

STRUCTURE OF A 1,4-DIAZABICYCLO[2,2,2]OCTANE-VERMICULITE INTERCALATE

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Abstract—1,4-diazabicyclo[2,2,2]octane dihydrochloride (DABCO·2HCl) was reacted with two vermiculite samples to produce intercalates which, at room temperature, had relatively sharp, single crystal X-ray diffraction patterns. At higher temperatures (250°C) the stacking order decreased, and consequently the $0kl$ reflections with $k \neq 3n$ became increasingly diffuse. The stacking order of previously heated samples returned when they were cooled. A superstructure was present in which DABCO cations occupied the corners and center of a cell $3a \times b$, compared with the standard vermiculite cell.

DABCO-intercalated Nyasaland vermiculite had the following monoclinic subcell (symmetry $C1$) parameters under ambient conditions: $a = 5.341(2)$, $b = 9.249(3)$, $c = 14.50(1)$ Å, and $\beta = 96.98(5)^\circ$. Differential Fourier analyses and least-squares refinement led to a final R value of 12.6% for 1814 reflections. The crystal structure analysis showed that individual DABCO ions were not symmetrically positioned between the silicate layers. A network of inorganic cations and water molecules was also present and governed the interlayer separation. At 250°C the d value was 13.7 Å, consistent with a dehydrated structure, in which each organic pillar has one amino group keyed into a ditrigonal cavity and the other amino group riding on the basal oxygens of an opposite tetrahedron.

Key Words—Crystal structure, DABCO, Intercalate, Stacking ordering, Vermiculite.

INTRODUCTION

Slade *et al.* (1978, 1987), Slade and Raupach (1982), and Slade and Stone (1983) made use of X-ray diffraction superlattice reflections to characterize the ordered interlayer arrays formed when certain organic species were reacted with vermiculites. For a vermiculite-anilinium intercalate, Slade and Stone (1984) found $0kl$ reflections which indicated that its structure was comparatively well-ordered, the majority of the silicate layers being stacked with their ditrigonal cavities essentially opposite each other, as in micas.

Shabtai *et al.* (1977) reported on a swelling-resistant molecular sieve formed by intercalating the cage-like 1,4-diazabicyclo[2,2,2]octane (DABCO) into montmorillonite (Volcay bentonite SPV, American Colloid Company). The product (DABCO-M) had a basal spacing of 14.8 Å and a calculated lateral distance of ~ 6 Å between the edges of adjacent organic cations. The intercalate acted as a molecular sieve in catalyzing the esterification of carboxylic acids.

Although the potential of DABCO to cross-link silicate layers probably enhances the stacking order between adjacent layers, the uniform interlayer pore size in DABCO-M (Shabtai *et al.*, 1977) implies that the organic cations must also form ordered arrays on the surfaces of the silicate layers. The present work examines these possibilities in more detail by studying the intercalates formed between DABCO and two differently charged vermiculites. Despite the difficulties associated with structural work on intercalated ver-

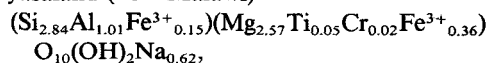
miculites, and bearing in mind that the structure of natural untreated vermiculite has only been refined to 9.1% on 822 reflections (Shirozu and Bailey, 1966), the interlayer structure of DABCO-intercalated vermiculite was examined and is described here.

EXPERIMENTAL

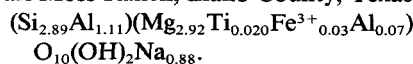
Materials and methods

The vermiculites used were taken from the mineral collection of the CSIRO Division of Soils. Prior to intercalation with DABCO, the vermiculite pieces were cut into flakes 1–2 mm across and refluxed with 2 M NaCl solution for a week at 80°C. Solutions were changed daily and the residual salt was removed by washing. The source localities and the structural formulae from electron microprobe analyses for the sodium-saturated materials are as follows:

Nyasaland (now Malawi)



Carl Moss Ranch, Llano County, Texas



DABCO·2HCl was prepared from the free diamine as described by Shabtai *et al.* (1977). The flakes of Na-saturated vermiculite were refluxed at 50°C with a 1% solution of DABCO·2HCl. The solution, which had a pH of 2.3, was changed daily for 10 days. At intervals

Table 1. Unit-cell parameters of DABCO¹-intercalated Llano (LV) and Nyalaland (NV) vermiculite samples.

	From powder and photographic single-crystal X-ray diffraction data	From 4-circle single-crystal diffractometer ²
	DABCO-LV	DABCO-NV
<i>a</i> (Å)	5.23(3) Å	5.341(2)
<i>b</i> (Å)	9.23(5)	9.249(3)
<i>c</i> (Å)	14.11(2)	14.50(1)
α	90.0°	90.0°
β	97.5(2)°	96.98(5)°
γ	90.0	90.0°

¹ 1,4-diazabicyclo[2,2,2]octane.

