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A new complex sheet of uranyl polyhedra in the structure of wölsendorfite

PETER C. BURNS*

Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana 46556-0767, U.S.A.

ABSTRACT

The structure of wölsendorfite, $Pb_{6.16}Ba_{0.36}[(UO_2)_{14}O_{19}(OH)_4](H_2O)_{12}$, $Z = 8$, orthorhombic, $a = 14.131(1)$, $b = 13.885(1)$, $c = 55.969(4)$ Å, $V = 10{,}982$ Å^3, space group *Cmcm*, was solved by direct methods and refined by full-matrix least-squares techniques to an agreement factor (R) of 6.4% and a goodness-of-fit (S) of 1.13 using 6215 unique observed reflections ($|F_o| \geq 4\sigma_F$) collected with Mo$K\alpha$ X-radiation and a CCD (charge-coupled device) detector. The structure contains eight unique U^{6+} positions, each of which is part of a nearly linear $(UO_2)^{2+}$ uranyl ion. The uranyl ions (Ur) are further coordinated by four or five anions (ϕ) arranged at the equatorial corners of square and pentagonal bipyramids, respectively. The structure contains two unique Urϕ_4 square bipyramids and six unique Urϕ_5 pentagonal bipyramids that link by the sharing of equatorial corners and edges to form infinite sheets that are parallel to (100). The sheets have a primitive repeat distance of $c = 55.969$ Å, and are by far the most complex sheet of uranyl polyhedra yet observed. The interlayer between the uranyl sheets contains Pb^{2+} and Ba cations, as well as H_2O groups that are either bonded to the interlayer cations or are held in the structure by H bonding only. There are eight unique cation positions in the interlayer that are coordinated by six to ten anions.

The structure of wölsendorfite is remarkable both in the complexity of the sheets of uranyl polyhedra and the connectivity of the interlayer. By using the sheet anion-topology approach, it is shown that the wölsendorfite sheet is composed of slabs of the simpler α-U_3O_8 and β-U_3O_8-type sheets. It is possible that many as yet unknown complex sheets of uranyl polyhedra exist that are based upon anion topologies that are combinations of slabs of simpler topologies, but it is currently not possible to distinguish which of these may be energetically favorable.