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The crystal structure of mercury(II)phosphate, $Hg_3(PO_4)_2$

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Auszug

Die Struktur des Quecksilber(II)phosphates, $Hg_3(PO_4)_2$, wurde mittels symbolischer Addition und Fouriermethoden bestimmt. Durch Verfeinerung aus 1491 unabhängigen Zählrohrintensitäten wurde ein R-Faktor von 0,043 erhalten. Die Kristalle sind monoklin, die Raumgruppe ist $P2_1/c$, mit vier Formeleinheiten pro Elementarzelle und den folgenden Zellparametern: $a = 9{,}737(2)$ Å, $b = 11{,}466(2)$ Å, $c = 6{,}406(1)$ Å und $\beta = 99{,}51(2)°$.

Die Quecksilberatome sind auf beinahe lineare Weise zweifach-koordiniert, die Abstände Quecksilber-Sauerstoff schwanken zwischen 2,06(1) Å und 2,13(1) Å und die O—Hg—O-Winkel zwischen 163,4(4)° und 169,9(5)°. Alle Sauerstoffatome gehören zu Phosphattetraedern. Jedes Quecksilberatom ist an je ein Sauerstoffatom von zwei Phosphattetraedern gebunden und jede Phosphatgruppe besitzt Bindungen zu drei Quecksilberatomen.

Die Struktur ist aus unendlichen, einander durchdringenden und gefalteten Netzen mit der Formel $[Hg_3(PO_4)_2]_n$ aufgebaut. Die Netze werden aus endlosen

–Hg—O—P—O—Hg–-Ketten, miteinander durch zusätzliche Quecksilberatome verbunden, gebildet. Die Hg—O-Abstände zwischen den Netzen sind $\geq 2{,}42(1)$Å.

Abstract

The structure of mercury(II)phosphate, $Hg_3(PO_4)_2$, has been determined by symbolic addition and Fourier methods and refined to an R value of 0.043 on the basis of 1491 independent counter intensities. The crystals are monoclinic, space group $P2_1/c$, with four formula units in a unit cell of the dimensions $a = 9.737(2)$, $b = 11.466(2)$, $c = 6.406(1)$ Å and $\beta = 99.51(2)°$.

The mercury atoms are two-coordinated in a nearly linear way; the mercury to oxygen distances vary between 2.06(1) and 2.13(1) Å, and the O—Hg—O angles between 163.4(4) and 169.9(5)°. All oxygen atoms belong to phosphate tetrahedra. Each mercury atom is bonded to one oxygen atom of each of two phosphate tetrahedra and each phosphate group is bonded to three mercury atoms.

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The structure is built up of infinite, interpenetrating puckered nets of formula $[Hg_3(PO_4)_2]_n$, formed from endless $-Hg-O-\underset{\vee}{P}-O-Hg-$chains, fused by additional mercury atoms. The Hg—O distances between the nets are $\geq 2.42(1)$ Å.

Introduction

In connection with several studies on mercury salts containing pyramidal or tetrahedral anions (BJÖRNLUND, 1971, 1974; AURIVILLIUS, 1972), it was found of interest to investigate some mercury phosphates. This paper deals with the structure of $Hg_3(PO_4)_2$. Work is in progress on a compound of formula $Hg_2(H_2PO_4)_2$, containing monovalent mercury.

Experimental

Single crystals of $Hg_3(PO_4)_2$ were prepared according to two different methods. First a synthesis suggested by KLEMENT and HASELBECK (1964) was tried, the procedure somewhat modified by the present authors, using a more dilute solution of mercury(II)oxide in phosphoric acid (3 g HgO in 50 ml concentrated H_3PO_4). Another method is to use an acidified solution of mercury(II)acetate and phosphoric acid (10 ml 0.3M $Hg(C_2H_3O_2)_2$, 10 ml 2.5M HNO_3, 10 ml conc. H_3PO_4). The crystallization proceeds very slowly in the last case, but gives a more well-formed product. The crystals thus obtained were in the form of thin, colourless plates. Weissenberg photographs showed the crystals to be monoclinic. The systematically absent reflections were $h0l$ with $l \neq 2n$ and $0k0$ with $k \neq 2n$, the extinctions consistent with the space group $P2_1/c$. X-ray powder photographs were taken in a Guinier-Hägg focusing camera with Cu$K\alpha_1$ radiation, using aluminium as internal standard ($a = 4.04934$ Å). The preliminary values of the cell dimensions were refined by least-squares calculations. The density was determined from the loss of weight in benzene. Some crystal data are given in Table 1.

Table 1. *Crystal data*

$Hg_3(PO_4)_2$, Formula weight 791.8
Monoclinic, $P2_1/c$
$a = 9.737(2)$, $b = 11.466(2)$, $c = 6.406(1)$ Å,
$\beta = 99.51(2)°$,
$V = 705.4$ Å^3, $Z = 4$.
$D_m = 7.32$, $D_x = 7.45$ g · cm^{-3}
μ(Mo$K\alpha$) = 669 cm^{-1}

