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THE CRYSTAL STRUCTURE OF A CLAY-ORGANIC COMPLEX OF 6-AMINO HEXANOIC ACID AND VERMICULITE

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ABSTRACT

The crystal structure of a 6-amino hexanoic acid-vermiculite complex has been determined using X-ray single crystal diffraction method.

The complex has a long spacing of 17.32 ± 0.04 Å and the monoclinic unit cell $a = 5.33 \pm 0.01$, $b = 9.18 \pm 0.02$, $c = 17.45 \pm 0.04$ Å, $\beta = 97°$, $Z = 2$. The probable space group is $C2$.

Electron density projections on (100) and (010) planes show that the organic molecules form two layers with long chains parallel to the b-axis. The plane of the zig-zag hydrocarbon chain is tilted at 50° from the (001) plane. Therefore the complex belongs to the α-configuration. Disorder and hydrogen bonding are discussed.

INTRODUCTION

The study of the crystal structure of clay organic complexes is limited by the difficulty in obtaining well-grown single crystals. Nevertheless, valuable information can be obtained with the use of oriented powder samples and the approximate orientation of the organic molecules between the silicate layers of micaceous type minerals can be established. From the one-dimensional electron density projections along the c axis and the Δ-value, the "clearance space" which is more or less equivalent to the space available for the absorbed molecules between the inorganic sheets, it was deduced that the orientation of the organic molecules can be placed in α- or β-categories corresponding respectively to the plane or chain of the organic molecule lying parallel or perpendicular to the silicate surface (MacEwan, 1948).

The single crystal determination of the structure of a silicate-organic complex, actually of vermiculite, by Haase, Weiss and Steinfink (1963) showed that the organic molecular chain was inclined to the clay surface at an angle of 32°, and the organic molecules were randomly distributed over the available crystallographic sites.

Weiss (1963) also found that alkylammonium ions took up both α- and β-configurations, depending on the degree of swelling with alkylamine. Brindley and Ray (1964) reported that the orientations of normal alcohol molecules depend on the chain length of the molecules and on the

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equilibration temperature. Brindley and Moll (1965) studied also complexes with carboxylic acids.

These results indicate that the investigation of clay organic complexes is very complex and that structure analyses using single crystals should be undertaken to study the bonding between the organic molecules and inorganic silicate surface.

Protein- or amino acid-clay complexes are very interesting problems from the viewpoint of the original synthesis of proteins and life from amino acids on the templates provided by the presence of clay particles in the primeval oceans. Talibudeen (1955) prepared amino acid- and protein-montmorillonite complexes, and decided the orientation of the –COOH group and the peptide radical.

In the present study a single crystal of the 6-amino hexanoic acid vermiculite was prepared and the configuration of the 6-amino hexanoic acid molecules in the interlayer region was elucidated.

EXPERIMENTAL

The starting material selected for this investigation was a vermiculite from Kenya obtained through the courtesy of Dr. V. C. Farmer. The approximate chemical composition under normal conditions was: $(Mg_{2.36}Fe_{0.48}Al_{0.16})(Al_{1.28}Si_{2.72})O_{10}(OH)_2Mg_{0.32}\cdot xH_2O$.

The large flake was cut into small fragments, about 0.3 mm×0.1 mm, and then reacted with 1 N-NaCl solution at room temperature for 2–3 weeks, replacing interlayer Mg^{2+} ions by Na^+ ions. Na-saturated vermiculite with $d_{(001)}=14.7$ Å was put into 1 N 6-amino hexanoic acid solution of pH=5.5 controlled with dilute sulfonic acid. Talibudeen (1955) found that amino acid and clay mineral interaction increases in extent, rapidity and stability as the pH of the equilibrium system is shifted from the isoelectric point of the amino acid towards more acidic values. In this case, pH=5.5 was enough for promoting the reaction and stabilizing the product. Replacement reaction was started at room temperature and proceeded until the X-ray diffraction pattern did not change (about 2 or 3 weeks). The single crystal X-ray photograph showed that this crystal was not a single phase, but a mixture of a long spacing phase ($d_{(001)}=17.32$ Å) and $d_{(001)}=14.2$ Å phase. The latter phase disappeared when treated with the same solution at 50°C for more than one week. The sample as grown at 50°C has a longer spacing ($d_{(001)}=21$ Å) than 17.32 Å. This phase was very unstable in air and changed rapidly to the stable $d_{(001)}=17.32$ Å phase during measurement of the X-ray diffraction pattern. This stable form in air was obtained also from Ba-saturated vermiculite by the same treatment.

