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CRYSTAL STRUCTURE OF KAOLINITE:DIMETHYLSULFOXIDE INTERCALATE

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Abstract—The crystal structure of the kaolinite:dimethylsulfoxide (DMSO) intercalate ($P1$, $a = 5.187(2)$, $b = 8.964(3)$, $c = 11.838(4)$ Å, $\alpha = 91.53(1)°$, $\beta = 108.59(2)°$, $\gamma = 89.92(1)°$) has been determined using spectroscopic and X-ray and neutron powder diffraction data. Both the X-ray and neutron powder diffraction patterns were refined. Solid-state ^{13}C, ^{29}Si, and ^{27}Al nuclear magnetic resonance data and previously collected infrared spectroscopic data provided a useful starting model for structural refinement. Due to the extreme overlap of reflections of this low-symmetry unit cell, the Rietveld method proved inadequate, and quasi-single crystal methods were employed. Each DMSO molecule was found to be triply hydrogen bonded above the octahedral vacancy in the gibbsitic sheet of the kaolinite layer. One methyl group is keyed into the ditrigonal hole in the tetrahedral sheet with the other S–C bond parallel to the sheet. The DMSO molecules are accommodated by significant horizontal displacement of individual kaolinite layers to achieve almost perfect overlap of the octahedral vacancy by the adjacent ditrigonal hole.

Key Words—Crystal structure, Dimethylsulfoxide, Infrared spectroscopy, Intercalate, Kaolinite, Neutron powder diffraction, Nuclear magnetic resonance, X-ray powder diffraction.

INTRODUCTION

The formation of a one-dimensionally (1-D) ordered intercalate between kaolinite and dimethylsulfoxide (DMSO) has been recognized for some time. The 1-D structure of this complex was proposed by Weiss *et al.* (1966). An electron microscope study by Sanchez Camazano and Gonzalez Garcia (1970) indicated that the kaolinite platelets assumed a tubular morphology similar to halloysite upon intercalation. Jacobs and Sterckx (1970) published an X-ray powder diffraction (XRD) pattern of the kaolinite:DMSO complex which displayed much more detail than would be expected from a 1-D ordered intercalate. Recently collected solid-state ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectra (Thompson, 1985) suggest a high degree of short-range ordering of the DMSO molecules within the intercalate structure. The only reported suggestion that the kaolin-group minerals (here dickite) formed 3-D ordered intercalates with DMSO appeared in the related publications of Adams (1979) and Adams and Waltl (1980).

A solution to the structure of the kaolinite:DMSO intercalate is important for five reasons:

(1) DMSO is one of a unique group of small, highly polar molecules which can be intercalated directly into kaolinite.
(2) The formation of the 11.2-Å intercalate has been used to differentiate kaolinite from chlorite and serpentine-group minerals (Jackson and Abdel-Kader, 1978; Calvert, 1984; Chang and Houng, 1984).
(3) The thermal decomposition of the kaolinite:DMSO intercalate, which was the subject of kinetic studies by Adams and Waltl (1980), displayed a surprisingly high activation energy compared with the kaolinite:*N*-methylformamide intercalate.
(4) The kaolinite:DMSO intercalate has recently been used as an intermediate in the formation of hydrated kaolinites (Costanzo *et al.*, 1984a, 1984b). The layer stacking adopted by the intercalate may have influenced the resultant hydrated kaolinite structures.
(5) The solution of the kaolinite:DMSO intercalate structure would provide the first example of a 3-D ordered kaolinite intercalate structure being solved independently, rather than by analogy with the corresponding dickite intercalate obtained by single crystal methods.

For those compounds where suitable single crystals are not obtainable, the Rietveld method (Rietveld, 1967, 1969) has been useful for structures of moderate unit-cell size (i.e., <500 Å^3), but less so for structures with larger, low-symmetry unit cells. In the latter materials, significant peak overlap severely limits the amount of extractable information from a powder diffraction profile. Other solid-state techniques can help elucidate these difficult structures by supplementing the limited structural information available from the powder diffraction profiles. Two spectroscopic techniques which provide useful supplementary bond-length

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information in the solid state are infrared (IR) spectroscopy and NMR spectroscopy. The former is well established, although it has become even more useful with the advent of Fourier-transform infrared spectroscopy (FTIR). The latter has only begun to contribute to crystal structure solutions since magic-angle spinning NMR spectroscopy (MAS/NMR) at high field has become routinely available to the solid-state chemist.

Using both the IR (Jacobs and Sterckx, 1970; Olejnik *et al.*, 1968) and solid-state ^{13}C and ^{29}Si NMR data (Thompson, 1985) available, an attempt was made to solve the crystal structure of the kaolinite:DMSO intercalate, based upon the basic knowledge of the structure of the raw materials, kaolinite (Brindley and Robinson, 1946; Zvyagin, 1960; Suitch and Young, 1983) and DMSO (Thomas *et al.*, 1966). In addition to the XRD data, neutron powder diffraction patterns were collected to refine the hydrogen atom positions as well as to provide a means of checking that the XRD profile refinements provided real structure solutions.

EXPERIMENTAL

Synthesis

Two different Georgia kaolinites were used to synthesize the kaolinite:DMSO intercalate. Kaolinite 1 was supplied by Ward's Natural Science Establishment Inc., Rochester, New York, as kaolinite #4, Oneal pit, Macon, Georgia. This kaolinite is relatively poorly crystallized, with a Hinckley crystallinity index of 0.43 (Hinckley, 1963). The measured cation-exchange capacity (CEC) was 11.2 meq/100 g; the particle size distribution was 56% <4 μm. Kaolinite 2, also from Macon, Georgia, was supplied by the Georgia Kaolin Company. Its crystallinity had been enhanced by dispersion and centrifugal fractionation to a Hinckley index of 1.40. Its CEC was 2.8 meq/100 g; its particle size distribution was 94% <4 μm.

