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The crystal structure of philolithite, a trellis-like open framework based on cubic closest-packing of anions

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ABSTRACT

The crystal structure of philolithite, $Pb_{12}O_6Mn(Mg,Mn)_2(Mn,Mg)_4(SO_4)(CO_3)_4Cl_4(OH)_{12}$, $P4_2/nnm$, a = 12.627(9), c = 12.595(9) Å, V = 2008(2) Å^3, Z = 2 has been solved by Patterson difference-Fourier syntheses and refined to R = 0.053 for 814 $F_o > 4\sigma_{Fo}$ using Mo$K\alpha$ X-ray data. In the structure, MnO_6 octahedra form straight chains parallel to [110] and [1$\bar{1}$0] by sharing opposite octahedral edges. Octahedra within the chains are further linked by sharing free corners with MnO_4 and SO_4 tetrahedra and CO_3 triangles. The MnO_4 and SO_4 tetrahedra also form bridging struts between octahedral chains, connecting them in the [001] direction into an open framework. The Pb, Cl, and non-framework O atoms occupy the open spaces within the framework. The 10- and 12-fold coordinations of the Pb atoms exhibit the lone-pair effect. Pb atoms link via short bonds to non-framework O atoms to form chains parallel to [110] and [$\bar{1}$10]. When viewed down [111], [$\bar{1}\bar{1}$1], [1$\bar{1}\bar{1}$], or [$\bar{1}$1$\bar{1}$], the framework (less the CO_3 groups) is seen to be based upon cubic closest-packing of anions. This open framework of composition $[^{[6]}(Mn,Mg)_{12}^{2+}{}^{[4]}(SO_4)_2^{2-}{}^{[4]}(Mn^{2+}O_4)_2^{6-}O_8(OH)_{24}]^{32-}$, referred to as a closest-packed trellis, is the fundamental unit for the structure.