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The Crystal Structure of Mercury(I) Sulphate and Selenate*

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Mercury(I) sulphate and mercury(I) selenate are isomorphous with monoclinic unit cells of the following dimensions $a=6.2802$ Å, $b=4.4273$ Å, $c=8.367$ Å, $\beta=91.76°$ (sulphate) and $a=6.3507$ Å, $b=4.5870$ Å, $c=8.499$ Å, $\beta=90.98°$ (selenate). The cells contain 2 formula units. The space group is $P2/c$. The mercury atoms are linked in pairs with Hg—Hg distances 2.500 Å and 2.51 Å, respectively. Each mercury atom has one oxygen neighbour at a short distance 2.24 Å (sulphate) and 2.21 Å (selenate). In this way infinite chains $-XO_4-Hg-Hg-XO_4-Hg-$ are formed which are almost perpendicular to the b axis. The Hg—Hg—O angles are 164.9° (sulphate) and 160° (selenate). The distances from a mercury atom in one chain to the closest situated oxygen atom in an adjacent chain are 2.49 Å and 2.50 Å, respectively.

The present investigation on mercury(I) sulphate and selenate is part of a research program on structures of inorganic and organic compounds containing monovalent mercury.[1] Very few such compounds have been studied previously. In structures reported so far the common feature is the pair of metal atoms, the bond length of which seems to depend on the nature of the ligand. A series of mercury(I) compounds with anions containing oxygen has been studied. The present structure and the previously published $Hg_2(BrO_3)_2$[2] have been investigated as to the influence of the anion on the mercury-mercury bond as well as to the coordination around mercury.

EXPERIMENTAL

Crystals were prepared through reaction between an aqueous mercury(I) nitrate solution — slightly acidified to avoid precipitation of basic salts — and sulphuric and selenic acid, respectively. The compounds differ greatly in solubility. The mercury(I) sulphate is easily prepared through slow evaporation of a dilute solution. The selenate is immediately precipitated from solutions of similar concentration. Since this precipitate yields very poor crystals a diffusion technique was applied. Two filter crucibles, one containing selenic acid and the other containing mercury(I) nitrate solution were placed in a large beaker partly filled with very dilute nitric acid. The three liquids were adjusted

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to the same level and the device set aside for two weeks. This method yielded great numbers of good crystals which grew downwards from the bottom of the crucible containing mercury nitrate. The sulphate formed colourless monoclinic crystals,[1] appearing as thick slightly elongated plates. The maximum length was 1.5 mm. The pale yellow selenate crystals were much smaller, similarly elongated, but rodlike rather than flat.

Table 1. Structural data for Hg_2SO_4 and Hg_2SeO_4.

Cell dimensions

Compound	a Å	b Å	c Å	$\beta°$	Z	d_{obs} g/cm³	d_{calc} g/cm³
Hg_2SO_4	6.2802±9	4.4273±5	8.367±2	91.76	2	7.05	7.10
Hg_2SeO_4	6.3507±8	4.5870±7	8.499±2	90.98	2	7.14	7.27

Positions used in space group $P2/c$.

4(*g*)	$\pm(x,y,z)$,	$\pm(\bar{x},y,\frac{1}{2}-z)$:	atoms Hg and O
2(*f*)	$(\frac{1}{2},y,\frac{1}{4})$,	$(\frac{1}{2},\bar{y},\frac{3}{4})$:	atoms S and Se

Final positional parameters and temperature factors.

Sulphate

	x	y	z	B Å²
Hg	0.1929±2	0.0524±4	−0.0203±2	*a*
S	—	0.566 ±3	—	1.4±2
O_1	0.693 ±4	0.394 ±8	0.262 ±3	2.5±5
O_2	0.497 ±4	0.767 ±7	0.104 ±3	1.4±4

[a]

b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
0.0097±4	0.031±2	0.0105±3	−0.006±1	0.0034±1	0.0018±9

Selenate

	x	y	z	B Å²
Hg	0.1939±9	0.0419±7	0.0138±3	*b*
Se	—	0.551 ±2	—	1.8±2
O_1	0.72 ±1	0.38 ±1	0.259 ±5	3.1±1
O_2	0.506 ±9	0.769 ±8	0.093 ±4	1.9±9

[b]

b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
0.020±3	0.048±2	0.0109±4	−0.0003±3	0.006±1	−0.006±1

The temperature factor expression used for the Hg atoms is

$$\exp-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)$$

All crystals obtained as described were twinned. Rodlike single crystals of the sulphate could, however, be cut with a razor blade from composite crystal plates parallel to the elongated direction. The selenate crystals were too small to adapt this method on but eventually a fragment of the conically shaped end of a composite crystal was found to be single.

