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Aggregation of Organometallic Complex Pillars in Synthetic Fluorhectorite and Montmorillonite

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Abstract: We report the first measurement of the inplane packing of pillars in smectites as a function of relative pillar charge (pillar ion charge/clay surface charge ratio). Sodium montmorillonite and a high-charge synthetic fluorhectorite were pillared with complex ions: Ir(diamsar)$^{3+}$, Hg(diamsarH$_2$)$^{4+}$, and Hg(diamsar)$^{2+}$ (diamsar denotes 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) resulting in well-oriented samples. Six orders of the *c*-axis X-ray diffraction were resolved as well as peaks corresponding to the lateral free distance between cations (in transmission mode). The peaks in plane have Warren line shapes, on analysis of which give the true interpillar distances. These are in a range 12.7-15 Å for pillared montmorillonite and 9.5-10.8 Å for pillared fluorhectorite. (Aggregate lengths vary between 19.7 and 62.3 Å for the systems measured.) The best three-dimensional order was achieved in cases where the distances determined by charge neutralization are near to the in-plane clay lattice parameters.

Clay minerals, pillared with polyhydroxy aluminum cations, have recently been shown[1] to be effective petroleum-cracking catalysts, and in such action the free lateral surface and pore size are important factors. For characterizing these quantities the average interpillar distance is calculated from the stoichiometry assuming a regular distribution of interlayer cations (e.g., Barrer[2]). Support for such regular packing comes from, e.g., Van Damme and Fripiat[3] who applied the concept of surface fractal dimension to pillared clays and found that the gas sorption data are consistent with a homogeneous distribution of pillars on the surface. However, analogy with the gallery structures formed by alkali metal intercalation into graphite where rather more is known structurally[4] suggests the possibility of more complex two-dimensional behavior. For graphites the first stage compounds are three dimensionally ordered at normal temperatures; the second and third stage materials (with *c*-axis distances between ionic layers more like the *c*-axis distances in clays) have an incommensurate two-dimensional liquid like cationic distribution at normal temperatures which breaks up into ordered commensurate domains at liquid nitrogen temperatures.[5]

By choosing pillaring cations with different charges and clay minerals of different exchange capacity we are, in principle, able to explore the two- and three-dimensional forces leading to pillar packing. In the present experiments the primary aim was to detect directly the lateral distribution of the pillars on smectite surfaces by using organic cations containing heavy metals. The smectites chosen were pillared by different cage compounds,[6] the structures of which are shown in Figure 1.

These compounds have a number of characteristics which make them useful as pillars. They are stable and rigid, and the charge is well defined at fixed pH in solution. The presence of two amino groups should raise the strength of adsorption on the clay surface, and the high atomic number of the central metal atom enhances the X-ray scattering of the pillars relative to the clay substrate.

The fluorhectorites have large platelet sizes (typically > 10000 Å), and so relatively well-oriented samples can be prepared by air drying. Well-oriented samples can also be prepared from montmorillonite under conditions of very slow drying. The high level of orientation and the high atomic number of iridium and mercury allow determination of the interpillar distances from the diffraction patterns in the transmission mode where the scattering vector is essentially in the plane of the clay sheet.

Experimental Section

The (Hg-diamsar)-montmorillonite, (Ir-diamsar)-fluorhectorite, and (Hg-diamsar)-fluorhectorite were prepared from sodium montmorillonite by the procedure of Callagan et al.[7] from Wy (Osage), bentonite (Wards Natural Science Establishment Inc. Rochester, NY) as starting material, and synthetic fluorhectorite (from Prof. T. J. Pinnavaia, Michigan State University). Deionized glass-distilled water was used in all experiments.

The cation exchange capacity (CEC) of the clays was determined initially by two methods. The first method as described by Callaghan et al.[7] for the preparation of homoionic clays consists of displacing exchangeable cations with ammonium acetate, followed by thorough washing with water. The amount of adsorbed nitrogen was determined in oven-dried (100 °C) samples by microanalysis. According to the alternative method developed by Rich[8] calcium-substituted clays were prepared and washed first with water and then several times with ethanol. The amount of Ca^{2+} was determined by flame ionization analysis of the solutions obtained by Ca^{2+} extraction to 1 N solution of magnesium acetate at pH 7 from these Ca-saturated samples.