The small planar crystal of 6-amino hexanoic acid vermiculite with $d_{(001)}=17.32$ Å, $0.3\times0.1\times0.02\sim0.03$ mm, was mounted on a goniometer head. Oscillation and Weissenberg photographs about a and b axes were taken using filtered Cu-Kα radiation. The dimensions of the monoclinic unit cell were determined to be: $a=5.33\pm0.01$ Å, $b=9.18\pm0.02$ Å, $c=17.45\pm0.04$ Å, $\beta=97°$, ($\lambda=1.5418$ Å), with $Z=2$. The space group corresponding to systematic absences (hkl: $h+k=2n+1$) are $C2$, Cm, and $C2/m$, the $C2$ space group being the most probable as the calculations using this space group give good agreement with observations. Since the crystals used had a platy habit and the linear absorption coefficient was not small, $\mu=100$, the intensity data were corrected using a method for estimating trasmission factors in a crystal of uniform cross section (Joel, Vera, and Garaycochea,

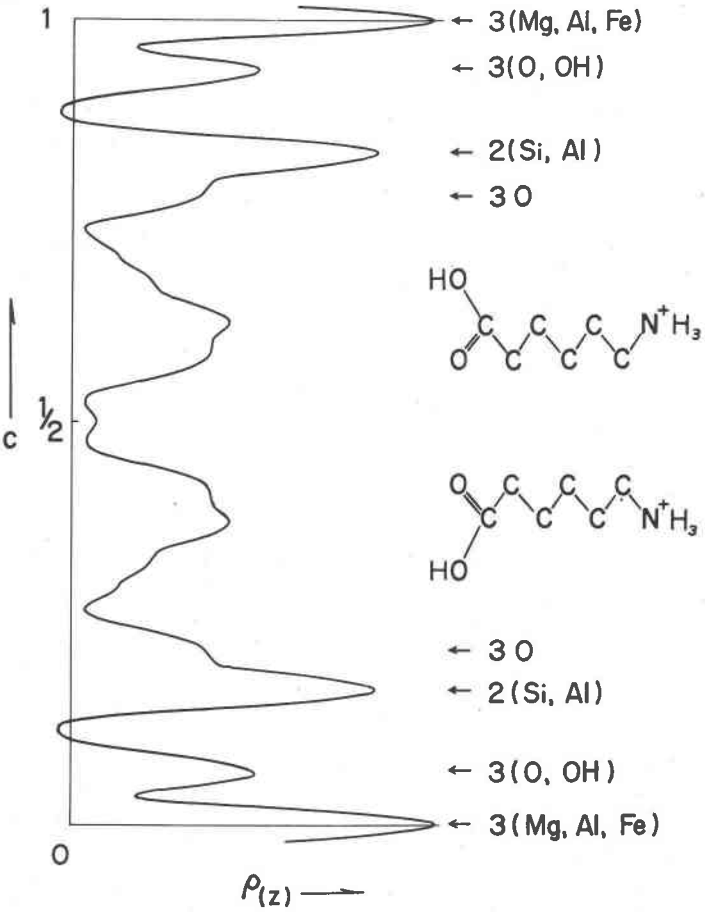

FIG. 1. One-dimensional electron density map.

