UNIFYING FEATURES RELATING TO THE 3D STRUCTURES OF SOME INTERCALATES OF KAOLINITE

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Abstract—The recent determination of the three-dimensional crystal structure of a dickite:formamide intercalate allows insight into the clay:organic bonding schemes of amides and other small organic molecule intercalates of the kaolin minerals. It is demonstrated that the observed basal spacings of intercalates with these molecules are consistent with hydrogen bonding schemes in which, if possible, triple hydrogen bonds from the clay hydroxyls to $O{=}C\!\!<$ are formed. Variations in basal spacing within a series of amides can be explained by considering the maximization of hydrogen bonding while avoiding close van der Waals contacts.

Key Words—Acetamide, Dickite, Formamide, Intercalate.

PREFACE

When a crystal is formed from *its* constituent elements, the fundamental quantity that is minimized is the total energy of the crystal i.e., the lattice or cohesive energy is increased: the crystal "chooses" out of possible structures the one with the maximum cohesive energy. Thus, in systems where the subunits are more or less invariable and are held together by hydrogen bonding, it is the hydrogen bonding scheme itself which must be varied to achieve the highest value of this cohesive energy. Now it is not the number of hydrogen bonds alone which will determine the energy, but (with other contributions neglected) the product of the number of hydrogen bonds and their individual strengths that is crucial. In many cases, however, little is known about the strengths of hydrogen bonds in a particular structure. Infrared (IR) spectra can be used to determine hydrogen bond distances, but in multiple hydrogen-bonding systems it will only give an average value. X-ray structural analysis also gives hydrogen bonding distances but in many systems (including clay intercalates) such studies are extremely difficult or even impossible. If, indeed we did have all of the hydrogen bond distances in a structure we could determine the energy of each bond from well-known strength/distance relationships (Pimentel and McClellan, 1960). With the lack of such information we must use the assumption (correct as a first approximation) that the number of hydrogen bonds that are formed determines the stability of the structure (Adams et al., 1976).

In the following note an attempt is made to unify and rationalize the available information relating to some of the simple organic intercalates of the kaolinite minerals. Certainly all the facts necessary for the fullest understanding are not available for these systems—neutron diffraction, for example, even on powder samples, would, when combined with X-ray results, allow a more penetrating interpretation. It may be that the ideas outlined below would be of value in studying other intercalates with different host materials e.g., phosphates or niobates.

INTRODUCTION

Recently the first full three-dimensional crystal structure of a kaolin mineral intercalate has been determined, the system studied being dickite:formamide (Adams and Jefferson, 1976). The most significant feature of the structural analysis is that the formamide molecules are completely ordered and are all bound to the mineral layers in the same way. In this context it may be significant to note that the amount of isomorphous substitution in kaolin minerals is generally small. There are, therefore, no random substitutional sites in these minerals; thus there is no obvious reason to expect lack of order in the position or orientation of the organic molecules. This contrasts with the case of the mica-type layered silicates in which there is considerable random isomorphous substitution; preferred sites for reaction with organic molecules being, presumably, also random. These facts are in accord with the crystallographic data obtained about intercalates of these structures, where it is found that there is order in a direction perpendicular to the silicate sheets, but considerable disorder in the two dimensions in the plane of the sheets (Kanamaru and Vand, 1970; Susa et al., 1967; Haase et al., 1963; Iglesias and Steinfink, 1974).

