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The Crystal Structure of a Dickite:Formamide Intercalate $Al_2Si_2O_5(OH)_4.HCONH_2$

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The structure of the title compound has been determined from film-microdensitometer measured intensities. It is the first three-dimensional crystal structure of a clay mineral intercalate in which the interlamellar molecules are ordered. The formamide molecules lie over vacant octahedral sites in the aluminosilicate layers. There are three hydrogen bonds from the OH groups of adjacent (AlO_6) octahedra to the formamide O and one from the amide N to one of these hydroxyls. A fifth hydrogen bond from the amide N to an O atom of the silica tetrahedra on the near side of the next silicate sheet bonds the layers together.

Introduction

There is currently much interest in the phenomenon of intercalation (Yoffe, 1973; Thomas, 1974) in general, and in the accommodation of guest molecules in the interlamellar region of sheet silicates in particular (Weiss, 1969; Tennakoon, Thomas, Tricker & Williams, 1974; Adams, 1974). Little structural work has been completed on such systems, partly because of the difficulty in obtaining good single-crystal specimens of the parent host, but more especially because of the tendency of the intercalates to be disordered with respect to the disposition of the guest molecules. The formamide complex of the mineral dickite (a two-layer monoclinic modification of kaolinite) is, however, an exception and it has proved possible to elucidate its three-dimensional crystallographic structure by conventional X-ray methods. The only previously successful three-dimensional studies of sheet silicate intercalates involve the mica-type layered solids (see *e.g.* Susa, Steinfink & Bradley, 1967). The crystal structure of dickite [$Al_2Si_2O_5(OH)_4$] is well known (Newnham & Brindley, 1956, 1957; Newnham, 1961): it has space group *Cc* with $a=5{\cdot}15$, $b=8{\cdot}95$, $c=14{\cdot}42$ Å, $\beta=96{\cdot}8°$.

Crystal data

Small ($\sim 0{\cdot}10\times0{\cdot}14\times0{\cdot}02$ mm) pseudo-hexagonal crystals of a naturally occurring dickite from Anglesey were immersed in formamide for several months. By Weissenberg photography, the space group was established as *Cc* or *C*2/*c* and, since the silicate sheets themselves were known to be non-centrosymmetric, *Cc* was chosen. Cell dimensions (Table 1) were obtained from high-angle reflexions on the Weissenberg films. Some diffuse streaking of the stronger spots parallel to **c*** was noted, but no maxima inconsistent with the determined cell constants were apparent.

Table 1. *Crystal data*

Space group *Cc*; $a=5{\cdot}17$ (1), $b=8{\cdot}97$ (2), $c=20{\cdot}19$ (2) Å
(Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å) $\beta=92{\cdot}8$ (1)°
$d_c=2{\cdot}16$ g cm^{-3} $\mu=59{\cdot}1$ cm^{-1}

Determination of the structure

Intensities were collected on a Stoe–Weissenberg camera about the [3$\bar{1}$0] axis together with the zero layer about [100] for scaling purposes. The data were measured on an Optronics International P1000 microdensitometer and processed to give 305 unique structure factors* by the SRC Microdensitometer Service. The intensities were not corrected for absorption. The structure solution followed the original method of Newnham & Brindley (1956). The two possible ways of arranging the OH ions in the layers (called *M* and *N*) were distinguished on the basis of 24 *h*0*l* reflexions; *M* gave $R=0{\cdot}31$, *N* gave $R=0{\cdot}47$. There are now three possible ways of ordering the two Al ions in the three available octahedral sites – designated *Ma*, *Mb* and *Mc* – together with an unknown shift of the whole aluminosilicate layer along **b**. Using 0*kl* data each of these models was shifted along **b** and on this basis *Mc* was eliminated (lowest $R=0{\cdot}44$), while there were five values of the shift that gave $R<0{\cdot}4$ for *Ma* and three for *Mb*. An attempt was made to distinguish these eight models on the basis of 15 low-order *hkl* reflexions and six were eliminated as $R>0{\cdot}4$. The two remaining models, both *Ma* type, with shifts $0{\cdot}04b$, $0{\cdot}12b$ were refined for two cycles of FMLS (full-matrix least squares) with an overall isotropic temperature factor. For ($Ma+0{\cdot}04b$), $R=0{\cdot}190$; for ($Ma+0{\cdot}12b$), $R=0{\cdot}167$. Difference maps revealed for ($Ma+0{\cdot}12b$) three large peaks in the interlayer region each of which was about twice background. These peaks were chemically reasonable since their distances and angles corresponded to an O=C–N group and the distances of the O and N atoms from the layer atoms were reasonable for hydrogen bonding. The *z* coordinates of these atoms correspond to those of the two major interlayer peaks in the one-dimensional Fourier synthesis (Fig. 1). The difference