Data were recorded on a Weissenberg camera using Cu$K\alpha$ radiation. The sulphate crystal was rotated around the rod axis and also around a perpendicular axis, using an integrating camera. The selenate was rotated around an axis normal to the extension of the rod. A non-integrating camera was used in the latter case. In this way data were collected for reflections $h0l-h3l$ and $0kl$ (sulphate) and for $0kl-3kl$ (selenate). Multiple film technique was applied. The number of independent reflections recorded was 309 and 232, respectively. The intensities were measured visually by comparison with an intensity scale. The data were corrected for Lorenz and polarization factors and for absorption.[3]

The Weissenberg photographs confirmed the monoclinic symmetry, and showed reflections $h0l$ to be present only for $l=2n$ which implies space group $P2/c$ or Pc, Nos. 13 and 7 of the *International Tables*. The cell constants obtained from Guinier powder photographs were refined through a least squares method program.[4] Densities were determined from the loss of weight in benzene. The cell dimensions are given in Table 1. For mercury sulphate these are in fair concordance with early optical measurements made by de Schulten.[5] The crystals studied by this author were obtained in the way described above. They were also analyzed for mercury and sulphur. The results corresponded to the formula Hg_2SO_4. De Schulten reports $a:b:c=1.4086:1:0.9002$ and $\beta=91°45'$. The c axis obtained from the present X-ray data is doubled, but this is shown only by the weak reflections hkl with $l=2n+1$. The strong reflections all of which have $l=2n$ indicate the presence of a pseudotetragonal substructure of the dimensions $a'=b$, $b'=c/2$ and $c'=a$.

This subunit was first studied by calculating the Patterson projection of the selenate along [100] using only $0kl$ reflections with $l=2n$. This exhibited broad major peaks only in the origin region and at $y=0$, $z=0.5$ in the true cell. A smaller peak appeared at $y=0.5$, $z=0.25$. The expected mercury doublet was therefore assumed to be oriented approximately in the [100] direction through (0,0,0) and (0,0,$\frac{1}{2}$). The selenium atoms were placed in the twofold position 2(*f*): ($\frac{1}{2}$,y,$\frac{1}{4}$)($\frac{1}{2}$,y,$\frac{3}{4}$) of space group $P2/c$ with y approximately 0.5.

Combinations of parameters close to $y=0$, $z=0$ were tried out for the mercury atoms using position 4(*g*) of space group $P2/c$, *i.e.* $\pm(x,y,z)$ $\pm(\bar{x},y,\frac{1}{2}-z)$ with $x=0.20$. The x parameter was chosen to give an Hg–Hg distance slightly above 2.5 Å. The selenium atoms were assumed to be situated at $\pm(\frac{1}{2},0.5,\frac{1}{4})$. Several sets of parameters were used for calculating Fourier maps $\varrho(yz)$ and $\varrho(xz)$, none of which gave any information as to the positions of the oxygen atoms.

Since the data from the sulphate were recorded around the more favourable b axis and of better quality than those of the selenate the $h0l$ data from the sulphate were evaluated. A Patterson projection along [010] made the principle of the structure obvious. A difference Fourier map $\varrho(xz)$ was calculated assuming space group $P2/c$ and using the structure factor signs obtained with the Hg parameters $x=0.195$, $z=-0.025$, and $\pm(\frac{1}{2},y,\frac{1}{4})$ for S. When the contributions from these atoms were subtracted, all oxygen atom peaks showed up on the resulting map.

