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The crystal structure of mercury(I) dihydrogenphosphate, $Hg_2(H_2PO_4)_2$

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Auszug

Die Struktur des Quecksilber(I)dihydrogenphosphates, $Hg_2(H_2PO_4)_2$, wurde mittels Patterson- und Fouriermethoden bestimmt. Die Verfeinerung bis zu einem R-Faktor von 0,059 erfolgte auf Grund von 996 unabhängigen Zählrohrintensitäten. Die Kristalle sind monoklin, die Raumgruppe ist $P2_1/n$ mit zwei Formeleinheiten pro Elementarzelle und den folgenden Zellparametern:

$$a = 6{,}0754(5)\ \text{Å},\ b = 14{,}5034(7)\ \text{Å},\ c = 4{,}7280(4)\ \text{Å},$$

$$\beta = 92{,}172(7)^\circ \quad \text{und} \quad V = 416{,}3\ \text{Å}^3.$$

Die Quecksilberatome sind paarweise über das Symmetriezentrum verbunden; der Quecksilber-Quecksilber-Atomabstand beträgt 2,499(1) Å. Jedes Quecksilberatom ist auch an ein Sauerstoffatom mit dem Abstand von 2,142(12) Å gebunden. Der Winkel Hg—Hg—O weicht mit 167,2(4)° nur wenig von der Geradlinigkeit ab. Der zweitnächste Nachbar des Quecksilbers ist ein Sauerstoffatom mit dem Abstand von 2,514(13) Å. Die Struktur ist aus $Hg_2(H_2PO_4)_2$-Molekülen aufgebaut, die wahrscheinlich durch ein Wasserstoffbrückensystem zusammengehalten werden. Mögliche Wasserstoffbrückenbindungen werden diskutiert.

Abstract

The structure of mercury(I) dihydrogenphosphate, $Hg_2(H_2PO_4)_2$, has been determined by Patterson and Fourier methods and refined to an R value of 0.059 on the basis of 996 independent counter intensities. The crystals are monoclinic, space group $P2_1/n$, with two formula units in a unit cell of the dimensions $a = 6.0754(5)$, $b = 14.5034(7)$, $c = 4.7280(4)$ Å, $\beta = 92.172(7)^\circ$, $V = 416.3$ Å^3.

The mercury atoms are linked in pairs across centres of symmetry, the mercury-mercury distances being 2.499(1) Å. Each mercury atom is also bonded to one oxygen atom at the distance 2.142(12) Å. The Hg—Hg—O angle deviates

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somewhat from linearity, being 167.2(4)°. The next-nearest neighbour to mercury is an oxygen atom at the distance 2.514(13) Å.

The structure is built up by $Hg_2(H_2PO_4)_2$ molecules, probably connected by a hydrogen bonding system. Possible hydrogen bonds are discussed.

Introduction

Only little information is given in the literature on the structures of mercury phosphates. The syntheses and analyses of many phases are described in reference books, however (GMELIN, *Handbuch der anorganischen Chemie*, 1969). In connection with the study of the crystal structure of $Hg_3(PO_4)_2$ (AURIVILLIUS and NILSSON, 1975), the present investigation of $Hg_2(H_2PO_4)_2$ was undertaken.

Experimental

Single crystals of $Hg_2(H_2PO_4)_2$ were prepared by dissolving $Hg_3(PO_4)_2$ in boiling concentrated H_3PO_4 and adding methyl alcohol to the solution. Mercury(II) was then reduced to the monovalent state. A heterogeneous sample was obtained, containing both $Hg_3(PO_4)_2$ and $Hg_2(H_2PO_4)_2$. The crystals of $Hg_2(H_2PO_4)_2$ thus obtained were colourless and rather irregular.

Weissenberg photographs showed the crystals to be monoclinic. The reflections with the following indices were systematically missing: $h0l$, $h+l$ odd; $0k0$, k odd. This is characteristic for the space group $P2_1/n$.

The cell dimensions, calculated by the method of least-squares, were obtained from the θ values of 58 reflections measured separately with the single-crystal diffractometer. The density of the crystals was determined from the loss of weight in benzene. Some crystal data are presented in Table 1.

