Dilead(II) hydrogenphosphite dinitrate

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In the title compound, $Pb_2(HPO_3)(NO_3)_2$, the two distinct Pb^{2+} ions (both with site symmetry m) adopt irregular PbO_{10} coordination polyhedra. The structure is completed by two distinct nitrate groups (in which one O atom and the N atom have m site symmetry for both ions) and an HPO_3^{2-} anion (in which one O atom and the P and H atoms have m site symmetry). The connectivity of the PbO_{10}, NO_3 and HPO_3 units in the crystal structure results in a three-dimensional network.

Related literature

For related structures, see: Ouarsal *et al.* (2005*a*,*b*); Vasić *et al.* (1981). For bond-valence sum calculations, see: Brown & Altermatt (1985).

Experimental

Crystal data

$Pb_2(HPO_3)(NO_3)_2$	$V = 404.94\ (4)$ Å³
$M_r = 618.4$	$Z = 2$
Orthorhombic, $Pmn2_1$	Mo $K\alpha$ radiation
$a = 5.4069\ (2)$ Å	$\mu = 41.76$ mm⁻¹
$b = 10.4079\ (6)$ Å	$T = 120$ K
$c = 7.1958\ (4)$ Å	$0.25 \times 0.10 \times 0.05$ mm

Data collection

Oxford Diffraction CCD diffractometer	6814 measured reflections
	932 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)	919 reflections with $I > 3\sigma(I)$
	$R_{int} = 0.026$
$T_{min} = 0.013$, $T_{max} = 0.156$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.012$	Only H-atom coordinates refined
$wR(F^2) = 0.030$	$\Delta\rho_{max} = 0.94$ e Å⁻³
$S = 1.25$	$\Delta\rho_{min} = -0.53$ e Å⁻³
932 reflections	Absolute structure: Flack (1983), with 431 Friedel pairs
78 parameters	Flack parameter: 0.01 (1)
1 restraint	

Table 1
Selected bond lengths (Å).

Pb1—O1	2.346 (6)	Pb2—O2^v	2.7756 (11)
Pb1—O1^i	3.042 (3)	Pb2—O3^{ii}	2.513 (4)
Pb1—O3^{ii}	2.418 (4)	Pb2—O4^{ii}	2.707 (4)
Pb1—O4^{iii}	2.884 (4)	Pb2—O5^{vi}	2.782 (4)
Pb1—O6^{iv}	2.881 (7)	Pb2—O5^{vii}	2.948 (4)
Pb1—O6^i	3.168 (4)		

Symmetry codes: (i) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$; (ii) $-x + 1, y, z$; (iii) $x - \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (iv) $x, y, z - 1$; (v) $x + 1, y + 1, z$; (vi) $x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (vii) $-x, y + 1, z$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006*.

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supplementary materials

Dilead(II) hydrogenphosphite dinitrate

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Comment

As part of our ongoing structural stuides of metal hydrogenphosphites (Ouarsal *et al.* 2005*a*,*b*) we now report on the preparation and crystal structure of the title compound, (I).

The structure of (I) consists of two symmetry-independent nitrate groups and one HPO_3 hydrogenphosphite tetrahedron. The Pb atoms are located between them in two different crystallographic positions, both of them being irregularly coordinated by ten O atoms (Fig. 1). In the coordination of Pb1, shorter bonds occur causing larger bond valence sum (Brown & Altermatt, 1985) [2.028 (10) and 1.917 (6) for $Pb(1)O_{10}$ and $Pb(2)O_{10}$, respectively]. On the other hand, the mean Pb—O distance is rather larger in $Pb(1)O_{10}$ than in $Pb(2)O_{10}$, respectively 2.835 (5) Å and 2.745 (6) Å. These values are comparable to those reported in $Pb(H_2PO_4)_2$, 2.617 Å (Vasić *et al.*, 1981). One can distinguish the two decahedrons by their respective coordination forms: one monodentate NO_3 and one monodentate HPO_3 occurs in the coordination of Pb1, while two bidentate NO_3 contribute to that of Pb2. Accordingly, the polyhedron $Pb(1)O_{10}$ turns to be more distorted as $Pb(2)O_{10}$.