DISCUSSION

Kaolinite:formamide

The formamide intercalate of kaolinite has been studied by IR by Ledoux and White (1966a, b) who found that the formamide carbonyl stretching frequency split into a triplet (at 1720, 1690 and 1675 cm^{-1}—although this was not confirmed by Olejnik et al., 1971) and that there was monomerization of the formamide together
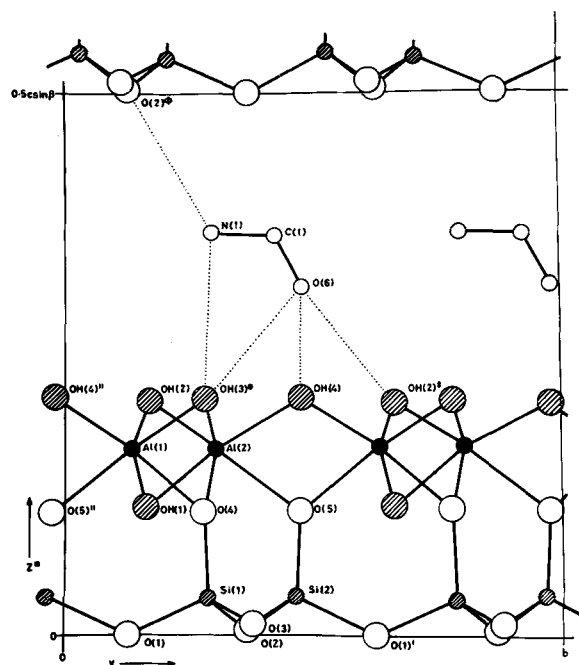
Fig. 1.   Projection of the structure of the dickite:formamide intercalate along the *a* axis.

with the breakdown of intermolecular hydrogen bonding. The N–H$\cdots$O bond was found to be weaker than the N–H$\cdots$O=C bond in liquid formamide and also the formamide molecules were shown to be at a large angle to the mineral sheets. This last point was also made by Weiss et al. (1963) who used a one-dimensional Fourier projection to show that the $-NH_2$ group was near the silicate oxygens of one sheet with the HCO group near the OH's of the neighboring layer.

The essential features of the bonding between formamide and the dickite brought out by the structural evaluation were (Figures 1, 2): (i) the three hydrogen bonds from the clay hydroxyls to the carbonyl oxygen, (ii) the hydrogen bond from the amide nitrogen to one of these three hydroxyls and (iii) the hydrogen bond from the amide nitrogen to the silicate oxygen of the next sheet. There seems no reason why elements of this bonding scheme should not be carried over into other members of the kaolin group of minerals since the hydroxyl surfaces are the same in all the members of this group—the only modification is that the oxygen atoms of the neighboring sheets are not in the same relative orientations to the first as in dickite. It seems likely, therefore, that the hydrogen bond to this second layer might have slightly different parameters than in the dickite:formamide example.
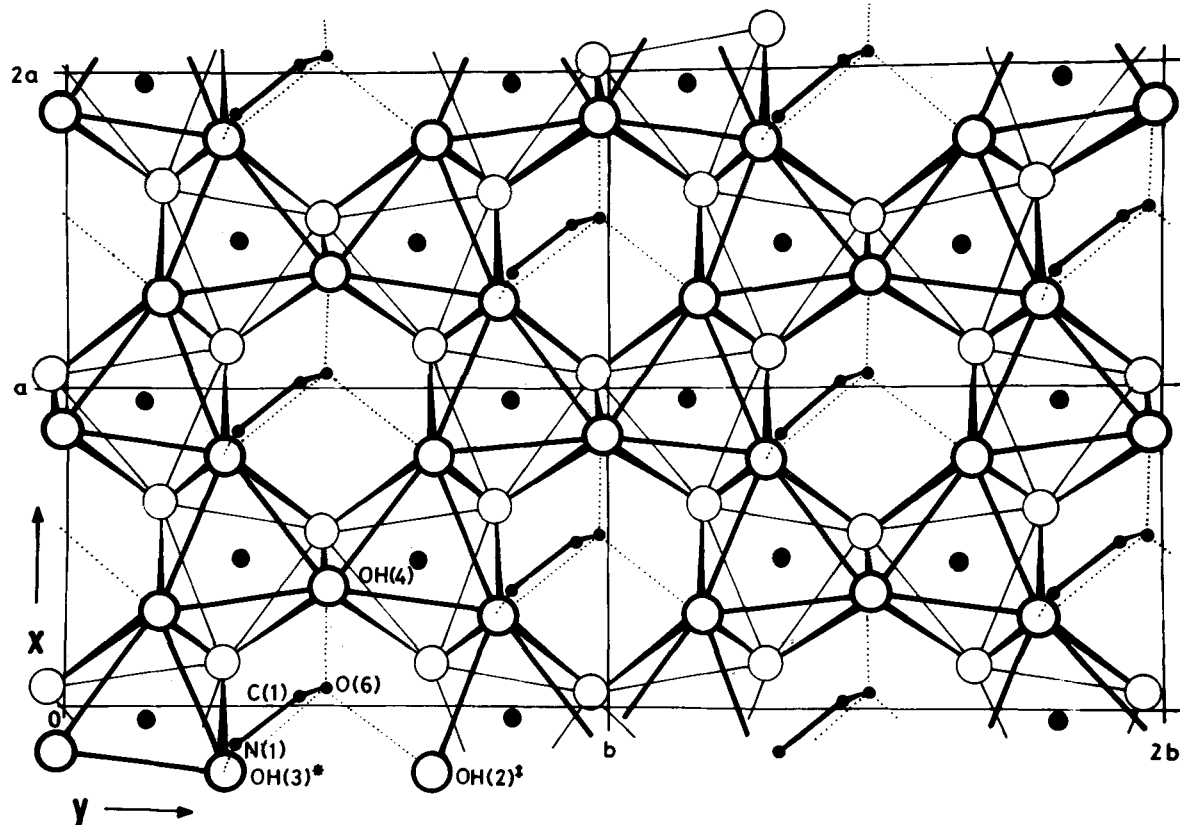

