A POLARIZED INFRARED AND X-RAY STUDY OF LYSINE–VERMICULITE

M. Raupach, P. G. Slade, L. Janik and E. W. Radoslovich*

C.S.I.R.O. Division of Soils, Glen Osmond, S. Australia 5064

Abstract—Lysine and vermiculite form a stable, ordered, interlamellar complex which has a well defined superlattice structure with respect to the *ab*-plane of vermiculite. The lysine molecules lie at a low angle to the silicate surfaces and establish a double layer network between such surfaces. I.R. and chemical data for the complex are given. The possible role of hydrogen bonds in linking the system together is considered.

INTRODUCTION

Walker (1961) and Garrett (1962) reported that the basic, soluble amino acids such as lysine and ornithine and also the ω-amino acids with chain lengths greater than β-alanine, form cationic complexes with vermiculite. Rausell-Colom and Salvador (1971) used the discrete basal spacings of vermiculite single crystals treated with amino acid solutions as guides for suggesting possible arrangements for the amino acid molecules in the interlamellar spaces. Mifsud *et al.* (1970) and Jang and Condrate (1972) have used i.r. spectra to identify adsorbed species.

Work has also been done on vermiculite–alkylammonium complexes (Walker, 1960; Garrett and Walker, 1962; Serratosa *et al.*, 1970; Walker, 1967; and Farmer, 1971). This paper reports a study by X-ray diffraction and i.r. spectroscopy of an *l*-lysine–vermiculite complex which displays a greater degree of order than previously observed for amino acid complexes with vermiculite.

EXPERIMENTAL

Preparation

Five differently charged vermiculites from the following localities: Llano, Texas; Santa Olalla, Spain; Beni Buxera, Spanish Morocco; Young River, Western Australia and Kapirikamodzi, Malawi (described and numbered as 1, 4, 14, 15 and 17 respectively by Norrish, 1972) were initially sodium saturated. Selected flakes about 0·5 mm across were reacted at 40°C for varying periods with a 0·5 M aqueous solution of *l*-lysine hydrochloride at the pH of maximum charge (5·57). The reactions were followed at 80× magnification by using a transmitted light microscope, fitted with a Leitz 10× U.M. objective with iris diaphragm adjusted to produce good contrast at the replacement boundary. This method allowed the reaction rim to be observed as it moved from the edge of a flake to its centre. At this stage the exchange

was assumed to be essentially complete. After reaction, the flakes were rinsed in cold water and air dried on filter paper; they were then rinsed with water at 40°C (to remove any expelled salts) and dried as before.

Methods

Chemical analyses were carried out with a combination of the methods detailed by Norrish and Hutton (1969) and conventional microanalytical procedures.

For X-ray diffractometry, single crystals (0·5 × 0·5 × 0·3 mm) were mounted on Mylar film stretched over specimen holders of the type usually used for packed powders. Iron filtered cobalt radiation was used in a Norelco diffractometer with the slit system as follows: divergence 0·25°, receiving 0·146 mm in front of a 1° slit. The scanning speed was 1°/min.

The a^*b^*-plane of the reciprocal lattice was recorded by mounting crystals in front of a collimated beam of iron-filtered cobalt radiation in a Unicam rotation camera. Crystals examined in this way were initially set with their basal planes perpendicular to the X-ray beam and were then oscillated through 7·5° either side of their median positions. By varying the initial position of the crystal from perpendicular to the beam, different portions of the a^* b^*-plane were observed as it contacted the Ewald sphere.

A Perkin–Elmer 521 double beam grating spectrophotometer, equipped with a wire grid polarizer, was used for the i.r. work. Single attenuated total reflectance (ATR) studies were made on films deposited upon the reflecting surface of a germanium hemicylinder. Films of the lysine-treated vermiculite were prepared by depositing them from aqueous suspensions, formed from lightly hand-ground solids. Films produced in this way were dried over P_2O_5 at 20°C. Deuteration of the complex was readily achieved by direct exchange between the films and D_2O. Single flakes of the complex were also deuterated on the reflecting surface of the hemicylinder and dried over P_2O_5. The swelling of single flakes both in water and

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* Division of Soils, C.S.I.R.O., Adelaide, Australia.