For montmorillonite the CEC per 100 g of clay found by these two methods was 80 and 118 mequiv (giving a charge per unit cell of 0.60 and 0.88, respectively). The cation exchange capacity measured by two methods for the synthetic fluorhectorite was 130 mequiv per 100 g and 210 mequiv per 100 g, respectively. The impurity content (mainly lithium metasilicate (Li$_2$SiO$_3$) and α-quartz) was estimated through observations with TEM and X-ray at about 13%. Thus for this clay the corrected CEC by the two methods is 150 mequiv per 100 g and 240 mequiv per 100 g (the charge per unit cell determined by the two methods is 1.1 and 1.8, respectively). In a third method—appropriate to our experiment, we assumed complete neutralization of the clay surface by [Hg(diamsarH$_2$)]$^{4+}$ ions and measured the pillar concentration in (Hg-diamsar)-fluorhectorite I and (Hg-diamsar)-montmorillonite I. The montmorillonite unit cell charge was found equal to 0.74, and the fluorhectorite unit cell charge was equal to 1.36. These values are close to the mean of the above experiments. We conclude that the washing procedures of the classical methods may lead to rather different results.

Preparation of Pillared Smectite. A 0.2% suspension of smectite was dripped slowly into a solution of pillaring agent under conditions of vigorous stirring, and stirring continued for 2 more h. Then the suspension was centrifuged, and the pillared clay was washed 4 times with water and air dried. The amount of cage molecule in solution usually exceeded the amount of the molecules which could be adsorbed on the surface under condition of chosen pH by a factor of four.

For preparation of (Ir-diamsar)-fluorhectorite a 15-mL portion of fluorhectorite suspension and 20 mL of a 4.1 mM solution of Ir(diamsarH$_2$)Cl$_5$ in water at pH 4.2 were taken. At this pH which is above pK_a the NH$_2$ groups should be unprotonated. Measurement of the pillar concentration on the surface (Table I) gives an average charge on the

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Table I. Interpillar Distances (*d*) and Coherent Lengths of Pillar Domains (L) Calculated by Line Shape Analysis

			2θ (deg)		*d* (Å)			L (Å)	
	p (Mpillar/Mclay)	$2\theta_{max}$ (deg)	1[a]	2[b]	1[a]	2[b]	av	1[a]	2[b]
Hg(diamsar)-montmorillonite I	0.186	7.2		5.88		15.0			19.7
Hg(diamsar)-montmorillonite II	0.225	8.00	6.88	7.01	12.8	12.6	12.7	24.1	27.6
Hg(diamsar)-fluorhectorite I	0.341	8.60		8.17		10.8			62.3
Hg(diamsar)-fluorhectorite II	0.392	8.79		8.20		10.77			45.7
Ir(diamsar)-fluorhectorite	0.417	9.42		8.83		10.01			45.4
Hg(diamsar)-fluorhectorite III	0.447	9.93		9.32		9.48			44.0

[a] Values obtained from the fitting of the large angles part of the peak. [b] Values obtained from the fitting of the whole peak.

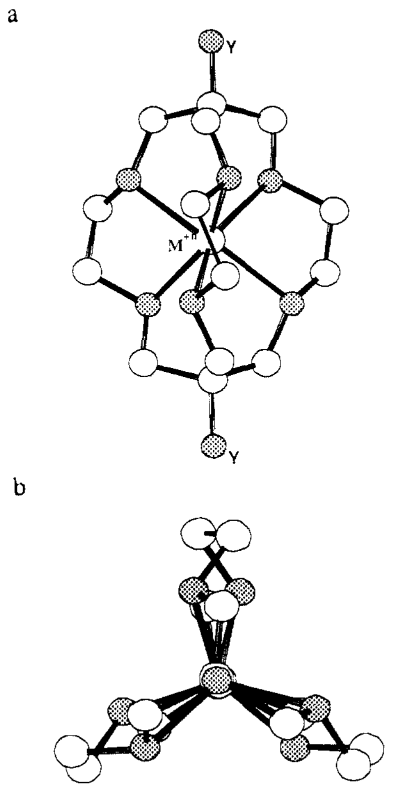

Figure 1. The structure of cage pillar, where M^{n+} is Ir^{3+}, Hg^{2+} and Y = NH_2, NH_3^+: (a) view perpendicular to Y-Y axis and (b) view along Y-Y axis. Shaded circles represent NH groups, and empty circles carbon atoms (C or CH_2, hydrogen atoms are omitted).

pillars +3.3. Thus not less than 70% of pillars are in the unprotonated form. The pillaring agent was in excess: 2.7 mmol per gram of clay.