² Crystal data derived from this unit cell are as follows: Unit-cell volume $V = 710.95 \text{ \AA}^3$, $Z = 2$, $D_m = 2.27 \text{ g/cm}^3$, $D_c = 2.17 \text{ g/cm}^3$, $\mu = 10.93 \text{ cm}^{-1}$ (MoK α).

a few flakes were removed for examination by X-ray powder diffraction. The reaction was judged to be complete when a rational set of 00 l reflections, based upon a fundamental spacing of 14.39 Å, was observed. The flakes were then washed until chloride free. Samples of the products were analyzed for C and N by the Canadian Microanalytical Service (Vancouver).

Data collection

A flake of DABCO-NV $0.06 \times 0.68 \times 0.88 \text{ mm}$ was selected for structure analysis on an ENRAF-NONIUS CAD4 diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Reflection intensities were measured between θ_{\min} of 1.5° and θ_{\max} of 30°; the indices ranged between $-6 \leq h \leq 6$, $-12 \leq k \leq 12$, and $-18 \leq l \leq 18$. The slit height used was 6 mm and the aperture width was $(3.00 + \tan \theta) \text{ mm}$. A total of 2570 reflections were considered to have been observed having $|F_o|/\sigma|F_o| > 5.0$. During the data collection standard reflections were regularly measured to check crystal and instrumental stability. Integrated intensities were corrected for Lorentz and polarization factors and for absorption ($\mu = 10.93 \text{ cm}^{-1}$); maximum and minimum transmission factors were 0.943 and 0.558, respectively.

RESULTS

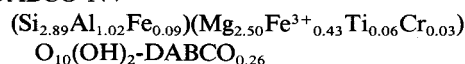
Preliminary study

By using a combination of X-ray Weissenberg photographs and powder diffractometry on orientated flakes, values for the unit-cell dimensions of DABCO-Llano vermiculite (DABCO-LV) were determined. Table 1 shows the results and also gives the values obtained by least-squares refinement using 25 low- to medium-angle reflections measured with a 4-circle diffractometer for the DABCO-Nyalaland vermiculite (DABCO-NV).

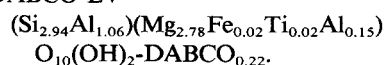
The analytical results for the DABCO-LV and DABCO-NV were as follows: C = 3.28, N = 1.27; C = 3.89 and N = 1.49%; respectively. From these analyses and

the single crystal data, the number of DABCO cations per unit-cell of DABCO-NV were calculated to be 0.517 from the nitrogen analysis and 0.525 from the carbon analysis. The corresponding numbers of DABCO cations per unit-cell for DABCO-LV were 0.430 and 0.430, respectively. The above figures, along with electron microprobe analyses, enabled the following structural formulae for the intercalated vermiculites to be computed:

DABCO-NV



DABCO-LV



Oscillation XRD photographs taken about the *a* axes of crystals of each DABCO-intercalated vermiculite, initially set with their basal planes perpendicular to the X-ray beam, not only showed the usual vermiculite reflections but also additional spots near the direct beam. These spots, sharpest for the DABCO-NV intercalate, are indicative of a superlattice arrangement with DABCO cations occupying the corners and center of a cell $3a \times b$ with respect to the standard vermiculite cell. The superlattice spots for the DABCO-LV intercalate were more diffuse than those for DABCO-NV, showing that the organic cations were ordered in smaller domains in the former material.

Figure 1 (left) shows the b^*c^* plane of the DABCO-NV intercalate under ambient conditions. The $0kl$ reflections, including the $k \neq 3n$ reflections, are reasonably discrete so that a relatively high degree of stacking order exists parallel to the *y*-axis. The pattern of the reflections is similar to that found by Slade and Stone (1983) for a vermiculite-anilinium intercalate and also to that described by de la Calle (1977) and Slade *et al.* (1985) for the two-layer hydrates of Na- and Ca-vermiculite. In all of these one-layer structures the ditrigonal cavities in adjacent layers are opposite each other. After the DABCO-NV crystals were heated to 250°C (Figure 1 (right)), their $k \neq 3n$ reflections became very diffuse, indicating greatly increased stacking disorder, and their basal spacings decreased to 13.7 Å. After cooling to room temperature, flakes again gave discrete $k \neq 3n$ reflections as in Figure 1 (left), and the basal spacings returned to 14.4 Å.

Transmission electron micrographs of edge-on flakes of the DABCO-intercalated vermiculites showed an unexpected repeat distance between the silicate layers of $\sim 12.5 \text{ \AA}$. This value differs markedly from that ($\sim 14.4 \text{ \AA}$) determined by X-ray diffraction and was unexpected because the cross-linking DABCO cations in the model of Shabtai *et al.* (1977) were reported to be stable to 345°C.