Since the y parameter for the mercury atom was found to be close to zero a value of 0.01 was tentatively chosen. With $y=0.5$ for the sulphur atom the sign for the mercury y parameter is arbitrary. In the Fourier map $\varrho(yz)$ thus calculated the sulphur atom peak came out at $y=0.55$, $z=0.25$. There was also a low broad peak at $y=0.70$, $z=0.25$. The latter was interpreted as corresponding to two overlapping peaks from oxygen atoms in 4(*g*) (x,y,z) $(x,y,\frac{1}{2}-z)$. It was now possible to estimate the y parameter of the second oxygen atom position from spatial considerations. However, the difference Fourier map $\varrho(xz)$ showed partial splitting of the oxygen atom peaks. This was tentatively interpreted as due to a lower symmetry, *viz.* that of the alternative space group Pc. Attempts were accordingly made to refine the sulphate structure with three dimensional data by the least squares method assuming the latter space group. The results were not satisfactory giving no improvement in the standard deviations and R factor and obviously erroneous sulphur-oxygen distances.

Taking the space group to be $P2/c$ further refinement brought the R factor down to 0.105. The splitting of the oxygen atom peaks was found to be due to minor discrepancies in the mercury atom parameters. A difference Fourier map $\varrho(xz)$ calculated with contributions from Hg and S in final positions subtracted did not show any splitting of peaks.

As in $Hg_2(BrO_3)_2$ previously investigated by the present author a total difference Fourier map $\varrho(xz)$ showed peaks which were interpreted as likely to be due to anisotropic vibration of the mercury atoms. For that reason a refinement was carried out applying a full matrix least squares program LALS,[6] allowing refinement of anisotropic temperature factors. In order to keep the number of parameters down all atoms except the mercury atoms were assumed to vibrate isotropically. The scale factors were not allowed to vary mutually. Their ratios were fixed at the values obtained with isotropic refinement but the overall scale factor was refined. The positional parameters came out practically unchanged. The largest oxygen atom shift was 0.02 Å . The isotropic temperature factor decreased slightly for the oxygen atom closest to mercury and all standard deviations decreased by 30—40 %. The R factor was 0.078. The structural parameters are listed in Table 1.

Table 2. Analysis of the weighting schemes used in the refinements.

Interval F_{obs}	Number of reflections	$\overline{w\Delta^2}$ normalized	Interval $\sin^2\theta$	Number of reflections	$\overline{w\Delta^2}$ normalized
		Sulphate			
0— 26	30	1.20	0.00—0.46	47	1.27
26— 35	32	0.65	0.46—0.57	41	0.91
35— 41	30	0.81	0.57—0.66	40	1.16
41— 48	30	1.16	0.66—0.72	27	0.64
48— 56	31	0.75	0.72—0.78	35	0.80
56— 67	31	0.99	0.78—0.83	22	1.15
67— 80	30	0.89	0.83—0.87	22	1.00
80— 97	31	1.31	0.87—0.91	28	1.10
97—131	31	1.18	0.91—0.95	28	1.13
131—238	31	1.06	0.95—0.98	15	0.82
		Selenate			
0— 22	23	1.56	0.00—0.46	44	1.00
22— 27	23	1.03	0.46—0.57	36	0.97
27— 35	23	1.18	0.57—0.66	26	1.37
35— 40	23	1.08	0.66—0.72	23	1.08
40— 47	24	1.01	0.72—0.78	29	1.02
47— 58	23	1.01	0.78—0.83	16	1.03
58— 69	23	1.08	0.83—0.87	12	1.01
69— 92	23	0.56	0.87—0.91	15	1.05
92—117	23	0.62	0.91—0.95	16	0.61
117—242	24	0.86	0.95—0.98	12	0.87

The weighting function used in the refinement was one recommended by Hughes, *i.e.* $w=1/h^2|F_o,\min|^2$ for $|F_o|\leq h|F_o,\min|$ and $w=1/|F_o|^2$ for $|F_o|\geq h|F_o,\min|$. The parameter h was given the value 4. The weighting analysis obtained in the last cycles is given in Table 2 and observed and calculated structure factors are listed in Table 3.

The thermal displacement of the mercury atom was calculated with the program ORFFE [7] as were also the directions of the principal axes of the thermal ellipsoid. One principal axis is shorter than the other two and deviates only 8° from the direction of the merucry doublet bond (Table 4).

Table 3. hkl, $|F_o|$, and $|F_c|$ for mercury(I) sulphate and selenate. The reflections marked with asterisks were excluded from the refinement since there were difficulties in measuring their intensities.