A single crystal with the dimensions $0.20 \times 0.075 \times 0.15$ mm along a, b and c, respectively, was used for the intensity data collection on a computer-controlled four-circle diffractometer (CAD-4) with Mo$K\alpha$

Table 1. *Crystal data*

$Hg_2(H_2PO_4)_2$, Formula weight 595.2
Monoclinic, $P2_1/n$
$a = 6.0754(5)$, $b = 14.5034(7)$, $c = 4.7280(4)$ Å,
$\beta = 92.172(7)°$,
$V = 416.3$ Å^3, $Z = 2$.
$D_m = 4.70$, $D_x = 4.75$ g · cm^{-3}
μ (Mo$K\alpha$) = 381 cm^{-1}

radiation ($\lambda = 0.71069$ Å) and a graphite monochromator. The intensities were recorded at a take-off angle of 3°. The ω-2θ scan technique was employed with a scan interval $\Delta\omega = (0.7 + 0.5 \tan\theta)°$. The background intensity was measured for 1/4 of the scan time at both ends of the interval. All independent reflections in the range $3° < \theta < 30°$ were measured. Of the 1221 reflections examined, 225 with $I < 2.58\sigma(I)$ were considered not observed. The values of $\sigma(I)$ are based on counting statistics. After each group of 25 reflections, the intensities of the standard reflections $\bar{1}3\bar{2}$, $\bar{2}51$ and $\bar{2}42$ were measured. The fluctuations in their intensities were random and the values of $(I_{max}-I_{min})/I_{max}$ were less than 6%.

The corrections for Lorentz, polarization and absorption effects were performed in the usual way. The transmission factors evaluated by numerical integration varied from 0.012 to 0.104.

All computations were made on the Univac 1108 computer in Lund. A short account of the program system used is given by STÅLHANDSKE, 1974.

Structure determination and refinement

A three-dimensional Patterson synthesis was used to find the preliminary positions of the mercury atoms. Least-squares refinement followed by difference Fourier synthesis revealed the positions of the phosphorus and oxygen atoms. The positional parameters for these atoms, their anisotropic temperature factors and an overall scale factor were then included in a full-matrix least-squares refinement, minimizing $\Sigma w_i(|F_o| - |F_c|)^2$ with the weights w_i calculated from the expression $w_i^{-1} = \sigma^2(F_o) + a|F_o|^2 + b$. The values $a = 0.004$ and $b = 4.0$ were chosen to make the average value of $w_i(|F_o| - |F_c|)^2$ nearly constant in the different intervals of $|F_o|$ and $\sin\theta$. The con-

Table 2. *Atomic coordinates obtained in the final least-squares refinement.* Estimated standard deviations are given in parentheses

Atom	x	y	z
Hg	0.30421(10)	0.01696(5)	0.05308(13)
P	−0.0114(7)	0.1523(3)	0.4050(8)
O(1)	0.001(2)	0.0677(11)	0.210(3)
O(2)	0.188(3)	0.1442(11)	0.624(3)
O(3)	0.771(2)	0.1379(11)	0.567(3)
O(4)	−0.008(2)	0.2450(9)	0.263(3)

Table 3a. *Thermal parameters β_{ij} with estimated standard deviations in parentheses.* The expression for the anisotropic thermal parameters used is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	0.0076(2)	0.0033(0)	0.0211(4)	0.0006(1)	0.0033(2)	0.0004(1)
P	70(9)	20(2)	92(13)	1(3)	17(9)	0(4)
O(1)	6(3)	52(9)	15(5)	−14(12)	3(3)	−46(16)
O(2)	19(4)	33(7)	24(5)	9(14)	−12(4)	−26(17)
O(3)	12(3)	29(7)	36(7)	−6(12)	13(4)	−3(16)
O(4)	10(3)	27(6)	31(6)	−2(11)	2(3)	22(16)

Table 3b. *The root-mean-square components R_i along the principal axes of the ellipsoids of thermal vibration*

Atom	R_1	R_2	R_3
Hg	0.111 Å	0.157 Å	0.189 Å
P	0.096	0.119	0.147
O(1)	0.096	0.115	0.249
O(2)	0.107	0.180	0.237
O(3)	0.102	0.174	0.228
O(4)	0.137	0.155	0.200

