The Surface and Intercalate Chemistry of the Layered Silicates. Part IV. Crystallographic, Electron-spectroscopic, and Kinetic Studies of the Sodium Montmorillonite–Pyridine System

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Neutron-diffraction studies of the stable pyridine (py) intercalate of Na^+-exchanged montmorillonite [basal-spacing 14.8 Å, idealized formula $Na^{+}_{0.5}(Al_{3.5}Mg_{0.5})Si_8O_{20}(OH)_4\cdot py\cdot 2H_2O$] have been carried out. It is shown that the plane of the guest aromatic molecule is perpendicular, and the long (C–N) axis inclined at 60°, to the aluminosilicate sheets. The kinetics of the conversion of the initially formed less-stable intercalate [basal-spacing 23.3 Å, idealized formula $Na^{+}_{0.5}(Al_{3.5}Mg_{0.5})Si_8O_{20}(OH)_4\cdot (py)_2\cdot H_2O$] to the more stable 14.8 Å intercalate has been followed by *X*-ray diffraction. *X*-Ray induced photoelectron spectroscopy (x.p.s.) has also been used to probe electronic changes in the environment of the Na^+ ions following intercalation. X.p.s. shows that the pyridine is retained even *in vacua* of 10^{-6} N m^{-2} at room temperature, and that the nitrogen atoms are situated within essentially one type of environment.

As part of our general investigation of sheet-silicate intercalates we have been prompted, for a variety of reasons, to re-examine the Na^+–montmorillonite–pyridine interlamellar complexes. First, there is the question of crystallographic structure, our knowledge of which derives entirely from the classical studies of Greene-Kelly,[1-3] who deduced that in the 14.8 Å intercalate the aromatic plane of the pyridine is perpendicular to the silicate layers and oriented such that the long (C–N) axis is parallel to the sheets. He was also able to demonstrate that, in the 23.3 Å intercalate, the stoicheiometric ratios of $Na^+ : py : H_2O$ were 1 : 4 : 2. We show below that neutron diffraction, which, for the kind of material that forms the subject of this series, is an intrinsically more powerful investigative tool for structural analysis [4] (especially in regard to the location of hydrogen atoms and to distinguishing carbon and nitrogen atoms) affords, for the first time, detailed insights into the siting of water molecules and organic entities which are intercalated in the sheet silicates, and that the conclusions of Greene-Kelly require some modification.

Secondly, there is the question of the electronic environment of the interlamellar pyridine and neutralizing Na^+ ions, and, in particular, the tenacity with which the organic base is retained by the sheet silicate. Moreover, it has recently been reported [5] that major changes in the core-electron binding energies of transition-metal ions that function as neutralizing cations accompany the process of intercalation. If this is indeed so, it signifies drastic charge-transfers and structural modifications which are not readily interpretable, during uptake of pyridine. Finally, our own preliminary studies,[6] along with those of Greene-Kelly,[1-3] indicated that the solid-state conversion of the 23.3 Å into the 14.8 Å basally-spaced pyridine intercalates was facile at room temperature and amenable to quantitative kinetic study by *X*-ray diffraction.

EXPERIMENTAL

Details of the origin of the montmorillonite and its conversion into the Na^+-exchanged form were given in Part III of this series.[7] Analysis of the ' cleaned ' clay gave in weight percent: 2.6(1) Fe, 24.6(2) Si, and 10.3(1)% Al. The clay was, therefore, dioctahedral, and its cation-exchange capacity was 70 milli-equivalents per 100 g clay.

Massive samples of the Na^+-exchanged clay (10 × 3 × 0.6 cm) were prepared, for the elastic neutron scattering studies, by sequential sedimentation, the sample being air-dried after each 1 mm deposition. The intercalation of pyridine was effected by immersing the cation-exchanged sample into the pure liquid for 24 h, followed by further equilibration at 45 °C for another 24-h period. The final intercalate was encapsulated within aluminium foil of 0.040 mm thickness. Well-resolved (00*l*) peaks (*l* up to 14) with a neutron wave-length of 1.18 Å were recorded on the Badger facility at Harwell. The intensities were corrected for Lorentz effects and the signs † for the reflections calculated from the contribution to the scattering caused by the aluminosilicate layers themselves and also by the interlamellar molecules, the approximate positions of which were known from prior *X*-ray studies.

