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STRUCTURAL STUDY OF TETRAMETHYLPHOSPHONIUM-EXCHANGED VERMICULITE

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Abstract—Vermiculite from Santa Olalla, Spain, was intercalated with tetramethylphosphonium [$P(CH_3)_4^+$ = TMP], using a TMP-bromide solution at 70°C for three weeks. The resulting TMP-exchanged vermiculite, which contained a small (<5% of a site) amount of residual interlayer Ca, showed near perfect three-dimensional stacking. Cell parameters are a = 5.3492(8) Å, b = 9.266(2) Å, c = 14.505(6) Å, β = 97.08(2)°, space group is *C2/m*, and polytype is *1M*. Single-crystal X-ray refinement (R = 0.052, wR = 0.061) located two crystallographically unique sites for the phosphorus atoms (TMP molecule). The phosphorus atoms are occupied partially [P1 = 0.146(6), P2 = 0.098(5)] and are offset from the central plane of the interlayer by 1.23 Å to form two P-rich planes in the interlayer. Electrostatic interactions between the P cations and basal oxygen atoms essentially balance the negative charge associated with Al for Si substitutions in the tetrahedral sites. In addition, the orientations of the TMP molecules are probably different owing to packing constraints. The H_2O site is located in the center of the interlayer, at the center of the silicate ring, and ~3.09 Å from the Ca, which is also located on the central plane of the interlayer. Other H_2O molecules are present in the interlayer, but could not be located by the diffraction experiment because they are randomly positioned in the interlayer. The tetrahedral rotation angle, α, is affected by the intercalation of TMP relative to tetramethylammonium (TMA), thus indicating that 2 : 1 layers are not simply rigid substrates, and that dynamic interactions occur during reactions involving adsorption and exchange.

Key Words—Organoclay, Tetramethylphosphonium, Tetramethylphosphonium Vermiculite, TMP-Vermiculite, Vermiculite.

INTRODUCTION

An important class of clays (Barrer, 1984) intercalated with organic cations is the class exchanged with small organic cations, such as tetramethylammonium (TMA) or teramethylphosphonium (TMP). The exchange cations are small and therefore do not completely fill the interlamellar space. The size and shape of the resultant cavities (sometimes referred to as "galleries") are determined by the shape and orientation of the organic molecules (or "pillars"). Thus, these molecules have a great influence on the adsorption behavior of the clay mineral (Barrer, 1989). Barrer and Macleod (1955), Barrer and Reay (1957), Barrer and Millington (1967), and others examined the adsorption properties of this class of sorbents, primarily montmorillonite, with aliphatic, aromatic, and polar organic species. Other workers, such as Gast and Mortland (1971), Rowland and Weiss (1961), Theng *et al.* (1967), and Diamond and Kinter (1961), characterized organo-montmorillonites based on their d(001)-values to obtain information about hydration states and structural features, such as the presence of multiple interlayer planes and possible orientations of the intercalated cations.

The galleries comprise both the surface of the organic molecule and the basal oxygen atom (siloxane) surface of the 2 : 1 layer. It is possible to calculate the spacing between the pillars and the surface area of the sorbate molecules (Barrer and Perry, 1961). More recently, Lee *et al.* (1989, 1990) showed that adsorption properties are functions of pore size and structure and the amount of adsorbed H_2O present. Thus, pillared clays are potentially important for shape-selective adsorption and molecule sieving of organic wastes.

This study examines a phosphorus-based tetrahedral compound, TMP, which is greater in size and consists of a different electronic configuration, than the previously studied (Vahedi-Faridi and Guggenheim, 1997) nitrogen-based compound, TMA, although both molecules have the same tetrahedral shape. Kukkadapu and Boyd (1995) suggested that different hydration properties of TMA-clays *vs.* TMP-clays may explain observed differences in adsorption behavior of these clays. Both this study and Vahedi-Faridi and Guggenheim (1997) involve the use of the same vermiculite starting material, so that structural differences can be observed.