Table 4. *Selected interatomic distances and angles in the structure of* $Hg_2(H_2PO_4)_2$. Estimated standard deviations are given in parentheses

The coordination of mercury

Distances	Hg—Hg		2.499(1) Å
		—O(1)	2.142(12)
		—O(1)	2.514(13)
Angle	Hg—Hg—O(1)		167.2(4)°

Distances and angles in the phosphate tetrahedron

P—O(1)	1.54(1) Å	O(1)—P—O(2)	106.3(8)°
—O(2)	1.57(1)	O(1)—P—O(3)	104.4(8)
—O(3)	1.57(1)	O(1)—P—O(4)	116.3(8)
—O(4)	1.50(1)	O(2)—P—O(3)	108.3(8)
Mean value	1.543(7)	O(2)—P—O(4)	109.7(8)
O(i)—O(j)	2.46(2)—2.58(2)	O(3)—P—O(4)	111.4(8)

Oxygen-oxygen distances outside the tetrahedron

O(1)—O(1)	2.79(3) Å
O(2)—O(4)	2.52(2)
O(3)—O(4)	2.59(2)

Table 5. *Observed and calculated structure amplitudes*

k	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0 k 0		
4	214	193
6	194	213
8	123	162
10	21	21
12	42	53
14	26	29
16	13	18
18	29	28
20	13	11
1 k 0		
1	31	34
2	51	53
3	139	143
4	100	105
5	70	79
6	111	137
7	27	32
8	104	140
9	43	58
10	93	130
11	27	35
12	90	118
13	19	22
14	77	97
16	61	71
18	49	50
19	14	14
20	34	35
2 k 0		
0	168	163
1	19	18
2	213	219
3	46	49
4	147	157
5	74	81
6	141	153
7	70	86
8	81	104
9	68	89
10	65	84
11	59	81
13	54	70
15	45	53
17	34	39
19	25	26
3 k 0		
1	224	227
2	22	22
3	170	175
4	41	42
5	148	153
6	57	61
7	98	110
8	54	65
9	44	56
10	45	58
11	29	35
12	43	54
13	28	32
14	42	51
16	31	36
17	17	18
18	25	24
4 k 0		
0	109	109
2	27	27
3	57	60
4	18	17
5	97	101
6	35	38
7	97	106
8	30	35
9	87	103
10	13	14
11	89	111
12	18	23
13	74	89
14	14	18
15	56	65
17	47	54
5 k 0		
1	141	141
2	23	24
3	181	189
5	134	138
7	80	83
8	27	28
9	74	84
10	14	18
11	45	54
6 k 0		
0	99	99
1	22	23
2	53	56
3	36	39
4	45	48
5	49	50
6	46	47
7	67	69
8	28	30
9	71	80
11	57	65
12	17	15
13	55	61
7 k 0		
1	93	94
2	18	18
3	68	69
4	37	40
5	66	67
6	46	49
7	54	55
8	50	52
9	27	28
10	51	56
11	20	22
8 k 0		
0	75	72
2	93	92
4	84	83
5	22	19
6	62	60
−8 k 1		
1	83	82
3	56	53
4	22	22
5	60	58
6	36	33
−7 k 1		
0	93	95
1	12	7
2	111	115
3	14	15
4	103	104
5	28	29
6	67	65
7	39	38
8	56	54
9	31	30
10	53	50
11	44	42
−6 k 1		
1	23	12
2	38	37
3	36	36
4	59	61
5	13	10
6	77	79
8	81	82
9	16	13
10	82	79
12	76	71
13	16	16
14	67	66
−5 k 1		
0	195	201
2	150	152
3	13	13
4	124	126
6	135	135
7	16	17
8	93	93
9	24	21
10	35	32
11	28	26
12	35	31
14	15	13
15	15	16
16	19	16
−4 k 1		
1	88	88
2	24	24
3	128	128
4	62	61
5	82	81
6	84	83
7	38	36
8	97	98
9	57	55
10	107	100
11	42	39
12	102	92
14	67	66
16	52	54
−3 k 1		
0	130	132
1	74	70
2	155	157