1953). The ratio of the maximum value and the minimum value of the transmission factors was 1.7.

DETERMINATION OF THE CRYSTAL STRUCTURE

1) *One-dimensional electron density projection.* The signs of the (00l) structure factors were computed from considering the whole contribution of the known silicate layer (Mathieson and Walker, 1954). The electron density distribution is shown in Figure 1. There are two low and four high peaks in the interlayer region between adjacent silicate layers. Since there are no high peaks around the middle of the interlayer $z=0.5$, the stair type configuration of 6-amino hexanoic acid cannot be fitted and

an α-configuration as shown in Figure 1 gives a reasonable model. Our result supports the well-known opinion that the c-spacing of the organo-clay complexes with a two-layer configuration of α-type are in the vicinity of 17 Å (*e.g.* Brindley and Ray (1964), Jordan, Hook and Finlayson (1950)).

2) *Two-dimensional analyses.* The signs of $h0l$ and $0kl$ structure factors were calculated by considering the "heavy atom" contribution from the silicate layer. Initial electron density projections on (010) and (100) planes again show that the 6-amino hexanoic acid molecules take an α-configuration, with zig-zag chain almost parallel to the b axis, and two layers of organic molecules in each interlayer. The (100) projection gives a rather complicated pattern which indicates stacking faults along c as described later. By considering the molecular structure of 6-amino hexanoic acid in α-configuration, all light atoms C, N, and O in–COOH were allotted to the peaks of each electron density map without difficulty.

Since the crystals were not good, the refinement of the atomic parameters proceeded using both the least squares method and "trial and error." The idealized y parameters, *e.g.* $y=0$, and $\frac{1}{3}$ for Si and Al atoms, were kept constant throughout the refinement process.

As described above, the $0kl$ reflections are very diffused with the exception of $06l$ reflections. Also, good agreement between F_o and F_c was obtained for the $k=3n$ reflections, but lack of agreement existed between F_o and F_c for the $k\neq 3n$ reflections. It is well known that the relative shifts of silicate layers by $\pm b/3$ along the b axis cause many different polytypes of clay minerals according to the ordering and probability of faults. The $0kl$ intensity data in this case seem to indicate some stacking faults connected with such shifts. If allowance was made for the stacking fault based on the $\pm b/3$ translation probability of $\frac{1}{6}$ and on the random distribution of it, the structure factors for $0kl$ were expressed as follows

$$A = 4\sum_i f_i \cos 2\pi l z_i \left\{\frac{2}{3}\cos 2\pi k y_i + \frac{1}{6}\cos 2\pi k\left(y_i + \frac{1}{3}\right) + \frac{1}{6}\cos 2\pi k\left(y_i - \frac{1}{3}\right)\right\}$$

$$B = 4\sum_i f_i \cos 2\pi l z_i \left\{\frac{2}{3}\sin 2\pi k y_i + \frac{1}{6}\sin 2\pi k\left(y_i + \frac{1}{3}\right) + \frac{1}{6}\sin 2\pi k\left(y_i - \frac{1}{3}\right)\right\}$$

$$F^2_{(0kl)} = A^2 + B^2$$

and the R-factor for $0kl$ was reduced by almost 17 percent. On the other hand, such stacking faults did not have any influence on the intensities of $h0l$ reflections. The R-factors for the $h0l$ and the $0kl$ reflections are 0.22. When the $0kl$ reflections $k=3n$ are omitted, $R_{0(kl)}=0.18$. The R values, although rather large, are about the best one can expect for work on this kind of substance. The isotropic temperature factor for atoms of the silicate layer is 3.5 and 5.0 Å^2 for carbon, oxygen and nitrogen atoms of the organic molecule. The latter are rather large, indicating that there may be a contribution not only from temperature motion, but also from disorder.