The preliminary study of DABCO-vermiculites

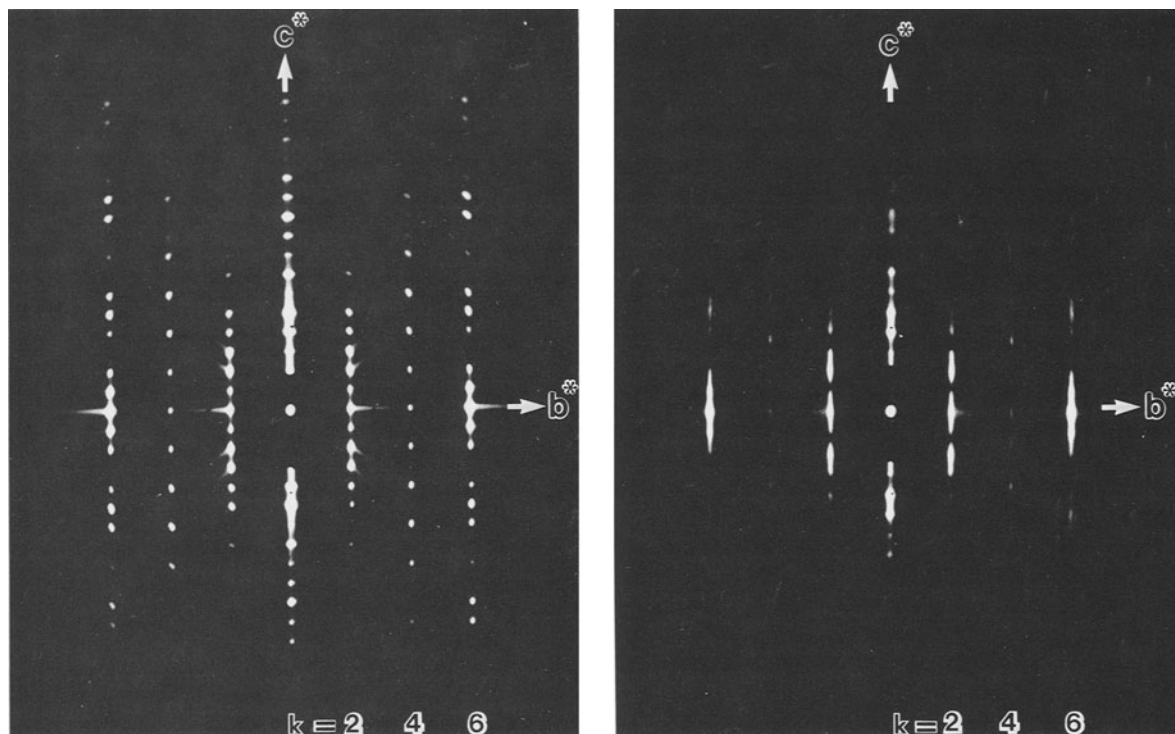


Figure 1. Precession X-ray diffraction photographs of the b^*c^* plane of DABCO-vermiculite at (left) room temperature and (right) 250°C. Conditions used were $\mu = 30^\circ$, $s = 26.0$ mm, $r = 15$ mm, MoK α radiation.

showed that their basal spacings differed, not only from each other, but also from the value of 14.8 Å, reported by Shabtai *et al.* (1977) for DABCO-M. The unexpected collapse of the spacings to about 12.5 Å in the electron microscope seemed incompatible with a model in which rigid, thermally stable, cage-like “pillars” determined the interlayer separation. Accordingly, the structure of DABCO-NV was further examined by collecting a set of three-dimensional X-ray diffraction intensity data for a Fourier analysis and refinement.

Structure determination: initial adjustment of silicate-layer parameters

A trial model for the silicate structure was derived from the atomic coordinates given by Slade *et al.* (1987). The asymmetric unit for the silicate-only part of the structure was chosen with the lowest likely symmetry, i.e., C1. Superlattice reflections were not taken into account, and therefore the interlayer structure to be described was averaged over sub-cells.

The scattering factors for the octahedral and the tetrahedral sites were in accord with the structural formula and fully ionized cations. For oxygen, the O $^{2-}$ curve of Tokonami (1965) was used; other curves were taken from the International Tables for X-ray Crystallography (1974).

The program SHELX 76 (Sheldrick, 1976) was used

for all structural refinements. After refining the positional parameters for all but one octahedral cation (fixed at 0, 1/2, 0) the isotropic temperature factors were adjusted in several further cycles. Weighting was not used, but reflections for which $I < 2.5\sigma(I)$ were excluded. The R factor at this stage was 22.8%. The adjusted model for the silicate-only part of the structure enabled the observed structure amplitudes to be converted to observed structure factors (F_o values). These, along with the F_c values from the silicate-only model, allowed sections through the three-dimensional (F_o - F_c) map to be calculated. The difference Fourier sections at the heights of the tetrahedral cations showed that the stacking order of the silicate layers was imperfect; the positions at the centers of the rings of tetrahedra were partially occupied. Residual disorder also showed up on other sections parallel to the basal plane. The disorder, associated with remaining $\pm b/3$ shifts, was modeled as well as possible, after which the R value fell to 16.1%.

