NOTES

THREE-DIMENSIONAL ORDER AND THE STRUCTURE OF ANILINE-VERMICULITE

Key Words—Aniline, Crystal structure, Intercalation, Ordering, Vermiculite.

An X-ray diffraction analysis of the structure of an intercalate of Llano vermiculite and aniline was described recently by Slade and Stone (1983). The analysis used superlattice reflections in the a*b* reciprocal plane and Fourier images obtained from $00l$ and $h0l$ reflections, to show that the aniline cations have an ordered arrangement on the silicate layers and are perpendicular to them. This note concerns further X-ray work recently made possible by finding unusually good flakes of the dark blue-colored intercalate in the original preparation. The new flakes show better $0kl$ reflections than seen previously and have enabled the structure proposed by Slade and Stone (1983) to be confirmed from Fourier projections along [100]. In addition, the $0kl$ reflections have revealed that the true unit cell ($a = 5.33$, $b = 9.268$, $c = 14.89$ Å, $\beta = 97°$) differs from that originally used and that neighboring silicate layers must be in well-defined positions with respect to each other.

$0kl$ DIFFRACTION PATTERN

Figure 1 shows that the intercalate formed between aniline and Llano vermiculite has $0kl$ reflections, including $k \neq 3n$ reflections, which are sharp and discrete. The structure therefore is three-dimensionally ordered. The pattern of these reflections suggests that the true unit cell contains but a single silicate layer and has a Z axis repeat of 14.89 Å. By considering the extinctions of the $0kl$ pattern in conjunction with those in the $h0l$ pattern, the space group can be deduced as $C2$ or $C2/m$. The mirror plane in $C2/m$, however, is incompatible with the ordering of silicon and aluminum found by Shirozu and Bailey (1966) in the tetrahedral sites for Llano vermiculite. When the interlayer region is considered in addition to the silicate portion of *any given unit cell*, the true space group is more likely to be $P1$ because the superlattice reflections in the a*b* plane show that the c-face centering has been destroyed (Slade and Stone, 1983). In addition, the presence of a single, non-centrosymmetric organic cation in the specified cell will not allow for a diad axis. The contents of a *collection of unit cells* are seen as averaged by the diffraction process; the most likely space group therefore is $C2$ and, thus, the present calculations were carried out for this symmetry. Three-dimensional order was described previously by de la Calle *et al.* (1975) in relation to the two-water layer

hydrates of Na and Ca-vermiculites. Such order was taken to confirm the existence of well-defined interlayer structures interacting with localized charges developed by substitutions in the tetrahedral sheets. In the present sample, the ordering allowed a good set of $0kl$ intensities to be measured with Mo radiation by using the methods detailed by Slade and Stone (1983).

FOURIER PROJECTION UPON THE (100) PLANE

With the structure amplitudes phased by only the silicate atoms, a difference Fourier projection of the electron density on the (100) face of the unit cell was calculated (Figure 2). The interlayer region of this projection was readily interpretable in terms of the structural model developed during the earlier study of the $00l$ and $h0l$ reflections. The aniline cations are positioned over the ditrigonal cavities in the silicate layers, to which the C–N bonds are perpendicular. The planes containing the benzene rings are either parallel or perpendicular to the b*c* plane.

On the assumption that a given aniline cation has a 50% probability of having one of these two possible
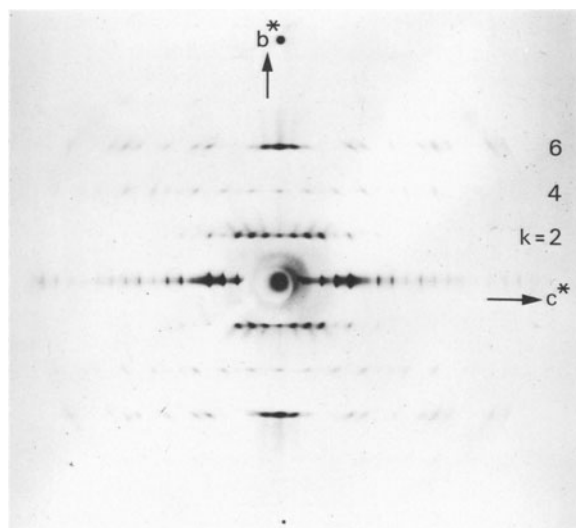