Sulphate

	h	k	l	$\|F_o\|$	$\|F_c\|$
	1	0	-10	41	37
	2	0	-10	44	49
	-1	0	8	79	75
	2	0	-8	71	73
	4	0	-8	81	81
	5	0	-8	32	36
	-1	0	6	17	27
	-2	0	6	159	153
	3	0	-6	30	27
	4	0	-6	75	75
	5	0	-6	105	102
	6	0	-6	26	29
	-1	0	4	40	44
	-2	0	4	180	191
	3	0	-4	87	85
	4	0	-4	100	94
	5	0	-4	109	114
	7	0	-4	95	83
	-1	0	2	57	58
	2	0	-2	205	218
	3	0	-2	161	154
	4	0	-2	53	55
	5	0	-2	157	168
	6	0	-2	23	26
	7	0	-2	79	71
	1	0	0	36	30
	2	0	0	153	163
	3	0	0	200	218
	4	0	0	53	55
	5	0	0	117	119
	6	0	0	90	89
	7	0	0	78	70
	8	0	0	79	67
*	0	0	2	177	211
	1	0	2	144	171
	2	0	2	117	128
	3	0	2	183	194
	4	0	2	34	33
	5	0	2	148	140
	6	0	2	78	73
	7	0	2	28	29
	0	0	4	184	198
	1	0	4	136	145
	2	0	4	66	68
	3	0	4	157	154
	4	0	4	40	40
	5	0	4	83	71
	6	0	4	98	86
	0	0	6	68	71
	1	0	6	141	143
	2	0	6	22	23
	3	0	6	96	92
	4	0	6	77	74
	5	0	6	71	61
	6	0	6	62	52
	0	0	8	58	66
	1	0	8	71	72
	3	0	8	81	71
	4	0	8	40	34
	1	0	10	63	53
	2	0	10	15	19
	1	1	-10	53	49
	2	1	-10	36	34
	1	1	-9	21	17
	3	1	-9	25	24
	-1	1	8	34	38
	2	1	-8	86	85
	4	1	-8	54	58
	5	1	-8	42	51
	-1	1	7	37	41
	4	1	-7	30	28
	5	1	-7	23	20
	-1	1	6	63	67
	2	1	-6	120	114
	3	1	-6	44	38
	4	1	-6	96	89
	5	1	-6	69	65
	-1	1	5	48	51
	3	1	-5	54	48
	4	1	-5	31	28
	6	1	-5	30	30
	2	1	-4	197	177
	3	1	-4	84	75
	4	1	-4	77	71
	5	1	-4	134	126
	7	1	-4	64	67
	-1	1	3	53	54
	2	1	-3	25	27
	3	1	-3	43	41
	4	1	-3	41	43
	6	1	-3	33	38
	7	1	-3	15	19
	-1	1	2	16	7
	2	1	-2	201	180
	3	1	-2	155	141
	4	1	-2	77	76
	5	1	-2	125	118
	6	1	-2	47	46
	7	1	-2	77	77
	1	1	-1	67	61
	2	1	-1	82	75
	3	1	-1	66	61
	4	1	-1	42	42
	6	1	-1	38	39
	7	1	-1	14	17
	1	1	0	126	114
	2	1	0	186	176
	3	1	0	170	169
	5	1	0	162	151
	6	1	0	57	49
	7	1	0	53	49
	0	1	1	17	21
*	1	1	1	81	93
	2	1	1	22	27
	4	1	1	69	66
	7	1	1	19	35
	0	1	2	238	267
	1	1	2	88	104
	2	1	2	101	108
	3	1	2	176	180
	5	1	2	94	95
	6	1	2	89	85
	7	1	2	37	36
	0	1	3	49	47
	1	1	3	55	61
	2	1	3	48	56
	4	1	3	52	50
	7	1	3	22	25
	0	1	4	131	128
	1	1	4	140	151
	2	1	4	60	60
	3	1	4	133	132
	4	1	4	59	58
	5	1	4	96	89
	6	1	4	66	62
	0	1	5	26	27
	1	1	5	29	32
	2	1	5	33	34
	4	1	5	32	32
	5	1	5	31	22
	0	1	6	98	109
	1	1	6	88	99
	3	1	6	95	102
	4	1	6	38	39
	5	1	6	33	29
	6	1	6	61	64
	2	1	7	39	46
	5	1	7	22	24
	0	1	8	27	29
	1	1	8	85	84
	3	1	8	55	49
	4	1	8	55	51