Position of DABCO ions

Figure 2, the difference Fourier section at $y = 1/2$, shows substantial peaks in the interlayer on either side of the middle at $z = 1/2$. The peaks, labeled A, B, C, and D in Figure 2, were attributed to the organic moieties. They were ascribed as follows: A and C to nitro-

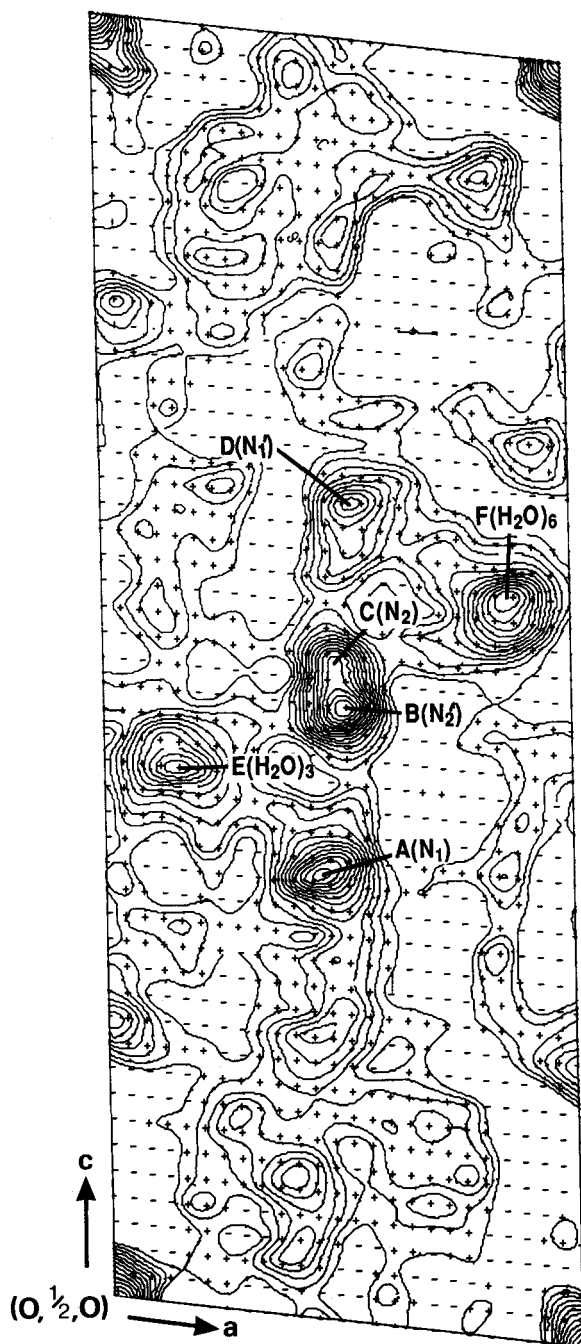


Figure 2. Section through a three-dimensional (Fo-Fc) synthesis at $y = \frac{1}{2}$. Contour interval = $0.1 \text{ e}/\text{\AA}^3$. Peaks A, B, C, and D are associated with organic cations, E and F with water molecules.

gens in a lower DABCO cation and B and D to nitrogens in an upper cation. This assignment was based on the distances between peaks A and C and B and D being the same as the distance (2.475 \AA) between the nitrogen atoms in a DABCO molecule (Kennedy *et al.*, 1987). The intramolecular N...N vectors were essen-

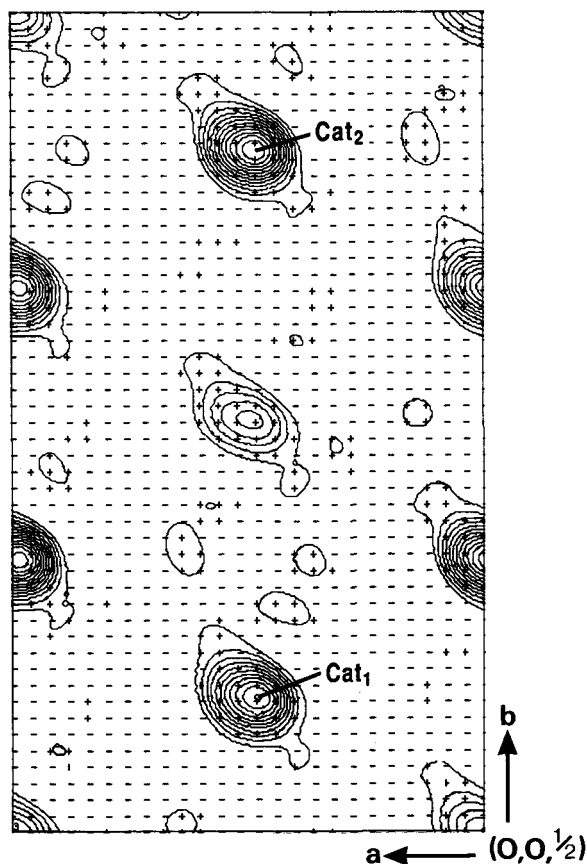


Figure 3. Section through a three-dimensional (Fo-Fc) synthesis at $z = \frac{1}{2}$. Contour interval = $0.3 \text{ e}/\text{\AA}^3$.

tially parallel to the c axis and directed towards the centers of the ditrigonal cavities in opposite silicate layers. The lower cation contacted the lower silicate surface and the upper cation contacted the upper silicate surface. Also implicit in this assignment was the concept that upper and lower cations were not present simultaneously in a single $5 \times 9 \text{ \AA}$ unit cell. Both cations appeared on the map because the X-ray structure was averaged over many cells, any one of which could only incorporate a single organic cation in one of four equivalent, potentially available, sites.

