

The crystal structure of anthropogenic $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, and a review of Pb-(O,OH) clusters and lead nitrates

U. KOLITSCH* AND E. TILLMANN

Institut für Mineralogie und Kristallographie, Universität Wien, Geozentrum, Althanstr. 14, A-1090 Wien, Austria

ABSTRACT

The previously unknown crystal structure of the basic lead nitrate $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ has been determined using single-crystal X-ray diffraction data (Mo-K α radiation, CCD area detector). The compound is orthorhombic, space group *Immm*, with $a = 8.314(2)$, $b = 8.545(2)$, $c = 17.210(3)$ Å ($R1 = 2.78\%$ for 940 ‘observed’ reflections with $F_o > 4\sigma(F_o)$). The layered structure contains a previously unknown cuboid $[\text{Pb}_8(\text{OH})_{12}]^{4+}$ cluster and NO_3 groups. The study used crystals formed by anthropogenic processes on a medieval mine dump, probably involving black gunpowder used in the blasting of ore. $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ is associated with a second nitrate, $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$, which was previously designated as “ $\text{Pb}_6\text{O}_3(\text{OH})_4(\text{NO}_3)_2$ ” or “ $\text{Pb}_3(\text{OH})_5(\text{NO}_3)$ ”. It is rhombohedral, space group $R\bar{3}$, with $a = 10.263(1)$, $c = 25.454(5)$ Å, and a structure solution is in complete agreement with an independent single-crystal study by Li *et al.* (2001). Probable hydrogen bonds in $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ are indicated. Reported data on $[\text{Pb}_x^+(\text{O,OH})_y]^{n+}$ clusters and lead hydroxide and oxide nitrates are summarized and discussed critically. The probable conditions of formation of the studied samples are evaluated.

KEYWORDS: $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, lead nitrates, crystal structure, cluster, review.

Introduction

RECENTLY, crystals of two Pb-rich basic lead nitrates, $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ (elongated tabular habit) and $\text{Pb}_6\text{O}_3(\text{NO}_3)_2(\text{OH})_4$ (pseudocubic to pseudocuboctahedral habit), were described briefly by Walenta (1998) from the Altemannfels dump of the medieval Pb-Zn-Ag mining district Badenweiler, Black Forest, Germany (Schloman and Steen, 1990). The identification of the crystals was based on X-ray powder patterns and microchemical spot test analyses which agreed with published data for $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ (Kwestroo *et al.*, 1967 and ICDD 22-661) and $\text{Pb}_6\text{O}_3(\text{NO}_3)_2(\text{OH})_4$ (ICDD 23-1558, unindexed). The overall appearance of the matrix of the specimens carrying these crystals strongly suggested that (post?)-medieval fire-setting methods of ore extraction had subjected the ore-bearing matrix to elevated

temperatures (Walenta, 1998; *cf.* also Wittern, 1994; Kolitsch, 1997). Several other oxide, carbonate and sulphate minerals occurring at the Altemannfels locality are known to have formed either directly by these processes or in their aftermath, e.g. elyite, hydrocerussite, shannonite, litharge, massicot, minium, tenorite and possibly lanarkite and chenite (Schloman and Steen, 1990). The origin of the two Pb nitrates was considered anthropogenic by Walenta (1998); he suggested that either black gunpowder (i.e. a nitrate explosive) or a nitrate fertilizer would be the most probable nitrogen source.

The pseudocubic lead nitrate compound has also been described as an unidentified compound from fire-setting assemblages in dump material of an old Pb-Zn mine at Bleialf, Eifel area, Germany (Graf, 1991) and of the Pb-Zn mine Churfürst Ernst near Bönkhausen, Sauerland, Germany (H.-W. Graf, pers. comm., 2000; see also Stieglitz and Metz, 1989). The occurrence of the compound in all these old mining districts strongly suggests that the use of a nitrate explosive is indirectly responsible for the occur-

* E-mail: uwe.kolitsch@univie.ac.at
DOI: 10.1180/0026461036710086

rence of these nitrates. The use of explosives in the mining districts of the Black Forest was introduced soon after 1623, when this technique was first used in the mines of the Harz mountains in northern Germany.

The $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ compound was characterized in some detail by Kwestroo *et al.* (1967) during a laboratory study of the system $\text{Pb}(\text{NO}_3)_2$ - $\text{Pb}(\text{OH})_2$, in which four phases with $\text{Pb}(\text{NO}_3)_2$: $\text{Pb}(\text{OH})_2$ ratios of 1:1, 2:5, 1:3 and 1:5 were detected. The 1:3 compound, i.e. $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, only crystallized from dilute solutions and was found to be insoluble in hot water. Its X-ray powder pattern was initially indexed with the orthorhombic cell $a = 4.310$, $b = 4.286$, $c = 4.164$ Å, but Kwestroo *et al.* (1967) noted that this cell indexes only the strong reflections and assumed the presence of a superstructure caused by the specific arrangement of non-Pb atoms. Several other hydrated Pb nitrates have been reported subsequently (see Discussion), but the atomic arrangement has been reported for only two of them before the present work was started: monoclinic $[\text{Pb}_4(\text{OH})_4](\text{NO}_3)_4$ (Grimes *et al.*, 1995; formula in previous publications generally given as $\text{Pb}_2(\text{OH})_2(\text{NO}_3)_2$ or $\text{Pb}(\text{OH})(\text{NO}_3)$) and orthorhombic $\text{Pb}_3\text{O}_2(\text{OH})(\text{NO}_3)$ (Krivovichev *et al.*, 2001). The structure of a related Pb carbonate-nitrate, $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$, was recently reported by Li *et al.* (2001).

The present work reports and discusses the previously unknown crystal structure of $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, based on single-crystal studies of the anthropogenic samples from the Black Forest (Walenta, 1998). The crystal structure of the pseudocubic lead nitrate described by Walenta (1998) was also solved during the present study ($\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$, space group $R\bar{3}$, $a = 10.263(1)$, $c = 25.454(5)$ Å, $V = 2321.9(6)$ Å³, $R1 = 4.38\%$), but the results will not be reported here since they show complete agreement with those of a very recent, independent structure determination using a hydrothermally synthesized crystal (Li *et al.*, 2001; $a = 10.283(1)$, $c = 25.471(4)$ Å, $V = 2331.6(5)$ Å³). However, some physical properties of anthropogenic $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ will be described, and comments will be made on the fact that the compound is identical to “ $\text{Pb}_6\text{O}_3(\text{OH})_4(\text{NO}_3)_2$ ” and “ $\text{Pb}_3(\text{OH})_5(\text{NO}_3)$ ” reported in the literature, a point not addressed by Li *et al.* (2001). $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ contains a unique, ball-shaped $[\text{Pb}_{13}\text{O}_8(\text{OH})_6]^{4+}$ cluster previously

unknown from oxidic Pb compounds; this cluster is characterized by a near-icosahedral arrangement of two non-equivalent Pb atoms around a third Pb atom at the centre of the cluster. In the present contribution, comparisons are drawn between the atomic arrangement in $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ and in related structures, and the published reports on $[\text{Pb}_x^+(\text{O},\text{OH})_y]^{n+}$ clusters and Pb nitrate compounds are summarized and discussed critically. The probable conditions of formation of the anthropogenic samples studied are also addressed.

Experimental

Characterization of the samples

The present study used several samples from the Altemannfels dump (see introduction), kindly provided by Mr R. Bayerl of Stuttgart, Germany and Mr. H.-W. Graf of Niederzier-Ellen, Germany. The first compound, $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, appears as colourless to whitish, transparent to translucent, approximately ruler-shaped crystals. They are up to 1 mm long. Optically, $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ is biaxial positive, with small 2V, relatively high birefringence and no discernible dispersion of the optical axes. The crystals show straight extinction and negative elongation. Based on the orthorhombic description (see below), the tabular form is {001} and the crystals are elongated along [100]. On {001} a weak striation parallel to [100] is seen. Cleavages were observed parallel to {010}, {100} and {001}(?). The optical orientation is $X = a$, $Y = b$, $Z = c$ (orientation of crystal axes were derived from single-crystal X-ray studies – see below). The second, pseudocubic to pseudo-cuboctahedral compound, designated as $\text{Pb}_6\text{O}_3(\text{NO}_3)_2(\text{OH})_4$ (Walenta, 1998), but found to be $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ in the present study, forms sharp, transparent colourless to pale yellowish crystals up to ~0.3 mm in size. Morphological studies showed that the pseudo-cuboctahedral habit of the crystals is the result of a combination of one positive rhombohedron and its negative counterpart, and generally small, triangular {001} faces. No distinct cleavage was observed. Optically, $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ is uniaxial negative, with medium-strong birefringence. The latter is explained by the orientation of both NO_3 groups parallel to (001) (Li *et al.*, 2001 and present study). No recognizable twinning features were present in either compound. Semi-quantitative energy-dispersive X-ray analyses of both

CRYSTAL STRUCTURE OF $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$

compounds showed only Pb to be present; no other elements with $Z > 10$ were detectable.

Both nitrates are grown on quartz or within the hollow centres of strongly corroded galena blebs in a quartz matrix. The major phases accompanying the two nitrates are acicular violet elyite, $\text{Pb}_4\text{Cu}(\text{SO}_4)\text{O}_2(\text{OH})_4 \cdot \text{H}_2\text{O}$ (Kolitsch and Giester, 2000), and scaly whitish hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$. On one specimen, an acicular elyite pierces crystals of the pseudocubic compound, indicating more or less simultaneous growth. The samples studied here also contain some massive reddish Pb oxides (not X-rayed) forming pseudomorphs after unidentified precursor phases grown within the quartz matrix, and rarely greenish pyromorphite.