3	68	66
4	133	132
5	72	74
6	80	80
7	85	86
8	65	62
9	119	116
10	61	56
11	70	68
13	75	72
15	66	65
17	50	49
18	13	13
−2 k 1		
1	239	248
2	81	75
3	214	207
4	31	32
5	203	196
6	38	36
7	154	150
8	64	64
9	77	74
10	46	44
11	56	49
12	21	18
13	36	34
14	38	39
15	14	10
16	28	29
17	22	21
18	17	14
−1 k 1		
0	66	56
1	19	14
2	23	23
3	91	88
4	35	32
5	96	96
6	39	36
7	148	145
8	15	13
9	142	134
10	33	29
11	174	155
13	110	104
14	11	11
15	78	83
16	13	13
17	62	64
19	46	47
0 k 1		
1	251	231
2	39	38
3	366	321
4	56	50
5	224	205
6	64	64
7	93	93
8	46	47
9	118	112
10	35	33
11	80	75
12	29	29
14	40	41
16	23	23
18	17	15
19	26	25
20	15	13
1 k 1		
0	234	212
1	92	80
2	170	152
3	74	70
4	121	118
5	113	108
6	138	136
7	98	100
8	82	86
9	123	125
10	25	25
11	75	75
12	24	25
13	74	85
15	62	71
16	17	17
17	46	51
18	12	14
19	30	29
2 k 1		
1	133	123
2	14	7
3	134	126
4	86	86
5	110	113
6	109	114
7	76	77
8	97	97
9	40	42
10	110	111
11	34	35
12	108	118
13	18	21
14	58	70
16	47	55
18	42	46
3 k 1		
0	238	219
1	45	42
2	229	215
4	188	184
5	20	19
6	125	130
7	21	20
8	103	104
10	69	70
11	44	48
12	21	22
13	21	19
4 k 1		
1	40	40
2	70	69
4	66	68
6	88	93
7	35	35
8	117	118
10	87	96
11	14	12
12	62	75
14	73	86
15	14	5
16	55	61
17	12	14
5 k 1		
0	181	170
1	23	19
2	134	133
3	19	19
4	99	102
5	41	41
6	119	119
7	41	42
8	82	82
9	29	32
10	31	32
11	53	60
12	22	25
13	30	35
14	16	17
15	13	21
6 k 1		
1	94	94
3	93	97
4	38	37
5	69	72
6	45	49
7	46	47
8	39	40
9	37	41
10	48	54
11	18	20
12	50	59
7 k 1		
0	49	48
1	28	28
2	46	45
3	35	36
4	39	41
5	44	45
6	31	30
7	57	60
8	29	31
9	61	69
10	18	22
8 k 1		
1	91	92
2	16	13
3	79	81
5	71	73
−8 k 2		
0	42	39
1	17	18
2	50	49
3	26	25
4	53	53
−7 k 2		
1	120	120
2	20	19
3	92	94
5	92	94
7	87	87
8	26	25
9	46	43
10	19	16
−6 k 2		
0	28	29
2	28	29
3	45	45
4	34	35
5	72	75
7	72	74
8	17	18
9	71	70
10	16	17
11	87	84
13	72	65
−5 k 2		
1	137	140
2	20	16
3	140	141
4	20	19
5	99	104
6	39	39
7	66	65
8	54	53
9	61	59
10	41	40
11	32	31
12	41	38
14	51	43
−4 k 2		
0	156	145
1	32	29
2	136	135
3	33	32
4	100	98
5	38	39
6	125	124
7	71	72
8	78	77
9	84	82
10	42	40
11	53	52
12	25	21
13	63	57
14	20	15
15	60	51
16	18	12
17	29	27
−3 k 2		
1	76	72
2	8	1
3	49	46
4	104	104
5	60	58
6	126	125
7	67	64
8	77	76
9	21	20
10	102	98
11	11	10
12	123	112
14	80	69
16	62	52
17	17	14
18	60	52
−2 k 2		
0	255	251
1	46	40
2	225	222
4	210	212
5	48	46
6	124	119
8	115	110
9	30	28
10	72	67
11	22	19
12	34	31
15	16	12
18	23	20
−1 k 2		
1	77	73
2	54	52
3	49	49
4	68	67