EXPERIMENTAL

Material

Lamellar flakes of high-crystallinity vermiculite from Santa Olalla, Spain, were used in this study. The Santa Olalla deposit is an alteration of pyroxenite, with the vermiculite weathering from phlogopite (Luque *et al.*, 1985). Norrish (1973) determined the structural formula of the vermiculite as $Ca_{0.85}(Si_{5.48},Al_{2.52})(Mg_{5.05}Ti_{0.03}Mn_{0.01}Fe^{3+}_{0.58}Al_{0.28})O_{22}$, based on 22 oxygens (ignited). For exchange experiments, flakes were cut from

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crystals several cm in size to squares of 0.7 mm with a thickness of ~0.05 mm.

Initial experiments at tetramethylphosphonium (TMP) cation exchange used Na intercalation as an intermediate cation-exchange step in an attempt to expand the interlayer to allow for the large TMP cations. However, TMP-exchange reactions yielded better stacking order when the Na intercalation step was omitted. Exchange with TMP was achieved by immersing in a 1M TMP-bromide solution at 70°C for 2–3 weeks. The progress of intercalation was monitored every 48 h, at which time the solution was changed and several individual crystals were examined with a Siemens D-5000 X-ray powder diffractometer. A $d(00l)$-value (= $c \sin \beta$) of 14.39 Å indicated maximum exchange. Approximately 60% of the examined crystals showed this spacing, with no additional lines observed.

A qualitative chemical analysis using an energy dispersive system (EDS) on a JEOL JSM 35C for three TMP-exchanged crystals showed the presence of phosphorous and traces of calcium.

X-ray study

Buerger precession photographs of the TMP-vermiculite crystal chosen for data collection showed a high degree of three-dimensional (stacking) ordering. There was no streaking for $k \neq 3n$ reflections, which is commonly observed for natural vermiculite and which indicates stacking disorder. Reflections of the type: $h + k = 2n$ indicated a *C*-centered lattice, and there was an apparent mirror plane perpendicular to a two-fold axis. This symmetry and the monoclinic cell geometry (see below) indicated space group $C2/m$ and a 1*M* polytype.

Unit cell dimensions were obtained from 216 reflections (27 unique reflections from 8 octants) at 2θ = 35–49° as measured from a Picker four-circle diffractometer with graphite monochromator (MoKα = 0.71069 Å): a = 5.3492(8) Å, b = 9.266(2) Å, c = 14.505(6) Å, β = 97.08(2)°. Data were collected from one-half the limiting sphere from 2θ = 4–60° with h = −14 to 14, k = −14 to 14, and l = 0 to 20. A total of 2278 reflections was collected. Three reference reflections were monitored every 300 min to check for system and crystal stability. Data reduction and refinement used the SHELXTL PLUS (Siemens, 1990) programs. The data were corrected for Lorentz and polarization effects. Psi-scans were taken in 10° intervals in psi and chosen to show variations in 2θ, χ, and ϕ. A total of about 400 psi-scan reflections was collected, which was used in the absorption correction procedures.

For the 2278 reflections measured, reflections were considered observed if the intensity is $>6\sigma$. After averaging to monoclinic symmetry and the rejection of unobserved reflection data, the 2278 reflections reduced to a data set of 967 independent reflections. An additional 40 reflections were rejected on the basis of unusual peak shapes.