Figure 1. Precession photograph of the b*c* plane of aniline-vermiculite ($\bar{\mu} = 25°$, s = 32.2 mm, r = 15 mm, MoKα radiation).
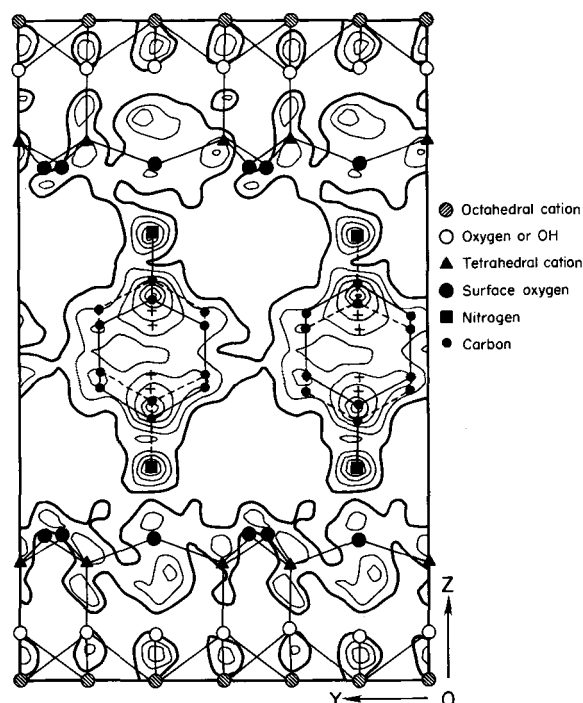
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Figure 2. Difference Fourier synthesis for aniline-Llano vermiculite projected upon the (100) plane; only positive contours are shown. The molecular model is outlined. Individual aniline cations in equivalent crystallographic positions are drawn either with solid or dashed lines. The projections of those aromatic rings whose planes are perpendicular to (100) are shown as crosses (+).

Legend:
- ⊘ Octahedral cation
- ○ Oxygen or OH
- ▲ Tetrahedral cation
- ● Surface oxygen
- ■ Nitrogen
- • Carbon

Table 1. Comparison of observed and calculated structure factors for aniline-Llano vermiculite. The level scale factor S = 17.99. F_{calc}, A_{calc}, and B_{calc} are multiplied by 10.

0	k	l	$|SF_{obs}|$	$|F_{calc}|$	A_{calc}	B_{calc}
0	0	1	1718	1695	1695	0
0	0	2	76	83	−83	0
0	0	3	484	432	−432	0
0	0	4	842	937	937	0
0	0	5	1346	1203	1203	0
0	0	6	178	50	50	0
0	0	7	572	643	−643	0
0	0	8	558	510	−510	0
0	0	9	328	320	320	0
0	0	10	545	523	523	0
0	0	11	502	549	549	0
0	0	12	363	422	422	0
0	0	13	289	336	336	0
0	0	14	164	141	141	0
0	0	15	294	198	198	0
0	2	0	324	420	231	−351
0	2	1	370	391	229	−318
0	2	2	491	581	−329	478
0	2	3	494	481	−271	398
0	2	4	224	182	99	−152
0	2	5	393	432	238	−361
0	2	6	166	187	108	−152
0	2	7	280	255	−165	194
0	2	8	164	188	−139	126
0	2	9	26	64	−5	4
0	2	10	177	148	95	−114
0	2	11	205	153	111	−105
0	2	12	17	25	19	−17
0	2	13	86	96	−67	69
0	2	14	92	80	−56	56
0	2	15	36	35	2	3
0	4	0	30	34	−16	−30
0	4	1	95	106	38	99
0	4	2	277	296	159	249
0	4	3	145	103	−32	−98
0	4	4	311	361	−180	−313
0	4	5	105	66	−39	−53
0	4	6	400	456	182	418
0	4	7	220	239	92	221
0	4	8	293	296	−157	−251
0	4	9	382	393	−196	−341
0	4	10	89	99	56	82
0	4	11	470	425	206	372
0	4	12	79	90	45	78
0	4	13	261	265	−130	−23
0	4	14	188	193	−89	−171
0	4	15	88	96	62	74
0	6	0	1385	1304	1298	131
0	6	1	892	840	840	17
0	6	2	359	376	373	−47
0	6	3	85	110	39	−103
0	6	4	178	205	204	−20
0	6	5	530	544	537	89
0	6	6	452	470	465	69
0	6	7	15	57	57	−3
0	6	8	392	326	−314	−89
0	6	9	93	74	−55	−49
0	6	10	405	382	381	33
0	6	11	534	588	584	75
0	6	12	336	365	365	17
0	6	13	153	83	73	−40
0	6	14	20	58	17	−55
0	6	15	260	234	234	7