D_2O, caused partial disintegration so that uniaxially oriented specimens tended to result. Transmission studies were made upon KBr discs, upon undeuterated self-supporting films and also upon single flakes. Because of their small cross section, the latter were mounted on a Nonius goniometer head in a reflecting beam condenser.

GENERAL RESULTS

Chemical analytical data for the complex obtained with the Young River vermiculite are given in Table 1. The Young River material was chosen for analytical work since it could be obtained in large flakes apparently free from inclusions.

The analyses reported are for material which had previously been sodium saturated and then reacted with lysine hydrochloride until the residual sodium concentration of the flakes was very low (0·02 per cent). Table 1 also sets out the number of atoms of each type within a vermiculite cell of 22 oxygens. On an average, the complex formed by the Young River material contains 8 carbon atoms, or 1 1/3 lysine molecules, per cell. This accords well with the charge of 1·31 units reported by Norrish (1972) for the same material (Sample 15).

All the vermiculites studied reacted readily with lysine after they had been sodium saturated, but the specimen with the highest charge (Llano) swelled greatly and disintegrated. Santa Olalla, a vermiculite of medium charge, showed some incipient disintegration.

After the washing and drying steps previously described, basal spacings of reacted flakes of the lower charged materials were measured from diffractometer traces. With cobalt radiation, these consistently produced an integral set of 001 peaks as far as the 21st order. Flakes were rewashed in a 1:1 water–ethanol mixture at 40°C for 4 hr and, following a final drying stage in air, the basal spacings were again measured. The constancy of the result (17·40 ± 0·1 Å) and the

integral set of orders, both before and after the water–ethanol wash, must be taken as evidence for the definite character and stability of the complex formed between lysine and vermiculite.

X-ray diffraction results

For the three lower charged vermiculites the diffraction patterns, obtained in the transmission mode described, consisted of the usual set of Bragg reflections for vermiculite but showed in addition, an array of superlattice reflections near the direct beam; see Fig. 1. These extra reflections degenerated into streaks for the medium-charged Santa Olalla vermiculite, in which the incipient disintegration during reaction increased stacking disorder. Single crystal work was not possible at all on the Llano material.

The superlattice pattern represents a direct projection onto the film of the reciprocal lattice plane nearest the Ewald sphere. By varying the initial position of the flakes, further portions of the superlattice along the a^*b^*-plane were observed as it contacted the Ewald surface.

The distortion produced as the flat plane of reciprocal space was projected onto the cylindrical surface of the film in the oscillation camera, was avoided by rephotographing with a precession camera. The problems of setting disordered specimens on a precession camera are well known, but they were overcome in the present work by using the technique due to Zoltai (1963) who blanked off half the circular screen slit to eliminate second reflections. Although images of the a^*b^*-superlattice plane were obtained with the precession instrument, exposure times were excessive (1 month).

The combined disadvantages of distortion of the geometry by the rotation camera and of weak incomplete reflections from the precession camera were removed upon transcribing the superlattice pattern onto a scale drawing of the vermiculite a^*b^*-plane (Fig. 2). By inspection of the array, the following selection rules were deduced:

$h\,0\,0$ with $h = 6\,n$
$0\,k\,0$ with $k = 2\,n$ $n =$ whole number
$h\,k\,0$ for which $-h + k = 12\,n$
     or $h + k = 12\,n$

Table 1. Chemical analysis and structural formula (O = 22) for the Young River vermiculite–lysine complex

