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VERMICULITE-ALKYL AMMONIUM COMPLEXES

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ABSTRACT

The structures of a series of alkyl ammonium-vermiculite complexes were examined by unidimensional Fourier methods, supplemented by microcarbon analyses to confirm alkyl ion content.

With any given alkyl ion, a series of complexes forms with differing 001 periodicities. In each case the alkyl chain orientation is maintained at 55 ± 5°. The variations in periodicity are due to variations in degree of interfingering of alkyl chains attached to each adjacent silicate surface.

The multiple series of alkyl-vermiculite complexes can be represented by the general formulae:

$$[Mg_6Al_2Si_6O_{20}(OH)_4]^{-2.00}\ {}^{+}[H_3N\text{-alkyl}]_2 \cdot 2\ \text{alkyl-}NH_2$$

$$[Mg_6Al_2Si_6O_{20}(OH)_4]^{-2.00}\ {}^{+}[H_3N\text{-alkyl}]_2 \cdot 1\ \text{alkyl-}NH_3Cl$$

$$[Mg_6Al_2Si_6O_{20}(OH)_4]^{-2.00}\ {}^{+}[H_3N\text{-alkyl}]_2 \cdot 2\ H_2O$$

$$[Mg_6Al_2Si_6O_{20}(OH)_4]^{-2.00}\ {}^{+}[H_3N\text{-alkyl}]_2$$

INTRODUCTION

There is a continuing and growing interest in the properties of organic-layer silicate complexes. Since the early studies by Bradley (1945) and MacEwan (1948) of alcohol montmorillonite complexes, interest has grown to include an ever widening circle of organic compounds and layer silicates species (Weiss, 1963).

Considerable attention has been given to the alkyl ammonium-silicate complexes generally formed in aqueous solution by exchange reactions in which the inorganic exchange ions are replaced by alkyl-ammonium ions. Montmorillonite-alkyl ammonium intercalcation has been studied in particular by Jordan (1949) and Weiss (1963); similar complexes with micas and vermiculites have been investigated by Weiss, Mehler, and Hofmann (1956), Sutherland and MacEwan (1961), and Garrett and Walker (1962), and others.

The intercalation of large alkyl-ammonium ions results in variable (00*l*) periodicities, which have been related in various instances to differences in alkyl chain length, layer silicate surface charge density, and method of preparation. In turn these observed variations can be rationalized in terms of different orientations with respect to layer silicate surfaces of the intercalated aliphatic chains. This rationale has led Weiss and his coworkers (1956, 1960) to suggest that alkyl chain orientation, as deduced from 00*l* periodicities, can be used to measure the magnitude

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of interlayer charge in micaceous layer silicates. It was this aspect which we set out to investigate further, hoping to be able to more fully characterize the micaeous constituents of polycomponent mixtures.

The normal procedure for studying organic-layer silicates, involving X-ray measurement of (001) periodicities, was employed first. The interlamellar space available for the organic molecule was determined and, along with the known dimensions of the organic molecule, molecular orientations were deduced which were compatible with the space limitations. In addition it was desirable to go beyond this procedural strategy to collect additional data to confirm postulated alkyl chain orientations. To this end the study was limited to a series of alkyl ammonium vermiculite single crystal complexes. From these appropriate X-ray data could be collected for unidimensional electron density determinations, and the identical single crystals could be subjected to micro-carbon analysis to confirm theoretical models.

EXPERIMENTAL MATERIALS

Most of this investigation involved complex formation, utilizing the Fe-free vermiculite from Llano Co., Texas (Clabaugh & Barnes, 1959; Bradley & Serratosa, 1960). In addition several complexes were made and studied using batavite (supplied by Dr. Sigmund Koritnig, Mineralogisches Institut, Goettingen) and West Chester, and Kenya vermiculites (supplied by Dr. G. F. Walker).

These vermiculities are different in their layer charges. The reported values per $O_{10}(OH)_2$ structural unit are as follows:

Llano	0.98	(Bradley & Serratosa, 1960)
Batavite	0.67	(Weiss, 1963)
	1.00	approx. (this study)
West Chester	0.7	(Garrett & Walker, 1962)
Kenya	0.65	(Garrett & Walker, 1962)

SAMPLE PREPARATION

All of these vermiculities have divalent Mg^{2+} and/or Ca^{2+} as exchangeable cations. In order to facilitate organic alkyl-ammonium exchange, the inorganic divalent ions were first replaced by Li, by reation at room temperature with 1N LiCl, and then washed to remove excess LiCl.

Several crystals of each Li-vermiculite were converted to alkyl ammonium complexes by reaction with the hydrochlorides of either butyl (C_4), hexyl (C_6), octyl (C_8), decyl (C_{10}) or dodecyl (C_{12}) normal amines. The reactions were carried out by refluxing the single crystals (2×2×0.1 mm) at 80°C in 3N amine hydrochloride. The progress of the reaction was monitored by periodically removing crystals from the reaction solution, and examining the (00*l*) X-ray reflections. Reaction was deemed complete when rational series of (00*l*) reflections were obtained which did not change with further reaction.

X-ray data were obtained from the alkyl ammonium complexes after reaction but prior to washing and drying, following various degrees of washing, and following complete removal of hydrochlorides and drying at 65°C.

X-RAY RESULTS

In Figure 1 are plotted the (001) spacings obtained with alkyl ammonium ions of differing chain lengths. The open circles represent data collected in this study from a number of different vermiculites. Llano complexes are designated by L, batavite by B, West Chester by W, and Kenya by K. All of these are (001) values from sequences showing perfect rational series of orders. The small points represent complexes made which exhibit departures from rationality. Additional data were taken from the literature and will be referred to later.