X-ray crystallography

Several small fragments of tabular $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ crystals were mounted on a

Nonius KappaCCD diffractometer equipped with a 300 μm diameter capillary-optics collimator to provide increased resolution. Preliminary studies showed a high crystal quality and consistently yielded an I -centred orthorhombic cell with $a = 8.31$, $b = 8.55$, $c = 17.2$ Å. For the intensity data collection, a full sphere of reciprocal space was measured from a suitably sized fragment (see Table 1 for details). The measured intensity data were processed with the Nonius program suite DENZO-SMN and corrected for Lorentz, polarization, background and absorption effects. Because the structure solution soon proved to be a challenge, two additional crystal fragments of different scattering volumes were also measured but gave comparable datasets.

The crystal structure was solved by direct methods (SHELXS-97, Sheldrick, 1997a) and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F^2 (SHELXL-97, Sheldrick, 1997b) (see

TABLE 1. Crystal data, data collection information and refinement details for $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$.

Crystal data	
Formula	$\text{Pb}_2(\text{OH})_3(\text{NO}_3)$
Space group	<i>Immm</i>
a , b , c (Å)	8.314(2), 8.545(2), 17.210(3)
V (Å ³), Z	1222.7(5), 8
$F(000)$, ρ_{calc} (g cm ⁻³)	1776, 5.73
μ (mm ⁻¹)	54.97
Absorption correction	multi-scan*
Crystal dimensions (mm)	$0.03 \times 0.05 \times 0.07$
Data Collection	
Diffractometer	Nonius KappaCCD system
T (K), λ (Mo- $K\alpha$) (Å)	293, 0.71073
Crystal-detector dist. (mm)	28
Rotation axis; rot. width (°)	ϕ , ω ; 2.0
Total no. of frames	461
Collect. time per frame (s)	125
Collection mode; $2\theta_{\text{max}}$	triclinic, sphere; 60
h , k , l ranges	-11 \rightarrow 11, -12 \rightarrow 12, -24 \rightarrow 24
Total reflections measured	7077
Unique reflections	1032 (R_{int} 5.48%)
Refinement	
$R1(F)$, $wR2(F^2)**$	2.78%, 7.45%
'Observed' reflections	940 [$F_o > 4\sigma(F_o)$]
Extinct. coefficient	0.00138(7)
No. of refined parameters	57
GoF; $(\Delta/\sigma)_{\text{max}}$	1.230; 0.001
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ (e/Å ³)	-3.05, 2.38

* Otwinowski and Minor (1997)

** $w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 11.4P]$, where $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$

TABLE 2. Fractional atomic coordinates and displacement parameters for $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$.

Atom	x	y	z	U_{eq}
Pb	-0.24201(3)	0.23782(3)	0.376017(9)	0.01715(14)
N(1)	-0.5	0.5	0.2720(5)	0.0203(18)
N(2)	0.0	0.5	0.2789(6)	0.024(2)
O(1)	-0.6310(7)	0.5	0.2360(3)	0.0300(13)
O(2)	-0.5	0.5	0.3451(5)	0.032(2)
O(3)	0.0	0.3740(7)	0.2440(3)	0.0312(14)
O(4)	0.0	0.5	0.3530(5)	0.039(2)
OH(5)	0.0	0.1592(6)	0.4231(3)	0.0188(10)
OH(6)	-0.3325(6)	0.0	0.4197(3)	0.0180(10)
OH(7)	-0.3109(7)	0.3277(6)	0.5	0.0229(11)

Oxygens of hydroxyl groups are designated as OH.

Table 1 for details). Analysis of the measured data of the tabular Pb nitrate indicated the centrosymmetric space group $Immm$. However, a solution of the structure in space group $Immm$ was only partially successful; although all Pb atoms could be found, not all N and O atoms were located, high residual electron densities were present close to some Pb positions, some unreasonably short O—O distances were obtained, anisotropic refinement was impossible and severe damping was necessary. The $R1$ value was always >8%. After similarly unsatisfactory trial solutions in $Imm2$, $I222$, $I2_12_12_1$, $C2/m$, Cm and $C2$ (C -centred monoclinic cell with $a = 19.113(4)$, $b = 8.545(2)$, $c = 8.314(2)$ Å, $\beta = 115.79(3)^\circ$, equivalent to the orthorhombic cell), and, finally, in $P\bar{1}$ (triclinic cell with $a = 8.314(2)$, $b = 8.545(2)$, $c = 10.467(2)$ Å, $\alpha = 114.08(3)$, $\beta = 113.40(3)$, $\gamma = 90.00(3)^\circ$, representing the cell with the lowest possible Bravais symmetry), the structure could be solved and smoothly refined in

space group $P1$ to $R1 = 3.95\%$. However, a search for higher symmetry with the ADDSYM module in the PLATON program suite (Spek, 2001) again indicated the space group $Immm$. Furthermore, the value of the refined Flack parameter, 0.49(2), pointed to the possibility of a centrosymmetric structure although no clear indication for the presence or absence of a centre of symmetry was obtainable from intensity statistics (these are known to be inconclusive especially in the presence of heavy atoms). At last, after some considerations of allowed space-group symmetries it was concluded that the two special 8-fold Pb positions detected in the initial trial solution in $Immm$ were in fact representing only one general 16-fold Pb position, and subsequent manual recalculations of the atomic coordinates, involving an origin shift, provided a correct set of atoms. In the last step of refinement in $Immm$, all atoms were treated anisotropically and the final residuals were $R1 = 2.78\%$ and $wR2 = 7.45\%$ for

TABLE 3. Anisotropic displacement parameters for $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb	0.01703(19)	0.01762(19)	0.0168(2)	0.00281(6)	-0.00137(6)	0.00121(6)
N(1)	0.015(4)	0.030(5)	0.016(4)	0.0	0.0	0.0
N(2)	0.018(4)	0.024(5)	0.032(5)	0.0	0.0	0.0
O(1)	0.026(3)	0.031(3)	0.033(3)	0.0	-0.007(3)	0.0
O(2)	0.033(5)	0.047(6)	0.017(4)	0.0	0.0	0.0
O(3)	0.034(3)	0.027(3)	0.033(3)	-0.009(3)	0.0	0.0
O(4)	0.062(7)	0.024(5)	0.029(4)	0.0	0.0	0.0
OH(5)	0.017(2)	0.021(3)	0.019(2)	0.003(2)	0.0	0.0
OH(6)	0.018(2)	0.015(2)	0.021(2)	0.0	0.001(2)	0.0
OH(7)	0.032(3)	0.018(3)	0.018(2)	0.0	0.0	0.003(2)

940 reflections with $F_o > 4\sigma(F_o)$ and 57 parameters (Table 1). Hydrogen atoms could not be located. All the largest residual peaks in the final electron density map were close to Pb atoms. The final positional and displacement parameters are given in Tables 2 and 3. Selected bond lengths, angles, calculated bond-valences and probable hydrogen bonds are presented in Table 4. A list of observed and calculated structure factors (Table 5) has been deposited with the Principal Editor of *Mineralogical Magazine* and is available upon request from him or from the Mineralogical Society website (http://www.minersoc.org/pages/e_journals/dep_mat.htm).

As a footnote, we point out that, after data collection of the $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ crystal, the originally pale yellowish crystal colour had turned into a brownish orange, without loss of transparency. However, no decay of the crystal quality during the measurement was noted. The brownish orange colour did not change within a period of several months. In contrast, in the case of

$\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, the colours of the three measured crystal fragments were unchanged after the respective data collections. Identical unit cells were obtained from the measured, brownish orange $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ crystal and from other, colourless or pale yellowish crystals removed from additional specimens from the same locality (Altemannfels dump) and from two other localities [Bleialf and Bönkhausen (see introduction)].

Results and discussion

The structure of $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$

The crystal structure of $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ contains one Pb atom, two non-equivalent N atoms, seven non-equivalent O atoms and three H atoms, which could not be located in the asymmetric unit. All atoms except Pb are in special positions, a fact that certainly explains the difficulties encountered during the structure solution. As calculated bond-valence sums for the three O atoms OH(5), OH(6) and OH(7) amount to 1.07, 1.02 and 0.92 v.u.

TABLE 4. Selected bond distances (Å) and angles ($^\circ$), calculated bond valence sums (v.u.) and probable hydrogen bonds for the coordination polyhedra in $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$.

Pb—OH(5)	2.271(2)	0.533	N(1)—O(1) $\times 2$	1.253(7)	1.622 $\times 2$
—OH(6)	2.294(2)	0.509	—O(2)	1.258(11)	<u>1.600</u>
—OH(7)	2.339(2)	0.464	<N(1)—O>	1.255	4.84 v.u.
—O(1)	2.950(4)	0.133			
—O(4)	3.0371(13)	0.112	N(2)—O(3) $\times 2$	1.233(7)	1.712 $\times 2$
—O(3)	3.127(4)	0.093	—O(4)	1.276(13)	<u>1.524</u>
—O(2)	3.1468(15)	0.089	<N(2)—O>	1.247	4.95 v.u.
—O(3)	3.251(5)	<u>0.072</u>			
<Pb—O>	2.30 + 3.10	2.01 v.u.			
	([3+5]-coord.)				

Bond-valence sums for O atoms O1—OH7 are 1.62, 1.60, 1.71, 1.52, 1.07, 1.02 and 0.92 v.u., respectively.