For the *X*-ray kinetics study, a sample of the Na^+-exchanged montmorillonite was first immersed in liquid pyridine for 20 min and then, at *ca.* 5-min intervals, the *X*-ray pattern was recorded in the 2—10° range of 2θ on a Philips PW1050 diffractometer. These measurements were continued until the peak corresponding to the 23.3 Å basal spacing disappeared and the 14.8 Å peak displayed no further change. Since the diffraction signals for the first few minutes were attenuated as a result of absorption by the unavoidable initial presence of some liquid pyridine, a calibration had to be performed on a solid sample which also possessed a pronounced 23 Å peak but which is not modified as a result of short exposures to pyridine. A sample of vermiculite (Palabora) was used for this purpose, and the necessary correction could therefore be applied to the raw data on the 23.3 Å-spaced pyridine-intercalated sample.

X.p.s. were recorded on an A.E.I. ES200 spectrometer employing Mg-K_α radiation (1 486.6 eV). The samples

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† As mentioned in Part III of this series,[7] it is tacitly and reasonably assumed that the intercalate is centrosymmetric in its projection on to a line perpendicular to the silicate sheets.

[1] R. Greene-Kelly, *Trans. Faraday Soc.*, 1955, **51**, 412.

[2] R. Greene-Kelly, *Trans. Faraday Soc.*, 1955, **51**, 424.

[3] R. Greene-Kelly, *Clay Mineral Bull.*, 1955, **2**, 226.

[4] T. H. B. Sanders, S. Spooner, and W. E. Moody, *19th Clay Minerals Conference*, Abstracts, 1970, 33.

[5] J. Escard, I. Mantin, and G. Mavel, *Bull. Groupe fran Argiles*, **t.XXV**, 1973, 181.

[6] J. M. Adams, unpublished work.

[7] J. M. Adams, *J.C.S. Dalton*, 1974, 2286.

consisted of flakes (1 × 0.5 × 0.05 cm) of sedimented clay and the stable intercalate. The flakes were directly attached to a copper probe which fitted inside the vacuum chamber, and was continuously pumped at a dynamic pressure of *ca* 3 × 10^{-6} N m^{-2}.

RESULTS AND DISCUSSION

Neutron Diffraction.—Figure 1, which shows the relevant one-dimensional Fourier map for the 14.8 Å-spaced intercalate, along with Tables 1—3, summarize the results. Peaks (A)—(I) (Figure 1) are labelled according to our internally consistent assignments (see below), and Table 2 presents our reason for concluding that the long C–C axis is parallel to the (001) aluminosilicate planes. The extent of agreement between experimentally observed and computed (on the basis of the orientation shown in the inset of Figure 1) peak intensities is encouraging. There are, however, some noteworthy features. First, the size of the octahedral atom peak (A) is greater, and, secondly, the projected distance of the silicon atoms from the octahedral atoms is *ca.* 0.2 Å less, than what we would have expected on the basis of the idealized structure of defect-free montmorillonite sheets.

TABLE 1

Structure factors for the intercalate

l	F_l	l	F_l
1	+16.4	8	−7.3
2	−2.0	9	+5.8
3	−8.5	10	+5.5
4	+7.7	11	−4.8
5	+12.1	12	+4.2
6	−7.5	13	+7.2
7	−9.8	14	+5.5

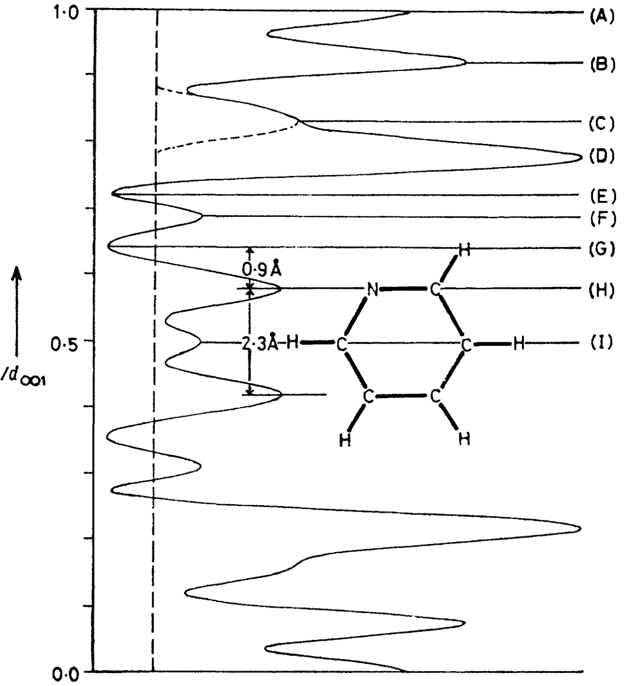

FIGURE 1 One-dimensional projection of nuclear scattering density perpendicular to (001)