arrangements and given also that chemical analysis allows for only one organic ion per single layer cell, a set of 0*kl* structure factors was calculated. With the organic atoms included for the model described, the R factor fell from 19.4 to 13.5%. A difference Fourier projection at this stage showed the interlayer region to be very nearly flat, but anisotropic peaks still remained in the silicate portion of the structure. These peaks were most prominent for the octahedral cations and are believed, to have resulted partly from disruption to the structure caused by acid attack during the preparation of the intercalate (Slade and Stone, 1983).

After a least-squares adjustment of the isotropic temperature factors was made, the factors were converted to their anisotropic forms. In a subsequent least-squares adjustment, only the appropriate anisotropic thermal components for the octahedral cations were allowed to vary. In a further least-squares cycle, in which the positional parameters of the organic atoms were relaxed, only small changes occurred. At this stage the R-factor was 10.8%, and a further difference map showed that the remaining differences were largely associated with the silicate region. Therefore, in view of the suspected disturbance to this portion of the structure by the acidic medium in which the intercalation process was con-

Table 1.   Continued.

0	k	l	$|SF_{obs}|$	$|F_{calc}|$	A_{calc}	B_{calc}
0	8	0	16	86	6	86
0	8	1	95	131	116	−62
0	8	2	47	72	−60	−40
0	8	3	134	107	−101	36
0	8	4	154	139	−90	106
0	8	5	90	55	52	−16
0	8	6	247	227	156	−165
0	8	7	120	82	−10	−82
0	8	8	162	156	−140	69
0	8	9	217	218	−163	145
0	8	10	81	88	70	−54
0	8	11	243	208	153	−141
0	8	12	51	70	56	−41
0	8	13	140	158	−119	105
0	8	14	102	102	−81	62
0	8	15	22	47	31	−35

Table 3.   Bond lengths between the aniline nitrogen or para carbon atoms and surface oxygens in aniline-Llano vermiculite.

Bond	Distance (Å)
O(X)–N	2.86
O(X′)–N	2.91
O(X″)–N	2.86
O[S(P_1)]–N	3.13
O[S(P_2)]–N	3.23
O[S(P_3)]–N	3.20
O(X)–C(4)	3.43
O(X′)–C(4)	3.71
O(X″)–C(4)	3.58
O[S(P_1)]–C(4)	3.57
O[S(P_2)]–C(4)	3.75
O[S(P_3)]–C(4)	3.87

Probable error in bond lengths: O–N, ± 0.05 Å; O–C, ±0.10.

ducted, further refinement was considered to be unprofitable. Table 1 shows the observed structure factors and those calculated from the parameters given in Table 2. The z positional parameters shown in Table 2 for the surface oxygen atoms were taken from Shirozu and Bailey (1966) and adjusted to the present unit cell. Their variations during refinement were insignificant. The z coordinates for the organic atoms differ slightly from the values obtained by averaging the figures quoted in Slade and Stone (1983). These small differences probably reflect the variable quality of the crystals upon

which the measurements were made; they do not significantly alter the impression of the structure.

From the relevant parameters listed in Table 2 the distances between the aniline nitrogen atoms and the surface oxygen atoms were calculated with the ORFFE program (Busing et al., 1964). The results are listed in Table 3 along with the distances between the para-carbon atoms of the aromatic rings and the surface oxygens. The notation for the oxygens follows that of Mathieson and Walker (1954). Nitrogen–oxygen distances less than 3 Å have values very close to 2.88 Å

Table 2.   Final positional and temperature parameters for aniline-Llano vermiculite.

