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A neutron diffraction study of boussingaultite, $(NH_4)_2[Mg(H_2O)_6](SO_4)_2$

G. DIEGO GATTA[1,*], GIORGIO GUASTELLA[2], ALESSANDRO GUASTONI[3], VALENTINA GAGLIARDI[4],
LAURA CAÑADILLAS-DELGADO[5], AND MARIA TERESA FERNANDEZ-DIAZ[5]

[1]Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, I-20133 Milano, Italy
[2]Agenzia delle Accise, Dogane e Monopoli, DTI–Lombardia, Ufficio Antifrode–Sezione Laboratori, Via Marco Bruto 14, I-20138 Milano, Italy
[3]Dipartmento di Geoscienze, Università degli Studi di Padova, Via G. Gradenigo 6, I-35131 Padova, Italy
[4]Istituto Gemmologico Italiano, Piazza San Sepolcro 1, I-20123 Milano, Italy
[5]Institut Laue-Langevin, 71 Avenue des Martyrs, F-38042 Grenoble, France

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 (NH_4,Rb,Cs,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: $[(NH_4)_{1.77}K_{0.22})_{\Sigma 1.99}[(Mg_{0.95}Mn_{0.06})_{\Sigma 1.01}(H_2O)_{5.7}](SO_4)_{1.99}$. Neutron data analysis confirms that the structure of boussingaultite is built up by isolated $Mg(H_2O)_6$-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 $H\cdots O_{acceptor}$ and $O_{donor}\cdots O_{acceptor}$ ranging between 1.72–1.87 and 2.70–2.84 Å, respectively, along with O_{donor}-$H\cdots O_{acceptor}$ angles between 168–178°. The four independent N-H···O bonds show $H\cdots O_{acceptor}$ and $N_{donor}\cdots O_{acceptor}$ distances ranging between 1.81–2.00 and 2.84–2.98 Å, respectively, with N-H···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 $Mg(H_2O)_6$ 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