Starting atomic coordinates for the refinement consisted of the 2:1 layer from Vahedi-Faridi and Guggenheim (1997). Scattering factors (Cromer and Mann, 1968) were based on half-ionized atoms using the averaging method for "mixed atom" sites (Sales, 1987). Unit weights for reflections and a single scale factor were used in the refinement process. Initially, only the scale factor and atomic positions were varied. After 9 cycles of refinement, which included the isotropic temperature factors, the R value ($R = \Sigma (|F_o| - |F_c|)/\Sigma |F_c|$) decreased to 0.133. A Fourier electron difference map showed positive electron density of 2.1 e/Å^3 and 1.6 e/Å^3 in the interlayer region near the silicate rings. Phosphorus cations were placed in these positions, and further refinement reduced the R value to 0.101, with a P-site occupancy of 0.15 and 0.10, respectively. A subsequent difference map showed positive electron density of 1.2 e/Å^3 at 0.5, 0.167, 0.5, which was interpreted as Ca (see below). Additional refinement indicated a 5% site occupancy. Anisotropic temperature factors were introduced, and R decreased to 0.052 (wR = 0.061). Finally, a difference map located an additional peak at 0, 0, 0.5 at 0.96 e/Å^3 in height, which is well above the background of 3s [the standard deviation, s, of a difference Fourier peak as given by Ladd and Palmer (1977) was calculated for this map at 0.083 e/Å^3]. The peak position does not correlate with any possible methyl-group site, and is believed to be a partially occupied interlayer H_2O site. To identify Ca *vs.* H_2O positions unambiguously, scattering factors for first Ca and then H_2O were considered at each of the two sites. The R factor improved considerably (by ~0.012) for the model where Ca was assigned to 0.5, 0.167, 0.5 and H_2O was assigned to 0, 0, 0.5 compared to alternative models.

Table 1 gives final atomic coordinates and displacement factors for TMP-exchanged vermiculite, and Table 2 gives important interatomic distances and angles.

DISCUSSION

An X-ray crystal structure analysis provides an average description of the structure. Two basic features of an average structure for all organo-exchanged 2:1 phyllosilicate structures determined to date are (a) that the organic molecules occur in sites that are partially occupied and (b) that these sites are located offset from the central plane of the interlayer so that the molecule is closer to one silicate layer than the other. As with previous studies, the average structure of TMP-exchanged vermiculite shows TMP molecules in interlayer sites of partial occupancy [P1 = 0.146(6), P2 = 0.098(5)] and with sites offset from the central plane of the interlayer. For TMP-vermiculite, the offset is 1.23 Å, and two P-rich planes are observed. In ad-

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Table 1. Atomic coordinates of TMP-vermiculite.

ATOM	*x*	*y*	*z*	K[1]	U_{11}[2]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M(1)	0.5	0	0	0.25	0.0095(9)	0.0051(9)	0.024(1)	0	0.0029(9)	0	0.0131(6)
M(2)	0	0.1686(2)	0	0.5	0.0089(7)	0.0052(6)	0.0251(8)	0	0.0024(6)	0	0.0130(4)
T	0.3965(2)	0.1667(1)	0.19010(8)	0.978(6)	0.0077(5)	0.0061(5)	0.0214(6)	0.0000(4)	0.0024(4)	0.0000(4)	0.0117(3)
O(1)	0.4438(9)	0	0.2301(3)	0.5	0.025(2)	0.012(2)	0.029(2)	0	0.002(2)	0	0.022(1)
O(2)	0.1424(5)	0.2329(4)	0.2304(2)	1.0	0.017(1)	0.021(1)	0.029(2)	0.002(1)	0.004(1)	0.005(1)	0.0223(9)
O(3)	0.3581(5)	0.1667(3)	0.0748(2)	1.0	0.011(1)	0.007(1)	0.022(1)	0.000(1)	0.0028(9)	0.0005(9)	0.0134(7)
OH	0.3576(7)	0.5	0.0712(3)	0.5	0.015(2)	0.009(2)	0.034(2)	0.03(9)	0.004(2)	0.003(8)	0.019(1)
P(1)	0.635(3)	0.337(2)	0.4168(8)	0.146(6)	0.115(7)	0.093(7)	0.061(6)	0.016(5)	0.022(5)	0.011(6)	0.089(4)
P(2)	0.649(4)	0	0.415(1)	0.098(5)	0.099(8)	0.096(9)	0.052(7)	0	0.009(7)	0	0.084(5)
Ca	0.5	0.167(2)	0.5	0.049(3)	0.062(8)	0.041(7)	0.028(6)	0	0.03(6)	0	0.44(4)
H_2O	0	0	0.5	0.039(4)	0.052(9)	0.049(9)	0.000(9)	0	0.000(9)	0	0.034(5)

