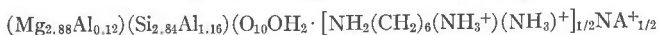


THE CRYSTAL STRUCTURE OF A HEXAMETHYLENE-DIAMINE-VERMICULITE COMPLEX

D. J. HAASE, E. J. WEISS AND HUGO STEINFINK, *Department of Chemical Engineering, The University of Texas, Austin, Texas.*

ABSTRACT

Single crystals of a naturally occurring magnesium vermiculite were converted to the sodium form and then reacted with a solution of hexamethylenediamine dihydrochloride until x -ray diffraction patterns indicated the presence of a single expanded phase. The monoclinic cell constants are: $a = 5.33 \text{ \AA}$, $b = 9.18 \text{ \AA}$, $c = 17.12 \text{ \AA}$, $\beta = 97.0^\circ$, and space group $C2$. There are two formula weights of the approximate composition



in the unit cell. The hexamethylenediamine molecule is inclined to the surface formed by the hexagonal array of oxygen atoms of the silicate layer. The inclination angle is 32° to the " ab " plane, and the projection of the organic molecule onto the " ab " plane is at an angle of 56° to the a axis. The organic molecule is randomly distributed over four crystallographic sites in the unit cell. The structure was determined from electron density projections on the (010) and (100) planes.

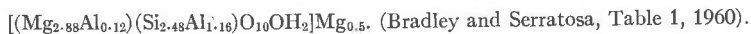
INTRODUCTION

The orientation of organic molecules which have been sorbed between the silicate layers of micaceous type minerals, such as vermiculite and montmorillonite, has been intensively investigated and many models have been proposed based on the analyses of one dimensional electron density projections along the c axis of the unit cell. (Bradley 1945; Walker 1950, 1956; Brindley and Hoffmann, 1962).

However, structures derived from one dimensional projections are subject to very large uncertainties because many different models of these proposed structures are nearly identical in such a projection. It was, therefore, desirable that a single crystal of a complex be prepared so that the structure could be determined at least from two dimensional projections.

EXPERIMENTAL

The vermiculite used in this investigation occurs as large white flakes in a deposit in Llano County, Texas, and has the approximate composition



The naturally occurring vermiculite was reacted with a concentrated sodium chloride solution and upon completion of the exchange reaction the flakes were placed in a hexamethylenediamine dihydrochloride solution of pH 6. The reaction was stopped when the x -ray diffraction dia-

gram showed that the material consisted essentially of a single phase which displayed a $d(001) = 16.98 \text{ \AA}$.

The reacted flakes were cut into small fragments (about $1 \times 2 \text{ mm}$) and mounted on glass fibers. Oscillation diagrams were obtained from these mounted crystals, and the one giving the best approximation to a single crystal diffraction pattern was chosen for the structural investigation. From oscillation, Weissenberg, and precession photographs, the dimensions of the monoclinic unit cell were determined to be: $a = 5.33 \text{ \AA}$, $b = 9.18 \text{ \AA}$, $c = 17.12 \text{ \AA}$, and $\beta = 97.0^\circ$, with two formula weights in the unit cell. The diffraction symmetry was $2/m C$. Three monoclinic space groups, $C2$, Cm $C2/m$, are consistent with the observed data.

The structure determination was begun by choosing a model based on the considerations of the known vermiculite structure (Mathieson and Walker, 1954) and the structure of hexamethylenediamine (Binnie and Robertson, 1950) together with the value of the c axis dimension of the unit cell of the complex. The model so constructed satisfied the symmetry required for space group $C2$. On several occasions during the refinement of the structure, models which fit in space groups Cm and $C2/m$ were tried, but always rejected because of the very poor agreement with the observed data.

