Surface and Intercalate Chemistry of the Layered Silicates. Part VI.[1] Tetrahydrofuran Intercalates of a Series of Cation-exchanged Montmorillonites

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Intercalates of tetrahydrofuran (THF) with nine distinct cation-exchanged montmorillonites have been prepared and may be divided into two classes depending upon the magnitude of the basal spacing, d_{001}. In one class (with NH_4^+, Na^+, Co^{2+}, Ni^{2+}, and Cu^{2+}) d_{001} lies close to 14.6 Å; in the other (with Ca^{2+}, Sr^{2+} and Ba^{2+}) the spacing is close to 19.0 Å, while Li^+-exchanged montmorillonites are capable of forming both types of intercalate. The orientation and position of the organic molecules for six of the intercalates (NH_4^+, Na^+, Co^{2+}, Ni^{2+}, Cu^{2+}, and Sr^{2+}) have been determined from one-dimensional electron density maps constructed from the results of *X*-ray diffraction measurements. The lower-spacing intercalates have one layer of organic molecules in the interlamellar region with the THF perpendicular to the sheets. The number of THF molecules per formula unit [idealised, $Al_4Si_8O_{20}(OH)_4$] ranges from 1.3 (NH_4^+) to 2.3 (Ni^{2+}), the corresponding figures per exchanged cation being 2.6 (NH_4^+) to 9.4 (Ni^{2+}). The higher spacing intercalates have a double layer of THF molecules inclined at *ca.* 55° to the sheets. There are, for example, 4.8 molecules per formula unit of the Sr^{2+}-exchanged clay. Electron spectroscopy demonstrates that the copper-exchanged clay and intercalate change from Cu^{2+} to Cu^+ under the influence of the incident, low energy, *X*-rays.

To date, it has been possible to elucidate the detailed structures of organic intercalates of layered silicates for only a few systems. Thus, whereas very precise data (obtained from 2-D or 3-D single crystal diffraction studies) on the aluminosilicate layers themselves are available,[2] the orientations of organic molecules intercalated by these layers have not been investigated in such detail, largely because of experimental difficulties:

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[1] Part V, D. T. B. Tennakoon and M J. Tricker, *J.C.S. Dalton*, 1975, 1802.

[2] S. W. Bailey, ' Clays and Clay Minerals, Proceedings 14th Conference,' Pergamon Press, New York, 1968, 1.

only five definitive studies have, to our knowledge, been derived from single-crystal data.[3-7]

The present report represents a continuation of our systematic investigation[8] of the structural aspects of some thermally stable intercalates of montmorillonites in which the organic molecules are simple and rigid, and the molecular dimensions of which, in the crystalline state, are known with some precision. We report here the results of our *X*-ray, and to a lesser extent, *X*-ray-induced photo-electron spectroscopic (x.p.s.) studies of a range of THF intercalates of nine cation-exchanged montmorillonites. X.p.s. was utilized in an effort to gain some insight into the environment of the copper ions in the intercalate. It is now well known[9] that the paramagnetic Cu^{2+} species is characterised by large, high-binding-energy, satellite peaks of the $2p$ levels, often with up to 50% of the main-peak intensities, together with significantly broadened lines (FWHM *ca.* 2 eV) relative to a Cu^+ species which shows no satellites and narrow (FWHM *ca.* 1 eV) lines.

EXPERIMENTAL

The preliminary treatment and characterisation of the Wyoming montmorillonite used has been described in previous parts[1,8] of this series. Cation exchange was effected by first treating portions of an aqueous suspension of the clay with solutions of appropriate salts and then centrifuging and washing the portions several times with deionised water until the excess of reagent was removed from the sample.

X-*Ray Diffraction*.—Suspensions of the untreated (sodium) clay and the exchanged clays were allowed to dry on glass slides; the intercalates were prepared by immersing the sample in laboratory reagent grade THF for several hours. Diffraction patterns, taken of the samples after they had been set aside in air for *ca* 1 h, were recorded on a Philips PW1050 Vertical Diffractometer using Cu-K_α radiation ($\lambda = 1.5418$ Å). Intensities were corrected for Lorentz and polarisation effects,[8] *i.e.* $2\,Lp = (1 + \cos^2 2\theta)/\sin 2\theta$.

