
Structural Study of Monomethylammonium and Dimethylammonium-Exchanged Vermiculites

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Abstract: Vermiculite crystals from Santa Olalla, Spain, were first Na exchanged and then intercalated with monomethylammonium ($= \text{NH}_3(\text{CH}_3)^+$, MMA) and dimethylammonium ($= \text{NH}_2(\text{CH}_3)_2^+$, DMA) molecules, respectively, by immersion in 1 M ammonium-chloride solutions at 65°C for 2–3 wk. MMA- and DMA-exchange with vermiculite resulted in crystals with near perfect three-dimensional stacking, suitable for single crystal X-ray diffraction analysis. Unit cell parameters are: $a = 5.353(2) \text{ \AA}$, $b = 9.273(3) \text{ \AA}$, $c = 11.950(6) \text{ \AA}$, and $\beta = 98.45(4)^\circ$ for MMA-exchanged vermiculite and $a = 5.351(2) \text{ \AA}$, $b = 9.268(4) \text{ \AA}$, $c = 12.423(8) \text{ \AA}$, and $\beta = 98.33(5)^\circ$ for DMA-exchanged vermiculite. Refinement results are $R = 0.059$ and $wR = 0.073$ (MMA-exchanged vermiculite) and $R = 0.059$ and $wR = 0.064$ (DMA-exchanged vermiculite). The results are based on structures which show substitutional disorder, and thus the presented models are derived from average structures.

There are two distinct sites for the MMA molecule in MMA-exchanged vermiculite. One crystallographically unique MMA is oriented such that the N-C axis of the molecule is perpendicular to the basal oxygen plane, with the N ion offset from the center of the interlayer by 1.04 \AA . The other MMA is located such that the N ion is at the center of the interlayer between adjacent 2:1 layers, presumably with the N-C axis of the molecule oriented parallel to the basal oxygen plane. This represents the first known occurrence of an organic molecule located exactly between the two adjacent 2:1 layers. Both sites are located between hexagonal cavities of adjacent layers. DMA molecules in DMA-exchanged vermiculite are located such that the N ion is offset from the central plane in the interlayer by 0.95 \AA . A static model is proposed with two orientations of DMA to produce a DMA "zigzag" orientation of molecules parallel to the (001) plane. The plane defined by the C-N-C atoms in the molecule is perpendicular to the (001) plane. An alternate model is more dynamic, and it involves the rotation of DMA molecules about one C-N axis.

Identical starting material was used in previous studies on tetramethylammonium (TMA)-exchanged vermiculite and tetramethylphosphonium (TMP)-exchanged vermiculite. The effect of onium-ion substitutions on the 2:1 layer shows that the tetrahedral rotation angle, α , is significantly smaller for MMA- and DMA-exchanged vermiculite *vs.* TMA and TMP-exchanged vermiculite. Tetrahedral and octahedral bond distances of the 2:1 layer of the TMA, TMP, MMA, and DMA-exchanged structures may be explained by the location of the organic cation relative to the basal oxygen atom plane and by the differences in the geometries of the organic molecule. Thus, the 2:1 layer is affected by the interlayer molecule, and the 2:1 layer is not a rigid substrate, but interacts significantly with the onium ions.

Key Words: Dimethylammonium-Exchanged Vermiculite • Monomethylammonium-Exchanged Vermiculite • Organoclay • Tetramethylammonium-Exchanged Vermiculite • Tetramethylphosphonium-Exchanged Vermiculite • Vermiculite • X-ray Diffraction

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