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NUCLEAR MAGNETIC RESONANCE, INFRARED, AND X-RAY POWDER DIFFRACTION STUDY OF DIMETHYLSULFOXIDE AND DIMETHYLSELENOXIDE INTERCALATES WITH KAOLINITE

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Abstract—Dimethylselenoxide (DMSeO) forms three structurally resolvable intercalates with kaolinite (d(001) = 10.95, 11.26, and 11.38 Å). The 11.26-Å kaolinite:DMSeO intercalate is structurally analogous to the 3-D ordered kaolinite:DMSO intercalate (d(001) = 11.22 Å). Infrared and solid-state ^{77}Se nuclear magnetic resonance data indicate that all DMSeO molecules are equivalent in the structure and, therefore, that the 11.26-Å kaolinite:DMSeO intercalate structure is C-face centered. Structural model refinement from X-ray powder diffraction (XRD) data further support this conclusion ($P1$, $a = 5.195(2)$, $b = 8.990(4)$, $c = 11.946(5)$ Å, $\alpha = 91.33(2)°$, $\beta = 109.39(2)°$, $\gamma = 89.77(2)°$). The kaolinite:DMSO intercalate structure was subsequently re-refined from the XRD profile in C-face centered $P1$. The derived orientation of the DMSO and DMSeO molecules with respect to the basal plane of their respective intercalates is in agreement with polarized infrared measurements of the angles with *ab* of S=O (40.3°) and Se=O (38.8°) for the 11.26-Å intercalate. The locations of the organic molecules also agree with observed infrared band splittings and perturbations. Interatomic distances calculated from the band shifts agree with those for the XRD derived structures.

The 11.38-Å kaolinite:DMSeO intercalate is closely related to the 11.26-Å intercalate, the main differences being a 2-fold disorder in the orientation of the DMSeO molecule and less penetration of the kaolinite ditrigonal cavity by that molecule. The 10.95-Å kaolinite:DMSeO intercalate, displaying disorder parallel to [110], was obtained from the 11.26- or 11.38-Å intercalates by removal of some DMSeO.

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

INTRODUCTION

Two aspects of the structural model of the kaolinite: dimethylsulfoxide (DMSO) intercalate proposed by Thompson and Cuff (1985) require further attention: (1) whether the intercalate structure is C-face centered, and (2) the precise orientation of the DMSO molecule. The successful refinement of structural models from X-ray powder diffraction (XRD) data is dependent on well-resolved profiles, moderate-size unit cells, and a high symmetry space group. The kaolinite: DMSO intercalate structure refinement had none of these and relied heavily on spectroscopic evidence in arriving at a plausible model. The choice of a non-centered cell over a centered cell was based on the preferred symmetry assigned to the starting material, kaolinite, by Suitch and Young (1983). For the intercalate refinement no direct evidence existed to support one over the other. Such direct evidence could be obtained by nuclear magnetic resonance (NMR) spectroscopy, should a suitable magnetic nucleus be available. In view of the above-mentioned limitations, independent verification of the orientation of the DMSO molecule in the intercalate is desirable, especially as previous spectroscopic studies (Jacobs and Sterckx, 1970; Olejnik *et al.,* 1968; Johnston *et al.,* 1984) arrived at divergent structural models to that of Thompson and Cuff (1985). Use of polarized infrared (IR) spectroscopy can, in favorable circumstances, allow comment to be made on molecular orientations with respect to the basal plane of clay minerals able to be oriented uniaxially in IR reflectance assemblies. Band splits may also indicate different environments for the intercalated molecules.

To this end the selenium analogue of the kaolinite: DMSO intercalate was synthesized to facilitate further investigation because of the following advantages: (1) ^{77}Se is an abundant, spin-1/2 nucleus, suitable for solid-state NMR and is very sensitive to changes in magnetic environment; (2) the Se=O stretching frequency is conveniently displaced from the silicate band near 1000 cm^{-1}, which overlaps with the S=O stretching vibration.

EXPERIMENTAL

Synthesis

The dimethylselenoxide molecule (DMSeO) (Hopf and Paetzold, 1972) has similar structure to dimethylsulfoxide (DMSO), but unlike DMSO, DMSeO is solid at room temperature, the melting point being 94°C (Paetzold and Bochmann, 1968), and it is not amenable to intercalation from a saturated vapor as used by Thompson and Cuff (1985) in their synthesis of the kaolinite : DMSO intercalate. Therefore, several standard alternative procedures (Theng, 1974) were attempted to prepare a kaolinite : DMSeO intercalate. Under various conditions, three structurally resolved DMSeO intercalates were obtained with basal dimensions of 10.95, 11.26, and 11.38 Å. Their XRD profiles are displayed in Figure 1.

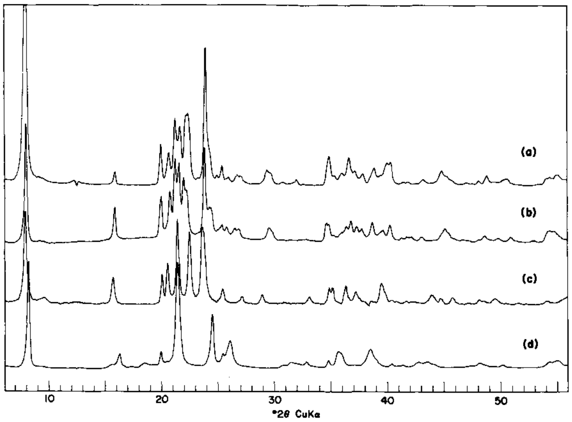

Figure 1. X-ray powder diffraction profiles of (a) kaolinite: dimethylsulfoxide intercalate and (b) 11.26-Å, (c) 11.38-Å, and (d) 10.95-Å kaolinite:dimethylselenoxide intercalates. Note close similarity between upper two profiles.

A 10.95-Å intercalate was prepared by repeated leaching of DMSeO from either of the other two intercalates with chloroform. This intercalate displayed a characteristically disordered XRD pattern. The 11.38-Å intercalate was obtained by reacting oven-collapsed kaolinite : hydrazine intercalate (d(001) = 7.8–8.0 Å, as a result of incomplete expulsion of hole water (Costanzo *et al.*, 1984)) with a 50% excess of DMSeO in aqueous solution at 60°C until all the water had evaporated. The XRD profile was characteristic of a 3-D ordered structure.

The 11.26-Å intercalate was obtained from the untreated kaolinite #2 of Thompson and Cuff (1985) instead of the oven-collapsed kaolinite : hydrazine used above. The XRD profile of this intercalate was almost identical to that reported for 3-D ordered kaolinite : DMSO intercalate (Thompson and Cuff, 1985) and was assumed to be its structural analogue. The IR spectra of the DMSeO intercalates indicated excess DMSeO to be present.

The DMSeO used in the above intercalation reactions was prepared by ozonolysis of dimethylselenide according to the method of Ayrey *et al.* (1962). Unlike DMSO, DMSeO is relatively reactive at room temperature and slightly above; e.g., it reacts with olefins at 60°C (Miyoshi *et al.*, 1975) and decomposes in air above ~60°C (Syper and Mlochowski, 1984). For this reason the attempted synthesis of kaolinite : DMSeO intercalates by the vapor method at elevated temperatures (Thompson, 1985) was unsuccessful. Furthermore, the removal of excess DMSeO from the 11.26- and 11.38-Å intercalates was not possible without collapse of the intercalate or decomposition of the selenoxide to higher molecular weight Se compounds, usually orange-red in color.

