

ORTHORHOMBIC JAHN-TELLER DISTORTION AND SI-OH IN MOZARTITE $\text{CaMn}^{3+}\text{O}[\text{SiO}_3\text{OH}]$ DUE TO TOPOLOGICAL STRESS: A STRUCTURE MODELING, SINGLE CRYSTAL X-RAY, AND IR STUDY

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Mozartite (described by BASSO et al., 1993) is tailor-made to elucidate how lattice stress can cause changes in the electronic properties of atoms. It is isostructural to vuagnatite, $\text{CaAl}(\text{OH})\text{SiO}_4$, (McNEAR et al., 1976) and four members of the adelite group. All these minerals are orthorhombic and consist of a linear chain of edge-sharing octahedra with attached single tetrahedra developed along a two-fold screw axis.

Three sets of single-crystal X-ray data were collected at 100°, 300°, and 500°K. Network calculations (program STRUMO, (BROWN, 1992)), allow a comparison of observed and calculated interatomic distances. Both powder and single-crystal FTIR absorption spectra were recorded.

The Mn^{3+}O_6 octahedron in mozartite shows distorted Mn-O distances but at a first glance it is not obvious whether an elongated or a compressed Jahn-Teller distortion has to be assumed. One diagonal is elongated, one is intermediate, and one is compressed. One could argue that such an unusual distortion is caused by static or dynamic disorder of differently oriented tetragonally compressed or elongated directions. However, such a disorder should lead to substantial electronic »smearing« which is not observed in mozartite, thus ruling out Jahn-Teller disorder. The same trend of elongated and compressed directions as observed in mozartite can also be seen in vuagnatite ($M = \text{Al}$). However, the elongated and compressed directions in vuagnatite are not as pronounced. If we compare the increase of the three O-M-O diagonals from vuagnatite to mozartite, the long and the intermediate diagonal increase in length by 0.22 Å or more whereas the short one increases only by 0.07 Å. It indicates that in mozartite the compressed Jahn-Teller variety is present but distorted due to structural stress. This stress is mainly caused by two interacting reasons, namely cation-cation repulsion and valence sum requirements. This is an example where the orientation of the electronic effect (Jahn-Teller distortion) follows the topologically induced distortion and enhances it. An octahedral geometry with two short, two intermediate, and two long M-O bonds as observed in mozartite is known for several Cu^{2+} compounds. Such orthorhombic distortions may occur as a consequence of the plasticity properties of the Cu^{2+} coordination sphere combined with the stabilization properties of the crystal lattice (HITCHMAN, 1994). Octahedral Mn^{3+} and Cu^{2+} have similar electronic properties, therefore, stable orthorhombic octahedral geometry can also be expected for compounds like mozartite.

The structure of mozartite produces an additional change of the atomic characteristics in comparison to the isostructural minerals; in the original publication (BASSO et al., 1993) we detected unreasonable valence sums for O atoms coordinating Si and Mn. The original geometry is characterized by the distances O5–H = 1.05, and H...O2 = 1.45 Å, O5 connects two Mn³⁺O₆ octahedra and bonds to one Ca and O₂ is part of a SiO₄ tetrahedron and bonds to two Ca. According to the bond valence concept of BROWN & ALTERMATT (1985) this arrangement would result in the following valence sums (excluding H): 1.376 v.u. for O2 and 1.878 v.u. for O5. For this reason the probability that the OH group is at position O2 rather than at O5 is considerably higher, thus forming a Si–OH group. Both the network calculations and the X-ray data confirm this suspicion. Two network calculations were performed, one based on the atomic setting as proposed by BASSO et al. (1993) a second in accord with our results. The calculated and observed interatomic distances are in a closer agreement for the second setting with the H assigned to the SiO₄ tetrahedron. Furthermore, H was located from difference Fourier maps and subsequently refined. The FTIR spectrum shows a broad peak at 1300–1700 cm⁻¹ which agrees with a short O–H...O distance of 2.501 Å (300°K).

- BASSO, R., LUCCHETTI, G., ZEFIRO, L. (1993): Mozartite, CaMn(OH)SiO₄, a new mineral species from the Cerchiara mine, Northern Apennines, Italy. - *Can. Min.*, **31**, 331–336.
- BROWN, I.D. (1992): Chemical and steric constraints in inorganic solids. - *Acta Cryst.*, B **48**, 553–572.
- BROWN, I.D., ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. - *Acta Cryst.*, B **41**, 244–247.
- HITCHMAN, M.J. (1994): The influence of vibronic coupling on the spectroscopic properties and stereochemistry of simple 4- and 6-coordinate copper(II) complexes. - *Comm. Inorg. Chem.*, **15**, 197–254.
- McNEAR, E., VINCENT, M.G., PARTHÉ, E. (1976): The crystal structure of vuagnatite. - *Am. Min.*, **61**, 831–838.