A single crystal with the dimensions $0.20 \times 0.07 \times 0.007$ mm was used for the intensity data collection on a Pailred linear diffractometer, using Mo$K\alpha$ radiation, monochromatized by reflection off the (002) planes of a graphite crystal, the monochromator angle being 6.08°. The crystal used was mounted along its longest edge, which coincides with the direction of the crystallographic b axis. The reflections of the layer lines $h0l$—$h\,11\,l$ were collected for the copper range, $(\sin\theta)/\lambda \leq 0.65$, using the equi-inclination and ω-scan technique with a scan rate of 1.0°/min. The scan range was 4.0° for all reflections. The stationary background counts were measured for 40 sec at each end of the scan interval. The aperture size of the detector was 2.0°. As a check of the electronic stability during the period of data collection, the intensity of two standard reflections, 400 and 050, were measured at regular intervals. The fluctuation of their intensities was random, and the values of $(I_{max} - I_{min})/I_{max}$ were less than 6%. A total of 2232 independent reflections were recorded ($h \geq 0$, $k \geq 0$). 209 reflections for which the two measured background values differed more than 3.09 times the estimated standard deviations of their difference were omitted. The integrated peak counts I were calculated from the total integrated peak counts, the background counts and the counting time in the usual way. 532 reflections with $I \leq 2.58\sigma(I)$ were considered unobserved. The values of $\sigma(I)$ were based on counting statistics. The remaining 1491 reflections were corrected for Lorentz, polarization and absorption effects. The transmission factors, evaluated by numerical integration, varied from 0.04 to 0.61.

Structure determination and refinement

The positions of the heavy atoms were determined by symbolic addition methods. The asymmetric part of the E map showed three maxima of nearly the same height, indicating the positions of the atoms Hg(1)—Hg(3) of the unit cell. Least-squares refinement followed by difference Fourier syntheses revealed the positions of the phosphorus and oxygen atoms. The positional parameters, the isotropic temperature factors and the inter-layer scale factors were then included in a full-matrix least-squares refinement, minimizing $\Sigma w_i(|F_o| - |F_c|)^2$ with weights $w_i = [\sigma^2(F_o) + a|F_o|^2]^{-1}$. A suitable value for a was found from an analysis of the weighting scheme. The discrepancy factors R and R_w, defined by $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w_i(|F_o| - |F_c|)^2/\Sigma w_i|F_o|^2]^{1/2}$, converged to $R = 0.064$ and $R_w =$

$= 0.083$. When anisotropic temperature factors were introduced for all atoms in a new refinement, the R value fell to 0.043 and R_w to 0.051. In the last cycle of refinement the value of a was 0.001. At the end of the refinement the value of S was 0.99. The expression for S (goodness of fit) is $S = [\Sigma w_i(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, where

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

Atom	x	y	z
Hg(1)	1.04137(7)	0.62072(5)	0.67502(8)
Hg(2)	0.69987(7)	0.39641(6)	0.82674(8)
Hg(3)	0.65409(7)	0.67005(6)	0.41226(9)
P(1)	0.6109(4)	0.4010(4)	0.3051(5)
P(2)	0.8972(4)	0.8666(3)	0.5987(5)
O(11)	0.551(1)	0.525(1)	0.249(2)
O(12)	0.716(1)	0.407(1)	0.511(2)
O(13)	0.698(1)	0.356(1)	0.139(2)
O(14)	0.492(1)	0.316(1)	0.317(2)
O(21)	1.034(1)	0.798(1)	0.583(2)
O(22)	0.783(1)	0.778(1)	0.632(2)
O(23)	0.916(1)	0.940(1)	0.804(2)
O(24)	0.860(1)	0.941(1)	0.399(2)

Table 3. *Thermal parameters β_{ij} with estimated standard deviations in parentheses.* The expression used is $\exp[-(\beta_{11} \cdot h^2 + \beta_{22} \cdot k^2 + \beta_{33} \cdot l^2 + 2\beta_{12} \cdot hk + 2\beta_{13} \cdot hl + 2\beta_{23} \cdot kl)]$. The β_{ij} values are multiplied by 10^5 for Hg, 10^4 for P and 10^3 for O. The root-mean-square components, R_i, of thermal vibration along principal axes of the ellipsoids of vibration are also given

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Hg(1)	276(6)	110(5)	734(12)	23(4)	30(6)	33(4)	0.126Å	0.083Å	0.113Å
Hg(2)	288(6)	282(5)	458(11)	29(4)	49(6)	−22(5)	0.139	0.096	0.114
Hg(3)	341(6)	228(6)	794(12)	114(4)	171(7)	121(5)	0.155	0.095	0.115
P(1)	19(4)	12(3)	38(7)	−4(2)	5(4)	−2(3)	0.104	0.077	0.088
P(2)	14(3)	6(3)	48(7)	0(2)	2(4)	−1(3)	0.100	0.062	0.081
O(11)	3(1)	3(1)	13(3)	0(1)	−1(2)	1(1)	0.183	0.108	0.145
O(12)	1(1)	4(1)	6(2)	0(1)	1(1)	1(1)	0.162	0.047	0.112
O(13)	3(1)	3(1)	5(2)	0(1)	2(1)	0(1)	0.142	0.088	0.124
O(14)	3(1)	5(1)	8(2)	−2(1)	4(1)	−1(1)	0.199	0.026	0.132
O(21)	2(1)	1(1)	12(3)	1(1)	1(1)	0(1)	0.155	0.075	0.119
O(22)	1(1)	3(1)	8(2)	−1(1)	1(1)	−1(1)	0.158	0.046	0.119
O(23)	2(1)	2(1)	8(2)	0(1)	2(1)	−1(1)	0.138	0.090	0.109
O(24)	1(1)	2(1)	8(2)	0(1)	−1(1)	0(1)	0.136	0.044	0.108

Table 4. *Selected interatomic distances and angles in the structure of* $Hg_3(PO_4)_2$. Estimated standard deviations are given in parentheses. For notations of the atoms, *cf.* Table 2