X.p.s.—The spectra were recorded on an AEI ES200 spectrometer using Mg-K_α radiation (1253.6 eV) as source. The samples used were in the form of small flakes (*ca.* $1 \times 5 \times 0.5$ cm) attached to a copper probe tip. A dynamic pressure of *ca.* 10^{-5} Pa was achieved by continuous pumping.

Analyses.—The stoicheiometries of the intercalates (Table 1) were deduced from the heights of the peaks on the electron-density projections (see Figure) and the known cation-exchange capacity of the clay of 79 mequiv. per 100 g dried clay.[8] Conventional chemical analyses were carried out for C and H on Na^+-exchanged and Co^{2+}-exchanged clays and their respective intercalates in order to check and confirm the reliability of this procedure; stoicheiometries obtained in this way are also given in Table 1. We have:

	% C	% H
Na^+-montmorillonite	0.50	1.92
Na^+-montmorillonite/THF	10.82	2.36
Co^{2+}-montmorillonite	0.48	1.61
Co^{2+}-montmorillonite/THF	13.13	2.57

RESULTS AND DISCUSSION

It is apparent from the elemental analysis that there is some carbon contamination present in the untreated clay: some of the hydrogen is bound to the carbon impurity, the remainder being attributable to hydroxyl ions in the structure and also interlayer water. An estimate of the number of water molecules before intercalation can be obtained by taking the amount of hydrogen present as water to be *ca* 1.4%, thereby giving an idealised formula for the original clay of $Al_4Si_8O_{20}(OH)_4{\cdot}3.5H_2O$. The

TABLE 1a

Basal spacings of the metal-exchanged montmorillonites and THF intercalates

Exchangeable cation	Basal spacing/Å	
	Clay	Intercalate
Li^+	12.5(1)	14.54(5), 19.0(1)
Na^+	12.5(1)	14.70(5)
NH_4^+	12.26(5)	14.53(5)
Ca^{2+}	15.8(1)	19.0(1)
Sr^{2+}	15.2(1)	18.95(5)
Ba^{2+}	12.5(1)	19.0(1)
Co^{2+}	15.2(1)	14.58(5)
Ni^{2+}	15.1(1)	14.50(5)
Cu^{2+}	12.5(1)	14.58(5)

TABLE 1b

Peak height ratios from the electron density projections

Exchangeable cation	B/A		C/A	
	Expt.	Model	Expt.	Model
NH_4^+	0.79	0.84		
Na^+	0.57	0.64		
Sr^{2+}	0.50	0.43	0.83	0.86
Co^{2+}	1.00	0.84		
Ni^{2+}	0.64	0.64		
Cu^{2+}				

TABLE 1c

Stoicheiometry of the intercalates: 0.5e charge per $Al_4Si_8O_{20}(OH)_4$ unit

Exchangeable cation	No. of THF molecules ‡	
	per unit cell	per cation
NH_4^+	1.3	2.6
Na^+	1.6 (1.8)	3.2 (3.6)
Sr^{2+}	4.8	19.2
Co^{2+}	2.2 (2.5)	8.8 (10.0)
Ni^{2+}	2.3	9.4
Cu^{2+}	2.1	8.4

‡ Figures obtained by conventional elemental analysis are given in parentheses.

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[3] F. Kanamaru and V. Vand, *Amer. Min.*, 1970, **55**, 1550.

[4] K. Susa, H. Steinfink, and W. F. Bradley, *Clay. Min.*, 1967, **7**, 145.

[5] D. J. Haase, E. J. Weiss, and H. Steinfink, *Amer. Min.*, 1963, **48**, 261.