Atom[1]	x^2	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
(Mg,Fe,Al)	0	0	0	0.0096	0.0022	0.0029	0.0000	0.0004	0.0000
(Mg,Fe,Al)	0	0.3333	0	0.0082	0.0007	0.0026	0.0000	0.0004	0.0000
(Mg,Fe,Al)	0	0.6667	0	0.0091	0.0018	0.0033	0.0000	0.0004	0.0000
O_1	0.3576	0.0000	0.0730	0.0172	0.0057	0.0022	0.0000	0.0007	0.0000
O_1	0.3590	0.3333	0.0730	0.0315	0.0104	0.0041	0.0000	0.0013	0.0000
O_1	0.3580	0.6667	0.0730	0.0213	0.0070	0.0028	0.0000	0.0009	0.0000
(Si,Al)	0.3974	0.3399	0.1837	0.0213	0.0070	0.0028	0.0000	0.0009	0.0000
(Si,Al)	0.3958	0.0053	0.1843	0.0123	0.0041	0.0016	0.0000	0.0005	0.0000
O_2A	0.1421	0.4013	0.2254	0.0179	0.0059	0.0023	0.0000	0.0008	0.0000
O_2B	0.1471	0.9360	0.2238	0.0179	0.0059	0.0023	0.0000	0.0008	0.0000
O_3	0.4407	0.1667	0.2252	0.0182	0.0060	0.0024	0.0000	0.0008	0.0000
	0.4500	0.6667	0.3219	2.00[3]					
$N^{\parallel+\perp}$	0.4779	0.6791	0.4235	2.13[3]					
$C_1^{\parallel+\perp}$	0.4912	0.8065	0.4644	2.13[3]					
$C_2^{\parallel}$	0.5074	0.8022	0.5594	2.13[3]					
$C_3^{\parallel}$	0.5221	0.6791	0.6069	2.13[3]					
$C_4^{\parallel+\perp}$	0.5074	0.5475	0.5541	2.13[3]					
$C_5^{\parallel}$	0.4912	0.5475	0.4617	2.13[3]					
$C_6^{\parallel}$	0.7088	0.6791	0.4617	2.13[3]					
$C_2^{\perp}$	0.7279	0.6706	0.5567	2.13[3]					
$C_3^{\perp}$	0.2794	0.6706	0.5567	2.13[3]					
$C_6^{\perp}$	0.2647	0.6791	0.4617	2.13[3]					

[1] The symbols ∥ or ⊥ refer to atoms in aromatic rings which are either parallel or perpendicular to the b*c* plane.

[2] The x positional parameters for the silicate atoms are derived from Shirozu and Bailey (1966). For the organic atoms they are from Slade and Stone (1983).

[3] Temperature factors for the organic atoms are from an isotropic refinement.

which is the average length, quoted by the International Tables for Crystallography (1962), for N–H–O bonds. The three amine-hydrogen atoms of an organic cation are therefore likely to be involved in the formation of hydrogen bonds to three surface oxygens of an adjacent silicate layer. The *para*-carbon–oxygen distances appear to be normal van der Waal contact distances when hydrogens are interposed between the carbon and oxygen atoms.

THREE-DIMENSIONAL ORDER

As mentioned above, Figure 1 shows that the $0kl$ reflections (including the $02l$ and the $04l$ reflections) for aniline-vermiculite are sharp and discrete. This sharpness of the $k \neq 3n$ reflections implies that the positions of adjacent silicate layers are rigorously determined by the characteristics of the interlayer region; random shifts, e.g., $\pm b/3$, do not occur. The present study shows that the ditrigonal cavities in adjacent silicate layers of aniline-vermiculite are positioned opposite to each other. The positions are controlled by the aniline cations which have quite specific linkages to the surface oxygen atoms surrounding the cavities. These linkages, which involve N–H–O bonds and van der Waal forces, combine with packing considerations to produce close-packed aniline groups along rows perpendicular to [010] (see Figure 3 in Slade and Stone,

1983). Therefore, the only translations parallel to [010] which can occur between adjacent layers must leave the ditrigonal cavities opposite each other. Such translations are $\pm b$ or $\pm(b/2 + a/2)$; hence aniline-vermiculite will be fully ordered because the silicate layers are c-face centered.

CSIRO Division of Soils   P. G. SLADE
Private Bag No. 2   P. A. STONE
Glen Osmond (5064)
South Australia, Australia

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