O(1)—N(1)—O(1)	120.7(9)	O(3)—N(2)—O(3)	121.7(10)
O(1)—N(1)—O(2) $\times 2$	119.6(5)	O(2)—N(2)—O(4) $\times 2$	119.2(5)
<O—N(1)—O>	120	<O—N(2)—O>	120

Probable hydrogen bonds

Intracluster bonds		Intercluster bonds	
OH(5)···OH(5)	2.647(9)*	bonds along <i>a</i>	
OH(5)···OH(5)	2.722(10)**	OH(6)···OH(6)	2.785(10)
OH(5)···OH(6)	3.082(5)	OH(7)···OH(7)	3.144(11)
OH(6)···OH(6)	2.763(9)		
OH(6)···OH(7)	3.128(5)	bonds along <i>b</i>	
		OH(7)···OH(7)	2.945(10)

The bond-valence parameters used are from Brese and O'Keeffe (1991) (for N^{5+} —O bonds) and from Krivovichev and Brown (2001) (for Pb^{2+} —O bonds).

* bond along [001]; ** bond along [010]

(valence units), respectively, they all represent OH groups. The dominant component in the structure is a previously unknown $[\text{Pb}_8(\text{OH})_{12}]^{4+}$ cluster which has eight equivalent Pb atoms at the corners of a fairly regular "Pb₈" cube (Fig. 1). The OH groups forming part of the cluster can be considered as the centres of kinked Pb-OH-Pb struts connecting the eight Pb atoms along the edges of the "Pb₈" cube (Fig. 1). Thus, each Pb atom is strongly bonded to three OH groups, OH(5), OH(6) and OH(7), at distances within a narrow range from 2.271(2) to 2.339(2) Å (Table 4).

The Pb atom also has five more remote O neighbours within 3.26 Å (Table 4). This coordination demonstrates that the 6s² lone electron pair on the Pb atom is stereochemically active. The lone pairs of electrons all point away from the corners of the cuboid cluster, approximately in the direction of the adjacent layers of NO₃ groups (see below). The calculated bond-valence sum for the [8]-coordinated Pb atom is 2.16 v.u., if the bond-valence parameters of Brese and O'Keeffe (1991) are used, and 2.01 v.u., if the new bond-valence parameters for Pb²⁺-O bonds suggested by Krivovichev and Brown (2001) are used. Each O atom involved in the cluster is only bonded to three cations: two Pb²⁺ and one H⁺. Strong to

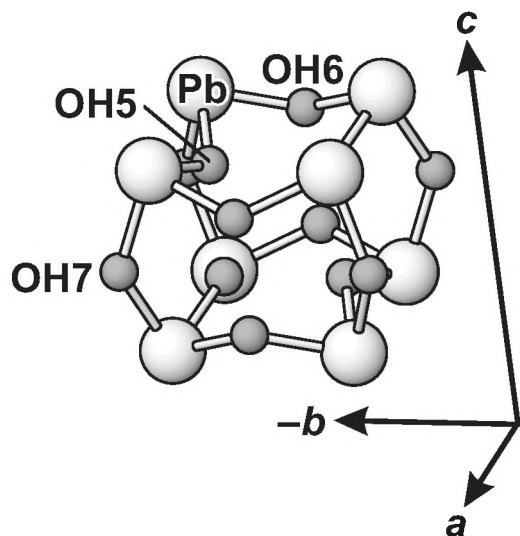


FIG. 1. The cuboid $[\text{Pb}_8(\text{OH})_{12}]^{4+}$ cluster in $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$. Pb atoms are shown as large spheres, O atoms of OH groups as small dark spheres. All drawings were created using ATOMS (Shape Software, 1999).

weak hydrogen bonds within the cluster provide considerable internal stability: intracuster OH...OH distances range from 2.647(9) to 3.128(5) Å (Table 4). Both of the strongest bonds involve OH(5)...OH(5) interactions along [001] and [010], respectively. Each $[\text{Pb}_8(\text{OH})_{12}]^{4+}$ cluster is surrounded within a plane parallel to (001) by eight other clusters to form Pb-OH 'layers' (Figs 2, 3). The clusters are connected to each other by weak to very weak hydrogen bonds within the Pb-OH 'layer', the bonds being directed approximately along the *a* and *b* axes (Figs 2, 3); intercluster OH...OH distances show a range from 2.785(10) to 3.144(11) Å (Table 4). Additional weak bonding contributions may be effected by van der Waals interactions between lone-pair orbitals on the Pb atoms (e.g. Pykkö, 1997). Furthermore, there is evidence that the lone electron pair of Pb²⁺ cations can act as a hydrogen-bond acceptor (Lutz *et al.*, 1995, 1996; Lutz and Jung, 1997).

The Pb-OH 'layers' parallel to (001) are separated by layers of NO₃ groups (Figs 2, 3), in which the planes of the NO₃ triangles are oriented perpendicular to the (100) and (010) planes in an alternating manner. There are weak to very weak bonds between the Pb atoms and the O atoms of the nitrate triangles (Table 4). The NO₃ groups are only slightly distorted, as seen from the narrow range of N-O bond lengths, 1.253(7) to 1.276(13) Å, and O-N-O angles, 119.2(5) to 121.7(10)° (average 120°, indicating no aplanarity; see Table 4). Considerably more distorted NO₃ groups were observed in $[\text{Pb}_4(\text{OH})_4(\text{NO}_3)_4]$ (Grimes *et al.*, 1995) and $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ (Li *et al.*, 2000). The calculated bond-valence sums of the two N atoms are 4.84 and 4.95 v.u. for N(1) and N(2) respectively, i.e. close to the ideal value. Bond-valence sums for the O ligands O(1)-O(4) of the two different NO₃ groups show a range of values from 1.52 to 1.71 v.u. Although O(1) and O(4) might obtain some bond strength contributions from possible hydrogen bonds, the distances between these two O acceptor atoms and suitable donor atoms, OH(5) and OH(6), are >3.15 Å, thus indicating only very weak, if any, hydrogen bonding.

The location of NO₃ (and CO₃) groups between Pb-(O,OH) layers has also been observed in the structure of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ (Li *et al.*, 2000). The strongly pronounced subcell of $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, previously noted by Kwestroo *et al.* (1967), is caused by the orthorhombic

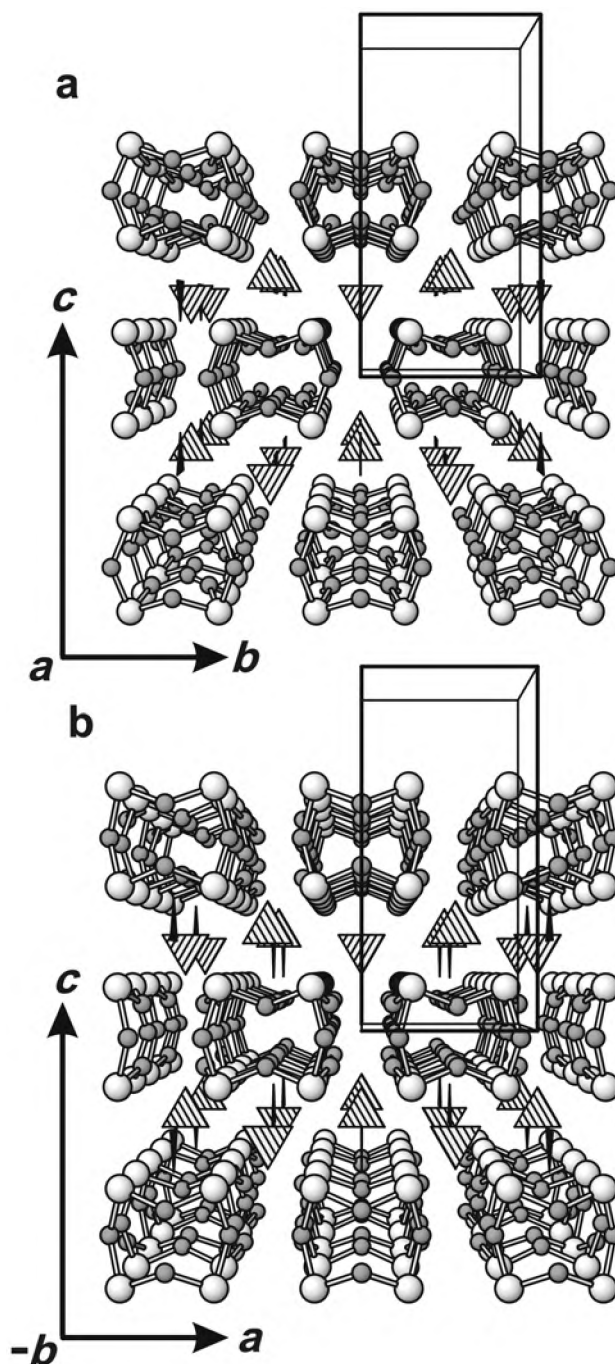
CRYSTAL STRUCTURE OF $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ 

FIG. 2. The structure of $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ in two perspective views: (a) along $[100]$, (b) along $[0\bar{1}0]$; unit cells are also shown. (001) layers composed of cuboid $[\text{Pb}_8(\text{OH})_{12}]^{4+}$ clusters, which are weakly hydrogen-bonded to each other, are separated by layers of NO_3 groups (striped triangles). Only the strong $\text{Pb}-\text{O}$ bonds within 2.35 \AA are shown. The remaining, very weak $\text{Pb}-\text{O}$ bonds ($2.95-3.26 \text{ \AA}$ long), which are only between the Pb atoms and the O atoms of the NO_3 groups, have been omitted for clarity.