Instrumental details

Solid-state ^{77}Se and ^{13}C NMR spectra were collected at 57.275 and 75.450 MHz, respectively, on a Brucker CXP-300 NMR spectrometer. ^{13}C NMR cross-polarized magic-angle spinning (CP/MAS) experiments were conducted on all intercalates using ^{1}H and ^{13}C H_1 fields of 12.5 and 50 G, respectively, 5-ms single contacts, and a recycle time of 1 s. ^{77}Se CP/MAS and dipolar decoupled magic-angle spinning (DD/MAS) experiments were run on all three DMSeO intercalates. CP/MAS experimental conditions were the same as for ^{13}C, except ^{1}H and ^{77}Se H_1 fields of 10 and 50 G, respectively, and a recycle time of 5 s were employed. T_1 measurements on the kaolinite:DMSO and 11.26-Å kaolinite : DMSeO intercalates were made using the normal ^{1}H-^{13}C cross-polarization method followed by a $\pi/2$ phase-shifted $[\pi/2\text{-}\tau\text{-}\pi/2]$ ^{13}C pulse sequence. Samples were packed in stabilized zirconia rotors equipped with Kel-F air bearings. Some solution/liquid ^{77}Se and ^{13}C spectra were collected at 38.15 and 50.30 MHz, respectively, on a Brucker CXP-200 spectrometer.

XRD data were obtained using Ni-filtered CuKα radiation on a Philips vertical goniometer diffractometer. Data were collected in the step-scan mode every 0.05°2θ from 6° to 56°2θ, with counting times of 30 s/step. XRD profile refinement was performed using the same approach reported by Thompson and Cuff (1985) in their investigation of the kaolinite : DMSO intercalate structure. The computer programs DBW3.2 (Wiles and Young, 1981) and SHELX (Sheldrick, 1976) were employed on a VAX 11/750 computer.

Attenuated total reflectance (ATR) IR spectra were

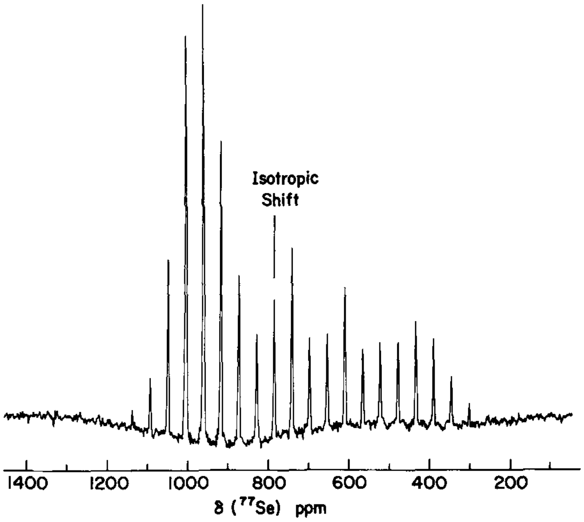

Figure 2. Cross-polarization ^{77}Se nuclear magnetic resonance spectrum of 11.26-Å kaolinite : dimethylselenoxide intercalate. Spinning sidebands result from the highly anisotropic magnetic environment of the ^{77}Se nucleus in dimethylselenoxide and trace out the static spectrum.

obtained on powdered samples lightly pressed against the plane face of a KRS-5 optical hemicylindrical element in a RIIC micro-ATR assembly. The angle of incidence was set at 40°, and a wire grid AgCl Perkin Elmer polarizer was placed between the hemicylinder and the detector of the Fourier-transform spectrometer with a Ge-coated KBr beam splitter operating over 4000–400 cm^{-1} (Digilab FTS15/90). Spectra were collected over 512 scans having resolution of 2 cm^{-1}. The intensities of reflectivity bands were recorded with the polarizer set at 0° and 90° to the plane of incidence of the KRS-5 element. These intensities were then used to calculate the angle of rise of transition moment directions from the basal plane of kaolinite by the methods given by Raupach and Janik (1987). Using this technique on O–H stretching and Si–O bands, untreated and treated kaolinite samples were shown to have uniaxial orientation about the hemicylinder plane. Where necessary, regions of the spectra containing overlapped bands were resolved into their components using a Digilab BANDFIT or equivalent program. The far-IR spectra were recorded on the Digilab FTS15/90 spectrometer using a Mylar beam splitter and a TGS detector fitted with a polythene window. The intercalate samples were placed in a diffuse reflectance (DRIFT) Digilab attachment.

RESULTS

Nuclear magnetic resonance

The CP/MAS ^{77}Se NMR spectra of the three kaolinite : dimethylselenoxide intercalates each gave a single resonance. The CP/MAS ^{77}Se spectrum of the 11.26-Å intercalate, shown in Figure 2, displayed spinning side-bands that result from the highly anisotropic chemical environment of the ^{77}Se nucleus. The isotropic chemical shifts of the 11.26- and 11.38-Å intercalate resonances were $\delta = 785$ and 788 ppm, respectively (relative to neat $(CH_3)_2Se$). The 10.95-Å intercalate also displayed a single resonance, but was significantly broader and deshielded ($\delta = 758$ ppm) relative to the other two intercalate resonances. The ^{77}Se chemical shift for DMSeO in aqueous solution has been reported at $\delta = 812$ ppm relative to neat $(CH_3)_2Se$ (McFarlane and Wood, 1972) using the ^{1}H-^{77}Se double-resonance technique, and $\delta = 819$ ppm relative to 20% $(CH_3)_2Se$ v/v in $CDCl_3$ from direct observation of ^{77}Se (Odom *et al.,* 1979). In the present study, relative to neat $(CH_3)_2Se$, 20% $(CH_3)_2Se$ v/v in $CDCl_3$ was found to resonate at $\delta = -6.0$ ppm.

The presence of only one ^{77}Se signal in both the 11.26- and 11.38-Å intercalates implies magnetically identical environments for Se in each half of their respective unit cells. This direct evidence justified the subsequent use of the C-face centered $P1$ space group in powder profile refinements of these two intercalate structures. Excess DMSeO was observed in the DD/MAS spectra of the 11.26-Å intercalate at $\delta = 813$ ppm, in good agreement with the chemical shifts reported for $(CH_3)_2SeO$ in aqueous solution (McFarlane and Wood, 1972; Odom *et al.,* 1979).

The ^{13}C CP/MAS NMR spectra of each of the intercalates were different (Figure 3). The 11.26-Å intercalate, like the kaolinite : DMSO intercalate (Thompson and Cuff, 1985), displayed two resolved resonances ($\delta = 37.6$ and 36.3, relative to tetramethylsilane (TMS)) of about equal intensity. Furthermore, spin-lattice relaxation times, T_1, were different for the two resolved carbon resonances in each of the above-mentioned intercalates, the more deshielded resonance having the greater T_1. The ^{13}C inversion-recovery experimental results for the kaolinite : DMSO intercalate are displayed in Figure 4. Like the ^{13}C resonance in the DMSO intercalate, the 11.26-Å kaolinite : DMSeO intercalate resonances were downfield of the ^{13}C signal for DMSeO in chloroform ($\delta = 33.8$ pm).

Intermediate between the two ^{13}C resonances for the 11.26-Å intercalate, the 11.38-Å intercalate gave a single, broader signal at $\delta = 36.8$. The 10.95-Å intercalate gave a broad resonance at $\delta = 34.1$, significantly shielded relative to the spectra of the other two kaolinite : DMSeO intercalates. A shoulder on the low-field side of this resonance is indicative of incomplete collapse of this intercalate to 10.95 Å.