[1] K = refined value of site occupancy, except where noted in text.
[2] Displacement parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

dition, Ca and H_2O were located at specific sites, with both situated on the central plane of the interlayer. Calculated layer charge using the occupancy factors of P1, P2, and Ca (Table 1) and associated charges of the cations are in fair agreement (0.97 electrostatic valency units, *evu*) with the layer charge of 0.85 *evu* as determined by chemical analysis (Norrish, 1973). We attribute the difference (0.12 *evu*) to the small scattering efficiencies for these sites, the resulting difficulties in refinement, and possible experimental errors in the chemical analysis.

TMP locations in the average structure

There is a TMP molecule associated with each basal oxygen. P–O distances (P1–O2 = 2.80(1) Å, P2–O1 = 2.77(2) Å) are essentially equal (within one standard deviation). The strong covalent character of the atoms within the molecular unit and the close similarities of the P–O distances for the two crystallographically unique TMP molecules suggest that the TMP and basal oxygen interactions are primarily electrostatic in nature. In addition, the tetrahedral site, which contains

Table 2. Selected calculated bond lengths and angles.

Bond length (Å)				Bond angles(°)
				About T
T-O(1)	1.658(2)	O(1)-O(2)′	2.693(4)	108.6(2)
O(2)′	1.658(3)	O(2)	2.694(4)	108.5(2)
O(2)	1.662(3)	O(3)	2.723(5)	110.3(2)
O(3)	1.660(3)	O(2)-O(2)′	2.693(3)	108.5(2)
	mean 1.660	O(3)	2.725(4)	110.5(2)
		O(2)′-O(3)	2.728(4)	110.5(1)
			mean 2.709	mean 109.5
		Shared		*About M(1)*
M(1)-O(3) × 4	2.084(3)	O(3)-O(3) × 2	2.797(4)	84.3(1)
OH × 2	2.059(4)	OH × 4	2.757(4)	83.4(1)
	mean 2.075		mean 2.777	
		Unshared		
		O(3)-O(3) × 2	3.089(4)	95.7(1)
		OH × 4	3.092(4)	96.6(1)
			mean 3.091	
		Shared		*About M(2)*
M(2)-O(3) × 2	2.070(3)	O(3)-O(3)	2.797(4)	85.0(1)
O(3)′ × 2	2.082(2)	O(3)′ × 2	2.795(4)	84.6(1)
OH × 2	2.069(3)	OH-O(3)′ × 2	2.757(4)	83.2(1)
	mean 2.074	OH	2.713(6)	82.0(1)
			mean 2.766	
		Unshared		
		O(3)-O(3)′ × 2	3.088(4)	96.1(1)
		OH × 2	3.089(3)	96.5(1)
		OH-O(3)′ × 2	3.086(4)	96.0(1)
			mean 3.088	

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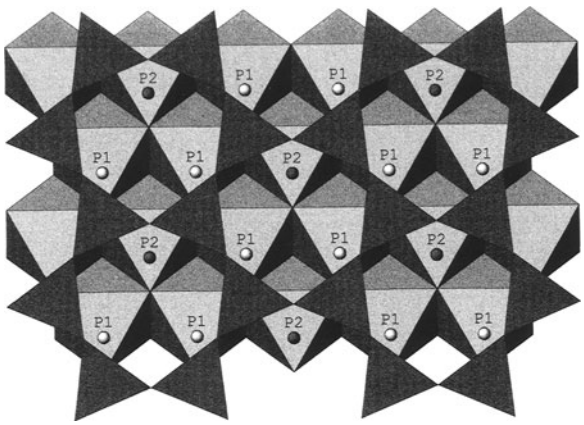