Fig. 2.   Projection of the AlO$_6$ octahedra (of the dickite:formamide intercalate) onto (001) showing the bonding of the formamide to the clay octahedral layer.
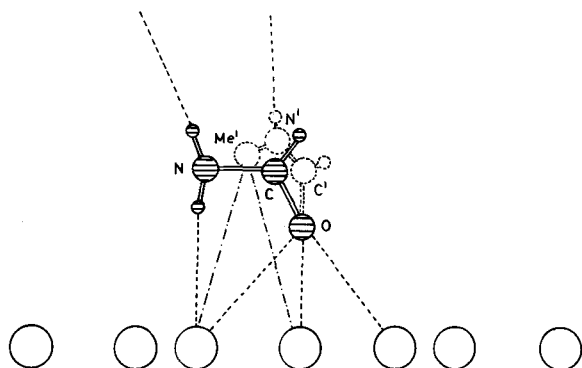
Fig. 3. Showing the reorientation necessary for N-methyl formamide molecules to maintain four of the five hydrogen bonds found in the formamide intercalates. Projection along a. (---hydrogen bonds, -·-· van der Waals distances).
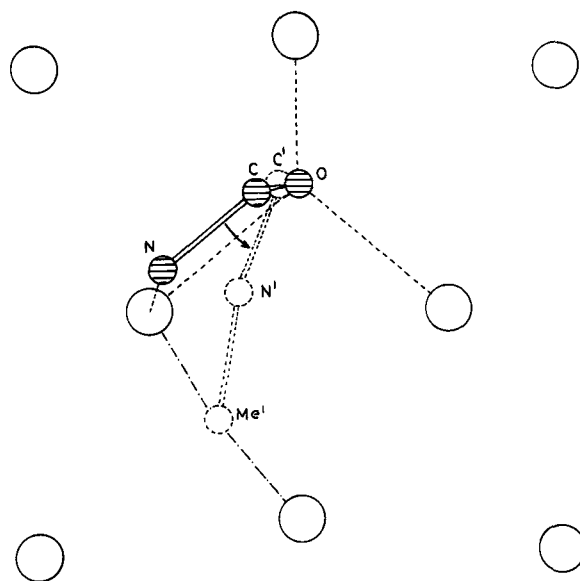

Fig. 4. Proposed rearrangement of the disposition of the organic molecules on going from formamide to N-methyl formamide. Projection onto the basal surface showing the bonding of the organic molecules to the clay hydroxyls. Note that there are six almost-equivalent positions for the N-methyl formamide molecules. (---hydrogen bonds, -·-· van der Waals distances).