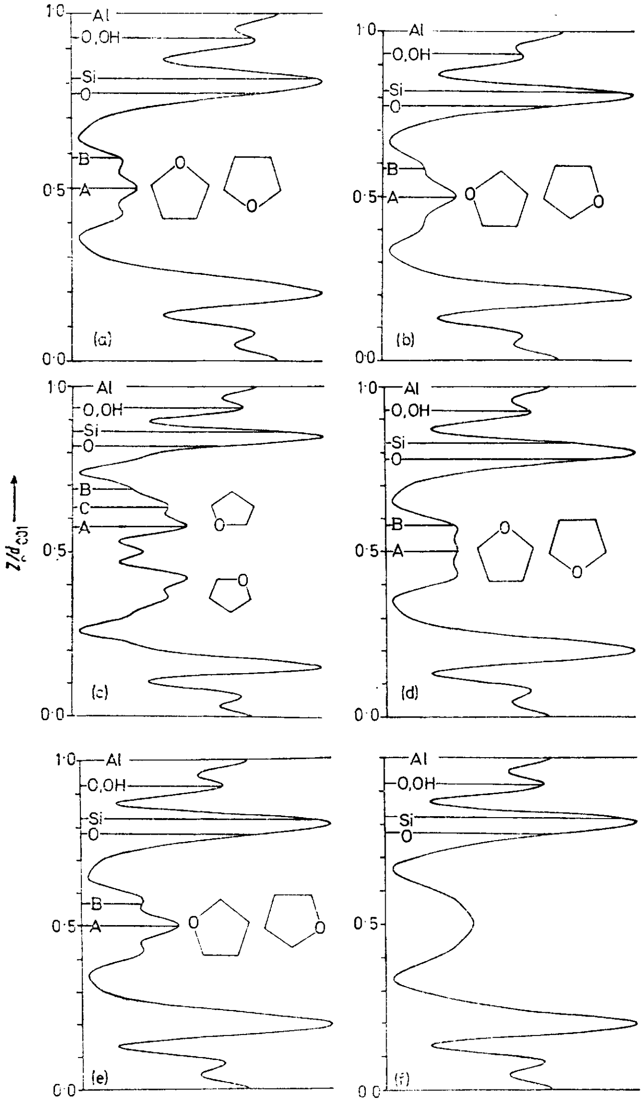
[6] J. E. Iglesias and H. Steinfink, *Clays and Clay Minerals*, 1974, **22**, 91.

[7] C. D. Brandle, MS Thesis, 1964, University of Texas, Austin, Texas.

[8] D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and (in part) J. O. Williams, *J.C.S. Dalton*, 1974, 2207; J. M. Adams, *J.C.S. Dalton*, 1974, 2286; J. M. Adams, J. M. Thomas, and M. J. Walters, *J.C.S. Dalton*, 1975, 1459.

[9] D. C. Frost, A. Iishitani, and C. A. McDowell, *Mol. Phys.*, 1972, **24**, 861.

amount of THF present may, therefore, be obtained from the difference in C before and after intercalation (but not from the difference in H, since some H will be lost as water is replaced in the interlayer region by THF). The stoicheiometries obtained (Table 1) confirm those obtained by X-ray analysis to within 10% and the further conclusion can be drawn that there is very little water left in the interlayer region after intercalation of THF since if the H content is computed assuming that the only hydrogen present is that of the layer and the organic moiety, we obtain 2.32% H in the Na^+-exchanged intercalate and 3.07% H in the Co^{2+}-exchanged intercalate. These figures are in reasonable agreement with those obtained by independent analysis.



(a) One-dimensional electron density map for the NH_4^+-montmorillonite/THF intercalate projected onto a line perpendicular to the aluminosilicate sheets. The orientation of a centrosymmetric pair of organic molecules is shown. (b) 1-D map for the Na^+-montmorillonite/THF intercalate. (c) 1-D map for the Sr^{2+}-montmorillonite/THF intercalate. (d) 1-D map for the Co^{2+}-montmorillonite/THF intercalate. (e) 1-D map for the Ni^{2+}-montmorillonite/THF intercalate. (f) 1-D map for the Cu^{2+}-montmorillonite/THF intercalate

