
Ordered and Disordered Organic Intercalates of 8.4-Å, Synthetically Hydrated Kaolinite

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Abstract: Stable, three-dimensionally ordered complexes were formed from synthetically hydrated, highly ordered kaolinite ($d(001) = 8.4 \text{ \AA}$) and several organic compounds. Removal of the intercalated organic compound by drying or by water washing recovered the 8.4-Å hydrate with its ordered layer stacking essentially unchanged. Some of the complexes were stable for less than a day, whereas others appeared to be stable indefinitely. The compounds that formed ordered complexes were dimethylsulfoxide, formamide, hydrazine-hydrate, 1,1-dimethylhydrazine, ethylene glycol, glycerol, and pyridine. Clay-organic complexes that were prepared from methanol, ethanol, 1- and 2-propanol, acetone, acetic acid, propionic acid, acetaldehyde, N-methylformamide, methylethyl ketone, tetrahydrofuran, and K-acetate were stable only if they were immersed in the intercalating medium and had little or no stacking order.

Many of the organic compounds intercalated by the 8.4-Å hydrate are not known to be intercalated by non-hydrated kaolinite either directly or indirectly. Isolated water molecules appear to be keyed into the ditrigonal holes formed by the basal oxygen of the silicate tetrahedra of the 8.4-Å hydrate. These water molecules, referred to as "hole water," and fluorine ions that had replaced ~20% of the inner-surface hydroxyls of the 8.4-Å phase sufficiently altered the interlayer bonding to allow an expansion of the inner-layer spaces by a variety of guest molecules. The presence of these guest molecules between the clay layers not only changed the basal spacing and perturbed the infrared (IR) bands arising from the inner-surface hydroxyls, it also shifted the position of the IR band arising from the inner hydroxyl.

Key Words: Dimethylsulfoxide • Formamide • Hydrate • Infrared spectroscopy • Intercalate • Kaolinite • N-methylformamide • Ordering

Clays and Clay Minerals; April 1990 v. 38; no. 2; p. 160-170; DOI: [10.1346/CCMN.1990.0380207](https://doi.org/10.1346/CCMN.1990.0380207)

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