The crystal structure of köttigite

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Abstract

Köttigite, (Zn_{2.04}Co_{0.42}Ni_{0.14})(AsO_{4})_{2}·8H_{2}O, from the type locality (Schneeberg, East Germany) crystallizes in space group C2/m with \(a = 10.241(3)\), \(b = 13.405(3)\), \(c = 4.757(2)\)Å, \(\beta = 105.21(2)^\circ\), and \(Z = 2\). Isotypy with vivianite is confirmed: the hydrogen atoms have been located and the crystal structure refined using 812 Zr-filtered MoKα data to an \(R\) value of 0.054 (\(R_w = 0.057\)). The transition metals are randomly distributed over insular single and double (edge-sharing) octahedral groups of O atoms and H₂O molecules connected by \(\delta\)O₄ tetrahedra to form complex slabs parallel to (010). These sheets are held together by hydrogen bonding alone, thereby accounting for the perfect (010) cleavage of the mineral. Shortening of the shared edge relative to the unshared edges within the octahedral dimer (0.139Å) is well within the rather wide range of values observed in other Zn compounds containing shared octahedral edges.

Introduction

The mineral köttigite, ideally Zn₆(AsO₄)₂·8H₂O, has long been recognized as a member of the vivianite group of minerals with the general formula M₆(TO₄)₂·8H₂O. The monoclinic members of this family include the phosphates vivianite (\(M = Fe\), bobberite (Mg), and barićite (Mg,Fe)), and the arsenates köttigite, parasymplesite (Fe), hoernesite (Mg), annabergite (Ni), and erythrite (Co). In addition, both vivianite and parasymplesite have been observed in a closely-related triclinic modification as the minerals metavivianite and symplecite (Ritz et al., 1974).

The topology of the monoclinic structure type was shown by Mori and Ito (1950) to consist of octahedral edge-sharing dimers, \(M_2O_6(H_2O)_4\), and insular octahedra, \(MO_2(H_2O)_4\), linked by \(TO_4\) tetrahedra into complex sheets parallel to (010). However, the atomic coordinates were not refined, and the details of this interesting structure remain in doubt. The structure of the triclinic dimorph is still unknown.

The structural analysis of köttigite was initiated as part of a continuing study of Zn stereochemistry and, in particular, of the characteristics of Zn octahedron shared-edge shortening. Material from the type locality in Schneeberg, East Germany, was kindly made available for study by B. D. Sturman of the Royal Ontario Museum (ROM specimen number M15537).

Experimental

The crystal selected for data collection was a pale red transparent platelet displaying well-developed (010) faces, and having the dimensions 0.098 × 0.093 × 0.037 mm. Detailed morphological, optical, chemical and X-ray data for the material have been reported by Sturman (1976); the chemical composition determined in that study has been included in the abstract. The crystal was oriented with the \(c^*\) axis slightly displaced from the \(\phi\) axis of a Picker FACS I four-circle diffractometer. Unit-cell parameters were refined by least-squares methods to give the best fit between calculated and observed angles \(2\theta, \chi, \phi\), measured at 25±2°C with MoKα radiation (\(\lambda = 0.70926\)Å), for 30 automatically centered reflections in the range \(2\theta = 30–45^\circ\). The resultant cell dimensions \(a = 10.241(3)\), \(b = 13.405(3)\), \(c = 4.757(2)\)Å, \(\beta = 105.21(2)^\circ\) [unit-cell volume = 630.2(2)Å³] agree well with values reported by Sturman (1976).

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\(^{2}\) Note that monoclinic Fe₅(AsO₄)₂·8H₂O is (incorrectly) referred to as symplecite rather than parasymplesite by Mori and Ito (1950).

\(^{3}\) E.s.d.'s, given in parentheses, refer to the last decimal place.