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A STRUCTURAL INVESTIGATION OF A VERMICULITE–PIPERIDINE COMPLEX*

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Abstract—A vermiculite–piperidine complex was investigated by a single crystal three dimensional X-ray diffraction procedure. The complex was prepared by ion exchange of a Na–vermiculite at pH 8. A total of 453 reflections was observed and used in the least squares refinement of the structure. The complex is monoclinic, $C2/m$, $a = 5{\cdot}346(2)$ Å, $b = 9{\cdot}256(3)$ Å, $c = 17{\cdot}57(1)$ Å, $\beta = 96{\cdot}29(9)°$. The final R value was 0·17 using anisotropic temperature factors for the silicate atoms and isotropic temperature factors for the carbon atoms. The occupancy factors of the C atoms were considered as variable parameters. The diffraction data were of poor quality because of stacking faults. The results show that the molecules are randomly distributed over the crystallographic sites in the interlayer space and the peaks appearing in the electron density maps can be interpreted as being due to 2 piperidine molecules and two H_2O molecules. The orientation of the organic molecules is ambiguous. The electron density peaks fit a model in which the molecules are vertical and their planes form a small dihedral angle, and also fit a model in which the plane of the molecules is parallel to (001). It is quite possible that both types of orientations are present.

INTRODUCTION

For more than three decades an enormous amount of work has been carried out on clay–organic complexes concerning their chemistry, the sorption mechanism of organic molecules into the layers of the clay mineral, and the reactions of such molecules with the clay surfaces. Numerous investigations using various physical techniques to elucidate the structures of these complexes have been reported. The most desirable technique and the one that would yield, under favorable conditions, an unequivocal answer to the structure of such complexes is single crystal, three-dimensional, X-ray diffractometry. However, clay minerals, e.g. montmorillonite, have particle sizes too small to lend themselves to single crystal analysis. Therefore, we and others have used vermiculite single crystals to prepare such complexes and then applied X-ray diffraction analysis to these single crystals. Under the best of circumstances, vermiculite crystals display X-ray diffraction data that reflect the inherent stacking disorders within the structure. This disorder is compounded when organic molecules are introduced between the silicate layers.

We have previously reported on a structural determination for complexes containing hexamethylenediamine and *n*-hexylamine using two-dimensional X-ray diffraction data (Haase *et al.*, 1963; Brandle, 1964). The arrangement of the organic molecules in the interlayer space was disordered but the orientation of the chain with respect to the oxygen clay surface could be inferred. Disordered arrangements were also reported by Moll (1963) who studied the orientation of cyclic amines and by Johns and Sen Gupta (1967) who investigated alkylammonium cations in vermiculite. Three-dimensional X-ray diffraction analysis of a pyridine–vermiculite complex was reported by Susa *et al.* (1967) where they found that the organic molecules were statistically distributed over the crystallographic sites and that part of the exchange positions were occupied by magnesium; water molecules were also present in the interlayer space. Kanamaru and Vand (1970) reported a X-ray analysis of the complex 6-aminohexanoic–vermiculite and from a two-dimensional analysis found that the molecules are distributed statistically over crystallographically equivalent positions in the unit cell but were also able to reach a conclusion regarding the orientation of the molecule. We report here the three-dimensional X-ray diffraction investigation of a vermiculite–piperidine complex.

EXPERIMENTAL

Flakes of vermiculite from the Llano, Texas, locality large enough for single crystal X-ray analysis were examined under the microscope for thinness and freedom from cracks. The (001) diffraction spectra of a