The two kaolinites gave XRD profiles almost identical to those of samples 2 and 1, respectively, reported by Plançon and Tchoubar (1977) in their study of types of structural defects in natural kaolinites. Based on their description, kaolinite 1 of the present study probably contained a significant number of nb/3 defects, whereas kaolinite 2 was probably relatively free of such defects. Kaolinite 1 intercalated to >95% upon exposure to a saturated vapor of laboratory grade DMSO for 48 hr at 60°C. It was then heated in air, also at 60°C, for 24 hr to remove excess DMSO. Kaolinite 2 did not intercalate spontaneously and had first to be expanded by saturation in hydrazine hydrate, collapsed, and subsequently treated as above. For neutron powder diffraction experiments DMSO-d6 >99.5% (from Fluka AG) was substituted for the laboratory grade DMSO during sample preparation because the substitution of deuterium for hydrogen is desirable in neutron elastic scattering experiments.

Data acquisition

XRD data were collected using graphite monochromated CuKα radiation on a Rigaku horizontal goniometer diffractometer (Model CN2155D5). Freeze drying was not attempted for the kaolinite:DMSO intercalate due to its instability in aqueous suspension. Preferred orientation, however, was not anticipated to be a major problem due to the apparently tubular morphology of the intercalate (Sanchez Camazano and Gonzalez Garcia, 1970). Data were collected in the step-scan mode every 0.05°2θ from 10° to 90°2θ with a counting time of 100 sec/step.

Neutron powder diffraction data were collected on a high-resolution powder diffractometer at the Australian Atomic Energy Commission's Lucas Heights Research reactor. The sample was mounted in a 16-mm vanadium can, and data were collected every 0.05°2θ up to a monitor count of 10^4/step. The eight counters used on this diffractometer enabled reasonable peak-to-background ratios to be achieved over the region of most interest (10° to 100°2θ) within 2 days running time. The wavelength of the irradiating neutron beam was 1.893 Å.

Powder diffraction profile refinement

Rietveld analysis of the powder diffraction data was performed on a DEC KL1091E computer using version 3.2 of the program (DBW3.2) written by Wiles and Young (1981). Due to the severe overlap of reflections and the large number of atoms in the kaolinite:DMSO intercalate's smallest asymmetric unit (34 atoms; 54, including H atoms), it was necessary to be able to constrain bond lengths according to the data supplied by IR and NMR spectroscopy and from the structure of the starting materials. Upon exhausting the usefulness of the Rietveld method, the simplest approach was to use quasi-single crystal methods. Program DBW 3.2 was used to refine the instrumental variables and the cell parameters to extract observed integrated intensities. The intensities and the refined unit cell were input into SHELX (Sheldrick, 1976). The refined atomic coordinates were then input into the DBW3.2 program to re-refine the instrumental variables and the cell dimensions. This two-step approach was performed cyclically two or three times until no significant improvement in the fit of the model to the raw data was achieved.

X-ray powder diffraction structure determination

The XRD pattern of the kaolinite:DMSO intercalate prepared using kaolinite 1 had greater peak overlap than that prepared using kaolinite 2. For this reason, structure refinement using the data set of the former

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was not attempted. This apparent broadening of the XRD pattern of the former intercalate could not be attributed to particle size effects. The significance of the poorer resolution is discussed below.

Reflections due to unreacted kaolinite were stripped out prior to refinement by subtracting an appropriately scaled powder diffraction pattern of freeze-dried kaolinite collected under identical conditions. The regions below 15.0°2θ and between 23.0° and 25.5°2θ were excluded. These excluded regions included the 001 and 003 reflections of the kaolinite:DMSO intercalate as well as the 101 reflection of the minor TiO_2 contaminant anatase. By excluding the two most intense reflections of the intercalate, 001 and 003, the reflections likely to be enhanced the most by preferred orientation of a platy nature were removed from the least squares refinement, thus minimizing unwanted preferred orientation effects.

During the early stages, the structure refinement was limited to the region below 36.0°2θ (55 reflections), being extended to 46.0°2θ (134 reflections) for the later stages. Several approximations were made to facilitate the extraction of observed intensities for input into SHELX. These were: no preferred orientation, a Lorentzian peak-profile function, constant peak half-widths, constant background, and a single wavelength (λ = 1.542 Å), the last three of which being reasonable between 15.0° and 46.0°2θ for CuKα radiation. The diffraction pattern was indexed by analogy with the kaolinite structure (Suitch and Young, 1983) using a locally written program for least squares refinement of $1/d^2$. The unit-cell dimensions obtained by this method were a suitable starting point for Rietveld refinement.

Table 1 compares the cell parameters for kaolinite derived by the Rietveld method (Suitch and Young, 1983) with the starting cell parameters derived using the least squares refinement of $1/d^2$. The crystallographic axes of dickite and the two 3-D ordered dickite intercalates mentioned above are approximately parallel from consideration of the relative positions of atoms of the dickite layer in their respective unit cells. Subsequently, this orientation was assumed for the kaolinite:DMSO intercalate such that intercalation by DMSO proceeded by a mechanism involving simple expansion normal to the *ab* plane and horizontal displacement parallel to *a*.

BOND LENGTH CONSTRAINTS

Three studies have discussed the IR spectrum of the kaolinite:DMSO intercalate (Olejnik *et al.*, 1968; Jacobs and Sterckx, 1970; Lipsicas, 1984). One notable feature, unique among kaolinite intercalates, is that new, sharp peaks at relatively low wave number, 3535 and 3499 cm^{-1}, formed upon intercalation (Olejnik *et al.*, 1968). Jacobs and Sterckx (1970) corrected these values to 3545 and 3505 cm^{-1}, respectively. The new, sharp peaks were unambiguously attributed to the formation of moderately strong hydrogen bonds between some of the inner-surface hydroxyls of the kaolinite and the sulfonyl oxygen.

Nakamoto *et al.* (1955) correlated O–H . . . O bond length with ν(OH). The two peaks which appeared upon intercalation at 3545 cm^{-1} and 3505 cm^{-1} corresponded on this basis to O–H . . . O interatomic distances of 2.94 and 2.91 Å, respectively. These distances provided a useful starting point for O–H . . . O bond lengths in a structural refinement.