| Analysis		Number of ions on basis of 22 oxygens	
SiO_2	33.14	Si	5.7
Al_2O_3	13.07	Al	2.3
		Tetrahedral ions	8.0
TiO_2	0.53	Al	0.35
		Ti	0.67
MgO	17.55	Mg	4.50
		Fe+3	1.24
Fe_2O_3	9.59	Fe+2	0.00
		Mn	0.04
		Octahedral ions	6.20
		Ca	0.00
MnO	0.28	Na	0.01
		K	0.00
CaO	0.01	C	8.12
		N	2.71
Na_2O	0.03	H	18.97
		O	2.71
K_2O	0.01	Interlayer lysine	1.3 molecules
P_2O_5	0.01		
		Structural (OH)	2.08 molecules
C	9.43		
N	3.67	Interlayer (H_2O)	1.57 molecules
H	1.85		
O	4.19		
H_2O	6.36		
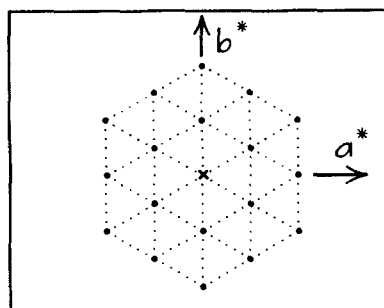
Fig. 2. Transcription of a^*b^* reciprocal plane of the superlattice for the vermiculite–lysine complex. Points for unreacted vermiculite are shown boldly.
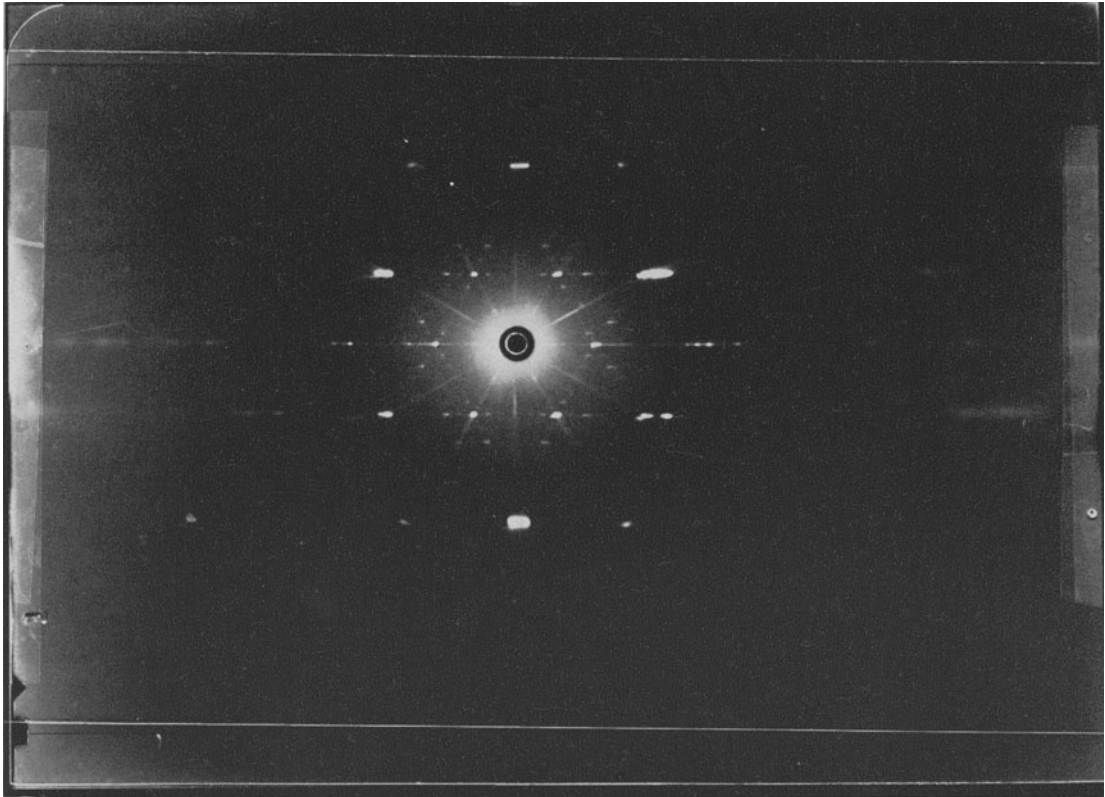
Fig. 1. Oscillation photograph taken with cobalt radiation of a flake of Nyasaland vermiculite after reaction with l-lysine monohydrochloride (0·5M) at pH=5·57. Oscillation axis = a and exposure time 3 hr.