Preparation of (Hg-diamsar)-fluorhectorite II and III was performed from 250 mL of fluorhectorite suspension and 300 mL of 5.3 mM [Hg-(diamsarH_2)]$(NO_3)_4$×$2H_2O$ in water at pH 6.0 and 8, respectively. Given that pK_{a1} = 5.44 and pK_{a2} = 6.32 these conditions should protonate one NH_2 group in case of (Hg-diamsar)-fluorhectorite II and no NH_2 groups in case of (Hg-diamsar)-fluorhectorite III. The microanalysis shows, however, an ion concentration consistent with more fully protonated pillars than expected present on the surface (average pillar charge +3.5 in case of (Hg-diamsar)-fluorhectorite II and +3.0 in case of (Hg-diamsar)-fluorhectorite III). An excess of pillaring agent was used: about 3.2 mmol per gram of clay.

(Hg-diamsar)-fluorhectorite I was prepared from a 250-mL portion of fluorhectorite suspension and 200 mL of 4 mM solution of [Hg-(diamsarH_2)]$(NO_3)_4$×$2H_2O$ in water at pH 3.5. At this pH the pillars are fully protonated in solution, and this form was assumed for their state on the surface. The pillaring agent was in excess: about 1.6 mmol per gram of clay.

(Hg-diamsar)-montmorillonite II was prepared from 250 mL of fluorhectorite suspension, and 250 mL of 3.6 mM solution of [Hg-(diamsarH_2)]$(NO_3)_4$×$2H_2O$ in water at pH 6.0 corresponds (as above) to ions with one protonated NH_2 group. The microanalysis showed, once again, an ion concentration consistent with a large amount of fully protonated pillars being present on the surface (average pillar charge +3.3). The pillaring agent was in excess: about 1.8 mmol of complex per gram of clay.

For preparation of (Hg-diamsar)-montmorillonite I were used 250 mL of fluorhectorite suspension and 200 mL of 2.3 mM solution of [Hg-(diamsarH_2)]$(NO_3)_4$×$2H_2O$ in water at pH 3.5. This pH gives the fully protonated form, and this we assumed to be present on the clay surface. The pillaring agent was used in excess: about 0.9 mmol per gram of clay.

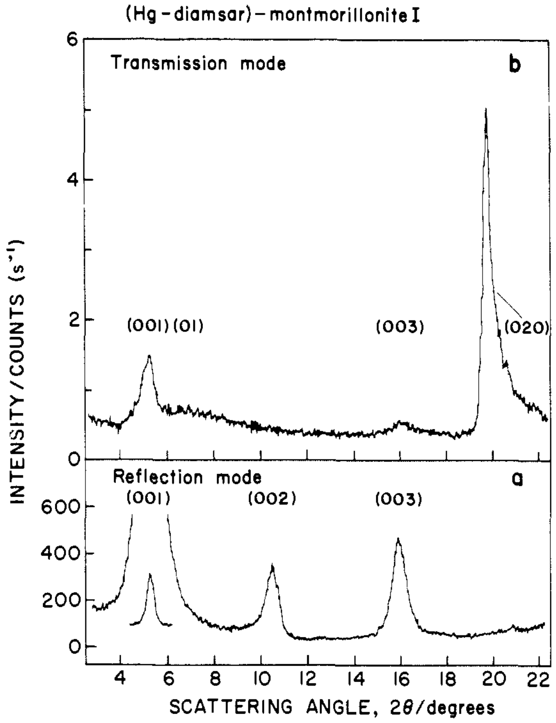

Figure 2. X-ray powder diffraction patterns of (Hg-diamsar)-montmorillonite I (a) in reflection mode and (b) on transmission mode: Cu Kα radiation. The intensity of small (001) peak in reflection mode is 20 times decreased.

