

# CRYSTAL STRUCTURE AND RAMAN SPECTRA OF $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{ClO}_4^-)_3 \cdot 3\text{H}_2\text{O}$

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Single crystal X-ray diffraction is used to study the structure of colorless crystals isolated from the saturated aqueous solution of trivalent iron perchlorate (TIP) in 67.5% perchloric acid. It is found that the compound crystallizes in the trigonal crystal symmetry; parameters of the hexagonal unit cell:  $a = b = 16.079(2) \text{ \AA}$ ,  $c = 11.369(2) \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ , space group  $R\bar{3} (S_6)$ ,  $Z = 6$ ,  $\rho_{\text{calc}} = 2.021 \text{ g/cm}^3$ . The structural form of the crystal hydrate is  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{ClO}_4^-)_3 \cdot 3\text{H}_2\text{O}$ . The structure contains two independent complex iron cations. Each of them is in the special position  $\bar{3}$ , but retains the regular octahedral structure: average bond lengths are  $r(\text{Fe}-\text{O}) = 1.997(1) \text{ \AA}$ ,  $\angle \text{O}-\text{Fe}-\text{O}$  bond angles differ from  $90^\circ$  by only  $0.93^\circ$ . Independent  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  cations form short H-bonds ( $\text{O} \dots \text{O} \ 2.64 \text{ \AA}$ ) with three crystallization water molecules and somewhat longer H-bonds ( $\text{O} \dots \text{O} \ 2.73 \text{ \AA}$ ) with three  $\text{ClO}_4^-$  anions. The  $\text{ClO}_4^-$  anion is disordered over two positions with occupancies of 0.62(2) and 0.37(2). Both positions correspond to the general position. The outer-sphere crystallization water molecule is characterized by the tetrahedral direction of H-bonds, which it forms with two anions and two independent  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  cations. All water molecules are in the general position. The Raman spectroscopic study of polycrystalline samples reveals weak bands belonging to the internal vibrations of two types of water molecules. The least broad bands are assigned to the transitions of crystallization water molecules whose symmetry is insignificantly lowered by two anion-molecular H-bonds. Anomalously broad bands are assigned to the transitions of a coordinated water molecule whose symmetry is more lowered by intermolecular and anion-molecular H-bonds.

**Keywords:** iron(III) perchlorate nonahydrate, crystal structure, Raman spectra.