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* A list of structure factors ($\times 10^2$) has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31353 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

map for the ($Ma + 0{\cdot}04b$) model produced a large, relatively diffuse tube of electron density in the interlayer region which could not easily be split into separate peaks although small, local, maxima were too close for atom–atom distances. Two further FMLS cycles of the layer atoms with individual isotropic temperature factors reduced R to 0·185 but produced severe bond length distortions [*e.g.* Al(2)–O lengths varied by 0·44 Å] and the temperature factors of O(1) and O(2) became negative. Inclusion of atoms at the 'best' places in the interlayer region reduced R to a final value of 0·165 but the bond length distortions remained, the temperature factor for O(1) remained persistently negative and the bond lengths and angles between the 'atoms' in the interlayer remained chemically unreasonable. This model ($Ma + 0{\cdot}04b$) was therefore rejected and refinement of the ($Ma + 0{\cdot}12b$) model attempted.

Refinement

Inclusion of the C, O, N atoms of the formamide molecules reduced R to 0·144; one cycle of FMLS reduced this to 0·124. At this stage the atoms were given isotropic temperature factors and refinement continued. The (002) plane was left out of the refinement and R value calculation, since it was considered to show pronounced secondary extinction. It did not prove possible to find any of the H atoms in difference syntheses. Any attempt at lowering the site occupancy factor of the formamide molecules raised R significantly. Unit weights were used throughout the refinement since if weights $\propto 1/\sigma(F)$ were used the standard deviations of the bond lengths remained about the same but R became slightly higher. The final value of R was 0·107. An alternative approach to the secondary extinction problem by use of an isotropic extinction parameter (Larson, 1967, 1970) did not effect a significant improvement. The scattering factors were those for neutral atoms for the formamide molecule and Si^{2+} (interpolated between Si and Si^{4+}), $Al^{1\cdot5+}$ (interpolated between Al and Al^{3+}) and O^- for the atoms of the mineral layers. All were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a CDC 7600 computer with the X-RAY System (1972). Atomic coordinates and thermal parameters are shown in Table 2.

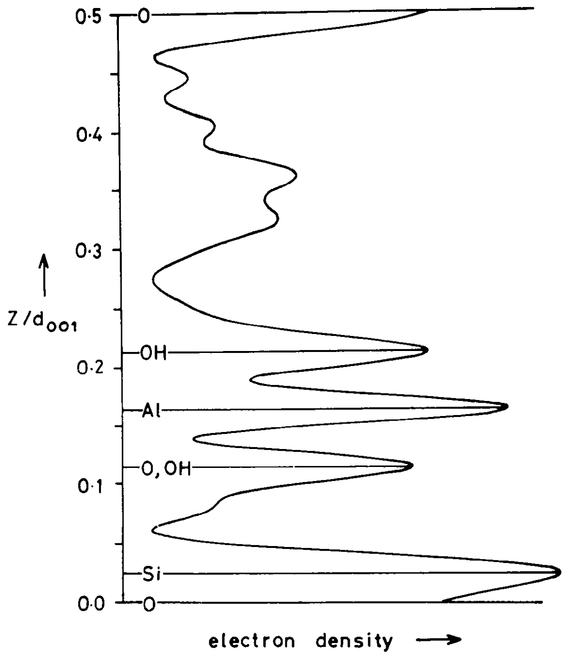

Fig. 1. One-dimensional F_o Fourier synthesis; phases taken from those predicted by an idealized layer. The two largest interlayer peaks have z coordinates of 0·32, 0·37.

Table 2. *Fractional atomic coordinates* ($\times 10^3$) *and thermal parameters* (Å²) *with their standard deviations*

	x	y	z	B
O(1)	0 (0)	124 (3)	0 (0)	1·7 (6)
O(2)	301 (10)	370 (4)	1 (2)	3·0 (7)
O(3)	816 (9)	385 (4)	9 (2)	1·5 (6)
O(4)	122 (9)	280 (3)	109 (2)	1·4 (7)
O(5)	553 (10)	467 (4)	111 (2)	2·3 (8)
OH(1)	626 (10)	160 (3)	114 (2)	1·5 (7)
OH(2)	291 (10)	159 (4)	212 (2)	2·4 (8)
OH(3)	794 (11)	286 (4)	213 (3)	2·6 (9)
OH(4)	375 (10)	472 (3)	215 (2)	0·6 (6)
Si(1)	47 (8)	288 (1)	30 (2)	1·7 (3)
Si(2)	548 (8)	459 (1)	35 (2)	1·6 (3)
Al(1)	960 (8)	136 (1)	167 (2)	1·5 (3)
Al(2)	467 (8)	303 (1)	167 (2)	1·4 (3)
O(6)	38 (11)	475 (5)	318 (3)	5·1 (1·1)
C(1)	26 (21)	419 (9)	371 (5)	8·5 (2·4)
N(1)	−128 (15)	297 (8)	371 (4)	7·5 (1·7)

