Clays and Clay Minerals, Vol. 31, No. 3, 200–206, 1983.

STRUCTURE OF A VERMICULITE-ANILINE INTERCALATE

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Abstract—A vermiculite-aniline intercalate with a basal spacing of 14.78 Å was investigated by one- and two-dimensional X-ray diffraction methods. The intercalate, prepared by ion exchange between Na-saturated vermiculite from Llano, Texas, and a 1% aniline hydrochloride solution, contains only one aniline cation per single layer cell. A reduced effective cell-charge is believed to be responsible for this. Structure factor calculations were made in space group $C2/c$ and with unit cell dimensions of $a = 5.33$, $b = 9.18$, $c = 29.78$ Å, and $\beta = 97.0°$. However, extra reflections in the a*b* plane, which are similar to those in a vermiculite-benzidine intercalate, showed that after aniline intercalation the true unit cell became primitive. The aniline cations are distributed statistically over equivalent crystallographic sites in the interlayer space. The organic molecules are orientated with their planes vertical and their nitrogen atoms over the projected centers of the ditrigonal cavities into which they key. The aniline cations form ordered arrays upon the silicate layers by packing into rows. Perpendicular to [010], populated and vacant rows alternate. Along populated rows aromatic ring planes are alternately parallel and perpendicular to [010]. With small adjustments this model is similar to that of benzidine-vermiculite.

Key Words—Aniline, Crystal structure, Intercalate, Vermiculite, X-ray diffraction.

INTRODUCTION

In vermiculites, the combination of high surface-charge density and a predominantly tetrahedral source for that charge is believed to be responsible for side or terminal $-NH_3^+$ groups on intercalated organic molecules being deeply keyed into the ditrigonal holes in the planes of surface oxygen atoms. For aromatic molecules these factors can result in packing arrangements in which the planes of the rings are almost vertical (Slade and Raupach, 1982; Iglesias and Steinfink, 1974). In montmorillonites, where the charge density is lower than in vermiculites, the packing arrangement resulting from the intercalation of a given organic species may differ from that in vermiculite. These packing differences can be responsible for different basal spacings (Slade and Raupach, 1982).

X-ray diffraction photographs of the a*b* planes of benzidine-vermiculite (Slade and Raupach, 1982) and those obtained during the present study of aniline-vermiculite show the same pattern of extra reflections between the normal Bragg reflections of vermiculite. The basal spacings of the two intercalates are, however, quite different (19.25 Å for benzidine-vermiculite and 14.78 Å for aniline-vermiculite). In addition, preliminary diffraction photographs of a 4,4′-diamino-*trans*-stilbene intercalate of vermiculite also show extra reflections which, in this case, are a subset of those found for the aniline and the benzidine intercalates. The basal spacing of the diaminostilbene-vermiculite is 21.8 Å.

The close similarity of the extra reflections in the a*b* planes for these three materials suggests that their intercalated organic molecules have a common orientation to the silicate surfaces. In benzidine-vermiculite the orientation of the long axes of the molecules were shown by Slade and Raupach (1982) to be essentially perpendicular to the silicate layers.

The present paper describes the use of chemical and X-ray data to establish the main aspects of the structure of an aniline intercalate of vermiculite from Llano, Texas.

EXPERIMENTAL

Material

The vermiculite used came from the Carl Moss Ranch, Llano County, Texas. When calcium-saturated this material has been reported (Norrish, 1973, Table II) as having the following composition:

$$[(Mg_{2.810}Al_{0.080}Fe^{3}{}_{0.065}Ti_{0.020}Mn_{0.005})(Si_{2.895}Al_{1.105})O_{10}(OH)_2]Ca_{0.465}K_{0.015}.$$

Sample preparation

Flakes were cut to approximately 1 × 1 mm before being sodium-saturated at 70°C. They were then refluxed in a 1% aniline hydrochloride solution for 10 weeks at 40°C. At intervals, when the supernatant solution was changed, some flakes were removed for examination on an X-ray powder diffractometer. In this way the exchange reaction could be monitored by following the development of a rational set of 00*l* reflections based upon a fundamental spacing of 14.78 Å. At the end of 10 weeks the dark, lilac-blue flakes were washed with hot distilled water until the filtrate was chloride free. They were then air dried and tested for sharp rational 00*l* reflections.