The chemical data and the principle of neutralization indicate that 6-amino hexanoic acid absorbed in the interlayer is present in about 1.2 mole per unit cell. But the space group, $C2$, demands four equivalent lattice sites per unit cell. It is therefore clear that the 6-amino hexanoic acid molecules are distributed statistically over four equivalent positions with a probability of 0.32 per lattice site. Furthermore, the contribution of 6-amino hexanoic acid to the structure factor is small. So it is not easy to determine the precise atomic parameters of carbon, nitrogen and oxygen of the carbonyl radical, but the final electron density maps shown in Figures 2, 3 suffice in deciding the orientation of 6-amino hexanoic acid and in assigning each atom of the organic molecule to the peaks of the electron density maps.

The atoms in the inorganic layer are well separated in the (010) projection, but the (100) projection shows extra peaks denoted by + in Figure 3 in addition to the main peaks corresponding to the ideal structure. The former peaks are related respectively to the latter peaks by the translation of $\pm b/3$ along b axis as described above.

Atomic parameters and significant interatomic distances are given in Table 1 and Table 2 respectively. Observed and calculated structure amplitudes are listed in Table 3.

DISCUSSION

One of the interesting problems in the organic clay complexes is the elucidation of the orientation of the organic molecules absorbed between the silicate layers and the interpretation of the driving forces which would account for their orientation. Haase *et al.* (1963) analyzed the crystal structure of a single crystal of hexamethylene diamine vermiculite complex and concluded that the organic chain is inclined to the silicate surface at an angle of 32°. However, the present result for 6-amino hexanoic acid vermiculite which is stable in air, shows that the organic molecules are laid in an α-fashion with two layers of organic molecules between the silicate layers. The zig-zag chain of the amino acid is nearly parallel to b

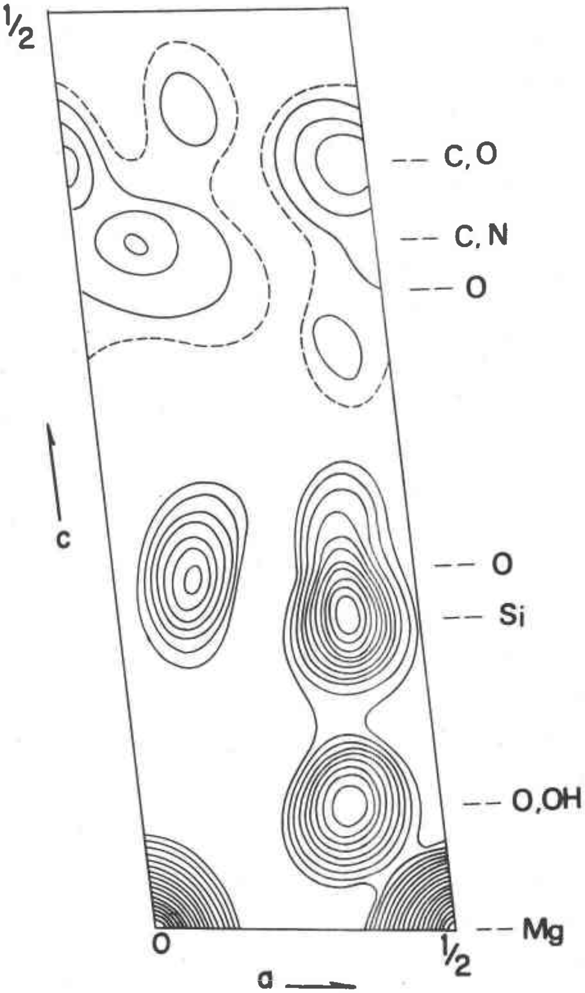

FIG. 2. Electron density projection on the (010) plane: solid contours are drawn at unit electron intervals and dashed contour at zero electron density.

axis, and tilts to the silicate layer by about 5°. The zig-zag plane also tilts to the silicate layer by about 50°. It is very interesting that this configuration is midway between the α_{II}-configuration (plane parallel to silicate layer) and the α_{I}-configuration (plane perpendicular to silicate layer). From the change of *c*-spacing of amino acid-montmorillonite complexes before and after reaction with amino acid, Talibudeen (1955) concluded that the carboxyl group, –COOH, lies parallel to the silicate layer.