	3	1	-9	11	12
	0	1	10	22	23
	1	1	10	36	39
	2	1	10	19	22
	1	2	-9	33	30
	2	2	-9	17	19
	3	2	-9	25	26
	-1	2	8	44	43
	2	2	-8	56	52
	4	2	-8	45	51
	-1	2	7	47	49
	3	2	-7	70	61
	2	2	-6	97	90
	4	2	-6	59	58
	5	2	-6	52	57
	-1	2	5	92	86
	3	2	-5	54	49
	4	2	-5	63	61
	6	2	-5	40	46
	-1	2	4	47	43
	2	2	-4	116	100
	3	2	-4	81	70
	4	2	-4	83	77
	5	2	-4	66	66
	-1	2	3	112	102
	2	2	-3	63	59
	3	2	-3	107	89
	4	2	-3	66	64
	6	2	-3	59	62
	-1	2	2	35	31
	2	2	-2	167	144
	3	2	-2	93	83
	4	2	-2	34	38
	5	2	-2	115	107
	7	2	-2	42	49
	1	2	-1	129	128
	2	2	-1	57	49
	3	2	-1	42	37
	4	2	-1	106	98
	6	2	-1	44	51
	7	2	-1	41	48
	1	2	0	67	60
	2	2	0	139	125
	3	2	0	125	114
	5	2	0	101	96
	6	2	0	41	42
	7	2	0	37	43
	0	2	1	20	21
	1	2	1	88	104
	2	2	1	104	111
	3	2	1	53	51
	4	2	1	73	82
	5	2	1	36	32
	6	2	1	41	47
	7	2	1	34	38
	0	2	2	133	132
	1	2	2	86	105
	2	2	2	89	93
	3	2	2	113	109
	5	2	2	93	93
	6	2	2	43	44
	7	2	2	22	19
	0	2	3	42	42
	1	2	3	89	92
	2	2	3	56	65
	4	2	3	75	80
	7	2	3	46	50
	0	2	4	141	133
	1	2	4	66	73
	3	2	4	111	115
	5	2	4	42	43
	6	2	4	55	61
	0	2	5	48	46
	2	2	5	90	89
	4	2	5	50	44
	5	2	5	39	41
	0	2	6	55	60
	1	2	6	80	80
	3	2	6	65	68
	4	2	6	44	38
	5	2	6	33	33
	0	2	7	48	45
	2	2	7	43	39
	4	2	7	32	30
	5	2	7	23	28
	0	2	8	24	34
	1	2	8	50	52
	3	2	8	39	43
	0	2	9	34	28
	2	2	9	33	39
	1	3	-8	20	20
	2	3	-8	30	34
	1	3	-7	61	55
	3	3	-7	50	50
	4	3	-7	29	35
	2	3	-6	39	43
	4	3	-6	36	41
	5	3	-6	25	25
	-1	3	5	76	78
	2	3	-5	25	24
	3	3	-5	104	86
	4	3	-5	43	45
	2	3	-4	75	67
	4	3	-4	41	37
	5	3	-4	38	43
	-1	3	3	168	130
	3	3	-3	54	50
	4	3	-3	107	96
	6	3	-3	54	54
	2	3	-2	76	65
	3	3	-2	57	52
	4	3	-2	47	34
	5	3	-2	51	52
	1	3	-1	132	122
	2	3	-1	103	82
	3	3	-1	85	73
	4	3	-1	90	90
	6	3	-1	57	63
	1	3	0	30	35
	2	3	0	82	74
	3	3	0	53	52
	5	3	0	54	58
	6	3	0	9	15
	1	3	1	105	117
	2	3	1	75	77
	4	3	1	105	100
	5	3	1	32	30
	6	3	1	38	44
	0	3	2	82	79
	1	3	2	41	42
	2	3	2	32	38
	3	3	2	67	69
	5	3	2	40	46
	6	3	2	24	28
	0	3	3	32	27
	1	3	3	56	61
	2	3	3	114	118
	3	3	3	35	29
	4	3	3	65	64
	5	3	3	50	52
	6	3	3	34	39
	0	3	4	61	59
	1	3	4	45	51
	3	3	4	52	51
	5	3	4	32	33
	0	3	5	60	58
	1	3	5	59	56
	4	3	5	55	60
	5	3	5	36	37
	0	3	6	39	37
	1	3	6	39	38
	3	3	6	41	43
	0	3	7	45	47
	2	3	7	68	61
	4	3	7	27	29
	1	3	8	30	35
	0	3	-9	48	42

Table 3. Continued.