$Pb_2(HPO_3)(NO_3)_2$ is characterized by a three-dimensional network. Although this is not a layer structure it is convenient from the explanatory point of view to distinguish two layers as indicated in Fig. 2. The slightly rotated view of a layer along [100] (Fig. 3) reveals strips extended in the c directions that are not interconnected within the same layer. Their connection in the b direction is mediated *via* the neighbouring layer which is shifted so that its Pb atoms fall into the holes. The shortest Pb—O bonds participate in the connection of the two PbO_{10} units and in the bond towards the HPO_3 tetrahedron. As expected, H1 atom bonded to P is not involved in any hydrogen bonding. Average P—O distance and O—P—O and H—P—O angles are 1.531 (5) Å, 110.4 (2)° and 108.6 (2)° respectively. $d_{P—H}$ = 1.20 (5) Å. These values lie in the same range as the ones previously reported in known phosphites (Ouarsal *et al.* 2005*b*).

Experimental

1.6161 g lead nitrate $Pb(NO_3)_2.6H_2O$ was dissolved in 6 ml of distilled water and added to a solution of 0.4 g phosphorous acid H_3PO_3, dissolved in 5 ml water. The mixture was stirred for 1 h at 333 K, after which time the precipitate obtained was filtered out of the solution. The filtrate was allowed to stand at room temperature until many large, colourless needles of (I) arose. The crystals were recovered by filtration and washed with a water–ethanol (80:20 v/v) mixture.

Refinement

The H atom was located in a difference map and its position and U_{iso} values were freely refined.

supplementary materials

Figures
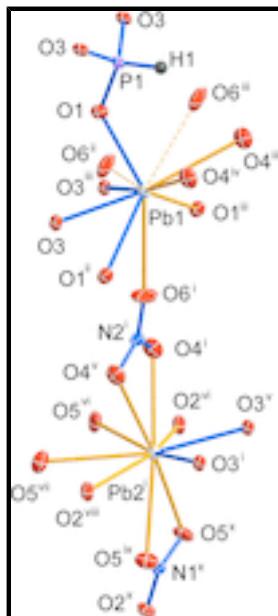
Fig. 1. A view of the asymmetric unit and some symmetry-related atoms of (I) showing 60% probability displacement ellipsoids. The various bonds lengths are distinguished by colours and style: indigo-thick up to 2.514 Å, yellow-thick from 2.707 Å to 3.042 Å, yellow-thin-dashed for 3.168 Å. [Symmetry codes: (i) x, y, -1 + z; (ii) 1/2 - x, 1 - y, -1/2 + z; (iii) 3/2 - x, 1 - y, -1/2 + z; (iv) -1/2 - x, 1 - y, -1/2 + z; (v) 1 - x, y, -1 + z; (vi) 1 + x, 1 + y, -1 + z; (vii) -x, 1 + y, -1 + z; (viii) x, 1 + y, -1 + z; (ix) 1/2 + x, 1 - y, -3/2 + z; (x) 1/2 - x, 1 - y, -3/2 + z]
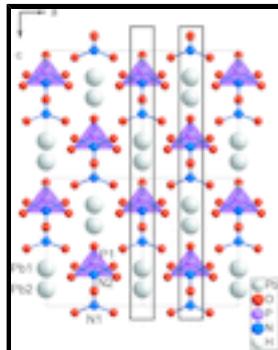
Fig. 2. A view of the structure of the title compound along [010]. The HPO_3 groups are indicated as pink tetraedra. The bonds to Pb are omitted for clarity. The black thick rectangles denote the layers that will be plotted in more details in Fig. 3.
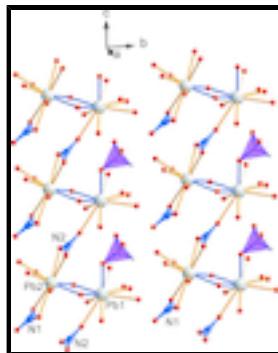
Fig. 3. The layers indicated in Fig. 2 in a view along the a direction. The first layer (grey, blue and red atoms) is plotted together with all coordinated O atoms. The various bonds lengths are distinguished by the same way as in Fig. 1.

Dilead(II) hydrogenphosphite dinitrate

Crystal data

$Pb_2(HPO_3)(NO_3)_2$ $F(000) = 532$

$M_r = 618.4$ $D_x = 5.070$ Mg m^{-3}

Orthorhombic, $Pmn2_1$

Hall symbol: P 2ac -2

$a = 5.4069$ (2) Å

$b = 10.4079$ (6) Å

$c = 7.1958$ (4) Å

$V = 404.94$ (4) Å^3

$Z = 2$

Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å

Cell parameters from 6814 reflections

$\theta = 3.4–26.5°$

$\mu = 41.76$ mm^{-1}

$T = 120$ K

Plate, colourless

$0.25 \times 0.10 \times 0.05$ mm

Data collection

Oxford Diffraction CCD diffractometer

Radiation source: X-ray tube

graphite

Detector resolution: 8.3438 pixels mm^{-1}

Rotation method data acquisition using ω scans

Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)