A recent study of kaolinite intercalation by ^{13}C and ^{29}Si NMR spectroscopy by Thompson (1985) provides important information on the orientation and positioning of the DMSO molecule between the kaolinite layers. The ^{29}Si spectrum displays a single resonance at $\delta = -93.1$ (ppm relative to TMS), significantly shielded relative to kaolinite which exhibited a split resonance centered on $\delta = -91.5$ (Barron *et al.*, 1983). These data were interpreted in the context of other kaolinite intercalate spectra as indicating little or no hydrogen bonding between the basal oxygens of the silicate sheet and the DMSO molecule. This information allowed interatomic distances between the basal oxygens of the silicate sheet and at least one methyl group to be constrained according to van der Waals interaction distances (CH_3 = 2.0 Å, O = 1.4 Å).

The ^{13}C NMR spectrum of the intercalate is even more significant in that the two methyl carbons, which were degenerate in the liquid state (δ = 40.3, ppm relative to TMS), are clearly resolved into two equally intense resonances at δ = 42.5 and 43.7 (Thompson, 1985). This resolution implies different magnetic environments for the two methyl carbons which is likely achieved, from consideration of the configuration of the DMSO molecule, by positioning one methyl group keyed into the ditrigonal holes in the silicate sheet with the other approximately parallel to the sheet.

Additionally solid-state ^{27}Al NMR spectra for both the starting material and the intercalate were collected at 78.18 MHz by P. F. Barron (Brisbane NMR Centre, Brisbane, Australia; personal communication, 1985). The resultant spectra were reported to be similar for both the static and magic angle spinning experiments. This similarity indicates that, upon intercalation, no major change exists in the magnetic environment or symmetry for the octahedrally coordinated aluminum in the gibbsitic sheet (cf. Lampe *et al.*, 1982).

The model derived in this present study from the IR and NMR spectra of the kaolinite:DMSO intercalate was not inconsistent with 1-D Fourier projection of Weiss *et al.* (1966) yet accounted for the 11.2-Å basal dimension more satisfactorily than the models described by them and by Olejnik *et al.* (1968). The constraints derived from the spectroscopic data were of

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Table 1. Comparison of kaolinite and starting kaolinite:dimethylsulfoxide (DMSO) cell dimensions.

	a (Å)	b (Å)	c (Å)	α	β	γ
Kaolinite	5.153	8.941	7.403	91.692°	104.860°	89.822°
Kaolinite:DMSO	5.203	8.927	11.838	90.902°	108.849°	89.838°

great assistance considering the complex nature of the XRD pattern, previously reported by Jacobs and Sterckx (1970).

STARTING MODEL

Due to the limitations of the Rietveld method, an effort was made to obtain the best possible starting model for the kaolinite:DMSO structure. For this reason, the recently published structure of kaolinite (Suitch and Young, 1983) was preferred to others (e.g., Zvyagin, 1960; Brindley and Robinson, 1946), by reason of the greater detail provided. Also, to avoid the possibility of false refinement minima, two parallel refinements were conducted throughout using the two different sets of refined positional parameters for kaolinite obtained by Suitch and Young (1983), henceforth referred to as BRR and ZRT.

The two sets of kaolinite positional parameters, BRR and ZRT, were translated into the new starting unit cell (Table 1). Full occupancy of the interlayer sites by DMSO was assumed, i.e., one DMSO per $Al_2Si_2O_5(OH)_4$. The space group $P1$ was chosen by analogy with kaolinite (Suitch and Young, 1983) because it was assumed that the intercalate would not have higher symmetry than the starting material. Due to the relatively high atomic number of sulfur, the two DMSO molecules were approximated in the early stages by placing two positionally unconstrained sulfur atoms between the positionally constrained kaolinite layers.

As discussed by Young and Wiles (1981), the R values used as fitting criteria were R_{wp} and R_B. The initial refinements of the BRR- and ZRT-derived models converged at $R_{wp} = 35\%$ and 33%, respectively. Release of the aluminum positional parameters resulted in these values dropping to 19% and 18%, respectively, with the four aluminum atoms undergoing a concerted displacement, as if rotating about a common axis. This apparent rotation resulted in a revision of the starting models and the rejection of the earlier assumption that the a and b axes of kaolinite were parallel to those of the kaolinite:DMSO unit cell. The BRR and ZRT starting parameters were rotated through $-\pi/3$ radians about the axis normal to the ab plane and passing through the center of the ditrigonal hole. The subsequent refinements with free-sulfur positional parameters converged at $R_{wp} = 21.0\%$ and 17.3% for the BRR- and ZRT-derived models, respectively. Further refinement was attempted with the addition of six unconstrained atoms, four carbon and two oxygen, adjacent to the sulfur atoms. R_{wp} values dropped to 12.5% and 11.8%, respectively, although the bond lengths and angles of the two DMSO molecules were quite unreasonable.

In view of the recent neutron profile refinement of hydrogen atom positions in kaolinite by Adams (1983) in the space group $C1$, the possibility of c-face centering was considered at this stage; however, R_{wp} values for such refinements in the space group $C1$ were typically 2% higher than those in $P1$. The least squares procedure employed by the Rietveld method (Rietveld, 1969) precluded the application of standard tests (e.g., Hamilton, 1965) for the significance of the refinement in $P1$ over $C1$. Subsequently, the possibility of c-face centering was not considered further.

The bond length and angle constraints were considered essential to the successful refinement of the intercalate model. As described above, these constraints were applied by extracting observed intensities using the DBW3.2 program and refining the atomic parameters via SHELX. Due to the relatively small number of reflections for the 34 non-hydrogen atom structure, it was necessary to start the refinement with DMSO bond lengths and angles constrained according to Thomas *et al.* (1966). For each DMSO molecule the three O . . . H–O hydrogen bond lengths were constrained at 2.94 Å, as suggested by the IR data. The sulfonyl oxygens were positioned above the vacant octahedral sites in a manner similar to the dickite:formamide (Adams and Jefferson, 1976) and dickite:*N*-methylformamide (Adams, 1979) intercalates. At the other end of the molecule one methyl carbon was keyed into the ditrigonal hole with methyl carbon-oxygen separation of 3.4 Å, the sum of the van der Waals radii. Not unexpectedly, these two constraints were remarkably compatible with each other and with the previously refined sulfur atom positions.

