The crystal structure of paulmooreite, Pb$_2$[As$_2$O$_5$]: dimeric arsenite groups

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Abstract

Paulmooreite, Pb$_2$[As$_2$O$_5$], 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 $P2_1$, or $P2_1/m$ including exceedingly weak reflections but refined in $P2_1/α$, $Z = 4$, $a = 13.584(4)$, $b = 5.650(2)$, $c = 8.551(3)$ Å, $β = 108.78(2)^°$, $R = 0.064$ ($R_w = 0.057$) for 2709 independent reflections. The structure was solved by Patterson, Fourier and least-squares refinement techniques.

The structure is based on [As$_2$O$_5$]$^{4-}$ corner-linked dimers which link to distorted Pb–O polyhedra, leading to the weakest links across [001], the plane of perfect cleavage. For [As$_2$O$_5$]$^{4-}$, bond distance averages are As(1)–O = 1.774, As(2)–O = 1.782, Pb(1)–O = 2.380, and Pb(2)–O = 2.436 Å. The [As$_2$O$_5$]$^{4-}$ groups are trigonal pyramids, and PbO$_4$ groups are distorted tetragonal pyramids. For bonds < 3.8 Å, distorted Pb(1)O$_5$ and Pb(2)O$_5$ 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 Långban, 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, Pb$_2$As$_2$O$_5$, 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 × 0.13 × 0.10 mm along its principal axes. Least-squares refinement employing 20 high-angle MoKα reflections from a Picker four-circle goniostat with a Kevek 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 filtered MoKα radiation, MoKβ being eliminated by a 400 V wide pulse-height analyzer window. Reflections were step-scanned in increments of 0.02° in $2θ$ over a range of $2θ = (3.3 × 114.6$ $\Deltaλ/λ)^°$. Each step was collected 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
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