

Details of interatomic distances and bond angles in these groups are reported in Table 2. They have no internal symmetry. Mixed layers containing both Cs atoms and water molecules correspond to  $z \sim 3n/12$  and  $(3n + 1)/12$ . Caesium coordination polyhedra located in layers separated by  $c/12$  share O atoms while between two layers separated by  $c/6$  only water molecules are shared. Cs—O distances in the various caesium polyhedra are given in Table 2.

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## Structure Refinement of Lead Nitrate

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**Abstract.**  $\text{Pb}(\text{NO}_3)_2$ ,  $M_r = 331.20$ , cubic,  $Pa3$ ,  $a = 7.8586(2) \text{ \AA}$ ,  $V = 485.33 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 4.535 \text{ Mg m}^{-3}$ , neutrons,  $\lambda = 0.8313(9) \text{ \AA}$ ,  $\mu = 0.0015 \text{ mm}^{-1}$ , room temperature. The atomic arrangement was refined with single-crystal neutron diffraction data to  $R = 0.019$  for 297 reflections. The structure is built up by a cubic face-centred-type arrangement of  $\text{Pb}^{2+}$  ions with nitrate groups in between. The N—O bond length (uncorrected for thermal vibration) is  $1.2469(6) \text{ \AA}$ , the deviation of the N atom from the  $\text{O}_3$  plane is  $0.0102(7) \text{ \AA}$ . The amplitudes of the thermal vibrations have normal values.

**Introduction.** In connection with recent structural work on  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Sr}(\text{NO}_3)_2$  (Nowotny & Heger, 1983) it seemed interesting to refine also the structure of  $\text{Pb}(\text{NO}_3)_2$  from carefully measured single-crystal neutron diffraction data. The structure of  $\text{Pb}(\text{NO}_3)_2$  was determined by Vegard & Bilberg (1931) from X-ray powder data and by Hamilton (1957) from

neutron powder data assuming space group  $Pa3$ . Weber & Haussühl (1977) found this space group compatible with careful determinations of physical properties, but Arkhipenko, Bokiy, Fyodorova & Shebanin (1983) recently reported space group  $P2_13$  for this compound.

**Experimental.** A single crystal of  $\text{Pb}(\text{NO}_3)_2$  (grown from aqueous solution at about 320 K, size approximately  $1.8 \times 2.9 \times 3.0 \text{ mm}$ ) was mounted on the  $P110$  neutron four-circle diffractometer at the 5C2 beam of the ORPHEE reactor at CEN Saclay (France) [wavelength, according to the lattice constant  $a = 7.8586(2) \text{ \AA}$  (Swanson, Gilfrich & Ugrinic, 1955),  $0.8313(9) \text{ \AA}$ ]. Before the measurements the crystal was quenched in liquid nitrogen (Heger & Kuhs, 1979). The remaining extinction effects had to be corrected in the structure refinement.

1296 reflections with  $\sin\theta/\lambda \leq 0.8 \text{ \AA}^{-1}$  were measured of which 195 were 'forbidden' reflections in space group  $Pa3$ ; range of  $hkl$ :  $0 \leq h \leq 12$ ,  $-12 \leq k \leq 0$ ,  $0 \leq l \leq 12$ . Standard reflection: 006, mean intensity measured 2995.12 counts,  $\sigma$  (calculated from counting statistics) 5.12.

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The intensities of the 195 'forbidden' reflections were found to describe very well a normal distribution with a mean of about zero [mean for 195  $I/\sigma(I)$ : 0.211, standard deviation: 1.266; omitting one reflection with  $I/\sigma(I) = 12.4$ † leads to a mean of 0.148 and a standard deviation of 0.917]. Fig. 1 shows a normal probability plot for 194 values of  $I/\sigma(I)$  for the reflections 'forbidden' in space group  $Pa3$ .‡ These 195 reflections, which fit into the distribution of all measured reflections, were then excluded from the following calculations.

Therefore, there is no indication against space group  $Pa3$  within the observed range by the occurrence of any reflections in contradiction to symmetry. Besides, a value of  $2.0\sigma(I)$  is confirmed as a (rather low) threshold for observed reflection intensities. [The maximum of the observed intensities was about  $100 \times \sigma(I)$ .]