This structural study firmly establishes the orientation already deduced for formamide in kaolinite (Weiss et al., 1963) and the small increase in the basal spacing (of only 2·9 Å) occurs due to the considerable hydrogen bonding between the layers. The carbonyl oxygen is only 2·1 Å out of the plane of the hydroxyls, approximately 1 Å less than that predicted from an impenetrable layer; the hydrogen atom involved in the hydrogen bond to the silicate oxygen is about 2·0 Å from this oxygen layer, approximately 0·5 Å less than that predicted on van der Waals radii grounds. The other observations of Ledoux and White (1966a, b) also can be rationalized: the monomerization of the formamide molecules is confirmed and the relatively weak N–H···O bonds (3·05 and 3·21 Å compared with 2·94 Å in solid formamide) (Ladell and Post, 1954) were also found. Knowledge of the structure has solved the problem (Olejnik et al., 1971) of whether these weak hydrogen bonds are to the clay sheets or to other formamide molecules.

Related kaolinite:amide complexes

Complexes of kaolinite with similar organic species have been studied (Olejnik et al., 1970; Weiss et al., 1966; Fennol Hach-Ali and Weiss, 1969) again by a combination of the X-ray and IR techniques. In N-methyl formamide the basal spacing is 0·6 Å greater than in the formamide case although the orientation deduced is similar, with the methyl group directed toward the hydroxyl rather than the oxygen surface. This scheme allows the three hydroxyl hydrogen bonds to the carbonyl oxygen to remain and also the N–H hydrogen bond to the next mineral layer. However, the organic molecule would have to be rotated and tilted backwards in its molecular plane to put the methyl group at sufficient distance (van der Waals) from the hydroxyl groups to which the carbonyl oxygen is hydrogen bonded. Simple calculations with such a model

(Figures 3, 4) show an increase in the basal spacing of about 0·8 Å compared with the 0·6 Å experimentally obtained.

Extending the analogy further to dimethyl formamide would result in a considerable increase in spacing for two reasons: (i) the N–H···O hydrogen bond to the next layer could no longer be formed—this part of the "keying" into the clay layer would therefore be lost and (ii) the methyl group has a considerably larger van der Waals radius than hydrogen. An increase of the order of 2·3 Å would be expected compared with the 2·0 Å found.

In the intercalate with acetamide the same general scheme for the hydroxyl to carbonyl–oxygen hydrogen bonding could be followed but the other elements of the bonding scheme need to be modified. If the fourth (N–H···OH) hydrogen bond was the same as in the formamide case then necessarily the basal spacing increase would have to be much larger than the 0·8 Å actually observed—a consequence of the fact that the formamide hydrogen (H–CO) is only 2·53 Å from a silicon oxygen. Substitution by a methyl would therefore give an increase of spacing of 1·6–2·0 Å even allowing for some relative shift of the aluminosilicate sheets. This would destroy any possibility of the hydrogen bond from the organic to the next layer (N–H···O–Si) since the distance would now be too great. On the other hand, if the acetamide was tilted backwards into its molecular plane, then the fourth hydrogen bond to the hydroxyl layer would be broken and the acetamide

Table 1. Summary of the hydrogen between the amide molecules and kaolinite.

Number of hydrogen atoms					
Involved in hydrogen bonds	Not involved in hydrogen bonds	Amide	3 $OH\cdots O=C$	Fourth bond $N-H\cdots OH$	Fifth bond $N-H\cdots O\text{-}Si$
5	–	formamide	Y	Y	Y
4	–	N-methylformamide	Y	N	Y
3	–	dimethylformamide	Y	N	N
4	1	acetamide	Y	N	Y
4	–	N-methylacetamide	Y	N	Y
3	–	dimethylacetamide	Y	N	N

Y indicates that these hydrogen bonds are formed.
N indicates these bonds are not formed.

would be free to rotate about the carbonyl bond to a different relative orientation to this layer, thus putting the NH_2 groups at greater than van der Waals distance from any of the hydroxyl groups. The hydrogen bond to the silicate oxygen, however, could be maintained by a movement of this next layer relative to the first and the increase in basal spacing would be approximately equal to that found.