The size of the peak (A) is, however, consistent with all the 2.6% Fe occupying octahedral sites. An alternative possible explanation for the shoulder (C) on the side of the main peak (C+D)—that it is due to hydrogen atoms of OH groups depressing an unresolved (Si + O) peak—cannot be sustained on two grounds: first because the clay is dioctahedral and the O–H bond in such minerals is approximately parallel to (001);[8] and, secondly, that if the hydrogen atoms are considered to be in such a position then the peak area ratios diverge much more from those expected theoretically (Table 3).

TABLE 2

Computed and experimental peak heights for the pyridine molecule (see Figure 1)

		Computed	
Peak	Expt.	Long C–N axis ‖ to sheets	Long C–C axis ‖ to sheets
(G)	−0.41 (5)	−0.57	−0.39
(H)	1.00	1.00	1.00
(I)	0.36 (5)	0.92	0.38

TABLE 3

Computed and experimental areas for the aluminosilicate peaks (see Figure 1)

Peak	Assignment	Expt.	Computed assuming all the 2.6% Fe is in octahedral sites
(A)	Al, Mg, Fe	2.0 (2)	1.71
(B)	O, OH	2.7 (2)	2.72
(C + D)	Si, O	5.16	5.16
(C)	Si	1.4 (2)	1.68
(D)	O	3.8 (2)	3.48

So far as the depression (E) and peak (F) (in Figure 1) are concerned, it is possible that (E) could arise from hydrogen atoms attached to the tetrahedrally bonded oxygens, thereby leaving peak (F) to be ascribed to the interlayer cation. But (F) is considerably too large (by a factor of five) for this to be so; and an alternative explanation is that (E) and (F) could both arise from interlamellar water molecules, which are hydrogen bonded to the silicate oxygen atoms, (E) being due to hydrogen and (F) to oxygen atoms. The geometry of the hydrogen-bonding scheme is as follows: the projected distance (D)–(F) is 1.3 Å and we can assume 2.8 Å for the O–H · · · O hydrogen bond distance (Figure 2a). We obtain an O–O distance in the layer of 5 Å and an O · · · O · · · O angle of 126°. The H–O–H angle in the water molecule is 104.5°, thus leaving us with a hydrogen bond which is *ca.* 11° out of linearity, not an unacceptable value. The Si–O–O–Si distance of 5 Å is in excellent agreement[9] with a unit-cell parameter in clays of *ca.* 5.2—5.4 Å and permits a bridging of the form schematized in Figure 2(b).

From the orientation of the pyridine molecules that has been deduced, it is possible to predict a projected position for the interlayer sodium ions. An Na^+–N

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[8] G. W. Brindley, *Mat. Res. Bull.*, 1972, **7**, 1191.

[9] 'The *X*-Ray Identification and Crystal Structures of Clay Minerals,' ed. G. Brown, Mineralogical Society, London, 1972, p. 55.

distance[10,11] of 2.5 Å gives a projected position for the cations of 4.1 Å from the octahedral atoms (Figure 3) compared with a value of 4.2 Å found by Pezerat and Méring[12] in the case of anhydrous and hydrated Na^+-exchanged montmorillonite. The projected position of the cations would thus be in the depression, (E) (Figure 1). The peak areas of (E) and (F) correspond almost exactly to 0.25 Na^+ and 1.0 H_2O per half-unit cell [(E) corresponding to (0.25 sodium ions + 2.0 hydrogen atoms), (F) corresponding to 1.0 oxygen atoms].