The electron density projection on the (100) plane is best suited for the elucidation of the structure because the short " a " axis minimizes overlap in this projection. The okl structure factors were calculated on the basis of the known silicate atomic positions. The contributions to the structure factors by the atoms of the hexamethylenediamine molecule were neglected. Applying the calculated phases to the observed structure factors, an electron density projection on the " bc " plane was calculated and plotted. The electron density projection on the (100) plane showed elongated peaks in the interlayer region parallel to the " c " axis and perpendicular to the " b " axis at intervals of $\frac{1}{6}b$. The orientation of the electron density peaks in the interlayer space could be interpreted as representing organic molecules laying parallel to " c " and at intervals of $\frac{1}{6}b$. The space group $C2$ demands the presence of at least four hexamethylenediamine molecules in the unit cell. It was clear that the organic molecules are present in crystallographic sites on a statistical basis, since the chemical analysis could be reconciled with the presence of only one molecule per unit cell.

Thus, the model chosen for the next structure factor calculation was selected so that the plane containing the C-C bonds of the diamine chain was parallel to the " ac " plane and the diamine chain was inclined at an angle of approximately 40° to the " ab " plane in order to fit the long direction of the molecule into the available space. The new electron

density projection was not consistent with the assumed model. High regions of electron density where atoms were assumed began to disappear while new electron density peaks appeared where no atoms had been placed.

A set of centrosymmetric hol structure factors was also calculated on the assumption that the neglect of the carbon contribution would not change the signs. An electron density projection on the (010) plane was constructed with these signs and from a comparison of the (100) and (010) projections, a new model was proposed. The model placed the organic chain in a stepwise manner in projection on the "bc" plane. This accounted for the $\frac{1}{6}b$ requirement since $\frac{1}{6}b$ is approximately the C-C or C-N bond length, 1.5 Å. The first nitrogen, N₁, and the first carbon, C₁, were placed at $\frac{1}{6}b$, whereas the second carbon C₂, was placed on $\frac{1}{3}b$. Further refinement of this model by difference maps proved it to be correct and yielded discrepancy coefficients for F(okl) and F(hol) of 0.18 and 0.14, respectively. When the okl reflections $k \neq 3n$ are omitted, R(okl) = 0.13, (Table 1). The isotropic temperature factor $B = 3.75 \text{ \AA}^2$ was used in the calculations of the structure factors. The final atomic parameters are given in Table 2.

The final electron density projections on the (100) and (010) planes are shown in Figs. 1 and 2, respectively. A schematic representation of the oxygen surfaces and of the hexamethylenediamine molecule projected on the "ab" plane is shown in Fig. 3.

DISCUSSION OF STRUCTURE

Most of the y parameters of the atoms of the silicate layer in vermiculite are multiples of $\frac{1}{6}b$ so that okl structure factors with $k = 3n$ constitute the most prominent amplitudes in the calculation of the electron density projections on the (100) plane. The determination of the true atomic parameters, which deviate slightly from $y = \frac{1}{6}b$, demands precise measurements of intensities obtained from good crystals. The crystals which were obtained after the introduction of hexamethylenediamine showed invariably elongated diffraction intensities which were difficult to measure. It is realized that precise atomic coordinates cannot be obtained from these data, but they do permit the determination of the orientation of the molecule with respect to the oxygen surface. The (100) projection did show that the carbon and nitrogen atoms had y parameters at or very close to multiples of $\frac{1}{6}b$ and this assumption together with the x and z values from the (010) projection fixed the orientation of the molecule in the unit cell. This model yielded good agreement between the observed and calculated structure factors but physically it was unreal because the chain length was much too short. Slight shifts on the y and x parameters

TABLE 1.