The intersecting lines of diffraction maxima, which in combination form the total pattern, are the Fourier transform of three lines of points in real space; these lines are perpendicular to the related point rows of the diffraction pattern. The arrangement of scattering centres in the new supercell (6 × 6 subcells) of vermiculite was established by firstly plotting planes of the type $-h + k = 12n$ and then $h + k = 12n$ on a drawing of the supercell. Planes within each group intersected in a common point at the centre of a subcell: one on either side of the b-axis adjacent to the origin. These starting positions enabled diagonal rows of points to be extended across the supercell to form a network which is 2-fold degenerate with respect to both the a and b-axes and therefore does not explain the $h\,0\,0$ reflections. To do this the model was further developed.

For the generalized space group $P\bar{1}$ the geometric part (A) of any structure factor has the form $A = 2\cos 2\pi\,(hx + ky + lz)$ such that A will have non-zero values for $k = 2$ when the repeating units are along planes perpendicular to b and intersecting it at intervals of $b/2$. Similarly, for h to be a multiple of 6, planes are required to intersect a at intervals of $a/6$.

The final model (Fig. 3) incorporating these restrictions, was tested by calculating geometric structure factors for all classes of reflections on a PDP 11/20 computer. The relationship between this geometrical array and the disposition of the lysine molecules in the interlamellar space of the vermiculite was then further investigated by i.r. spectroscopy.

I.r. results

(1) Band resolution. Figure 4(a and b) shows the deuterated and undeuterated ATR spectra, at polarizations of 0° and 90°, for the lysine–vermiculite complex formed by the Young River material. The spectra were resolved into a maximum of 22 bands by assuming each component band to be a linear combination of a Cauchy and Gauss function defined, according to Fraser and Suzuki (1969), by height, position and width at half height and with a Cauchy proportion of 0·7. Reiteration was continued until the variance was less than 0·1 per cent. The highly overlapped
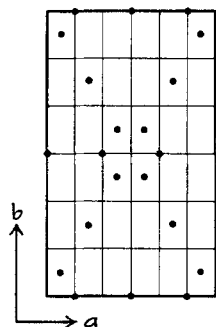

Fig. 3. The *ab* plane of the lysine–vermiculite supercell, showing the imposed geometrical array of points deduced from the observed extinction criteria for the diffraction pattern.
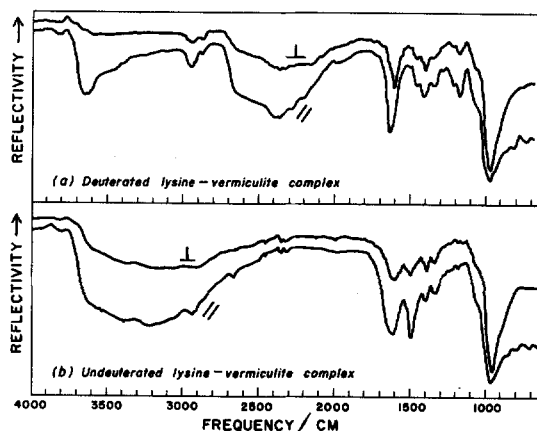

Fig. 4. Perpendicular and parallel polarized ATR spectra of (a) deuterated and (b) undeuterated lysine–vermiculite films at a 30° incident angle.

region near 1600/cm caused some uncertainty, but the defining parameters were changed minimally for the various spectra.

(2) Assignments. The assignments for the deuterated and undeuterated spectra of the complex were made by using published data for pure lysine (Pearson and Slifkin, 1972; Tsuboi *et al.*, 1963), other amino acids (Suzuki and Shimanouchi, 1963; Adamowicz and Fishman, 1972), amino acid complexes (Mifsud *et al.*, 1970; Jang and Condrate, 1972) and alkylammonium–vermiculite complexes. The results are given in Table 2.

Table 2. I.r. frequencies, band assignments and transition moment directions of lysine–vermiculite complex as determined by polarized ATR

Frequency cm-1	Band Assignment	Transition Moment Direction ($\psi°$)
2949 2910	tertiary αCH and antisymmetric CH_2 stretching	35
2875	symmetric CH_2 stretching	25
1653	H_2O deformation	51
1635		71
1610	$COO^{\ominus}$ antisymmetric stretching	30
1590	$NH_3^{\oplus}$ antisymmetric deformation	43
1560		19
1540		36
1501	$NH_3^{\oplus}$ symmetric deformation	41
1473		44
1450	CH_2 scissoring deformation	29
1415		41
1400	$COO^{\ominus}$ symmetric stretching	15
1360		28
1340	CH_2 wagging deformation	24
1320		32
1290	$NH_3^{\oplus}$ rocking	21
1260		
1230		35
1210	* $ND_3^{\oplus}$ antisymmetric deformation	45
1185	C-C-N stretching	22
1169	* D_2O and $ND_3^{\oplus}$ symmetric deformation	31
1060		

* Bands appearing on deuteration.