The basal spacings of the cation-exchanged clays (Table 1) can be seen to fall into two groups, one of which has spacings close to 12.5 and the other close to 15.2 Å (the ' single-layer ' and ' double-layer ' of MacEwan [10]). This is a well documented phenomenon [11,12] and the point of changeover for any particular cation-exchanged montmorillonite depends on the relative humidity (*ca.* 50% in this study). Unfortunately clay–water systems give poor diffraction data and consequently it is difficult to obtain much meaningful information about them by X-ray methods. The basal spacings for the intercalates again fall into two classes near 14.6 and 19.0 Å, the latter being associated with the Li^+- (which also gives the lower spacing), Ca^{2+}-, Sr^{2+}-, and Ba^{2+}-exchanged intercalates. It is quite unusual to have spacings this large, in that very few simple organic moieties give spacings greater than *ca.* 15 Å with inorganic cation-exchanged clays. The way in which the intercalates sub-divide into two groups is not in agreement with the early work of Barshad,[13] who suggested that, for a given organic compound, the ' ease of interlayer expansion ' is greater the smaller the cation and the greater the charge on the cation. The various cation-exchanged silicates demonstrably do not fall readily into the two groups distinguished by such parameters as ionic radii or polarisabilities. It is however possible that the two values for lithium might be attributable to Li^+ ions in one case and $Li^+(H_2O)$ ions in the other.

The signs of the structure factors (Table 2) were predicted from the scattering from the aluminosilicate layers only but were recalculated including the contribution of the organic molecules, the positions of which had been deduced from electron density maps using the first set of signs.

It can be seen that the electron distributions (see Figure) are readily interpretable for the NH_4^+-, Na^+-, Sr^{2+}-, Co^{2+}-, and Ni^{2+}-exchanged intercalates on the basis of THF molecules ordered, at least along the axis perpendicular to the silicate layers (although it is possible that there could be rotation about this axis), this being contrasted with the free rotation postulated for THF when held, presumably much less securely, at room temperature in the clathrate cage of H_2S.[14] The Cu^{2+}-exchanged clay, however, gave a less well-defined structure in the interlayer region, the map being best explained by the organic molecules taking up two or three orientations, related by ring rotation about an axis parallel to the silicate layers, rather than one stable, well defined, orientation.

The positions and orientations of the THF molecules

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[11] S. B. Hendricks, R. A. Nelson, and L. T. Alexander, *J. Amer. Chem. Soc.*, 1940, **62**, 1457.

[12] R. W. Mooney, A. G. Keenan, and L. A. Wood, *J. Amer. Chem. Soc.*, 1952, **74**, 1371.

[13] I. Barshad, *Proc. Soil Sci. Soc.*, 1952, 176.

[14] T. C. W. Mak and R. K. McMullan, *J. Chem. Phys.*, 1965, **42**, 2732.

postulated for the NH_4^+-, Na^+-, Co^{2+}-, and Ni^{2+}-intercalates are basically similar except for the position of the oxygen in the ring; in all cases the THF is seen to be essentially perpendicular to the aluminosilicate sheets with two of the ring atoms lying on a line midway between the sheets. For each pair of centrosymmetric THF molecules ‡ we have on either side of the central plane of the expanded clay, for sodium and nickel, three carbon atoms arranged in a line, whereas for the ammonium and cobalt intercalates (of essentially equal spacing) there are two atoms of carbon and one of oxygen in each of the two lines. Although the general structural pattern of the sodium and nickel intercalates is similar [Figures (b) and (e)], their stoicheiometries are different (Table 1), the same being true of the ammonium and cobalt intercalates [Figures (a) and (d)]. It is not possible to denote positions for the interlayer cations on any of the electron-density maps for these 14.6 Å intercalates, although the cation-exchange capacity of 0.5 e per $Al_4Si_8O_{20}(OH)_4$ unit would require peaks totalling between about 4 and 7 electrons per cell. If the cations were in two positions per cell in the manner obtained by Pezerat and Méring[15] at *ca.* 4.2 Å projected distance from the Al atoms in the centre of the layer then they would be hidden in the large Si/O peak.