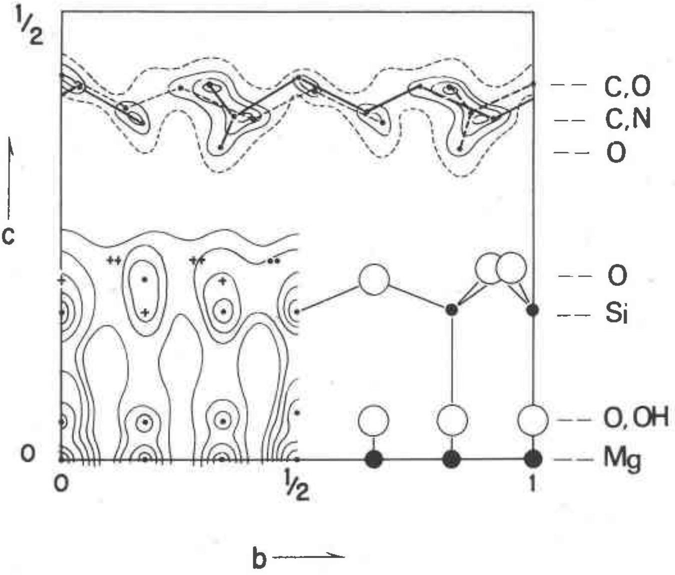

FIG. 3. Electron density projection on the (100) plane: solid contours are drawn at unit electron intervals and dashed contour at zero electron density. Small crosses represent the $\pm b/3$ translated atoms.

Brindley and Hoffmann (1962) also reported that neutral organic molecules with polar group such as ketones, C=0, take up the α_{II}-orientation, and deduced that the polar group must play a dominant role for the configuration of organic molecules in the interlayer. Bradley (1945), MacEwan (1948), and Talibudeen (1955) suggested that a kind of hydrogen bonding, C–H—O, may be important in stabilizing the organic molecule and shortening the basal spacing. However, as described by Emerson (1957), it seems to be reasonable that the hydrogen bonding of O–H—O or N–H—O type is preferred to the C–H—O interaction. In fact the O–O distance in O–H—O assumed by Emerson (1957) and Brindley and Ray (1964), and N–O distance in N–H—O observed by Haase, Weiss and Steinfink (1963) and Johns and Sen Gupta (1967) indicate respectively that there is a strong hydrogen bonding between the O or N atom of the organic molecule and the O atom of the silicate surface. The 6-amino hexanoic acid vermiculite has O–H—O hydrogen bonding with a short distance, 2.82 Å. This interaction may be enough for attracting the OH group in –COOH toward the silicate surface, causing the –COOH plane to tilt to the silicate layer. The other terminal group of 6-amino hexanoic acid, NH_3^+, is also close to the silicate layer. The N–O distance of 2.86 Å indicates that ionic charges and N–H—O hydrogen

TABLE 1. FINAL ATOMIC COORDINATES

Atom	x	y	z
(Mg, Fe, Al)$_{oct}$(1)	0.000	0.000	0.000
(Mg, Fe, Al)$_{oct}$(2)	.000	.333	.000
(Mg, Fe, Al)$_{oct}$(3)	.000	.667	.000
(Si, Al)$_{tet}$(1)	.393	.000	.160
(Si, Al)$_{tet}$(2)	.393	.333	.160
O$_{oct}$(1)	.352	.000	.061
O$_{oct}$(2)	.352	.333	.061
O$_{oct}$(3)	.352	.667	.061
O$_{tet}$(1)	.136	.464	.189
O$_{tet}$(2)	.136	.929	.189
O$_{tet}$(3)	.412	.167	.218
OH	.715	.332	.330
O	.465	.298	.432
C(0)	.600	.366	.392
C(1)	.480	.505	.422
C(2)	.595	.633	.383
C(3)	.475	.763	.413
C(4)	.590	.900	.375
C(5)	.470	.038	.405
N	.585	.167	.367

bonding play an important role. From these results, it is reasonable to conclude that the 6-amino hexanoic acid molecules are fixed tightly on the silicate surface through two kinds of hydrogen bonding, O–H—O and N–H—O.