The cyclic refinement of the powder profile of the kaolinite:DMSO intercalate, using the DBW3.2 program to extract observed integrated intensities followed by the SHELX program to refine the positional parameters, proceeded initially for the region 15.0° to 36.0°2θ, excluding the region from 23.0° to 25.5°2θ (55 reflections), and then for the region 15.0° to 46.0°2θ. This approach was applied identically to both the BRR- and ZRT-derived starting models. Due to the small

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Table 2. Positional parameters of the kaolinite : dimethylsulfoxide intercalate for structural models from X-ray (BRR- and ZRT-derived) and neutron (BRRN and ZRTN) powder diffraction data.

	BRR[1] and BRRN[2]			ZRT[1] and ZRTN[2]		
	x	y	z	x	y	z
Al1	0.538	0.636	0.278	0.547	0.650	0.270
Al2	0.026	0.849	0.260	0.009	0.834	0.279
Al3	0.032	0.146	0.277	0.035	0.153	0.282
Al4	0.512	0.345	0.277	0.524	0.356	0.265
Si1	0.058	0.663	0.045	0.030	0.654	0.029
Si2	0.572	0.809	0.038	0.572	0.807	0.034
Si3	0.544	0.177	0.042	0.533	0.169	0.030
Si4	0.072	0.301	0.040	0.085	0.315	0.035
O1	0.143	0.677	0.198	0.149	0.679	0.179
O2	0.647	0.802	0.184	0.666	0.816	0.179
O3	0.267	0.739	−0.020	0.297	0.722	−0.023
O4	−0.007	0.483	0.004	−0.022	0.481	0.003
O5	0.776	0.747	−0.025	0.788	0.759	−0.023
O6	0.667	0.178	0.191	0.649	0.182	0.186
O7	0.181	0.311	0.182	0.161	0.298	0.182
O8	0.803	0.225	−0.024	0.780	0.243	−0.019
O9	0.502	−0.012	0.011	0.479	−0.016	0.008
O10	0.287	0.260	−0.020	0.269	0.249	−0.026
OH1	0.094	−0.011	0.181	0.079	−0.002	0.171
OH2	−0.087	0.698	0.376	−0.080	0.688	0.358
OH3	0.414	0.800	0.380	0.425	0.794	0.378
OH4	−0.022	−0.007	0.370	−0.035	0.001	0.351
OH5	0.579	0.489	0.169	0.585	0.486	0.177
OH6	0.413	0.196	0.372	0.409	0.201	0.367
OH7	−0.083	0.295	0.379	−0.093	0.310	0.380
OH8	0.463	0.505	0.356	0.462	0.506	0.361
	BRRN (BRR in parentheses)			ZRTN (ZRT in parrentheses)		
	x	y	z	x	y	z
C1	−0.064	−0.039	−0.188	−0.064	−0.037	−0.190
	(−0.123	−0.013	−0.203)	(−0.095	−0.013	−0.216)
H1C1	−0.110	−0.046	−0.105	−0.101	−0.037	−0.104
H2C1	0.090	0.046	−0.179	0.092	0.045	−0.187
H3C1	0.011	−0.147	−0.209	0.004	−0.148	−0.209
C2	−0.565	−0.152	−0.292	−0.568	−0.153	−0.294
	(−0.562	−0.169	−0.339)	(−0.562	−0.148	−0.350)
H1C2	−0.621	−0.139	−0.211	−0.631	−0.141	−0.215
H2C2	−0.445	−0.253	−0.287	−0.445	−0.253	−0.287
H3C2	−0.748	−0.161	−0.369	−0.748	−0.163	−0.373
C3	0.423	0.503	−0.193	0.427	0.501	−0.193
	(0.404	0.495	−0.215)	(0.294	0.501	−0.207)
H1C3	0.376	0.503	−0.109	0.577	0.591	−0.178
H2C3	0.579	0.587	−0.186	0.516	0.397	−0.213
H3C3	0.498	0.394	−0.209	0.368	0.489	−0.113
C4	−0.092	0.395	−0.296	−0.084	0.397	−0.298
	(−0.088	0.380	−0.341)	(−0.136	0.364	−0.368)
H1C4	−0.206	0.432	−0.238	−0.192	0.436	−0.238
H2C4	0.035	0.300	−0.257	0.039	0.301	−0.261
H3C4	−0.232	0.362	−0.383	−0.230	0.366	−0.385
S1	−0.367	0.007	−0.307	−0.373	0.008	−0.305
	(−0.399	0.007	−0.340)	(−0.374	0.020	−0.350)
S2	0.121	0.545	−0.313	0.133	0.544	−0.317
	(0.136	0.528	−0.352)	(0.093	0.517	−0.361)
OS1	−0.294	−0.038	−0.418	−0.298	−0.032	−0.418
	(−0.270	−0.009	−0.440)	(−0.256	−0.001	−0.452)
OS2	0.221	0.498	−0.417	0.229	0.491	−0.421
	(0.250	0.478	−0.451)	(0.276	0.464	−0.433)
H1	0.139	0.089	0.148	0.118	0.102	0.142
H2	0.024	0.647	0.444	−0.005	0.658	0.438
H3	0.524	0.874	0.433	0.518	0.874	0.429
H4	−0.106	0.017	0.429	−0.107	0.013	0.416
H5	0.724	0.570	0.171	0.739	0.557	0.172

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Table 2. Continued.

	BRRN (BRR in parentheses)			ZRTN (ZRT in parentheses)		
	x	y	z	x	y	z
H6	0.473	0.134	0.440	0.475	0.141	0.437
H7	0.074	0.355	0.415	0.084	0.352	0.415
H8	0.331	0.510	0.396	0.334	0.521	0.403

Cell parameters	*a* (Å)	*b* (Å)	*c* (Å)	α	β	γ
BRR and BRRN	5.186(1)	8.965(2)	11.835(3)	91.52(1)°	108.57(2)°	89.93(1)°
ZRT and ZRTN	5.189(2)	8.963(2)	11.841(3)	91.53(1)°	108.60(2)°	89.92 (1)°

[1] BRR- and ZRT-derived models employed the positional parameters of kaolinite (BRR and ZRT, respectively) published by Suitch and Young (1983).