Description and discussion of the structure

The general structure of the mineral sheets themselves is identical with that found earlier by Newnham (1961) and although a closer examination of the bonding (Table 3) within these sheets does reveal some discrepancies in bond lengths, the standard deviations of these are too high for much detailed discussion. The bonding of the formamide molecules to the sheets (Figs. 2 and 3) is ordered and the hydrogen-bond lengths (Table 4) are all acceptable, except perhaps for the bond N(1)...OH(3)^{ii} which is slightly longer than usually found; the standard deviation is, however, relatively high. There are four hydrogen bonds between the formamide and the hydroxyls of the sheets; the organic molecules must therefore be relatively strongly bonded to this sheet. There is only one hydrogen bond per formamide linking this mineral:organic 'open-sandwich' to the next mineral sheet, presumably resulting in the interlamellar forces being somewhat less than in the original dickite. The angle found between the formamide and the layers is 79° and the minimum distance between formamide molecules is 4·79 Å between C(1) and N(1)^{vi}. The H–CON hydrogen atom, predicted from the geometry of the molecule at (0·1147, 0·4571, 0·4112) has nearest neighbours O(1)^{vii}, O(2)^{viii}, O(3)^{ix} at 2·72, 2·53, 2·93 Å; the contact with O(2)^{viii} is the closest and is near to the sum of the van der Waals radii. It may be predicted, therefore, that the replacement of this H by, say, a methyl group would destroy the possibility of hydrogen bonding to the next mineral layer in the manner found in this structure, although the bonding to the OH's of the first layer would remain unaffected. Any intercalate formed might be disordered in that the positions of the sheets would bear no simple relation to each other. It should be noted that the final difference synthesis did not show any peaks that were significantly above background – the possibility of water being inserted between the sheets at the same time as the formamide can therefore be ruled out.

Table 3. *Bond distances* (Å) *and angles* (°) *with standard deviations*

Si(1)–O(1)	1·60 (3)	Al(1)–OH(2)^{i}	1·92 (7)
Si(1)–O(2)	1·64 (6)	Al(1)–OH(3)	1·86 (5)
Si(1)–O(3)^{ii}	1·52 (5)	Al(1)–OH(4)^{v}	1·83 (4)
Si(1)–O(4)	1·64 (6)	Al(2)–O(4)	2·08 (6)
Si(2)–O(1)^{iii}	1·66 (3)	Al(2)–O(5)	1·92 (5)
Si(2)–O(2)	1·63 (6)	Al(2)–OH(1)	1·88 (5)
Si(2)–O(3)	1·65 (6)	Al(2)–OH(2)	1·85 (5)
Si(2)–O(5)	1·53 (6)	Al(2)–OH(3)	1·90 (7)
Al(1)–O(4)^{i}	1·95 (5)	Al(2)–OH(4)	1·87 (4)
Al(1)–O(5)^{v}	1·96 (5)	C(1) –O(6)	1·20 (11)
Al(1)–OH(1)	1·99 (6)	C(1) –N(1)	1·36 (12)