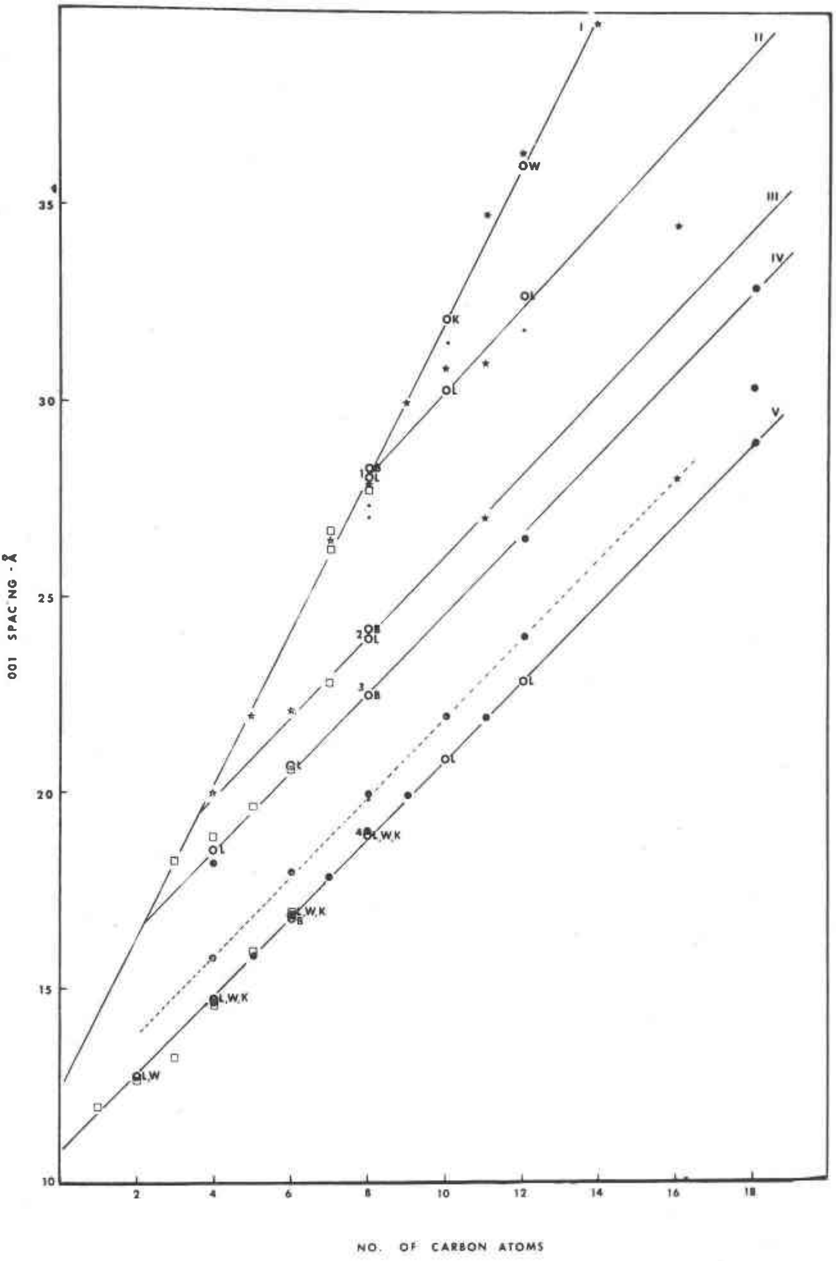
The complexed crystals which had been extensively washed and dried, gave (001) values lying along line $\overline{V}$ of Figure 1. The points lying above this reference line are from crystalline phases that had been for the most part either insufficiently washed to remove excess amine hydrochloride or had not been dried to remove excess H_2O.

Two observations of significance can be made immediately, referring to Figure 1:

1) For each alkyl ammonium complex the minimum basal (001) spacing falls on the straight line $\overline{V}$.
2) Each alkyl ammonium-vermiculite complex (butyl, hexyl, octyl, decyl, dodecyl) exhibits more than one crystalline phase. This had been noticed previously by others (Weiss, *et al.*, 1956; Sutherland and MacEwan, 1961; and Garrett and Walker, 1962). In fact Weiss (1956) has interpreted these multiple spacings to represent significant variation in the inclinations of the long aliphatic chains. Such an interpretation does not appear alone to be compatible with the cumulative data and we shall propose an alternative interpretation.

Line $\overline{V}$ of Figure 1, determined by regression analysis of the data for the C_4, C_6, C_8, C_{10} and C_{12} Llano vermiculite complexes, has the form $y=10.184+1.013x$. The slope of this line is determined by and, therefore, fixes the orientation of the aliphatic chains relative to the layer silicate surface for this series of complexes. This slope, representing incremental increases of d_{001} of 2.03 Å per increase in aliphatic chain length from C_4 to C_6, etc., indicates a chain orientation of $54^\circ 48^1$ relative to the layer silicate surface. The theoretical increase for this orientation is 2.05 Å. Thus the orientation indicated is as illustrated in Figure 2 for a hexyl complex. With this orientation the C–N bond of the alkyl ammonium ion is perpendicular to the silicate substrate.

