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 (*P*l, a = 5.195 (2), b = 8.990(4), c = 11.946(5) Å, α = 91.33(2) °, β = 109.39(2) °, γ = 89.77(2) °). The kaolinite: DMSO intercalate structure was subsequently re-refined from the XRD profile in C-face centered *P*l. 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

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