5	66	64
6	110	107
7	75	70
8	143	139
9	25	22
10	120	115
11	14	14
12	106	96
14	115	97
16	81	65
17	18	13
18	39	36
0 k 2		
0	200	185
1	20	15
2	204	186
3	66	65
4	133	125
5	79	76
6	176	162
7	71	68
8	102	96
9	75	73
10	56	54
11	92	86
12	21	21
13	61	55
14	19	16
15	48	41
16	17	15
17	51	45
18	18	13
19	31	28
1 k 2		
1	227	210
3	209	190
4	80	73
5	156	146
6	83	78
7	94	92
8	38	36
9	74	70
10	62	62
11	41	38
12	75	71
13	17	15
14	40	36
16	32	31
18	37	37
19	19	19
2 k 2		
0	100	89
1	72	65
2	43	40
3	79	74
4	46	44
5	45	44
6	20	17
7	126	120
8	34	33
9	151	146
11	91	86
12	15	13
13	90	83
15	94	86
17	47	48
3 k 2		
1	193	178
2	27	24
3	184	170
4	38	38
5	159	150
6	37	35
7	125	119
8	14	13
9	76	73
10	15	14
11	49	46
12	31	29
13	15	16
15	15	15
4 k 2		
0	84	78
2	73	71
3	46	45
4	83	79
5	90	86
6	28	27
7	71	68
8	28	27
9	71	70
10	16	17
11	96	89
13	71	66
15	45	45
5 k 2		
1	110	99
2	38	33
3	103	99
4	30	28
5	82	78
6	48	48
7	50	49
8	77	76
9	43	42
10	59	57
11	32	29
12	51	45
14	54	51
6 k 2		
0	102	92
1	17	17
2	115	106
3	13	15
4	92	90
6	79	77
7	30	30
8	50	50
9	38	37
10	38	39
11	16	17
7 k 2		
3	19	15
4	48	49
5	14	12
6	60	59
8	44	43
8 k 2		
0	92	87
−7 k 3		
0	103	97
2	100	99
4	95	98
5	17	16
6	69	69
7	14	14
−6 k 3		
1	64	65
2	39	37
3	58	60
4	29	29
5	49	50
6	45	45
7	34	35
8	78	79
9	26	25
10	64	63
11	25	20
−5 k 3		
0	94	91
2	97	95
3	30	30
4	78	78
5	69	70
6	61	59
7	46	47
8	34	36
9	56	57
10	30	29
11	69	66
12	13	13
13	56	50
−4 k 3		
1	144	140
3	138	140
4	44	43
5	120	120
6	43	43
7	90	90
8	13	13
9	65	63
10	37	36
11	38	37
12	39	38
13	14	12
−3 k 3		
0	13	11
1	42	39
3	67	67
4	17	16
5	33	32
7	107	107
9	121	118
11	88	82
13	80	72
15	95	81
−2 k 3		
1	195	187
2	19	18
3	179	164
4	50	49
5	132	132
6	56	56
7	99	98
9	67	66
10	30	29
11	42	39
12	48	42
13	19	18
14	18	16
17	18	12
−1 k 3		
0	135	125
1	20	19
2	109	104
3	46	43
4	99	97
5	102	100
6	91	89
7	66	66
8	71	67
9	82	80
10	31	28
11	91	84
12	20	16
13	73	67
15	48	41
17	65	50
18	20	12
0 k 3		
1	111	103
2	37	35
3	88	83
4	47	45
5	90	86
6	78	75
7	79	76
8	115	107
9	41	39
10	85	80
11	23	21
12	81	75
13	14	14
14	86	76
16	60	51
18	30	24
1 k 3		
0	185	179
1	19	17
2	105	186
3	25	23
4	167	156
5	33	30
6	113	108
7	37	36
8	80	79
9	38	35
10	63	61
12	25	23
13	15	14
15	37	32
2 k 3		
1	21	18
3	9	6
4	100	94
5	15	17
6	122	115
7	21	22
8	65	63
10	92	89
12	106	100
14	66	61
16	51	44
3 k 3		
0	150	141
1	20	19
2	136	127
3	32	32
4	121	115
6	107	104
7	54	51
8	77	75
9	55	52
10	41	39
11	33	31
12	24	23
13	29	27
15	44	38