Chemical Analyses. All samples were analyzed after air drying and after oven drying (100 °C, 24 h). The pillar concentrations were determined by C, N, H analyses of oven-dried samples. The automatic analyzer used was a Carlo Erba 1106: sample combustion was followed by gas chromatographic separation of the resultant gases, and a thermal conductivity detector gave the C, H, N determination. Metals were determined by flame atomic absorption spectroscopy of solutions obtained by dissolving the sample in concentrated nitric acid.

Instruments. An X-ray powder diffractometer Siemens D501-K710 with a Cu target was used in both transmission (scattering vector in the layer plane) and reflection (scattering vector perpendicular to the layer plane) mode. Samples were thin films of the clays produced by evaporation—freely mounted in the X-ray beam. Line shape analysis was performed from the shape of reflections described by Warren[9] by using a VAX 11-750 computer.

Results and Discussion

(Ir-diamsar)-fluorhectorite, (Hg-diamsar)-montmorillonite I and -II, and (Hg-diamsar)-fluorhectorite I-III were prepared under conditions of different pH and initial ion concentrations. In all cases where the ion was not fully protonated in solution we noted extra protonation upon sorption. This effect has been reported before.[10] The charge of the pillar ions varies from +3

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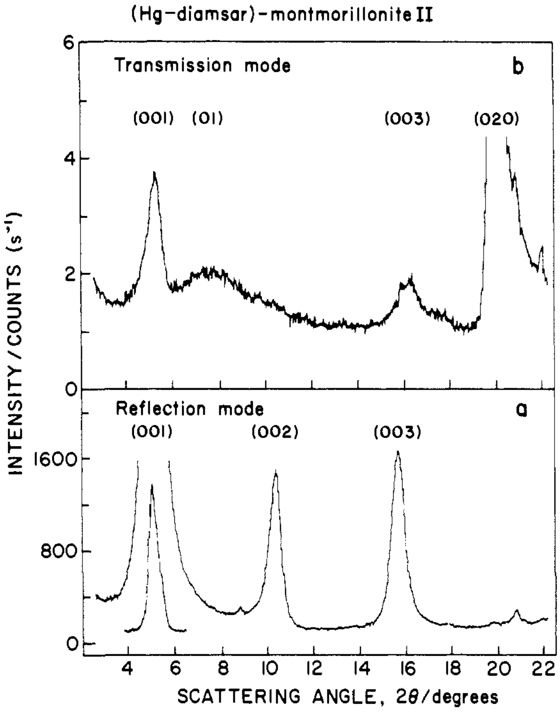

Figure 3. X-ray powder diffraction patterns of (Hg-diamsar)-montmorillonite II (a) in reflection mode and (b) on transmission mode: Cu Kα radiation. The intensity of small (001) peak in reflection mode is 20 times decreased.

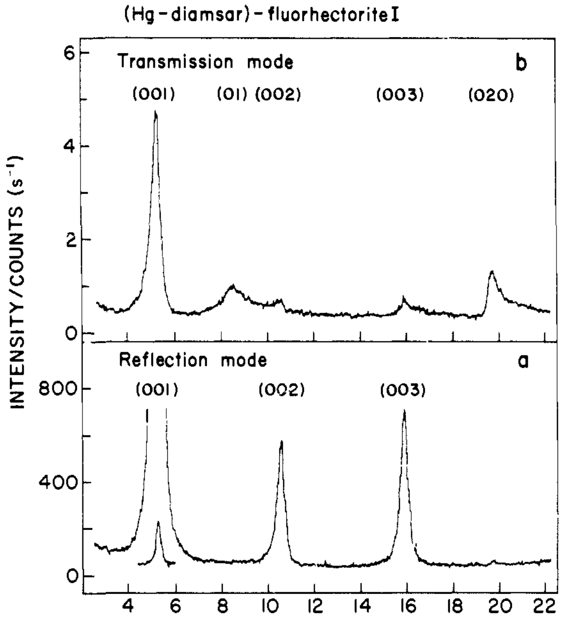

Figure 4. X-ray powder diffraction patterns of (Hg-diamsar)-fluorhectorite I (a) in reflection mode and (b) on transmission mode: Cu Kα radiation. The intensity of small (001) peak in reflection mode is 20 times decreased.