a) okl Structure Factors					b) hol Structure Factors				
h	k	l	$ F_o $	$ F_c $	h	k	l	F_o	F_c
0	2	0	49	63	0	0	1	154	184
0	2	1	40	39	0	0	2	49	43
0	2	3	73	63	0	0	3	56	- 65
0	2	4	15	11	0	0	5	116	118
0	2	5	33	34	0	0	6	100	107
0	2	6	19	29	0	0	8	65	- 65
0	2	8	11	22	0	0	9	55	- 61
0	2	9	14	18	0	0	11	39	44
0	4	0	46	37	0	0	12	48	54
0	4	2	36	24	0	0	13	38	48
0	4	4	29	14	0	0	14	23	21
0	4	5	22	28	0	0	15	19	19
0	4	7	26	34	0	0	16	18	14
0	4	8	15	30	0	0	17	27	19
0	4	10	20	25	0	0	18	21	26
0	4	12	17	12	0	0	19	25	22
0	4	13	17	20	0	0	20	17	11
0	4	15	15	15	2	0	0	58	50
0	6	0	113	92	2	0	1	97	100
0	6	1	65	76	2	0	2	104	112
0	6	2	50	37	2	0	3	67	85
0	6	5	29	20	2	0	4	64	55
0	6	6	57	45	2	0	5	41	30
0	6	7	36	36	2	0	6	54	57
0	6	9	28	30	2	0	7	79	94
0	6	12	33	42	2	0	8	65	86
0	6	13	33	36	2	0	9	42	33
0	6	14	17	13	2	0	11	33	- 37
0	6	17	11	15	2	0	14	36	30
0	6	18	12	20	4	0	0	46	- 41
0	8	6	15	5	4	0	2	46	50
0	8	7	17	14	4	0	3	46	41
0	8	9	14	12	4	0	7	38	34
0	8	10	14	16	4	0	8	46	47
0	8	12	13	8	4	0	9	46	43
0	8	13	12	12	-2	0	0	58	50
0	10	2	14	7	-2	0	1	30	- 7
					-2	0	2	61	- 53
					-2	0	3	45	- 57
					-2	0	5	62	63
					-2	0	6	68	73
					-2	0	8	30	- 12
					-2	0	10	73	72
					-2	0	11	90	106
					-2	0	12	69	80
					-4	0	0	46	- 41
					-4	0	1	36	- 44
					-4	0	3	58	62
					-4	0	4	54	84
					-4	0	8	41	32
					-4	0	9	50	55
					-4	0	10	40	45

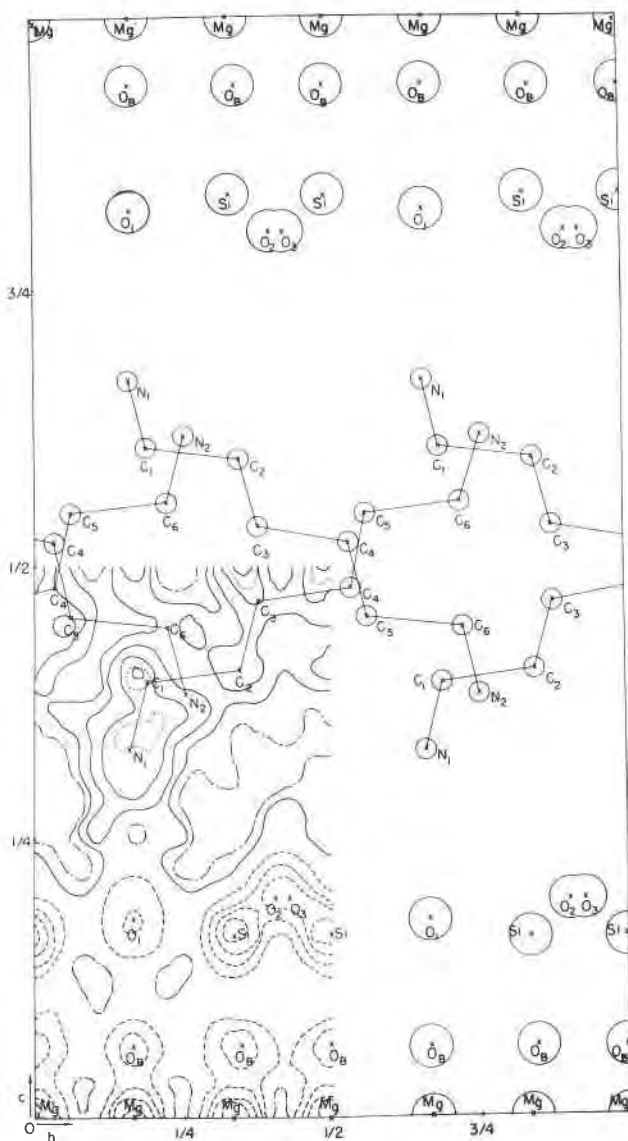


FIG. 1. Electron density projection on (100). Solid contours at intervals of $1e \text{ \AA}^{-2}$. Small dashed contours at $1/2e \text{ \AA}^{-2}$. Large dashed contours at $4e \text{ \AA}^{-2}$. Dash-dot contours are $0.5e \text{ \AA}^{-2}$ contours. Crosses mark final atomic positions.

