

A neutron diffraction study of boussingaultite, $(\text{NH}_4)_2[\text{Mg}(\text{H}_2\text{O})_6](\text{SO}_4)_2$

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ABSTRACT

The crystal structure and chemical composition of boussingaultite from Pécs-Vasas, Mecsek Mountains, South Hungary, were investigated by single-crystal neutron diffraction (at 20 K) along with a series of chemical analytical techniques [i.e., gravimetric determination of sulfates, EDTA titrimetric determination of magnesium, ion selective electrode for F and Cl, indirect gravimetric determination of ammonium as $(\text{NH}_4, \text{Rb}, \text{Cs}, \text{K})$ tetraphenylborate, inductively coupled plasma atomic emission spectroscopy for REE and other minor elements, elemental analysis for C, N, and H content, high- T mass loss for H_2O content]. The concentrations of more than 50 elements were measured. The experimental formula of the boussingaultite is: $[(\text{NH}_4)_{1.77}\text{K}_{0.22}]_{\Sigma 1.99}[(\text{Mg}_{0.95}\text{Mn}_{0.06})_{\Sigma 1.01}(\text{H}_2\text{O})_{5.7}](\text{SO}_4)_{1.99}$. Neutron data analysis confirms that the structure of boussingaultite is built up by isolated $\text{Mg}(\text{H}_2\text{O})_6$ -octahedra, along with isolated NH_4 - and SO_4 -tetrahedra connected by a complex H-bonds network. Mg^{2+} is completely solvated by H_2O molecules in a typical octahedral bonding configuration. All the seven independent oxygen sites in the structure are involved in H-bonds, as donors or as acceptors. The geometry of all the H_2O molecules, bonded to Mg, is in line with that usually observed in crystalline compounds. The H_2O molecules show moderate-strong H-bonds, with $\text{H}\cdots\text{O}_{\text{acceptor}}$ and $\text{O}_{\text{donor}}\cdots\text{O}_{\text{acceptor}}$ ranging between 1.72–1.87 and 2.70–2.84 Å, respectively, along with $\text{O}_{\text{donor}}\text{-H}\cdots\text{O}_{\text{acceptor}}$ angles between 168–178°. The four independent N-H \cdots O bonds show $\text{H}\cdots\text{O}_{\text{acceptor}}$ and $\text{N}_{\text{donor}}\cdots\text{O}_{\text{acceptor}}$ distances ranging between 1.81–2.00 and 2.84–2.98 Å, respectively, with N-H \cdots O angles between 158–176°. All the H-bonds of the H_2O molecules and of the NH_4 -group involve the oxygen sites of the SO_4 -group as acceptors: the SO_4 -group is, therefore, the “bridging unit” between the NH_4 and the $\text{Mg}(\text{H}_2\text{O})_6$ units, via H-bonds. Our structure refinement proved, unambiguously, that the partial K^+ vs. NH_4^+ replacement generates a local disorder. K lies at the N site, and its bonding configuration can be described by a distorted polyhedron with CN = 8. However, the K^+ vs. NH_4^+ replacement implies a change in the configuration of the SO_4 -tetrahedron, through a sort of rotation of the polyhedron. This is the first evidence of the presence of a partial picromerite component in the boussingaultite structure, which gives rise to a local disorder likely due to the significantly different bonding configurations of the two cations. Our refinement also revealed that Mn^{2+} replaces Mg^{2+} at the Mg site. No evidence of distortion of the octahedron is observed in response to such a replacement, but the fraction of Mn^{2+} is modest. An analysis of previous Raman and IR results is provided, and is compared with the experimental results of this study.

Keywords: Boussingaultite, sulfate, neutron diffraction, crystal chemistry, hydrogen bonding