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large number of flakes selected on this basis were then examined and any flakes exhibiting a trace of a 10 Å peak were discarded. Crystals were cut to suitable size before forming the complex to allow them to recover from the distortions that are invariably introduced when cutting. We did not notice that this procedure produced better crystals than carrying out the ion-exchange step first and cutting the crystals afterwards. Crystals of the proper size were placed in concentrated NaCl solutions at 70°C for 2 days, with changes of the NaCl solution every 12 hr. Exchange was judged complete when an 11·8 Å spacing was observed in an atmosphere of 40–50 per cent r.h. The Na–vermiculite crystals were then placed in a solution of piperidine hydrochloride which was buffered to a pH of 8·0. This pH was chosen in order to prevent the exsolution of Mg^{2+} from the silicate layer and subsequent ion exchange competition with the piperidinium ion. The system was held at 70°C for 4–5 days with changes of the soaking solution every 12 hr. After this treatment, the crystals were washed with hot, distilled water 5 or 6 times; a cold water wash produced exfoliation. After thorough desiccation the flakes were found to have a basal spacing of about 17·5 Å.

About 25 flakes were selected and mounted on glass fibers and X-ray oscillation pictures were taken. The diffraction pictures were of rather poor quality and further experimentation to improve the shape of the diffraction spots by varying the preparative conditions proved to be of no avail. Three crystals judged to be best on the basis of the least distortion in the X-ray diffraction spectra were selected and zero and upper level Weissenberg photographs and precession pictures were taken. The diffraction symmetry and systematic absences indicated the diffraction symbol $2/mC$ which is compatible with the space groups $C2$, Cm and $C2/m$. On the basis of the more extensive data, the best of these crystals was selected for mounting on a single crystal diffractometer. The crystal, 0·20 × 0·20 × 0·04 mm, was aligned along the b axis and about 30 reflections were selected whose 2θ angles were accurately measured with the instrument set at a 1° take off angle and a 0·02° receiving slit in front of the counter. The measured values were then used in a least squares program to determine the lattice parameters, $a = 5{\cdot}346(2)$ Å, $b = 9{\cdot}256(3)$ Å, $c = 17{\cdot}57(1)$ Å, $\beta = 96{\cdot}29(9)°$. Data were collected with nickel-filtered CuK_α radiation using a scintillation counter and with the pulse height discriminator set to accept about 80 per cent of the incident radiation. For each reciprocal lattice point the peak intensity and the background intensities on both sides of the peak were measured. There were 1034 reflections measured. Because of the poor quality of the crystal, care had to be taken to locate the intensity by maximizing the positions of the crystal and the counter for each peak. A peak was considered observed if the number of counts obtained in 20 sec was 10–20 counts greater than the number of background counts obtained in the same length of time. On this basis 453 reflections were observed. During the course of the measurements a standard reflection, (005), was checked every hour to monitor the alignment of the crystal and the constancy of the intensity of the primary beam. The intensity of the standard reflection remained constant within experimental error during the course of the data collection. The reflections were broad and strong overlapping among neighboring reflections was observed. However, the overlapping was not uniform in reciprocal space and was sufficiently small in most instances so that peak intensities could be measured. In some cases it was impossible to achieve an intensity maximization because of the severe overlap. An α splitting correction and Lorentz and polarization corrections were made to convert the intensities to structure factors.

STRUCTURE DETERMINATION AND REFINEMENT

Structure factors and phases for the complete set of data were calculated using the space group $C2/m$ and silicate layer parameters only. The positional parameters for the atoms in the silicate layer were taken from Shirozu and Bailey (1966) and modified for space group $C2/m$ and $c = 17{\cdot}5$ Å. The selection of space group $C2/m$ was influenced by the result obtained by Susa *et al.* (1967) and by the fact that the piperidine molecule possesses mirror symmetry. Full matrix least squares refinement of the scale factor and the silicate positional parameters resulted in $R = 0{\cdot}36$; $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, function minimized $= \Sigma w(|F_o| - |F_c|)^2$, $w = 1$. This value is unexpectedly large, even considering that only the silicate layer was used to calculate the structure amplitudes, and must be due to the poor quality of the data.