for (Hg-diamsar)-fluorhectorite III with one unprotonated amino group to +4 for $(\text{Hg-diamsarH}_2)^{4+}$-fluorhectorite I and $(\text{Hg-diamsarH}_2)^{4+}$-montmorillonite I where all amino groups are protonated. Figures 2-7a represent diffraction patterns of these compounds. Six orders of the *c*-axis were resolved in reflection mode for all samples that have been checked (namely (Ir-diamsar)-fluorhectorite and (Hg-diamsar)-montmorillonite II). The increased *c*-axis spacings of these compounds show the penetration of cage molecules into interlayer space. The values are 16.4 Å for $(\text{Ir-diamsar})^{3+}$-fluorhectorites and (Hg-diamsarH_2)-fluorhectorite III and 16.8 Å for other clays pillared with mercury-containing ions.

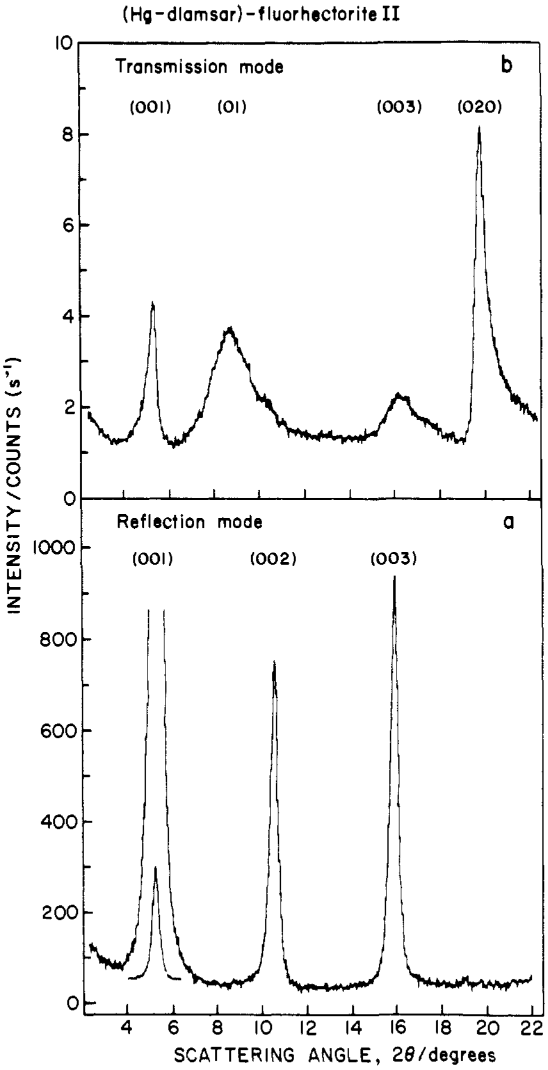

Figure 5. X-ray powder diffraction patterns of (Hg-diamsar)-fluorhectorite II (a) in reflection mode and (b) on transmission mode: Cu Kα radiation. The intensity of small (001) peak in reflection mode is 20 times decreased.

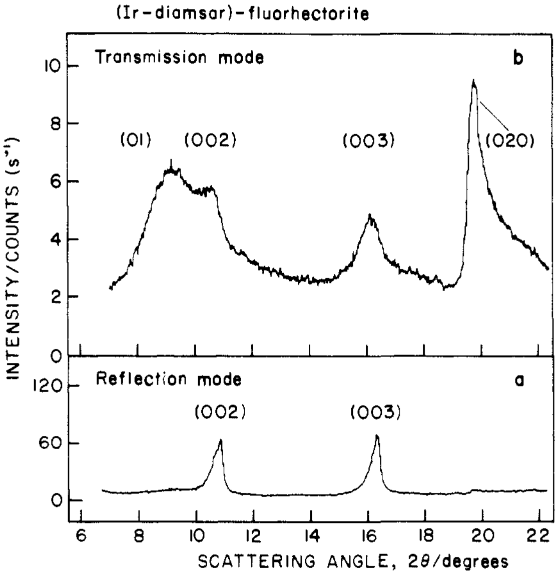

Figure 6. X-ray powder diffraction patterns of (Ir-diamsar)-fluorhectorite (a) in reflection mode and (b) on transmission mode: Cu Kα radiation.