Mercury to oxygen distances		O—Hg—O angles	
within the nets		O(21)—Hg(1)—O(23)	163.4(4)°
		O(13)—Hg(2)—O(12)	169.9(5)
Hg(1)—O(21)	2.11(1) Å	O(11)—Hg(3)—O(22)	163.9(5)
Hg(1)—O(23)	2.11(1)		
Hg(2)—O(13)	2.06(1)		
Hg(2)—O(12)	2.06(1)		
Hg(3)—O(11)	2.13(1)		
Hg(3)—O(22)	2.12(1)		
between the nets			
Hg—O	≥ 2.42(1) Å		

Distances and angles within the PO_4 tetrahedra

P(1)—O(11)	1.55(1) Å	P(2)—O(21)	1.56(1) Å
—O(12)	1.53(1)	—O(22)	1.55(1)
—O(13)	1.55(1)	—O(23)	1.55(1)
—O(14)	1.53(1)	—O(24)	1.53(1)
Mean values	1.541(6)		1.545(6)
O(1*i*)—O(1*j*)	2.43(2)—2.57(2) Å	O(2*i*)—O(2*j*)	2.43(2)—2.58(2) Å
O(11)—P(1)—O(12)	109.2(7)°	O(21)—P(2)—O(22)	108.3(6)°
O(11)—P(1)—O(13)	111.8(7)	O(21)—P(2)—O(23)	110.2(6)
O(11)—P(1)—O(14)	109.5(8)	O(21)—P(2)—O(24)	108.3(6)
O(12)—P(1)—O(13)	104.0(6)	O(22)—P(2)—O(23)	103.3(6)
O(12)—P(1)—O(14)	113.1(6)	O(22)—P(2)—O(24)	113.9(6)
O(13)—P(1)—O(14)	109.3(7)	O(23)—P(2)—O(24)	112.7(6)

m denotes the number of observations and n the number of parameters varied. Thus the errors seem to be correctly estimated. All parameter shifts were less than 5% of the estimated standard deviations. Corrections for extinction and for anomalous dispersion were not included in the calculations, however. A final three-dimensional difference synthesis was calculated, with the contributions of all atoms subtracted. The highest remaining peak had an approximate height of $3 e/Å^3$. The scattering factors were those of CROMER and WABER