O(1)——Si(1)–O(2)	113 (3)	O(4)—Al(2)—OH(1)	90 (2)
O(1)——Si(1)–O(3)^{ii}	109 (3)	O(4)—Al(2)—OH(2)	77 (2)
O(1)——Si(1)–O(4)	111 (2)	O(4)—Al(2)—OH(3)	169 (2)
O(2)——Si(1)–O(3)^{ii}	106 (3)	O(4)—Al(2)—OH(4)	98 (2)
O(2)——Si(1)–O(4)	102 (3)	O(5)—Al(2)—OH(1)	94 (3)
O(3)^{ii}—Si(1)–O(4)	116 (3)	O(5)—Al(2)—OH(2)	164 (3)
O(1)^{iii}–Si(2)–O(2)	99 (2)	O(5)—Al(2)—OH(3)	97 (3)
O(1)^{iii}–Si(2)–O(3)	109 (2)	O(5)—Al(2)—OH(4)	76 (2)
O(1)^{iii}–Si(2)–O(5)	112 (2)	OH(1)–Al(2)—OH(2)	92 (2)
O(2)——Si(2)–O(3)	109 (3)	OH(1)–Al(2)—OH(3)	79 (2)
O(2)——Si(2)–O(5)	115 (3)	OH(1)–Al(2)—OH(4)	167 (3)
O(3)——Si(2)–O(5)	111 (3)	OH(2)–Al(2)—OH(3)	98 (3)
O(4)^{i}—Al(1)–O(5)^{v}	93 (2)	OH(2)–Al(2)—OH(4)	99 (3)
O(4)^{i}—Al(1)–OH(1)	90 (2)	OH(3)–Al(2)—OH(4)	93 (2)
O(4)^{i}—Al(1)–OH(2)^{i}	79 (2)	Si(1)—O(1)—Si(2)^{iv}	130 (2)
O(4)^{i}—Al(1)–OH(3)	92 (2)	Si(1)—O(2)—Si(2)	133 (3)
O(4)^{i}—Al(1)–OH(4)^{v}	166 (3)	Si(1)^{i}—O(3)—Si(2)	143 (3)
O(5)^{v}—Al(1)–OH(1)	91 (2)	Si(1)—O(4)—Al(1)	121 (3)
O(5)^{v}—Al(1)–OH(2)^{i}	97 (2)	Si(1)—O(4)—Al(2)	134 (3)
O(5)^{v}—Al(1)–OH(3)	167 (3)	Al(1)—O(4)—Al(2)	97 (2)
O(5)^{v}—Al(1)–OH(4)^{v}	76 (2)	Si(2)—O(5)—Al(1)^{vi}	128 (3)
OH(1)–Al(1)–OH(2)^{i}	167 (2)	Si(2)—O(5)—Al(2)	124 (3)
OH(1)–Al(1)–OH(3)	77 (2)	Al(1)^{vi}–O(5)—Al(2)	101 (3)
OH(1)–Al(1)–OH(4)^{v}	98 (2)	Al(1)—OH(1)–Al(2)	100 (2)
OH(2)^{i}–Al(1)–OH(3)	96 (2)	Al(1)^{ii}–OH(2)–Al(2)	106 (3)
OH(2)^{i}–Al(1)–OH(4)^{v}	93 (2)	Al(1)—OH(3)–Al(2)	104 (3)
OH(3) –Al(1)–OH(4)^{v}	100 (3)	Al(1)^{vi}–OH(4)–Al(2)	107 (3)
O(4)——Al(2)–O(5)	88 (2)		

Symmetry operations for tables and figures

(i)	$x+1$	y	z	(vi)	$x-\frac{1}{2}$	$y+\frac{1}{2}$	z
(ii)	$x-1$	y	z	(vii)	$x+\frac{1}{2}$	$-y+\frac{1}{2}$	$z+\frac{1}{2}$
(iii)	$x+\frac{1}{2}$	$y+\frac{1}{2}$	z	(viii)	x	$-y+1$	$z+\frac{1}{2}$
(iv)	$x-\frac{1}{2}$	$y-\frac{1}{2}$	z	(ix)	$x-1$	$-y+1$	$z+\frac{1}{2}$
(v)	$x+\frac{1}{2}$	$y-\frac{1}{2}$	z				

Table 4. *Hydrogen-bond distances* (Å) *and related angles* (°)

OH(2)^{vi}···O(6)	2·93 (7)	C(1)–O(6)···OH(2)^{vi}	149 (6)
OH(3)^{ii}···O(6)	2·95 (7)	C(1)–O(6)···OH(3)^{ii}	112 (5)
OH(4)····O(6)	2·77 (8)	C(1)–O(6)···OH(4)	137 (6)
N(1)······OH(3)^{ii}	3·21 (9)	C(1)–N(1)···OH(3)^{ii}	94 (7)
N(1)······O(2)^{vii}	3·05 (8)	C(1)–N(1)···O(2)^{vii}	119 (7)

The presence of some disorder in the crystal under investigation is indicated by a diffuse streaking of the strongest spots in a direction parallel to **c***, but no