With the structure factors phased by the silicate atoms only, a Fourier electron density map and a difference Fourier map were computed. The interlayer region in both maps showed density distributions that were very similar. The peaks observed in the interlayer space were broad and in most instances unresolved. The electron density represented by the peaks was generally low, about 1e/Å^3 for most and 3e/Å^3 for two of them. A careful study of the interlayer region in the difference map yielded thirty peaks, representing more than 0·8e/Å^3, which could be possible carbon locations. These peaks were fed into a least squares program and refinement was made on the positional parameters and occupancy factors of the atoms while holding the silicate atom parameters constant. The large

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Table 1. Final parameters with S.D.

Atom	Multiplicity [σ(Mult.)]	x [σ(x)]	y [σ(y)]	z [σ(z)]	B [σ(B)]
2 MgI	0·25	0	0	0	1·55
					(0·39)
4 MgII	0·5	0	0·3334	0	1·54
			(0·0018)		(0·25)
8 OI	4·0	0·3527	0·3352	0·0641	1·85
		(0·0035)	(0·0025)	(0·0012)	(0·36)
4 OH	0·5	0·3494	0·5	0·0551	1·45
		(0·0055)		(0·0019)	(0·53)
8 Si	1·0	0·3858	0·3332	0·1563	2·14
		(0·0015)	(0·0010)	(0·0005)	(0·18)
4 OII	0·5	0·4338	0·5	0·1906	3·27
		(0·0054)		(0·0018)	(0·70)
8 OIII	1·0	0·1261	0·2693	0·1893	3·10
		(0·0035)	(0·0023)	(0·0012)	(0·47)
8 C1	0·1932	−0·0112	0·4794	0·2742	4·55
	(0·0773)	(0·0265)	(0·0223)	(0·0117)	—
4 C2	0·2288	0·4291	0	0·3124	3·77
	(0·0577)	(0·0169)		(0·0069)	—
8 C3	0·2554	0·2476	0·4671	0·3444	2·62
	(0·0612)	(0·0194)	(0·0122)	(0·0065)	—
4 C4	0·1705	0·4414	0·5	0·3617	3·77
	(0·0570)	(0·0253)		(0·0098)	—
8 C5	0·2290	0·2512	0·2246	0·3864	2·54
	(0·0681)	(0·0242)	(0·0157)	(0·0083)	—
4 C6	0·2560	0·1282	0	0·4023	4·27
	(0·0529)	(0·0177)		(0·0060)	—
4 C7	0·1600	0·4576	0·5	0·4135	3·26
	(0·0571)	(0·0284)		(0·0109)	—
8 C8	0·2585	0·1424	0·3243	0·4157	3·48
	(0·0687)	(0·0211)	(0·0143)	(0·0071)	—
8 C9	0·1234	0·2922	0·0783	0·4312	2·82
	(0·0667)	(0·0448)	(0·0275)	(0·0157)	—
8 C10	0·3464	−0·0216	0·1696	0·4384	0·85
	(0·0663)	(0·0153)	(0·0114)	(0·0053)	—
4 C11	0·2232	0·4777	0	0·4708	3·14
	(0·0481)	(0·0197)		(0·0059)	—

Atom	B_{11} [σ(B_{11})]	B_{22} [σ(B_{22})]	B_{33} [σ(B_{33})]	B_{12} [σ(B_{12})]	B_{13} [σ(B_{13})]	B_{23} [σ(B_{23})]
MgI	0·0224	−0·0023	0·0023	0	0·0013	0
	(0·0061)	(0·0013)	(0·0008)		(0·0018)	
MgII	0·0179	−0·0024	0·0032	0	0·0018	0
	(0·0035)	(0·0008)	(0·0005)		(0·0011)	
OI	0·0095	−0·0014	0·0046	−0·0002	0·0029	−0·0002
	(0·0046)	(0·0012)	(0·0008)	(0·0023)	(0·0015)	(0·0011)
Si	0·0206	0·0015	0·0032	0·0015	0·0019	−0·0006
	(0·0020)	(0·0006)	(0·0003)	(0·0012)	(0·0006)	(0·0006)
OII	0·0473	0·0037	0·0026	0	0·0031	0
	(0·0123)	(0·0028)	(0·0012)		(0·0031)	
OIII	0·0331	0·0057	0·0027	−0·0013	−0·0007	0·0008
	(0·0071)	(0·0020)	(0·0007)	(0·0032)	(0·0018)	(0·0012)
OH	0·0322	−0·0008	0·0009	0	0·0012	0
	(0·0099)	(0·0021)	(0·0009)		(0·0025)	