The section at $y = \frac{1}{2}$ also showed a series of diffuse interlayer peaks which may have been associated with pairs of ethylene carbons. Their images, however, were not clear, perhaps because of positional disorder, but more certainly because there were other interlayer components (see below) producing overlapping images in the sub-cell used to represent the structure.

Additional interlayer components

The difference Fourier section at $z = \frac{1}{2}$ (Figure 3) showed a series of well-defined peaks which, with the exception of the weaker one at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, are of equal strength. The stronger peaks corresponded with sites

Table 2. Positional and thermal parameters for DABCO-NV¹ intercalate.

Atom	x	y	z	B
Mg ₁	0.0000	0.5000	0.0000	0.16
Mg ₂	0.000(1)	0.8329(8)	0.0012(7)	0.16
Mg ₃	-0.003(1)	-0.3850(8)	0.0008(6)	0.16
T ₁	0.391(1)	0.1628(6)	0.1867(5)	0.26
T ₂	0.392(1)	0.8304(7)	0.1864(5)	0.26
T ₃	0.594(2)	0.161(1)	0.808(1)	1.26
T ₄	0.598(2)	0.830(1)	0.8068(8)	1.26
O ₁	0.360(2)	0.163(1)	0.0740(9)	0.51
O ₂	0.361(2)	-0.170(1)	0.0734(9)	0.51
O ₃	0.859(2)	-0.001(1)	0.072(1)	0.51
O ₄	-0.353(3)	0.165(1)	-0.074(1)	0.51
O ₅	-0.353(3)	-0.168(2)	-0.076(1)	0.51
O ₆	-0.855(3)	-0.001(2)	-0.075(1)	0.51
O ₇	0.145(2)	0.234(1)	0.227(1)	3.2
O ₈	0.144(2)	-0.242(2)	0.226(1)	3.2
O ₉	0.431(3)	-0.005(1)	0.227(1)	3.2
O ₁₀	-0.143(6)	0.219(4)	-0.234(3)	3.2
O ₁₁	-0.151(7)	-0.221(6)	-0.241(4)	3.2
O ₁₂	-0.032(7)	0.505(6)	-0.233(4)	3.2
Cat ₁	0.487(4)	0.160(2)	-0.495(2)	2.3
Cat ₂	0.487(4)	-0.172(2)	-0.498(2)	2.3
(H ₂ O) ₁	0.115(8)	0.159(6)	-0.575(5)	0.83
(H ₂ O) ₂	0.113(8)	-0.174(6)	-0.576(5)	0.83
(H ₂ O) ₃	0.623(8)	-0.005(6)	-0.573(5)	0.83
(H ₂ O) ₄	0.841(8)	0.159(6)	-0.439(5)	0.83
(H ₂ O) ₅	0.849(8)	-0.176(6)	-0.437(5)	0.83
(H ₂ O) ₆	0.337(8)	-0.010(6)	-0.437(5)	0.83
N ₁	0.469(8)	0.491(6)	0.349(5)	0.45
N ₂	0.476(8)	0.497(7)	0.514(6)	0.45
N ₁ '	0.566(9)	0.489(8)	0.638(7)	0.45
N ₂ '	0.488(8)	0.497(7)	0.467(6)	0.45

¹ 1,4-diazabicyclo[2,2,2]octane-Nyasaland vermiculite.

mid-way between the tetrahedral bases and therefore were associated with inorganic interlayer cations. The peak at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ resulted from overlap of the nitrogen peaks B and C referred to above.

Further evidence for the structure of the interlayer appeared on sections at $z = 0.43$, $z = 0.57$, and $y = \frac{1}{2}$. Collectively, these sections showed peaks at positions where water molecules, octahedrally coordinated at distances ≈ 2.05 Å from the interlayer inorganic cations, were expected. The interlayer structure therefore included not only DABCO cations, but also a network of inorganic cations and water molecules. A full trial-set of positional coordinates for each of the interlayer members was obtained from the difference Fourier sections and then refined. For these calculations the isotropic thermal parameters belonging to similar kinds of atoms were adjusted in groups and the inorganic interlayer cations were, as explained later, assigned to the Fe³⁺ scattering curve.