Selenate

0	-1	0	193	187	1	-1	-1	40	37	2	-1	-3	11	13	2	-2	0	109	100
0	-2	0	195	196	1	-5	-1	23	24	2	-3	-7	22	13	3	-1	-9	23	18
0	-3	0	85	81	1	-5	-5	15	18	2	-1	-2	125	144	3	-2	-9	14	14
0	-4	0	55	50	1	-4	-6	26	8	2	-5	-5	14	19	3	-2	-8	42	35
0	-4	1	26	18	1	-1	-3	44	46	2	-5	5	9	14	3	-2	-7	54	51
0	-4	2	35	41	1	-1	-5	32	30	2	0	-10	53	61	3	-2	-6	35	31
0	-3	2	93	102	1	-1	-6	69	51	2	0	-8	64	70	3	-3	-7	27	26
0	-4	3	41	38	1	-1	-7	47	37	2	0	-6	140	165	3	-3	-6	47	42
0	-5	5	30	30	1	-1	-9	22	14	2	0	-4	143	156	3	-2	-4	105	99
0	-2	2	119	120	1	-1	-10	43	39	2	0	4	56	68	3	-3	-5	69	65
0	-3	4	60	62	1	-2	-9	38	31	2	0	6	72	68	3	-2	-3	70	76
0	-2	3	43	41	1	-2	-8	44	33	2	-1	8	39	28	3	-3	-4	33	28
0	-3	5	59	48	1	-2	-7	40	31	2	-1	7	45	40	3	-4	-5	20	21
0	-4	7	43	39	1	-2	-5	95	78	2	-1	6	31	15	3	-4	-4	27	25
0	-3	6	52	62	1	-3	-7	65	53	2	-2	9	34	34	3	-2	-2	60	64
0	-2	4	166	161	1	-3	-6	28	16	2	-1	4	104	103	3	-1	-1	38	53
0	-1	2	241	299	1	-2	-4	46	32	2	-2	7	28	20	3	-4	-3	58	54
0	-3	9	36	36	1	-4	-7	20	19	2	-2	6	45	42	3	-3	-2	76	73
0	-2	6	59	67	1	-3	-5	57	47	2	-3	8	21	20	3	-3	-1	57	64
0	-1	3	35	36	1	-2	-3	70	62	2	-2	5	73	75	3	-5	-1	38	36
0	-2	7	45	38	1	-4	-5	79	69	2	-3	7	50	50	3	-4	0	42	41
0	-2	8	60	64	1	-3	-3	123	115	2	-2	4	34	23	3	-3	0	40	41
0	-1	4	116	120	1	-2	-2	71	70	2	-1	2	105	93	3	-2	0	131	128
0	-1	6	125	144	1	-4	-3	52	45	2	-4	7	15	15	3	-1	0	113	125
0	-1	10	42	47	1	-5	-3	58	54	2	-3	5	34	30	3	-4	1	35	43
0	0	8	95	95	1	-2	-1	123	114	2	-4	6	20	23	3	-5	2	15	8
0	0	6	64	70	1	-4	-1	93	95	2	-3	4	55	53	3	-2	1	57	50
0	-1	1	24	22	1	-1	0	136	138	2	-4	5	51	58	3	-4	2	21	20
0	-4	4	24	31	1	-2	0	52	40	2	-3	3	88	98	3	-3	2	77	78
0	-3	1	35	24	1	-3	0	59	54	2	-4	3	27	29	3	-3	3	35	39
0	-3	7	23	21	1	-4	1	42	37	2	-3	2	38	32	3	-2	2	85	78
0	-3	8	17	23	1	-3	1	117	104	2	-5	3	31	40	3	-4	4	24	25
0	-2	5	16	23	1	-2	1	70	64	2	-2	1	104	98	3	-3	4	38	39
0	-2	9	15	14	1	-4	2	63	67	2	-4	2	32	35	3	-3	6	50	50
0	-1	5	28	28	1	-2	2	138	114	2	-3	1	35	36	3	-2	4	111	118
0	-1	8	31	38	1	-5	5	22	34	2	-4	1	60	72	3	-3	8	15	17
0	-5	1	27	26	1	-1	1	83	87	2	-1	0	184	196	3	-1	2	157	184
1	-1	-4	54	45	1	-3	3	33	29	2	-3	0	98	94	3	-2	6	54	51
1	-4	7	29	31	1	-3	4	56	55	2	-5	-1	35	40	3	-2	7	25	19
1	-1	2	67	61	1	-4	6	26	22	2	-3	-1	68	77	3	-2	8	56	52
1	-2	4	39	39	1	-2	3	100	89	2	-2	-1	16	16	3	-1	4	102	92
1	-3	8	38	35	1	-3	5	59	58	2	-4	-2	45	38	3	-1	6	111	108
1	-1	3	37	45	1	0	-2	91	97	2	-3	-2	51	50	3	-1	8	44	36
1	-2	7	32	31	1	0	-4	34	36	2	-4	-3	44	42	3	0	8	86	77
1	-2	6	73	78	1	0	-6	30	22	2	-1	-1	58	71	3	0	6	61	62
1	-1	4	138	148	1	0	-10	17	13	2	-2	-2	159	161	3	0	4	126	158
1	-2	8	35	31	1	-1	8	79	83	2	-3	-3	20	5	3	-3	5	23	19
1	-1	5	37	37	1	-3	-1	69	71	2	-2	-3	78	64	3	-5	3	11	16
1	-1	10	26	27	1	0	-8	70	55	2	-4	-4	24	22	3	-1	-2	158	166
1	-1	6	58	62	2	-2	-9	23	18	2	-3	-4	93	80	3	-2	-5	27	26
1	0	10	53	54	2	-2	-8	47	44	2	-4	-6	34	33	3	-1	-3	26	27
1	0	8	57	49	2	-2	-7	22	13	2	-3	-5	40	32	3	-1	-4	68	67
1	0	6	143	140	2	-2	-6	112	100	2	-4	-7	17	14	3	-1	-5	46	45
1	0	4	85	94	2	-1	-10	29	35	2	-2	-4	84	79	3	-1	-6	93	76
1	-2	10	51	43	2	-1	-8	96	97	2	-3	-8	48	45	3	0	-2	120	126
1	-3	9	17	20	2	-1	-6	104	96	2	-3	-6	38	35	3	0	-4	112	125
1	-3	2	29	23	2	-2	-10	19	49	2	-1	3	39	48	3	0	-6	41	31
1	-5	1	47	60	2	-1	-4	198	185	2	-2	2	125	125	3	0	-8	49	44