Table 5. *(Continued)*

k	$\|F_o\|$	$\|F_c\|$
4 k 3		
1	100	97
2	25	22
3	98	93
4	23	22
5	73	68
6	41	39
7	47	45
8	68	62
9	39	38
10	48	47
12	46	45
14	54	47
5 k 3		
0	49	43
2	58	53
3	32	31
4	53	49
5	69	66
6	30	25
7	52	51
8	25	25
9	61	60
10	28	28
11	65	61
13	56	50
6 k 3		
1	106	101
2	12	11
3	80	75
5	81	77
7	75	71
8	15	10
9	34	34
7 k 3		
0	13	11
1	16	15
2	25	23
3	30	28
4	20	23
5	22	17
-6 k 4		
0	84	85
2	74	75
4	56	58
5	45	48
6	64	67
7	32	33
8	44	45
-5 k 4		
1	50	49
2	39	40
3	24	24
4	36	37
5	28	31
6	53	53
7	39	39
8	72	74
10	56	57
-4 k 4		
0	130	131
1	13	13
2	130	127
3	14	13
4	123	121
6	78	77
7	14	13
8	65	65
9	12	7
10	46	43
12	22	19
-3 k 4		
1	42	40
3	36	35
4	58	58
5	39	37
6	77	77
7	33	32
8	61	61
10	81	79
11	16	14
12	88	82
14	57	51
-2 k 4		
0	122	120
1	29	28
2	113	111
3	43	44
4	85	85
5	25	23
6	100	97
7	56	56
8	58	58
9	62	59
10	33	33
11	39	36
12	21	20
13	40	36
15	52	44
-1 k 4		
1	117	115
2	35	34
3	145	141
4	29	29
5	101	97
6	41	39
7	52	49
8	55	54
9	58	58
10	38	38
11	58	54
12	33	31
14	45	41
16	31	29
0 k 4		
0	23	20
2	46	39
3	36	34
4	58	57
5	75	73
7	70	69
8	14	14
9	85	82
10	23	24
11	95	89
13	73	67
15	51	45
16	18	11
1 k 4		
1	144	146
2	30	30
3	110	112
5	111	111
7	102	100
8	26	24
9	47	48
11	29	30
13	22	21
14	16	15
2 k 4		
0	53	56
1	32	32
2	55	56
3	50	50
4	60	61
5	37	35
6	18	20
7	20	68
8	26	26
9	78	76
10	18	18
11	52	52
13	50	49
15	60	54
3 k 4		
1	80	79
2	11	5
3	92	91
4	34	35
5	64	64
6	47	48
7	38	38
8	46	45
9	44	43
10	53	52
11	24	24
12	62	51
14	37	33
4 k 4		
0	105	105
2	87	86
4	65	62
5	15	15
6	84	82
7	19	18
8	49	48
9	30	27
10	21	20
11	30	27
5 k 4		
1	19	17
2	24	24
3	14	9
4	36	35
6	50	47
7	26	25
8	55	53
10	51	47
6 k 4		
0	65	64
2	77	74
4	79	77
5	16	16
6	39	37
-5 k 5		
3	28	27
4	16	19
5	46	47
6	13	9
7	49	50
-4 k 5		
1	103	109
3	73	76
5	71	74
6	19	16
7	63	65
8	24	21
9	28	29
-3 k 5		
0	50	50
1	15	17
2	59	61
3	26	26
4	61	65
5	40	39
6	36	37
7	48	48
8	38	39
9	55	55
10	28	29
11	42	42
-2 k 5		
1	44	46
2	14	12
3	71	72
4	38	38
5	45	48
6	49	49
7	27	28
8	50	49
9	39	39
10	54	52
11	16	19
12	59	54
-1 k 5		
0	136	141
2	100	102
4	68	69
5	13	10
6	91	91
8	56	55
10	17	16
11	20	20
12	20	21
13	14	12
0 k 5		
1	12	10
2	27	27
3	30	32
4	40	41
5	13	10
6	58	57
8	65	65
9	16	15
10	62	61
12	54	52
13	17	16
1 k 5		
0	67	75
2	82	92
3	14	15
4	87	94
5	19	21
6	53	56
7	26	27
8	50	51
9	21	21
10	42	42
11	33	31
13	26	22
2 k 5		
1	70	78
2	11	10
3	49	52
4	24	24
5	48	52
6	33	33
7	42	43
8	35	37
9	17	15
10	35	36
12	39	38
3 k 5		
0	53	57
2	33	35
3	21	21
4	19	20
5	42	45
6	36	38
7	43	42
9	46	47
4 k 5		
1	57	61
3	82	87
5	60	61
7	33	34
5 k 5		
0	30	34
3	22	21
-3 k 6		
1	64	72
2	17	18
3	46	49
4	15	18
5	52	54
-2 k 6		
0	32	37
2	12	13
3	16	17
5	36	38
6	25	25
7	38	40
-1 k 6		
1	60	68
3	82	90
5	58	61
7	34	33
0 k 6		
0	45	51
1	11	12
2	23	25
3	24	27
4	19	18
5	27	30
6	29	31
7	40	42
8	22	20
1 k 6		
1	47	38
3	33	40
4	18	22
5	36	44
6	26	29
7	35	39
8	25	26
2 k 6		
0	42	51
2	54	63
4	46	54
5	15	19
6	34	36
3 k 6		
2	24	25