Remaining data averaged to give 334 unique reflections ( $R_{\text{int}} = 0.026$ ) of which 310 had  $I > 2\sigma(I)$ . Structure refinement performed (on  $F$ ) with *RFINE4* (Finger & Prince, 1975), using anisotropic thermal parameters for all atoms and an isotropic extinction correction [ $r^* = 0.11 (5) \times 10^{-6}$ ], and converged to give  $R = 0.019$  ( $wR = 0.015$ ) for 297 accepted (criterion:  $w|F_o - F_c| \leq \Delta F_{\text{max}}$ ) reflections [ $R = 0.034$  ( $wR =$

† The 003 reflection showed an intensity of 99 (8) counts, while the equivalent 030 and 300 had 7 (4) and 9 (4) respectively. A similar phenomenon occurs at the (not 'forbidden') reflections  $\overline{10}, 0, 0$ ,  $0, \overline{10}, 0$ ,  $0, 0, 10$ , and  $10, 0, 0$  with intensities 0 (10), 10 (8), 294 (16), and 16 (7), respectively.

‡ As the results of repeated measurements are expected to resemble a normal distribution around a 'true' value, intensity calculation, which was performed in principle as subtracting 'background' from 'peak' counts, resulted in both negative and positive intensities with low absolute values within the distribution around zero (not dependent on whether the reflection was 'forbidden' or not).

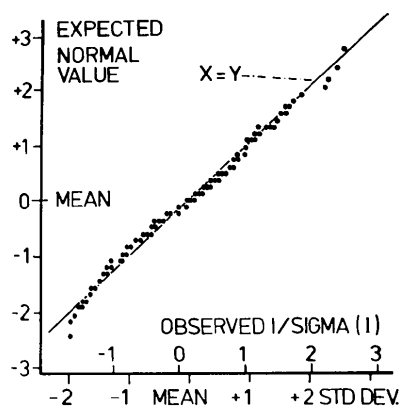


Fig. 1. Normal plot for 194 'forbidden' reflections expressed in units of mean [ $0.148I/\sigma(I)$ ] and standard deviation [ $0.917I/\sigma(I)$ ]. Units of  $I/\sigma(I)$  are given additionally on the horizontal axis. (One point may mean more than one reflection.)

0.037) for all 334 reflections]\* and 16 variables. There was no need to apply an absorption correction (see *Abstract*). Neutron scattering lengths from Koester (1977). Parameters for weighting scheme chosen to give a balanced error distribution [ $p = 0.0103$ ,  $\Delta F_{\text{max}} = 3.0$ , for details see Nowotny & Heger (1983)].  $(\Delta/\sigma)_{\text{max}}$  in final cycle  $-0.04$ ,  $(\Delta/\sigma)_{\text{av}}$  0.02. CDC Cyber 170-720 computer at the Interuniversitäres EDV-Zentrum of the University of Vienna used for the refinement.

The use of an anisotropic extinction correction caused no significant changes of the structure parameters.

The final refined parameters (based on isotropic extinction correction) are given in Table 1. [As similar corrections – using in fact the same refinement program – were applied, they are comparable with the structure parameters of  $\text{Sr}(\text{NO}_3)_2$  and  $\text{Ba}(\text{NO}_3)_2$  (Nowotny & Heger, 1983).]

Merging and suitable preparation of the data were performed by programs newly written by one of us (HN), intensity statistics and intensity-data overview calculations by *BMDP* (Dixon, 1981), and geometrical calculations by *KRISTALLCHEMIE* (Nowotny & Zobetz, 1984).

**Discussion.** The interatomic distances and angles are given in Table 2. Data relating to space-filling polyhedra and coordination [closely related to those for  $\text{Sr}(\text{NO}_3)_2$  and  $\text{Ba}(\text{NO}_3)_2$ ] are given in Table 3.

The structure is built up by a cubic face-centred-type arrangement of  $\text{Pb}^{2+}$  ions with nitrate groups in between (perpendicular to threefold axes), resulting in a cuboctahedral twelve-coordination of O around Pb. Six of the 24 edges of this distorted cuboctahedron are remarkably shorter than the others; these are joined edges with nitrate groups [for a more detailed description and discussion of the structure type, see Nowotny & Heger (1983)].

As the nitrates of Sr, Pb, and Ba are isotopic with relatively small differences of the lattice constants  $a$ , one might suspect a more or less linear relation between the atomic coordinates of these substances. In fact, the structural parameters obtained for  $\text{Pb}(\text{NO}_3)_2$  (the cell dimensions of which are intermediate between the two others) differ slightly from those expected from such a linear interpolation and look closely related to those of  $\text{Sr}(\text{NO}_3)_2$ .