The anti-symmetric carbonyl stretching vibration, normally near 1720/cm in pure lysine at low pH (Pearson and Slifkin, 1972), was absent in lysine–vermiculite films: the acid group of the interlamellar lysine molecules is therefore in an ionized form.

In accordance with this ionization state two carboxyl stretching frequencies were observed; an anti-symmetric vibration at 1610/cm and a symmetric vibration at 1400/cm. These agree with the frequencies at 1615 and 1395–1416/cm for intercalated lysine–montmorillonite complexes (Jang and Condrate, 1972). Two other bands at 1630 and 1415/cm could also be carboxyl stretching frequencies.

The symmetric deformation modes of the α and the ϵ amino groups in lysine hydrochloride (Tsuboi et al., 1963) absorb near 1516 and 1529/cm respectively. The corresponding vibration in lysine–montmorillonite complexes is near 1497/cm. For the lysine–vermiculite complex a strong highly dichroic band occurred at 1501/cm. On deuteration this shifted to 1169/cm and has been assigned to the symmetric deformation of the NH_3^+ groups. From the above evidence we assume the lysine molecules exist in their cationic form, in agreement with their ability to satisfy the charge found by Norrish (1972) for this material.

The absorption frequencies of most importance in determining the orientation of the organic molecules with respect to the silicate surface are the methylene stretching and bending modes. The bands at 2949 and 2875/cm in the spectra of the deuterated complex were assigned to the methylene antisymmetric and symmetric stretching modes, in agreement with assignments of similar frequencies in the lysine–montmorillonite complexes. Deuteration was necessary to

Mg–K depleted phlogopite. We have no evidence to suggest perturbation of the lattice hydroxyls as observed in the alkylammonium complexes which also have a band near 3700/cm.

In pure lysine hydrochloride, lysine molecules are bonded into chains by a hydrogen bond network with an average bond length of about 2·8 Å (Koetzle et al., 1972). According to the Leonard–Jones potential function, the frequency of such NH–O bonds should be about 3100/cm. For the lysine–vermiculite complex the broad NH stretching region is centred at 3150/cm, together with the OH stretch of hydrogen bonded water. Therefore a hydrogen bond environment similar to lysine and involving amino groups, and interlamellar water could be present in the lysine–vermiculite complex. Fripiat et al. (1969) have shown that water molecules possess a strong tendency to form hydrogen bonds with ammonium groups. Such hydrogen bonded water molecules can be expected to show an antisymmetric hydroxyl deformation and hence be responsible for the band observed at 1653/cm in our complex. This band was shifted by a factor of 1·41 on deuteration, to give a peak at 1060/cm.

(3) Bond orientation. When single flakes of the complex were rotated about their c crystallographic axes, no significant dichroism was observed in the polarized transmission spectra. This suggested that the lysine cations are either randomly orientated about c or distributed with a three-fold or higher symmetry.

From perpendicular and parallel polarized ATR spectra, transition moment directions of the resolved bands could be calculated with respect to the c-axis, by using the optical equations given by Flourney et al. (1966):

$$\ln R_\perp = -\frac{4n_x^2 k_x}{n_1^2 \tan\theta \left(1 - \frac{n_x^2}{n_1^2 \sin^2\theta}\right)^{1/2} \left(1 - \frac{n_x^2}{n_1^2}\right)}$$

$$\ln R_\parallel = -\frac{4n_y n_z \left[k_z + \left(1 - \frac{n_z^2}{n_1^2 \sin^2\theta}\right) k_y\right]}{n_1^2 \tan\theta \left(1 - \frac{n_z^2}{n_1^2 \sin^2\theta}\right)^{1/2} \left(1 - \frac{n_z^2}{n_1^2 \sin^2\theta} + \frac{n_y^2 n_z^2 \cot^2\theta}{n_1^4}\right)}$$

verify the bands of methylene due to overlap with neighboring bands. Of the deformation modes, the bands at 1450–70 and 1340–60/cm are probably due to CH_2 scissoring and wagging vibrations respectively (Jang and Condrate, 1972, and Pearson and Slifkin, 1972).