A portion of the product was analyzed for C and N by the Australian Microanalytical Service. They re-

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ported 9.06% C and 1.82% N on a vacuum-dry basis, whereas the structural formula for the Llano vermiculite requires 15.22% C and 2.96% N to satisfy the layer charge fully if the exchange reaction is complete, as our X-ray diffraction evidence suggested. To check that equilibrium had been reached, the intercalate from the first reaction was refluxed for an additional 10 weeks at a higher temperature (60°C). Again the supernatant solution was regularly changed and finally the product was washed and analyzed as before. The second analysis (8.94% C and 1.77% N) was essentially the same as the first and showed that no additional aniline had been taken up by further reaction.

Single crystal X-ray diffraction methods

To check the quality of their diffraction patterns, a number of aniline-vermiculite flakes were mounted on glass fibers for oscillation and Weissenberg photographs. Compared to the diffraction patterns of other vermiculite-organic intercalates investigated in this laboratory, the patterns of the aniline intercalate of the Llano vermiculite were reasonably sharp. Nevertheless, some overlapping of neighboring reflections was evident. Finally, two good flakes (one large and one small) were selected for mounting on a Supper Two-Circle Single Crystal Diffractometer.

The true Y axis of the small crystal, upon which the $h0l$ reflections were measured, was found by examining three $0kl$ photographs. These photographs were obtained by mounting the flake successively upon the [100], [110], and [$\bar{1}$10], axes. To minimize the crowding of reflections and to take advantage of an available high intensity X-ray tube the $h0l$ intensities were measured with cobalt radiation.

The $00l$ reflections, used to prepare the one-dimensional electron density projections, were measured upon the larger flake which was also mounted upon a "Y" axis. No attempt was made to establish that this was the unique axis, but for $00l$ reflections this is irrelevant.

For the one-dimensional electron density projections, intensity data for the $00l$ orders 3 to 38 were collected automatically with filtered MoKα radiation and orders 1 to 15 with filtered CoKα radiation. A full set of intensities for orders 1 to 38 were therefore obtained by mutually scaling these two data sets after Lp and absorption corrections had been applied. In this way the problem of the beam trap obscuring the first two orders was overcome, and a data set to give the highest possible resolution was obtained.

The electron density projections on the (010) face of the unit cell were prepared from the unique set of $h0l$ reflections obtained by averaging all symmetry related reflections measurable with CoKα radiation. The algorithm for the data collection program was a substantially altered version of that described by Freeman *et al.* (1970). The modifications incorporated for this study were: (1) an $\omega/2\theta$ scan; this scan was more suitable than the original ω scan for the measurement of the Bragg diffraction from an imperfect flake; (2) a peak-search routine combined with an integrating step-scan; (3) an automated procedure for any peak with one overlapping neighbor by which the integrated intensity on the clear side of the peak was simply doubled. A standard reflection was checked periodically to monitor the constancy of the primary beam, the crystal alignment, and the stability of the counting circuits. Experimental intensities were corrected for Lp factors, and absorption corrections were made by using a linear absorption coefficient of $\mu = 8.89$ cm^{-1} for MoKα, or $\mu = 106.23$ cm^{-1} for CoKα radiat, and the algorithm of Burnham (1963).

STRUCTURE DETERMINATION AND REFINEMENT

All structure factors were calculated with the ORFLS program of Busing *et al.* (1962) in space group $C2/c$. Initially only the parameters for the silicate atoms were used and the values were taken from Shirozu and Bailey (1966), but modified for a unit cell with a "Z" axis repeat of 29.78 Å. However for the $h0l$ data and this silicate-only model, a least squares refinement of the scale factor returned an R factor of 0.29. The positional parameters of Mathieson (1958) were then tried, and the R factor dropped to 0.23. The Mathieson parameters were therefore taken as the basis for all the subsequent structure factor calculations.

One-dimensional electron density projection

The electron density distribution (Figure 1) shows two high, broad regions each apparently composed of three overlapping peaks. Adjacent to these peaks, but nearer to the silicate regions, are four weaker peaks. There is no peak at the middle of the interlayer region.

To interpret this image, the electron densities given by various models were compared with the observed data. This comparison was greatly assisted by making difference Fourier projections and eventually resulted in a good fit when the C–N bonds of the aniline molecules were inclined about 6° to the Z direction.

Because a difference Fourier projection based upon many terms is sensitive to fine details in an atomic model, the z coordinates for both the organic and the silicate atoms could be refined. It was found that each site for an atom in an aniline molecule had to be split into two and the components slightly offset from their mean positions.

