Surface and Intercalate Chemistry of Layered Silicates. Part III.[1] *X*-Ray Investigation of Tetrahydropyran and 1,4-Dioxan Intercalates of Montmorillonite

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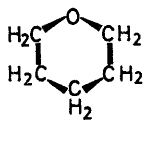
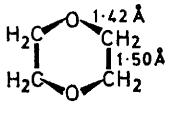
Electron-density maps of intercalates of sodium- and strontium-exchanged montmorillonites show that both the interlamellar tetrahydropyran, (I), and 1,4-dioxan molecules, (II), are oriented essentially perpendicular to the aluminosilicate layers. The number of organic molecules per formula unit of silicate [idealised $Al_4Si_8O_{20}(OH)_4$] lies between 1·0 and 1·3. It is also demonstrated that changes in basal spacings, used alone, yield misleading information concerning the orientation taken up by the organic guest species.

SINCE very little information is currently available concerning the structure of even the simplest intercalates formed by sheet silicate minerals, we have concentrated our early *X*-ray studies on systems in which thermally stable silicate–organic complexes are formed, and which also yield well oriented samples which, in turn, permit ready accumulation of 00*l* intensity data (to quite high order). The related molecules tetrahydropyran, (I), and 1,4-dioxan, (II), are particularly appropriate for our purposes partly because their precise molecular parameters are already known,[2] and also because they offer a ready means of determining how the orientation of essentially rigid organic molecules between the sheets varies with respect to both slight molecular modification and the nature and position of interlayer (inorganic) cations present in the parent silicate.



(I)



(II)

The intercalate with (II) was first studied with *X*-rays by MacEwan[3] who postulated from the basal spacing of 15 Å for the complex that the short axis of the organic molecule was approximately perpendicular to the aluminosilicate layers. Brindley and Tsunashima[4] studied the uptake of (II) from aqueous solution with a differential refractometer and, on comparing their results with electron counts obtained from a one-dimensional electron-density map, they deduced that they had considerable amounts of water in the interlayer region. They did not, therefore, deduce an orientation for the intercalating molecule.

We set out to obtain more complete information by preparing electron-density maps from Fourier summation of structure factors of the 00*l* reflections. It should be noted that calculation of the electron-density maps assumes the distribution to be centrosymmetric. This assumption has a physical basis since the layers themselves are centrosymmetric. However, the interpretation of these maps is often difficult since if we have a non-centrosymmetric molecule we obtain only the average of the two orientations of the molecule.

EXPERIMENTAL

Montmorillonite from Upton, Wyoming, was obtained as a Clay Mineral Standard (No. 25) from Wards Natural Science Establishment. The clay was sedimented overnight in water and the top 5 cm fraction collected (particle size < 1 μm). The suspension was concentrated by warming for several hours. A portion of the clay was treated with a strong strontium dinitrate solution and was then washed many times with deionised water until the *X*-ray diffraction pattern of a portion of the solid was free of peaks from $Sr(NO_3)_2$. The cation-exchange capacity (c.e.c.) of this clay has been determined[5] as 70 millequivalents per 100 g air-dried clay. A sample of this clay was dried for 24 h at 110 °C and from the weight loss the new c.e.c. was established to be 79 milliequivalents per 100 g of dehydrated clay. Samples of suspensions of the untreated (sodium) and strontium-exchanged clays were allowed to dry on glass slides and intercalates were prepared by immersing the sample on its slide in the laboratory-reagent-grade organic liquid for several hours.

Diffraction patterns were recorded on a Philips PW1050 Vertical Diffractometer using Cu-K_α radiation (λ 1·5418 Å). It was possible to observe up to the 12 or 13th order of diffraction in all cases, corresponding to spacings of *ca.* 1·1 Å. Intensities were corrected for Lorentz and polarisation effects using the expression appropriate for diffraction from planes parallel to the surface of an extended, infinitely thick, crystal plate, *i.e.* $2Lp = (1 + \cos^2 2\theta)/\sin 2\theta$ (where θ is the Bragg reflection angle and the intensity, I, is related to the structure factor, F, by $I = Lp|F|^2$). This expression is not exact in our case since the samples were only *ca.* 0·3 mm thick.

RESULTS

The basal spacings (Table 1) for the air-dried sodium- and strontium-exchanged clays, and also the intercalates were obtained by extrapolating a graph of $d_{obs.}$ against cot ($\theta_{obs.}$) to $\theta = 90°$ following Bracher and Small.[6] The signs of the structure factors (Table 2) were predicted from scattering due to the aluminosilicate layers only. The signs were recalculated including the contribution due to

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[1] Part II, D. T. B. Tennakoon, J. M. Thomas, and M. J. Tricker, *J.C.S. Dalton*, 1974, 2211.

[2] R. E. Cobbledick and R. W. H. Small, *Acta Cryst.*, 1973, **B29**, 2585.

[3] D. M. C. MacEwan, *Trans. Faraday Soc.*, 1948, **44**, 349.