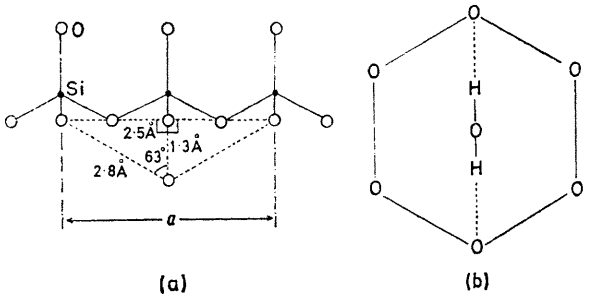

FIGURE 2 (a) Hydrogen bonding scheme for water molecules to the tetrahedral oxygen atoms: projection along *b* axis; (b) bridging role of the water molecules

X-Ray Studies.—Figures 4 and 5 show, respectively, the variations in the 23.3 and 14.8 Å peaks with time and the correction curve obtained by monitoring the time dependence of the Palabora vermiculite deliberately contaminated with pyridine. Owing to experimental difficulties, kinetic measurements could be recorded only at room temperature and humidity (295 K, relative humidity 59%). The respective kinetic plots derived from Figure 4 are presented in Figures 6 and 7, from which it is seen that the rate of conversion of the larger spaced (23.3 Å basal spacing) to the more stable intercalate is kinetically a ' first-order ' process. Although it is strictly not legitimate to treat first-order processes in solid-state decomposition reactions or phase transformations (see refs. 13 and 14) as analogous to kinetic first-order reactions in dispersed phases (where there is complete mixing both energetically and spacially), it is safe to conclude that the rate of breakdown of the parent initially formed pyridine complex {composition

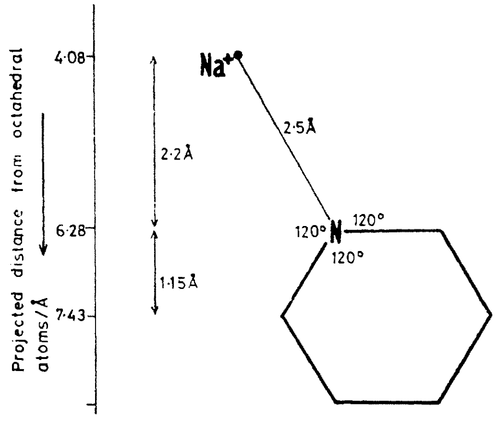

FIGURE 3 Prediction of the position of the interlayer cation

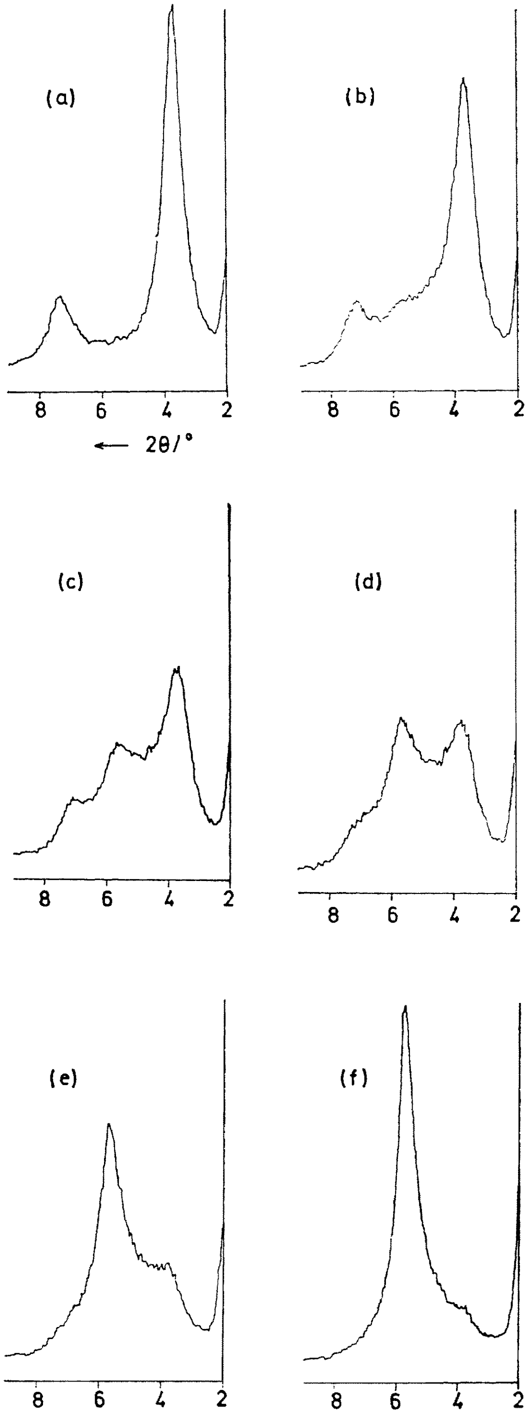

FIGURE 4 (a) *X*-Ray diffractometer traces of pyridine intercalate after (a) 8 min, (b) 85 min, (c) 119 min, (d) 145 min, (e) 214 min, and (f) 373 min

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[10] J. A. J. Jarvis and P. G. Owston, *Chem. Comm.*, 1971, 1403.