Table 5. *Observed and calculated structure amplitudes*

k	$\|F_o\|$	$\|F_c\|$
	1 k -9	
1	107	110
2	136	135
3	132	132
6	86	85
7	63	66
	2 k -9	
1	110	112
3	45	31
4	62	64
5	189	187
	3 k -9	
2	181	174
3	53	38
6	57	49
7	66	62
	4 k -9	
2	78	78
3	80	82
5	67	61
	5 k -9	
1	74	68
	1 k -8	
2	62	55
3	126	126
6	110	112
7	184	181
10	68	69
11	132	133
	2 k -8	
0	84	88
2	45	46
3	47	46
4	48	43
5	48	49
6	87	88
8	46	52
9	94	96
	3 k -8	
0	193	192
1	155	161
3	96	98
4	123	128
5	135	136
6	43	47
10	78	76
11	44	40
	4 k -8	
2	44	49
3	173	175
4	44	46
6	93	93
7	246	245
8	56	62
9	43	33
10	52	49
11	177	175
	5 k -8	
0	209	210
1	48	39
4	125	124
5	81	80
9	94	93
	6 k -8	
0	121	123
1	105	109
4	57	58
5	97	98
7	47	29
	7 k -8	
0	42	31
3	139	133
7	191	190
8	43	40
11	141	130
	8 k -8	
0	226	227
4	171	165
5	41	45
8	44	48
	1 k -7	
1	51	53
2	86	89
4	139	141
5	49	43
6	192	190
8	132	133
10	193	193
11	62	61
	2 k -7	
1	187	186
2	247	245
3	184	184
5	64	63
6	148	151
7	52	39
10	66	59
11	64	65
	3 k -7	
1	47	60
4	86	90
5	180	180
8	88	85
9	193	193
11	50	42
	4 k -7	
2	93	92
4	86	87
5	47	50
7	56	63
8	62	60
10	106	107
11	75	73
	5 k -7	
1	131	133
2	193	195
3	172	172
5	40	45
6	81	79
7	79	84
8	52	50
	6 k -7	
2	67	70
4	48	51
5	262	261
6	68	69
8	59	57
9	254	249
10	58	59
	7 k -7	
2	236	236
3	78	78
4	53	54
5	43	36
6	83	84
7	75	78
11	79	73
	8 k -7	
1	69	69
2	135	138
3	117	111
7	72	75
10	98	93
	9 k -7	
1	95	90
2	75	69
5	214	211
6	62	58
9	199	193
	10 k -7	
2	227	216
3	62	62
6	110	111
7	50	44
	1 k -6	
0	197	202
1	259	260
3	181	184
4	154	157
5	123	125
7	50	45
8	100	106
9	68	72
	2 k -6	
0	44	46
1	127	137
2	83	85
5	58	65
6	155	152
7	64	67
9	72	74
10	96	93
11	42	48
	3 k -6	
0	131	130
2	151	152
3	54	51
4	187	193
5	37	34
6	235	238
7	60	60
8	236	237
9	73	76
10	125	125
	4 k -6	
0	305	314
1	258	262
3	196	200
4	229	233
5	146	151
6	37	37
7	110	114
8	82	84
11	68	73
	5 k -6	
1	44	37
2	52	55
3	86	92
6	114	114
7	195	201
9	68	71
10	94	98
11	156	153
	6 k -6	
0	48	56
2	75	72
3	55	49
5	81	81
6	136	135
7	46	44
8	107	104
9	73	68
10	56	54
	7 k -6	
0	202	206
1	155	158
3	121	122
4	140	144
5	124	125
7	57	59
10	46	53
11	58	60
	8 k -6	
0	102	108
3	182	180
4	82	83
6	68	65
7	262	259
8	50	51
11	175	170
	9 k -6	
0	266	267
1	72	71
4	172	168
5	87	81
6	51	42
7	51	49
9	63	58
	10 k -6	
0	149	152
1	64	67
4	47	49
5	69	69
8	84	81
9	58	51
10	51	47
	11 k -6	
0	86	86
3	171	171
4	63	71
7	215	210
8	55	45
	12 k -6	
0	240	232
	1 k -5	
1	273	277
2	146	152
3	253	250
4	100	99
5	127	133
6	85	83
7	84	83
8	45	45
9	43	44
10	34	18
	2 k -5	
1	57	56
2	127	134
3	51	57
4	215	220
5	50	52
6	230	232
8	246	250
9	47	45
10	252	253
	3 k -5	
1	199	204
2	209	214
3	200	204
4	94	99
5	78	75
6	117	120
10	57	54
11	120	122
	4 k -5	
1	67	71
2	57	56
3	155	157
4	123	125
5	79	79
7	129	128
9	134	138
10	124	126
11	99	98
	5 k -5	
2	118	116
3	69	72
4	223	227
5	63	66
6	205	209
7	77	76
8	200	205
9	62	66
10	209	213
11	74	76
	6 k -5	
1	273	277
2	302	311
3	226	225
4	70	68
5	171	174
6	135	133
7	56	60
9	114	112
11	56	58
	7 k -5	
2	49	44
3	39	40
4	100	94
5	172	173
6	109	110
8	35	33
9	63	67
11	112	112
	8 k -5	
3	83	83
4	123	126
5	78	78
6	77	73
7	103	101
8	128	127
9	56	59
10	111	111
11	60	63
	9 k -5	
1	175	178
2	206	202
3	153	151
4	42	43
5	138	134
6	58	59
7	50	43
9	83	89
	10 k -5	
1	47	55
2	127	129
4	54	48
5	185	184
6	80	72
8	89	77
9	216	204
11	58	63
	11 k -5	
2	160	151
3	92	95
4	72	69
5	78	80
6	73	75
9	57	50
	12 k -5	
2	78	86
3	75	61
7	67	37
	1 k -4	
0	149	151
2	182	185
4	185	194
5	65	67
6	296	307
8	257	266
9	100	105
10	167	174
	2 k -4	
0	65	64
1	108	109
2	106	104
4	64	65
5	37	35
6	197	200
7	129	128
9	134	138
10	124	126
11	99	98
	3 k -4	
0	233	236
1	342	347
3	275	282
4	177	181
5	240	245
6	69	72
7	115	117
8	95	96
11	60	57
	4 k -4	
0	186	192
2	153	157
4	240	242
6	308	313
8	294	298
9	51	58
10	189	189
11	44	38
	5 k -4	
0	222	228
1	206	214
2	72	71
3	125	126
4	129	134
5	99	104
6	109	110
8	35	33
9	63	67
10	36	32
	6 k -4	
0	62	67
1	194	198
4	58	60
5	106	104
6	56	61
7	100	103
8	49	50
9	65	66
10	40	47
11	64	68
	7 k -4	
0	58	58
1	99	101
2	130	131
4	155	151
5	116	115
6	220	220
7	63	62
8	208	212
9	58	53
10	128	123
	8 k -4	
0	275	278
1	235	233
2	60	46
3	185	181
4	181	180
5	165	162
6	70	67
7	142	140
11	93	96
	9 k -4	
0	92	89
3	119	113
