

Fig. 3. The packing of the layers.

are impossible (dotted lines in Fig. 3). It is convincing from Fig. 3 that there is strong correlation, be it dynamic or static, between the positions of the terminal methyl groups in the *y* as well as in the *x* direction. Each methyl group has four neighbours belonging to the adjacent layer at distances of approximately 4.5 Å. Thus, the packing is rather loose. With the arguments given in D79 this kind of neighbourhood results in a stability less than in  $(C_2H_5NH_3)_2MnCl_4$  or  $(C_3H_7NH_3)_2MnCl_4$ .

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## The Crystal Structure of a Dickite:*N*-Methylformamide Intercalate [Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>·HCONHCH<sub>3</sub>]

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### Abstract

The structure of the intercalate has been solved with film-scanned data. The final *R* is 9.4%. The organic molecules are regularly ordered, the threefold hydrogen bonds from the clay OH groups to the amide O atom found in the formamide intercalate being retained. The remaining part of the *N*-methylformamide molecule rotates with respect to the OH groups since there is no hydrogen bonding from the N atom to these OH groups. There are no hydrogen bonds from the amide to the SiO<sub>4</sub> tetrahedra of the neighbouring layer.

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DTA measurements have shown that C4Mn undergoes some structural phase transitions at lower temperatures. It should be of interest to see whether the all-*trans* conformation is reached at some lower temperature. This work is in progress.

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The organic molecules themselves are non-planar (at the N atom). The stacking of the octahedral (AlO<sub>6</sub>) part of the clay layers upon the SiO<sub>4</sub> tetrahedra is different from that previously found for dickite itself and the dickite : formamide intercalate.

### Introduction

Recently there has been considerable interest in intercalates, *i.e.* materials in which molecules are inserted between the sheets of a basically unchanged host material. These guest species are often small organic

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molecules, but it is possible (sometimes by successive displacement reactions) to intercalate rather larger entities. In the montmorillonite class of minerals it is possible to swell the layers from an original 9.6 Å to 50 or 60 Å by the use of suitable long-chain alkylamines. The driving force behind much of the recent work has been the discovery and characterization of very selective and clean catalysis of organic reactions by layered materials: a recent example is the conversion of alk-1-enes to di(2-alkyl) ethers by certain ion-exchanged montmorillonites (Adams, Ballantine, Graham, Laub, Purnell, Reid, Shaman & Thomas, 1978).

Despite this chemical interest there appears to have been little structural work on intercalates. The structure of a transition-metal chalcogenide intercalate with pyridine has been solved by neutron diffraction (Riekel, 1979) and in the clay field there have been several studies on vermiculite intercalates (*e.g.* Susa, Steinfink & Bradley, 1967), although in this case the interlamellar molecules have invariably been found to be disordered. In the kaolin group of clay minerals, only the dickite:formamide intercalate (Adams & Jefferson, 1976) has been studied and in this case a very regular arrangement of the amide molecules was found. There were several noteworthy features of this structure: there were three hydrogen bonds formed from the clay OH groups to each amide O atom and the amide N atom donated a hydrogen bond to one of these OH groups. It was also suggested that there was a hydrogen bond formed with the remaining amide H atom to an O atom of the neighbouring sheet of SiO<sub>4</sub> tetrahedra. This hydrogen bond was rather long (3.2 Å) but it was considered to be responsible for keeping the layer stacking sequence regular.

The structural investigation of the title compound was prompted by the following considerations: (i) was the amide again regularly arranged between the clay sheets, (ii) were features of the hydrogen-bonding scheme for the formamide intercalate carried over into this structure, (iii) was the amide again bonded to both interlamellar surfaces by hydrogen bonds?

### Experimental

Small pseudo-hexagonal flakes of naturally occurring dickite (Anglesey) were immersed in liquid *N*-methylformamide at 323 K for 7 months. Two crystals (each approximately 0.17 × 0.09 × 0.01 mm) were chosen for data collection. The space group (determined by systematic absences) was *Cc* or *C2/c*. Since the mineral layers were known to be noncentrosymmetric, *Cc* was preferred. The crystals were mounted about *a* and *b* respectively, and *0kl-3kl* and *h0l-h5l* data collected on a Stoe Weissenberg camera with Cu *Kα* radiation. The cell dimensions (Table 1) were determined by least

squares from high-angle film data and the films were scanned by the SRC Microdensitometer Service, Daresbury. The data were corrected for Lorentz and polarization effects and for absorption ( $\mu = 4.82 \text{ mm}^{-1}$ ). Although there was some diffuse streaking on the films of the stronger spots parallel to *c*\*, this was considerably less than was observed for the dickite:formamide intercalate (Adams & Jefferson, 1976). Again the simplest explanation for this is a non-intercalation of some of the mineral layers at random throughout the crystal.