The structural interpretation of the high spacing complexes (points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NO. OF CARBON ATOMS

Fig. 1

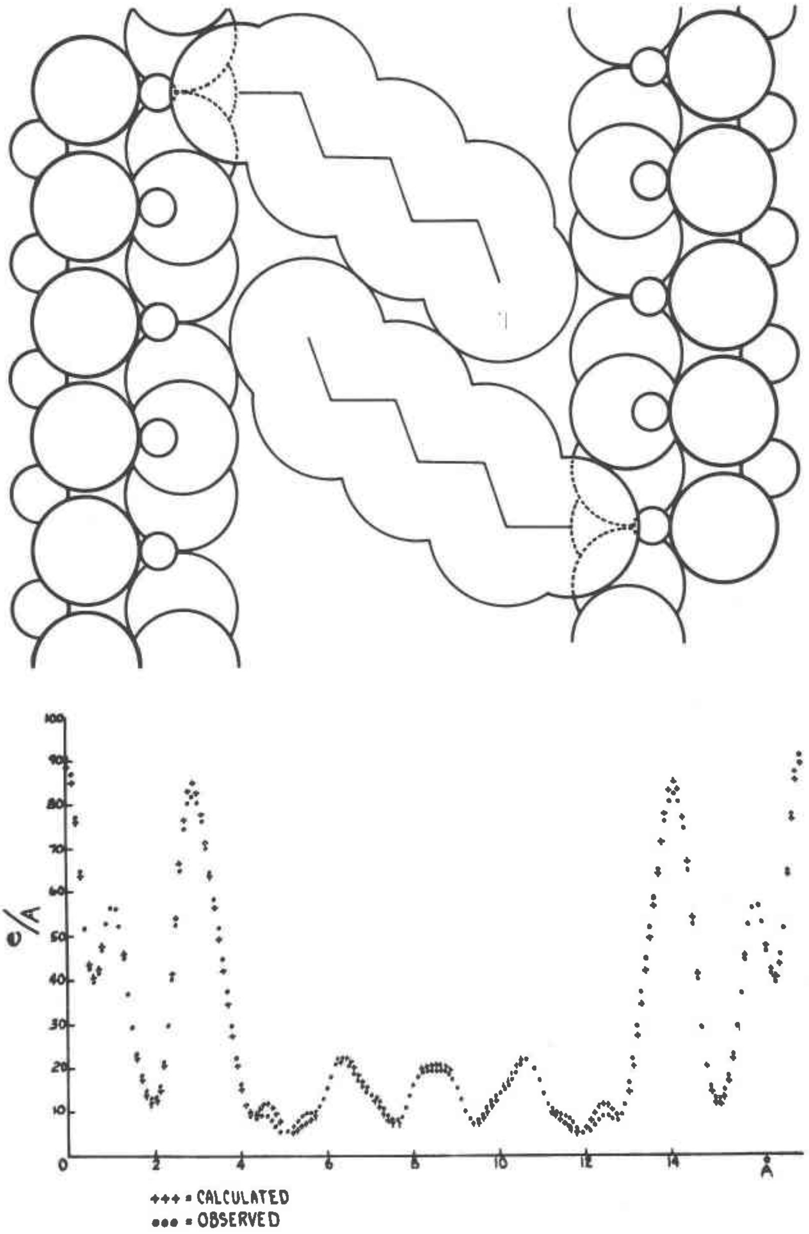

FIG. 2. Structure of hexyl complex (fully collapsed).

lying above line $\overline{V}$ of Figure 1) is far less certain. In order to ascertain the structures of these phases, to examine the low spacing phases in more detail, and to interrelate the structures of all phases, a suite of selected alkyl ammonium complexes was singled out for more detailed structural analysis.

STRUCTURAL ANALYSIS

For more detailed structural interpretation, appropriate X-ray data were collected which permitted [001] electron density distributions to be ascertained by Fourier methods. For the Fourier calculations atomic scattering factors for inorganic atoms from Bragg & West (1929) were used; for the organic atoms, values based on those from the International Tables were derived. Calculated F factors were modified by application of a temperature correction term, $B = 3.75$ Å^2.

Single crystals of the 14.75 Å butyl-, 17.0 Å hexyl-, 19.0 Å octyl-, 20.95 Å decyl-, and 22.9 Å dodecyl- Llano vermiculite complexes were used for this study. These will be referred to as the *fully collapsed phases.* In addition the 28.1 Å and 24.0 Å octyl complexes (indicated by points 1 and 2 in Figure 1) were selected as key representatives of the higher spacing complexes, the "expanded" phases, along with the 20.75 Å hexyl Llano complex. These were chosen because each phase produced an extended series of 001 orders necessary for significant resolution in the electron density plots.

The orientation of the organic cation intercalated in vermiculite can be determined if the coordinates of the atoms of the entire crystal are ascertained. The coordinates of the atoms in the vermiculite silicate skeleton were taken as those previously determined by Mathieson Å Walker (1954) and later refined by Mathieson (1955). Dimensions of intercalated organic cations were determined from the data of Kitaigorodskii (1961), using the radii of C (1.82 Å) and N (1.57 Å), bond angle (109°28^1), C–C bond length (1.54 Å) and N–C bond length (1.47 Å).

Observed (001) reflection intensities were converted to structure factors and with normalization, compared to calculated F factors for a large number of trial models. Further refinement was achieved from [001] electron density plots, calculated from separate sets of observed and calculated F values. These had additional value in denoting in a semi-quantitative manner the presence or absence of the more highly scattering Cl^- ion (present as alkyl amine hydrochloride).

In every case trial models were proposed, assuming organic chain orientations relative to the silicate substrate of 45°, 50°, 55°, 60° and 65°. A large number of trial models was made feasible by applying computer techniques.

Fully Collapsed Phases. The structures of the butyl- (14.75 Å), hexyl- (16.98 Å), octyl- (19.03 Å), decyl- (20.95 Å), and dodecyl- (22.90 Å) ammonium Llano vermiculite were examined in greater detail. Various trial models were proposed, varying the angle of aliphatic chain inclination by as much as $\pm 10°$ from the 55° orientation indicated from the slope of line $\overline{V}$ of Figure 1. Although [001] electron density plots for the shorter chain complexes are not very sensitive to small variations in chain orientation, significant variations in atomic coordinates for the longer chains (C_{10}, C_{12}) result in more definitive interpretations in these cases. The results of these studies indicate that all of the fully collapsed Llano vermiculite complexes exhibit chain orientations of $55 \pm 5°$.

