The role of water in the structures of synthetic hallimondite, Pb$_2$[(UO$_2$)(AsO$_4$)$_2$](H$_2$O)$_n$ and synthetic parsonsite, Pb$_2$[(UO$_2$)(PO$_4$)$_2$](H$_2$O)$_n$, 0 ≤ $n$ ≤ 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 (I$F$) ≥ 4σ(I), respectively. Hallimondite is triclinic, space group P$ar{T}$, Z = 2, a = 7.1153(8), b = 10.4780(12), c = 6.8571(8) Å, α = 101.178(3), β = 95.711(3), γ = 86.651(3)°, V = 498.64(3) Å$^3$, and is isostructural with parsonsite, triclinic, space group P$ar{T}$, Z = 2, a = 6.8432(5), b = 10.4105(7), c = 6.6718(4) Å, α = 101.418(1), β = 98.347(2), γ = 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$_2$O 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$_2$O. The presence of H$_2$O in synthetic hallimondite, and its absence in synthetic parsonsite, is 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$_2$O)$_n$, and hallimondite, Pb$_2$[(UO$_2$)(AsO$_4$)$_2$](H$_2$O)$_n$, with 0 ≤ $n$ ≤ 0.5 in each case.

INTRODUCTION

The crystal chemistry of hexavalent uranium has attracted considerable attention in recent years (Burns et al. 1996, 1997; Burns 1999; King 2002). Four major structural classes of inorganic uranyl phosphates and uranyl arsenates have been recognized: (1) structures containing the autunite-type sheet (autunite and meta-autunite groups), (2) structures containing the phosphuranylite-type sheet (phosphuranylite group), (3) structures containing the uranophane sheet-anion topology, and (4) chain structures. Sheets of polyhedra dominate the structures of uranyl phosphates and arsenates. The autunite sheet involves the sharing of vertices between uranyl square bipyramids and phosphate or arsenate tetrahedra. The phosphuranylite sheet contains uranyl pentagonal bipyramids that share edges to form pentagonal and hexagonal bipyramids that share edges to form uranyl arsenate tetrahedra. The phosphuranylite sheet involves the sharing of vertices between uranyl square bipyramids and phosphate or arsenate tetrahedra. The phosphuranylite sheet contains uranyl pentagonal and hexagonal bipyramids that share edges to form chains that are cross-linked by sharing vertices and edges with phosphate or arsenate tetrahedra. In some cases, sheets in minerals of the phosphuranylite group are linked by bonds to U$^{6+}$ in the interlayer, resulting in framework structures. The uranophane-type sheet that involves chains of edge-sharing uranyl pentagonal bipyramids linked by sharing edges and vertices with tetrahedra has been found in only a few inorganic uranyl phosphates and uranyl arsenates, and in uranyl phosphate or arsenate minerals is only represented by ulrichite, Cu[Ca(H$_2$O)$_2$(UO$_2$)(PO$_4$)$_2$](H$_2$O)$_4$ (Kolitsch and Giester 2001), and the mixed arsenate-arsenite seelite, Mg(UO$_2$)$_2$(AsO$_4$)$_4$,(AsO$_4$)$_6$(H$_2$O)$_7$ (Piret and Piret-Meunier 1994).

Chain structures are relatively uncommon in uranyl phosphate or arsenate minerals, and occur only in walpurgite, (UO$_2$)Bi$_4$O$_6$(AsO$_4$)$_2$(H$_2$O)$_2$ (Mereiter 1982), orthowalpurgite, (UO$_2$)Bi$_4$O$_6$(AsO$_4$)$_2$(H$_2$O)$_2$ (Krause et al. 1995), and parsonsite, Pb$_2$[(UO$_2$)(PO$_4$)$_2$] (Burns 2000). The structures of the phosphate analogue of walpurgite, IMA2001-062, (UO$_2$)Bi$_4$O$_6$(PO$_4$)$_2$(H$_2$O)$_2$, and of the arsenate analogue of parsonsite, hallimondite, Pb$_2$[(UO$_2$)(AsO$_4$)$_2$] (Walenta 1965) have not been reported previously. As part of our ongoing research into the structures of uranyl phosphates and arsenates, we have synthesized hallimondite and parsonsite, and herein present the structure of hallimondite and a new refinement of parsonsite.

PREVIOUS WORK

Hallimondite was first mentioned by Walenta and Wimmenauer (1961) as a new lead uranyl arsenate hydrate. Walenta (1965) provided a formal description of hallimondite using material from the type locality of the Michael mine, near Reichenbach, east of Lahr in the Black Forest, Baden-Württemberg, Federal Republic of Germany. He reported morphologic data, physical and optical properties, synthesis methods, the formula Pb$_2$[(UO$_2$)(AsO$_4$)$_2$], and the following crystallographic data: triclinic, space group P$ar{T}$, α = 7.123(11), β = 10.469(16), γ = 6.844(10) Å, α = 100.57(17)°, β = 94.80(17)°, γ = 91.27(17)°, V = 499.6 Å$^3$, Z = 2, $D_{\text{calc}}$ = 6.39 g/cm$^3$, $D_{\text{calc}}$ = 6.40 g/cm$^3$. In addition to the Reichenbach locality, hallimondite has been found in uranium mineralization at Buehlskopf, near Ellweiler, Federal Republic of Germany (Büttlemann 1970).

The unit-cell dimensions of hallimondite are larger than those