As described above, 6-amino hexanoic acid is distributed statistically over four equivalent positions in the unit cell. There are three types of arrangements permitted cyrstallographicaly (Fig. 4*a*). Among them, *A*

TABLE 2. INTERATOMIC DISTANCES

O–C(0)	1.24 Å
O$_H$–C(0)	1.34
C(0)–C(1)	1.55
C(1)–C(2)	1.52
C(2)–C(3)	1.48
C(3)–C(4)	1.58
C(4)–C(5)	1.54
C(5)–N	1.52
O$_H$–O$_{tet}$(1)	2.82
N–O$_{tet}$(3)	2.86

TABLE 3. STRUCTURE FACTORS

h k l	F_{calc}	F_{obs}	*h k l*	F_{calc}	F_{obs}
0 0 1	198	196	4 0 0	−39	56
0 0 2	28	29	4 0 2	54	49
0 0 3	−28	31	4 0 3	49	51
0 0 4	7	35	4 0 7	31	43
0 0 5	158	162	4 0 8	46	40
0 0 6	96	74	4 0 9	47	37
0 0 8	−43	36	−4 0 1	−33	55
0 0 9	−41	31	−4 0 2	44	75
0 0 12	54	43	−4 0 3	84	102
0 0 13	50	41	−4 0 4	81	81
0 0 14	37	34	−4 0 7	23	30
0 0 16	15	18	−4 0 8	42	48
0 0 17	21	20	−4 0 9	63	55
0 0 18	76	80			
			0 2 0	29	19
2 0 0	76	80	0 2 1	18	23
2 0 1	82	107	0 2 2	12	16
2 0 2	130	106	0 2 3	30	19
2 0 3	82	87	0 2 4	16	16
2 0 4	58	46	0 2 6	24	18
2 0 5	85	60	0 4 1	6	18
2 0 6	44	47	0 4 2	12	12
2 0 7	92	65	0 4 3	16	15
2 0 8	88	52	0 4 4	12	11
2 0 10	18	28	0 4 5	13	17
2 0 11	−30	19	0 4 7	22	17
2 0 13	18	19	0 4 8	10	12
2 0 14	38	28	0 4 12	12	16
−2 0 1	−18	23			
−2 0 2	−44	62	0 6 0	109	116
−2 0 3	−25	41	0 6 1	76	76
−2 0 5	61	40	0 6 2	31	33
−2 0 6	51	53	0 6 3	14	12
−2 0 7	35	30	0 6 5	33	20
−2 0 8	18	28	0 6 6	40	26
−2 0 9	21	43	0 6 10	13	15
−2 0 10	53	53	0 6 12	25	22
−2 0 11	98	70	0 6 13	32	23
−2 0 12	90	67	0 6 14	19	18

and *B* are unreasonable since the intermolecular distance is less than the van der Waals distance. In case *C*, the intermolecular distance between organic molecules is larger than 4.0 Å as shown in Figure 4*b*, which means that there are no strong interactions between adjacent organic molecules.