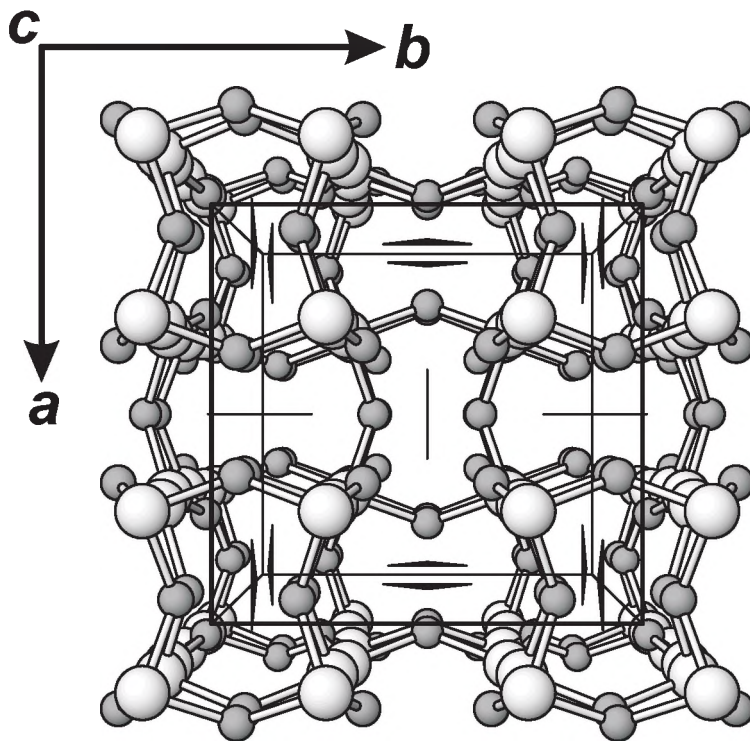


FIG. 3. The structure of $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ in a perspective view along $[001]$. Note that the NO_3 groups are arranged in layers parallel to (010) (compare the layering in Fig. 2).

arrangement of the Pb atoms in its structure. This is especially evident in the views shown in Figs 2 and 3. The X-ray powder diffraction data for $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ given by Kwestroo *et al.* (1967) (ICDD 22-661) and Michell (1974) (ICDD 27-273), which are identical to data calculated from the present results, were indexed by Kwestroo *et al.* (1967) on an orthorhombic subcell with $a_{\text{sub}} = 4.31$, $b_{\text{sub}} = 4.286$, $c_{\text{sub}} = 4.164$ Å, $V_{\text{sub}} = 76.9$ Å³. This subcell is obviously related to the orthorhombic cell found in the present work, $a = 8.314(2)$, $b = 8.545(2)$, $c = 17.210(3)$ Å, $V = 1222.7(5)$ Å³, as follows: $a \approx 2c_{\text{sub}}$, $b \approx 2b_{\text{sub}}$, $c = 4a_{\text{sub}}$, $V \approx 16V_{\text{sub}}$. The conclusions of Kwestroo *et al.* (1967) that the subcell dimensions are caused by the arrangement of the Pb atoms, are confirmed by the present structure determination. The Pb–Pb–Pb angles within the $[\text{Pb}_8(\text{OH})_{12}]^{4+}$ cluster are all 90.0°, and the atomic arrangement of the Pb atoms in the cluster is in accordance with *mmm* symmetry. The three intracluster Pb–Pb distances are 4.0241(11), 4.0643(11) and 4.2675(8) Å, while

the two shortest intercluster Pb–Pb distances are 4.2899(11) and 4.4807(12) Å. Not surprisingly, these distances are similar to the unit-cell parameters of the orthorhombic subcell reported by Kwestroo *et al.* (1967). X-ray single-crystal studies of the crystal morphology showed that the compound is tabular on $\{001\}$ and elongated along $[100]$, i.e. along the direction of the strongest intercluster hydrogen bond (Table 4). Observed orthorhombic forms are $\{001\}$, $\{010\}$ and $\{100\}$.

Relationship with other compounds, and a review of $[\text{Pb}_x^2+(\text{O},\text{OH})_y]^{n+}$ clusters

As already mentioned above, the $[\text{Pb}_{13}\text{O}_8(\text{OH})_6]^{4+}$ cluster in $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ is unique. The $[\text{Pb}_8(\text{OH})_{12}]^{4+}$ cluster found in $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ has also not been previously identified in inorganic Pb compounds. However, a discrete unit $\text{Pb}_8(\text{OH})_{12}\text{Cl}_4$ was characterized by Raman spectroscopy in studies of basic Pb^{2+} chloride solutions (Tsai and Cooney, 1976); the

four Cl^- anions in this unit compensate for the four positive charges on the core cluster $[\text{Pb}_8(\text{OH})_{12}]^{4+}$.

A cluster consisting also of eight Pb atoms but only four O atoms, $[\text{Pb}_8\text{O}_4]^{8+}$, occurs in the structure of $\text{Pb}_9\text{O}_4\text{Br}_{10}$ (Keller, 1983) and $\text{TlPb}_8\text{O}_4\text{Br}_9$ (Keller, 1982). This cluster can be conveniently described considering the presence of oxocentred OPb_4 groups [see O'Keeffe and Hyde (1985), Hyde and Andersson (1989), Krivovichev *et al.* (1998) and Krivovichev and Filatov (1999*a,b*) for the high usability of the concept of oxocentred $[\text{OM}_4]$ groups in the description of inorganic crystal structures]: four OPb_4 tetrahedra share edges to form a poly-tetrahedral $[\text{Pb}_8\text{O}_4]^{8+}$ cluster. A comparable $[\text{Sn}_8^+\text{O}_4]^{8+}$ cluster occurs in $\text{Sn}_2^+\text{OSO}_4$ (Lundgren *et al.*, 1982). In large cavities in Pb-exchanged, vacuum-dehydrated (at 380°C) variants of zeolite X, the occurrence of $[\text{Pb}_4\text{O}_4(\text{Pb}^{2+}, \text{Pb}^{4+})_4]$ clusters has been reported (Yeom *et al.*, 1997, 1999). These are also topologically identical to the $[\text{Pb}_8\text{O}_4]^{8+}$ cluster. The cited authors assumed the presence of Pb^{4+} within the cluster because of the observation of small Pb–O bond lengths, which range from 2.24(2) to 2.32(2) Å (Yeom *et al.*, 1997) and from 2.11(7) to 2.23(2) Å (Yeom *et al.*, 1999). However, they neglect the stereochemical activity of the $6s^2$ lone electron pair on Pb^{2+} , and the observation that M –O bonds in oxocentred OM_4 groups are always shorter than in non-oxocentred groups (Krivovichev *et al.*, 1998). In $[\text{Pb}_4(\text{OH})_4](\text{NO}_3)_4$ (Grimes *et al.*, 1995), one Pb–O distance is also extremely short, 1.97 Å, but no indication for the presence of tetravalent Pb is present.

Several $[\text{Pb}_x^+(\text{O}, \text{OH})_y]^{m+}$ clusters with fewer than eight Pb atoms ($x < 8$) have been found in the crystal structures of other lead oxide hydroxide nitrates and lead oxysalts. Isolated $[\text{Pb}_4\text{O}]$ clusters (i.e. isolated OPb_4 tetrahedra) were found in $\text{Pb}_4\text{O}(\text{Pb}_2(\text{BO}_3)_3\text{Cl})$ (Behm, 1983), $\text{Pb}_8\text{Bi}_2(\text{PO}_4)_6\text{O}_2$ (Moore *et al.*, 1982) and $\text{Pb}_6\text{Re}_6\text{O}_{19}$ (Abakumov *et al.*, 1998). A simple linear $[\text{Pb}_2(\text{OH})]^{3+}$ unit occurs in $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ (Krivovichev and Burns, 2000*c*). A disordered $[\text{Pb}_2(\text{OH})(\text{H}_2\text{O})_3]^{3+}$ cluster has been observed in lead hydro sodalite, $[\text{Pb}_2(\text{OH})(\text{H}_2\text{O})_3]_2[\text{Al}_3\text{Si}_3\text{O}_{12}]_2$ (Eiden-Assmann *et al.*, 2000). A cluster with four Pb atoms, $[\text{Pb}_4(\text{OH})_4]^{4+}$, occupies the sodalite cage in another variant of zeolite X (Nardin *et al.*, 1995) and is present in maricopaite,

$(\text{Pb}_7\text{Ca}_2)[\text{Al}_{12}\text{Si}_{36}(\text{O}, \text{OH})_{100}] \cdot n(\text{H}_2\text{O}, \text{OH})$, $n \approx 32$ (Rouse and Peacor, 1994) and in $[\text{Pb}_4(\text{OH})_4](\text{NO}_3)_4$ (Grimes *et al.*, 1995). Such a cluster also forms part of the structures of $[\text{Pb}_4(\text{OH})_4]_3(\text{CO}_3)(\text{ClO}_4)_{10} \cdot 6\text{H}_2\text{O}$ (Hong and Olin, 1973) and $[\text{Pb}_4(\text{OH})_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ (Hong and Olin, 1974). In fact, the $[\text{Pb}_4(\text{OH})_4]^{4+}$ unit represents the predominant Pb-containing species in non-dilute aqueous solutions of Pb^{2+} salts (Johansson and Olin, 1968; Baes and Mesmer, 1976; Grimes *et al.*, 1995). A related unit, $[\text{Pb}_4(\text{OH})_2\text{F}_2]^{4+}$, was recently detected in the structure of bideauxite, $\text{Pb}_2^+\text{Ag}^+\text{Cl}_3\text{F}(\text{OH})$ (Cooper *et al.*, 1999). Hydrogen-free varieties of the $[\text{Pb}_4(\text{OH})_4]^{4+}$ cluster occur as “electrically neutral” $[\text{Pb}_4\text{O}_4]$ units in the structure of flux-grown aluminat sodalites $\text{Ln}_4[\text{Al}_{12}\text{O}_{24}](\text{Pb}_4\text{O}_4)_2$ ($\text{Ln} = \text{Nd}, \text{Sm}$) (Werner and Müller-Buschbaum, 1997); however, these $[\text{Pb}_4\text{O}_4]$ units cannot be considered as independent clusters, since their O atoms are also closely bonded (2.33 Å) to Nd atoms to form OPb_3Ln tetrahedra linked into a three-dimensional framework (Krivovichev *et al.*, 1998).