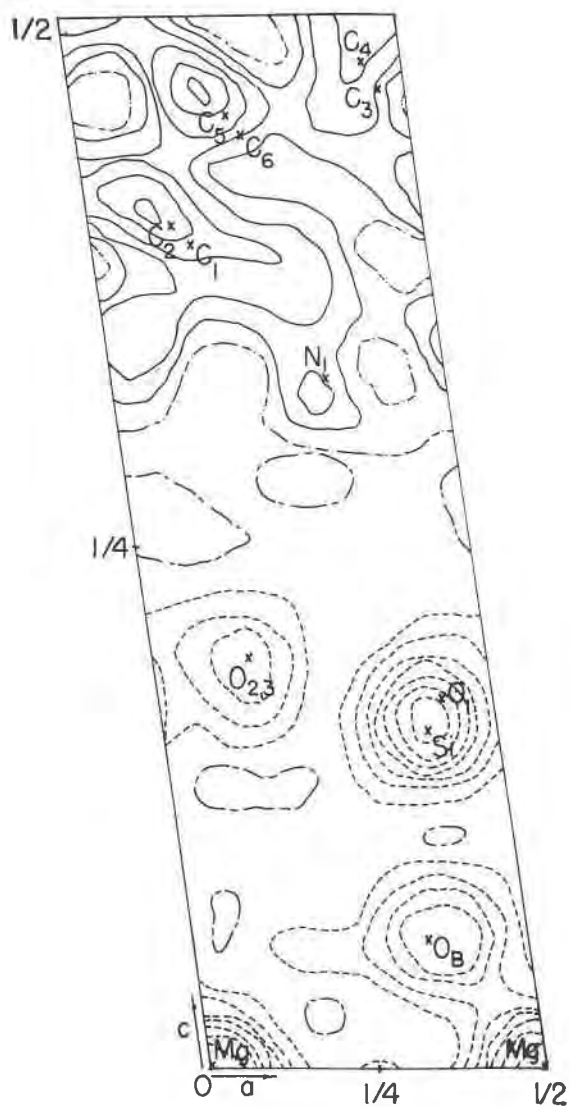


FIG. 2. Electron density projection on (010). Solid contours at intervals of $1e \text{ \AA}^{-2}$. Dashed contours at intervals of $5e \text{ \AA}^{-2}$. Dash-dot contours are $0e \text{ \AA}^{-2}$ contours.

TABLE 2. FINAL COORDINATES

Atom	x	y	z
<i>Silicate Layer</i>			
C-octahedral (Mg ²⁺)	0	0	0
C-octahedral (Mg ²⁺)	0	.333	0
C-octahedral (Mg ²⁺)	0	.667	0
D-tetrahedral (Si ⁴⁺)	.3967	.9920	.1607
D-tetrahedral (Si ⁴⁺)	.3967	.3330	.1607
O _B	.3579	.9920	.0624
O _B	.3579	.3480	.0624
O _B	.3579	.6617	.0624
O ₁	.4322	.1775	.1775
O ₂	.1482	.4040	.1960
O ₃	.1482	.9290	.1960
<i>Hexamethylenediamine Chain</i>			
N ₁	.3200	.1600	.3300
C ₁	.1500	.1875	.3925
C ₂	.1300	.3475	.4035
C ₃	-.0400	.3750	.4690
C ₄	-.0600	.5350	.4800
C ₅	-.2300	.5625	.5455
C ₆	-.2500	.7225	.5565
N ₂	-.4200	.7500	.6190