### Structure determination

The data were put on a common scale and merged (Rae & Blake, 1966); there were 1343 reflections which reduced to 663 on taking symmetry into account. The 00*l* data were used to calculate a one-dimensional electron density projection (Fig. 1) perpendicular to the basal surface, the phases being predicted from the structure of an idealized layer. This projection was consistent with that given by Weiss, Thielepape & Orth (1966) for the kaolinite:*N*-methylformamide intercalate (dickite is a two-layer monoclinic modification of kaolinite).

Table 1. *Crystal data*

Space group <i>Cc</i>	
<i>a</i> = 5.14 (2) Å	$\beta = 92.3 (1)^\circ$
<i>b</i> = 8.94 (2)	<i>Z</i> = 4
<i>c</i> = 21.45 (3)	$d_c = 1.60 \text{ Mg m}^{-3}$

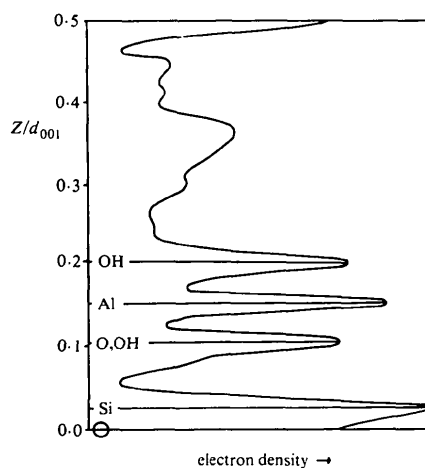


Fig. 1. One-dimensional electron density projection along the normal to the basal planes. The phases used were calculated from an idealized aluminosilicate layer. The largest peaks in the inter-layer region have *Z* = 0.30 and 0.36 although the width of the latter suggests non-resolved individual peaks.

Table 2. Final fractional coordinates ( $\times 10^3$ ) and their e.s.d.'s

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	0 (0)	83 (3)	0 (0)
O(2)	214 (6)	346 (2)	7 (1)
O(3)	698 (6)	312 (3)	3 (1)
O(4)	-34 (6)	235 (4)	106 (1)
O(5)	526 (6)	429 (4)	105 (1)
O(6)	459 (6)	116 (3)	111 (1)
O(7)	858 (6)	119 (4)	202 (1)
O(8)	353 (6)	235 (4)	206 (1)
O(9)	779 (7)	430 (5)	202 (1)
Si(1)	-26 (5)	243 (2)	35 (1)
Si(2)	486 (4)	412 (2)	29 (1)
Al(1)	154 (5)	92 (2)	156 (1)
Al(2)	657 (5)	259 (2)	162 (1)
O(10)	164 (7)	413 (6)	302 (2)
C(1)	160 (11)	403 (8)	362 (3)
C(2)	-268 (14)	338 (9)	364 (4)
N(1)	-64 (11)	462 (7)	386 (3)
H(1)*	205	350	405
H(2)	-90	500	433
H(3)	735	50	233
H(4)	290	333	238
H(5)	835	430	235

\* The positions of the H atoms were not refined.

The structure solution followed the method used by Newnham & Brindley (1956, 1957) for dickite itself. There are two possible ways of arranging the OH groups in the clay layers (described by *M* and *N*); these were distinguished on the basis of 65 *h0l* reflections. Contrary to the previous findings for dickite and for dickite:formamide the *N* model gave a much lower *R*, 36% compared with 53%. There are three possible ways (*a, b, c*) of arranging the two Al ions in three octahedral sites together with a shift of the whole layer parallel to *b*. The *0kl* data (61 reflections) were used with each of the models shifted in small increments along *b*. Two models ( $\text{Na} + 0.08b$ ,  $\text{Nb} + 0.42b$ ) gave  $R = 30.9\%$  and were in fact equivalent. After least-squares refinement with an overall temperature factor (all data) with this model *R* was 19%. At this stage a difference map enabled the non-hydrogen atoms of the organic intercalate to be found. Refinement (after deletion of several reflections suffering from extinction effects – marked on the structure factor tables) reduced *R* to 10.6% with individual isotropic temperature factors. Five of the nine H atoms were located from a difference synthesis and refinement terminated at  $R =$