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number of parameters involved relative to the rather small number of observations caused many elements of the correlation matrix to be larger than 0·3. Peaks were eliminated on the basis of poor convergence of the positional parameters and/or occupancy factors, and they were eliminated if the latter became very small. Of the original 30 peaks, 19 were eliminated through successive refinements. After twelve cycles of refinement 11 peaks were considered acceptable. The R value was now 0·23 and did not change with any subsequent elimination or addition of peaks. Six cycles of refinement were then calculated using isotropic temperature coefficients for the atoms in the silicate layer and the 11 carbon atoms. Although the standard deviations were very large for the temperature coefficients of the carbon atoms, none of the coefficients became negative or so large that they were unacceptable. The R value at the end of this cycle of refinements had decreased to 0·22. A new difference Fourier synthesis was computed on the basis of the silicate structure and the eleven carbon atoms and the residual electron density in the interlayer region was now essentially zero. Six additional cycles of refinement were carried out using anisotropic temperature factors for the atoms in the silicate layer and R dropped to 0·169. Table 1 lists the final atomic parameters and temperature factors.

DISCUSSION

No peaks were observed in the Fourier map which could be interpreted in terms of Mg^{2+} in exchangeable sites; therefore, the vermiculite structure was not degraded during the several exchange steps.

Eleven carbon peaks with occupancy factors ranging from 0·12 to 0·34 were found by the least squares refinement in the asymmetric unit. In space group $C2/m$ this result amounts to a total of 119 electrons per unit cell or about 2·5 piperidine molecules. The maximum exchange capacity of vermiculite (200 m-equiv/100 g) would be satisfied by 2 piperidine molecules per unit cell. The interlayer volume of the complex under investigation is about 420 $Å^3$ and since the volume of a piperidine molecule is 165 $Å^3$ there is an additional 90 $Å^3$ per unit cell which could accommodate up to 4 water molecules. The 2 piperidine molecules plus 2 water molecules represent a total of 116 electrons, close enough to the value of 119 found by the analysis.

If only the peaks are considered which lie on the mirror plane or close to it, about 81 electrons per unit cell are accounted for while 2 piperidine molecules would yield a total of 96 electrons. The distribution of the peaks around the mirror plane can be interpreted in terms of 2 vertically oriented molecules which, because of the disorder, produce peaks indicating that they form a small dihedral angle. This model leaves several peaks unaccounted for which are either spurious or represent possible additional locations of the piperidine molecules with a much lower occupancy factor. Another interpretation is possible if the assumption is made that all peaks are significant. Distorted hexagonal outlines of horizontal molecules lying nearly in the (001) plane can be obtained and because of statistical disorder each sequence of peaks represents the outline of about 1/4 of a piperidinium ion. Serratosa (1966) found by i.r. study of a pyridine–montmorillonite complex that the pyridinium ions are nearly parallel to (001). A similar situation may exist here.

We conclude from this investigation that the organic molecules are statistically distributed over a large number of positions and that some may be in a vertical position and some parallel to the (001) plane. It appears that on the basis of four complexes studied by us by single crystal X-ray diffraction techniques, and from results reported by other investigators, that the statistical distribution of organic molecules is inherent in the nature of these complexes and that probably no crystallographically ordered complexes can be prepared by the usual ion exchange techniques.