TABLE 3. INTERATOMIC DISTANCES

Atom	Distance
N ₁ -C ₁	1.51
C ₁ -C ₂	1.49
C ₂ -C ₃	1.56
C ₃ -C ₄	1.49
C ₄ -C ₅	1.59
C ₅ -C ₆	1.49
C ₆ -N ₂	1.51
N ₁ -O ₁	2.82
N ₁ -O ₂	3.26
N ₁ -O ₃	3.17
N ₂ -O _{1'}	3.92
N ₂ -O _{2'}	3.50
N ₂ -O _{3'}	3.65
C ₁ -O ₂	3.91
C ₁ -O ₃	3.59

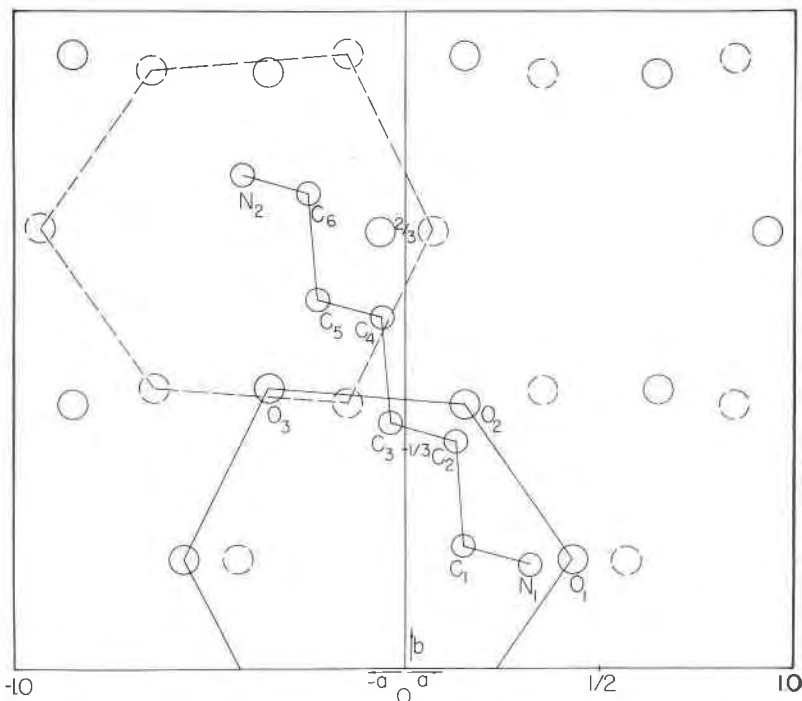


FIG. 3. Projection on ab of O_1 , O_2 , O_3 , and one hexamethylenediamine molecule for which atomic coordinates are given in Table 2. The larger solid circles are oxygen O_1 , O_2 and O_3 at $z=0.1775$ and 0.1960 , respectively. The dashed circles are O_1 and O_2 and O_3 at $z=0.6775$ and 0.6960 , respectively. N_1 is at $z=0.3300$. N_2 is at $z=0.6190$.

did yield a physically possible model, but the discrepancy coefficient remained unchanged. The orientation of the molecule changed only very slightly as a result of these adjustments.

The hexamethylenediamine chain is located in a stairway fashion between the hexagonal network of oxygens on the silicate interlayer surfaces. The N_1 , nitrogen, is located on a line parallel to a , at an angle of 83° to the " ab " plane, and intersecting the lower O_2O_3 plane, Fig. 3, near the middle of the base of the triangle, $O_1O_2O_3$, formed by the projection of O_1 on the O_2O_3 plane. The N_2 , nitrogen, is similarly located with respect to the upper distorted hexagonal oxygen network, Fig. 3. The shortest nitrogen-oxygen distance, Table III, is 2.82 \AA , the shortest nitrogen-oxygen approach on the other side of the chain is 3.50 \AA . The interatomic distances suggest that at one end of the hexamethylenediamine chain the nitrogen atom forms an N-H-O bond and at the other end the N-O distance indicates a van der Waals contact only.