[4] G. W. Brindley and A. Tsunashima, *Clays and Clay Minerals*, 1973, **21**, 233.

[5] D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and (in part) J. O. Williams, *J.C.S. Dalton*, 1974, 2207.

[6] B. H. Bracher and R. W. H. Small, *Acta Cryst.*, 1967, **23**, 410.

the intercalating molecules [the orientation of which had been deduced from electron-density maps (Figures 1 and 2) using the first set of signs] but none of the signs changed.

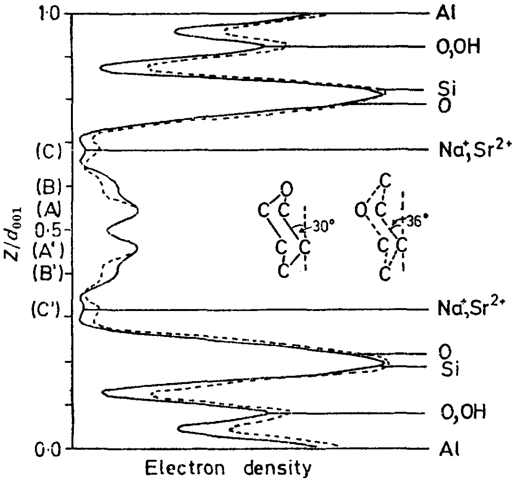

FIGURE 1 Electron-density maps for tetrahydropyran intercalates, with Na^+-exchanged (——) and Sr^{2+}-exchanged clay (- - - -). Calculated (A)–(B), (A)–(A¹), and (A¹)–(B¹) distances (observed values in parentheses) are 0·87 (0·88), 1·32, and 0·87 (0·88) for Na^+-exchanged clay and 0·97 (0·96), 1·23, and 0·97 (0·96) Å for Sr^{2+}-exchanged clay

TABLE 1

Basal spacings and stoicheiometry

(*a*) Basal spacings (Å) of montmorillonite and its intercalates

(Na) Montmorillonite	12·5 (1)
(Na) Montmorillonite–Tetrahydropyran	14·99(5)
(Na) Montmorillonite–1,4-Dioxan	14·94 (5)
(Sr) Montmorillonite	15·2 (1)
(Sr) Montmorillonite–Tetrahydropyran	14·81 (5)
(Sr) Montmorillonite–1,4-Dioxan	15·00 (5)

(*b*) Stoicheiometry of the intercalates

	Number of organic molecules	
	Per formula unit	Per cation
(Na) Montmorillonite–Tetrahydropyran	1·3 (1)	2·3 (2)
(Sr) Montmorillonite–Tetrahydropyran	1·0 (1)	3·5 (4)
(Na) Montmorillonite–1,4-Dioxan	1·1 (1)	1·9 (2)
(Sr) Montmorillonite–1,4-Dioxan	1·1 (1)	3·8 (4)

TABLE 2

Structure factors of the intercalates

l	Na Clay–Tetrahydropyran	Na Clay–1,4-Dioxan	Sr Clay–Tetrahydropyran	Sr Clay–1,4-Dioxan
1	+5·57	+6·55	+7·51	+7·38
2	−1·02	−1·14	−0·98	−1·41
3	−3·58	−4·01	−3·77	−4·90
4	+2·24	+2·49	+2·33	+2·80
5	+4·52	+4·34	+4·19	+4·48
6	+0·42	+0·84	+0·82	+0·62
7	−2·33	−2·02	−2·12	−2·51
8	−1·99	−1·54	−1·96	−1·90
9	+0·56	0·00	+0·47	0·00
10	+1·59	+1·21	+1·08	+1·61
11	+1·82	+1·20	+1·45	+1·10
12	+1·32	+0·91	+1·16	+1·35
13	+1·13		+1·22	+0·87

(Na) *Montmorillonite–Tetrahydropyran* (*Figure* 1).—The distance between the peaks (A) and (A¹) on the electron-density map was 1·32 Å. If we take the known C–C distance of 1·50 Å found in (II) [2] and assign these peaks as each being due to 2C or C + O then the angle α shown in Figure 1 can be calculated: it was *ca.* 30°. Using this angle, the predicted distance from (A) to (B) is 0·87 Å compared with an experimental value of 0·88 Å. We expect the peak-height ratio of (B) : (A) to be *ca.* 0·58 : 1 if the ring oxygen atom is nearest the layers (O + C)/4C or *ca.* 0·46 : 1 if a ring carbon atom is nearest the layers 2C/(3C + O). The experimental value was 0·66(5) : 1. A comparison of the peak heights of (A) and (B) with the aluminium peak enabled an estimate to be made of the number of organic molecules per formula unit [idealised $Al_4Si_8O_{20}(OH)_4$]. The number of organic molecules per cation was also estimated from the c.e.c. and the number of molecules per formula unit derived above (see Table 1). Results estimated from an electron-density map derived for an intercalate that had been left to stand in air for 1 week were indistinguishable from those of a freshly prepared sample. Peaks (C) and (C¹) are considered to be due to the sodium ions. The projected distance of the ions from the oxygen atoms on the outside of the layers was 1·53 Å.