Figure 1. Average structure of TMP-exchanged vermiculite along [001] direction showing the distribution of partially-occupied phosphorus (P) atoms of the interlayer plane most closely associated with the underlying 2:1 layer (upper tetrahedral sheet and octahedral sheet of 2:1 layer shown). Within the 2:1 layer, the polyhedral corners represent oxygen-atom centers. Octahedra represent M sites and shaded overlying triangles represent the basal oxygen triad of the tetrahedra containing T sites (Si, Al).

the O1 and O2 anions as a portion of its polyhedron, is very regular (T–O distances ranging from 1.658 to 1.662 Å), suggesting that neither O1 or O2 are sufficiently affected by the TMP neighbor to distort the tetrahedron. This strongly suggests that the P remains in four-coordination. Thus, an interesting question is: what is the effect of the electrostatic interactions between the TMP molecule and the associated oxygen?

In most vermiculites, the major source of the layer charge is Al^{3+} for Si^{4+} substitutions, and this is what commonly distinguishes vermiculite from montmorillonite, where the charge originates from the octahedral sheet due to Mg for Al substitutions. In common vermiculites, for a given pair of linked tetrahedra, Pauling bond summations of 2.0 *evu* (two Si cations, each contributing 1.0 *evu*) occurs for oxygen shared between two Si tetrahedra. A summation of 1.75 *evu* occurs for oxygen shared between Al and Si tetrahedra (Al = 0.75 *evu*, Si = 1.0 *evu*), resulting in an undersaturated oxygen at each corner of the tetrahedron, including those of the basal plane (bridging oxygen). It is this undersaturated charge that must be offset by interlayer cations or molecules. For the Santa Olalla vermiculite, Al for Si substitutions represent an average Al tetrahedral occupancy of about 1/3 per site (2.52 ^{IV}Al/8 sites = 0.315). On the average, there will be four bridging oxygen at 1.75 *evu* and two bridging oxygen at 2.0 *evu* around a six-ring with two of the six tetrahedra occupied by Al, resulting in an average Pauling bond summation of 1.83 *evu* per bridging oxygen. This is in close agreement with calculated summations from P-site occupancies (O2: 1.75 + 0.146 = 1.90 *evu*; O1: 1.75 + 0.098 = 1.85 *evu*), where TMP will associate with a bridging oxygen linked between an Al-substituted tetrahedron and a Si tetrahedron. It is well known (Brown, 1977) that bond distances will compensate for a charge-undersaturated or oversaturated ion. Since the calculated summations indicate that the bridging oxygens are nearly saturated with respect to charge, the P1–O2 or P2–O1 distances (~2.78 Å) are neither shortened nor lengthened significantly from unbalanced electrostatic interactions.

TMP orientation

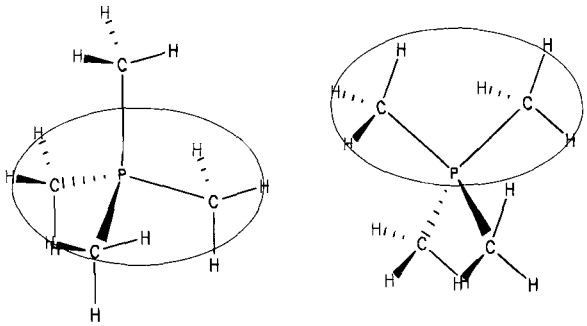
Determining the orientation of the TMP molecule is problematic due to the difficulty in locating the methyl groups. These groups were not located because of the very light elements (C, H) present and because the sites are partially filled, as indicated by the occupancy refinement of the respective P sites. In addition, the molecule may be dynamic. Nonetheless, some constraints may be placed on the orientation of the molecule. The known tetrahedral geometry of TMP and the location of the P atom with respect to the adjacent basal oxygen plane places steric constraints on the orientation of the methyl groups. The TMP molecule (P1 in Figure 1) located most closely to a bridging oxygen of the adjacent basal plane is probably oriented such that two methyl groups "straddle" the bridging oxygen in projection. Thus, each of these methyl groups may point towards the center of a neighboring silicate ring, so that the methyl groups can pack efficiently with the oxygen of the basal plane. In contrast, we believe that the TMP molecule (P2 in Figure 1) located more closely to the ring center in projection can pack most efficiently if there is only one methyl group associated with the ring. In this case, the TMP molecule must tilt somewhat and thus, the basal plane of the TMP tetrahedron is not parallel to the (001) plane. We tentatively conclude that the TMP molecules at site P1 do not have the same orientation as at site P2.