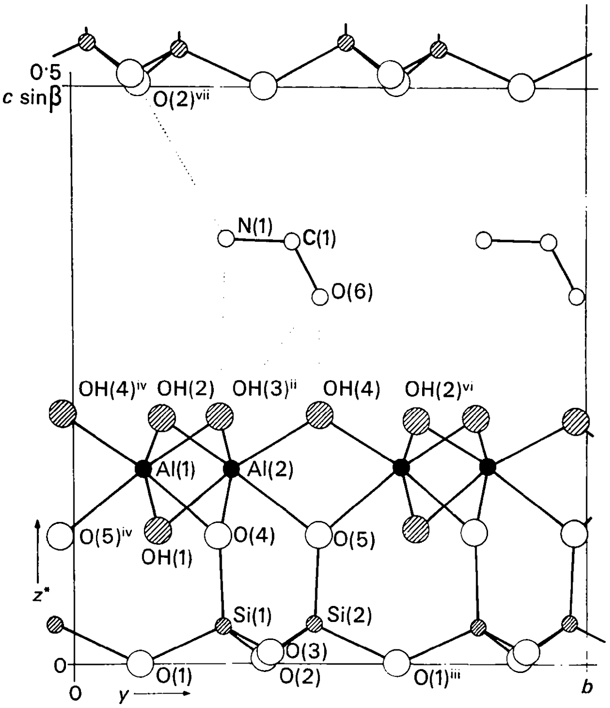

Fig. 2. Projection of the structure of the dickite:formamide intercalate down **a** showing the hydrogen-bonding scheme.

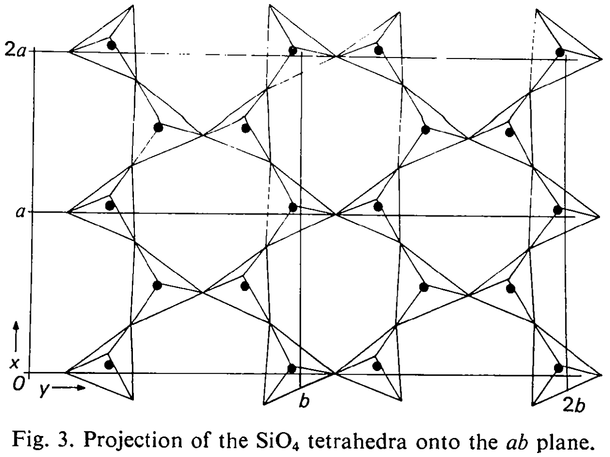

Fig. 3. Projection of the SiO_4 tetrahedra onto the *ab* plane.

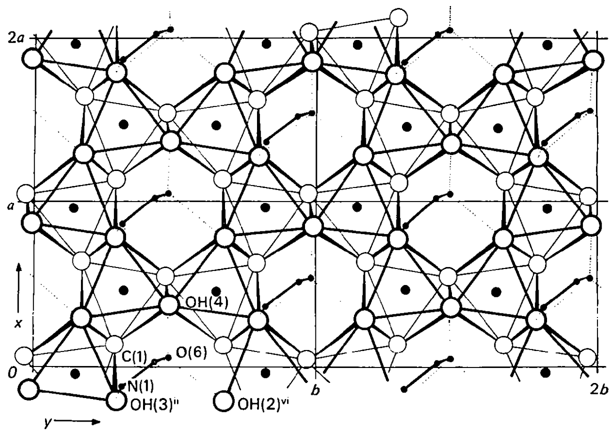

Fig. 4. Projection of the AlO_6 octahedra onto the *ab* plane. The bonding of the formamide molecules is also shown.

extra maxima were discernible on those streaks, suggesting that macroscopic regions of an alternative polytype were definitely absent. There are two possible causes of this kind of diffuse streaking, the simplest being merely a non-intercalation of certain layers distributed at random within the crystal. An alternative mechanism for disorder could involve the positioning of the formamide molecules in one of the two alternative orientations with respect to the octahedral component of the layers (Fig. 4). Such a disorder would not necessarily involve a change in cell constants or symmetry, but the alternative structures would be crystallographically distinct, and intergrowths of these on a fine scale would produce a diffuse streaking of the type observed. However, the lack of refinement of the alternative model for the structure ($Ma+0{\cdot}04b$) would appear to indicate that the former explanation is the more likely. The equations of planes are shown in Table 5.

Table 5. *Equations of planes*

(*a*) Through the groups OH(2)^{vi}, OH(3)^{ii}, OH(4)
$-0{\cdot}0818x+0{\cdot}0058y+20{\cdot}1789z=4{\cdot}3079$

(*b*) Through the formamide molecule O(6), C(1), N(1)
$-4{\cdot}1042x+5{\cdot}1866y+4{\cdot}5832z=3{\cdot}7657$

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