A similar argument to that used above for N-substituted formamide can also be used for the mono and di N-substituted acetamide. The increase in spacings for intercalates with the three members of this series are found to be $0\cdot8$, $1\cdot2$, and $2\cdot2$ Å relative to that found for formamide (Olejnik et al., 1970) again showing the small increase from the first to the second member of the series and a larger increase on going to the third member where the hydrogen bonding between the clay layers has been broken.

A summary of the hydrogen bonds formed by the various amides discussed here is given in Table 1.

Intercalates with other small molecules

With small molecules other than amides there still appears to be evidence for the triple hydroxyl$\cdots$O bonding of the type found for dickite:formamide. With dimethyl sulphoxide (Weiss et al., 1966; Olejnik et al., 1968; Sanchez Camazano and Gonzalez Garcia, 1966) it was found that the $S=O$ bond was perpendicular to the clay sheets with the oxygen atom $1\cdot8$ Å from the plane containing the hydroxyl groups, a geometry almost identical to that found for the $C=O$ in formamide. Pyridine N-oxide (Olejnik et al., 1970, 1971; Weiss and Orth, 1973) also forms an intercalate with kaolinite and the available evidence shows that the molecule has its long axis almost perpendicular to the clay sheets with the oxygen atom at $2\cdot0$ Å from the hydroxyl plane.

CONCLUSIONS

In cases where there is no functional group capable of hydrogen bond formation to the silicate oxygens (dimethyl formamide, dimethylacetamide, dimethyl sulphoxide, and pyridine N-oxide) there is less reason to expect crystallographically ordered structures (since

there are only van der Waals forces to keep neighboring layers in register) capable of giving *hkl* reflections and therefore suitable for study by single crystal X-ray techniques.

It can be seen (Figure 2) that if the type of triple $O-H\cdots O$ bonding from the clay layer to the organic is maintained for these other organic species, it implies that there should be a stoichiometry of $Al_2Si_2O_5(OH)_4\cdot(\text{organic})_{1\cdot0}$. Such stoichiometries are often not reported in work on these systems but have been noted for formamide, N-methyl formamide, pyridine N-oxide, and dimethyl sulphoxide.

It should be noted that this ordered scheme (Figure 2) would break down if the dimensions of the organic species (parallel to the plane of the clay sheets) were too large, i.e., for close molecular packing the oxygen atoms of the organic molecules would be at too great a separation to fit into the correct relation with respect to the silicate hydroxyls. The likely result in such a case would be maintenance of the triple hydrogen bonds from the layers but irregular packing of the organics, i.e., all of the available sites (Figure 2) would not be filled. It would be possible, however, instead of an irregular filling of sites for more long range order to occur with the subsequent formation of a superlattice.

ACKNOWLEDGMENTS

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Резюме- Недавнее определение трехразмерной кристаллической структуры включений диккита:формамида позволяет детальнее изучить глину:органические связывающие схемы амидов и других малых органических молекулярных включений каолиновых минералов. Показывается,что наблюдаемые основные промежутки между включениями и этими молекулами согласуются с водородными связывающими схемами,в которых,если возможно,из глинистых гидроксилов формируются тройные водородные связи O=C⟨. Различия в основных промежутках в пределах серий амидов могут быть объяснены максимизацией водородных связей при отсутствии тесных контактов Ван дер Ваалса.

Kurzreferat- Die neue Bestimmung der dreidimensionalen Kristallstruktur einer Dickit-Formamideinbettung erlaubt Einblicke in die Bindungsweise der Einbettungen von organischen Amiden und anderen kleinen organischen Molekülen mit Kaolinmineralien.Es wurde gezeigt,daß die erhaltenen Basisabstände von Einbettungen mit diesen Molekülen im Einklang mit Wasserstoffbrückenschemen sind, in welchen,wenn möglich,dreifache Wasserstoffbrücken von den Tonhydroxylgruppen zu den Karbonylgruppen geformt werden.Variationen in den Basisabständen innerhalb einer Serie von Amiden können erklärt werden,indem die Maximisation von Wasserstoffbrücken und zur selben Zeit das Vermeiden von zu nahen van der Waalschen Kontakten berücksichtigt werden.