(Sr) *Montmorillonite–Tetrahydropyran* (*Figure* 1).—Following the same procedure as above, from the measured distance of 1·23 Å for the peak separation (A) to (A¹) we deduce a value for α of 36° and a predicted distance (A) to (B) of 0·97 Å which matches the experimental value of 0·96 Å. The peak-height ratio (B) : (A) was 0·45(5) : 1 which suggests that a ring carbon atom is nearest the layers. The strontium-ion peaks (C) and (C¹) were a projected distance of 1·47 Å from the oxygen atoms on the outside of the layers.

(Na) *Montmorillonite*–1,4-*Dioxan* (*Figure* 2).—The distance between peaks (A) and (B) was 1·17 Å which is comparable with a value of 1·22 Å calculated on the basis that the molecules of (II) are perpendicular to the layers and using a C–O distance of 1·42 Å previously found for (II).[2] The ratio of the peak heights (B) : (A) should be

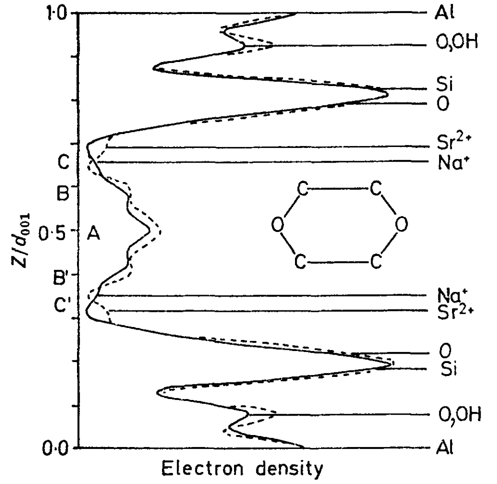

FIGURE 2 Electron-density maps for the 1,4-dioxan intercalates with Na^+-exchanged (——) and Sr^{2+}-exchanged clay (- - - -). Calculated (A)–(B) and (A)–(B¹) distances (observed values in parentheses) are 1·22 (1·17) and 1·22 (1·17) for Na^+-exchanged clay and 1·22 (1·27) and 1·22 (1·27) Å for Sr^{2+}-exchanged clay

ca. 0·75 (2C/2O) whereas the experimental value was 0·72(5) : 1. The sodium peaks, (C) and (C^1), were a projected distance of 1·94 Å from the oxygen atoms on the outside of the layers.

(Sr) *Montmorillonite*–1,4-*Dioxan* (*Figure* 2).—The distance found between peaks (A) and (B) was 1·27 Å (*cf.* 1·22 Å above). The ratio of the peak heights (B) : (A) was found to be *ca.* 0·65(5) : 1 which is rather lower than the theoretical value of 0·75 : 1. The strontium-ion peaks were a projected distance of *ca.* 1·35 Å from the oxygen atoms on the outside of the layers.

DISCUSSION

The montmorillonite intercalates studied in this work provide a good illustration of the necessity of obtaining, and interpreting, electron-density functions wherever possible, since the detailed orientations of the guest molecules differ considerably whereas the interlayer spacings are virtually the same. Indeed, if basal spacings alone were used, it would have been difficult to decide with certainty if the strontium–montmorillonite formed an intercalate with (II).

The two interlayer cations used, sodium and strontium, have ionic radii that are not too dissimilar (0·98 and 1·13 Å) but possess different charges. This study has shown that different cations can have some effect on the type of intercalate formed. In the intercalates of (I) it seems probable that the oxygen-ring atom lies closest to the silicate layer when the cation is sodium and a carbon-ring atom lies closest to the layer when the cation is strontium. In the intercalates of (II), however, the orientation of the organic molecules remains the same for both these ions. The distances between the inorganic cation and the silicate layers (varying from 1·4 to 2·0 Å) are all greater than those (1·0 Å) found by Pezerat and Méring[7] in the case of anhydrous and hydrated sodium-exchanged montmorillonite. They are, however, comparable with the 2·0 Å found in a sodium vermiculite–ethylene glycol intercalate by Bradley *et al.*[8]

In three of the intercalates both the number of guest molecules per unit cell and per cation are nearly whole numbers. With (Na) montmorillonite–tetrahydropyran we have neither a whole number of molecules per formula unit or per cation. Brindley and Tsunashima[4] showed that for Li^+- and Ca^{2+}-exchanged montmorillonite the uptake of (II) from aqueous solution was *ca.* 0·85 molecules per unit cell, which corresponded closely with the c.e.c. of their clay (125 milliequivalents per 100 g). In this study we have shown that a slightly greater uptake has occurred, although the c.e.c. of our clay is considerably smaller (79 milliequivalents per 100 g). Parallel to the layers the organic molecules would take up an area of *ca.* 6 × 5 Å^2 compared with 9 × 5 Å^2 for the ' unit mesh ' of the layer; the remaining space is then available for interlayer exchangeable cations which are invariably present.

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