The diffraction patterns in the transmission mode showed the (001) peaks greatly reduced in intensity and also new broad peaks,

Table II. Calculated and Observed Interpillar Distances (Å)

	calculated from microanalysis				experimental (X-ray data)			
	p (Mpillar/Mclay)	S_{av} A/p (Å^2)	$S^{1/2}$ (Å)	d_{hex},[a] (Å)	d_{exp} (Å)	d,[b] (Å^2)	S_{hex},[b] (Å^2)	a[c] (Å)
(Hg-diamsar)–montmorillonite I	0.186	250	15.8	14.7	15.0	225	260	17.3
(Hg-diamsar)–montmorillonite II	0.225	207	14.4	13.4	12.7	172	199	14.7
(Hg-diamsar)–fluorhectorite I	0.341	141	11.9	11.0	10.8	117	135	12.47
(Hg-diamsar)–fluorhectorite II	0.392	122	11.1	10.3	10.77	116	134	12.44
(Ir-diamsar)–fluorhectorite	0.417	115	10.7	10.0	10.0	100	115	11.55
(Hg-diamsar)–fluorhectorite III	0.447	107	10.4	9.6	9.48	90	104	10.95

[a] $d = 0.93(S)^{1/2}$. [b] $S = 2(3)^{1/2}\cdot a^2 = (2/(3)^{1/2})\cdot d^2 = 1.155\ d^2$. [c] $a = 1.155\ d$.

not observed in the reflection mode (see Figures 2–7). These peaks correspond to diffraction from the lateral ordering of the pillars. The peaks are broad, especially for montmorillonite-containing samples, where the concentration of the pillars is at least 50% lower. Diffraction patterns of fluorhectorite samples have well-defined shape, which is well represented by Warren's formula[9] for diffraction by two-dimensional lattices (eq 1). Least-squares fitting to the data gives the real $2\theta_0$ corresponding to the distances "d" of the pillar lattice (see Table I) and the coherence length "L" corresponding to the coherence length of the two-dimensional diffracting particle. The pattern of (Hg-diamsar)–montmorillonite II was fitted in the range 6° < 2Θ < 12° and 7° < 2Θ < 12° to avoid interference from the 001 peak.

The intensity of X-ray diffraction by a two-dimensional layer lattice is given by

$$P = KmF^2\{(1 + \cos^2 2\theta)/(2 \sin^{3/2} \theta)\}\{L/(\pi^{1/2}\lambda)\}^{1/2}F(a) \qquad (1)$$

where K = constant, m = two-dimensional multiplicity, F = the structure factor, θ = scanning Bragg angle (e.g., half the diffraction angle 2θ), and $2\theta_0$ = diffraction angle corresponding to the minimum distance.

$$F(a) = \int \exp[-(x^2 - a)^2]\ dx, \text{ for } a < 6.2$$

$$\text{and } F(a) = (\pi/4a)^{1/2} \text{ for } a \geq 6.2 \qquad (2)$$

where

$$a = (2L(\pi)^{1/2}/\lambda)(\sin \theta - \sin \theta_0)$$

In our calculations we assumed that $c = KmF^2$ is a constant, apart from an atomic scaling factor, because all pillars have the same shape. The distances observed are not commensurate with either fluorhectorite or montmorillonite basal plane spacings. The dimensions of the fluorhectorite unit cell measured in the present work for the unpillared clay are a = 5.29 Å and b = 9.07 Å, quite similar to those reported by Barrer et al.[11] a = 5.16 Å, b = 9.08 Å. For montmorillonite, the unit cell has a = 5.18 Å and b = 9.00 Å.[12] The dependence of d on pillar concentration measured by microanalysis (Figure 8) indicates the formation of a two-dimensional pillar lattice on the smectite surface whose characteristic scale is a function of a pillar charge.