Starting with the structural parameters derived from Hg_2SO_4 it was possible to refine the Hg_2SeO_4 structure to an R factor of 0.12 assuming isotropic thermal motion. With anisotropic temperature factors for mercury the R factor decreased to 0.106. However, as only data registered with rotation around the a axis were available the latter refinement is somewhat inappropriate with thermal vibration of the character present and it was carried out only for comparison. The positional parameters are not significantly different from those obtained through isotropic refinement.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The present investigation shows mercury(I) sulphate and selenate to have the mercury atoms arranged in doublets the bond distances within which are 2.500 ± 3 Å (sulphate) and 2.51 ± 1 Å (selenate). The metal atom doublets are oriented so as to be nearly parallel to the a axis. The distances between

Table 4. Interatomic distances and angles calculated with parameters shown in Table 1. X=S, Se.

Distances Å

	sulphate	selenate
Hg—Hg	2.500±3	2.51±1
Hg—O_1	2.93 ±3	2.90±5
Hg—O_1'	2.72 ±3	2.71±5
Hg—O_2	2.24 ±2	2.21±5
Hg—O_2'	2.49 ±2	2.50±5
X—O_2	1.51 ±3	1.67±4
X—O_1	1.43 ±3	1.61±7
O_1—O_1 with XO_4 group	2.43 ±5	2.8 ±1
	2.44 ±4	2.67±7
O_2—O_2 with XO_4 group	2.34 ±4	2.65±7
O_1—O_2 with XO_4 group	2.43 ±4	2.63±7
O_2—O_2 between XO_4 groups	2.70 ±5	2.65±7

