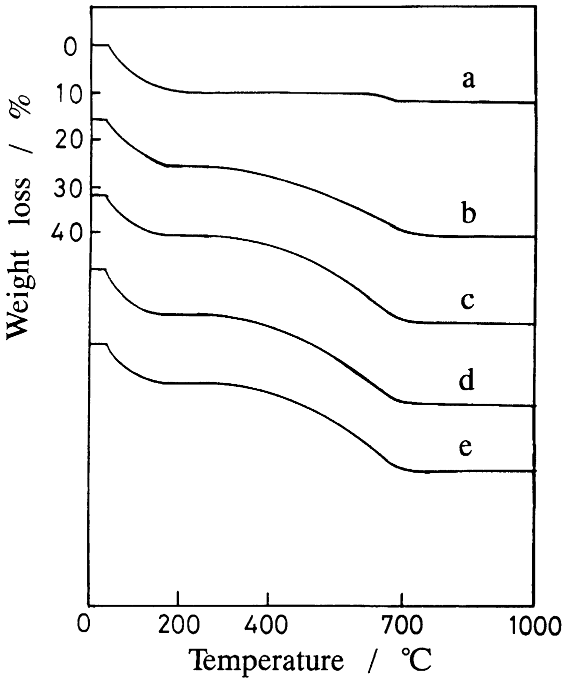


Fig. 3. TG curves for Cu(II)–montmorillonite (a) and its intercalates with calixareneoctol **1**. Calixareneoctol addition levels (mmol g^{-1}): 0.25 (b), 0.5 (c), 0.75 (d), and 1.0 (e).

is cited in Table 1, along with the initial amounts of the metal ions held as interlayer cations, and as any neutralized species on the external surface of the crystals. The amount of interlayer Cu^{2+} ions desorbed by ion exchange with calixareneoctol molecules was obtained by subtracting the amount of neutral species from the total amount of desorbed metal ions. Here we can assume that the calixareneoctol molecules are taken up as a mono- (m=1), di-(m=2), tri- (m=3), or tetra- (m=4) valent cation with the composition CLX-$(NH_3^+)_m(NH_2)_{4-m}$ or their mixture, where CLX refers to the macrocyclic moiety of **1** or **2**. Thus, if the average valence of intercalant species is taken as n, the calixareneoctol content evaluated from the TG data and that evaluated from the Cu^{2+} release data can be related to the intercalant valence n by a straight line and by a curve, respectively, as shown in Fig. 4(A), including the case of $n=m$ (indicated by open or closed symbols). The curve and straight line for the solids formed as a single phase intercept at $n=+2$, indicating that the calixareneoctol molecules are intercalated in the divalent form, with the intercalant content of about 0.23 mmol g^{-1} at the full uptake stage. The uptake parameters thus obtained are summarized in Table 1.

Calixareneoctol 2. X-Ray diffraction patterns of the resulting solids with **2** indicated that the intercalation of **2** proceeds in two steps, in contrast to that of **1** (Fig. 2(B)). At addition levels as low as 0.20—0.25 mmol g^{-1}, the host phase is fully converted into an intercalated phase with an interlayer spacing of about 18.2 Å. With further addition of **2** the intercalated phase increases in interlayer spacing from 18.2 to 19.1 Å. The structural data derived from the X-ray observations are listed in Table 2. Assuming that the calixareneoctol molecules are taken up as a mono- (m=1), di- (m=2), tri- (m=3), or tetra- (m=4) valent cation with the composition $CLX^{4+}(4\text{-}m)Cl^-$ or their mixture, the calixareneoctol contents evaluated from TG and Cu^{2+} release data for the intercalated solids give a straight line or curve as a function of the valence of intercalant species, n, as shown in Fig. 4(B). Each curve and straight line for the solids formed at the low and high uptake stages intercept at $n=+2$ and $n=+1.7$. This indicates that the calixareneoctol molecules in the low- and high-spacing phases are taken up in the divalent and the di- and monovalent mixed forms, respectively. The calixareneoctol content data thus obtained are in Table 2.