All our experiments are carried out in the regime of excess of pillaring agent and dilute clay suspension where clay layers are totally delaminated, i.e., total electroneutrality of clay surface was obtained by its neutralization with pillaring ions. Let S be a total area of the clay sample and m—the number of adsorbed pillars. Total charge on S will be $Q^- = (S/A)\cdot q^-$, where A is a unit cell area and q^- is the charge per unit cell. Thus one needs $m = Q^-/q^+$ pillars to neutralize the surface, where q^+ is a charge of one pillar. In this case the average electrostatic area occupied by one pillar molecule is

$$S_{av} = S/m = (Q^-\cdot A\cdot q^+)/(q^-\cdot Q^-) = (A\cdot q^+)/q^- \qquad (3)$$

The characteristic interpillar distance is proportional to $(S)^{1/2}$ depending on the geometry of the packing (Table II).

For a hexagonal lattice with side = a the area occupied by one pillar molecule is $(3)^{1/2}a^2/2$. The observed distance between

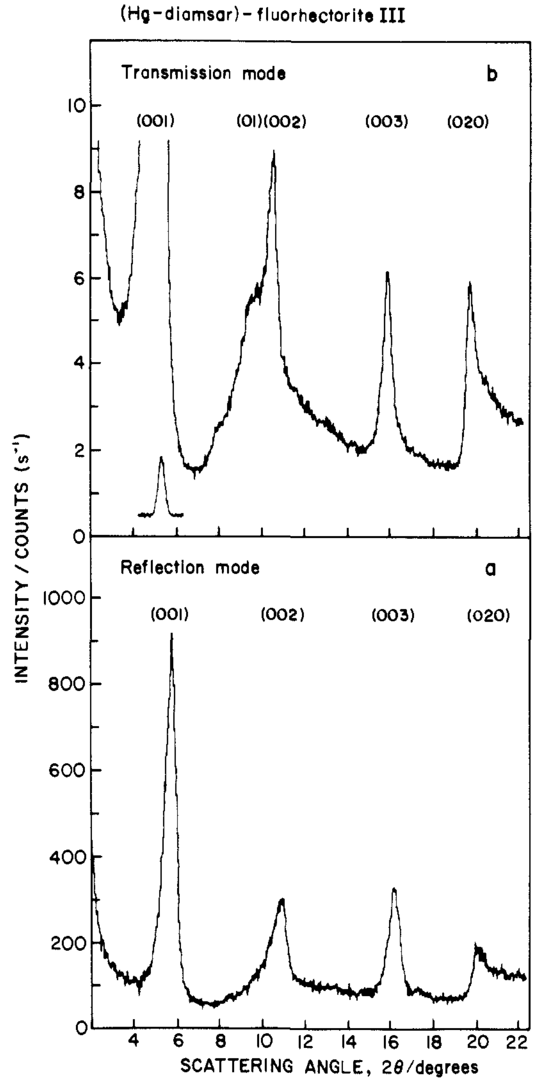

Figure 7. X-ray powder diffraction patterns of (Hg-diamsar)–fluorhectorite III (a) in reflection mode and (b) on transmission mode: Cu Kα radiation. The intensity of small (001) peak in reflection mode is 20 times decreased.

molecules $d = (3)^{1/2}a/2$ and area per one molecule $S_{eff} = 2/(3)^{1/2}d^2$ or

$$A\cdot q^+/q^- = (2/(3)^{1/2})d^2$$

$$d^{-1} = (2/(3)^{1/2}A)^{1/2}\cdot(q^-/q^+)^{1/2} \text{ or}$$

$$d^{-1} = \text{const}\cdot p^{1/2}$$

where const = 0.155, when A = 48 Å^2 and const = 0.157, when A = 46.6 Å^2, p is a pillar concentration given in Mol pillar per Mol clay units. Experimentally (Figure 8) we found by least-squares fitting to the data that the constant is equal to 0.156. This supports the above proposal of pillars packing into an incommensurate hexagonal lattice, the lattice parameter being determined by the criterion of charge neutrality.