In addition, organic atomic coordinates were varied, positioning the NH_3 group at various levels relative to the silicate surfaces. Electron density plots were calculated placing the N atom at distances from the origin (center of silicate sheet) varying between 4.60 and 4.85 Å. Best agreement between calculated and observed electron densities was achieved with the N at 4.65 Å from the origin. This parameter places the - NH_3 group well within the hexagonal (trigonal) "hole" on the layer silicate surface.

In making the structure factor calculations, and ultimately the electron density plots, it was assumed that the number of alkyl ammonium ions present is in compliance with the charge of 0.98 per O_{10} $(OH)_2$ structural unit.

In summary, for each of the fully collapsed phases studied (C_4, C_6, C_8, C_{10}, C_{12}) the following structural arrangement was confirmed:

1. Alkyl chains inclined at 55° to the silicate surface.
2. N–C bond perpendicular to the silicate surface, with N located at 4.65 Å from the center of the silicate sheet.
3. Compositions are represented by the formula $[\text{vermiculite}]^{-2.00}$ $[^{+}H_3N\text{-alkyl}]_2$.

For comparison the calculated and observed structure factors are compiled for each complex.[1] Figure 2 shows schematically the accepted structure, illustrated by the hexyl ammonium complex. In addition the calculated and observed electron density plots are shown, based on this proposed model. Thus these collapsed phases exhibit an interfingering of organic chains, with each of the chains making contact with the opposite basal oxygen surface, extending from the surface to which it is bonded.

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[1] A table listing calculated and observed structure factors has been deposited as Document No. 9657 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington, D. C. 20540. Copies may be secured by citing the document number, and remitting in advance $1.25 for photoprints or $1.25 for microfilm.

Expanded Octyl Ammonium Complexes. The following sequence of treatments produced a series of octyl amine vermiculite-complexes with progressingly decreasing basal spacings.

1. Following reaction with octyl amine hydrochloride, an unwashed crystal, dried at 65°C produced a sequence of ordered (00l) reflections related to a 28.13 Å periodicity.
2. When this crystal, or a duplicate was soaked in H_2O and heated overnight at 65°C, a new phase with a rational sequence of orders gave a d_{001} value of 24.00 Å.
3. When this crystal (actually a duplicate crystal of batavite) was subjected to additional washing and *air dried*, a 22.6 Å spacing resulted.
4. Subsequent drying at 65°C, resulted in further reduction in d_{001} to 19.03 Å, producing the fully collapsed phase described above.

This sequence of octyl amine complexes is indicated by points 1, 2, 3, and 4 respectively in Figure 1. The reduction in spacing and consideration of the washing and drying sequence, suggest that the former was related to removal of water soluble (amine HCl) material and/or water from interlayer space.

It was felt that more detailed structural analyses of these octyl amine phases held the key to the structural interpretation of the total data represented in Figure 1.

Fully-expanded (28.13 Å) Phase (point 1, Fig. 1). In considering possible structures, it was apparent that no simple change in the angle of chain inclination could account for the large basal spacing. This spacing was, however, compatible with a model derived from the collapsed phase by spreading the silicate sheets apart, until interfingering chains stand end on end, still maintaining approximately their 55° inclination. It would seem likely that the vacated space might be filled with neutral octylamine hydrochloride molecules, standing parallel to the octyl ammonium ions. However, since this assemblage of organic molecules would completely fill the interlayer space, there would be no room to accommodate the large Cl^- ions. Accordingly it was assumed that neutral octyl amine molecules were intercalated, apparently produced upon heating from initially absorbed hydrochloride by volatilization of HCl. We might expect that the organic assemblage would exhibit packing analogous to that in long chain organic crystals.

Trial models were proposed, maintaining a projected 2.90 Å separation between the terminal C atoms of opposing organic molecules. This separation distance is maintained in the structure of n-hexadecanol, determined by Abrahamson, *et al.* (1960). Having fixed the coordinates of the terminal carbon atoms, various trial structures were proposed, varying chain inclinations to the extent compatible with d_{001} spacings. After numerous trials, the model shown in Figure 3 was accepted. Terminal C atoms are at 12.62 Å and N atoms at 4.80 Å from the origin. These parameters result in an aliphatic chain inclination of 51° relative to the substrate surface. It is to be noted that two organic molecular orientations are involved. Half of the molecules have their C–N bonds essentially perpendicular to the silicate substrate, the other half highly inclined to it. The analysis does not permit specific assignment of either orientation to octyl ammonium ions or neutral octyl amine molecules. Because C atoms are fairly evenly distributed in projection along 001, electron density plots are uninteresting due to lack of resolution, and are thus omitted. Calculated and observed F values ($B = 5.0$ Å^2) based on this model are tabulated in Table 1. The resulting composition of this complex can be represented as:

$$[Mg_6Al_2Si_6O_{20}(OH)_4]^{-2.00}\ {}^+[H_3N\text{-octyl}]_2\cdot 2\ \text{octyl-}NH_2$$

Partially Collapsed (24.00 Å) Phase (point 2, Fig. 1). Various models were considered involving changes in alkyl chain orientation, but none were compatible with the electron density distributions based on the observed data. After many trials, the model depicted diagramatically in Figure 4 was confirmed by comparison of calculated and observed [001] electron density plots (also shown in Fig. 4). Washing of the fully expanded phase had resulted in removal of one-half of the adsorbed neutral octyl-amine HCl. The remaining neutral molecules change their inclined orientation and now lie parallel to the silicate surface. The octyl ammonium ions begin to interfinger still maintaining their 55° inclination. Each approaches to within 5 Å of the opposite silicate sheet. This would suggest that the neutral molecules are lying with their plane of symmetry perpendicular to the silicate surface (van der Waals diameter approx. 5 Å). Calculated and observed structure factors for this model are compared in Table 1.