Table 3. Bond lengths (Å) and angles (°)

Si(1)–O(1)	1.62 (3)	O(1)–Si(1)–O(2)	104 (2)	O(4 <sup>iv</sup> )–Al(2)–O(5)	89 (1)
Si(1)–O(2)	1.68 (3)	O(1)–Si(1)–O(3 <sup>i</sup> )	102 (2)	O(4 <sup>iv</sup> )–Al(2)–O(6)	90 (1)
Si(1)–O(3 <sup>i</sup> )	1.68 (4)	O(1)–Si(1)–O(4)	116 (2)	O(4 <sup>iv</sup> )–Al(2)–O(7)	76 (2)
Si(1)–O(4)	1.52 (4)	O(2)–Si(1)–O(3 <sup>i</sup> )	105 (2)	O(4 <sup>iv</sup> )–Al(2)–O(8)	166 (2)
Si(2)–O(1 <sup>ii</sup> )	1.66 (4)	O(2)–Si(1)–O(4)	116 (2)	O(4 <sup>iv</sup> )–Al(2)–O(9)	96 (2)
Si(2)–O(2)	1.57 (4)	O(3 <sup>i</sup> )–Si(1)–O(4)	112 (2)	O(5)–Al(2)–O(6)	90 (2)
Si(2)–O(3)	1.53 (4)	O(1 <sup>ii</sup> )–Si(2)–O(2)	106 (1)	O(5)–Al(2)–O(7)	164 (2)
Si(2)–O(5)	1.65 (3)	O(1 <sup>ii</sup> )–Si(2)–O(3)	111 (2)	O(5)–Al(2)–O(8)	97 (2)
Al(1)–O(4)	1.91 (4)	O(1 <sup>ii</sup> )–Si(2)–O(5)	106 (2)	O(5)–Al(2)–O(9)	76 (1)
Al(1)–O(5 <sup>iii</sup> )	1.92 (4)	O(2)–Si(2)–O(3)	108 (2)	O(6)–Al(2)–O(7)	95 (2)
Al(1)–O(6)	1.90 (4)	O(2)–Si(2)–O(5)	115 (2)	O(6)–Al(2)–O(8)	77 (1)
Al(1)–O(7 <sup>i</sup> )	1.85 (4)	O(3)–Si(2)–O(5)	111 (2)	O(6)–Al(2)–O(9)	165 (2)
Al(1)–O(8)	1.93 (4)	O(4)–Al(1)–O(5 <sup>iii</sup> )	92 (2)	O(7)–Al(2)–O(8)	99 (2)
Al(1)–O(9 <sup>iii</sup> )	1.84 (4)	O(4)–Al(1)–O(6)	92 (2)	O(7)–Al(2)–O(9)	100 (2)
Al(2)–O(4 <sup>iv</sup> )	2.04 (4)	O(4)–Al(1)–O(7 <sup>i</sup> )	79 (2)	O(8)–Al(2)–O(9)	98 (2)
Al(2)–O(5)	2.04 (4)	O(4)–Al(1)–O(8)	96 (2)	O(10)–C(1)–N(1)	113 (5)
Al(2)–O(6)	1.94 (3)	O(4)–Al(1)–O(9 <sup>iii</sup> )	169 (2)	C(1)–N(1)–C(2)	100 (6)
Al(2)–O(7)	1.82 (4)	O(5 <sup>iii</sup> )–Al(1)–O(6)	94 (2)	O(10)–C(1)–H(1)*	153 (7)
Al(2)–O(8)	1.87 (4)	O(5 <sup>iii</sup> )–Al(1)–O(7 <sup>i</sup> )	98 (2)	N(1)–C(1)–H(1)*	90 (5)
Al(2)–O(9)	1.85 (4)	O(5 <sup>iii</sup> )–Al(1)–O(8)	168 (2)	C(1)–N(1)–H(2)*	127 (5)
O(10)–C(1)	1.28 (7)	O(5 <sup>iii</sup> )–Al(1)–O(9 <sup>iii</sup> )	79 (2)	C(2)–N(1)–H(2)*	114 (5)
C(1)–N(1)	1.38 (8)	O(6)–Al(1)–O(7 <sup>i</sup> )	166 (2)	Al(1 <sup>iv</sup> )–O(7)–H(3)*	137 (3)
N(1)–C(2)	1.59 (9)	O(6)–Al(1)–O(8)	77 (2)	Al(2)–O(7)–H(3)*	110 (2)
C(1)–H(1)*	1.06 (6)	O(6)–Al(1)–O(9 <sup>iii</sup> )	95 (2)	Al(1)–O(8)–H(4)*	132 (2)
N(1)–H(2)*	1.08 (6)	O(7 <sup>i</sup> )–Al(1)–O(8)	93 (2)	Al(2)–O(8)–H(4)*	118 (2)
O(7)–H(3)*	1.13 (3)	O(7 <sup>i</sup> )–Al(1)–O(9 <sup>iii</sup> )	96 (2)	Al(1 <sup>ii</sup> )–O(9)–H(5)*	127 (4)
O(8)–H(4)*	1.17 (3)	O(8)–Al(1)–O(9 <sup>iii</sup> )	94 (2)	Al(2)–O(9)–H(5)*	123 (4)
O(9)–H(5)*	0.76 (3)				