In the projection illustrated (Figure 1), the P2 site projects nearly over the octahedral cation of the underlying 2:1 layer. It is noteworthy, however, that the distance between the P2 site and the Mg^{2+} cation is large ($\gg$3.5 Å), and any repulsive effects between the Mg and the TMP are small.

Calcium and H_2O site

In addition to the TMP molecules, the calcium cations are required in the interlayer to offset the charge on the 2:1 layer. The Ca sites are directly over the tetrahedral sites in projection, thereby helping to saturate the source of the charge deficiency of the layer. However, because the residual negative charges on the tetrahedra are mostly compensated by the TMP, Ca to basal-oxygen-atom distances are large. Also, there is probably a hydration shell around Ca that acts to shield the charge on Ca (see below). Thus, the location of the Ca may not be completely dictated by charge bal-

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r-TMP(2) = 2.81 Å **r-TMP(1) = 2.79 Å**

Figure 2. Rotational radii of TMP(1) and TMP(2).

ance considerations alone. We note that the Ca site location also may be a result of the position of Ca in the parent (unexchanged) vermiculite phase. For comparison, Ca was located (de la Calle *et al.,* 1977; Slade *et al.,* 1985) in two sites in Ca-exchanged vermiculite in coordination with H_2O: one site was in distorted cubic coordination between the ditrigonal cavities and the other was in octahedral coordination between the bases of tetrahedra in adjacent layers. It is this latter site with the more regular polyhedron that is consistent with the Ca site located in the present study (shifted by 0.55 Å).

The H_2O site is located in the center of the interlayer ~3.09 Å from the Ca and ~2.10 Å from P1 and P2. Because the sites (P1, P2, Ca) are partially occupied, it is problematic to discuss this structural water as belonging to a coordination sphere of these sites.

Although the present study did not locate a coordination sphere about Ca, it is unlikely that the Ca can exist in this hydrous interlayer environment without a coordination shell of H_2O. TGA data (not shown) indicate weight loss at 100°C (6.1% wt. loss), 217°C (1.5% wt. loss), 422°C (0.6% wt. loss), 716°C (2.7% wt. loss) and 939°C (0.7% wt. loss). We interpret these data as reactions involving adsorbed unbonded (surface?) water (100°C), adsorbed interlayer water (217°C), decomposition of TMP (422°C and 716°C), and dehydroxylation (939°C). We note that in another TGA experiment involving Santa Olalla vermiculite that had undergone Na-exchange (for Ca, *etc.*) followed by TMP exchange, neither the peaks at 217°C nor 422°C occurred. Therefore, it is likely that the peak at 217°C is related to Ca and H_2O, and the peak at 422°C is related to interactions between Ca and TMP decomposition. The weight loss of 1.5% (at 217°C) is too great to attribute to the small amount of H_2O located at the center of the hexagonal ring, indicating that additional H_2O is present in the interlayer. In addition, the thermal analysis suggests that the relationship between Ca and the interlayer structure under dynamic heating conditions appears quite complex. A full description of the thermal analysis data and additional X-ray data will be presented in another paper.

TMP pillaring and constraints to determine the local pillar structure

Rotational radii within the (001) of the two TMP orientations are shown in Figure 2. In this figure, the TMP molecule associated with P2 is assumed to have its basal plane parallel to the (001) plane, although it is apparent from the discussion above that this is only an approximation. Calculated rotational radii values are nearly equal at 2.79 Å and 2.81 Å. These values determine the minimum TMP to TMP distance of 5.6 Å. However, TMP to TMP distances (or P1 to P2 distances) for the average structure that are below this value (apparent TMP to TMP distances are: 2.94, 3.02, 3.12, 4.21, 4.32, 5.26, 5.27, 5.29, and 5.35 Å) indicate that these sites cannot be simultaneously occupied. Distances >5.6 Å may be occupied simultaneously (nearest neighbor values range from 6.14 to 7.59 Å).