XRD profile refinement

Because the XRD profile of the kaolinite : DMSeO intercalate was nearly identical to that used in the structure refinement of the kaolinite : DMSO intercalate by

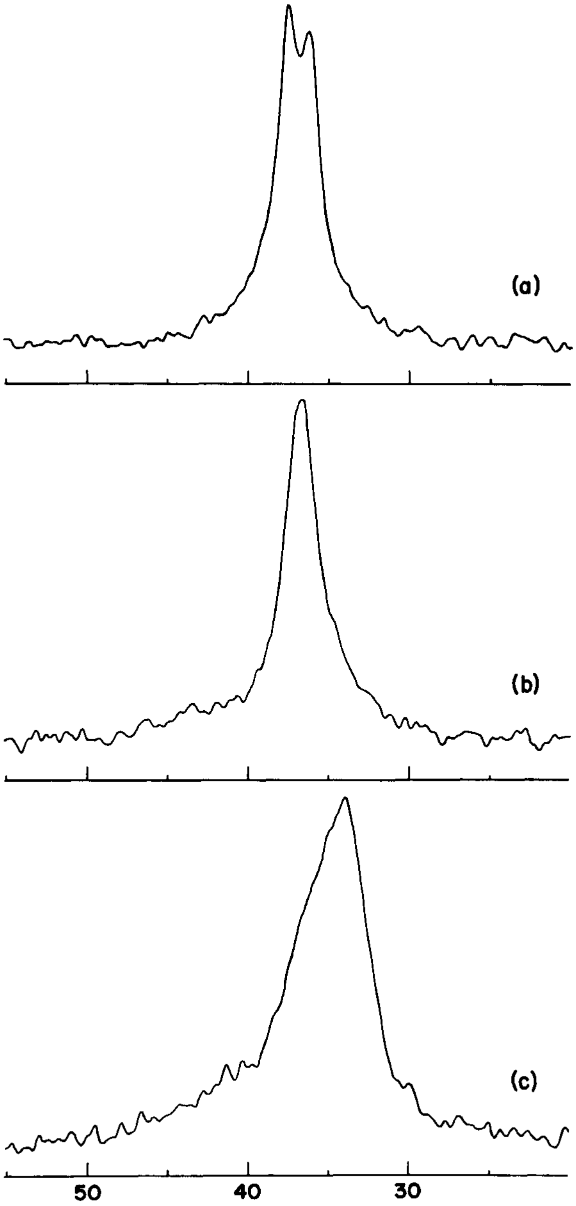

Figure 3. Cross-polarization ^{13}C nuclear magnetic resonance spectrum of (a) 11.26-Å, (b) 11.38-Å, and (c) 10.95-Å kaolinite : dimethylselenoxide intercalates.

Thompson and Cuff (1985), the structural models proposed in this previous work (BRR- and ZRT-derived) were used as starting models for the refinement of the Se analogue. During the early stages of refinement DMSeO bond lengths and angles were constrained according to Hopf and Paetzold (1972), although they were fully released during later stages. Loose constraints were placed on the positions of oxygen atoms in the kaolinite layer throughout the refinement such that Si–O and Al–O bond lengths were maintained at 1.62 ± 0.20 and 1.92 ± 0.15 Å, respectively. Because all structural refinement was conducted with respect to the C-face cell, the degrees of freedom were almost halved compared with those allowed in the previous work on kaolinite : DMSO intercalate (Thompson and Cuff, 1985), thus improving the reliability of the atomic coordinates obtained by this approach. This improvement was reflected in the agreement between the refined coordinates using the two different starting models (BRR- and ZRT-derived). Of the 48 structural parameters released during the SHELX refinement all agreed within 2σ; in fact only three were $>1\sigma$.

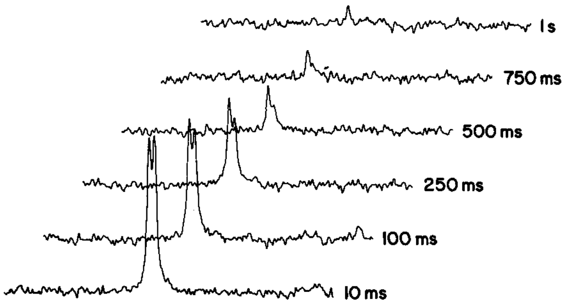

Figure 4. ^{13}C T_1 experiment for the kaolinite : dimethylsulfoxide intercalate using the normal ^{1}H–^{13}C cross-polarization method followed by the $\pi/2$-τ-$\pi/2$ ^{13}C pulse sequence. Relaxation difference can be confidently attributed to different internal rotation rates of methyl groups affecting the efficiency of the ^{13}C–^{1}H dipolar relaxation mechanism.

The resultant R-factors, R_{wp} and R_B (Young and Wiles, 1981), for the parallel refinements were R_{wp} = 11.0% and R_B = 5.2% for the ZRT-derived starting model from 18.0° to 56.0°2θ, excluding the region 23.0° to 26.0°2θ. R_{wp} values were at least 1.0% better than those obtained in attempted refinements in the non-centered cell.

While reworking the kaolinite : DMSO structure in C-face centered $P1$ we observed that exclusion of the intense 02(l), 11(l) band of reflections greatly improved the refinement. The structure was subsequently refined from the 107 reflections included in the powder profile between 26° and 56°2θ. The same starting models and the same methodology as used for the 11.26-Å kaolinite : DMSeO refinement were used for kaolinite : DMSO, except that for kaolinite : DMSO starting bond lengths and bond angles for DMSO were taken from Thomas *et al.* (1966). For the parallel refinements, of the 48 structural parameters released during the SHELX refinement, three $>3\sigma$ and eight $>2\sigma$. R_{wp} and R_B for the ZRT-derived model over the 2θ range mentioned above were 15.0% and 5.6%, respectively.

Inasmuch as no such difficulty with the 02(l), 11(l) region was encountered for the 11.26-Å kaolinite : DMSeO intercalate, two possible explanations are proposed: (1) the 11.26-Å kaolinite : DMSeO intercalate is more completely ordered than the kaolinite : DMSO intercalate; (2) the background in the 02(l), 11(l) region of the 11.26-Å kaolinite : DMSeO intercalate profile is

Table 1. Positional parameters of 11.26-Å kaolinite : dimethylselenoxide (DMSeO) and kaolinite : dimethylsulfoxide (DMSO) intercalates.

	11.26-Å kaolinite : DMSeO				Kaolinite : DMSO		
Si1	0.037	0.653	0.039	Si1	0.024	0.654	0.029
Si2	0.085(14)	0.296(7)	0.042(6)	Si2	0.064(6)	0.310(3)	0.033(2)
Al1	0.534(13)	0.648(7)	0.273(6)	Al1	0.534(5)	0.646(3)	0.272(2)
Al2	0.017(13)	0.834(7)	0.272(6)	Al2	0.014(5)	0.841(3)	0.270(2)
C1	0.355(25)	0.488(13)	−0.201(12)	C1	0.345(11)	0.499(6)	−0.211(5)
C2	−0.153(28)	0.361(16)	−0.397(12)	C2	−0.116(11)	0.361(6)	−0.356(4)
Se	0.068(9)	0.506(5)	−0.354(4)	S	0.093(4)	0.513(2)	−0.357(2)
OSe	0.258(19)	0.485(10)	−0.447(8)	OS	0.250(8)	0.476(4)	−0.446(3)
O1	0.154(18)	0.678(10)	0.189(8)	O1	0.136(7)	0.686(5)	0.176(3)
O2	0.662(15)	0.818(8)	0.183(7)	O2	0.665(7)	0.800(4)	0.174(3)
O3	0.267(17)	0.741(9)	−0.028(7)	O3	0.288(8)	0.730(4)	−0.018(3)
O4	−0.016(17)	0.468(9)	−0.003(8)	O4	−0.019(8)	0.477(5)	0.011(4)
O5	−0.210(16)	0.762(10)	−0.029(7)	O5	−0.231(7)	0.745(5)	−0.016(3)
OH1	0.527(18)	0.490(10)	0.161(8)	OH1	0.574(8)	0.479(5)	0.173(3)
OH2	0.934(17)	0.696(10)	0.369(7)	OH2	0.905(8)	0.689(5)	0.356(3)
OH3	0.410(16)	0.790(9)	0.385(7)	OH3	0.405(6)	0.799(5)	0.371(3)
OH4	0.462(17)	0.484(9)	0.364(8)	OH4	0.459(8)	0.495(5)	0.356(3)