vergence was checked by the agreement indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w_i(|F_o| - |F_c|)^2/\Sigma w_i|F_o|^2]^{1/2}$. The refinement resulted in $R = 0.068$ and $R_w = 0.097$. The atomic scattering factors were those of CROMER and WABER (1965) for neutral mercury and of HANSON *et al.* (1964) for neutral phosphorus and oxygen. At this stage, an isotropic secondary-extinction parameter was included in the refinement, resulting in $R = 0.059$, $R_w = 0.086$ and the goodness of fit $S = 1.00$. The refined value of the extinction parameter, $g = 0.35(4) \cdot 10^4$, corresponds to a mosaic spread of 17 seconds or a domain size of $2.5 \cdot 10^{-5}$ cm. Correction for the anomalous dispersion of mercury was then attempted, but had no effect on the refinement. All parameter shifts were less than 0.01 of their estimated standard deviations. A final three-dimensional difference synthesis was calculated with the contributions of all located atoms subtracted. The map showed residual peaks of the heights ≈ 4 e/Å^3 between the positions of the mercury atoms in the doublets and some peaks of ≈ 2 e/Å^3 in the neighbourhood of the positions of the oxygen atoms of the phosphate tetrahedra. No attempt has, however, been made to try to find the positions of the eight hydrogen atoms of the unit cell. The

final positional and thermal parameters are given in Tables 2 and 3, and selected interatomic distances and angles in Table 4. Observed and calculated structure amplitudes are given in Table 5.

Description and discussion of the structure

The mercury-mercury distance found in the structure is 2.499(1) Å, indicating that the metal atoms are in the monovalent state forming the ordinary mercury doublet. The value obtained compares well with those reported by DORM (1967, 1969, 1971) for oxygen and fluorine compounds of Hg(I), *e.g.* for $Hg_2(BrO_3)_2$ [2.507(6) Å], Hg_2SO_4 [2.500(3) Å], $HgSeO_4$ [2.51(1) Å and $Hg_2SiF_6 \cdot 2H_2O$ [2.495(3) Å]].

Each mercury atom is also bonded to one oxygen atom O(1) at the distance 2.142(12) Å, implying the frequently occurring two-coordination. The group O(1)—Hg—Hg—O(1) deviates somewhat from linearity, the angle Hg—Hg—O(1) being 167.2(4)°. The mercury-to-oxygen distance and the Hg—Hg—O angle are about the same as found in *e.g.* Hg_2SO_4 [2.24(2) Å, 164.9(6)°] and $Hg_2(BrO_3)_2$ [2.16(4) Å, 174(1)°].

The oxygen atoms O(1)—O(4) are part of phosphate tetrahedra. The mercury doublet is thus bonded to two phosphate tetrahedra through the oxygen atom O(1) [Hg—O(1) = 2.142(12) Å]. For the sake of electrical neutrality the anions of the structure must be $H_2PO_4^-$ and the structure is in this manner built up by discrete $Hg_2(H_2PO_4)_2$ groups.