[11] B. Berking, *Angew. Chem. Internat. Edn.*, 1971, **10**, 814.

[12] H. Pezerat and J. Méring, *Compt. rend.*, 1967, 265, 529.

[13] D. A. Young, ' Decomposition of Solids,' Pergamon Press, London, 1966.

[14] T. A. Clarke and J. M. Thomas, *Nature*, 1968, **219**, 1149.

$M(py)_4\cdot 2H_2O$, $M \equiv 2[Na^+_{0.5}(Al_{3.5}Mg_{0.5})Si_8O_{20}(OH)_4]\}$ is directly proportional to the amount of parent complex present. This is reasonable in the light of the general nature of *n*-stage intercalates in other solids (notably graphite), the kinetics of interconversion of which have not, unfortunately, been reported. It is clear that the conversion

$$\begin{array}{ccc} M(py)_4\cdot 2H_2O & \xrightarrow[+H_2O]{-py} & M(py)_2\cdot 4H_2O \\ (23.3\ \text{Å spacing}) & & (14.8\ \text{Å spacing}) \end{array}$$

proceeds in an unhindered fashion * for a substantial range of the process (from $\alpha = 10\%$ to $\alpha = 97\%$), and that the rates of diffusion of the pyridine out from, and of the water vapour into, the interlamellar regions are not rate limiting (otherwise different functional dependences on time, involving square-root terms, would prevail).

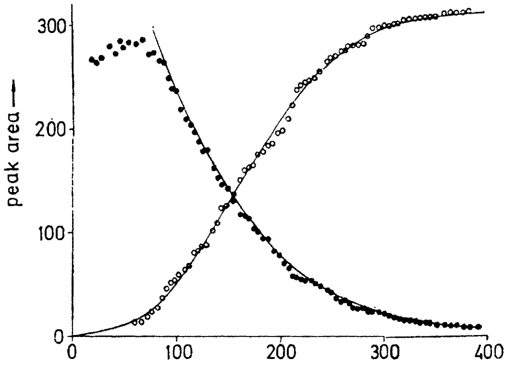

FIGURE 4 (b) Variation of 23.3 Å (filled circles) and 14.8 Å (empty circles) peak areas with time

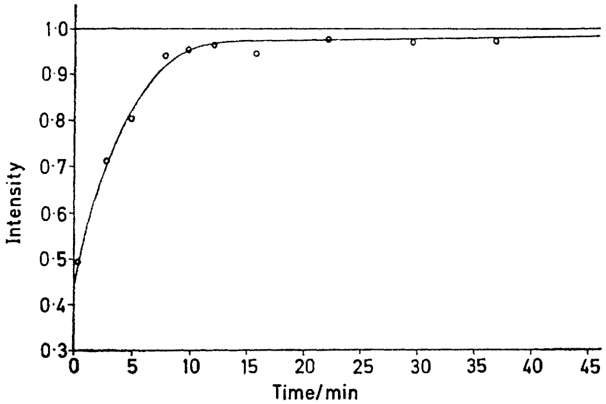

FIGURE 5 Time dependence of the Palabora vermiculite 23 Å-peak intensity after surface exposure to pyridine

In the absence of crystal-structure data on the parent pyridine intercalate, it is not possible to formulate detailed mechanisms for the transformation. However, recent results in these laboratories [15,16] on lattice-imaging electron microscopy of graphite–ferric chloride complexes reveal that, at the unit-cell level, a given phase of intercalate, corresponding for example to an *n*th-stage material as studied by *X*-ray diffraction, consists in reality, as studied by lattice imaging, of coherent 'mixtures' such as $n-1$, $n-2$, . . ., $n+1$, $n+2$ . . . stage phases. Whilst it is dangerous to press the analogy between graphite intercalates and sheet-silicate intercalates too far, it is, nevertheless, instructive to consider such ultra-microstructural factors as they do indicate how in principle the transformation may occur smoothly within the entire bulk of the parent pyridine–montmorillonite intercalate and thereby simulate the kinetic situations that obtain in dispersed phases.