less significant due to the dominant X-ray scattering contribution of Se, compared with that of S. This background is possibly due to nonintercalated, disordered kaolinite, which probably introduced an unrefinable background hump in this region (Plançon and Tchoubar, 1977).

Because of the good agreement between the two parallel refinements in a C-face centered cell for both the 11.26-Å kaolinite : DMSeO and the kaolinite : DMSO intercalate refinements, the atomic coordinates and unit cell parameters of only the ZRT-derived models of each are reported here (Table 1). Standard deviations of the positional parameters of unconstrained atoms from SHELX are presented; bond lengths and angles and interatomic distances of interest are listed for these intercalate structures in Table 3.

Preliminary refinement of the XRD profile of the 11.38-Å kaolinite : DMSeO intercalate gave significantly different unit-cell dimensions for the 11.26-Å intercalate (see Table 2). Subsequent refinement commenced with the refined 11.26-Å structural model translated into the new unit cell. A value of 90.3° for α suggested the existence of two DMSeO sites symmetrically related by the mirror plane *ac* through the center of the molecule. Refinement of the 11.38-Å intercalate profile in a C-face centered cell with these two half-filled DMSeO positions unconstrained decreased R_{wp} from 16.3 to 14.5% over the same range of 2θ used for the 11.26-Å intercalate, the two DMSeO positions retaining their symmetry-related positions. Further improvement in R_{wp} was achieved by releasing the constraint of exactly half occupancy. The fractional occupancies refined to 0.5 and 0.4, the former applying to the orientation of DMSeO observed for the kaolinite : DMSO and 11.26-Å kaolinite : DMSeO intercalates, the latter to its mirror image (see Figure 8). Thus, the small amount of unexpelled water prevented complete ordering of the DMSeO molecules as was achieved in the 11.26-Å intercalate.

The 10.95-Å intercalate lacked the degree of ordering evident from the other intercalate XRD profiles (Figure 1); however, the presence of strong non-basal reflections indicated partial ordering in the *ab* plane. The observed profile fitted the unit cell listed in Table 2. All of the relatively intense reflections were of the type $00l$ or hkl: $h + k = 0$, notably $1\bar{1}0$ and $1\bar{1}2$ at 21.2°, $1\bar{1}\bar{3}$ at 25.9°, and $1\bar{1}3$ at 38.4°2θ, consistent with disorder parallel to [110].

Infrared

The kaolinite : DMSeO intercalates gave IR spectra (Figure 5) showing perturbation of the 3689-cm^{-1} ka-

Table 2. Comparison of unit-cell dimensions and areas $a \times b$ of kaolinite intercalates with kaolinite.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	$a \times b$ (Å)	% increase[1]
Kaolinite[2]	5.153(1)	8.941(1)	7.403(1)	91.692(3)	104.860(3)	89.822(3)	46.07(2)	
Kaolinite : DMSO	5.197(4)	8.960(6)	11.866(7)	91.63(2)	108.74(2)	89.91(2)	46.56(6)	1.1(1)
Kaolinite : DMSeO, 11.26 Å	5.195(2)	8.990(4)	11.946(5)	91.33(2)	109.39(2)	89.77(2)	46.70(4)	1.4(1)
Kaolinite : DMSeO, 11.38 Å	5.188(2)	8.961(4)	11.894(5)	90.27(2)	106.82(2)	90.03(2)	46.49(4)	0.9(1)
Kaolinite : DMSeO, 10.95 Å	5.177(5)	8.968(7)	12.037(9)	90.00	114.52(4)	90.00	46.43(8)	0.8(2)

[1] Percentage increase in area $a \times b$ relative to kaolinite.

[2] Suitch and Young, 1983.

Table 3. Bond lengths (Å) and angles (°) in the kaolinite: dimethylselenoxide (DMSeO) and kaolinite: dimethylsulfoxide (DMSO) intercalates, interatomic distances (Å), and angles (°) of S=O and Se=O with the *ab* plane.

11.26-Å kaolinite: DMSeO		Kaolinite: DMSO	
Se=O	1.72(10)	S=O	1.55(5)
Se–C1	1.95(17)	S–C1	1.81(6)
Se–C2	1.70(17)	S–C2	1.75(6)
O–Se–C1	100(6)	O–S–C1	105(2)
O–Se–C2	102(6)	O–S–C2	109(2)
C1–Se–C2	115(7)	C1–S–C2	100(3)
O···H–O			
O–OH3′	2.80(12)	O–OH3′	2.79(6)
O–OH4	2.80(13)	O–OH4	2.89(7)
O–OH2	3.00(12)	O–OH2	3.15(6)
C1···O <4 Å			
C1–O5′	3.03(16)	C1–O3	3.13(7)
C1–O3	3.17(16)	C1–O5	3.39(7)
C1–O3′	3.32(16)	C1–O5′	3.40(7)
C1–O4	3.35(17)	C1–O4	3.51(8)
C1–O5	3.49(16)	C1–O3′	3.64(7)
C1–O4	3.53(16)	C1–O4	3.71(8)
C2···O <4 Å			
C2–OH3′	2.79(16)	C2–OH3′	3.32(6)
C2–OH4	3.12(17)	C2–OH4′	3.66(6)
C2–OH2′	3.24(16)	C2–OH2′	3.81(6)
Angle of Se=O with *ab* plane 37(6)°		Angle of S=O with *ab* plane 40(2)°	

Table 4. Se=O bond lengths (Å) calculated from frequencies of Se=O stretching bands.

	ν_{SeO} (cm^{-1})	Angle to kaolinite surface (*ab*)	Se=O distance (Å)	Found by XRD (Å)
Kaolinite: DMSeO, 11.38 Å	847 811	34.6°	1.693 1.707	
Kaolinite: DMSeO, 11.26 Å	831.3	38.8°	1.707	1.72(10)
Kaolinite: DMSeO, 10.95 Å	834 827	31.9°	1.704 1.711	
Liquid DMSeO	820		1.717	

The above distances were deduced from a combination of the equations for simple diatomic oscillators and the results of Paetzold (1968, 1970) relating the Se=O force constant to frequency.

olinite band by ~6 cm^{-1} due to the close approach of the Se=O linkage of the DMSeO molecule. The relative intensity of this kaolinite band was reduced because hydrogen bonding displaced many of these OH vibrators to ~3400 cm^{-1}. This tendency was most clearly shown by DMSO in which the H-bond displacement was to two frequencies (having corresponding O...H–O bond lengths (Bellamy and Owen, 1969) based on a "free" OH frequency of 3750 cm^{-1}) of 3536.5 cm^{-1} (2.85 Å) and 3503.7 cm^{-1} (2.83 Å) (cf. 2.89(7) and 2.79(6) Å in Table 3).