The composition of this phase can be represented as

$$[Mg_6Al_2Si_6O_{20}(OH)_4]^{-2.00}[{}^+H_3N\text{-octyl}]_2\cdot 1\ \text{oct-}NH_3Cl.$$

Partially Collapsed (20.8 Å) Llano Hexyl Complex (point 3, Fig. 1). From Figure 1 it is clear that another partially collapsed phase forms alkyl complexes with somewhat reduced spacing. No Llano complex was produced in this case, but a batavite (octyl) complex with a 22.6 Å spacing was formed. Several crystals of this complex were analyzed chemically as referred to later. The remaining crystals did not give a sufficiently extended series of orders for good electron density resolution.

Consequently an analogous Llano-hexyl complex with a 20.8 Å spacing (point 3, Fig. 1) was used for more detailed analysis. Observed electron density plots indicated the presence of moderately scattering atoms at the 6.1 Å level, suggestive of water. This seemed reasonable also in light of the fact that drying at 65°C converted this phase to the fully collapsed form. After numerous trial models, the one depicted in Figure 5 was accepted as essentially correct. The aliphatic chains maintain their 55° orientation, interfingering with one another. Full collapse is prevented by the presence of H_2O molecules. In Figure 5 the calculated and ob-

TABLE 1. STRUCTURE FACTORS, EXPANDED AND PARTIALLY COLLAPSED PHASES

Order	1 Octyl amine-vermiculite (fully expanded) $d_{001}=28.13$ Å		2 Octyl amine-vermiculite (partially collapsed) $d_{001}=24.00$ Å		3 Hexyl amine-vermiculite (partially collapsed) $d_{001}=20.79$ Å	
	$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$
000	—	+677	—	+623	—	+490
001	+283	+255	211	+220	177	+219
002	145	+130	78	+ 90	60	+ 87
003	62	+ 64	10	+ 28	15	− 35
004	15	− 33	27	− 14	41	− 36
005	40	− 38	86	− 87	9	+ 5
006	67	− 50	51	+ 42	127	+119
007	38	+ 54	166	+158	139	+143
008	131	+102	133	+118	43	+ 34
009	118	+123	55	+ 52	38	− 27
0010	82	+ 83	6	− 10	69	− 60
0011	23	+ 40	45	− 19	59	− 63
0012	19	− 21	94	− 94	10	− 15
0013	43	− 31	46	− 58	39	+ 38
0014	79	− 82	3	+ 7	46	+ 50
0015	53	− 69	32	+ 43	42	+ 36
0016	8	+ 10	46	+ 38	40	+ 32
0017	15	+ 15	46	+ 38	35	+ 36
0018	22	+ 33	43	+ 42	23	+ 19
0019	28	+ 31	33	+ 36	16	+ 7
0020	34	+ 33			18	+ 17
0021	26	+ 29			17	+ 13
0022	22	+ 26			26	+ 16
0023					24	+ 17
0024					25	+ 15

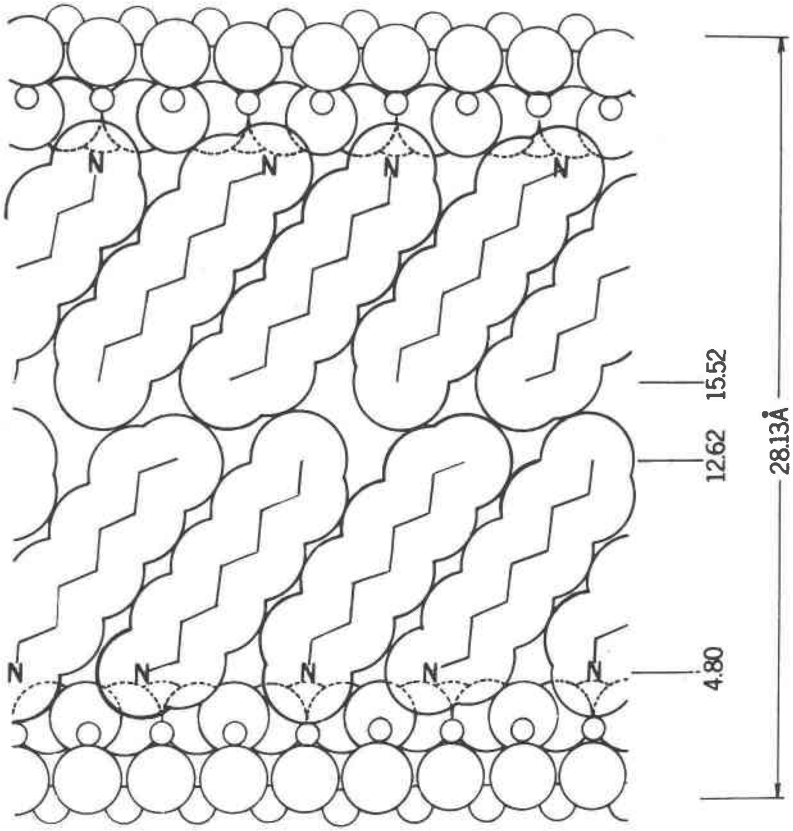

Fig. 3. Structure of octyl complex (fully expanded).

served electron density plots, based on this model are given also for comparison. Calculated and observed F factors are listed in Table 1.

The composition of this phase can be represented as:

$$[\text{vermiculite}]^{-2.00} + [\text{H}_3\text{N-hexyl}]_2 \cdot 2\text{H}_2\text{O}$$

Carbon Analyses

Further confirmation of these structural interpretations comes from direct carbon micro-analysis of the crystals used for structure determination. Utilizing a F&M model 800 Analyser, carbon analyses could be made on complexed crystals weighing as little as 0.5 mg. The procedure involved oxidation of the organic complex using an oxidizing catalyst. The CO_2 produced was automatically collected and measured quantitatively by gas chromatography. Table 2 shows the results of the analysis, each value representing the mean of two separate analyses.