$T_{min} = 0.013$, $T_{max} = 0.156$

6814 measured reflections

932 independent reflections

919 reflections with $I > 3\sigma(I)$

$R_{int} = 0.026$

$\theta_{max} = 26.5°$, $\theta_{min} = 3.4°$

$h = -6 \rightarrow 6$

$k = -13 \rightarrow 13$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.012$

$wR(F^2) = 0.030$

$S = 1.25$

932 reflections

78 parameters

1 restraint

1 constraint

Only H-atom coordinates refined

Weighting scheme based on measured s.u.'s $w = 1/[\sigma^2(I) + 0.0004I^2]$

$(\Delta/\sigma)_{max} = 0.013$

$\Delta\rho_{max} = 0.94$ e Å^{-3}

$\Delta\rho_{min} = -0.53$ e Å^{-3}

Extinction correction: B-C type 1 Lorentzian isotropic (Becker & Coppens, 1974)

Extinction coefficient: 48 (5)

Absolute structure: Flack (1983), with 431 Friedel pairs

Flack parameter: 0.01 (1)

Special details

Refinement. The refinement was carried out against all reflections. The conventional R-factor is always based on F. The goodness of fit as well as the weighted R-factor are based on F and F^2 for refinement carried out on F and F^2, respectively. The threshold expression is used only for calculating R-factors *etc*. and it is not relevant to the choice of reflections for refinement.

The program used for refinement, JANA2000, uses the weighting scheme based on the experimental expectations, see _refine_ls_weighting_details, that does not force S to be one. Therefore the values of S are usually larger then the ones from the *SHELX* program.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Pb1	0.5	0.47428 (2)	0.20948	0.01003 (7)
Pb2	0.5	0.84356 (2)	0.37011 (5)	0.01002 (8)
O1	0.5	0.4667 (5)	0.5354 (8)	0.0147 (15)
P1	0.5	0.34607 (15)	0.6573 (3)	0.0083 (5)
N1	0	−0.0035 (6)	0.4972 (8)	0.0103 (17)
O2	0	−0.0975 (5)	0.3893 (8)	0.0155 (14)
N2	0.5	0.7144 (6)	0.7547 (8)	0.0134 (18)
O3	0.2358 (7)	0.6561 (4)	0.2748 (5)	0.0109 (10)
O4	0.7011 (7)	0.7548 (3)	0.6898 (6)	0.0205 (11)
O5	−0.2007 (7)	0.0434 (3)	0.5539 (6)	0.0194 (11)
O6	0.5	0.6317 (6)	0.8801 (10)	0.033 (2)
H1	0.5	0.248 (4)	0.568 (10)	0.0099*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.00890 (14)	0.01098 (13)	0.01022 (12)	0	0	−0.00077 (12)
Pb2	0.00891 (15)	0.01137 (12)	0.00978 (12)	0	0	−0.00032 (9)
O1	0.012 (3)	0.020 (2)	0.013 (2)	0	0	0.002 (2)
P1	0.0048 (9)	0.0110 (8)	0.0091 (9)	0	0	0.0017 (5)
N1	0.011 (3)	0.013 (2)	0.007 (3)	0	0	0.000 (2)
O2	0.012 (3)	0.015 (2)	0.019 (2)	0	0	−0.006 (2)
N2	0.019 (4)	0.011 (3)	0.010 (3)	0	0	0.000 (2)
O3	0.0055 (18)	0.0151 (16)	0.0123 (17)	−0.0002 (15)	0.0003 (14)	−0.0033 (11)
O4	0.0123 (19)	0.0226 (16)	0.027 (2)	−0.0012 (15)	−0.0004 (16)	0.0012 (17)
O5	0.013 (2)	0.0235 (17)	0.0222 (16)	0.0054 (16)	0.0001 (18)	−0.0102 (17)
O6	0.049 (4)	0.030 (3)	0.019 (3)	0	0	0.015 (3)

Geometric parameters (Å, °)