Other OH-stretching bands of kaolinite were modified by DMSeO intercalation. For the 10.95- and 11.38-Å kaolinite: DMSeO intercalates the inner-OH kaolinite band at 3621 cm^{-1} gave two bands centered at 3627.5 and 3593.4 cm^{-1}. In contrast, the 11.26-Å intercalate had two adjacent and relatively intense bands at 3623.1 and 3616 cm^{-1}, together with a hydrogen bond frequency centered at 3388 cm^{-1}. The 10.95-Å intercalate probably contained unoccupied ditrigonal cavities, which gave rise to the inner-OH band at 3593.3 cm^{-1}. As can be seen from the IR spectrum of the 11.38-Å intercalate, fewer unoccupied ditrigonal cavities were present as evidenced by the relative intensity of this band. Further, most of the cavities were occupied in the 11.26-Å kaolinite: DMSeO intercalate.

The clay surface stiffened the CH-stretching and -bending vibrations of the DMSeO intercalates, giving them additional (perturbed) frequencies displaced upwards and downwards respectively. The perturbations were caused by dispersion forces resulting from the interaction of carbon atoms of the methyl groups with neighboring dipoles (Raupach, 1986), here located in the surface oxygen atoms or OH groups of the clay. Various interatomic distances may be calculated from these perturbations using polarizabilities, as shown by Raupach (1986). Briefly, the distance *R* between dipoles A and B may be calculated from shifts, $\Delta\nu$, of perturbed frequencies from an underlying unperturbed frequency, ν, and from their polarizabilities, α_A and α_B (Raupach, 1986). For $\alpha = (\alpha_A\alpha_B)^{0.5}$, dipoles in line with *R* give $\Delta\nu/\nu = \alpha/R^3$; those perpendicular to *R* give $\Delta\nu/\nu = \alpha/2R^3$. The results for C···O, Se=O···HO–Al, and S=O···HO–Al distances (Table 5) are in very good agreement with those found by XRD.

Shorter C...O distances correspond to strong perturbation of methyl groups located within the confines of ditrigonal holes. Methyl groups free of the holes but still constrained in the interlayer space are less perturbed (e.g., <10 cm^{-1} shift) by the surface oxygen atoms, but their frequency may shift because of interaction with hydroxyl groups on the opposing interlayer surface. Nonintercalated DMSeO gave frequencies of 3000 and 2915 cm^{-1} for the asymmetric and symmetric CH-stretching vibrations and 1430–1420 cm^{-1} and 1271–1248 cm^{-1} for the bending or deformation vibrations, as found by Paetzold *et al.* (1967) for DMSeO melt. From the data in Table 5 and Figure 6, the CH-stretching and -deformation frequencies and related distances correspond to the various degrees of constraint for the methyl groups, as indicated above. This interpretation of the IR spectra and distances calculated are in accord with the models proposed below.

The above calculations may also be used to make an additional estimate of the length of the hydrogen bond between the oxygen atom of the 11.26-Å inter-

Table 5. Observed infrared bands with calculated and observed interatomic distances.

	Frequency (cm^{-1})			Distance (Å)	
	Perturbed	Unperturbed	Proposed dipole interaction	Calculated from infrared spectroscopy[2]	Found by X-ray powder diffraction
Kaolinite : DMSeO, 11.38 Å	3033	3000[3]	C···O<	3.26	
	1404	1421[4]	C···O<	3.12	
	1394	1421	C···O<	3.41	
Kaolinite : DMSeO, 11.26 Å	3388	3620[4]	Se=O···HO–Al	2.30 + 0.5[1] = 2.80	2.80, 2.80, 3.00
	3041	3000	C1···O<	3.04	3.03
	3026	3000	C1···O<	3.52	3.49, 3.53
	3012	3000	C2···O<	4.59	4.34, 4.60, 4.71
	2946	2915[3]	C1···O<	3.29	3.32, 3.35
	1402	1421	C1···O<	3.07	3.03
	1386	1421	C1···O<	3.15	3.17
Kaolinite : DMSeO, 10.95 Å	3042	3000	C···O<	3.01	
	1408	1421	C···O<	3.47	
Kaolinite : DMSO	3536	3750	S=O···HO–Al	2.39 + 0.5[1] = 2.89	2.89
	3504	3750	S=O···HO–Al	2.28 + 0.5[1] = 2.78	2.79
	3030	2994[5]	C1···O<	3.17	3.13
	3022	2994	C1···O<	3.44	3.39, 3.40
	3018	2994	C1···O<	3.62	3.51, 3.64
	2936	2913[5]	C1···O<	3.64	3.64
	1437	1445[5]	C···O<	4.10	
	1433	1445	C1···O<	3.58	3.51, 3.64
	1428	1445	C1···O<	3.19	3.13
	1408	1414[5]	C···O<	4.48	
	1393	1414	C1···O<	3.72	3.71

[1] Half the OH bond length is taken as 0.5 Å.
[2] Using the following polarizabilities (Å^3): C, 0.7; O, 0.83; OH, 0.728.
[3] From DMSeO (Paetzold *et al.*, 1967).
[4] From the present spectra.
[5] From liquid DMSO (Olejnik *et al.*, 1968).

calate and the hydroxyl groups of the clay. As shown in Table 5, this estimate is 2.80 Å, in good agreement with 2.75 Å estimated from the empirical calculation of Bellamy and Owen (1969) and 2.80(12) estimated from XRD.

For the kaolinite : DMSO intercalate a main band at 3001 cm^{-1} and weak minor bands at 3006 and 3116 cm^{-1} have been reported (Johnston *et al.*, 1984). In the 11.26-Å DMSeO intercalate, a medium asymmetric CH-stretching band at 3012 cm^{-1} was noted, along with two equally intense, strong bands at 3041 and 3026 cm^{-1}; the equivalent symmetric bands were at 2946 and 2920 cm^{-1}. The bands of the first set are regarded as perturbed upwards from 3000 cm^{-1} for DMSeO (Paetzold *et al.*, 1967); calculations based on these perturbations are shown in Table 5. The other unperturbed frequencies in Table 5 were obtained similarly.

The CH-deformation vibrations had small polarization splittings for the 11.38- and 11.26-Å kaolinite : DMSeO intercalates indicating two different Se-C angles and, hence, two environments for the –CH$_3$ groups.

The Se=O stretching band at 820 cm^{-1} in the IR spectrum of DMSeO was perturbed to 831.3 cm^{-1} in the 11.26-Å kaolinite : DMSeO intercalate (see Figure 7). As also shown in Figure 7, this vibration occupied two nearby frequencies at 834 and 827 cm^{-1} for the 10.95-Å intercalate, and at 847 and 811 cm^{-1} for the 11.38-Å intercalate, showing that the Se=O bond lengths were different in the three intercalates.

Combining the expression for the frequency of a simple diatomic oscillator with the force constant vs. bond length relationship for the Se=O bond derived by Paetzold (1968, 1970), this bond length may be estimated for the three intercalates (Table 4). The value of 1.71 Å for the 11.26-Å intercalate agrees with that found by XRD (1.72(10) Å), and the estimated bond lengths for the other two intercalates are in accord with the structural models given below.

Far-IR bands for the O=Se–C deformation vibration were observed at 298, 270, 246, 216, and 207 cm^{-1} in the spectrum of the 11.26-Å intercalate. Untreated kaolinite had bands at 278, 248, and 195 cm^{-1}, the latter two frequencies being poorly resolved.