The deuterated complex has a strong, highly polarized, broad band near 3620–60/cm which we have assigned to the lattice OH stretching frequency. Hydrogen bonding could possibly be responsible for the lowering of this frequency from 3635–77/cm which was the value assigned by Raussell-Colom and Salvador (1971) to the lattice OH stretching vibration of

where subscripted n is the refractive index in the x, y and z directions (and z is perpendicular to the crystallographic ab-plane), n_1 is the refractive index of germanium, θ is the angle of incidence, k is the absorption index in the x, y and z directions and R is the perpendicular or parallel reflectivity. An isotropic refractive index was used since this assumption was found to be valid by other workers (Takenaka et al., 1971). The value 1·52, used in the calculations, was found by an oil immersion technique using single crystals of lysine hydrochloride. With the equations of Takenaka et al. (1971) values of k_x, k_y and k_z were used to calculate the transition moment direction (ψ), with respect to the ab-plane, for each vibration.

Table 2 gives ψ for the transition moment directions of the resolved bands.

The geometrical relationship between a lysine cation and the silicate surface, as deduced from the transition moment directions for CH_2 groups, is illustrated in Fig. 5. Table 2 sets out the directions of other modes of vibration which relate to the orientation of the organic molecule with respect to the ab-plane. The angle ($25°$) between the lysine chains and the silicate surface is considerably less than the value of $54°$ deduced by Walker (1967) for octylammonium chains in vermiculite. Such a shallow angle makes it difficult for the ϵ amino group of the lysine chain to key deeply into the holes of the silicate surface. This is supported not only by the lack of evidence for perturbation of the lattice hydroxyl groups but also by the position of the NH_3^+ symmetrical deformation mode at 1501/cm. Serratosa et al. (1970) found that for collapsed octylammonium–vermiculite complexes the NH_3^+ deformation mode absorbed at 1570/cm; this represented a shift of 65 from 1505/cm for the expanded film in which the ammonium groups were believed not to be deeply buried in the surface.

Two possibilities exist for the disposition of the lysine molecules; either their α and ϵ amino groups are arranged in a cis- or a trans-configuration to the silicate surface. The tilt of the molecule is the same in either case since one configuration is a mirror image of the other except for the α-$(H–C–NH_3^+)$ group.

DISCUSSION

Although vermiculite complexes containing ornithine, histidine, arginine and 6-aminohexanoic acid have also been investigated, superlattice reflections have only been observed for the lysine complex. This is believed to indicate that the dimensions and bonding capabilities of the lysine molecule are such as to match the geometrical arrangement of active points in the system of hexagonally arranged oxygen atoms which form the surfaces of the silicate sheets. If l-lysine molecules are hydrogen bonded in pairs, units suitable to span centres of hexagonal oxygen rings result. These units can be arranged to form linear members, ordered in at least three possible ways to produce the X-ray and i.r. spectra:-

(a) The pattern may be the statistical resultant produced by stacking a number of sheets, on each of which there is a parallel arrangement of linear members. Between sheets the lineation is randomly rotated through $60°$ in the basal plane.

(b) The spectra may arise from a pattern within single sheets on which the organic molecules are grouped in parallel arrangements of linear members within domains, each domain being rotated $60°$ to a neighboring domain.

(c) Again within single sheets, the organic molecules may be arranged on a repeating superlattice pattern. This superlattice array is continuous over each and every sheet but the sheets can be randomly stacked.