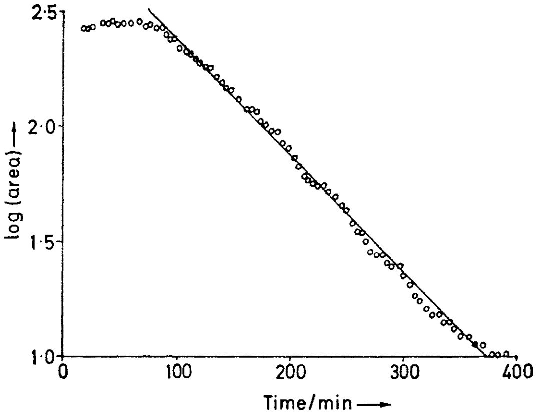

FIGURE 6 Variation of log (23.3 Å peak area) with time

X.p.s. Studies.—Figures 8 and 9 summarize the relevant results upon which we shall comment. It is to be noted that the technique is sufficiently sensitive to detect the photo-electrons emitted from both the Na 2*s* and 2*p* core levels even though the sodium is present in relatively small (1 atom per 80 non-hydrogen atoms) amounts. Owing to the difficulties encountered with differential charging across the surfaces of the alumino-silicate samples—a universal problem associated with all insulators studied by x.p.s. and u.p.s.—peaks are

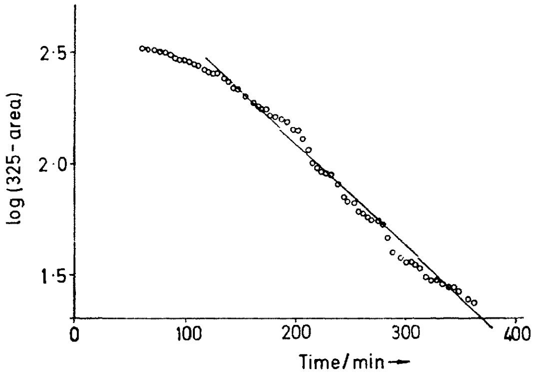

FIGURE 7 Variation of log [325 − (14.8 Å peak area)] with time

* In view of the uncertainties in the *X*-ray results at small times of conversion it is difficult to assess whether there exists an induction period in this reaction.

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[15] N. C. Davies, Ph.D. Thesis, University of Wales, Aberystwyth, 1974.

[16] N. C. Davies, E. L. Evans, and J. M. Thomas, in preparation.

artificially broadened and consequently tend to obscure genuine splitting, if it is present. The problem of charging also complicates the determination of absolute binding energies,[17,18] but this may be largely circumvented, for the purpose of assessing whether the Na^+ ions suffer major electronic environmental changes upon uptake of pyridine, by measuring the separation between Na 2*p* and the Au $4f_{7/2}$ signal from a thin layer of gold evaporated on the surface of the sample. On this basis it is found that both for the Na^+-exchanged montmorillonite and for the stable 14.8 Å-spacing intercalate the Na 2*p* binding energy turns out to be identical, and may be assigned a value of 31.6(4) eV if the Au $4f_{7/2}$ level is taken [19] to be 84.0 eV. Our results, therefore, do not agree with the recent claims that a binding-energy shift of *ca.* 2 eV occurs upon intercalation of an organic base. It clearly follows that the potential field seen by the Na^+ ions before and after intercalation is essentially the same, even though the local environment must obviously change. This is readily interpretable in terms of modern theories which seek to explain the origin of changes in binding energy in terms of change of charge, of Madelung contributions, and other more subtle effects (see, *e.g.* Parry [18] and Gelius [20]). Although the profiles of the N 1*s* signal change slightly with changing conditions, the differences are not significant. The width of the peak [full width at half maximum, 2.2(2) eV] is rather broad, because of differential charging, and there is no definite indication for the occurrence of more than one type of N atom in the intercalate. (There is a suggestion of a shoulder on the high binding energy side of the peak, which could even arise from the monopole governed shake-up process.[21]) Of particular interest, however, is the fact that the N 1*s* signal remains almost undiminished after the intercalate had been held in a vacuum of *ca.* 3×10^{-6} N m^{-2} for 1 h at 370 K, showing that the strength of the chemical binding of the organic moiety is exceptionally high.