Pb1—O1	2.346 (6)	Pb2—O4^{iii}	2.707 (4)
Pb1—O1^{i}	3.042 (3)	Pb2—O5^{vii}	2.948 (4)
Pb1—O1^{ii}	3.042 (3)	Pb2—O5^{i}	2.782 (4)
Pb1—O3	2.418 (4)	Pb2—O5^{viii}	2.782 (4)
Pb1—O3^{iii}	2.418 (4)	Pb2—O5^{ix}	2.948 (4)
Pb1—O4^{ii}	2.884 (4)	P1—O1	1.532 (6)
Pb1—O4^{iv}	2.884 (4)	P1—O3^{x}	1.530 (4)
Pb1—O6^{v}	2.881 (7)	P1—O3^{xi}	1.530 (4)
Pb1—O6^{i}	3.168 (4)	P1—H1	1.20 (5)
Pb1—O6^{ii}	3.168 (4)	N1—O2	1.249 (8)
Pb2—O2^{vi}	2.7756 (11)	N1—O5	1.258 (5)
Pb2—O2^{vii}	2.7756 (11)	N1—O5^{xii}	1.258 (5)

Pb2—O3	2.513 (4)	N2—O4	1.255 (5)
Pb2—O3^{iii}	2.513 (4)	N2—O4^{iii}	1.255 (5)
Pb2—O4	2.707 (4)	N2—O6	1.247 (9)
O1—Pb1—O1^{i}	114.73 (10)	O2^{vii}—Pb2—O5^{i}	64.37 (14)
O1—Pb1—O1^{ii}	114.73 (10)	O2^{vii}—Pb2—O5^{viii}	109.11 (14)
O1—Pb1—O3	80.31 (13)	O2^{vii}—Pb2—O5^{ix}	110.88 (13)
O1—Pb1—O3^{iii}	80.31 (13)	O3—Pb2—O3^{iii}	69.28 (12)
O1—Pb1—O4^{ii}	91.22 (13)	O3—Pb2—O4	101.25 (12)
O1—Pb1—O4^{iv}	91.22 (13)	O3—Pb2—O4^{iii}	74.85 (12)
O1—Pb1—O6^{v}	147.26 (18)	O3—Pb2—O5^{vii}	169.07 (12)
O1—Pb1—O6^{i}	66.48 (13)	O3—Pb2—O5^{i}	109.08 (12)
O1—Pb1—O6^{ii}	66.48 (13)	O3—Pb2—O5^{viii}	83.30 (11)
O1^{i}—Pb1—O1^{ii}	125.41 (13)	O3—Pb2—O5^{ix}	110.97 (11)
O1^{i}—Pb1—O3	52.92 (13)	O3^{iii}—Pb2—O4	74.85 (12)
O1^{i}—Pb1—O3^{iii}	116.57 (13)	O3^{iii}—Pb2—O4^{iii}	101.25 (12)
O1^{i}—Pb1—O4^{ii}	130.14 (13)	O3^{iii}—Pb2—O5^{vii}	110.97 (11)
O1^{i}—Pb1—O4^{iv}	69.42 (12)	O3^{iii}—Pb2—O5^{i}	83.30 (11)
O1^{i}—Pb1—O6^{v}	63.03 (9)	O3^{iii}—Pb2—O5^{viii}	109.08 (12)
O1^{i}—Pb1—O6^{i}	58.09 (14)	O3^{iii}—Pb2—O5^{ix}	169.07 (12)
O1^{i}—Pb1—O6^{ii}	171.25 (15)	O4—Pb2—O4^{iii}	47.35 (12)
O1^{ii}—Pb1—O3	116.57 (13)	O4—Pb2—O5^{vii}	68.85 (11)
O1^{ii}—Pb1—O3^{iii}	52.92 (13)	O4—Pb2—O5^{i}	133.06 (12)
O1^{ii}—Pb1—O4^{ii}	69.42 (12)	O4—Pb2—O5^{viii}	174.94 (11)
O1^{ii}—Pb1—O4^{iv}	130.14 (13)	O4—Pb2—O5^{ix}	94.59 (12)
O1^{ii}—Pb1—O6^{v}	63.03 (9)	O4^{iii}—Pb2—O5^{vii}	94.59 (12)
O1^{ii}—Pb1—O6^{i}	171.25 (15)	O4^{iii}—Pb2—O5^{i}	174.94 (11)
O1^{ii}—Pb1—O6^{ii}	58.09 (14)	O4^{iii}—Pb2—O5^{viii}	133.06 (12)
O3—Pb1—O3^{iii}	72.44 (12)	O4^{iii}—Pb2—O5^{ix}	68.85 (11)
O3—Pb1—O4^{ii}	171.11 (12)	O5^{vii}—Pb2—O5^{i}	81.63 (12)
O3—Pb1—O4^{iv}	109.00 (12)	O5^{vii}—Pb2—O5^{viii}	106.42 (11)
O3—Pb1—O6^{v}	73.43 (14)	O5^{vii}—Pb2—O5^{ix}	66.57 (11)
O3—Pb1—O6^{i}	72.12 (14)	O5^{i}—Pb2—O5^{viii}	45.92 (11)
O3—Pb1—O6^{ii}	134.56 (15)	O5^{i}—Pb2—O5^{ix}	106.42 (11)
O3^{iii}—Pb1—O4^{ii}	109.00 (12)	O5^{viii}—Pb2—O5^{ix}	81.63 (12)
O3^{iii}—Pb1—O4^{iv}	171.11 (12)	Pb1—O1—P1	126.8 (3)
O3^{iii}—Pb1—O6^{v}	73.43 (14)	O1—P1—O3^{x}	109.20 (18)
O3^{iii}—Pb1—O6^{i}	134.56 (15)	O1—P1—O3^{xi}	109.20 (18)
O3^{iii}—Pb1—O6^{ii}	72.12 (14)	O1—P1—H1	113 (3)
O4^{ii}—Pb1—O4^{iv}	68.18 (11)	O3^{x}—P1—O3^{xi}	112.8 (2)
O4^{ii}—Pb1—O6^{v}	115.45 (13)	O3^{x}—P1—H1	106.4 (16)
O4^{ii}—Pb1—O6^{i}	102.09 (13)	O3^{xi}—P1—H1	106.4 (16)