[2] BRRN and ZRTN employed the refined non-hydrogen atom positional parameters from the BRR- and ZRT-derived models, respectively.

amount of extractable information, DMSO bond lengths and angles were not released, and constraints were placed on Si–O and Al–O bond lengths according to those observed in kaolinite (Suitch and Young, 1983).

The final atomic parameters for the two models are presented in Table 2, and the corresponding pattern-fitting plot of the better-fitting ZRT-derived model is shown in Figure 1. An overall isotropic temperature factor was used, and no allowance was made for preferred orientation other than the omission of the 001 and 003 reflections at the intensity extraction stage. When the site occupancy of the DMSO was refined at various stages it did not deviate significantly below n = 1.0 for $Al_2Si_2O_5(OH)_4 \cdot [(CH_3)_2SO)]_n$. For this reason,

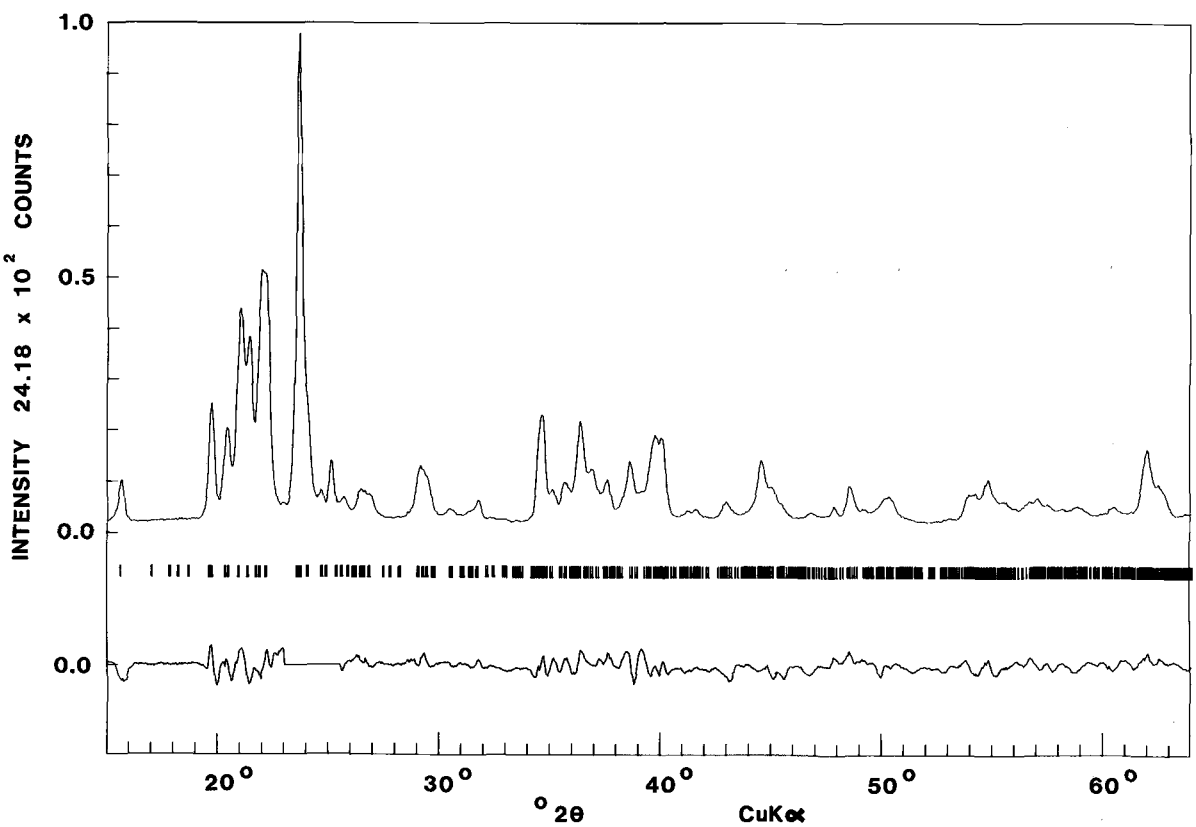


Figure 1. Pattern-fitting plot for refinement of the kaolinite:dimethylsulfoxide intercalate structure from the ZRT-derived starting model, based on data from Suitch and Young (1983), using X-ray powder diffraction data. Only observed data and difference (observed minus calculated) plots are displayed. Refinement of this model using data to 64°2θ converged to R values of R_{wp} = 10.60% and R_B = 6.57% (cf. R_{wp} = 11.28% and R_B = 7.08% for starting model BRR).

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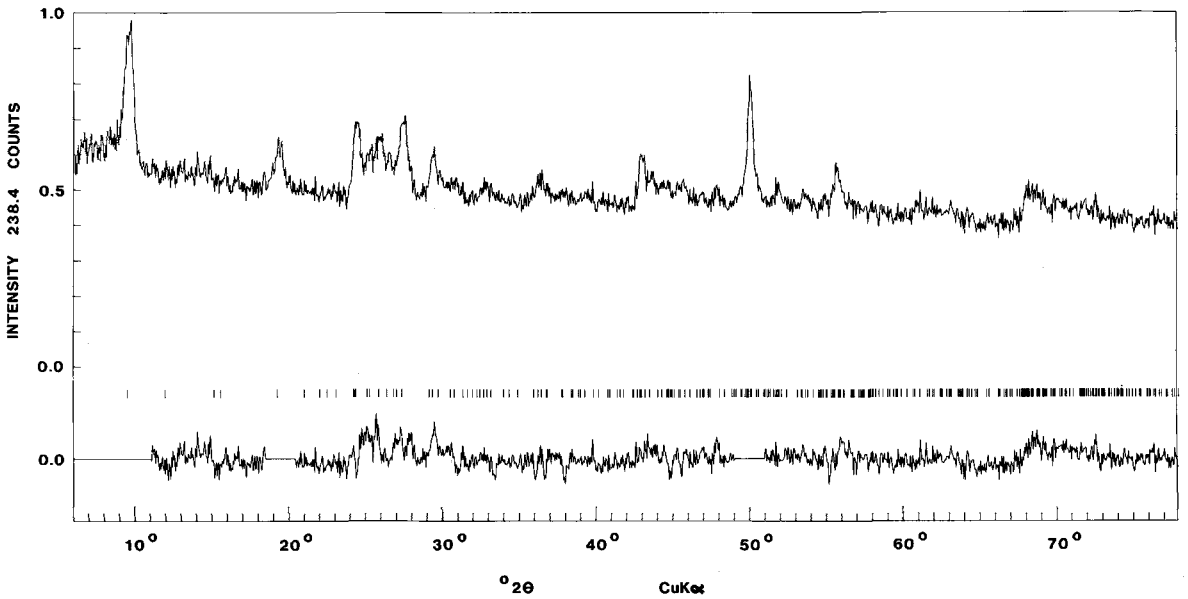