Another constraint for TMP occupancy is determined by the layer charge of the vermiculite. In addition to the charge associated with the Ca, TMP-TMP distances must allow a sufficient density of TMP molecules to balance the layer charge. This constraint places an upper limit on TMP to TMP distances of ~8.8 Å. Figure 3 shows the four different positions of TMP1 and TMP2 in the interlayer. A strict occupation of only the lower or upper plane is unlikely for two reasons: (1) $d(00l)$-values suggest the occupation of both planes, and (2) local charge balance is better maintained by occupying two interlayer planes. Thus, the TMP molecules randomly alternate between occupying the lower and upper interlayer planes within the limits discussed above. Figure 3 shows one such interlayer arrangement.

Silicate layer

Table 3 provides the calculated structural parameters for TMP-vermiculite. Most noteworthy is the 6.75° value for the tetrahedral rotation angle, α. The value of this angle is usually related to the misfit between the octahedral and tetrahedral sheets of the 2:1 layer, where it is possible to reduce the lateral dimensions of a larger tetrahedral sheet by rotating adjacent tetrahedra in opposite directions in the (001) plane. Interestingly, however, the value of α for TMP-vermiculite is 0.35° smaller than for TMA-vermiculite (Vahedi-Faridi and Guggenheim, 1997), although both exchanged vermiculite samples were derived from the same crystal of Santa Olalla vermiculite and the 2:1 layers are identical in composition. Because TMP molecules affect the 2:1 layer differently than TMA molecules, we conclude that 2:1 layers are not simply rigid substrates, and that dynamic interactions occur during reactions involving adsorption and exchange.

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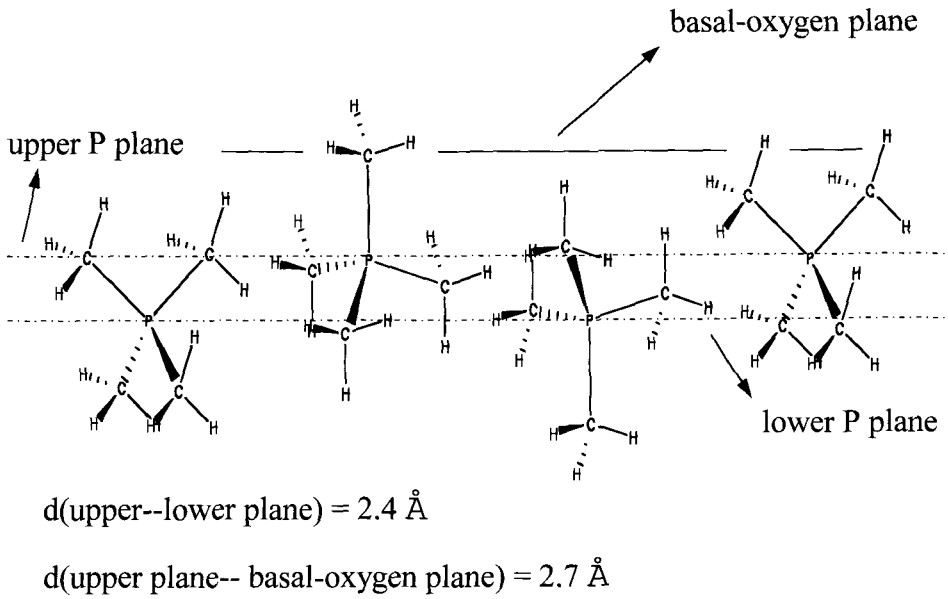


Figure 3. The interlayer of TMP-vermiculite along the [110] direction.

