MITT.ÖSTERR.MINER.GES. 146 (2001)

STRONG PSEUDOSYMMETRY IN THE CRYSTAL STRUCTURE OF ANTHROPOGENIC $Pb_2(OH)_3(NO_3)$ FROM A MEDIEVAL MINE DUMP

by

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Recently, an anthropogenic occurrence of the well-known synthetic basic lead nitrate $Pb_2(OH)_3(NO_3)$ was briefly described from the Altemannfels dump of the medieval Pb-Zn-Ag mining district Badenweiler, Black Forest, Germany [1]. The ruler-shaped colourless crystals have formed by anthropogenic processes, probably involving black gunpowder used in the blasting of ore. $Pb_2(OH)_3(NO_3)$ is associated with elyite, $Pb_4Cu(SO_4)O_2.(OH)_4.H_2O$, hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, and, rarely, another anthropogenic lead nitrate with formula $Pb_{13}O_8(OH)_6(NO_3)_4$ (rhombohedral, space group $R\bar{3}$, a = 10.263(1), c = 25.454(5) Å); its recently solved crystal structure contains a unique $[Pb_{13}O_8(OH)_6]^{4+}$ cluster characterised by a near-icosahedral arrangement of two Pb atoms around a third Pb atom at the centre of the cluster [2, 3].

The previously unknown crystal structure of $Pb_2(OH)_3(NO_3)$ was determined from single-crystal X-ray intensity data (CCD detector, MoKα radiation). The compound is metrically orthorhombic, with a = 8.31, b = 8.55, c = 17.19 Å, but is strongly pseudosymmetric (pseudo-space group *Immm*). The true space group is P1, with a = 8.314(2), b = 8.545(2), c = 10.467(2) Å, α = 114.08(3), β = 113.40(3), γ = 90.00(3)°, V = 611.3(2) Å^3 and Z = 4 (R1 = 3.95 % for 4759 'observed' reflections).

The dominant structure element is a cuboid $[Pb_8(OH)_{12}]^{4+}$ cluster previously unknown from inorganic lead compounds. The cluster can be described as eight Pb atoms at the corners of a 'cube', with kinked Pb–OH–Pb bonds representing the cube edges. Strong to weak hydrogen bonds within the cluster provide an internal stabilisation. The clusters are arranged in a plane parallel to (001) to form Pb–OH 'layers', which are separated by layers composed of fairly distorted NO_3 groups. Connection between the $[Pb_8(OH)_{12}]^{4+}$ clusters is achieved by weak hydrogen bonds within the Pb–OH 'layer'. Linkage to the NO_3 groups is achieved by very weak Pb–$O_{nitrate}$ bonds. All Pb atoms exhibit stereochemical activity of their $6s^2$ lone electron pairs. The distinct pseudosymmetry results from the orthorhombic arrangement of the Pb atoms. Reported data on $[Pb_x^{2+}(O,OH)_y]^{n+}$ clusters and basic lead nitrates are summarised and critically discussed. The probable conditions of formation of $Pb_2(OH)_3(NO_3)$ and $Pb_{13}O_8(OH)_6(NO_3)_4$ are evaluated, and Raman spectroscopic data for both compounds are reported.

Hans-Werner Graf of Niederzier-Ellen, Germany, is thanked for kindly furnishing the studied samples. The financial support of the Deutsche Forschungsgemeinschaft (DFG) via a Research Fellowship to the author is gratefully acknowledged.

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