Orthorhombic Jahn-Teller distortion and Si-OH in mozartite, CaMn$^{3+}$O[SiO$_3$OH]: A single-crystal X-ray, FTIR, and structure modeling study

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ABSTRACT

The structure of mozartite, CaMn$^{3+}$O[SiO$_3$OH], was refined in space group $P2_12_12_1$ from X-ray single-crystal data collected at 100 K ($R = 2.45\%$, $R_w = 2.62\%$), 300 K ($R = 2.60\%$, $R_w = 2.68\%$), and 500 K ($R = 2.79\%$, $R_w = 2.81\%$). The Mn$^{3+}$O$_6$ octahedron shows approximately orthorhombic geometry, which is explained by a combination of a tetragonally compressed Jahn-Teller effect with lattice-induced stress. Comparison with isostructural vuagnatite, CaAl(OH)SiO$_4$, which shows no distortions due to electronic effects, indicates that the distorted octahedral geometry in mozartite causes shifts in valence sums of the O atoms that are hydrogen bonded. As a result, the OH group in mozartite is located at the isolated SiO$_4$ apex and is not linked to the octahedron as reported for isostructural minerals. Isostructural minerals of the adelite group with tetrahedral As$^{5+}$ and V$^{5+}$ exhibit a different Jahn-Teller distortion with tetragonally elongated geometry for octahedral Cu$^{2+}$O$_6$.

The O-H...O distance of $<2.5$ Å in mozartite is one of the shortest hydrogen bonded O...O distances in minerals and leads to a diffuse FTIR absorption peak (stretching mode) polarized parallel to $b$ between 1300 and 1700 cm$^{-1}$.

INTRODUCTION

The structure of mozartite, CaMn$^{3+}$O[SiO$_3$OH], was first studied by Basso et al. (1993) using crystals from the Cerchiara mine, Northern Apennines, Italy. Mozartite is isostructural with vuagnatite, CaAl(OH)SiO$_4$ (McNear et al. 1976) and four members of the adelite group: vanadate calciovolborthite, CaCu(OH)VO$_4$ (Basso et al. 1976) and four members of the adelite group: vanadate calciovolborthite, CaCu(OH)VO$_4$ (Basso et al. 1976) and four members of the adelite group: vanadate calciovolborthite, CaCu(OH)VO$_4$ (Basso et al. 1976) and four members of the adelite group: vanadate calciovolborthite, CaCu(OH)VO$_4$ (Basso et al. 1976) and four members of the adelite group: vanadate calciovolborthite, CaCu(OH)VO$_4$ (Basso et al. 1976). These minerals, with the edge-sharing octahedral chains are formed by trivalent cations (Al, Mn$^{3+}$), whereas in the adelite group divalent cations (Cu, Ni, Zn) form the chains. The deficit of positive charges is stoichiometrically balanced by the valence of the tetrahedral cations (As$^{5+}$, V$^{5+}$) in the minerals of the adelite group, whereas tetrahedral Si$^{4+}$ occurs in vuagnatite and mozartite. In the adelite group of minerals, this higher valence state of the tetrahedral cation leads to electrostatically more saturated O atoms forming the tetrahedron and their affinity for protonization becomes negligible. The divalent octahedral cation, on the other hand, yields a formal undersaturation of one of its next O atoms, favoring the formation of an OH group.

Our attention was focused on mozartite when we detected unreasonable valence sums for O atoms coordinating Si and Mn (Basso et al. 1993). The original geometry described by Basso et al. (1993) is characterized by the distances O5-H = 1.05 Å and H...O2 = 1.45 Å. The O5 atom connects two Mn$^{3+}$O$_6$ octahedra and bonds to one Ca atom. Another O atom, O2, is part of a SiO$_4$ tetrahedron and bonds to two Ca atoms. This arrangement, according to the bond valence concept of Brown and Altermatt (1985), results in the following valence sums (excluding H): 1.376 valence units (v.u.) for O2 and 1.878 for O5. This suggests that the OH group is at O2 rather than at O5 as hitherto assumed.

In addition to the proton position, the Jahn-Teller distortion of the Mn$^{3+}$O$_6$ octahedron is discussed in this paper. To elucidate the influence of lattice stress on the orientation of the Jahn-Teller distortion, network calculations were performed. Single-crystal X-ray data were collected at three temperatures (100, 300, and 500 K) to test the temperature dependence of the Jahn-Teller distortion. The short hydrogen bonded O-H...O distance of $<2.50$ Å initiated an IR spectroscopic investigation.