Refinement of the final model led to an R value = 12.6% for 1814 reflections³ and 220 parameters; unit

³ A list of calculated and observed structure factors is available from the authors.

Table 3. Bond lengths involving a selection of interlayer atoms in DABCO-NV¹ intercalate.

Atoms	Distance (Å)
N ₁ -O ₇	3.08(5)
N ₁ -O ₈	3.04(5)
N ₁ -O ₉	3.21(5)
N ₁ '-O ₁₀	3.12(6)
N ₁ '-O ₁₁	2.95(6)
N ₁ '-O ₁₂	2.97(6)
Cat ₁ -(H ₂ O) ₁	2.17(5)
Cat ₁ -(H ₂ O) ₂	2.09(6)
Cat ₁ -(H ₂ O) ₃	2.08(7)
Cat ₁ -(H ₂ O) ₄	1.97(5)
Cat ₁ -(H ₂ O) ₅	1.93(7)
Cat ₁ -(H ₂ O) ₆	1.99(6)
Mean	2.04
Cat ₂ -(H ₂ O) ₁	2.08(5)
Cat ₂ -(H ₂ O) ₂	2.17(5)
Cat ₂ -(H ₂ O) ₃	2.07(7)
Cat ₂ -(H ₂ O) ₄	1.99(6)
Cat ₂ -(H ₂ O) ₅	2.03(5)
Cat ₂ -(H ₂ O) ₆	1.96(6)
Mean	2.05

¹ 1,4-diazabicyclo[2,2,2]octane-Nyasaland vermiculite.

weights were used throughout. Table 2 shows the resulting positional and thermal parameters. The bond lengths are given in Tables 3 and 4.

The relatively large temperature factors for the surface oxygen atoms was associated with some remaining positional disorder caused by $\pm b/3$ translations.

DISCUSSION

The X-ray diffraction analysis reported here unambiguously located the positions of the pivotal nitrogen atoms, as well as those of the inorganic cations and water molecules. The ethylene carbon atoms, however, were not clearly seen, even in the Fourier images calculated after the final refinement. The DABCO cation has three vertical mirror planes at 120° to each other. In the intercalate, therefore, despite any rotational disorder which may be present, one of these mirror planes is always likely to be coplanar with the plane through the unit cell at $y = \frac{1}{2}$. With the ethylene bridges so positioned, Figure 4 shows that a DABCO cation keys into a ditrigonal cavity in the surface of a silicate layer. The ethylene carbon atoms then make van der Waals contact with the surface oxygens.

Superstructure

In the C-face-centered supercell DABCO cations appeared to be in sites over the ditrigonal cavities, with the adjacent equivalent surrounding sites unoccupied. This arrangement apparently prevents steric hinderances, but it may also better satisfy the charge distribution in local domains. Alcover *et al.* (1973) suggested that the exchangeable inorganic cations and water molecules in a Kenya vermiculite were also distributed

Table 4. Interatomic distances (Å) for silicate layer atoms in DABCO-NV¹ intercalate.

Tetrahedron about T ₁		Tetrahedron about T ₂	
T ₁ -O ₁ *	1.62(1)	T ₂ -O ₂ *	1.63(1)
-O ₇	1.64(1)	-O ₇	1.67(1)
-O ₈	1.65(1)	-O ₈	1.65(1)
-O ₉	1.66(1)	-O ₉	1.64(1)
Mean	1.64	Mean	1.65
Tetrahedron about T ₃		Tetrahedron about T ₄	
T ₃ -O ₄ *	1.70(2)	T ₄ -O ₅ *	1.69(2)
-O ₁₀	1.68(4)	-O ₁₀	1.70(2)
-O ₁₁	1.79(5)	-O ₁₁	1.65(5)
-O ₁₂	1.58(5)	-O ₁₂	1.74(5)
Mean	1.69	Mean	1.69
Octahedron about Mg ₁		Octahedron about Mg ₂	
Mg ₁ -O ₁	2.04(1)	Mg ₂ -O ₁	2.08(1)
-O ₂	2.08(1)	-O ₂	2.08(1)
-(OH) ₁	2.07(1)	-(OH) ₁	2.04(1)
-O ₄	2.08(2)	-O ₄	2.11(2)
-O ₅	2.11(2)	-O ₅	2.07(2)
-(OH) ₂	2.07(2)	-(OH) ₂	2.09(2)
Mean	2.08	Mean	2.08
Octahedron about Mg ₃		* apical oxygens	
Mg ₃ -O ₁	2.09(1)		
-O ₂	2.04(1)		
-(OH) ₁	2.04(1)		
-O ₄	2.05(1)		
-O ₅	2.12(2)		
-(OH) ₂	2.10(2)		
Mean	2.07		

¹ 1,4-diazabicyclo[2,2,2]octane-Nyasaland vermiculite.

over the lattice points in a C-face centered cell with dimensions $3a \times b$, which, by inference, represented the charge distribution in the silicate layers. For the vermiculite from Llano County, Texas (LV), de la Calle *et al.* (1976), Thompson (1984), and Slade *et al.* (1987) showed that only short-range ordering of tetrahedral cations exists in local domains. Consequently, if local charge balance operates in LV, its interlayer cations should also be ordered only in local domains; however, for the Nyasaland and Kenya vermiculites, the local domains of short-range order may well be larger. The superlattice spots for DABCO-NV were indeed sharper than for DABCO-LV, which is consistent with the local domains being larger in DABCO-NV.