Clusters with composition $[\text{Pb}_6\text{O}(\text{OH})_6]^{4+}$ were found in both polymorphs of $[\text{Pb}_6\text{O}(\text{OH})_6]$ $(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ (Spiro *et al.*, 1969; Olin and Söderquist, 1972) and in $[\text{Pb}_6\text{O}(\text{OH})_6]$ $(\text{ReO}_4)_4 \cdot \text{H}_2\text{O}$ (Haag-Bruhl *et al.*, 1988). The six Pb atoms in $[\text{Pb}_6\text{O}(\text{OH})_6]^{4+}$ occupy the corners of three distorted Pb_4 tetrahedra connected by common faces. In $\text{Pb}_3\text{O}_2(\text{OH})_2$, a topologically different and electrostatically neutral cluster, $[\text{Pb}_6\text{O}_4(\text{OH})_4]$, was found (Hill, 1985); it can be described as an almost regular Pb_6 octahedron whose eight triangular faces are ‘topped’ by O atoms or OH groups. Isolated $[\text{Pb}_6\text{O}_2]$ clusters occur in Pb_3UO_6 (Sterns *et al.*, 1986). A $[\text{Pb}_7\text{O}(\text{OH})_3]^{9+}$ cluster is present in a Pb-exchanged variety of zeolite A (Ronay and Seff, 1993) and in synthetic ‘plumbonacrite’, $\text{Pb}_5\text{O}(\text{OH})_2(\text{CO}_3)_3$ (Krivovichev and Burns, 2000*b*; see also Brooker *et al.*, 1983).

Most of the above clusters have also been identified in aqueous solutions by various methods; additional discrete $[\text{Pb}_x^+(\text{O}, \text{OH})_y]^{m+}$ units found are as follows: $[\text{Pb}(\text{OH})]^{+}$, $[\text{Pb}_3(\text{OH})_4]^{2+}$, $[\text{Pb}_3(\text{OH})_5]^{+}$ and $[\text{Pb}_6(\text{OH})_8]^{4+}$ (e.g. Johansson and Olin, 1968; Baes and Mesmer 1976; Gyunner *et al.*, 1978; Cruywagen and van de Water, 1993; Arbatskii *et al.*, 1995; Grimes *et al.*, 1995 and references cited therein). Most of these results were obtained by analysing products of the reaction of aqueous lead nitrate

solutions with NaOH or concentrated NH_3 . In molten $\text{NH}_4\text{NO}_3 + 1.5\text{H}_2\text{O}$ mixtures and in water-bearing (K,Na) NO_3 melts, the species $[\text{Pb}(\text{OH})]^+$, $[\text{Pb}_2(\text{OH})_3]^+$ and $[\text{Pb}_2(\text{OH})_2]^{2+}$ have been detected (Bengtsson and Holmberg, 1990; Frostemark *et al.*, 1994).

Summarizing the data available on these clusters, it is seen that discrete units containing 1, 2, 3, 4, 6, 7, 8 and 13 Pb atoms are known. It seems probable that ongoing research on the crystallography of Pb oxysalts will lead to the detection of further, possibly larger $[\text{Pb}_x^+(\text{O},\text{OH})_y]^{n+}$ clusters with unusual configurations. A cluster containing three Pb atoms has seemingly not been found yet in crystalline Pb oxysalts, although the $[\text{Pb}_7\text{O}(\text{OH})_3]^{9+}$ cluster described by Ronay and Seff (1993) can be visualized as a central $[\text{Pb}_3\text{O}(\text{OH})_3]^+$ cluster surrounded by four Pb atoms. The configuration of the central cluster is basically identical to that of $[\text{Sn}_3^{2+}(\text{OH})_4]^{2+}$ in $[\text{Sn}_3^{2+}(\text{OH})_4](\text{NO}_3)_2$ (Donaldson *et al.*, 1995).

The crystal structures of other structurally characterized lead oxide hydroxide nitrates are based on O–Pb chains. For instance, orthorhombic $\text{Pb}_3\text{O}_2(\text{OH})(\text{NO}_3)$ is based on $[\text{O}_2\text{Pb}_3]$ chains of edge-sharing OPb_4 tetrahedra which are linked by $(\text{OH})\text{Pb}_2$ dimers into $[\text{Pb}_3\text{O}_2](\text{OH})$ sheets (Krivovichev *et al.*, 2001). The structure of $\text{Pb}_3\text{O}_2(\text{OH})(\text{NO}_3)$ is closely related to that of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ (Li *et al.*, 2000). Both O–Pb chains and Pb-based sheets also occur in structurally related, basic lead carbonates (e.g. Krivovichev and Burns, 2000*a,b,c* and references cited therein).

Formulae for presently and previously studied lead nitrates

The structure solution of the pseudocubic compound (Li *et al.*, 2001 and present study) shows that the previously reported formulae for this phase, “ $\text{Pb}_6\text{O}_3(\text{OH})_4(\text{NO}_3)_2$ ” (ICDD 23-1558) and “ $\text{Pb}_3(\text{OH})_5(\text{NO}_3)$ ” (ICDD 23-1558; Kwestroo *et al.*, 1967, and ICDD 22-659; Gyunter *et al.*, 1978; Narita *et al.*, 1984; Arbatskii *et al.*, 1995; Uchida *et al.*, 1997; Sugiyama *et al.*, 1999) both need to be revised. The correct formula, $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$, contains more Pb by comparison [Pb:(NO_3) ratio = 3.25:1] and also fewer OH groups. The identity of $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ with “ $\text{Pb}_6\text{O}_3(\text{NO}_3)_2(\text{OH})_4$ ” and “ $\text{Pb}_3(\text{OH})_5(\text{NO}_3)$ ” was not discussed by Li *et al.* (2001). The formula reported for the tabular Pb nitrate,

$\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, originally proposed by Kwestroo *et al.* (1967) and reproduced by later authors (Michell, 1974, and ICDD 27-273; Cram and Davies, 1976; Narita *et al.*, 1984; Garcia-Clavel *et al.*, 1985; Arbatskii *et al.*, 1995; Uchida *et al.*, 1997; Sugiyama *et al.*, 1999), was confirmed by the present structure determination.

Table 6 provides an overdue critical compilation on the confusing variety of reported lead nitrate compounds, the formulae of some of which are now known to be erroneous (see previous paragraph) or may be considered doubtful (see bottom of Table). The data in Table 6 show that none of the crystal structures are known for any of the H-free Pb oxide nitrates such as $\text{Pb}_6\text{O}_5(\text{NO}_3)_2$ and $\text{Pb}_3\text{O}_2(\text{NO}_3)_2$. The structures of the following two hydrous Pb nitrate compounds are also still undetermined: $\text{Pb}_3\text{O}_2(\text{NO}_3)_2 \cdot 1.5\text{H}_2\text{O}$ (also described as $\text{Pb}_5\text{O}_3(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$, see Table 6), and $\text{Pb}_2(\text{OH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. The Pb:(NO_3) ratio of 1.5:1 characteristic of $\text{Pb}_3\text{O}_2(\text{NO}_3)_2 \cdot 1.5\text{H}_2\text{O}$ suggests that it may be isostructural with $[\text{Sn}_3^{2+}(\text{OH})_4](\text{NO}_3)_2$ (Donaldson *et al.*, 1995). On the other hand, it was suggested that $\text{Pb}_3\text{O}_2(\text{NO}_3)_2 \cdot 1.5\text{H}_2\text{O}$ contains $[\text{Pb}_6\text{O}(\text{OH})_6]^{4+}$ clusters and probably has the formula $\text{Pb}_6\text{O}(\text{OH})_6(\text{NO}_3)_4$ (Grimes *et al.*, 1995). The existence of the four basic compounds described by Kwestroo *et al.* (1967) can be considered as established, as their occurrence was later reported by several workers (e.g. Narita *et al.*, 1984; Arbatskii *et al.*, 1995; Uchida *et al.*, 1997; Sugiyama *et al.*, 1999). Clearly, more crystallographic work is necessary to obtain correct formulae for all of the reported Pb hydroxide and oxide nitrates.

Conditions of formation of the studied samples

The probable conditions of formation of the two Pb nitrates on the mine dump may be deduced by comparison to data on their syntheses (Pauley and Testerman, 1954; Kwestroo *et al.*, 1967; Michell, 1974; Narita *et al.*, 1984; Arbatskii *et al.*, 1995; Grimes *et al.*, 1995; Uchida *et al.*, 1997; Sugiyama *et al.*, 1999). The formation of “ $\text{Pb}_3(\text{OH})_5(\text{NO}_3)$ ” (= $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$) at comparatively high pH values and high Pb:(NO_3) ratios was reported by Kwestroo *et al.* (1967), who concluded that this compound is fairly stable. According to Kwestroo *et al.* (1967), $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ crystallizes only from dilute solutions, unlike the other nitrates characterized by them, i.e. $\text{Pb}(\text{OH})(\text{NO}_3)$, $\text{Pb}_7(\text{OH})_{10}(\text{NO}_3)_4$ and “ $\text{Pb}_3(\text{OH})_5(\text{NO}_3)$ ” (=

CRYSTAL STRUCTURE OF $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$

 TABLE 6. Reported Pb hydroxide and oxide nitrates, arranged according to their $\text{Pb}:(\text{NO}_3)$ elemental ratio*.