6	63	61
7	220	215
8	50	38
9	63	72
10	91	79
11	167	161
	10 k -4	
1	77	73
5	123	120
6	97	91
7	64	76
8	112	105
9	83	81
	11 k -4	
0	221	200
1	160	150
3	164	156
4	158	147
5	100	95
7	100	106
9	68	25
	12 k -4	
0	163	148
3	118	136
7	183	197
10	100	78
11	137	143
	13 k -4	
0	116	117
1	62	54
4	88	87
6	79	42
7	97	91
	1 k -3	
1	110	111
2	118	124
3	102	98
4	173	177
5	308	321
6	127	133
8	165	173
9	266	279
10	102	104
11	120	126
	2 k -3	
1	441	463
2	246	256
3	414	428
5	206	207
6	106	108
7	88	91
9	92	91
11	91	94
	3 k -3	
2	130	130
4	261	270
6	283	294
7	45	49
8	244	248
9	51	53
10	252	256
11	109	113
	4 k -3	
1	103	103
2	80	83
3	97	97
4	218	222
5	45	49
6	199	202
7	113	113
10	35	21
11	133	137
	5 k -3	
1	357	364
2	180	177
3	334	339
4	58	58
5	169	170
6	169	167
7	94	96
8	35	39
9	69	67
10	116	116
11	136	138
	6 k -3	
2	285	285
4	272	269
6	328	329
8	285	284
9	66	65
10	282	279
11	69	66
	7 k -3	
1	202	207
2	206	199
3	158	155
4	158	158
5	133	132
6	57	59
8	128	128
11	118	114
	8 k -3	
1	179	175
3	220	216
6	52	55
8	54	44
9	63	53
10	72	70
11	141	141
	9 k -3	
1	68	53
2	170	151
3	118	118
4	212	207
5	56	42
6	182	177
7	60	55
8	208	200
10	174	162
	10 k -3	
1	215	205
2	196	182
3	175	165
4	120	106
5	193	187
9	137	129
	11 k -3	
5	106	123
9	134	147
11	126	111
	12 k -3	
4	67	72
7	96	98
8	86	86
	13 k -3	
1	125	134
2	153	153
3	87	102
4	67	49
5	129	126
6	58	35
7	54	67
9	96	93
	1 k -2	
0	344	349
1	436	457
2	45	40
3	210	214
4	148	156
5	349	366
6	45	49
7	73	75
8	69	71
9	76	80
10	138	140
11	82	88
	2 k -2	
0	369	376
2	117	121
3	39	36
4	172	174
5	135	139
6	184	188
7	27	27
8	60	57
9	179	187
10	23	17
11	51	53
	3 k -2	
0	37	33
1	47	48
2	136	157
3	315	318
4	131	131
6	235	245
7	395	406
8	169	166
9	52	54
10	125	127
11	247	254
	4 k -2	
0	317	316
1	457	471
3	258	255
4	202	200
5	268	272
6	92	92
7	67	67
8	62	65
10	116	116
11	103	101
	5 k -2	
1	66	69
2	126	125
3	44	45
4	116	111
6	224	224
7	50	51
8	224	224
9	117	113
10	132	122
11	45	42
	6 k -2	
0	196	186
1	68	67
2	120	120
3	64	53
4	102	103
5	72	62
6	235	230
7	126	120
10	100	99
11	111	108
	7 k -2	
0	227	219
1	286	269
3	195	187
4	205	188
5	194	182
8	146	141
	8 k -2	
0	263	237
1	87	79
2	140	119
4	251	231
6	249	238
8	287	271
10	158	156
	9 k -2	
0	222	244
4	145	157
6	136	158
	10 k -2	
1	176	174
3	84	82
5	86	80
8	103	100
9	68	69
	11 k -2	
0	129	124
1	105	106
2	80	79
4	157	158
5	92	85
6	186	181
7	70	63
8	152	155
10	153	159
	12 k -2	
0	144	146
1	143	152
2	75	68
3	175	183
4	84	83
5	69	62
6	90	99
7	150	161
11	96	100
	13 k -2	
0	121	125
4	66	73
7	80	85
9	50	68
10	52	51
	14 k -2	
1	75	91
	1 k -1	
2	470	523
	2 k -1	
1	224	231
3	28	31
4	191	198
5	434	456
6	188	194
7	31	28
8	235	235
9	368	384
10	174	174
	3 k -1	
1	442	442
2	250	246
3	388	385
5	168	162
6	86	85
7	184	180
8	71	69
9	33	32
11	70	68
	4 k -1	
2	271	255
4	235	219
5	62	52
7	177	164
8	138	131
10	133	126
11	222	220
	5 k -1	
1	247	218
4	326	297
5	366	343
6	128	123
7	83	75
8	242	226
9	307	291
10	117	105
11	117	109
	6 k -1	
1	415	358
2	223	206
3	440	397
4	94	68
5	196	173
6	195	188
7	127	122
8	111	115
9	79	87
11	95	83
	7 k -1	
1	140	111
3	104	87
4	220	189
6	183	159
7	87	82
8	193	170
10	197	188
11	173	162
	8 k -1	
2	91	81
4	204	187
5	88	93
8	179	181
9	117	113
10	50	37
	9 k -1	
1	191	186
2	200	196
3	198	200
4	78	76
5	78	77
6	174	168
8	59	54
10	129	133
11	126	123
	10 k -1	
1	104	103
2	160	163
3	109	117
4	149	153
6	198	200
8	149	155
9	189	196
10	61	65
	11 k -1	
2	169	176
3	57	66
4	106	114
5	77	71
6	67	61
8	107	112
	12 k -1	
1	83	94
3	96	100
6	102	111
7	48	45
8	101	106
10	101	108
	13 k -1	
1	52	60
2	105	111
3	85	105
4	78	86
6	121	122
7	48	45
8	101	106
10	101	108
	14 k -1	
1	97	100
2	99	106
3	49	59
	2 k 0	
5	307	237
7	321	256
10	57	44
	3 k 0	
0	780	685
2	100	76
3	92	62
4	540	487
6	60	39
7	90	81
8	114	102
9	83	77
10	141	128
11	79	75
	4 k 0	
1	214	188
2	81	72
3	398	356
4	64	55
6	191	180
7	438	412
8	198	186
10	109	103
11	299	290
	5 k 0	
0	274	254
1	384	361
3	154	148
4	199	187
5	305	289
8	45	33
10	55	52
11	44	30
	6 k 0	
0	233	221
2	102	99
4	105	104
6	127	129
7	71	67
8	93	84
9	167	162
11	88	87
	7 k 0	
0	63	60
1	150	143
2	159	158
3	234	227
5	64	67
6	227	228
7	265	267
8	107	104
9	65	61
10	113	106
11	201	204
	8 k 0	
0	192	186
1	374	378
2	49	59
3	229	225

