# Crystal Structure of Tetramethylammonium-Exchanged Vermiculite

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**Abstract:** Vermiculite crystals from Santa Olalla, Spain, were intercalated with tetramethylammonium (TMA) after Na saturation. The resulting TMA-vermiculite showed near perfect 3-dimensional stacking order with cell parameters of $a$ = 5.353 (1) Å, $b$ = 9.273(2) Å, $c$ = 13.616(6) Å, β = 97.68(3) °, and space group $C2/m$, which indicated a *1M* polytype. Single crystal X-ray refinement ($R$ = 0.073, $wR$ = 0.082) located the central atom (N) of the TMA (occupancy at 0.418) and the C atom of 1 methyl group (occupancy at about 0.35). The TMA is offset from the center plane between 2 silicate layers by 1.52 Å, and the methyl group is keyed into the silicate ring of the adjacent silicate layer. This arrangement constrains the positions of the C atoms of the other methyl groups to an opposing plane parallel to the oxygen basal plane. Associated $H_2O$ is randomly located between the TMA pillars, and no scattering from these molecules was observed. The calculated height of the TMA molecule is shown to be 4.15 Å.

Steric and electrostatic arguments suggesting that adjacent TMA molecules must alternate apex directions ($\pm c$) allow for a description of the local TMA arrangement. This model involves the keying of TMA molecules laterally, thereby explaining why perfect 3-dimensional stacking occurs. The offset of TMA from the center of the interlayer region produces a cavity suitable as an adsorption site for small molecules, such as benzene, which is consistent with the higher than expected adsorption of these molecules in TMA-smectites of high layer charge. This offset also explains the easy expandability of TMA-clays, since only very weak interactions occur between TMA and 1 adjacent silicate layer, thereby allowing molecules to enter the interlayer.

**Key Words:** Tetramethylammonium Vermiculite • TMA-Vermiculite • Vermiculite

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