For the silicate layer it appeared that neither the octahedral oxygens nor the tetrahedral oxygens were strictly coplanar. This situation could not adequately be modeled by using large temperature factors. In a refined model, a fraction of the atomic population associated with the layer structure was offset along the Z axis. Apparently the "planes" of atoms within the silicate layers are buckled, and some of the disorder in the sites

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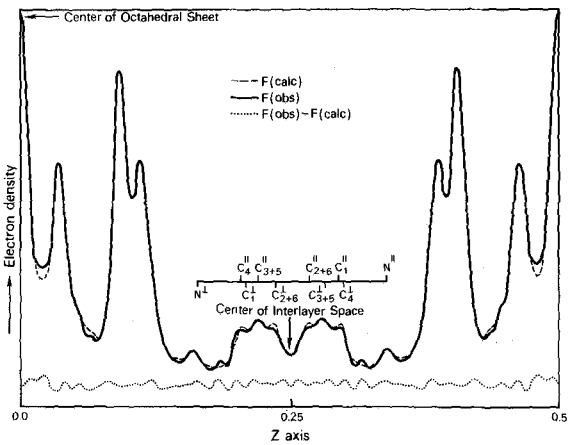


Figure 1. One-dimensional Fourier projection onto the Z axis of the electron density in aniline-vermiculite. The positions of the organic atoms in the model are shown for comparison. The superscripts to their labels indicate whether the atom is in a ring parallel or perpendicular to (010).

for the organic atoms is probably related to this buckling. Apart from these structural imperfections, the difference Fourier images showed a substantial amount of scattering material (equivalent to 8 electrons) at z/c = 0.063. Empirically this was modeled by inserting a sodium ion with a multiplier of 0.2.

The dashed curve in Figure 1 shows the calculated electron density distribution for the refined model. The dotted curve is the final difference image plotted on the same scale. The final R factor is 0.05.

Two-dimensional analyses

With the structure factors phased by only the silicate atoms, a Fourier map and a difference Fourier map of the electron density on the (010) face of the unit cell were calculated (Figure 2). The high areas in the interlayer regions of these maps were similar, but before they were considered in detail, the structure of the silicate layer was refined by using a combination of least squares adjustments and difference Fourier maps. The temperature factors were maintained in the isotropic form, and the scattering curve for O^{1-} was used in conjunction with the mean values of fully ionized and neutral atoms from the International Tables for X-ray Crystallography (1974) for Si, Al, Mg, and Fe. The R factor at the end of these refinements decreased from 0.23 to 0.14.

A new difference Fourier synthesis based upon the refined silicate structure showed two broad unresolved peaks adjacent to the center of the interlayer and two well-resolved peaks over the ditrigonal holes in the surface oxygen network. The z coordinates for the well-resolved peaks corresponded to the mean of those obtained from the one-dimensional work for the nitrogen atoms. The unresolved areas were in the regions of the z coordinates previously obtained for ring carbon atoms.

