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Structural features in Tutton's salts $K_2[M^{2+}(H_2O)_6](SO_4)_2$, with M^{2+} = Mg, Fe, Co, Ni, Cu, and Zn

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Abstract

The crystal chemistry of six crystals of general formula $K_2[M^{2+}(H_2O)_6](SO_4)_2$, with M^{2+} = Mg, Fe, Co, Ni, Cu, and Zn, was investigated by single-crystal structure analysis to determine the effects of the chemical variation of M^{2+} on the structural environment surrounding K, *M*, and S sites. Results indicate that the distortion in the SO_4 tetrahedron and the MO_6 octahedron is very small, except for CuO_6 where it is pronounced because of the Jahn-Teller effect. The KO_8-octacoordinate polyhedron has the highest degree of distortion, and its idealized shape may be referred to as a bicapped trigonal prism. The SO_4 size is not affected by changes in cation occupancies at the adjacent *M* site. In contrast, changes in the KO_8 size, which are accompanied by changes in the bond valence sum at K, depend on interaction with the first and second coordination sphere of *M*. This interaction results by changes in *M*-O individual lengths, by expansion of the second coordination sphere of *M*, and by changes in the distribution of the bond strengths over the O atoms coordinated to K. The MO_6 size follows the expected trend from the increased ionic radius at the *M* site. The latter is also correlated with the unit-cell volume except for the Cu- and Mg-phase, which show a larger cell volume with respect to that expected. Although the relevant octahedral distortion around the Cu^{2+} cation explains the volume excess in the Cu-phase, an expansion of the second coordination sphere of Mg^{2+}, compared to those of cations of larger ionic radius (such as Zn and Co), explains the excess of the unit-cell volume in the Mg-phase. As the CuO_6 distortion can be caused by the Jahn-Teller effect, the higher ionicity of the Mg atom could be the cause for its anomalous behavior observed in Tutton's salts. This stereochemical behavior of the Mg atom seems to be consistent with the weakening of the hydrogen bonds in the structure connected to differences in the bonding character of Mg and transition metals when coordinated by water molecules.

Keywords: Crystal synthesis, Tutton's salts, crystal structure, bond valence