Discussion

The Δ value of 10.8 Å observed for the intercalate with **1** agrees with 11.0 Å for the thickness of the cone conformer of **1**, estimated according to its CPK molecular model. The observed values of 9.6 and 8.7 Å for the high- and low-spacing intercalates with **2** formed at the high- and low-uptake stages are also nearly equal to or slightly less than 9.8 Å for the thickness of the cone conformer of **2**. These observations indicate that the calixareneoctol molecules in both systems are arranged as a monolayer with their cone conformation and with their cavity axes perpendicular to the silicate layers in montmorillonite, with or without molecular deformation due to the interlayer compression. A similar monolayered structure was observed on the Cu–montmorillonite/trimethylammoniomethylated calix[4]arenetetrol (**3**) system.[5]

If the maximum diameter of the calixareneoctol molecule is taken as D, the actual area per molecule A_0 is $\pi\times(D/2)^2$ and the effective area per molecule A for hexagonal close packing of callixarene molecules in the monolayer, A is given by $A=2\sqrt{3}\times(D/2)^2$. As the unit cell weight of Cu–montmorillonite is 756 and the surface area of one face of the unit cell is estimated to be 46 $Å^2$, the spatially maximum content of calixareneoctol x can be evaluated from the equation $x=(46/A)/756$. The calculated A and x values for **1** and **2** are listed in Table 3, along with those for **3**. The observed calixareneoctol content of 0.23 mmol g^{-1} for **1** is not only much less than 0.54 mmol g^{-1} expected for the full ion exchange of divalent intercalants with interlayer Cu^{2+} ions but also much less than the spatial limit of 0.36 mmol g^{-1}. The observed content of **1** leads to the arrangement of calixareneoctol molecules with an interlayer porosity of 1 minus $0.23/\{(46/A_0)/756\}$ or 42%, as illustrated in Fig. 5(A). For **2**, the observed calixareneoctol content of 0.45 mmol g^{-1} for the high-spacing phase is comparable to the calculated value of 0.43 mmol g^{-1} for the full-uptake phase, as shown

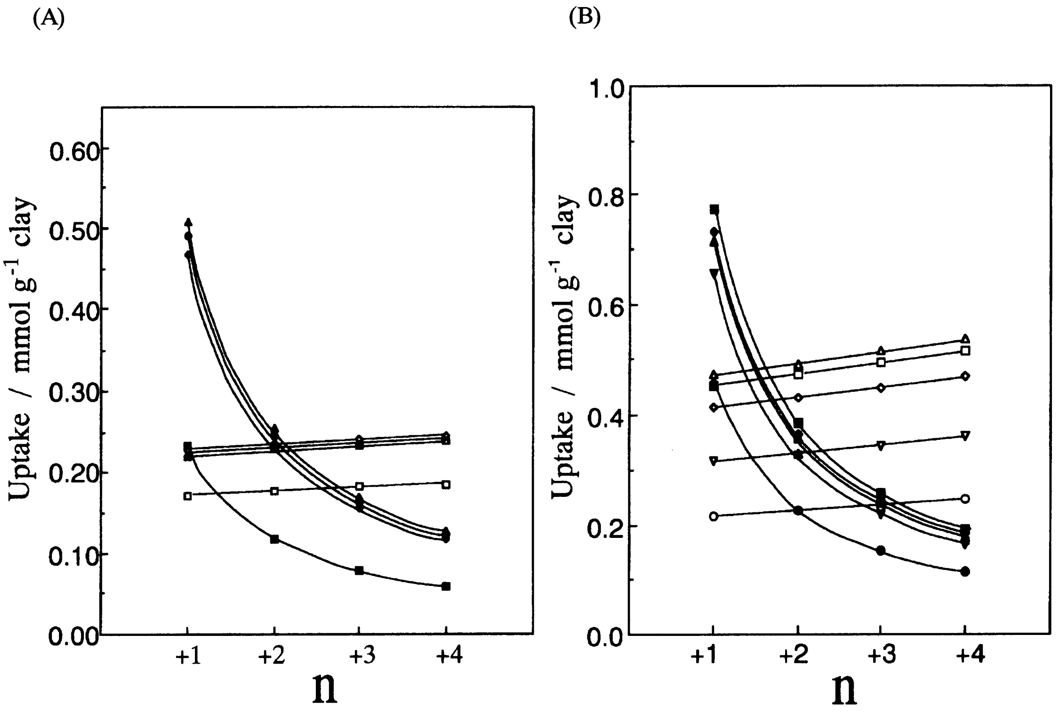


Fig. 4. Calixareneoctol uptake by Cu(II)–montmorillonite as a function of the average valence (n) of the intercalant molecule for **1** (A) and **2** (B). The calixareneoctol uptakes were evaluated from the TG (open symbols) and the Cu^{2+} ion release (closed symbols) data. Calixareneoctol addition levels (mmol g^{-1}): (A) 0.25 (-□-,-■-), 0.5 (-○-, -●-), 0.75 (-△-,-▲-), and 1.0 (-◇-,-◆-); (B) 0.20 (-○-,-●-), 0.25 (-▽-,-▼-), 0.5 (-□-,-■-), 0.75 (-◇-,-◆-), and 1.0 (-△-,-▲-).

