

CRYSTAL STRUCTURE OF SYNTHETIC HYDROTUNGSTITE, [WO₃(H₂O)](H₂O)

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Hydrotungstite, WO₂(OH)₂(H₂O) or H₂WO₄(H₂O) (PDF 00-016-0166 and 00-018-1420) occurs as an alteration product in the oxidized zone of a hydrothermal tungsten ore deposit at the Calacalani mine in Bolivia, and thin films of hydrotungstite have been used as humidity sensors. It is reported to crystallize in *P2/m* with $a = 7.379(5)$, $b = 6.901(5)$, $c = 3.748(5)$ Å, and $\beta = 90.36(16)^\circ$. The powder pattern of a greenish yellow precipitate from an inductively-coupled plasma (ICP) specimen preparation of a W-containing sample matched that of hydrotungstite well, but the unit cell and powder pattern were more complicated than had been reported. Application of lattice matching techniques to the reported unit cell yielded the chemically-plausible analogue “yellow molybdic acid”, MoO₃(H₂O)₂, which has the ICSD formula type AX5. A further search for Mo-containing compounds having this formula type yielded the mineral sidwellite, MoO₃(H₂O)₂, which crystallizes in *P2₁/n* with $a = 10.487(1)$, $b = 13.850(1)$, $c = 10.617(1)$ Å, and $\beta = 91.62(9)^\circ$, and has been studied using neutron powder diffraction. The sidwellite cell is an 8× supercell of the reported hydrotungstite cell, and the sidwellite structure served as a good initial model for a Rietveld refinement of the hydrotungstite structure. The hydrogen positions were determined by a quantum chemical geometry optimization, which permitted analysis of the hydrogen bonding pattern. The structure consists of corner-sharing layers of tilted WO₆ octahedra in the *ac* plane. Pointing into the interlayer region *trans* to each tungsten atom are a coordinated water molecule and a W=O group. The interlayer region is occupied by water molecules, which are hydrogen bonded to the layers. Hydrotungstite is properly formulated [WO₃(H₂O)](H₂O). The structure of the mineral tungstite, WO₃(H₂O), has been reported, but the topologies of the layers in sidwellite and tungstite differ. A combination of quantum calculations and Rietveld refinement was used to determine the best model for the topology of the hydrotungstite layer. The quantum calculations help establish the relative energies of hydrotungstite and tungstite.