The phosphate tetrahedra are quite regular, the mean distance P—O being 1.543(7) Å (Table 4), in a very good agreement with *e.g.* the mean value 1.546(3) Å calculated for Li_3PO_4 (KEFFER *et al.*, 1967). No extension of the P—O bond was observed for the P—O—Hg bridging oxygen atom in this structure.

As mentioned above, no attempt was made to locate the hydrogen atoms in the unit cell. It is, however, possible to draw some conclusions about the hydrogen bonding system by studying the oxygen-oxygen distances. As the anion must be $H_2PO_4^-$, two corners of the tetrahedral group are formed from the positions of OH groups and two from those of oxygen atoms. As hydrogen bonding between O and OH of the same tetrahedron is most unlikely to occur, there remain only three oxygen-oxygen distances short enough for hydrogen bonding, *viz.* O(1)—O(1′) 2.79(3), O(2)—O(4′) 2.52(2) and O(3)—O(4′) 2.59(2) Å (*cf.* Fig. 1). (The primed atoms belong to adjacent molecules.) It is scarcely likely that the atoms O(1), bonded to mercury at short distances, are also bonded to hydrogen. On the other hand,

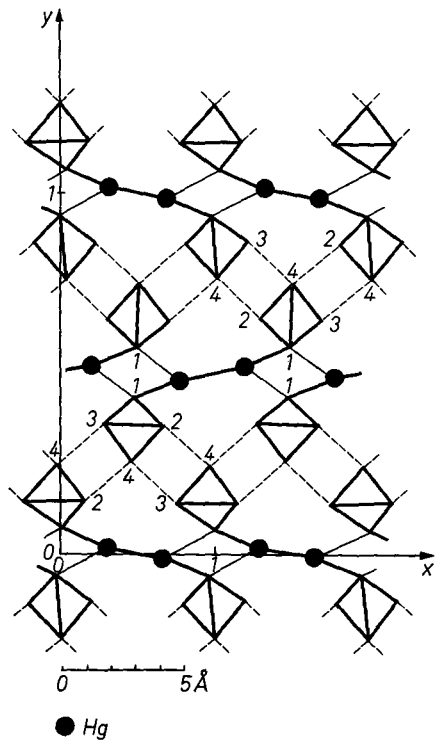

Fig. 1. Projection of the structure of $Hg_2(H_2PO_4)_2$ along the z axis. Thin lines indicate weak interactions Hg—O, and dotted lines possible hydrogen bonds. The numbers 1, 2, 3, 4 indicate the oxygen atoms identified in Table 2

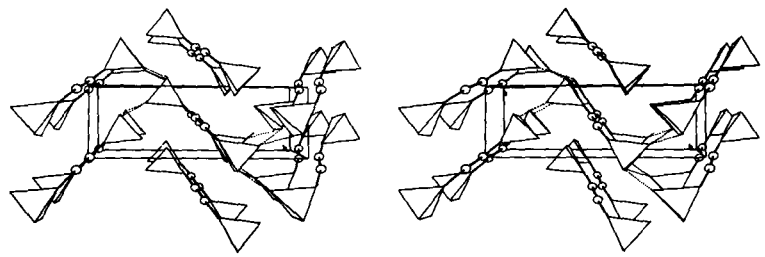

Fig. 2. Stereoscopic view of the structure of $Hg_2(H_2PO_4)_2$ along the x axis. Possible hydrogen bonds from the molecules in the center of the drawing are indicated with dotted lines

it is very probable that the short oxygen-oxygen distances between the tetrahedra, 2.52 and 2.59 Å, are caused by hydrogen bonding. The hydrogen atoms of the structure would then be bonded to the

oxygen atoms O(2) and O(3), forming hydrogen bonds O(2)—H···O(4′) and O(3)—H···O(4′) (Fig. 1). The shortest hydrogen-hydrogen distance would then be about 2.3 Å.

The crystal structure is then built up by separate $Hg_2(H_2PO_4)_2$ molecules, which are fused to a three-dimensional network by the hydrogen bonds, the proposed hydrogen bonding system being shown in a stereoview given in Fig. 2. There are also weak interactions between different molecules, as the next-nearest neighbour of mercury is an oxygen atom O(1) outside its molecule at the distance 2.514(13) Å (Fig. 1).

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