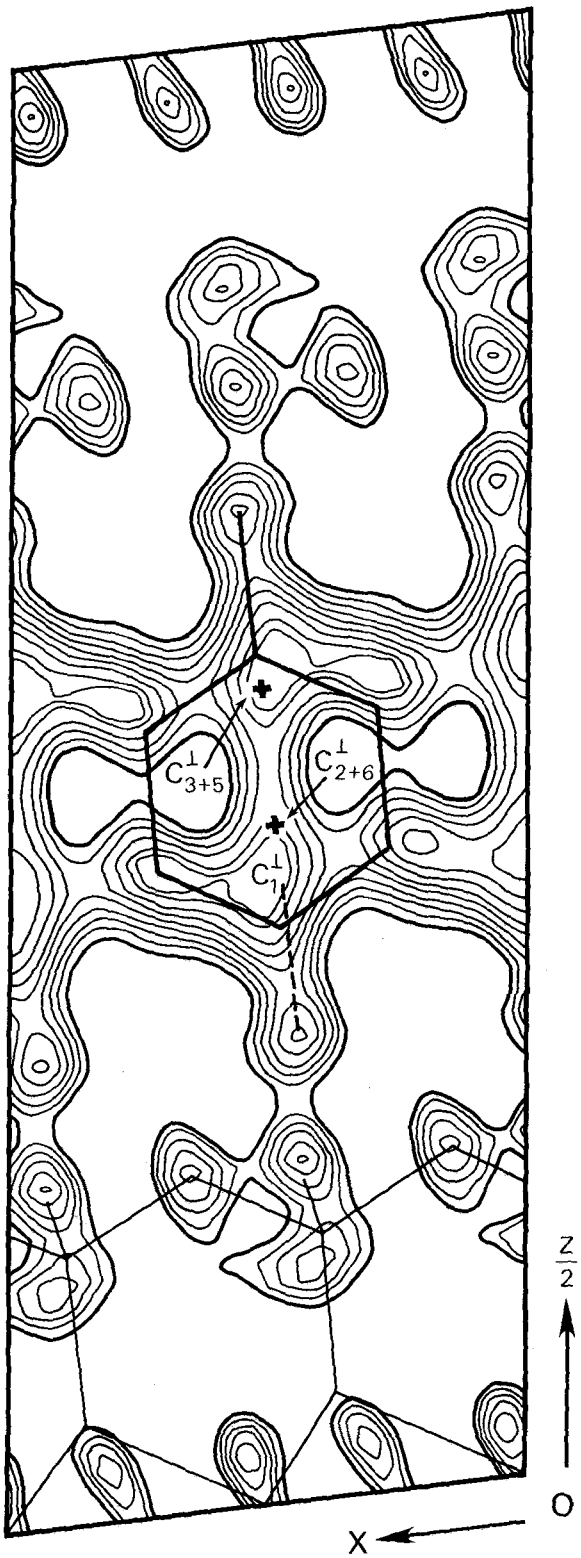


Figure 2. Difference Fourier synthesis for aniline-Llano vermiculite projected upon the (010) plane; only positive contours are shown. The molecular model is outlined.

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Table 1. Atomic positions in fractional coordinates and isotropic temperature factors (B).

Atom	Multiplicity	x/a	z/c	B (Å²)
3(Mg,Fe,Al)	0.4116	0	0	1.38
3(Mg,Fe,Al)	0.0884	0.0422	0.0190	1.38
3 O_1	1.0000	0.3580	0.0356	1.98
2(Si,Al)	1.0000	0.3960	0.0927	1.23
O_{2AB}	1.8000	0.1411	0.1108	1.68
O_{2AB}	0.0800	0.1411	0.0820	1.28
O_{2AB}	0.1200	0.1411	0.1322	1.28
O_3	1.0000	0.4195	0.1137	1.68
N (‖)	0.125	0.4500	0.1598	1.28
C_1(‖)	0.125	0.4779	0.2044	1.48
C_2(‖)	0.125	0.7088	0.2325	1.58
C_3(‖)	0.125	0.7279	0.2788	1.58
C_4(‖)	0.125	0.5221	0.2956	1.48
C_5(‖)	0.125	0.2794	0.2788	1.58
C_6(‖)	0.125	0.2647	0.2325	1.58
N (⊥)	0.125	0.4500	0.1635	1.28
C_1(⊥)	0.125	0.4779	0.2081	1.48
C_2(⊥) + C_6(⊥)	2(0.125)	0.4912	0.2362	1.58
C_3(⊥) + C_5(⊥)	2(0.125)	0.5074	0.2825	1.58
C_4(⊥)	(0.125)	0.5221	0.2993	1.48

The symbols (‖) or (⊥) refer to atoms in the aromatic rings which are either parallel or perpendicular to (010).

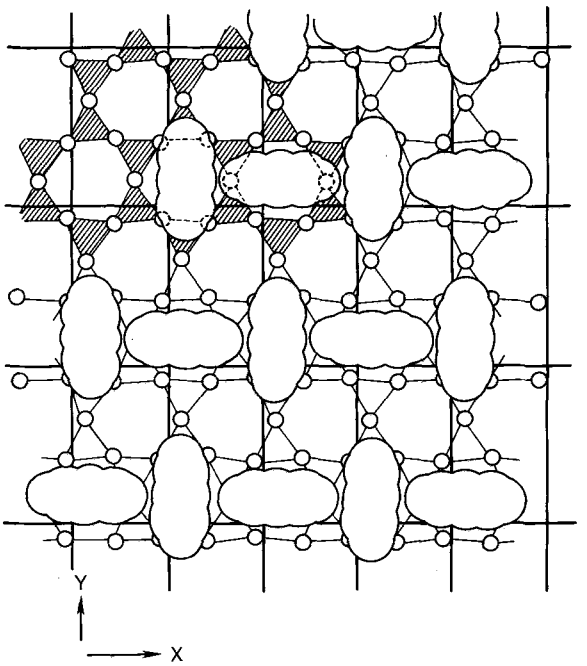


Figure 3. Schematic representation of the interlayer cation arrangement with a domain aniline-Llano vermiculite. The aniline cations are drawn from their van der Waals radii reduced to the same scale as that used for the vermiculite cell.

