The crystal structure of paulmooreite, Pb₂[As₂O₅]: dimeric arsenite groups

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Abstract

Paulmooreite, Pb₂[As₂O₅], was studied in detail by three-dimensional X-ray diffractometry on a Picker four-circle goniostat using MoKα radiation. The new mineral is monoclinic, space group P2₁, or P2₁/m including exceedingly weak reflections but refined in P2₁/a, Z = 4, a = 13.584(4), b = 5.650(2), c = 8.551(3)Å, β = 108.78(2)°. R = 0.064 (Rw = 0.057) for 2709 independent reflections. The structure was solved by Patterson, Fourier and least-squares refinement techniques.

The structure is based on [As₂O₅]₄⁻ corner-linked dimers which link to distorted Pb-O polyhedra, leading to the weakest links across [001], the plane of perfect cleavage. For Pb³⁺As₂O₅, bond distance averages are As(1)-O = 1.774, As(2)-O = 1.782, Pb(1)-O = 2.380, and Pb(2)-O = 2.436Å. The [As₂O₅]₄⁻ groups are trigonal pyramids, and PbO₄ groups are distorted tetragonal pyramids. For bonds < 3.8Å, distorted Pb(O)O₄ and Pb(2)O₄ polyhedra occur. Due to lone-pair electrons about the cations, the coordination polyhedra are "one-sided," the electron pairs presumably residing around the empty vertices.

Introduction

About a decade ago, an unknown mineral from Längban, Sweden was investigated in a cursory fashion and subsequently reported as likely being a new species, corresponding to Flink unknown 49 (Moore et al., 1971). Later study revealed the mineral to be the same as Flink unknown 305. A more detailed examination led to an electron microprobe study which revealed only lead and arsenic in the atomic ratio 1:1. Owing to the extreme rarity of the mineral we despaired of obtaining a more detailed wet-chemical analysis, especially for water and elements with atomic number less than 9, so we undertook a formal three-dimensional crystal structure analysis. Shortly after the structure was solved, the species was announced as the new mineral paulmooreite, Pb₂As₂O₅, by Dunn et al., 1979. These authors also noted its occurrence on Flink unknown 305, a specimen from which our crystal was taken for structure analysis (Riksmuseet Stockholm No. 252356) before it was submitted to their study and recatalogued (NMNH # 142974). Thus, by a remarkable coincidence, the new species and the structure were determined independently almost simultaneously.

Experimental section

Single crystals of the type specimen were examined and a suitable fragment was ground into an ellipsoid which measured 0.059 x 0.13 x 0.10 mm along its principal axes. Least-squares refinement employing 20 high-angle MoKα, reflections from a Picker four-circle goniostat with a Kevex Si-Li solid-state detector led to determination of the cell parameters a = 13.584(4), b = 5.650(2) and c = 8.551(3)Å, β = 108.78(2)°.

Three-dimensional data were collected with unfiltered MoKα radiation, MoKβ being eliminated by a 400V wide pulse-height analyzer window. Reflections were step-scanned in increments of 0.02° in 2θ over a range of 2θ = (3.3 x 114.6 Δλ/λ)°. Each step was counted for one second, and background was counted on each side of a reflection for fifteen seconds. The variance whose reciprocal was used in least-squares adjustment of structure parameters was...