Table 5. *(Continued)*

k	$\|F_o\|$	$\|F_c\|$
4	173	170
5	232	232
6	93	96
7	82	83
8	136	138
10	63	70
11	81	82
	9 k 0	
0	49	51
1	80	93
2	76	80
4	101	107
6	161	164
7	49	51
8	134	136
9	112	118
10	115	115
11	50	51
	10 k 0	
0	59	63
2	95	90
6	187	189
8	44	43
10	87	91
11	71	70
	11 k 0	
1	185	198
3	145	152
4	124	127
5	98	101
6	77	80
7	48	48
8	119	126
9	57	54
10	43	50
	12 k 0	
0	154	165
1	123	124
2	54	57
3	66	70
4	147	152
5	80	85
6	125	134
8	145	156
10	105	119
	13 k 0	
0	84	96
1	59	58
2	76	78
3	83	85
4	51	62
6	117	131
7	67	71
10	57	53
	0 k 1	
2	90	95
3	221	227
4	31	34
6	124	126
	1 k 1	
1	36	38
2	100	102
3	202	195
4	146	148
	2 k 1	
2	686	784
4	110	104
5	72	72
6	354	363
8	59	55
9	46	50
10	69	67
11	43	44
	3 k 1	
1	209	195
3	47	38
4	152	146
5	356	349
6	245	241
8	46	43
9	302	299
10	295	285
	4 k 1	
0	283	261
4	55	46
5	185	177
6	109	103
7	149	142
8	76	76
9	185	179
10	140	135
	5 k 1	
2	562	522
6	273	269
9	74	84
11	132	127
	6 k 1	
1	246	251
4	159	156
5	395	378
6	111	118
8	91	111
9	327	312
10	192	181
	7 k 1	
1	189	173
2	181	162
3	267	243
4	91	74
6	120	110
7	158	155
8	111	101
	8 k 1	
2	194	184
3	58	45
5	69	72
7	77	86
9	92	85
10	106	106
11	141	150
	9 k 1	
1	175	173
2	103	100
3	97	95
4	174	173
5	227	230
8	126	126
9	217	223
10	55	53
	10 k 1	
1	172	177
2	159	156
3	219	232
4	99	100
5	68	68
6	158	163
7	127	129
8	98	101
10	105	104
	11 k 1	
1	62	61
2	50	52
3	53	52
4	80	74
6	77	77
7	66	62
8	52	61
9	65	65
10	102	109
11	120	127
	12 k 1	
2	71	73
4	102	105
5	50	55
8	96	102
	13 k 1	
1	107	124
2	78	82
3	106	111
4	64	74
5	73	73
6	90	91
8	57	66
	0 k 2	
4	312	290
7	122	115
8	107	113
9	105	105
10	74	73
11	75	68
	8 k 2	
1	114	130
3	246	236
6	129	144
7	240	244
8	148	141
11	196	189
	9 k 2	
1	188	169
4	107	95
5	162	153
6	115	108
10	69	73
	10 k 2	
0	137	135
1	76	73
4	92	84
7	61	61
9	110	104
	11 k 2	
0	93	86
1	123	127
2	71	82
3	160	156
4	50	40
5	57	43
6	132	134
7	156	164
10	69	75
11	141	145
	12 k 2	
0	131	133
1	134	145
2	57	68
3	70	76
4	147	148
5	116	117
6	105	106
8	130	139
10	56	60
	13 k 2	
1	60	60
	0 k 3	
0	597	625
2	244	249
3	68	70
4	250	255
5	47	49
6	29	25
7	110	114
8	113	115
10	93	96
11	102	106
	1 k 3	
1	292	298
2	221	223
3	347	350
5	136	141
7	165	173
8	43	46
9	66	67
10	160	165
	2 k 3	
1	221	220
2	245	252
4	85	86
5	394	409
6	213	218
7	149	144
8	138	141
9	368	381
10	153	155
11	80	81
	3 k 3	
1	59	54
2	464	482
3	82	81
4	63	61
5	84	89
6	204	205
7	110	112
9	58	59
11	80	84
	4 k 3	
1	85	84
2	185	183
3	143	144
5	46	43
6	39	30
7	123	126
9	71	72
10	180	183
	5 k 3	
1	110	106
2	181	178
3	77	76
5	334	337
6	130	131
7	67	63
8	89	82
9	270	269
10	123	123
	6 k 3	
1	57	57
2	446	446
4	48	16
5	169	171
6	231	224
8	77	68
9	132	128
10	49	51
	7 k 3	
1	151	140
2	120	115
3	55	48
4	79	75
5	175	168
6	73	72
9	167	157
10	170	170
	8 k 3	
1	65	34
2	91	84
3	157	150
5	103	114
7	104	108
9	105	114
	9 k 3	
2	315	285
5	109	114
6	165	162
9	107	127
11	124	105
	10 k 3	
1	168	152
3	114	97
4	115	94
5	172	172
9	169	164
10	108	115
	11 k 3	
1	63	77
3	126	132
4	81	67
7	81	84
8	69	64
	12 k 3	
2	79	76
	0 k 4	
0	300	303
1	399	413
2	83	80
3	334	337
4	176	180
5	289	239
6	58	56
7	185	188
11	129	132
	1 k 4	
0	113	117
1	96	92
2	91	88
3	137	134
4	138	143
6	194	194
7	253	261
8	79	85
9	122	121
10	153	156
11	180	183
	2 k 4	
0	166	170
2	115	115
3	55	58
4	53	51
5	111	115
6	213	218
7	65	57
8	63	61
9	72	76
10	105	110
	3 k 4	
0	157	162
1	262	269
2	52	51
3	218	224
