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The role of water in the structures of synthetic hallimondite, $Pb_2[(UO_2)(AsO_4)_2](H_2O)_n$ and synthetic parsonsite, $Pb_2[(UO_2)(PO_4)_2](H_2O)_n$, $0 \le n \le 0.5$

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ABSTRACT

The crystal structures of synthetic hallimondite and synthetic parsonsite have been refined by full-matrix least-squares techniques to agreement indices (hallimondite, parsonsite) wR_2 of 5.5, and 7.6% for all data, and $R1$ of 2.7 and 3.4%, calculated for 3391 and 3181 unique observed reflections ($|F_o| \ge 4\sigma_F$), respectively. Hallimondite is triclinic, space group $P\overline{1}$, $Z = 2$, $a = 7.1153(8)$, $b = 10.4780(12)$, $c = 6.8571(8)$ Å, $\alpha = 101.178(3)°$, $\beta = 95.711(3)°$, $\gamma = 86.651(3)°$, $V = 498.64(3)$ Å^3, and is isostructural with parsonsite, triclinic, space group $P\overline{1}$, $Z = 2$, $a = 6.8432(5)$, $b = 10.4105(7)$, $c = 6.6718(4)$ Å, $\alpha = 101.418(1)°$, $\beta = 98.347(2)°$, $\gamma = 86.264(2)°$, $V = 460.64(5)$ Å^3. In both structures, hexavalent uranium occurs as a uranyl pentagonal bipyramid. The uranyl polyhedra share an edge, forming dimers that are linked by edge- and vertex-sharing with arsenate or phosphate tetrahedra to form chains along [001]. Two symmetrically distinct Pb positions connect the chains. In hallimondite, a partially occupied oxygen atom is located in the cavity between the uranyl arsenate chains and Pb positions, and is attributed to an H_2O group. The crystal of synthetic parsonsite investigated does not have appreciable electron density at this position, but its structural cavity is large enough to contain H_2O. The presence of H_2O in synthetic hallimondite, and its absence in synthetic parsonsite, are supported by the results of FTIR spectroscopy. In conjunction with thermogravimetric results from the literature, we suggest that the formula of parsonsite should be considered $Pb_2[(UO_2)(PO_4)_2](H_2O)_n$, and hallimondite, $Pb_2[(UO_2)(AsO_4)_2](H_2O)_n$, with $0 \le n \le 0.5$ in each case.