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Résumé—Un complexe vermiculite–pipéridine a été étudié par diffraction X dans les trois dimensions sur monocristal. Le complexe a été préparé par échange d'ion d'une vermiculite Na à pH = 8. Un total de 453 réflexions a été observé et utilisé pour le raffinement de la structure par la méthode des moindres carrés. Le complexe est monoclinique, $C\ 2/m$, a = 5,436 (2) Å, b = 9,256 (3) Å, c = 17,57 (1) Å, β = 96,29 (9)°. La valeur finale de R est de 0,17, en utilisant des facteurs de température anisotropes pour les atomes du silicate, et des facteurs de température isotropes pour les atomes de carbone. Les facteurs d'occupation des atomes de C ont été considérés comme des paramètres variables. Les données de diffraction sont de mauvaise qualité à cause des défauts d'empilement. Les résultats montrent que les molécules sont distribuées au hasard sur les sites cristallographiques dans l'espace interfeuillet et les pics apparaissant dans les cartes de densité électronique peuvent être interprétés comme étand dus à 2 molécules de pipéridine et deux molécules de H_2O. L'orientation des molécules organiques est ambigue. Les pics de densité électronique s'accordent avec un modèle dans lequel les molécules sont verticles et dont les plans forment un angle dièdre petit et s'accordent aussi avec un modèle où les plans des molécules sont parallèles à 001. Il est tout à fait possible que les deux types d'orientation existent.

Kurzreferat—Mit einem dreidimensionalen Röntgenbeugungsverfahren wurden Einkristalle eines Vermiculit–Piperidinkomplexes untersucht. Der Komplex wurde durch Ionenaustausch bei pH 8 aus einem Na–Vermiculit hergestellt. Insgesamt wurden 453 Reflexe beobachtet und zur Strukturverfeinerung nach der Methode der kleinsten Abweichungsquadrate herangezogen. Der Komplex ist monoklin, $C2/m$, a = 5,346(2) Å, b = 9,256(3) Å, c = 17,57(1) Å, β = 96,29(9)°. Der letzte R-Wert betrug 0,17 bei Benutzung anisotroper Temperaturfaktoren für die Silicatatome und isotroper Temperaturfaktoren für die Kohlenstoffatome. Die Besetzungsfaktoren der C-Atome wurden als variable Parameter betrachtet. Die Beugungsdaten waren wegen Fehlern in der Schichtzuordnung von geringer Qualität. Die Ergebnisse zeigen, daß die Moleküle über die kristallographischen Plätze im Zwischenschichtraum zufällig verteilt sind, und daß die in der Elektronendichtekarte erscheinenden Maxima als durch zwei Piperidinmoleküle und zwei Wassermoleküle verursacht interpretiert werden können. Die Orientierung der organischen Moleküle ist nicht eindeutig. Die Elektronendichtemaxima passen in ein Modell, in dem die Moleküle vertikal stehen und ihre Ebenen einen kleinen Winkel bilden. Sie passen auch in ein Modell, in dem die Ebene der Moleküle parallel zu (001) angeordnet ist. Es ist gut möglich, daß beide Arten der Orientierung vorliegen.

Резюме — Методом трехмерной дифракции рентгеновских лучей на одном кристалле исследовали комплекс вермикулита-пипердина. Комплекс приготовили путем ионообмена Na вермикулита при pH = 8. В общем итоге обнаружили 453 отражений, а структуру уточняли методом наименьших квадратов. Комплекс является моноклинным, С2/м, a = 5,346(2)Å; b = 9,256(3)Å; c = 17,57(1)Å; β = 96,29(9)°. Для атомов силиката конечное значение R = 0,17 при использовании анизотропических факторов температуры, а для атомов углерода то же самое только при изотропических факторах температуры. Фактор заполненности атомов С считали переменным параметром. Данные дифракции были плохого качества, вследствие погрешности в группировании. По результатам видно, что в межслойном пространстве молекулы распределены по кристаллографическим узлам произвольно, а максимумы концентрации электронов выявленные на отображениях могут быть объяснены двумя молекулами пиперидина и двумя молекулами H_2O. Ориентация органических молекул неясная. Максимумы концентрации электронов соответствует модели в которой молекулы вертикальные и их плоскости образуют небольшой двугранный уголок, и также модели в которой плоскость молекул параллельная (001). Очень возможно, что присутствуют оба типа ориентации.

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