## Symmetry code

- (i)  $-1 + x, y, z$       (iii)  $-\frac{1}{2} + x, -\frac{1}{2} + y, z$       (v)  $\frac{1}{2} + x, -\frac{1}{2} + y, z$   
(ii)  $\frac{1}{2} + x, \frac{1}{2} + y, z$       (iv)  $1 + x, y, z$

\* The hydrogen positions were not refined. The e.s.d.'s are estimated and are derived from the errors in the heavy-atom positions.

9.48% with anisotropic thermal parameters for Al and Si.\*

Unit weights were used. Scattering factors were for neutral atoms for the formamide molecule but were for  $\text{Si}^{2+}$ ,  $\text{Al}^{1.5+}$  (interpolated),  $\text{O}^-$  and H for the atoms of the mineral layers (*International Tables for X-ray Crystallography*, 1974). A dispersion correction was applied. Values of  $f'$  and  $f''$  were from the above source. An examination of a final difference map revealed no peaks above the fluctuating background.

The final atomic coordinates are in Table 2, and bond distances and angles in Table 3.

### Discussion

The structure of the aluminosilicate layers themselves is different in this intercalate from the arrangement in dickite and in the dickite:formamide intercalate (*N* instead of *M*, in Newnham & Brindley's notation). This corresponds to a rotation of the octahedra compared to the other structures and could be due to two causes: (i) natural dickite itself could consist of *M*-type and *N*-type crystals and the intercalate formed would thus be *M* or *N* type, or (ii) the dickite could be altered upon the intercalation of certain organic species. The first alternative seems more plausible since the second would either require the making and breaking of many strong covalent bonds or the rotation of whole mineral sheets upon intercalation, an unlikely event since the crystals maintain their shape in the basal plane upon intercalation. It is possible, therefore, that a reinvestigation of the structure of dickite is needed to determine whether *N*-type dickite crystals do exist.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34185 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

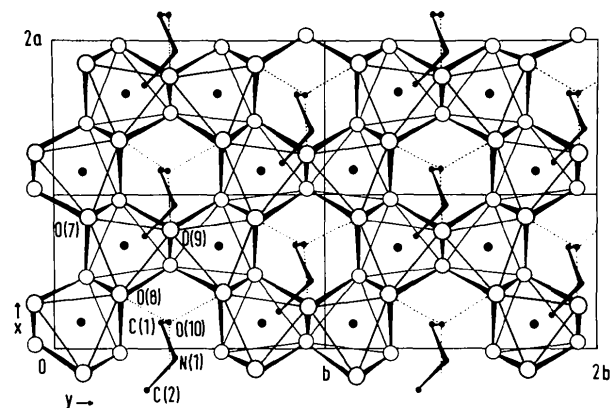


Fig. 2. Projection of the octahedral layer and the intercalated organic molecules on to the basal plane. The amide molecules are arranged in a completely regular fashion.

This intercalate is only the second clay mineral complex in which ordered interlamellar species have been found (Fig. 2), the dickite:formamide intercalate being the first. The minimum intermolecular distances found for the interlamellar molecules are 2.88 Å between H(1) and C(2) at  $1 - x, y, z$  and 3.00 Å between C(2) and C(1) at  $-1 + x, y, z$ . The shape of the amide molecule itself is somewhat unusual since it is not planar but is almost tetrahedral at the N atom. However, C(1)–N(1) is midway between the normal single C–N bond length of 1.47 Å and the 1.31–1.32 Å usually found in partly conjugated related *N*-methylamides (Harada & Iitaka, 1974*a,b*; Ichikawa & Iitaka, 1969; Iwasaki, 1974; Matsuzaki & Iitaka, 1971). It is difficult to argue about this point, however, since the e.s.d.'s of the bonds involved are large. It is true that there was a small peak in the final electron density map at the position that C(2) would adopt if the amide molecule were planar; it was, however, only  $\sim 1 \text{ e } \text{Å}^{-3}$ . We must, therefore, conclude either that this small molecule (the three-dimensional structure of which has not been investigated) is always non-planar in contrast to other *N*-methylamides or that it is deformed in order to fit more easily between the constraining clay mineral layers.