Compound	$\text{Pb}:(\text{NO}_3)$	References
$\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ previously described as "Pb ₆ O ₃ (OH) ₄ (NO ₃) ₂ " or "Pb ₃ (OH) ₅ (NO ₃)"	3.25:1 "3:1" "3:1"	This work; Li <i>et al.</i> (2001) ICDD 23-1558 (unindexed) Pauley and Testerman (1954); Kwestroo <i>et al.</i> (1967), ICDD 22-659; Gyunner <i>et al.</i> (1978); Narita <i>et al.</i> (1984); Arbatskii <i>et al.</i> (1995); Uchida <i>et al.</i> (1997); Sugiyama <i>et al.</i> (1999)
$\text{Pb}_3\text{O}_2(\text{OH})(\text{NO}_3)$	3:1	Krivovichev <i>et al.</i> (2001)
$\text{Pb}_6\text{O}_5(\text{NO}_3)_2$ *	3:1	Brusset <i>et al.</i> (1967), ICDD 22-390; Kwestroo <i>et al.</i> (1967); Newkirk and Hughes (1970), ICDD 23-1159; Martin <i>et al.</i> (1972a,b); Garcia-Clavel <i>et al.</i> (1985, 1986a); Sugiyama <i>et al.</i> (1999)
$\text{Pb}_2(\text{OH})_3(\text{NO}_3)$	2:1	This work; Kwestroo <i>et al.</i> (1967), ICDD 22-661; Michell (1974), ICDD 27-273; Cram and Davies (1976); Narita <i>et al.</i> (1984); Garcia-Clavel <i>et al.</i> (1985); Uchida <i>et al.</i> (1997); Arbatskii <i>et al.</i> (1995)
$\text{Pb}_4\text{O}_3(\text{NO}_3)_2$ *	2:1	Garcia-Clavel <i>et al.</i> (1985), ICDD 39-543
$\text{Pb}_7(\text{OH})_{10}(\text{NO}_3)_4$ **a	1.75:1	Kwestroo <i>et al.</i> (1967), ICDD 23-461; Narita <i>et al.</i> (1984); Uchida <i>et al.</i> (1997); Sugiyama <i>et al.</i> (1999)
$\text{Pb}_{3.2}\text{O}_{2.2}(\text{NO}_3)_2$ **b	1.6:1	Garcia-Clavel <i>et al.</i> (1986c), ICDD 40-553
$\text{Pb}_3\text{O}_2(\text{NO}_3)_2 \cdot 1.5\text{H}_2\text{O}$ = $\text{Pb}_6\text{O}(\text{OH})_6(\text{NO}_3)_4$ *	1.5:1	Garcia-Clavel <i>et al.</i> (1986a,b), ICDD 39-635; Grimes <i>et al.</i> (1995) Brusset <i>et al.</i> (1967), ICDD 22-667
$\text{Pb}_3\text{O}_2(\text{NO}_3)_2$ *	1.5:1	Brusset <i>et al.</i> (1967), ICDD 22-666; Garcia-Clavel <i>et al.</i> (1986a), ICDD 40-614
also described as $\text{Pb}_{10}\text{O}_7(\text{NO}_3)_6$	1.66:1	Martin <i>et al.</i> (1972a)
$\text{Pb}_{2.4}\text{O}_{1.4}(\text{NO}_3)_2$ *	1.2:1	Garcia-Clavel <i>et al.</i> (1986c), ICDD 40-552
$[\text{Pb}_4(\text{OH})_4][\text{NO}_3]_4$ = $\text{Pb}_2(\text{OH})_2(\text{NO}_3)_2$ = $\text{Pb}(\text{OH})(\text{NO}_3)$	1:1	Pauley and Testerman (1954); Kwestroo <i>et al.</i> (1967), ICDD 22-388; Michell (1974), ICDD 27-272; Gyunner <i>et al.</i> (1978); Narita <i>et al.</i> (1984); Garcia-Clavel <i>et al.</i> (1986c), ICDD 40-550; Arbatskii <i>et al.</i> (1995); Grimes <i>et al.</i> (1995), ICDD 83-1100
$\text{Pb}_2(\text{OH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ *	1:1	Michell (1974), ICDD 27-274; Cram and Davies (1976)
$\text{Pb}_2\text{O}(\text{NO}_3)_2$ *	1:1	Garcia-Clavel <i>et al.</i> (1986c), ICDD 40-551

The Pb oxide nitrates are mainly prepared by dehydration of the Pb hydroxide nitrates at elevated temperatures. Complete pyrolysis leads to the formation of PbO.

* An asterisk after the formula signifies unknown symmetry and/or crystal structure. The formulae of most of these compounds probably need confirmation.

^a According to Grimes *et al.* (1995), " $\text{Pb}_7(\text{OH})_{10}(\text{NO}_3)_4$ " is more likely to be $[\text{Pb}_3(\text{OH})_4](\text{NO}_3)_2$.

^b see also $\text{Pb}_3\text{O}_2(\text{NO}_3)_2$, which has $\text{Pb}:(\text{NO}_3) = 1.5:1$.

$\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$, and is insoluble in hot water. This agrees qualitatively with the observation of Arbatskii *et al.* (1995) that titration of a 0.005 M solution of PbNO_3 with NaOH gave the precipitates $\text{Pb}(\text{OH})(\text{NO}_3)$ and " $\text{Pb}_3(\text{OH})_5(\text{NO}_3)$ "

(= $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$), whereas titration of a 0.05 M solution (which may still be considered "dilute") yielded $\text{Pb}(\text{OH})(\text{NO}_3)$ and $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$. Michell (1974) observed that $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ formed from PbO and cold

aqueous $\text{Pb}(\text{NO}_3)_2$ solutions in the molar range of 3:1 at all temperatures between 15 and 30°C, whereas $\text{Pb}_2(\text{OH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Pb}(\text{OH})_3(\text{NO}_3)$ crystallized from solutions with a molar range from 1:3 to 1:1. $\text{Pb}_2(\text{OH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ was found to be stable only at <20°C, while $\text{Pb}(\text{OH})_3(\text{NO}_3)$ was stable at 25–30°C.

The above data suggest that $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$, which contains relatively more Pb than $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, has crystallized from comparatively Pb-rich, concentrated and fairly basic aqueous nitrate solutions, possibly at somewhat elevated temperatures. $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ then must have crystallized either after the solution was depleted in Pb, or at a greater distance from the primary source of the Pb^{2+} ions. Intergrowth of both nitrates on the studied samples are very rare, but provide no clear indication on which crystallized first. The suggested conditions of crystallization are consistent with formation associated with fire-setting and/or gun-powder blast mining. The association with elyite and hydrocerussite, typical indicator phases for the use of fire-setting methods, confirms this scenario. $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ is the most basic Pb hydroxide nitrate known and addition of NaOH to $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ results in the formation of $\text{Pb}(\text{OH})_2$ or polymorphs of PbO (Kwestroo *et al.*, 1967; Gyunner *et al.*, 1978; Narita *et al.*, 1984; Grimes *et al.*, 1995). Pb-O phases such as litharge, massicot or minium are in fact often identified from fire-setting dump material at the mine localities mentioned in the introduction. The majority of the Pb-O phases has, however, formed due to the dehydration and/or decarbonization of naturally crystallized lead oxysalts such as cerussite (with shannonite, $\text{Pb}_2\text{O}(\text{CO}_3)$, as an intermediate product) or anglesite (Wittern, 1994). Interaction of the Pb-O phases with water subsequently produced high-pH solutions and caused the crystallization of basic lead oxysalts such as elyite, hydrocerussite and lanarkite [compare also the observation of the direct influence of concrete on recently-mined ore at the operational Clara baryte and fluorite mine, Black Forest, Germany, which led to the crystallization of elyite, hydrocerussite, plumbonacrite, massicot, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, ettringite and calcite from high-pH solutions (Kolitsch, 2000)]. Only if nitrate ions were also present in the solutions, were $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ and $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ able to crystallize.

The fact that $\text{Pb}(\text{OH})(\text{NO}_3)$ is not observed in the anthropogenic Pb nitrate assemblage is

probably explained by its formation at comparatively low pH (5–7 according to Pauley and Testerman, 1954, and 5.3 according to Grimes *et al.*, 1995) and its solubility in water (Kwestroo *et al.*, 1967). Thus, $\text{Pb}(\text{OH})(\text{NO}_3)$ may have formed initially during the interaction of Pb- and nitrate-bearing solutions, but was later dissolved. Similarly, $\text{Pb}_7(\text{OH})_{10}(\text{NO}_3)_4$ (Table 6) has probably not been found because it decomposes in larger amounts of water to (unstable) $\text{Pb}(\text{OH})(\text{NO}_3)$ and (stable) $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$ (Kwestroo *et al.*, 1967). The compounds found on the dumps, $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ and $\text{Pb}_2(\text{OH})_3(\text{NO}_3)$, are both insoluble in (hot) water (Kwestroo *et al.*, 1967) and therefore obviously have survived weathering solutions for more than 100 years.

Acknowledgements

The author is very grateful to Mr Richard Bayerl of Stuttgart, Germany, and to Mr Hans-Werner Graf of Niederzier-Ellen, Germany, for providing the samples investigated. Dr Sergey Krivovichev is thanked for kindly supplying a copy of the final manuscript of his publication on $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$, and for helpful discussions. Prof. Dr Herta Effenberger, Dr Allan Pring and Dr Sergey Krivovichev are thanked for their comments on the manuscript. Constructive comments by the referees Dr Ian Steele and Dr Mark D. Welch also helped to improve the manuscript.