These data confirm the proposed structural compositions of the various octyl ammonium Llano complexes. Indirectly they confirm also the layer charges assigned to Llano vermiculite, and our supposition that the batavite studied by us has the same interlayer charge, essentially that of an ideal mica, 2.00 per $O_{20}(OH)_4$ structural unit.

The structural studies show that the multiplicity of phases with a particular alkyl ion is not related so much to significant variation in alkyl

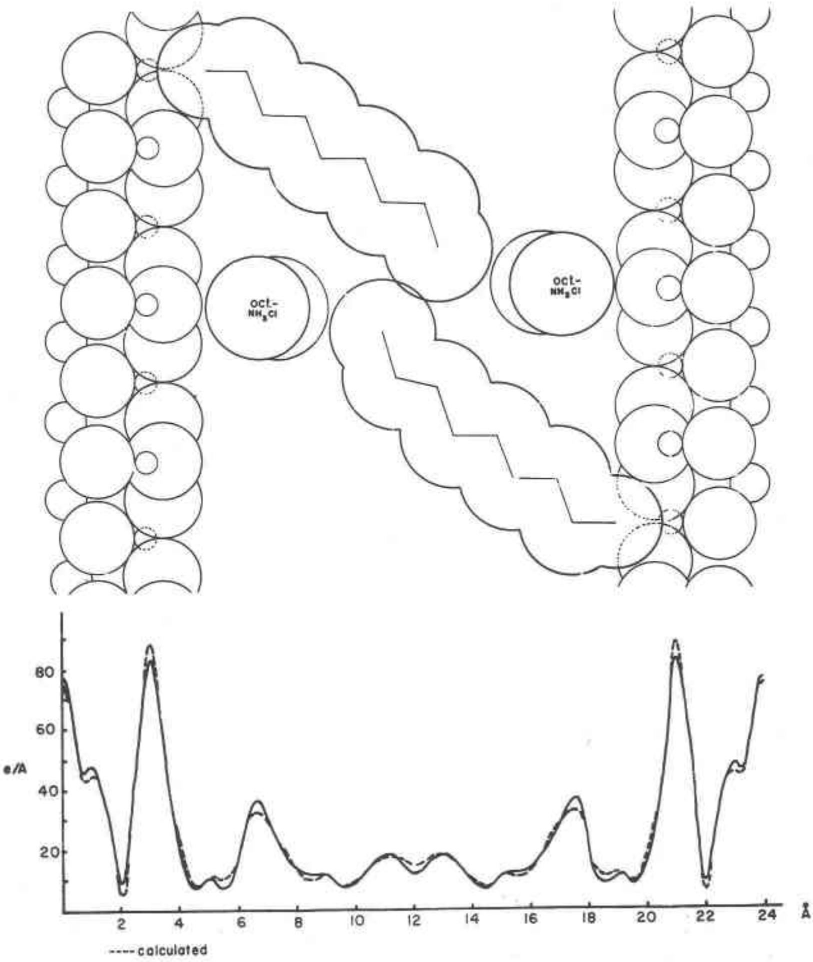

FIG. 4. Structure of octyl complex (partially collapsed).

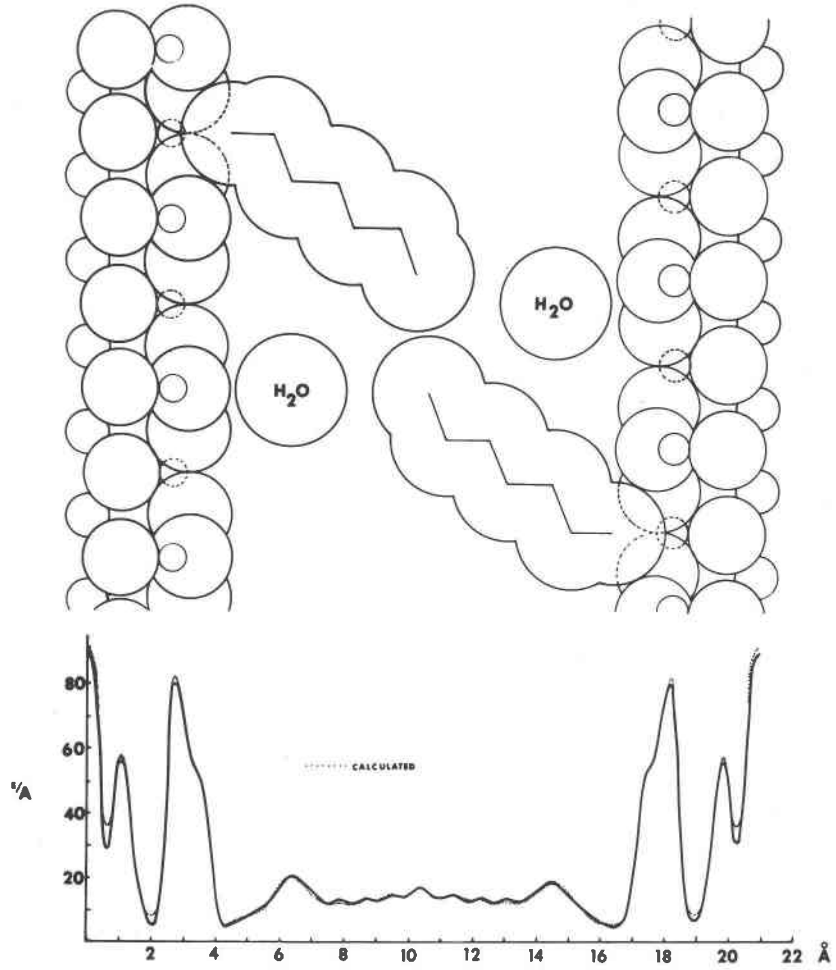

Fig. 5. Structure of hexyl complex (partially collapsed).

chain orientation, as interpreted by Weiss, *et al.* (1960), but is more simply related to varying degrees of interfingering of alkyl chains, which in all cases approximate the ideal 55° inclination.