The N–O bond length within the nitrate group [ $1.2469 (6) \text{ \AA}$ ] is practically the same; the deviation of the N atom out of the plane of the O atoms of the nitrate group ['height' of the 'nitrate pyramid' =

\* Lists of structure factors and an analysis of the anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42467 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters

Occupied positions [after *International Tables for X-ray Crystallography* (1952)]: Pb 4(a), N 8(c), O 24(d).

Pb: $x = y = z$	0	O: $x$	0.27772 (8)
$\beta_{ii}$	0.00648 (5) Å <sup>2</sup>	$y$	0.28869 (8)
$\beta_{ij}$	0.00004 (5)	$z$	0.47730 (7)
N: $x = y = z$	0.34865 (4)	$\beta_{11}$	0.01139 (8) Å <sup>2</sup>
$\beta_{ii}$	0.00643 (5) Å <sup>2</sup>	$\beta_{22}$	0.01076 (8)
$\beta_{ij}$	0.00027 (4)	$\beta_{33}$	0.00717 (7)
		$\beta_{12}$	0.00246 (6)
		$\beta_{13}$	0.00272 (6)
		$\beta_{23}$	0.00210 (6)

The temperature factor is of the form  
 $T = \exp[h^2\beta_{11} + \dots + 2hk\beta_{12} + \dots]$ .

Table 2. Selected interatomic distances (Å) and angles (°)

$t$ : type of Pb—O distance(s) defined by first occurrence in table. Because of the point symmetry of the Pb position the 12 surrounding O atoms build up a 6 + 6 coordination with two different types ( $a$ ,  $b$ ) of Pb—O distances within each PbO<sub>12</sub> polyhedron.

$r$ : remark.

$n$ : number of equivalent values.

	$t$	$r$	$n$
PbO <sub>12</sub> polyhedron			
Pb—O	$a$		6
Pb—O	$b$		6
Pb—N			6
O—O	$a, b$	1	6
O—O	$b, b$	2	6
O—O	$a, a$	2	6
O—O	$a, b$	2	6
O—O	$a, b$	3	6
Nitrate group			
N—O			3
O—O			3
O—N—O			3
Short N—N distances			
N—N		4	1
N—N		5	6

Remarks: (1) Joined edge between cuboctahedron around Pb and nitrate group. (2) Edge of cuboctahedron. (3) Closest O—O distance not within the same coordination polyhedron. (4) *Via* centre of symmetry (on the same threefold axis). (5) Nearest N neighbours not on the same threefold axis.

Table 3. Data for space-filling polyhedra (based on equal radii for all atoms) and coordination

	Pb	N	O
Coordination numbers			
Referred to greatest gap ( $Ad/d$ )	18	3	1
Referred to Hoppe (1970)	11.0	3.6	4.8
Referred to O'Keeffe (1979)	10.8	3.3	3.3
Space-filling polyhedra			
Total number of faces (n.o.f.)	12	16	21
N.o.f. > 1% of greatest face	12	10	15
N.o.f. > 10% of greatest face	12	7	12
Volume (Å <sup>3</sup> )	15.905	7.315	15.132
Faces of space-filling polyhedron around Pb			
N.o.f.	Superficial area (Å <sup>2</sup> )	Normalized superficial area (%)	
6	3.108	100.0	
6	2.567	82.6	

0.010 (1) Å] remains very low (see Jarosch & Zemann, 1983) but is approximately twice the value determined for the two isotopic nitrates [*i.e.* 0.006 (1) and 0.005 (1) Å]. This is the most significant difference between these closely related structures and may indicate a difference in the metal—O bond between Pb and the alkaline-earth metals Sr and Ba.

The metal—O and O—O distances have intermediate values. The r.m.s. amplitudes (obtained from the anisotropic temperature factors) are approximately 16% greater than for the corresponding Sr and Ba compounds. The shape of the thermal vibration ellipsoid is nearly spherical for Pb and N and clearly anisotropic for O (the longest axes of the ellipsoids are 1%, 6%, and 63% longer than the shortest axes). As in Ba(NO<sub>3</sub>)<sub>2</sub>, the longest axis of the ellipsoid for O points approximately perpendicular to the plane defined by the O atoms of the nitrate group. So the suggestion of a remarkably large oscillation (libration) of the nitrate group as a whole around the N atom (Hamilton, 1957) is not confirmed.

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