Figure 2. Pattern-fitting plot for refinement of the kaolinite:dimethylsulfoxide intercalate structure from the starting model BRRN using neutron powder diffraction data. Refinement of this model using data to 78°2θ converged to R values of R_{wp} = 5.36% and R_B = 3.32% (cf. R_{wp} = 5.43% and R_B = 3.37%).

during refinement of the final models full occupancy was assumed. The final R-values for the two models below 46°2θ, maintaining the previously stated approximations, were R_{wp} = 12.07% and R_B = 6.36% for the BRR-derived model and R_{wp} = 11.57% and R_B = 5.92% for the ZRT-derived model. The pattern-fitting plot in Figure 1 was achieved using two wavelengths, a polynomial background function, a pseudo-Voigt profile function, and a profile asymmetry factor. Whereas the final refinements of instrumental parameters were somewhat artificial, they did verify that the kaolinite:DMSO structural models, calculated from

Table 3. Relevant interatomic distances (Å) and angles (°) for the kaolinite:dimethylsulfoxide (DMSO) intercalate.

O–C distances (<3.6 Å)			OH–O distances (H-bonded)		
	BRRN[1]	ZRTN[1]		BRRN	ZRTN
O3–C1	2.98	3.15	OS1–OH3	2.76	2.82
O3–C3	3.18	3.02	OS1–OH4	3.27	3.44
O4–C3	3.13	3.06	OS1–OH6	3.28	3.31
O4–C4	3.50	3.54	OS2–OH7	2.99	2.87
O5–C1	3.05	3.00	OS2–OH2	3.09	3.18
O5–C3	3.09	3.20	OS2–OH8	3.31	3.18
O5–C2	3.25	3.27			
O8–C1	3.24	3.44			
O8–C3	3.44	3.28			
O9–C1	3.13	3.04			
O10–C3	3.26	3.31			
O10–C1	3.45	3.31			
O10–C4	3.49	3.46			
	DMSO				
	BRRN	ZRTN			
OS1–S1–C1	102.5	101.3			
OS1–S1–C2	101.4	101.8			
C1–S1–C2	96.4	97.6			
OS2–S2–C3	98.5	100.2			
OS2–S2–C4	105.9	105.1			
C3–S2–C4	98.5	97.3			

[1] Refer to footnote 2 of Table 2.

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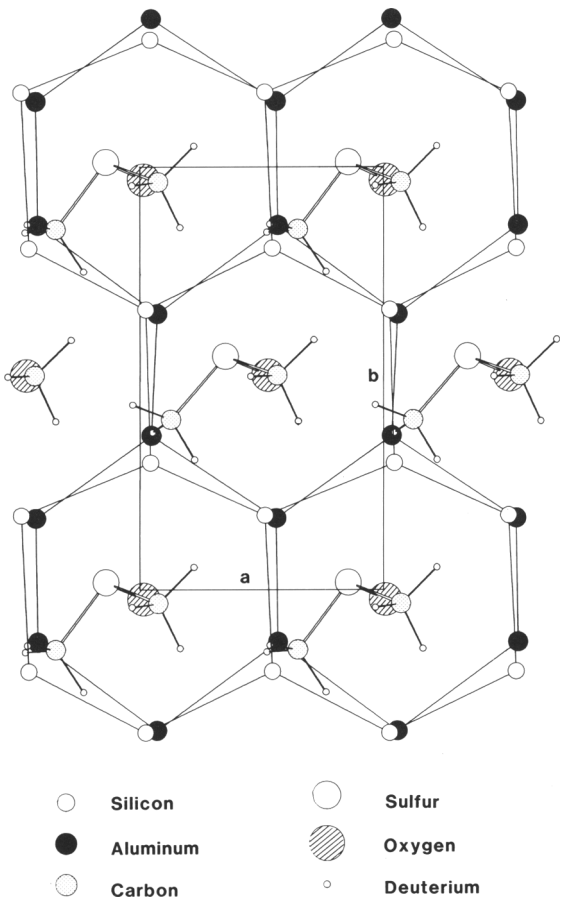


Figure 3. Schematic projection of the kaolinite:dimethylsulfoxide (DMSO) intercalate (refined model BRRN) onto the *ab* plane. Only the aluminum, silicon, and the DMSO molecules are included. Lines are drawn between adjacent silicon and aluminum atoms to accentuate the positions of the ditrigonal holes in the tetrahedral layer and the octahedral vacancies in the gibbsitic layer, respectively.