DISCUSSION

Two previously reported structures of 3-D ordered kaolin-group intercalates, dickite : formamide (Adams

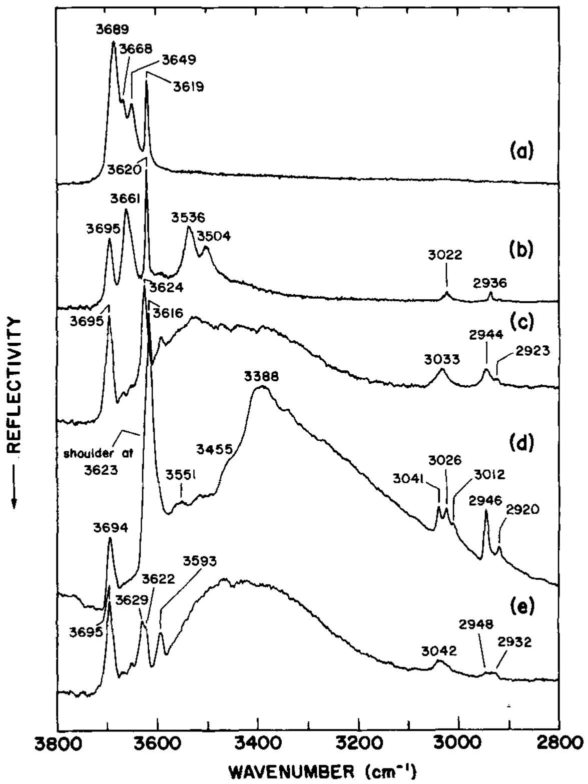

Figure 5. Attenuated total reflectance infrared spectra of (a) well-crystallized kaolinite, (b) kaolinite: dimethylsulfoxide intercalate, and (c) 11.38-Å, (d) 11.26-Å, and (e) 10.95-Å kaolinite: dimethylselenoxide intercalates. Spectra were obtained by lightly pressing powdered samples against the plane face of a KRS-5 optical hemicylindrical element.

and Jefferson, 1976) and dickite: *N*-methylformamide (Adams, 1979), were both refined in the monoclinic space group *Cc*, like the dickite (Newnham and Brindley, 1956) used in the preparation of the two intercalates. The structure of the parent material used in the present study, kaolinite, has usually been reported using a C-face centered triclinic cell (Zvyagin, 1960; Drits and Kashaev, 1960; Brindley and Robinson, 1946; Adams, 1983). Suitch and Young (1983) released the constraint of C-face centering in their X-ray and neutron powder diffraction profile refinement of kaolinite, although this approach was questioned by Thompson and Withers (1987) who suggested from electron diffraction data that the non-hydrogen atoms in kaolinite must be related by C-face centering.

The 11.26-Å kaolinite: DMSeO intercalate structure appears to possess C-face centering for the following reasons: (1) the observation of only one ^{77}Se signal in the CP/MAS NMR spectrum; (2) a single Se=O stretching vibration in the IR spectrum; (3) a single, dominant hydrogen-bonded O–H absorption rather than a spread of frequencies; (4) the improvement in profile refinement of this intercalate when the structure was constrained to be C-face centered; and (5) the parent material, kaolinite, is almost certainly C-face centered.

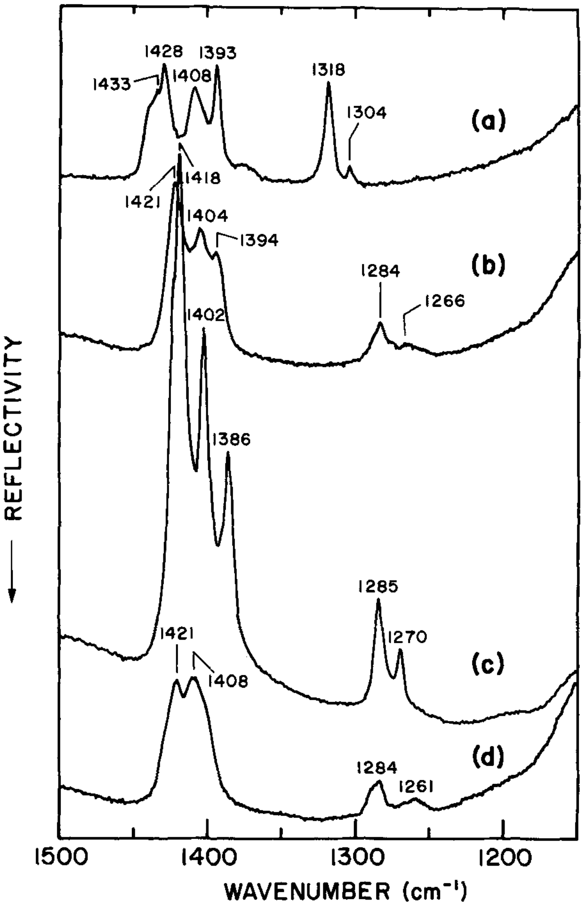

Figure 6. Attenuated total reflectance infrared spectra of (a) kaolinite: dimethylsulfoxide intercalate, and (b) 11.38-Å, (c) 11.26-Å, and (d) 10.95-Å kaolinite: dimethylselenoxide intercalates.

Because of the structural and spectroscopic similarities between the 11.26-Å kaolinite: DMSeO and kaolinite: DMSO intercalates, the structures appear to be analogous. The apparent improvement in the structure refinement of kaolinite: DMSO reported by Thompson and Cuff (1985), obtained when they released the constraint of C-face centering, was probably a result of increasing the number of parameters (cf. Hamilton, 1965). Additionally, the spectroscopic evidence does not preclude C-face centering in the DMSO intercalate.

The structural models for the three kaolinite: DMSeO intercalates prepared in this study are shown in Figure 8. The structural description previously given for the kaolinite: DMSO intercalate (Thompson and Cuff, 1985) applies equally to the 11.26-Å kaolinite: DMSeO intercalate, in which the seleninyl oxygen is triply hydrogen bonded to the inner-surface hydroxyls and one methyl group is keyed into the ditrigonal hole in the