The triple hydrogen-bonding scheme (Fig. 3, Table 4) between the clay OH groups and the amide O atom is a feature which is carried over from the formamide intercalate. The bond lengths are comparable with those found for that material, but in this case the H atoms involved have been located, albeit poorly. The remainder of the organic molecule has tilted away from, and rotated relative to, the OH groups so that the free, methyl end of the molecule does not come close to the

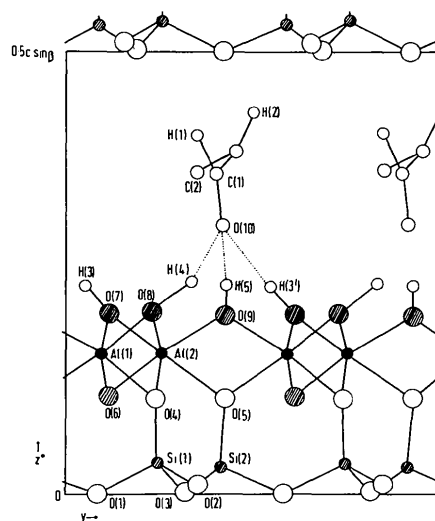


Fig. 3. Projection of the structure along *a*. The triple hydrogen bonding from the OH groups to the amide O atom is shown. The almost tetrahedral arrangement at N(1) can be seen.

Table 4. *Hydrogen-bond geometry*

The e.s.d.'s do not contain contributions from the H-atom positions.

<i>A</i> — <i>B</i> ... <i>C</i>	<i>B</i> ... <i>C</i>	<i>A</i> ... <i>C</i>	∠ <i>A</i> — <i>B</i> ... <i>C</i>
O(7)—H(3)...O(10)	1.97 (5) Å	3.04 (9) Å	156 (2)°
O(8)—H(4)...O(10)	1.70 (7)	2.81 (9)	156 (2)
O(9)—H(5)...O(10)	2.18 (11)	2.86 (16)	151 (3)

Table 5. *Least-squares planes (in direct space) and deviations of atoms from them*

(a) Defined by O(10), C(1), N(1)

$$2.263x + 7.989y + 1.482z = 4.1183$$

C(2)	-1.49 (6) Å	H(1)	-0.26 (1) Å
		H(2)	0.31 (1)

The angle between this plane and the basal surface is 85 (1)°.

(b) Defined by O(10), C(1), N(1), C(2)

$$-1.515x + 8.136y - 5.994z = 1.1895$$

O(10)	0.16 (4) Å	C(2)	-0.11 (7) Å
C(1)	-0.35 (1)	H(1)	-1.08 (10)
N(1)	0.29 (1)	H(2)	0.42 (10)

OH groups. Weiss, Thielepape & Orth (1966) first suggested, on the basis of one-dimensional Fourier analysis, that the methyl groups were close to the octahedral layer component. Indeed, in all *N*-methylamides the methyl is *cis* rather than *trans* to the carboxyl O atom. Details of least-squares planes are in Table 5.

There is definitely no N—H...O—Si hydrogen bond. In the formamide intercalate there was a short N...O—Si contact of 3.2 Å which was interpreted as a weak hydrogen bond. However, in this case the closest such contact is 3.38 Å [N(1)...O(2) at  $x, 1 - y, \frac{1}{2} + z$ ] with H(2)...O = 2.57 Å, both of which are equal to the sum of the van der Waals radii and similar to the C(1)—H(1)...O(1) at  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$  distances of 3.36 and 2.56 Å. The layers must, therefore, be held together in good register only by van der Waals forces.

The suggestions then about the three-dimensional bonding in such kaolin intercalates made by Adams (1978) are supported by these results in so far as the bonding to the OH group layer is concerned but are not confirmed in the speculation about the hydrogen bonding to the SiO<sub>4</sub> tetrahedra of the next layer. There appears to be no reason why the dimethyl sulphoxide intercalate and possibly others (where hydrogen bonding to the silicate layer would not be possible) should not be ordered.

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