Although we have discussed here in some detail the octyl ammonium complexes, a series of analogous phases should be expected also for the entire homologous series. Based on the proposed structures for the octyl phases, curves I, III, and IV were constructed (Fig. 1). From these d_{001} spacings can be predicted for analogous phases of a wide variety of alkyl ammonium vermiculite complexes.

The previous published data of Weiss, *et al.* (1956), Sutherland and MacEwan (1960), and Garrett and Walker (1962) are plotted also in Figure 1. These include data for both odd and even numbered aliphatic, chains, ranging from butyl to octadecyl.

It is noteworthy that essentially all data group themselves along the theoretical curves. It is now possible to interrelate structurally the studies of vermiculite complexes carried out by numerous investigators. Line I, representing fully expanded phases, and line V (fully collapsed phases) represent boundary situations, all intermediate points representing partially collapsed phases.[1] The group of points (Figure 1, dotted line) representing batavite complexes produced by Weiss, *et al.* (1956), are the only data inconsistent with our structural interpretations. We have no satisfactory explanation for these, although we were able to produce an octyl-ammonium baravite phase with an 18 Å (001) spacing that gave an irrational sequence of orders, indicating mixed layering.

Table 2

Inter-layer composition per $O_{20}(OH)_4$ structural unit	Theoretical %C	Measured %C
1. $2[^{+}H_3N\text{-octyl}]\text{-}2\ \text{octyl-}NH_2$ (28.1 Å)	29.5	28.7 (L)[a] 28.8 (B)[a]
2. $2[^{+}H_3N\text{-octyl}]\text{-}1\ \text{octyl-}NH_3Cl$ (24.00 Å)	23.4	21.9 (L)
3. $2[^{+}H_3N\text{-octyl}]\text{-}2\ H_2O$ (22.6 Å)	18.3	18.45 (B)
4. $2[^{+}H_3N\text{-octyl}]$ (19.03 Å)	18.9	19.34 (L) 19.35 (B)

[a] (L) Llano, (B) Batavite.

Slight departures of points from the theoretical curves may be due to variations in layer charge among the various vermiculites represented, or may be the result of slight amounts of mixed layering. Spacings represented by the small dots in Figure 1 represent mixed layer phases produced by us.

Another grouping of spacings occurs around curve II. Scatter about this curve is more severe than in all other cases. Data were insufficient

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[1] The upper boundary was called to our attention in discussions with Dr. G. F. Walker who produced the boundary curves also with a more complete series than our own of alkyl ammonium Llano vermiculite complexes.

to make detailed structural interpretations of these phases. We would presume that these phases, representing the longer chain complexes, represent varying degrees of interfingering of organic ions, intermediate between full expansion and the partial collapsed phases interpreted earlier.

In summary, phases falling along curves I, III, IV, and V can be represented respectively by the following compositions:

I. $[\text{vermiculite}]^{-2.00}\ {}^{+}[H_3N\text{-alkyl}]_2 \cdot 2\ \text{alkyl-}NH_2$
III. $[\text{vermiculite}]^{-2.00}\ {}^{+}[H_3N\text{-alkyl}]_2 \cdot 1\ \text{alkyl-}NH_3Cl$
IV. $[\text{vermiculite}]^{-2.00}\ {}^{+}[H_3N\text{-alkyl}]_2 \cdot 2H_2O$
V. $[\text{vermiculite}]^{-2.00}\ {}^{+}[H_3N\text{-alkyl}]_2$

The structural interpretations of aliphatic chain orientation lead to two further structural implications:

1) The organic molecules in the interlayer region of vermiculites must be close packed.
2) H-bonding must be involved between NH_3^+ groups of the amine and oxygen of the basal oxygen surfaces of the silicate layers.

INTERMOLECULAR PACKING

It is possible to denote the extent of intermolecular packing from knowledge of the number of molecules associated with each silicate interface, their orientation, and their molecular dimensions. All of these factors are known from the structural studies. It has been pointed out that the organic ions enter the interlayer region by ion exchange. In Llano and batavite vermiculite the silicate surfaces are very densely populated with exchange sites. From the layer change, confirmed by the micro-chemical carbon analyses, these vermiculites have a layer charge approaching an ideal 2.00 per $O_{20}\,(OH)_4$ structural unit. This means that there is one exchange site per each oxygen surface per unit cell. Since these exchange sites must be regularly distributed, the organic cations must likewise be arranged in an orderly manner. This regularity is shown by the well-ordered sequence of 001 orders of each complex.

From the molecular dimensions of the organic cations and their orientation relative to the silicate substrate, the surface area occupied by each molecule can be calculated. By assuming the alkyl chain to have a rectangular cross-section perpendicular to the chain axis, with the dimensions 4.0×4.9 Å, and an angle of inclination of $54°48^1$, the surface area per molecule is 24.00 $Å^2$. (51° and 25.1 $Å^2$ in case of the fully expanded phases). These values agree very well with the value of 24.46 $Å^2$

per exchange site, based on the lattice dimensions of vermiculite (Mathieson & Walker, 1954) and the assignment of two alkyl groups per unit cell (5.33×9.18/2). Thus it appears that the interlayer organic population and orientation is such as to permit van der Waals contact between molecular groups. Minor adjustment of the organic groups from the idealized arrangements shown in Figures 2–5 could result in more perfect close packing. Inasmuch as this study revealed no significant differences, in organic molecular orientation between high and lower charge vermiculites, one can speculate that in the latter, alkyl groups occur as clusters over the silicate surfaces, maintaining van der Waals contact within clusters, or that close packing is maintained by adsorption of neutral molecules.