At this stage a complete set of atoms for an aniline cation was added to the model. The *z* coordinates for these atoms were obtained from the one-dimensional work and, in conformity with the Fourier maps, their *x* coordinates were such that the plane of the cation was parallel to the (010) face. The multiplier for each atom was initially set to 0.25 to allow, on average, one aniline cation per single-layer unit cell with a total of four equivalent positions. After a least squares adjustment of the positional parameters the atom multipliers were released in a further cycle of refinement. Although the values for N, C_1, and C_4 did not alter significantly the multipliers for C_2, C_3, C_5, and C_6 changed to 0.125. The R factor dropped to 0.12. A difference Fourier synthesis based upon the model now showed residual peaks along a line joining the C_1 sites above and below the mid-plane of the interlayer region. On the assumption that these peaks were associated with carbon atoms, their coordinates were added to the model. The multipliers were set to 0.25, and the positional parameters were released in a refinement cycle; the changes, however, were not significant. The atom multipliers were then released, but again the changes were not significant. No attempt was made to use anisotropic temperature factors for the silicate atoms because, to satisfy the difference Fourier images, these had already been modeled as having substantial shifts from sharply defined planes. Table 1 lists the final atomic parameters and temperature factors. Table 2 lists the observed and calculated structure factors. The overall R factor for the *h0l* data was 0.116.

*The diffraction pattern in the a*b* plane*

It was pointed out above that the a*b* planes of aniline and benzidine-vermiculites show a similar pattern of extra reflections between the normal Bragg reflections of vermiculite. For benzidine-vermiculite, Slade and Raupach (1982) concluded that the pattern could be understood in terms of a primitive unit cell with the same *a* and *b* dimensions as the vermiculite cell. The c-face centering of normal vermiculite unit cells was destroyed by the intercalation process. In the aniline intercalate with the Llano vermiculite there is only one aniline molecule per unit cell which will, of necessity, be primitive.

A coherent, two-dimensional diffraction effect will be given by an arrangement of the primitive cells if, within a domain and normal to [010] for example, the adjacent rows of ditrigonal holes in the surface oxygen sheet are populated differently. Such a pattern of rows may have all of the holes along one row populated with aniline cations, with their ring planes orientated parallel to [010], and all of the holes in the adjacent row vacant. However, this pattern does not allow for those aniline cations required, by the two-dimensional Fourier synthesis, to have their ring planes orientated perpendicular to [010]. In fact, rows containing aniline cations arranged in this way, in each ditrigonal hole can not exist because the distance between hole centers (5.33 Å) is less than the van der Waals width of a cation (6.2 Å). Therefore, the aniline cations along populated rows

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Table 2. Comparison of observed and calculated structure amplitudes for aniline-vermiculite, (a) values for large crystal measured with MoKα radiation; (b) values for small crystal measured with CoKα radiation.