Full occupancy of the all available sites in a $3a \times b$ supercell requires a total of two DABCO units or on average $\frac{2}{3}$ of a unit in each sub-cell. At this theoretical maximum level of occupancy, the layer charge (1.22 electrons per sub-cell) of Nyasaland vermiculite should be satisfied by divalent cations; however, chemical analysis showed that on average, a sub-cell contained only 0.5 of a DABCO cation. The difference between the actual level of occupancy and the theoretical maximum should lead to a charge imbalance if inorganic cations were not present. In DABCO-LV, the organic cations were only imperfectly ordered, which may re-

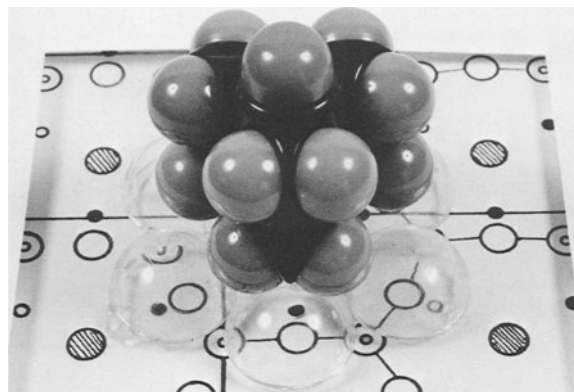


Figure 4. Model showing 1,4-diazabicyclo[2,2,2]octane molecule in contact with surface oxygens. Molecule and oxygens at the same scale.

fect the natural layer charge distribution of the material over only short distances or, its more limited uptake of DABCO ions. The high layer charge for LV may have inhibited a free exchange between the inorganic cations and the more bulky organic cations.

The X-ray diffraction data collected for DABCO-NV were only indexed for a sub-cell; hence, the Fourier images obtained were the average of those for the sub-cells comprising the supercell. The structure of the larger cell, however, was inferred as shown in Figure 5 in which, for improved clarity, DABCO ions have been omitted. The packing of the water molecules about the organic cations is more clearly demonstrated by the scale model shown in Figure 6. Here, the water molecules, whose images appear as peaks E and F on Figure 2, are marked for reference.

Relative positions of the silicate layers

The spacings between adjacent silicate layers of the DABCO-vermiculite intercalate are apparently governed by the presence of water molecules and cations. The differences between the basal spacings of DABCO-M, -NV, and -LV under ambient conditions can be attributed to charge differences between the parent silicate layers. At a given relative humidity an increase in the attraction between more highly charged silicate layers and a specific interlayer cation can be reflected by smaller basal spacings (MacEwan and Wilson, 1980).

Samples in the electron microscope showed layer separations of only ~ 12.5 Å. Apparently a high vacuum and the damage caused by the beam destroyed the interlayer structure so that the silicate layers were separated only by organic "fragments". Scale models (Figure 4) show that DABCO units, by keying into opposed silicate surfaces, can produce an interlayer spacing of 12.5 Å, a value considerably less than that suggested by Shabtai *et al.* (1977). Samples heated with warm air for X-ray diffraction examination at 250°C had a higher spacing (13.7 Å), a value retained even

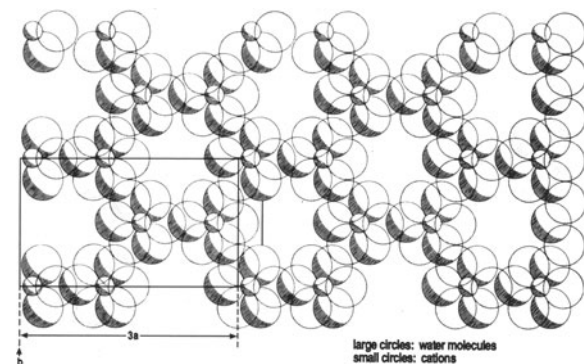


Figure 5. Computer drawing (PLUTO 78; Motherwell, 1978) showing water molecules and cations forming a superstructure in the interlayer of DABCO-vermiculite.

at 350°C. These relatively moderate conditions apparently removed enough interlayer water to weaken substantially the linkages holding the ditrigonal cavities in adjacent silicate layers opposite each other. With reference to Figures 5 and 6, for a silicate layer having an attached single sheet of water molecules, to move by either $\pm b/3$ requires that some water be lost. The disordering produced by this dehydration will bring the bases of tetrahedra opposite ditrigonal cavities. With such stacking, only one amino group per DABCO ion can key into a silicate surface; the second group will ride upon the oxygen atoms forming a tetrahedral base. The average N...O (basal) distances will then be about 2.9 Å. Scale models show that such an arrangement will produce a spacing of ~ 13.7 Å. Water molecules therefore have an important structural role in DABCO-vermiculite and, by inference, also in DABCO-montmorillonite.