HYDROGEN BONDING

The role of hydrogen bonding, involving polar groups and silicate basal oxygen atoms, has been considered often in connection with studies of organic-layer silicate complexes. Bradley (1945), MacEwan (1948), Green-Kelly (1955) and others have postulated C–H · · · O bond formation between alcohols and similar compounds and layer silicates. In determining the orientation of adsorbed polar molecules, Emerson (1957) focused on the directional orientation of potential hydrogen bonds formed between oxygen atoms of the silicate substrate and electronegative atoms in the adsorbed molecule. He assumed that OH · · · O bonds are formed with alcohols, and suggested that these must be essentially linear and directed to form at the tetrahedral angle dictated by the oxygen sp^3 orbitals. Brindley and Ray (1964) accepted Emerson's model for OH · · · O bonds and could infer molecular orientations for long chain primary alcohol complexes with montmorillonite which were consistent with experimental data. Weiss, *et al.* (1957) likewise discussed the role of hydrogen bonding in alkyl ammonium-vermiculite complexes.

As we look at the structures of the alkyl ammonium-vermiculite complexes it seems significant that the alkyl chain orientation always assumed leaves the C–N bond essentially perpendicular to the silicate substrate. It is important that with this orientation, the three hydrogen atoms of the NH_3^+ group are disposed tetrahedrally, constituting the corners of the base of the nitrogen coordination tetrahedron. In these positions they are capable of forming essentially linear bridges between the N of the organic molecule and the tetrahedrally disposed hybrid sp^3 orbitals of oxygen. It appears likely that the triads of -N–H · · · O bonds form at alternate sites in the hexagonal array of potential sites about the "holes" in the oxygen surface, stablizing the observed organic molecular orientation.

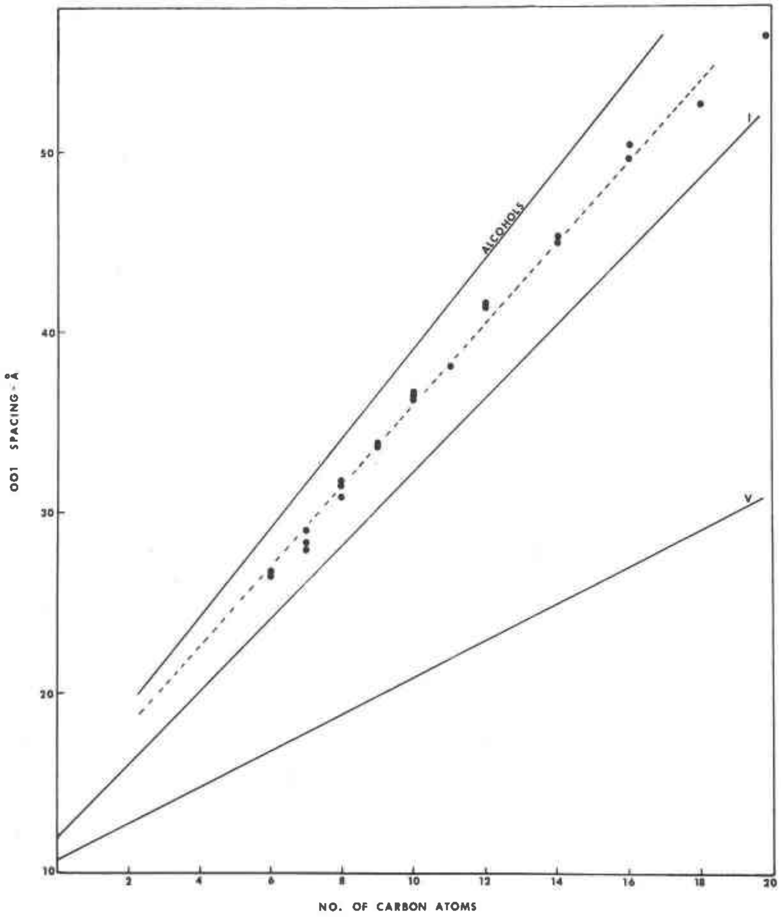

FIG. 6. Variations of d_{001} spacings with aliphatic chain length. (Neutral amines in vermiculite); points from Sutherland & MacEwan (1961); alcohol curve from Brindley & Ray (1964).

From the structures adopted it is possible to evaluate H · · · O bond formation in the conventional manner, by looking for shortening of N–O distances. The z parameters for N and basal O are 4.65 Å and 3.28 Å respectively. Assuming that the NH_3^+ groups are symmetrically located at the centers of the hexagonal holes, simple calculation shows that the N–O distance is 3.00 Å, indicative of hydrogen bond formation. By comparison, Fourier analysis of diffraction data from NH_4^+-vermiculite places the N in this case at 5.15 Å from the origin. This leads to a N–O distance of 3.26 Å, the difference being attributable to lack of N · · · O bonding with the spinning, effectively spherical NH_4^+ ion. The 55° orientation of the alkyl chains thus permits localization of the three equivalent N–H · · · O bonds. It might be expected that as the number of H atoms associated with the electronegative atom of the organic molecule decreases, different chain orientations would be permissible. This seems to be the case. In Figure 6 a series of curves represents 001 spacings for a number of organo-layer silicate complexes. Curves I and IV correspond to the limiting curves from Figure 1. Points indicated represent the data of Sutherland and MacEwan (1961) for neutral amine-vermiculite complexes, and the additional curve analogous data from Brindley and Ray (1964) for alcohol-montmorillonite complexes. Thus it appears that as the number of hydrogen atoms per organic group decreases from three ($-NH_3$) to two ($-NH_2$) to one (OH), a systematic increase in aliphatic chain orientation follows. Presumably appropriate spatial distributions of N–H · · · O or OH · · · O bond are still permitted. The greater slope of the Brindley and Ray curve also reflects influence of the smaller *a* and *b* dimensions of montmorillonite. Equal populations of molecules per unit cell must stand more nearly vertical on the smaller basal area.

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