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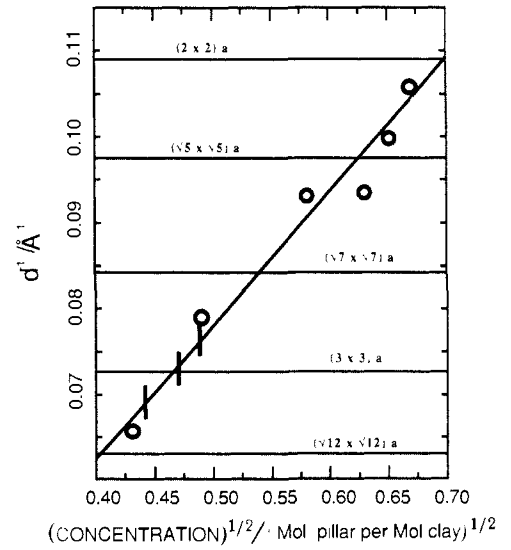

Figure 8. Dependence of $1/d$ on $(p)^{1/2}$, where p is pillar concentration given in Mol pillar per Mol clay and d is the experimental distance between pillars centers.

In the above no assumptions about pillar or clay charges have been made—only the X-ray and microanalysis results have been used. The slope of the line in Figure 8, however, does allow some further conclusion about relative charge on clay and pillar to be drawn following eq 3. Taking the determined values of the CEC's of the clays (which correspond with the usual values for these materials) we can say that the pillar charges are much higher than the ionic charges in solutions at the preparative pH. Thus acidity of the clay surface probably influence more protonation—as have been found elsewhere.[10]

In Figure 8 we show lines corresponding approximately to possible commensurate lattices on the clay surface. The fluorhectorites fall close to the $(5)^{1/2}\cdot(5)^{1/2}$ structure and the (Hg-diamsar)-fluorhectorite III close to the (2 × 2) structure. It may be that this correlates with the more perfect two-dimensional lattices (narrower Bragg peaks) in this case. The present work thus points to a general conclusion that the most rigid and stable pillared clay systems could be obtained when interpillar distances—determined primarily by charge balance—are equal very precisely to the clay basal plane lattice parameters. Conversely for regions of a clay particle surface where this obtains the most stable pillaring will result. Support for this statement comes from recent work of Pinnavaia et al.[13] For one out of the three Al-pillared clays described the interpillar distance calculated from Al concentration (Al_{13}^{7+} pillar) was equal to the clay lattice parameter. These pillared clays gave the biggest surface area and the best stacking order.

Acknowledgment. We thank C. Foudoulis for running X-ray powder diffraction spectra and Dr. I. Creaser for supplying us with the diamsar cage compounds. We also thank Prof. T. Pinnavaia (Michigan State University) for the fluorhectorite sample.

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Metal Ion Lability Constant Derived from a Linear Free Energy Relationship between Ligand-Substitution Rates of Tris(acetylacetonato) and Aqua Complexes of Various Tervalent Metal Ions

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Abstract: A linear relationship is found between the first-order rate constants of the ligand exchange of tris(acetylacetonato) complexes of tervalent metal ions $[M^{III}(acac)_3]$ (M = Sc, V, Cr, Mo, Mn, Fe, Ru, Co, Rh, Al, Ga, and In) in acetylacetone and/or acetonitrile and those of substitution reactions of their aqua complexes in water. The slope is very close to unity over the range of 10^{14}. The former is shifted invariably by about $10^{-4.5}$ to the latter. The finding shows that the nature of central metal ions dominates the lability of complexes over the great differences in ligands and reactive environment around the ions. A metal ion lability constant σ is proposed and evaluated for each M^{III} as a measure of the lability of octahedral M^{III} complexes.

Taube[1] first classified metal complexes by the central metal ion into substitution labile and inert on the basis of the observations on the rate of their ligand-substitution processes. He pointed out that complexes of metal ions with d^3 and low-spin configurations of d electrons are inert. A large amount of kinetic results accumulated since then clarified that other natures of metal ions such as charge and ionic radii as well as the electronic and structural character of ligands also have a considerable effect on the rate.[2] Replacement of chelate ligands is understood to proceed considerably slower than that of unidentates in complexes of a given metal ion.[2b] For evaluation of the kinetic nature of metal ions separately, it is essential to compare more than one series of rates for complexes of various metal ions with common ligands of different character.

We have chosen the acetylacetonate ion ($acac^-$) as the common chelating ligand, because it gives octahedral tris(bidentate)-type complexes $[M(acac)_3]$ with a variety of tervalent metal ions.

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