O4^{ii}—Pb1—O6^{ii}	41.64 (14)	O2—N1—O5	120.4 (3)
O4^{iv}—Pb1—O6^{v}	115.45 (13)	O2—N1—O5^{xii}	120.4 (3)
O4^{iv}—Pb1—O6^{i}	41.64 (14)	O5—N1—O5^{xii}	119.3 (5)
O4^{iv}—Pb1—O6^{ii}	102.09 (13)	Pb2^{xiii}—O2—Pb2^{xiv}	153.8 (2)
O6^{v}—Pb1—O6^{i}	121.12 (11)	Pb2^{xiii}—O2—N1	101.78 (11)
O6^{v}—Pb1—O6^{ii}	121.12 (11)	O4—N2—O4^{iii}	120.0 (5)
O6^{i}—Pb1—O6^{ii}	117.19 (15)	O4—N2—O6	120.0 (3)
O2^{vi}—Pb2—O2^{vii}	153.82 (14)	O4^{iii}—N2—O6	120.0 (3)
O2^{vi}—Pb2—O3	68.37 (13)	Pb1—O3—Pb2	108.96 (14)
O2^{vi}—Pb2—O3^{iii}	137.63 (13)	Pb1—O3—P1^{i}	111.9 (2)
O2^{vi}—Pb2—O4	115.10 (14)	Pb2—O3—P1^{i}	129.5 (2)
O2^{vi}—Pb2—O4^{iii}	69.02 (14)	Pb1^{xv}—O4—Pb2	123.29 (14)
O2^{vi}—Pb2—O5^{vii}	110.88 (13)	Pb1^{xv}—O4—N2	101.0 (3)
O2^{vi}—Pb2—O5^{i}	109.11 (14)	Pb2—O4—N2	94.7 (3)
O2^{vi}—Pb2—O5^{viii}	64.37 (14)	Pb2^{xiii}—O5—Pb2^{x}	151.56 (16)
O2^{vi}—Pb2—O5^{ix}	44.54 (13)	Pb2^{xiii}—O5—N1	93.1 (3)
O2^{vii}—Pb2—O3	137.63 (13)	Pb2^{x}—O5—N1	95.3 (3)
O2^{vii}—Pb2—O3^{iii}	68.37 (13)	Pb1^{xvi}—O6—N2	171.0 (5)
O2^{vii}—Pb2—O4	69.02 (14)	Pb1^{xvi}—O6—O4	148.84 (17)
O2^{vii}—Pb2—O4^{iii}	115.10 (14)	Pb1^{xvi}—O6—O4^{iii}	148.84 (17)
O2^{vii}—Pb2—O5^{vii}	44.54 (13)		

Symmetry codes: (i) −x+1/2, −y+1, z−1/2; (ii) −x+3/2, −y+1, z−1/2; (iii) −x+1, y, z; (iv) x−1/2, −y+1, z−1/2; (v) x, y, z−1; (vi) x, y+1, z; (vii) x+1, y+1, z; (viii) x+1/2, −y+1, z−1/2; (ix) −x, y+1, z; (x) −x+1/2, −y+1, z+1/2; (xi) x+1/2, −y+1, z+1/2; (xii) −x, y, z; (xiii) x−1, y−1, z; (xiv) x, y−1, z; (xv) −x+3/2, −y+1, z+1/2; (xvi) x, y, z+1.

Fig. 1

Fig. 2

Fig. 3