The three alternatives are sketched in Fig. 6. Although possibilities (a) and (b) cannot be dismissed entirely, they are not favoured as the distribution of intensities within the X-ray superlattice reflections has not been found to vary in any of the photographs obtained from the many crystals of the complex formed by the different vermiculites examined. The favoured possibility (c) is shown in detail in Fig. 7, which illustrates the configuration proposed for a
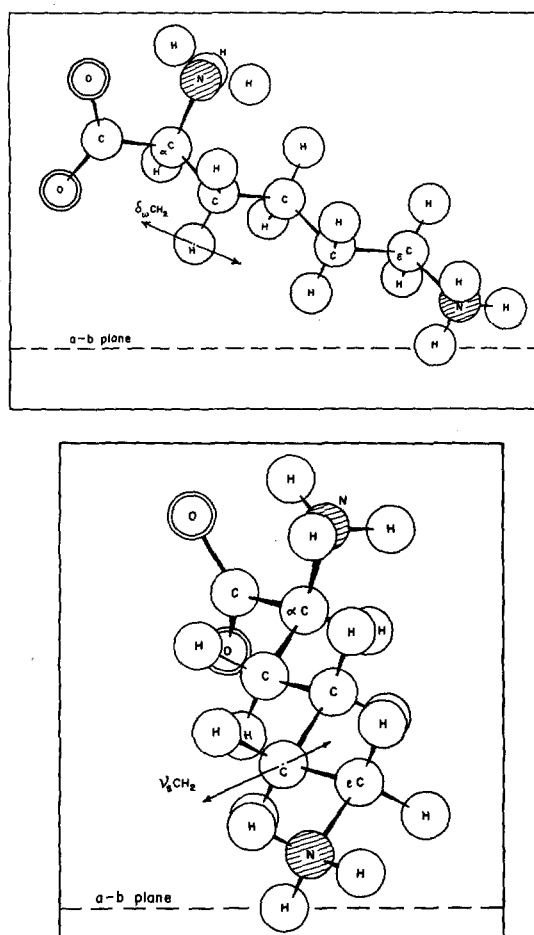

Fig. 5. Two views of a lysine molecule in the interlamellar region of vermiculite; normal to (a) the CH_2 wagging and (b) the symmetric stretching transition moment direction.
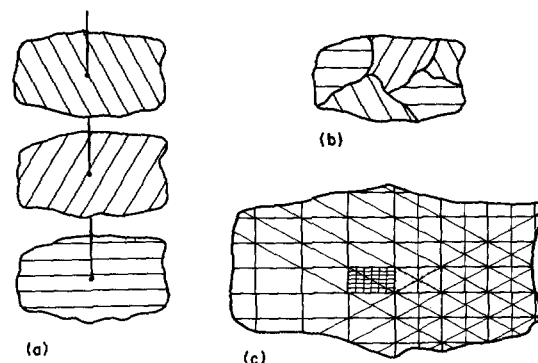

Fig. 6. Three ways in which linear groups of organic molecules might combine to produce X-ray and i.r. spectra. Only half sheets are shown and linear arrangements of organic molecules are represented thus ——
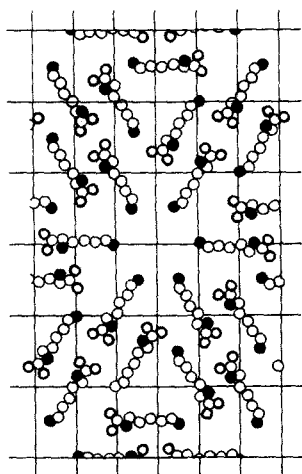
Fig. 7. Proposed configuration for hydrogen bonded pairs of lysine molecules on the surface of a silicate sheet. Amino groups are represented thus ●, with the ϵ amino groups positioned over centres of hexagonal rings of oxygen atoms. This has been achieved by shifting the origins of subcells by $a/3$ and $b/3$ cf. Mathieson and Walker's (1954) cell.

single half layer of 6×6 subcells. On average, such a single half layer will have $2/3$ of a lysine molecule per subcell. The relationship between this configuration of lysine molecules and the formal geometric array of scattering centres can be seen by comparing Fig. 7 with 3. The total interlamellar region is believed to result from regular interlinking of two half layers, perhaps through water molecules.

In the proposed model, the role of the α amino group is crucial, not only for the grouping of lysine molecules into pairs but also for the interlinking of half layers. Work on the role of this group is continuing.

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