4	48	57
5	159	167
6	58	60
7	131	136
8	102	103
10	67	66
11	97	98
	4 k 4	
0	261	272
2	69	72
3	182	183
4	224	230
6	113	115
7	285	292
8	145	147
9	56	55
10	100	100
11	191	191
	5 k 4	
0	339	344
1	45	54
3	46	39
4	260	262
5	80	79
6	78	75
7	107	105
8	90	88
9	67	63
	6 k 4	
0	127	130
1	98	94
3	53	54
5	79	87
8	139	143
10	47	49
	7 k 4	
0	166	163
1	175	169
4	136	130
5	71	74
7	223	220
8	105	104
10	72	70
11	136	136
	8 k 4	
0	318	307
3	95	94
4	266	256
7	129	132
8	122	115
11	71	65
	9 k 4	
0	122	126
1	89	79
3	137	126
4	67	32
7	125	119
8	108	107
11	90	93
	10 k 4	
5	96	100
9	87	84
	11 k 4	
0	236	223
4	177	163
7	138	120
	0 k 5	
2	62	71
3	82	80
4	103	106
5	102	103
6	31	36
8	116	121
9	128	131
10	34	34
11	162	164
	1 k 5	
1	61	68
2	87	89
3	119	116
4	209	213
6	181	179
7	87	91
8	199	204
10	193	195
11	97	98
	2 k 5	
1	317	320
2	238	241
3	275	277
4	57	56
5	197	204
6	46	46
7	95	99
9	138	136
10	36	28
11	48	45
	3 k 5	
2	116	117
3	45	50
4	94	96
5	197	203
6	79	73
8	150	153
9	214	216
11	105	106
	4 k 5	
2	70	71
3	92	94
4	141	145
5	103	105
7	91	93
8	110	114
9	44	45
10	55	63
11	55	54
	5 k 5	
1	187	189
2	120	121
3	172	174
4	40	43
5	162	162
7	55	51
9	121	119
10	123	118
11	43	39
	6 k 5	
1	57	55
2	240	244
4	61	66
5	165	168
6	157	156
8	104	106
9	204	199
10	85	81
11	55	49
	7 k 5	
2	201	203
3	53	59
4	68	63
5	111	106
6	122	118
7	62	52
9	96	90
11	45	24
	8 k 5	
1	86	75
3	67	60
6	53	59
10	149	146
	9 k 5	
2	188	177
5	124	122
6	107	107
9	129	131
10	66	67
	10 k 5	
2	204	184
5	103	104
6	129	117
	0 k 6	
0	154	157
1	82	83
2	129	126
3	79	78
4	208	210
5	47	50
6	263	263
7	47	47
8	233	233
10	178	178
11	49	50
	1 k 6	
0	70	72
1	219	222
2	48	52
3	186	187
4	35	40
5	139	141
6	119	121
7	92	89
10	47	44
11	53	53
	2 k 6	
1	110	110
5	39	40
6	51	56
7	80	83
9	111	110
10	50	46
11	67	69
	3 k 6	
0	75	79
1	113	119
2	103	105
3	45	52
4	110	112
5	107	112
6	195	195
8	158	158
9	71	67
10	124	124
11	56	54
	4 k 6	
0	148	146
1	232	231
2	62	57
3	214	219
4	72	72
5	168	171
6	74	70
7	155	158
9	39	45
11	95	97
	5 k 6	
3	95	96
4	76	77
6	80	73
7	165	166
9	83	79
10	82	94
11	129	127
	6 k 6	
7	60	52
9	90	90
11	45	24
	8 k 6	
1	68	59
2	48	47
5	89	91
6	87	80
7	61	58
8	48	45
10	55	51
	9 k 6	
7	62	57
10	94	88
	10 k 6	
1	122	121
3	144	145
4	70	63
5	66	70
7	117	108
8	51	56
10	56	37
11	69	65
	11 k 6	
3	193	187
4	104	104
6	159	158
7	56	53
8	151	154
9	68	75
10	96	87
	12 k 6	
0	42	33
1	81	83
2	65	65
3	64	62
4	73	80
6	113	109
8	150	145
9	65	55
10	60	61
	2 k 8	
0	90	86
1	54	49
2	74	74
4	55	51
5	51	50
6	123	119
7	53	50
8	119	115
9	50	47
	4 k 8	
0	98	99
1	82	79
2	56	57
3	55	52
4	123	121
5	47	48
6	120	119
8	137	137
	0 k 9	
8	96	89
9	69	62
11	47	43
	4 k 7	
1	83	83
3	83	86
8	40	36
9	57	53
10	47	29
11	138	132
	5 k 7	
1	71	70
2	101	98
3	111	109
4	144	142
6	96	96
7	60	56
8	167	167
9	123	124
10	57	48
	7 k 7	
2	65	55
4	83	85
5	174	173
7	81	77
8	50	53
9	123	124
10	57	48
	8 k 7	
0	213	214
1	157	157
3	100	98
4	181	183
5	93	88
6	52	51
8	91	92
9	68	71
11	41	27
	1 k 8	
0	193	187
3	104	104
4	159	158
6	56	53
7	151	154
8	68	75
10	96	87
	9 k 6	
0	149	143
	0 k 7	
1	63	66
2	88	86
3	89	91
4	137	138
6	37	30
8	108	109
9	66	61
10	39	34
11	61	56
	1 k 7	
1	165	167
2	146	145
3	176	174
5	54	56
6	130	126
10	90	91
11	112	109
	2 k 7	
1	75	80
2	169	167
3	52	54
4	166	166
6	187	183
8	183	183
10	170	169
11	42	40
	3 k 7	
1	166	169
2	70	65
3	131	135
4	101	102
5	123	130
7	40	36
8	96	89
9	69	62
11	47	43