Table 2. Characterization of Intercalates of Cu–Montmorillonite with **2** at Various Loadings

Amount of **2** added	Interlayer spaceing	Δ	Amount of **2**	Amount of releasable Cu^{2+}ion/mmol g^{-1} clay					Cu^{2+} ion /**2** ratio
				Initial			Desorbed	Remaining	
mmol g^{-1} clay	Å	Å	mmol g^{-1} clay	Total	Int.	Ext.			
0.20	18.3	8.8	0.23	0.63	0.54	0.09	0.23	0.40	1.9
0.25	18.1	8.6	0.33	0.63	0.54	0.09	0.33	0.30	0.9
0.50	19.0	9.5	0.47	0.63	0.54	0.09	0.39	0.24	0.5
0.75	19.2	9.7	0.43	0.63	0.54	0.09	0.37	0.26	0.6
1.00	19.0	9.5	0.48	0.63	0.54	0.09	0.36	0.27	0.6

Table 3. Comparison of Parameters for Intercalates of Cu–Montmorillonite with **1**, **2**, and **3**

Guest	D / Å	A[a)] / Å	x_{max}[a)] / mmol g^{-1}	Valence[b)] n	x_{obsd}[b)] / mmol g^{-1}	Cu/Guest[b)]
1	14.0	170 (154)	0.36 (0.40)	+2	0.23	1.6
2	12.8	142	0.43	+2 +1.7	0.33 0.45	1.0 0.5
3	16.0	205	0.30	+4 +3	0.13 0.25	2.8 1.1

a) Values in parentheses were calculated on the basis of $A=\pi(D/2)^2$ for the molecular diameter. b) Values for the low- and high-uptake phases are given above and below the line, respectively.

in Fig. 5(B). While the value of 0.33 mmol g^{-1} for the low-spacing phase is much less than the latter value and leads to an interlayer porosity of 1 minus $0.33/\{(46/A_0)/756\}$ or 28%.

The intercalation of **1** occurs in one step by a mode in which the calixareneoctol molecules are taken up in the same divalent form as that in an aqueous solution, without carrying counter anions. Coulomb repulsion

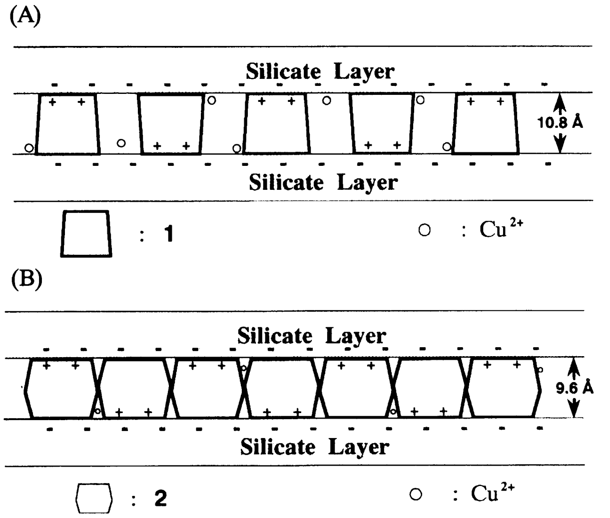


Fig. 5. Schematic representation of the probable arrangement of calixareneoctol molecules and interlayer Cu^{2+} ions (○) in the interlayer space of montmorillonite for the intercalates with **1** (A) and **2** (B) at their full loadings. The charge distribution is also illustrated by symbolsi + (positive) and − (negative).

between the cationic ammonio groups of neighboring intercalated molecules is probably responsible for the loose packing of the intercalated molecules, described above. On the other hand, the intercalation process for **2** consists of two steps, as described above. At the low uptake stage to form a porous low-spacing phase, the calixareneoctol molecules are taken up in the divalent form in which two Cl^- ions per molecule are co-intercalated as a counter anion for the cationic dimetylammonio group. The counter Cl^- anions would be stably held through the hydrogen bonding to the hydroxyl group of the resorcinol ring. In contrast to the **1**-based system, Coulomb repulsion between the co-intercalated chloride anion and the negatively charged silicate layer would also be considerably weakened because they are spatially separated by the bulky dimethylammnoium group. As a result of these effects, further uptake of **2** occurs until the initial porous phase is finally converted into the full-uptake phase.

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