TABLE 2

Structure factors (for the 00*l* planes) of the intercalates *

Interlayer cation	NH_4^+		Na^+		Sr^{2+}		Co^{2+}		Ni^{2+}		Cu^{2+}	
l	$\lvert F_o \rvert$ †	F_c †	$\lvert F_o \rvert$	F_c	$\lvert F_o \rvert$	F	$\lvert F_o \rvert$	F_c	$\lvert F_o \rvert$	F_c	$\lvert F_o \rvert$	F_c
1	6.78	+5.03	5.23	+4.84	3.57	+3.42	3.32	+3.31	2.86	+2.85	3.84	+3.85
2	0.46	−0.94	0.32	−0.56	2.11	+1.10	0.40	−0.20	0.29	−0.16	0.29	−0.21
3	3.01	−2.68	3.10	−3.02	0.91	−0.64	2.40	−2.43	2.30	−2.21	2.98	−2.95
4	2.55	+2.25	2.46	+2.24	2.63	−2.86	2.18	+1.83	2.02	+1.80	2.47	+2.37
5	2.85	+3.34	3.50	+3.33	1.74	+1.83	2.60	+2.69	2.30	+2.24	2.71	+2.79
6	0.38	−0.28	0.50	+0.05	2.14	+2.14	0.47	−0.26	0.00	−0.16	0.38	−0.06
7	1.72	−2.30	2.06	−2.31	1.23	+1.97	1.52	−1.69	1.47	−1.72	1.82	−2.12
8	1.19	−1.43	1.45	−1.57	0.70	−0.79	1.23	−1.25	1.09	−0.92	1.50	−1.43
9	0.25	+0.40	0.00	+0.22	1.27	−1.52	0.36	+0.32	0.00	+0.21	0.00	+0.42
10	1.17	+1.42	1.42	+1.43	1.04	−1.48	1.01	+1.12	1.07	+1.14	1.38	+1.24
11	0.66	+0.79	0.87	+0.82	0.78	−0.49	0.54	+0.59	0.59	+0.47	1.17	+0.85
12	0.62	+0.75	0.30	+0.82	0.74	+0.76	0.36	+0.66	0.53	+0.64	0.43	+0.68
13					0.78	+0.61						
14					1.24	+1.25						
B/Å^2 ‡	5.5		5.5		5.0		5.5		5.2		5.0	
R §	0.23		0.13		0.18		0.09		0.11		0.11	

* The interlayer cations have not been used in the calculations. In the Cu^{2+} intercalate half the THF molecules have been taken in an orientation similar to that for the Co^{2+} case and the other half in an orientation rotated by 90° in the plane of the figures. † F_o Is the observed structure factor, F_c is the calculated structure factor. ‡ B Is the isotropic temperature factor. § R Is $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

The strontium intercalate is, however, very different with the organic molecules forming a double layer between the sheets and the distances A–B–C (Figure (c)] suggest that the organic molecules are at *ca.* 55° to the sheets. The small peak midway between the layers is approximately the correct size for the exchangeable cations.

It was noteworthy that the basal spacings of the Cu^{2+}- and Ba^{2+}-exchanged clays were less than those commonly found with double-charged cations at a relative humidity of *ca.* 50%, and the opportunity was taken of investigating the Cu 2*p* region of the Cu^{2+}-exchanged materials by x.p.s. It was shown that during the time usually taken to record a reasonable spectrum (*ca.* 1 h) the spectrum changed drastically from one characteristic of paramagnetic Cu^{II} species to a spectrum typical of diamagnetic Cu^{I}. This process occurred not only with the parent Cu^{II}-exchanged clay but also with Cu^{II}-exchanged intercalated samples and was thought to be due to photoreduction[9,16] by the incident *X*-ray photons. That the process was *X*-ray induced was confirmed by the observation that the same sequence of events occurred with a Cu^{II}-exchanged montmorillonite–pyridine sample, where it is corroborated by e.s.r. measurements[17] that the copper is initially present as Cu^{II}.

Although the use of the *X*-ray diffraction technique has elucidated considerable detail about these intercalates, such chemical information as the mode of interactions (if any) between the exchangeable cations and THF or the possible hydrogen bonding schemes between the THF molecules and the OH of the sheets, remains unanswered because of the limitations of the method when applied to relatively disordered systems.

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‡ The electron density distribution perpendicular to the aluminosilicate layers is centrosymmetric and the maps produced [Figures (a)—(f)] always show centrosymmetric pairs of organic molecules in the interlayer regions.

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