(1965) for neutral mercury and of HANSON *et al.* (1964) for neutral phosphorus and oxygen. The final positional and thermal parameters, together with the root-mean-square components, are given in Tables 2

and 3 and selected interatomic distances and angles in Table 4. Observed and calculated structure amplitudes are presented in Table 5.

Description and discussion of the structure

As seen from Table 4 the mercury atoms are each coordinated to two oxygen atoms, the Hg—O distances varying from 2.06(1) to 2.13(1) Å and the O—Hg—O angles from 163.4(4) to 169.9(5)°. The values of the distances are in good agreement with those found in the infinite –O—Hg—O– chains of orthorhombic HgO [2.04(3), 2.07(3) Å] (AURIVILLIUS, 1956, 1964), and in the –Hg—O—Cr—O—Hg– chains of $HgCrO_4 \cdot \frac{1}{2} H_2O$ [2.055(1), 2.064(1) Å] (AURIVILLIUS and STÅLHANDSKE). The values of the O—Hg—O angles are more distorted in the present compound, however [179.5(1.1)° in HgO; 179.95(5)° in $HgCrO_4 \cdot \frac{1}{2} H_2O$]. A dominant feature of the structure of $Hg_3(PO_4)_2$ is thus the frequently occurring two-covalency of mercury(II).

The structure is built up of infinite puckered nets of formula $[Hg_3(PO_4)_2]_n$. Two such nets, related by $\bar{1}$, run through the unit cell. The nets are interpenetrating and the Hg—O distances between them are $\geq$ 2.42(1) Å.

The nets are formed from fused endless chains –Hg—O—P—O—Hg– in the following way: All oxygen atoms of the structure belong to phosphate tetrahedra; one of them consists of the atoms P(1), O(11)—O(14), and the other of the atoms P(2), O(21)—O(24). Each mercury atom is bonded to one oxygen atom of each of two phosphate groups, while three oxygen atoms of each phosphate group are bonded to mercury. The atoms Hg(1), bridging between the atoms O(21) and O(23), form separate endless –Hg—O—P—O—Hg– chains related to each other through $\bar{1}$. They run approximately parallel to [010]. In the same way, infinite chains, nearly parallel to [001], are formed as the atoms Hg(2) bridge the atoms O(12) and O(13) (*cf.* Table 2 for labelling of the atoms). The endless puckered nets are formed from –O(21)—Hg(1)—O(23)– and –O(12)—Hg(2)—O(13)– chains, fused by additional mercury atoms, Hg(3), which in turn are bonded to the atoms O(22) and O(11). The fourth corner of each tetrahedron, the atom O(24) or O(14), is not bonded to any mercury atom at short distance. The Hg—O distances within the nets are 2.06(1)—2.13(1) Å.

If the shortest mercury to oxygen distance between the nets of 2.42(1) Å is also considered as a coordination distance, the structure

may be described as built up of a three-dimensional network of formula $[Hg_3(PO_4)_2]_n$. A stereoscopic view of the structure is given in Fig. 1.

The phosphate tetrahedra are rather regular (Table 3), the mean P(1)—O and P(2)—O distances being 1.541(6) and 1.545(6) Å, respectively. These values are in good agreement with mean P—O values calculated from data given for other phosphates, *e.g.* Li_3PO_4 [1.546(3) Å] (KEFFER *et al.*, 1967), $Mg_3(PO_4)_2$ [1.527(3) Å] (NORD and

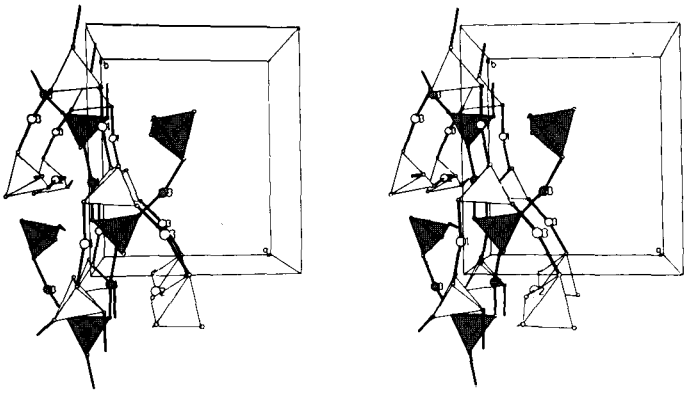

Fig. 1. Stereoscopic view along the *c* axis, showing two endless puckered nets of formula $[Hg_3(PO_4)_2]_n$, related by $\bar{1}$. The three mercury atoms are indicated as 1, 2 and 3. The nets are shadowed and unshadowed in the drawing. The *c* axis points against the reader

KIERKEGAARD, 1968) and $Zn_3(PO_4)_2$ [1.533 Å] (CALVO, 1965). There is, however, a small tendency towards elongation of the P—O bonds for the P—O—Hg bridging oxygen atoms, the largest difference in the bonds being about 3σ in the distances (0.036 Å). Much larger deformations of the tetrahedral groups are found in *e.g.* $HgCrO_4 \cdot \frac{1}{2} H_2O$, where the elongation of the Cr—O bonds for the two Cr—O—Hg bridging oxygen atoms in the infinite —Hg—O—Cr—O—Hg— chains amount to 0.12 Å ($\approx 60\sigma$ in the distances). In $Hg(OH)_2 \cdot 2\,HgSO_4 \cdot H_2O$, one oxygen atom of each sulfate tetrahedron bridges between sulfur and mercury in the limited chains O(SO$_4$)—Hg—O(OH)—Hg—O(OH)—Hg—O(SO$_4$), giving an elongation of 0.08 Å ($\approx 8\sigma$ in the distances).

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