References

- Abakumov, A.M., Shpanchenko, R.V. and Antipov, E.V. (1998) Synthesis and structure of the double oxide $\text{Pb}_6\text{Re}_6\text{O}_{19}$. *Zeitschrift für Anorganische und Allgemeine Chemie*, **624**, 750–753.
- Arbatskii, A.P., Benson, V.V. and Bol'shakova, E.V. (1995) Compositions and solubility products of lead nitrate hydroxides and hydroxide. *Russian Journal of Physical Chemistry*, **69**, 1730–1732.
- Baes, C.F., Jr. and Mesmer, R.E. (1976) *The Hydrolysis of Cations*. Wiley-Interscience, New York.
- Behm, H. (1983) Hexalead chloride triorthoborate oxide, $\text{Pb}_4\text{O}[\text{Pb}_2(\text{BO}_3)_3\text{Cl}]$. *Acta Crystallographica*, **C39**, 1317–1319.
- Bengtsson, L. and Holmberg, B. (1990) Cationic lead(II) hydroxide complexes in molten alkali-metal nitrate. *Journal of the Chemical Society, Faraday Transactions*, **86**, 351–359.
- Brese, N.E. and O'Keeffe, M. (1991) Bond-valence

- parameters for solids. *Acta Crystallographica*, **B47**, 192–197.
- Brooker, M.H., Sunder, S., Taylor, P. and Lopata, V.J. (1983) Infrared and Raman spectra and X-ray diffraction studies of solid lead(II) carbonates. *Canadian Journal of Chemistry*, **61**, 494–502.
- Brusset, H., Martin, J.J.P. and Peltier, C. (1967) Lead oxide nitrate hydrates. *Bulletin de la Société Chimique de France*, **1967**, 1127–1133 (in French).
- Cooper, M.A., Hawthorne, F.C., Merlino, S., Pasero, M. and Perchiazzi, N. (1999) Stereoactive lone-pair behavior of Pb in the crystal structure of bideauxite: $\text{Pb}^{2+}_2\text{Ag}^+\text{Cl}_3\text{F}(\text{OH})$. *The Canadian Mineralogist*, **37**, 915–921.
- Cram, A.G. and Davies, M.B. (1976) A Raman and IR spectrophotometric study of some basic lead nitrate compounds and their thermal decomposition products. *Journal of Inorganic and Nuclear Chemistry*, **38**, 1111–1117.
- Cruywagen, J.J. and van de Water, R.F. (1993) The hydrolysis of lead(II). A potentiometric and enthalpimetric study. *Talanta*, **40**, 1091–1095.
- Donaldson, J.D., Grimes, S.M., Johnston, S.R. and Abrahams, I. (1995) Characterisation of the tin(II) hydroxide cation $[\text{Sn}_3(\text{OH})_4]^{2+}$, and the crystal structure of tritin(II) tetrahydroxide dinitrate. *Journal of the Chemical Society, Dalton Transactions*, **1995**, 2273–2276.
- Eiden-Assmann, S., Schneider, A.M., Behrens, P., Wiebcke, M., Engelhardt, G. and Felsche, J. (2000) Lead hydro sodalite $[\text{Pb}_2(\text{OH})(\text{H}_2\text{O})_3]_2[\text{Al}_3\text{Si}_3\text{O}_{12}]_2$: synthesis and structure determination by combining X-ray Rietveld refinement, ^1H MAS NMR FTIR and XANES spectroscopy. *Chemistry – A European Journal*, **6**, 292–297.
- Frostemark, F., Bengtsson, L.A. and Holmberg, B. (1994) Formation and structure of mono- and di-lead hydroxide and fluoride complexes in molten $\text{NH}_4\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ at 50°C . *Journal of the Chemical Society, Faraday Transactions*, **90**, 2531–2539.
- Garcia-Clavel, M.E., Martinez-Lope, M.J., Casais-Alvarez, M.T. and Kilany, A. (1985) Thermoanalytical and structural study of lead trioxynitrates. Pp. 547–551 in: *Thermal Analysis, Proceedings ICTA, 8th, Vol. 1* (A. Blazek, editor).
- Garcia-Clavel, M.E., Martinez-Lope, M.J., Casais-Alvarez, M.T. and Kilany, A. (1986a) Obtention, thermal behavior and structural study of the dioxynitrates of lead. *Thermochimica Acta*, **105**, 111–116.
- Garcia-Clavel, M.E., Martinez-Lope, M.J., Casais-Alvarez, M.T. and Kilany, A. (1986b) Study of the degradation in open atmosphere of the hydrated dioxynitrate of lead. *Thermochimica Acta*, **108**, 29–32.
- Garcia-Clavel, M.E., Martinez-Lope, M.J., Casais-Alvarez, M.T. and Kilany, A. (1986c) Thermoanalytical study of lead monohydroxynitrate. *Thermochimica Acta*, **98**, 205–212.
- Graf, H.-W. (1991) Die Grube "Neue Hoffnung" zu Bleialf/Eifel. *Lapis*, **16**(2), 13–18 (in German).
- Grimes, S.M., Johnston, S.R. and Abrahams, I. (1995) Characterisation of the predominant low-pH lead(II)-hydroxo cation, $[\text{Pb}_4(\text{OH})_4]^{4+}$; crystal structure of $[\text{Pb}_4(\text{OH})_4][\text{NO}_3]_4$ and the implications of basic salt formation on the transport of lead in the aqueous environment. *Journal of the Chemical Society, Dalton Transactions*, **1995**, 2081–2086.
- Gyunner, E.A., Tsareva, A.I., Bakina, N.B. and Vel'mozhnyi, I.S. (1978) Reaction of lead nitrate with some bases in aqueous solutions. *Ukrainskii Khimicheskii Zhurnal (Russian edition)*, **44**, 348–352 (in Russian).
- Haag-Bruhl, C., Fuess, H., Lightfoot, P. and Cheetham, A.K. (1988) Preparation and structure of lead oxide hydroxide perrhenate hydrate $(\text{Pb}_6\text{O}(\text{OH})_6(\text{ReO}_4)_4 \cdot \text{H}_2\text{O})$. *Acta Crystallographica*, **C44**, 8–11.
- Hill, R.J. (1985) Structure of $\text{Pb}_5\text{O}_2(\text{OH})_2$ by Rietveld analysis of neutron powder diffraction data. *Acta Crystallographica*, **C41**, 998–1003.
- Hong, S.-H. and Olin, A. (1973) Crystal structure of $[\text{Pb}_4(\text{OH})_4]_3(\text{CO}_3)(\text{ClO}_4)_{10} \cdot 6\text{H}_2\text{O}$. *Acta Chemica Scandinavica*, **27**, 2309–2320.
- Hong, S.-H. and Olin, A. (1974) Crystal structure of $[\text{Pb}_4(\text{OH})_4](\text{ClO}_4)_4(\text{H}_2\text{O})_2$. *Acta Chemica Scandinavica*, **A28**, 233–238.
- Hyde, B.G. and Andersson, S. (1989) *Inorganic Crystal Structures*. Wiley Interscience, New York, 302 pp.
- Johansson, G. and Olin, A. (1968) Structures of the dominating hydrolysis products of lead(II) in solution. *Acta Chemica Scandinavica*, **22**, 3197–3201.
- Keller, H.L. (1982) Darstellung und Kristallstruktur von $\text{TlPb}_8\text{O}_4\text{Br}_9$. *Zeitschrift für Anorganische und Allgemeine Chemie*, **491**, 191–198 (in German).
- Keller, H.L. (1983) Eine neuartige Blei-Sauerstoff-Baugruppe: $(\text{Pb}_8\text{O}_4)^{8+}$. *Angewandte Chemie*, **95**, 318–319 (in German).
- Kolitsch, U. (1997) Neufunde von Mineralien aus einigen Vorkommen der Vogesen, Frankreich: Triembach, Blüttenberg und Val d'Ajol. *Aufschluss*, **48**, 65–91 (in German).
- Kolitsch, U. (2000) Eine durch Betoneinwirkung entstandene Paragenese von Blei-Verbindungen aus der Grube Clara im mittleren Schwarzwald. *Erzgräber*, **14**, 48–53 (in German).
- Kolitsch, U. and Giester, G. (2000) Elyite, $\text{Pb}_4\text{Cu}(\text{SO}_4)\text{O}_2(\text{OH})_4 \cdot \text{H}_2\text{O}$: crystal structure and new data. *American Mineralogist*, **85**, 1816–1821.
- Krivovichev, S.V. and Brown, I.D. (2001) Are the compressive effects of encapsulation an artifact of the bond valence parameters? *Zeitschrift für*