The TMP-vermiculite structure differs significantly from the TMA-vermiculite structure (Vahedi-Faridi and Guggenheim, 1997), although both structures have exchangeable organic cations of similar geometry (Table 4). The TMA molecule is positioned in the ditrigonal ring, whereas TMP is located more closely to an individual bridging oxygen. Thus, the TMA molecule can charge-balance the bridging oxygen in TMA-vermiculite by distributing its positive charge equally over the three nearest bridging oxygens around the ditrigonal ring. Therefore, the centrally located TMA molecule has an electrostatic attraction to each of the bridging oxygen atoms, which allows greater tetrahedral rotation than would be required from misfit between the octahedral and tetrahedral sheets alone. TMA can obtain this configuration because of its relatively small size and spherical charge.

TMA in TMA-vermiculite is "keyed" into the 2:1 layer by being located within the ditrigonal ring, whereas the TMP in TMP-vermiculite is bonded to the surface of the 2:1 layer by attraction to the bridging oxygen of the basal surface. In either case, the exchangeable cation position is fixed laterally, thereby allowing three dimensional stacking order.

Table 3. Calculated structural parameters for TMP-vermiculite.

Parameter	Value
$\alpha(^\circ)$[1]	6.75
$\psi(^\circ)$[2]	59.57 M(1)
	59.55 M(2)
$\tau_{tet}(^\circ)$[3]	110.4
Sheet thickness[4]	
octahedral (Å)	2.102
tetrahedral (Å)	2.264
Interlayer separation (Å)	7.764
Δz_{ave} (Å)[5]	0.004
$\beta_{ideal}(^\circ)$[6]	97.06

[1] α = 1/2[120° − mean O_b-O_b-O_b angle].
[2] ψ = $\cos^{-1}$[(oct. thickness)/(2(M-O)$_{ave}$)].
[3] τ = mean O_b-T-O_a.
[4] Tetrahedral thickness includes OH.
[5] Δz_{ave} = Basal oxygen corrugation.
[6] β_{ideal} = 180° − $\cos^{-1}$[a/3c].

CONCLUSION

In contrast to TMA-vermiculite, the pillar interstices in TMP-vermiculite are irregular in shape and size, where pillar-to-pillar distances range between 5.6–8.8 Å. Overall, the galleries are smaller in size in TMP-vermiculite due to the larger dimensions of TMP *vs.* TMA. However, since there is a variety in gallery sizes in TMP-vermiculite, a larger range of molecule sizes can be adsorbed than in the case of TMA-vermiculite. For example, Kukkadapu and Boyd (1995) found that larger molecules like styrene and ethyl benzene are more readily adsorbed by TMP-clays in comparison to TMA-clays when adsorbed from aqueous solution. Thus, it becomes possible to clarify the nature of the

Table 4. TMP- *vs.* TMA-Vermiculite.

	d(001)-value	P,N–CH_3	Pillar-height	P,N–Basal-oxygen plane	P,N–Interlayer-center
TMP	14.394 Å	1.87 Å	4.68 Å	2.7 Å	1.2 Å
TMA	13.494 Å	1.47 Å	4.16 Å	1.92 Å	1.53 Å
Δ	0.900 Å	0.4 Å	0.52 Å	0.78 Å	0.33 Å

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exchange and adsorption processes by developing a systematic understanding of the various exchanged structures.

We emphasize several important results of this study: (1) Researchers often consider the intercalation of pillars as involving an exchange reaction where the 2:1 layer acts as a static substrate. Clearly, the pillars interact with the 2:1 layer beyond simply balancing charges. This result indicates that these interactions must be considered in the molecular modeling of these materials. (2) Small amounts of interlayer material, *i.e.,* Ca, may produce significant differences in the properties of a pillared clay. Even small changes in the procedure used to synthesize an organoclay may greatly affect the product. (3) Differences in structure between TMP and TMA exchanged vermiculites (two interlayer sites *vs.* one site) indicate the need for caution in assuming that organoclay structures are isostructural, even for exchangeable cations of similar shape.

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