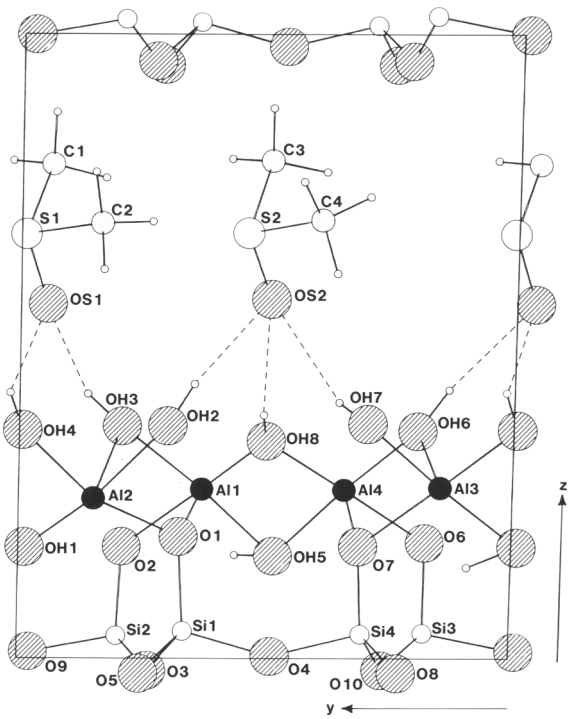


Figure 4. Projection of the kaolinite:dimethylsulfoxide intercalate (refined model BRRN) onto the *bc* plane. Where possible labels used by Suitch and Young (1983) have been retained for atoms of the kaolinite layer.

data below 46.0°2θ, were not inconsistent with the excessively overlapped data not used in the structure refinement.

NEUTRON STRUCTURE DETERMINATION

The neutron powder diffraction pattern provided a means of testing the refined X-ray diffraction models as well as determining the position of the 20 hydrogen atoms in the structure. The same cyclic approach used for the X-ray data refinement was applied to the neutron powder diffraction data. The reflections due to unreacted kaolinite were stripped prior to refinement, and three strong 00*l* reflections, 001, 002 and 005, from the kaolinite:DMSO intercalate were excluded to minimize preferred orientation effects. The refinement was restricted to the region below 49.0°2θ (88 reflections). The approximations made for the neutron data refinements were the application of a Gaussian peak profile function, a previously determined peak width function, and no preferred orientation.

As discussed above, it was necessary to constrain the bond lengths and angles for the DMSO molecules according to Thomas *et al.* (1966), although in the final stages C–S–O and C–S–C angle constraints were relaxed. The 12 deuterium atoms were left free to rotate about their S–C axes. The 8 hydrogen atoms from the kaolinite were fixed by means of O–H bond-length constraints with 0.95 Å for the six interlayer hydrogen atoms and 1.04 Å for the other two. The 26 kaolinite atom positions were fixed according to the X-ray refined models. As most of the neutron scattering for the intercalate was located in the four CD_3 groups, the DMSO molecules were allowed to refine unconstrained as well.

The refined atomic coordinates for the two models, BRRN and ZRTN, are also listed in Table 2. The final R values for the two models out to 49.0°2θ were R_{wp} = 5.38% and R_B = 3.64% for BRRN and R_{wp} = 5.43% and R_B = 3.74% for ZRTN. The validity of these models was tested by refinement of the instrumental parameters out to 78.0°2θ. The pattern-fitting plot of the better-fitting model BRRN is presented in Figure 2. Relevant bond length and bond angle information for both the X-ray and neutron diffraction-derived models is listed in Table 3.

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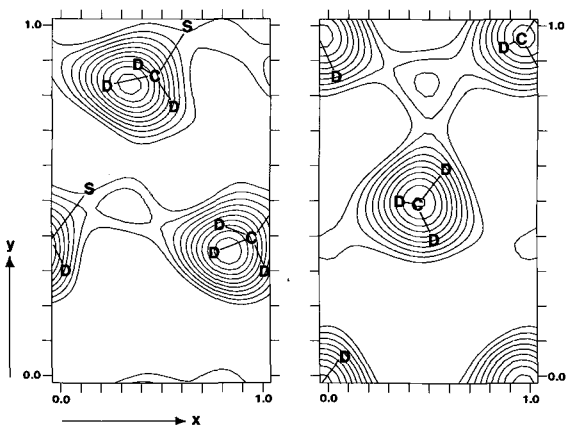


Figure 5. Profile maps of nuclear scattering density, parallel to the *ab* plane, generated from the extracted observed intensities using refined model BRRN. Only positive contours are displayed. Left-hand map (z = 0.670) shows the two sulfur atoms and the two CD_3 groups bonded parallel to the kaolinite layers. Right-hand map (z = 0.800) displays the two CD_3 groups keyed into the ditrigonal holes.

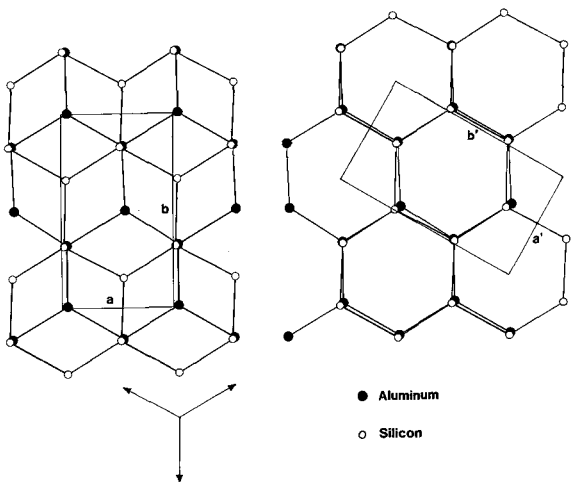


Figure 6. Schematic structure of kaolinite (Suitch and Young, 1983) projected onto the *ab* plane. Left-hand diagram illustrates the position of the silicate layer relative to the octahedral vacancy in the adjacent kaolinite layer. Three vectors ($a/2 + b/6$, $-a/2 + b/6$, $-b/3$) indicate the horizontal displacement required to achieve the overlap observed in the kaolinite: dimethylsulfoxide intercalate. Right-hand diagram illustrates the overlap achieved after the silicate layer has been displaced by $a/2 + b/6$. a' and b' represent the resultant unit cell for the intercalate.