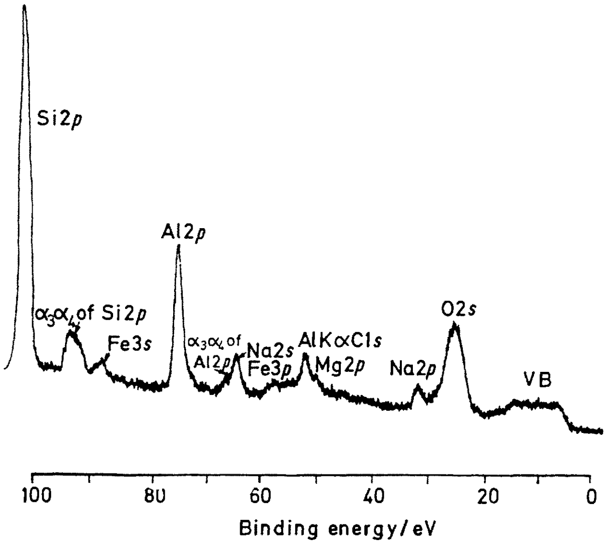

FIGURE 8 X.p.s. spectrum of the binding-energy range 100 ⟶ 0 eV for montmorillonite

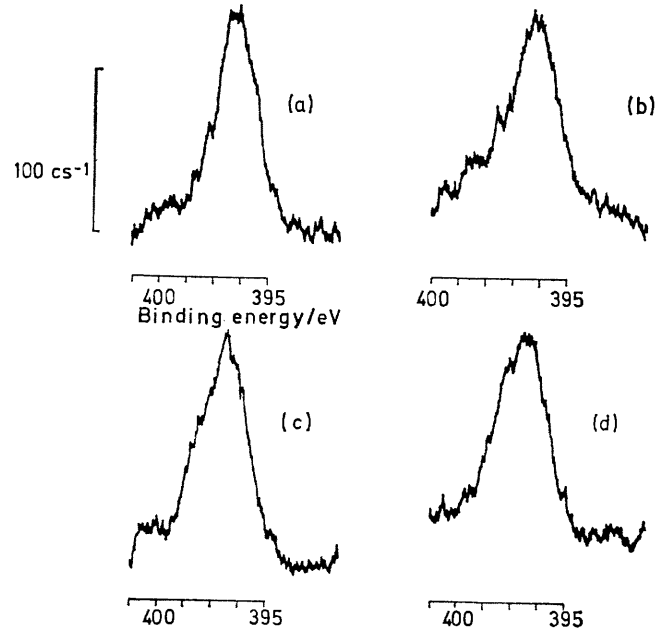

FIGURE 9 N 1*s* Signal for the stable intercalate (a) at 220 K, (b) 290 K after 16 h, (c) 370 K after a further few minutes, and (d) after 1 h at 370 K

Conclusions.—(i) From a one-dimensional Fourier analysis of the elastic neutron scattering of $M(py)_2{\cdot}4H_2O$ $\{M \equiv 2[Na^+_{0.5}(Al_{3.5}Mg_{0.5})Si_8O_{20}(OH)_4]\}$ the precise orientation and siting of an organic intercalate of a sheet silicate has, for the first time, been elucidated.

(ii) From the *X*-ray studies of variation in peak areas with time of the 23.3 and 14.8 Å basally-spaced pyridine intercalates the kinetics of the conversion

$$M(py)_4{\cdot}2H_2O \xrightarrow[+H_2O]{-py} M(py)_2{\cdot}4H_2O$$

has been followed and shown to be ' first order '.

(iii) From the x.p.s. studies of $M(py)_2{\cdot}4H_2O$ it is shown that: (*a*) contrary to a recent report, the electrostatic potential seen by the Na^+ ions prior to and following intercalation of pyridine is essentially the same; and (*b*) the pyridine is tenaciously bound to the silicates and survives heating to 370 K in a vacuum of 10^{-6} N m^{-2}.

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[4/2266 *Received, 4th November*, 1974]

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[17] J. M. Thomas, E. L. Evans, M. Barber, and P. Swift, *Trans. Faraday Soc.*, 1971, **67**, 1875.

[18] D. E. Parry, *J.C.S. Faraday II*, 1975, 337.

[19] S. Evans, unpublished work.

[20] U. Gelius, *Physica Scripta*, 1974, **9**, 133.

[21] L. J. Aarons, M. Barber, J. A. Connor, M. F. Guest, I. H. Hillier, I. Ikemoto, and J. M. Thomas, *J.C.S. Faraday I*, 1973, 270.