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Studtite, $[(UO_2)(O_2)(H_2O)_2](H_2O)_2$: The first structure of a peroxide mineral

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ABSTRACT

Studtite, $UO_4 \cdot 4H_2O$, and metastudtite, $UO_4 \cdot 2H_2O$, are the only minerals thought to contain peroxide. Determination of the structure of studtite has shown it to contain peroxide, with the structural formula $[(UO_2)(O_2)(H_2O)_2](H_2O)_2$. The structure is monoclinic, space group $C2/c$, $a = 14.068(6)$, $b = 6.721(3)$, $c = 8.428(4)$ Å, $\beta = 123.356(6)°$, $V = 665.6(3)$ Å^3, $Z = 4$. It was refined on the basis of F^2 for 1398 unique reflections collected using Mo$K\alpha$ X-radiation and a CCD-based detector to $R_1 = 3.66\%$, calculated for the 716 unique observed reflections ($|F_o| \geq 4\sigma_F$). The structure of studtite contains one symmetrically distinct U^{6+} cation and four O atoms, two of which occur as H_2O groups. The O-O bond-length in the peroxide group is 1.46(1) Å. The U^{6+} cation occurs as part of a linear $(UO_2)^{2+}$ uranyl ion, and each U^{6+} cation is bonded to six additional O atoms, two of which are H_2O groups, and four of which are O atoms of peroxide groups. The O-O bonds of two peroxide groups constitute two equatorial edges of each distorted uranyl hexagonal bipyramid. Uranyl polyhedra are polymerized into chains extending along [001] by sharing peroxide groups. Chains are linked by H bonds extending to and from an interstitial H_2O group. It is proposed that studtite forms by incorporating peroxide created by alpha-radiolysis of water, and that radiation is necessary for its formation in nature.