DISCUSSION

Structural description

The derived structural model of the kaolinite:DMSO intercalate is shown in Figures 3 and 4. The two halves of the unit cell are, as for kaolinite, approximately related by *c*-face centering. As mentioned above, the structure refined more comfortably in the space group *P*1, precluding the above symmetry constraint; however, the approach to structural model refinement used in this investigation did not allow the significance of this result to be tested rigorously using, for example, the method of Hamilton (1965). The sulfonyl oxygens are triply hydrogen bonded to the inner-surface hydroxyl groups in a similar manner to the dickite:formamide and dickite:*N*-methylformamide intercalates, i.e., the oxygen is positioned approximately above the octahedral vacancy (Figure 3) with relatively short hydrogen bond lengths as predicted from the IR data (cf. Table 3). One methyl group, positioned directly above the sulfonyl oxygen, is keyed into the ditrigonal hole in the silicate sheet with the other methyl carbon-sulfur bond lying parallel to the kaolinite layers. This positioning of the methyl groups was predicted by the ^{13}C NMR datum. Also, the methyl carbon-oxygen distances (Table 3) are in reasonable agreement with the premise that hydrogen bonding between such species is not possible. These data justify the interpretation given to the ^{29}Si NMR spectrum of the intercalate by Thompson (1985).

Figure 5 shows two nuclear scattering maps parallel to the *ab* plane through the center of the CD_3 groups. Due to the small number of reflections (72) used in generating these maps and the freedom of rotation about the S–C bonds, the CD_3 groups appear as single, intense nuclear scattering centers; however, they unequivocably verify the site inequivalence of the two methyl groups in the kaolinite:DMSO intercalate.

Comparison of the kaolinite and kaolinite:DMSO intercalate bond lengths and angles in the aluminosilicate framework indicates that individual kaolinite layers undergo little distortion, as suggested by the ^{27}Al NMR data, upon intercalation by DMSO. Even the ripple effect observed in the silicate sheet of kaolinite, which is reflected in the z-coordinates of the basal oxygens (cf. Figure 4), is preserved in the intercalate. It is likely that this feature facilitates the keying of the methyl groups into the silicate sheet of the intercalate.

Figure 3 illustrates the almost perfect overlap of the octrahedral vacancy with the ditrigonal hole in the adjacent layer in order to accommodate the DMSO molecules in their potential energy minimizing orientation (cf. Adams, 1978). An individual kaolinite layer can be displaced in three different directions to accommodate DMSO in its energetically favorable orientation. The mechanism of intercalation requires expansion to an 11.2-Å structure with corresponding horizontal displacement as illustrated in Figure 6. The ability of the intercalate to achieve 3-D ordering by these three different displacements enables the individual crystallites to minimize distortion upon intercalation. From this illustration it is clear why the *a* and *b* crystallographic axes of the kaolinite:DMSO intercalate cannot be parallel to those of kaolinite.

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One implication of this simple mechanism of intercalation is that a kaolinite specimen containing layer stacking disorder of the n*b*/3 type would result in a completely 3-D ordered kaolinite:DMSO intercalate. Because 3-D ordering was not apparent for the DMSO intercalate of kaolinite 1, the probable reason for the poorly resolved XRD pattern was a broadening effect due to a more tube-like morphology. The overall larger particle size and greater disorder of kaolinite 1 may have contributed to enhanced crystallite bending. Alternately, some disorder phenomenon other than n*b*/3 type, discussed by Plançon and Tchoubar (1977), may have been responsible for the diminished resolution. Furthermore, during collapse of the intercalate, individual kaolinite layers would be expected to adopt both kaolinite stacking order and n*b*/3 stacking disorder. This effect was observed by both Olejnik *et al.* (1968) using IR and Jacobs and Sterckx (1970) using XRD.

Significance of extracted data

The main criticism of the present approach to powder diffraction profile refinement has been the small number of reflections used for the refinement and the large number of approximations and assumptions. Data extraction from a powder diffraction profile must always be a compromise between minimizing the regions of severe peak overlap and maximization of data points. In this investigation the useful number of data points was very small by single crystal standards. Therefore, it was necessary to apply the constraints provided by spectroscopic data to lower the degrees of freedom and to commence with a plausible starting model. This latter condition was vital to the extraction of reasonable intensity data from the powder profile. For regions of extreme peak overlap, which included most of the diffraction patterns, the observed intensities extracted were very much starting model dependent.

Considering the above limitations, some doubt must be raised as to the uniqueness of the refined structural model achieved by this crystallographic approach. The two factors which provide confidence in both the uniqueness of the structural solution and the validity of the approach used are: (1) the starting model is soundly based upon spectroscopic evidence; and (2) good agreement exists between the X-ray and neutron powder profile refinements. This latter factor grows in significance when it is considered that, for the intercalate, the large scatterers of X-rays have small neutron scattering lengths, and vice versa.

Standard deviations

Although it is customary to publish the values of σ with the refined atomic positional parameters and bond lengths, we have not done this for the refined kaolinite:DMSO intercalate data for the following reason. In the latter stages of data refinement when the DBW3.2 program was used to refine instrumental variables and unit-cell parameters, atomic positional parameters were not varied. When the SHELX program was used to refine atomic positions, the entire structure was never released without some constraints. The uncertainties in atomic coordinates during the least constrained cycles, however, equated to values for σ of between 0.05 and 0.15 Å. The reliability of the positional parameters in this investigation could best be gauged from the approximate convergence of positional parameters of atoms from two different starting models (Table 2). As conventional reliability tests were not appropriate, this convergence was significant.

CONCLUSIONS

Given the severe limitations of the powder diffraction data in providing extractable information, the reasonable agreement between the two derived structural models of the kaolinite:DMSO intercalate for both X-ray and neutron scattering experiments indicates a plausible solution. It is because this structural solution concurs with the spectroscopic data that some degree of confidence can be attached to it. The application of this kind of eclectic approach to crystal structure solution, particularly using solid-state NMR and FTIR, gives some hope in deriving structural models for elusive structures which cannot be solved using single crystal methods. In particular, the present approach will likely prove useful for future investigations of 3-D ordered clay mineral and clay mineral-organic intercalate structures. It now remains to be seen whether the dickite:DMSO intercalate is a 2-layer analogue to the structure described in this work.

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