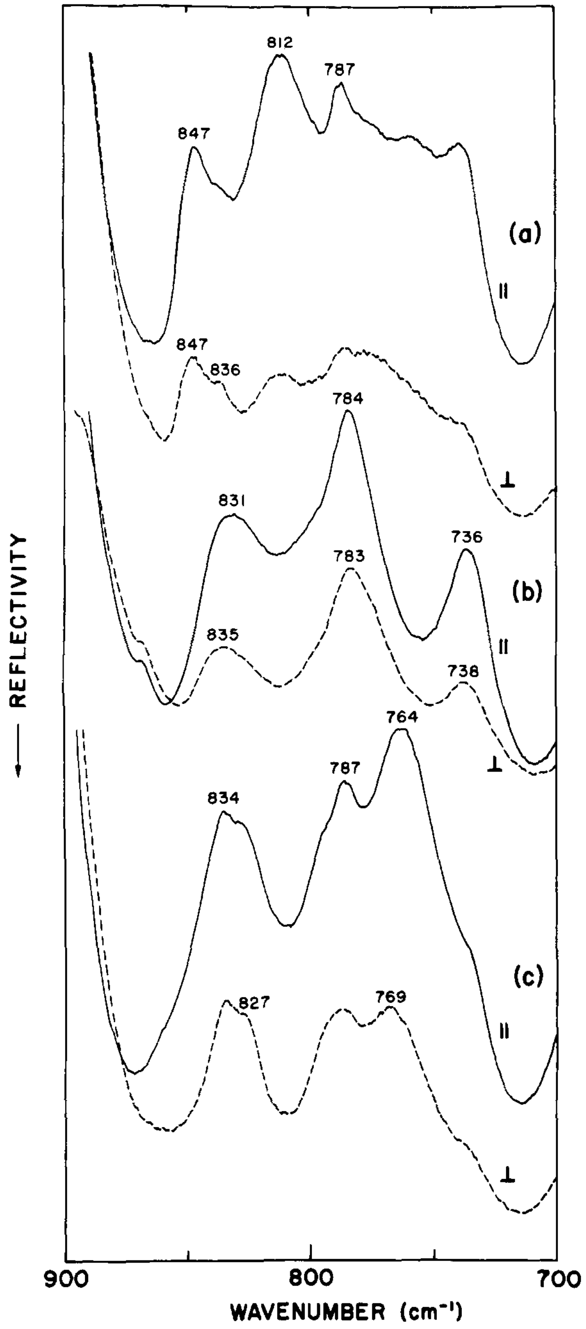

Figure 7. Attenuated total reflectance infrared spectra of (a) 11.38-Å, (b) 11.26-Å, and (c) 10.95-Å kaolinite : dimethylselenoxide intercalates. For each specimen spectra were recorded with a polarizer set both parallel and perpendicular to the plane of incidence of the hemicylindrical element.

silicate sheet above the seleninyl oxygen, as shown in Figure 8. The present results are fully consistent with the orientation of the DMSO molecule given by Thompson and Cuff (1985), a conclusion that is further supported by the IR results for both the DMSO intercalate and its Se analogue.

The structure of the 11.38-Å kaolinite : DMSeO intercalate, from consideration of the XRD and spectroscopic evidence, is closely related to the structure of the 11.26-Å intercalate. The similar ^{77}Se NMR spectra (δ = 788 vs. 785) and the same average ^{13}C chemical shift demonstrate this relationship. In particular, the similarity in the Se environments in these two intercalates is particularly surprising in view of the sensitivity of ^{77}Se to minor changes in magnetic environment, as evident from the large relative chemical shifts of unreacted excess DMSeO, 25–28 ppm downfield, and the 10.95-Å kaolinite : DMSeO intercalate, 27–30 ppm upfield. The increasing relative shielding of the ^{77}Se signal in DMSeO in the following order, aqueous DMSeO (δ = 813), 11.38-Å intercalate (δ = 788), 11.26-Å intercalate (δ = 785), 10.95-Å intercalate (δ = 758), correlates with the increasing distortion of the DMSeO molecule in the respective structural models. The main differences observed for the 11.38-Å intercalate relative to the 11.26-Å intercalate are the multiplicity of DMSeO orientation by the introduction of a mirror image DMSeO site, incomplete occupancy of the ditrigonal cavity, and slightly less distortion of the DMSeO bond angles.

The 10.95-Å intercalate, however, on the basis of the NMR and IR evidence discussed below, has equivalent DMSeO methyl groups in contact with the silicate sheet, but which do not penetrate the ditrigonal cavities. Adjacent cavities cannot be fully occupied because of the space taken by each DMSeO molecule in this orientation; hence, the formula $Al_2Si_2O_5(OH)_4 \cdot [(CH_3)_2SeO]_{\sim 0.5}$. The disorder parallel to [110] can be accounted for by the lack of keying of one of DMSeO methyl groups into the ditrigonal cavities. Assuming that the seleninyl oxygen is triply hydrogen bonded to the octahedral sheet above the octahedral vacancy, as for the other models, and that the DMSeO dipoles tend to align at a low angle to the *ab* plane in the absence of keying as indicated by the IR evidence, translational stacking disorder of n*a* + n*b* ($-1.0 < n < 1.0$) is expected.

In the 11.26-Å kaolinite : DMSeO intercalate, as in kaolinite : DMSO, the two methyl groups are structurally and spectroscopically resolved. The ^{13}C methyl resonances are different by 1.2 ppm for DMSO (Thompson, 1985) and 1.3 ppm for DMSeO, as well as resolved T_1's in each material, suggesting that one methyl group is more sterically hindered than the other. This hindrance is clearly seen from the splittings of the far-IR bands, the different polarizations of the deformation vibrations, and the two symmetric CH_3-bending vibrations at 1386 and 1402 cm^{-1} (see Table 5) in the 11.26-Å intercalate.

The symmetric and asymmetric O=Se–C deformation vibrations, expected at 249 and 283 cm^{-1}, respectively, for DMSeO (Paetzold *et al.*, 1967; Hopf and Paetzold, 1972) were both split into at least two

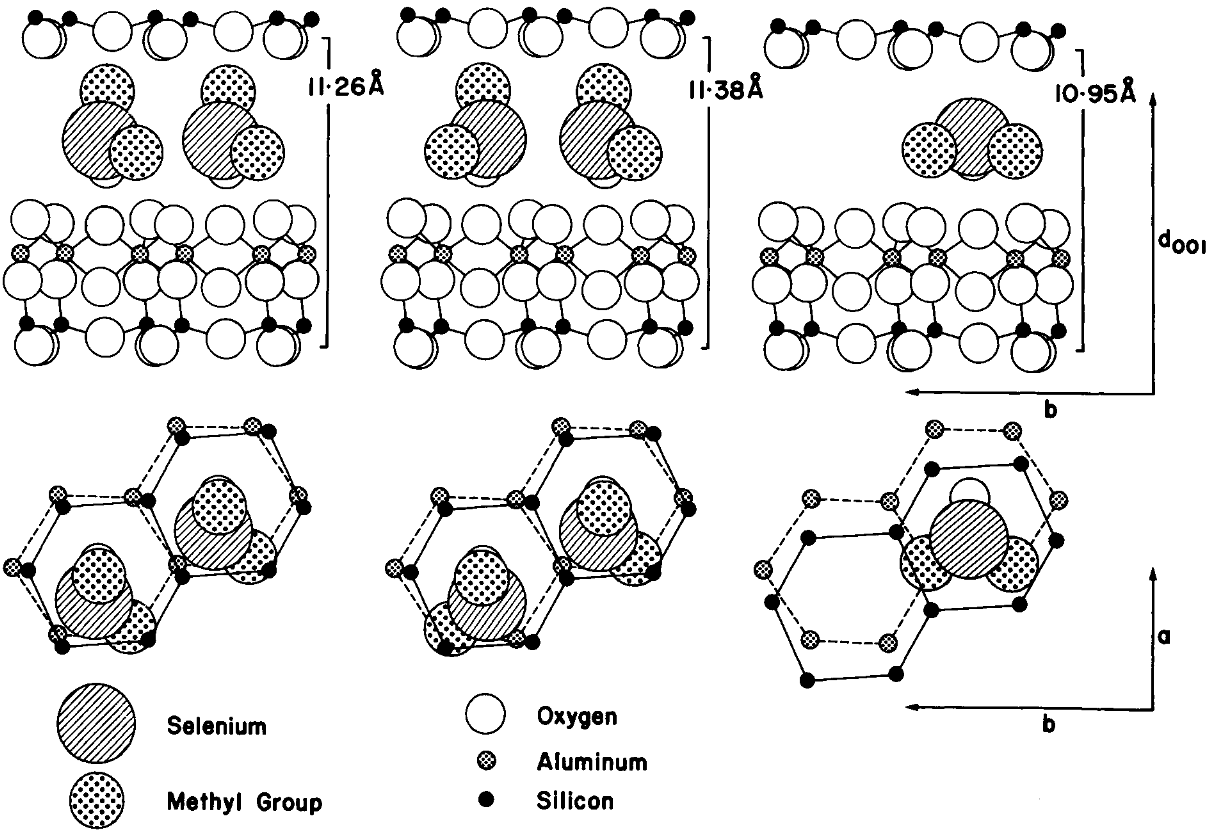

Figure 8. Comparison of the three kaolinite : dimethylselenoxide (DMSeO) intercalate models, projected along [100] (upper) and projected onto (001) with kaolinite oxygens omitted (lower). Selenium and oxygen atoms and methyl groups have been set to half their van der Waals radius. In the 11.38-Å intercalate each intercalant site may be occupied by a DMSeO molecule in either orientation.