(a)			(b)					
00*l*	F_{obs}	F_{calc}	*h*0*l*	F_{obs}	F_{calc}	*h*0*l*	F_{obs}	F_{calc}
0 0 2	341	348				2 0 $\overline{24}$	2	5
0 0 4	16	9	0 0 4	25	−22	2 0 24	64	87
0 0 6	101	−104	0 0 6	130	−120	2 0 $\overline{26}$	7	−15
0 0 8	189	185	0 0 8	169	159	2 0 26	38	39
0 0 10	265	260	0 0 10	254	237	4 0 0	135	−116
0 0 12	21	17	0 0 12	21	22	4 0 $\overline{2}$	136	−127
0 0 14	119	−119	0 0 14	94	−116	4 0 2	43	23
0 0 16	124	−123	0 0 16	99	−107	4 0 $\overline{4}$	139	126
0 0 18	69	68	0 0 18	46	45	4 0 4	160	156
0 0 20	114	116	0 0 20	81	98	4 0 $\overline{6}$	266	228
0 0 22	98	103	0 0 22	70	90	4 0 6	81	84
0 0 24	84	84	0 0 24	58	67	4 0 $\overline{8}$	167	154
0 0 26	64	64	0 0 26	44	44	4 0 8	28	−37
0 0 28	34	38	0 0 28	29	37	4 0 $\overline{10}$	21	20
0 0 30	64	73	0 0 31	49	70	4 0 10	22	−30
0 0 32	90	93	2 0 0	162	145	4 0 $\overline{12}$	26	12
0 0 34	91	94	2 0 $\overline{2}$	70	−83	4 0 12	78	63
0 0 36	17	18	2 0 2	236	241	4 0 $\overline{14}$	122	117
0 0 38	37	−38	2 0 $\overline{4}$	161	−144	4 0 14	129	143
0 0 40	39	−38	2 0 4	244	245	4 0 $\overline{16}$	164	149
0 0 42	20	20	2 0 $\overline{6}$	55	−58	4 0 16	99	99
0 0 44	54	53	2 0 6	179	171	4 0 $\overline{18}$	85	100
0 0 46	13	14	2 0 $\overline{8}$	81	95	4 0 18	39	40
0 0 48	26	−26	2 0 8	108	78	4 0 $\overline{20}$	3	5
0 0 50	1	−10	2 0 $\overline{10}$	151	164	4 0 $\overline{22}$	29	22
0 0 52	27	28	2 0 10	109	105			
0 0 54	58	56	2 0 $\overline{12}$	43	51			
0 0 56	30	29	2 0 12	171	167			
0 0 58	1	−2	2 0 $\overline{14}$	41	−18			
0 0 60	2	−3	2 0 14	159	173			
0 0 62	5	10	1 0 $\overline{16}$	59	49			
0 0 64	18	23	2 0 16	49	53			
0 0 66	2	1	2 0 $\overline{18}$	167	188			
0 0 68	10	−4	2 0 18	49	−64			
0 0 70	10	−11	2 0 $\overline{20}$	186	215			
0 0 72	3	−1	2 0 20	45	−51			
0 0 74	8	6	2 0 $\overline{22}$	77	94			
0 0 76	7	5	2 0 22	16	16			

must have their ring planes alternately parallel and perpendicular to [010] in Figure 3. This arrangement (Figure 3) results in a larger face-centered cell with dimensions $2a \times 2b$, where a and b are the dimensions of a normal vermiculite cell. However, the basic cell (with dimensions $a \times b$) remains primitive.

An increase in the effective cell charge allows aniline to fill vacant rows progressively. In these filling rows the planes of the aromatic rings must alternate (as in the previously filled rows) to keep the basic cell primitive. With the increased density of packing, Slade and Raupach's work (1982) on benzidine-vermiculite suggests that the aromatic rings rotate slightly about their steeply inclined C–N bonds. After this small adjustment a closest-packed array of aniline cations in aniline-vermiculite would be similar to the array illustrated for benzidine-vermiculite in Figure 5a of Slade and Raupach (1982). The comparison requires that the array for aniline-vermiculite be rotated 60° clockwise to bring it into coincidence with that shown for benzidine-vermiculite. On the surface of a silicate layer the [100], [110], and [$\bar{1}$10] directions are structurally equivalent.

DISCUSSION

In the Llano vermiculite intercalate, the aniline cations have a 25% probability of being located at any one of the four available equivalent positions in a single layer unit cell. The planes of the aromatic rings may be either parallel to the (010) face of the cell or parallel to its b*c* plane. The C–N bonds are steeply inclined to the silicate layers, and the nitrogen atoms are located over the centers of ditrigonal holes formed by the surface oxygen atoms. The average position for the nitrogen atom, at 4.78 Å from the center of the octahedral sheet, is intermediate between that found by Johns and Sen Gupta (1967) in alkylammonium complexes with

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the Llano vermiculite and that found in a butylammonium complex with vermiculite from Beni-Buxera, Spanish Morocco, by Martin-Rubi *et al.* (1974). These two values were reported to be 4.65 and 4.85 Å, respectively. At 4.78 Å, the nitrogen atoms are more deeply keyed into the ditrigonal cavities than are the carbon atoms on the opposite sides of the rings. These carbons have their centers at 5.99 Å from the center of octahedral sheets.