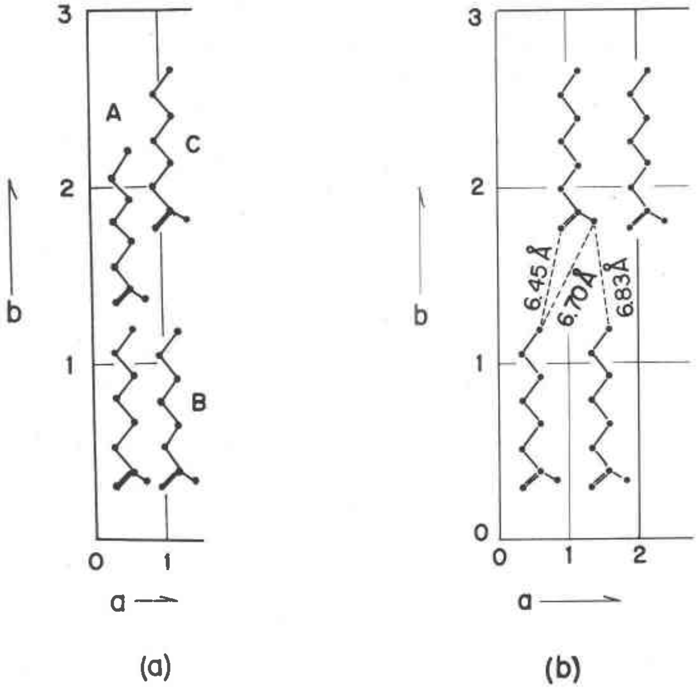

FIG. 4. Molecular arrangements of 6-amino hexanoic acid: (a) crystallographically permitted arrangement (b) interatomic distances between organic molecules in *C* configuration.

This is also reasonable since both ends of the amino acid have strong interactions with the silicate layer. The arrangement of *C* shows that three unit cells contain only four organic molecules; the number of organic molecules per unit cell is 1.24 and is very near to $\frac{4}{3}$. However, this agreement may be due to chance. If configuration *C* held throughout the whole crystal, it would result in a larger unit cell, three times that of the original cell. But, in fact, no superlattice was observed on the diffraction patterns. It is therefore concluded that a short-range order with *C*-configuration takes place, but from a point of view of long-range order, 6-amino hexanoic acid should be distributed statistically with the same probability over four equivalent lattice sites.

The configuration of absorbed organic molecules depends strongly on the charge density of the silicate layer and the degree of saturation of organic molecule or swelling solutions. Furthermore, slight grinding of the organic clay complex and evaporation of the absorbed liquid often yield another arrangement of organic molecules (Brindley and Ray, 1964). In this experiment, two more phases of 6-amino hexanoic acid vermiculite were observed in addition to the $d_{(001)} = 17.32$ Å phase; one has the 14.2 Å spacing and the other has a longer spacing than 17.32 Å. Since the $d_{(001)} = 14.2$ Å phase disappears by prolonged treatment at 50°C, this may be a metastable phase in which the replacement of Na by organic cation is not complete. The value of $d_{(001)} = 14.2$ Å corresponds to the *c*-spacing of a one-layer configuration or organic clay complex. Another phase is stable only in the presence of solution or water. This phase has a *c*-spacing of about 21 Å, but when kept in air for a few minutes, it changes rapidly to the $d_{(001)} = 17.32$ Å phase which is a stable form in air. This change in *c*-spacing may be caused by evaporation of a part of interlayer water molecules or neutral 6-amino hexanoic acid molecules from the interlayer region. In this phase, a stepwise configuration might be stabilized with water molecules or 6-amino hexanoic acid molecules. The $d_{(001)} = 17.32$ Å phase may contain some interlayer water molecules. The (010) electron density projection shows small peaks which may be interorganic molecules. If this is true, water molecules might play an important role for stabilizing the interlayer structure with making the hydrogen bonding with O in $-C{=}O$ and N in NH_3^+.

The 6-amino hexanoic acid vermiculite used for X-ray analysis was obtained by oriented solid state reactions containing cationic replacement and dehydration. The interlayer diffusion of big organic molecules with polar groups and water molecules probably loosens the interlayer structure. Furthermore, the lattice distortion may also be introduced in the crystal when cutting the flake of vermiculite. These factors might have an influence on the observed stacking faults.

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