bands in the far-IR spectrum of the 11.26-Å intercalate but no split was found for the 10.95-Å intercalate. Furthermore, in the kaolinite : DMSO, 11.26- and 11.38-Å DMSeO intercalates the CH_3-deformation bands were more perturbed and split than in the 10.95-Å intercalate, suggesting that the last of these intercalates contains equivalent methyl groups that do not penetrate the ditrigonal holes, in agreement with the above structural models.

The only previous spectroscopic study that proposed an orientation of the DMSO molecule in the kaolinite : DMSO intercalate based on experimental data (Jacobs and Sterckx, 1970) concluded that the S=O bond was nearly normal to the *ab* plane of the kaolinite. In contrast, our ATR polarized IR results suggested that S=O lies at 40.3° to *ab,* in good agreement with 40(2)° derived from the C-face centered model from XRD profile refinement. The Se analogue, the 11.26-Å DMSeO intercalate, provides similarly convincing agreement between IR (38.8°) and XRD (37(6)°) derived angles for Se=O with *ab.*

The observation of a single, broadened ^{13}C resonance for the 11.38-Å intercalate, although surprising given the model described above, is possibly due to the increase in basal dimension ($\Delta d(001) = 0.12$ Å) over the 11.26-Å intercalate, thereby requiring less penetration of the ditrigonal cavity by methyl groups. The above observation is compatible with the IR results (Table 5, Figure 6) which show less perturbation for these particular CH_3 groups.

The OH-stretching region in the IR spectra of each of the kaolinite : DMSeO intercalates indicated hydrogen bonds of moderate length, centered around a single frequency, 3388 cm^{-1}, in the 11.26-Å intercalate, and over a range of frequencies in the other two complexes, 3520 to 3375 cm^{-1} for the 11.38-Å intercalate, and 3475 to 3375 cm^{-1} for the 10.95-Å intercalate. Based on an unperturbed OH frequency of 3620 cm^{-1} and calculating from polarizabilities, the above frequencies corresponded to hydrogen bond lengths of 2.80 Å for the 11.26-Å intercalate, in agreement with 2.80(12) Å from the XRD profile refinement, 3.55–2.84 Å for the 11.38-Å intercalate, and 3.19–2.76 Å for the 10.95-Å intercalate. The positional multiplicity for DMSeO in the 11.38-Å structural model is consistent with the spread of hydrogen-bonded OH frequencies, compared with the 11.26-Å intercalate where only one dominant hydrogen-bonded OH frequency was observed. In the kaolinite : DMSO intercalate two clearly resolved hydrogen bond lengths of 2.89 and 2.79 Å may be calculated similarly using a free OH frequency of 3750 cm^{-1}; the corresponding lengths from the powder profile refinement reworked in the C-face centered $P1$ space group were 2.89(7) and 2.79(6) Å. The third refined hydrogen-bond length of 3.04 Å corresponds to the small and broader band at 3440 cm^{-1}, which gives 3.01 Å with respect to an unperturbed band at 3620 cm^{-1}, thereby supporting the proposed structural model for the kaolinite : DMSO intercalate.

Comparing the *a* and *b* cell dimensions of kaolinite (Suitch and Young, 1983) with those of the various kaolinite : $(CH_3)_2XO$ intercalates demonstrates that the close packing of the organic molecules between the kaolinite layers must determine the *a* and *b* dimensions of the resultant intercalate unit cell (Table 2). The increase in the area $a \times b$ relative to kaolinite increases in the following order: 10.95-Å kaolinite : DMSeO, 11.38-Å kaolinite : DMSeO, kaolinite : DMSO, 11.26-Å kaolinite : DMSeO. These last two intercalates, both fully occupied, should provide the largest increase, with the DMSeO intercalate area exceeding the DMSO intercalate area by reason of DMSeO being the larger molecule.

This evidence suggests that the 3-D ordering of kaolinite : DMSO and 11.26-Å kaolinite : DMSeO intercalates is driven by the coincidence of the 2-dimensional DMSO and DMSeO arrays, with the array of triply hydrogen bonding sites and ditrigonal cavities provided by the kaolinite. That the former array is of larger dimensions than the latter requires the kaolinite layer to distort somewhat to be commensurate with the close packed molecules, in agreement with the choice of C-face centered $P1$ for these two intercalate structures. Further, the ability of the DMSO and DMSeO molecules to "organize" the kaolinite layers would explain the observation of a 3-D ordered intercalate from apparently disordered halloysite (Costanzo and Giese, 1986).

CONCLUSIONS

This work has helped elucidate the two aspects of the kaolinite : DMSO intercalate which were uncertain, namely, the space group of the intercalate structure and the precise orientation of the DMSO molecule. The structural analogue of the kaolinite : DMSO intercalate, 11.26-Å kaolinite : DMSeO, is concluded to be C-face centered, based on ^{77}Se NMR, IR, and XRD profile-refinement data. Therefore, the kaolinite : DMSO intercalate probably possesses the same symmetry. The XRD profile refinement of the kaolinite : DMSO intercalate, constrained to be C-face centered, is an acceptable result given the uncertainty in atomic positions reported by Thompson and Cuff (1985) for the refinement in the non-centered cell.

The orientation of the DMSO molecule is central to the structural model proposed by Thompson and Cuff (1985). The non-equivalence of the two methyl groups is clearly demonstrated by the ^{13}C NMR data for the DMSO intercalate and its Se (11.26-Å) analogue; it is further supported by IR observations. The molecular orientations of DMSO and DMSeO in these two intercalates, with respect to the basal plane of kaolinite, derived from polarized IR results provide remarkable agreement with the structural models refined in C-face centered $P1$ proposed in this study. For the 11.26-Å kaolinite : DMSeO intercalate the reported standard deviations appear to have been overestimated. Given the different perspective of each of the analytical approaches used in this investigation a great deal of confidence can be attached to the structural models proposed herein.

The formation of two other DMSeO intercalates of kaolinite, 11.38- and 10.95-Å, is surprising in view of the absence of similar intercalates with DMSO. The 11.38-Å intercalate is clearly a result of remnant hole water molecules (Costanzo *et al.*, 1984) initiating 2-fold disorder of the DMSeO molecules between the kaolinite layers and thereby preventing the intercalate from adopting its energetically more favorable 11.26-Å arrangement. Also the presence of Se, the dominant X-ray scatterer in the intercalate, assisted in our being able to resolve the 11.38-Å intercalate as a distinct structure. On the other hand, the 10.95-Å intercalate is unlikely to have a sulfur analogue because the "size" of selenium, by reason of selenium-silicate bonding interaction, must be the controlling factor in forming a comparatively stable intercalate depleted in DMSeO.

The structures of the three DMSeO intercalates suggest that close packing of the intercalating molecules is necessary for 3-D order.

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