If the y coordinates for the nitrogen atoms are taken to be 1/6 or 2/3, the calculated distances between the nitrogen atoms and the oxygen atoms in an adjacent ditrigonal ring range between 2.58 and 3.17 Å. Hydrogen bonding is therefore strongly indicated.

Although the charge per single layer cell for the Llano vermiculite used in the present work is 1.90, on average, only one aniline cation could be introduced into such a cell. This result does not reflect a packing difficulty, because additional (unpublished) work in these laboratories has shown that a similar exchange reaction between aniline hydrochloride and the lower-charged Young River vermiculite (Western Australia) produces an intercalate in which the number of aniline cations per cell is close to the charge per single layer cell (1.45).

The restricted uptake of aniline by the Llano vermiculite may be due to either a decrease in its exchange capacity caused by migration of cations into hexagonal cavities or charge transfer effects. Of these possibilities, the former seems more likely because the electron density maps showed significant peaks near the bottoms of hexagonal cavities. Although the one-dimensional difference Fourier images were satisfied when these positions were populated with Na^+ with multipliers of 0.2, any comparable scatterer could have been used. Over the four sites in a single layer cell the charge equivalent of the Na^+ is 0.8 electrons, approximately equal to the portion of the total charge unsatisfied by aniline.

Calvet and Prost (1971) concluded from their study of the thermal migration of exchangeable cations in montmorillonite, that non-exchangeable lithium moved into vacant octahedral positions and deep into hexagonal cavities. However, Na^+ is too large to enter either of these positions, so in the present case Mg^{2+} or Al^{3+} are probably being trapped in the hexagonal cavities. Inasmuch as the exchange reactions were carried out for long periods at 40°C with aniline hydrochloride at pH 2.8, Mg^{2+} or Al^{3+} may have been liberated from the octahedral layer by acid attack. The high tetrahedral charge of the Llano vermiculite may initially draw liberated cations into the silicate layer. The attractive forces will be relatively high because the dielectric constant of the interlayer region will be reduced by the presence of organic cations and low water content. As the effective layer charge falls, the overall electric field drawing cations into the silicate layers will weaken, and any remaining cations, when released from their octahedral sites, will escape completely.

The intense colors of the aniline intercalates formed by both the Llano and the Young River vermiculites are probably indicative of charge transfer between the organic and the silicate parts of the structure. However, for the intercalate formed between aniline and the Young River vermiculite, in which an appreciable Fe^{3+} content may favor charge transfer, chemical analysis showed that the full cell charge is balanced by an equal number of aniline cations. The effective exchange capacity of a vermiculite therefore seems more important than charge transfer in regulating the extent of aniline uptake. Further, more detailed work is needed to establish how the exchange capacity of the Llano vermiculite was modified by entrapped ions.

As reported above, the $h0l$ structure factors calculated from the Shirozu and Bailey (1966) model for the Llano vermiculite, did not fit the observed values for the aniline intercalate or those calculated from the Mathieson (1958) model. The two models differ mainly because the former has its origin on a center of symmetry in the interlayer region, whereas the latter has its origin on the mid-plane of an octahedral sheet within a silicate layer. The presence of a single non-centrosymmetric aniline cation per single layer cell should therefore favor the Mathieson model. Also, a center of symmetry in the interlayer region may not be favored if the corrugations observed in the sheets do not intermesh across the interlayer. Such corrugations may be enhanced by the presence of the organic component.

This study, like those of other vermiculite-organic intercalates, has shown that the organic cations are statistically distributed over crystallographically equivalent sites; the extra reflections in the a*b* plane of aniline-vermiculite require the organic cations to have an ordered arrangement within the interlayer domains.

ACKNOWLEDGMENTS

Valuable discussions with Dr. M. Raupach and Dr. E. W. Radoslovich are gratefully acknowledged.