Cationic charge

Each organic cation in DABCO-vermiculite has one of its nitrogen atoms linked directly to a silicate surface; however, the second nitrogen atom is near the interlayer mid-plane so that the latter atom's attachment to a silicate surface is less direct. These different situations imply that the nitrogen atoms may carry different charges. The total number of charges carried by an intercalated DABCO unit is difficult to determine, but the site multiplicities (0.35) found for the inorganic interlayer cations, when assigned to the Mg^{2+} scattering curve, exceed the result expected (0.11) if the organic cations were divalent. The argument is not conclusive, however, because the interlayer inorganic cations were not identified beyond the fact that they were not Na (electron microprobe examination of the intercalates showed them to contain $<0.1\%$ Na). Previously, Slade *et al.* (1987) reported that Al, Mg, and Fe can be lost from phyllosilicates if they are intercalated in acidic media. These ions may then be co-adsorbed with the organic cations onto the exchange sites. In the present

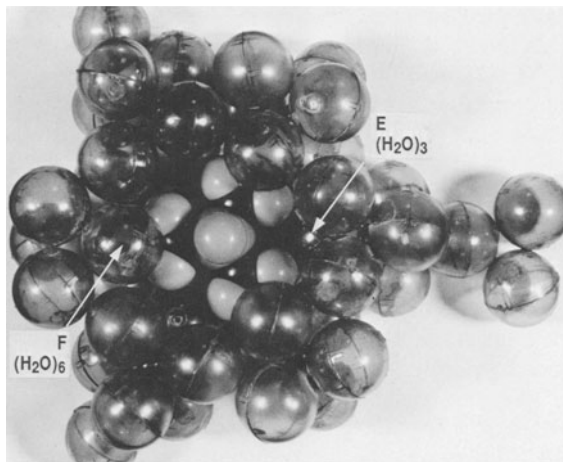


Figure 6. Scale model of 1,4-diazabicyclo[2,2,2]octane molecule embedded in the water network illustrated in Figure 5.

study, the Mg^{2+} scattering curve was arbitrarily used initially, but subsequently, to obtain more meaningful temperature factors, the sites were assigned to the Fe^{3+} scattering curve. Although the crystallographic evidence for the charge status of the organic cations was not conclusive, the asymmetry of the structural environment about their N atoms may indicate that these ions were not divalent.

The dissociation constants for DABCO ($pK_1 = 8.19$, $pK_2 = 4.18$; Terrin, 1965), however, indicate that the dication was favored by $\sim 10^4:1$. Hence, a mechanism to neutralize the cationic charges furthest from the silicate surfaces must be considered. The model illustrated in Figure 6 allows three extra water molecules to be accommodated in a trigonal close-packed formation above the DABCO unit. Such water molecules, being polar, will diffuse any adjacent positive charge upon the organic dications. Of necessity, the water molecules involved will be slightly displaced out of the planes of the main water sheets. Diffuse peaks on difference Fourier sections at $z = 0.37$ and $z = 0.63$ provide evidence for appropriate displacements of the water network.

CONCLUSIONS

DABCO cations had an interpillar distance of ~ 9.3 Å in the two-dimensional array which they formed between the silicate layers of vermiculite. This interpillar distance corresponds to an edge-to-edge distance of ~ 3.0 Å, a considerably smaller value than the 6.0 Å given by Shabtai *et al.* (1977) for DABCO-intercalated montmorillonite. The vermiculites' higher density of charge, compared with the montmorillonite, could have produced the closer packing.

By locating, at ambient conditions, the amine groups of the intercalated organic cations, the present study showed that individual cations were not symmetrically

positioned between the silicate layers in vermiculite. This model differs from that proposed by Shabtai *et al.* (1977) who suggested that the silicate layers in montmorillonite are cross-linked by DABCO cations whose opposite amino group are in direct contact with adjacent silicate layers. The likelihood of water not only being present, but also controlling the interlayer separation under ambient conditions, is not considered. In vermiculite, a single DABCO ion had only one amino group keyed into a ditrigonal cavity of a silicate surface. The other end of the dication was linked to the opposite silicate layer via hydrogen bonds through water molecules.

When the water-cation network was destroyed by heating, the spacing fell to 13.7 Å. At this spacing each DABCO ion was effectively in contact with the silicate layers adjacent to it, with one amino group embedded into a ditrigonal hole and the other group riding on the oxygen atoms forming the base of an opposite tetrahedron. The changes in the intercalate structure on dehydration were reversed on returning to ambient conditions.

Overall, this crystallographic study implies that the structural details for a pillared clay must be known if its properties as a molecular sieve are to be understood. It also highlights how water molecules and different kinds of cations interact to determine the interlayer structure.

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