In space group $C2$, there should be four hexamethylenediamine molecules in the unit cell; however, the nitrogen analysis can be reconciled with only one organic molecule per unit cell. The molecule therefore must be statistically distributed over the available crystallographic sites. The volume available between the silicate sheets when the "c" axis is 17.12 Å is approximately 370 Å³, and the molecular volume of the hexamethylenediamine is approximately 192 Å³, permitting two diamine molecules per unit cell. Therefore, the remainder of the volume is probably occupied by sodium ions and water molecules. A chemical analysis of the exchanged material was not available to test this hypothesis. The water molecules are probably randomly distributed in the unit cell, because no definite peaks could be assigned to these molecules in the (100) and (010) electron density projections.

At the pH of the base exchange reaction, only one of the amine groups of the hexamethylenediamine molecule can be considered as positively charged, so that the layer charge of -2 , which was formerly neutralized by the sodium ions, is now partially satisfied by the hexamethylenediamine and the remainder of the charge must be neutralized by the sodium ions left within the structure. It is believed that the sodium ion is randomly distributed over several possible positions because no distinct position for Na appeared on the Fourier electron density projections. However, on the (010) electron density projection, a low area of electron density and a possible sodium location occurs at $x=0.020$ and $z=0.350$. The only possible location for the assumed sodium in the (100) projection would be at $y=0.1667$. At this location, Na⁺ would be superimposed on a nitrogen and carbon peak so that its presence cannot be confirmed from this projection. A set of $h0l$ and okl structure factors were calculated and $R(okl)$ dropped to 0.165 while $R(h0l)$ increased to .15, indicating that the y and z parameters were probably correct, but the x parameter was incorrect.

The experimental data definitely leads to the conclusion that the hexamethylenediamine chain is oriented at an angle of 32° to the "ab" plane and the projection of the molecule on the "ab" plane is at an angle of 56° to the "a" axis. The vertical height of the hexamethylenediamine molecule in this orientation is 4.9 Å from center of nitrogen to center of nitrogen, thereby fitting excellently the available height of 7.6 Å when the nitrogen radii of the hexamethylenediamine molecule are considered. The second carbon of the hexamethylenediamine molecule on the end near the bonded nitrogen, N₁, exhibits an interatomic distance of 3.59 Å to O₂ of the hexagonal network. It is believed that this C₂ and N₁ form the support for holding the chain in its orientation, thereby preventing the collapse of the vermiculite-diamine complex to another configuration.

The standard deviations of the various interatomic distances were not calculated because of the poor quality of the single crystal data. A comparison of the calculated interatomic distances of the hexamethylenediamine molecule and of the silicate layer, respectively, with the reported values, should yield an estimate of the accuracy obtained. Considering the reported values as being correct, the largest error in the interatomic distances of the hexamethylenediamine molecule is 0.01 Å. It is felt that this is fortuitous and that the error is probably of the order of 0.1 Å.

REFERENCES

- BINNIE, W. P. AND J. MONTEATH ROBERTSON (1950) The crystal structure of hexamethylenediamine. *Acta Cryst.* **3**, 424-429.
- BRADLEY, W. F. (1945) Molecular association between montmorillonite and some polyfunctional organic liquids, *Jour. Am. Chem. Soc.* **67**, (6), 975.
- AND J. M. SERRATOSA (1960) A discussion of the water content of vermiculite. *Proc. Seventh Natl. Conf. Clays and Clay Minerals*, Pergamon Press, pp. 260-270.
- BRINDLEY, G. W. AND R. W. HOFFMAN (1962) Orientation and packing of aliphatic chain molecules on montmorillonite, *Proc. Ninth Natl. Conf. Clays and Clay Minerals*, Pergamon Press, pp. 546-556.
- MATHIESON, A. McL. AND G. F. WALKER (1954) Crystal structure of magnesium-vermiculite, *Am. Mineral.* **39**, 231-255.
- WALKER, G. F. (1950) Vermiculite-organic complexes, *Nature*, **166**, 695-697.
- (1956) Reactions of expanding-lattice clay minerals with glycerol and ethylene glycol, *Clay Mineral. Bull.* **3**, (20).

Manuscript received September 29, 1962; accepted for publication January 11, 1963.