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(Received 31 August 1982; accepted 3 November 1982)

Резюме—Прослойка вермикулит-анилин с промежутком 14,78 Å исследовалась при помощи одно- и двухразмерного порошкового рентгеновского анализа. Прослойка, подготовленная при помощи обмена ионов между Na-насыщенным вермикулитом из Ддано, Тексас, и 1% расивором анилинового хлоргидрата, содержит только один анилиновый катион в ячейке одиночного слоя. Кажется, что уменьшенный эффективный заряд ячейки является ответственным за это. Расчеты структурального фактора были проведены в пространственной группе $C2/c$ при размерах элементарной ячейки a = 5,33, b = 9,18, c = 29,88 Å, и β = 97,0°. Однако, добавочные отражения в плоскости a* b*, похожие на отражения для прослойки вермикулит-бензидин, указывали на то, что после внедрения анилина истинная ячейка является первозданной. Катионы анилина распределены статистически по эквивалентных кристаллографических местах в межслойной области. Органические молекулы ориентированы вертикально своими плоскостями и атомы азота распределены по центрам дитригональных полостей, в которых они заклиниваются. Катионы анилина образуют упорядоченные ряды над силикатовыми слоями. Перпендикулярно к [010] заполненные и пустые ряды заменяются. Проскости ароматических колец чередуются перпендикулярно и параллельно к [010] вдоль заполненных рядов. С малыми поправками эта модель похожа на модель для прослойки бензидин-вермикулит. [E.G.]

Resümee—Eine Vermiculit-Anilin-Wechsellagerung mit einem Basisabstand von 14,78 Å wurde mittels ein- und zweidimensionalen Röntgendiffraktionsmethoden untersucht. Die Wechsellagerung, die durch Ionenaustausch zwischen Na-gesättigtem Vermiculit von Llano, Texas, und 1%iger Anilinhydrochloridlösung hergestellt wurde, enthält nur ein Anilinkation pro einzelner Zellschicht. Eine reduzierte effektive Zell-Ladung wird dafür verantwortlich gemacht. Berechnungen des Strukturfaktors wurden in der Raumgruppe $C2/c$ und mit einer Elementarzelle von a = 5,33, b = 9,18, c = 29,78 Å, sowie mit einem β von 97,0° durchgeführt. Zusätzliche Reflexe in der a*b*-Ebene, die denen in einer Vermiculit-Benzidin-Wechsellagerung ähneln, zeigen jedoch, daß nach dem Einbau von Anilin die eigentliche Elementarzelle primitiv wird. Die Anilinkationen sind statistisch auf kristallographisch gleichwertigen Plätzen zwischen den Schichten verteilt. Die organischen Moleküle sind so orientiert, daß ihre Ebenen vertikal stehen, und ihre Stickstoffatome über den projezierten Mittelpunkten der ditrigonalen Hohlräume liegen, in die sie hineinreichen. Die Anilinkationen sind strukturell in Reihen auf den Silikatschichten angeordnet. Senkrecht zu [010] wechseln sich besetzte und leere Reihen ab. Entlang den besetzten Reihen sind die aromatischen Ringebenen abwechselnd parallel und senkrecht zu [010] angeordnet. Mit geringen Angleichungen ähnelt dieses Modell dem von Benzidin-Vermiculit. [U.W.]

Résumé—On a investigué un intercalat vermiculite-aniline ayant un espacement de base de 14,78 Å par des méthodes de diffraction de rayons-X à une et deux dimensions. L'intercalat, préparé par un échange d'ions entre une vermiculite saturée de Na provenant de Llano, Texas et une solution d'hydrochloride aniline à 1%, ne contient qu'un cation d'aniline par maille à couche unique. On croit qu'une réduction de l'éfficacité de la charge de maille est responsable pour ceci. Des calculs de facteur structural ont été faits sur le groupe d'espace $C2/c$, et avec des dimensions de maille mère de a = 5,33, b = 9,18, c = 29,78 Å, et β = 97,0°. Cependant, d'avantage de réflections dans le plan a*b*, qui sont semblables à celles dans un intercalat vermiculite-benzidine, ont montré qu'après intercalation d'aniline, la maille mère réelle devenait primitive. Les cations aniline sont distribués statistiquement sur des sites cristallographiques équivalents dans l'espace intercouche. Les molécules organiques sont orientées de manière que leurs plans sont verticaux et que leurs atomes nitrogènes sont sur les centres projetés des cavités ditrigonales dans lesquelles ils s'insèrent. Les cations d'aniline forment des ordres rangés sur les couches silicates en s'empillant en rangées. Des rangées occupées et vides alternent perpendiculairement à [010]. Le long des rangées occupées, des plans d'encerclement de composes arômatiques sont alternativement parallèles et perpendiculaires à [010]. Avec des petits ajustements, ce modèle est semblable à celui de la benzidine-vermiculite.

https://doi.org/10.1346/CCMN.1983.0310305 Published online by Cambridge University Press