- Kristallographie*, **216**, 245–247.
- Krivovichev, S.V. and Burns, P.C. (2000a) Crystal chemistry of basic lead carbonates. I. Crystal structure of synthetic shannonite, $\text{Pb}_2\text{O}(\text{CO}_3)$. *Mineralogical Magazine*, **64**, 1063–1068.
- Krivovichev, S.V. and Burns, P.C. (2000b) Crystal chemistry of basic lead carbonates. II. Crystal structure of synthetic "plumbonacrite". *Mineralogical Magazine*, **64**, 1069–1075.
- Krivovichev, S.V. and Burns, P.C. (2000c) Crystal chemistry of basic lead carbonates. III. Crystal structures of $\text{Pb}_3\text{O}_2(\text{CO}_3)$ and $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$. *Mineralogical Magazine*, **64**, 1077–1088.
- Krivovichev, S.V. and Filatov, S.K. (1999a) Metal arrays in structural units based on anion-centered metal tetrahedra. *Acta Crystallographica*, **B55**, 664–676.
- Krivovichev, S.V. and Filatov, S.K. (1999b) Structural principles for minerals and inorganic compounds containing anion-centered tetrahedra. *American Mineralogist*, **84**, 1099–1106.
- Krivovichev, S.V., Filatov, S.K. and Semenova, T.F. (1998) Types of cationic complexes based on oxocentred tetrahedra $[\text{OM}_4]$ in the crystal structures of inorganic compounds. *Russian Chemical Reviews*, **67**, 137–155.
- Krivovichev, S.V., Li, Y. and Burns, P.C. (2001) Crystal chemistry of lead oxide hydroxide nitrates. III. The crystal structure of $\text{Pb}_3\text{O}_2(\text{OH})(\text{NO}_3)$. *Journal of Solid State Chemistry*, **158**, 78–81.
- Kwestroo, W., Langereis, C. and van Hal, H.A.M. (1967) Basic lead nitrates. *Journal of Inorganic and Nuclear Chemistry*, **29**, 33–38.
- Li, Y., Krivovichev, S.V. and Burns, P.C. (2000) Crystal chemistry of lead oxide hydroxide nitrates. I. The crystal structure of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$. *Journal of Solid State Chemistry*, **153**, 365–370.
- Li, Y., Krivovichev, S.V. and Burns, P.C. (2001) Crystal chemistry of lead oxide hydroxide nitrates. II. The crystal structure of $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$. *Journal of Solid State Chemistry*, **158**, 74–77.
- Lundgren, G., Wernfors, G. and Yamaguchi, T. (1982) The structure of ditin(II) oxide sulfate. *Acta Crystallographica*, **B38**, 2357–2361.
- Lutz, H.D. and Jung, C. (1997) Lattice vibration spectra. Part XCII. High-pressure Raman spectroscopic studies on laurionite-type $\text{Pb}(\text{OD})\text{Cl}$, $\text{Pb}(\text{OD})\text{Br}$, $\text{Pb}(\text{OD})\text{I}$, and $\text{Sr}(\text{OD})\text{I}$, pressure dependence of the directionality of lone pairs. *European Journal of Solid State and Inorganic Chemistry*, **34**, 1179–1185.
- Lutz, H.D., Beckenkamp, K. and Peter, S. (1995) Laurionite-type $\text{M}(\text{OH})\text{X}$ ($\text{M} = \text{Ba}, \text{Pb}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{Sr}(\text{OH})\text{I}$. An IR and Raman spectroscopic study. *Spectrochimica Acta*, **51A**, 755–767.
- Lutz, H.D., Beckenkamp, K., Kellersohn, T., Moeller, H. and Peter, S. (1996) Neutron and X-ray structure determination of laurionite-type $\text{Pb}\{\text{O}(\text{H},\text{D})\}\text{X}$, with $\text{X} = \text{Cl}, \text{Br}$, and I , hydrogen bonds to lead(II) ions as a hydrogen-bond acceptor. *Journal of Solid State Chemistry*, **124**, 155–161.
- Martin, J.J.P., Martin-Lefevre, C., Repelin, Y. and Husson, E. (1972a) Lead oxynitrates. Thermal analysis of hydrated lead heptoxynitrate. *Bulletin de la Société Chimique de France*, **1972**, 3341–3342 (in French).
- Martin, J.J.P., Martin-Lefevre, C. and Despagne, B. (1972b) Lead oxynitrates. Thermal analysis of hydrated lead pentoxynitrate. *Bulletin de la Société Chimique de France*, **1972**, 2573–2574 (in French).
- Michell, E.W.J. (1974) Basic lead nitrates. I. Compounds formed by reaction of orthorhombic lead monoxide with cold aqueous lead nitrate. *Journal of Applied Chemical Biotechnology*, **24**, 571–581.
- Moore, E.P., Chen, H.Y., Brixner, L.H. and Foris, C.M. (1982) The crystal structure of $\text{Pb}_8\text{Bi}_2(\text{PO}_4)_6\text{O}_2$. *Materials Research Bulletin*, **17**, 653–660.
- Nardin, G., Randaccio, L. and Zangrando, E. (1995) Lead clustering in a zeolite X. *Zeolites*, **15**, 684–688.
- Narita, E., Okayasu, H. and Naito, H. (1984) The formation and solubility of various lead(II) compounds prepared by the hydrolysis of lead(II) nitrate. *Bulletin of the Chemical Society of Japan*, **57**, 309–310.
- Newkirk, A.E. and Hughes, V.B. (1970) Identification of the "lead(II) hydroxide" of Robin and Theolier. *Inorganic Chemistry*, **9**, 401–404.
- O'Keefe, M. and Hyde, B.G. (1985) An alternative approach to non-molecular crystal structures with emphasis on the arrangements of cations. *Structure and Bonding*, **61**, 77–144.
- Olin, A. and Söderquist, R. (1972) Crystal structure of β -lead hydroxide oxide perchlorate hydrate (β - $[\text{Pb}_6\text{O}(\text{OH})_6](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$). *Acta Chemica Scandinavica*, **26**, 3505–3514.
- Otwinowski, Z. and Minor, W. (1997) Processing of X-ray diffraction data collected in oscillation mode. *Methods in Enzymology*, **276**, 307–326.
- Pauley, J.L. and Testerman, M.K. (1954) Basic salts of lead nitrate formed in aqueous media. *Journal of the American Chemical Society*, **76**, 4220–4222.
- Pyykkö, P. (1997) Strong closed-shell interactions in inorganic chemistry. *Chemical Reviews*, **97**, 597–636.
- Ronay, C. and Seff, K. (1993) Lead oxide hydroxide clusters in lead hydroxide oxide ($\text{Pb}_9\text{O}(\text{OH})_4$)-A, zeolite A exchanged with Pb^{2+} at pH 6.0. *Zeolites*, **13**, 97–101.
- Rouse, R.C. and Peacor, D.R. (1994) Maricopaite, an unusual lead calcium zeolite with an interrupted

- mordenite-like framework and intrachannel Pb_4 tetrahedral clusters. *American Mineralogist*, **79**, 175–184.
- Schlomann, C. and Steen, H. (1990) Neue Mineralfunde aus dem Bergbauggebiet von Badenweiler im Südschwarzwald. *Lapis*, **15**(12), 13–20; 50 (in German).
- Shape Software (1999) *ATOMS for Windows and Macintosh V5.0.4*. Kingsport, TN 37663, USA.
- Sheldrick, G.M. (1997a) *SHELXS-97, a program for the solution of crystal structures*. University of Göttingen, Germany.
- Sheldrick, G.M. (1997b) *SHELXL-97, a program for crystal structure refinement*. University of Göttingen, Germany.
- Spek, A.L. (2001) *PLATON, a multipurpose crystallographic tool*. Utrecht University, Utrecht, The Netherlands.
- Spiro, T.G., Templeton, D.H. and Zalkin, A. (1969) Crystal structure of a hexanuclear basic lead(II) perchlorate hydrate: $\text{Pb}_6\text{O}(\text{OH})_6(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$. *Inorganic Chemistry*, **8**, 856–861.
- Sterns, M., Parise, J.B. and Howard, C.J. (1986) Refinement of the structure of trilead(II) uranate(VI) from neutron powder diffraction data. *Acta Crystallographica*, **C42**, 1275–1277.
- Stieglitz, H. and Metz, W. (1989) Die Mineralien der Grube Churfürst Ernst in Bönkhausen. *Lapis*, **14**(2), 22–27, 33, 42 (in German).
- Sugiyama, S., Nakanishi, T., Ishimura, T., Moriga, T., Hayashi, H., Shigemoto, N. and Moffat, J.B. (1999) Preparation, characterization, and thermal stability of lead hydroxyapatite. *Journal of Solid State Chemistry*, **143**, 296–302.
- Tsai, P. and Cooney, R.P. (1976) Raman spectra of polynuclear hydroxo-compounds of lead(II) chloride. *Journal of the Chemical Society, Dalton Transactions*, **1976**, 1631–1634.
- Uchida, M., Minakata, N. and Okuwaki, A. (1997) Recovery of ammonia and nitrate ion from ammonium nitrate in wastewater by steam distillation adding lead(II) oxide. *Hydrometallurgy*, **45**, 239–247.
- Walenta, K. (1998) Neue Mineralfunde aus dem Schwarzwald. 7. Folge, 2. Teil. *Lapis*, **23**(12), 43–48 (in German).
- Werner, J.P. and Müller-Buschbaum, H. (1997) Elektroneutrale Pb_4O_4 -Heterokubaneinheiten in den Aluminatsodalithen $\text{Ln}_4[\text{Al}_{12}\text{O}_{24}](\text{Pb}_4\text{O}_4)_2$ (Ln = Nd, Sm). *Zeitschrift für Naturforschung*, **B52**, 449–452 (in German).
- Wittern, A. (1994) Sekundärminerale durch Feuersetzen in Oberschulenberg, Bönkhausen, Bleialf und Badenweiler. *Aufschluss*, **45**, 36–42 (in German).
- Yeom, Y.H., Kim, Y. and Seff, K. (1997) Crystal structure of zeolite X exchanged with Pb(II) at pH 6.0 and dehydrated: $(\text{Pb}^{4+})_{14}(\text{Pb}^{2+})_{18}(\text{Pb}_4\text{O}_4)_8 \text{Si}_{100}\text{Al}_{92}\text{O}_{384}$. *Journal of Physical Chemistry*, **B101**, 5314–5318.
- Yeom, Y.H., Kim, Y. and Seff, K. (1999) Crystal structure of $\text{Pb}^{2+}_{44}\text{Pb}^{4+}_5\text{Ti}^+_{18}\text{O}^{2-}_{17}-\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$, zeolite X exchanged with Pb^{2+} and Ti^+ and dehydrated, containing $\text{Pb}_4\text{O}_4(\text{Pb}^{2+}, \text{Pb}^{4+} \text{ mixed})_4$ clusters. *Microporous and Mesoporous Materials*, **28**, 103–112.

[Manuscript received 20 April 2001;
revised 17 December 2002]