Angles, degrees

Hg—Hg—O_2	164.9±6	160±1
Hg—Hg—O_2'	125.7±6	131±1
Hg—Hg—O_1	103.1±4	99±1
Hg—Hg—O_1'	193.2±6	101±1
O_1—X—O_1	116 ±3	121±4
O_1—X—O_2	105 ±1.5	108±3
O_1—X—O_2	111 ±1.5	107±3
O_2—X—O_2	108 ±2	106±3

RMS components Å (sulphate)

r_1	0.130±5
r_2	0.180±6
r_3	0.194±3

them in the *b* and *c* directions are 4.3 Å and 4.2 Å, respectively. The tendency towards linear coordination of two ligands obviously is the cause of the short distance between mercury and the closest oxygen atom, O_2. These distances are 2.24±3 Å and 2.21±5 Å, respectively. Thus the mercury doublets form part of infinite chains $-XO_4-Hg-Hg-XO_4-Hg-Hg-\cdots$ (X denoting S or Se) where the mercury atoms from different doublets are linked each to one oxygen of a XO_4 group (see Fig. 1). The Hg—Hg—O angle is 165°±1 in the sulphate and 160°±1 in the selenate. The chain crosses the unit cell diagonally and runs nearly parallel to the *ac* plane. Each mercury atom in the sulphate is also fairly close to an oxygen atom O_2' of an adjacent chain — 2.49±3 Å — and there are another two oxygen atom neighbours at 2.72 Å — O_1' and 2.93 Å — O_1. The mercury sulphate structure is best described as composed of infinite molecular chains held together by weak Hg—O interactions. The calculated distances (Table 4) are within standard deviations of the same values as those of the mercury(I) selenate.

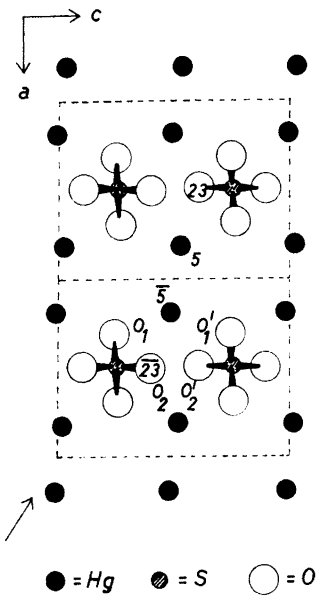

Fig. 1. Two unit cells of Hg_2SO_4. The arrow shows the direction of the chain. The starting point for the discussion of distances is the doublet in the centre of the figure.

The XO_4 group is slightly distorted. In the sulphate structure S—O_1 is 1.43±3 Å while S—O_2 is 1.51±3 Å. The difference in bond lengths is only possibly significant but it should be observed that the same distortion was found in mercury(I) bromate where the difference in Br—O distances is 0.11 Å. In both anion groups there is a larger distance between the central atom and the oxygen ligand closest to the mercury doublet. Consequently it seems likely that the weakening of the S—O bond is due to the influence of the mercury atom.

In an article by Potts and Allred [11] an infrared study on mercury(I) sulphate is reported. The sulphate group is described as restrained and not acting as a single anion but coordinated to mercury, a fact which is emphasized by the present investigation.

The "thermal ellipsoid" of the mercury atom indicates the possibility of a vibration which is more pronounced in planes perpendicular to the mercury doublet than along the metal-metal bond direction. The RMS components are given in Table 4. The result is the same as that obtained for mercury(I) bromate which also shows the same ratio, 1.5, between the largest and the smallest component. This type of thermal vibration is also reported for the mercury atoms in a recent article on 1,10-phenanthroline mercury(I) nitrate,[12] $Hg_2(phen)(NO_3)_2$.

The occurrence of metal atom doublets is a common feature in all mercury(I) compounds studied so far. Several of these contain close Hg—O contacts and as stated in a previous article [2] the Hg—Hg bond distances in this type of compound are all in agreement with each other. The constant value of the bond distance is closely associated with the presence of fairly linear O—Hg—Hg—O

groups. Such groups have been found in $Hg_2(BrO_3)_2$,[2] $Hg_2(ClO_4)_2 \cdot 4H_2O$,[9] $Hg_2(NO_3)_2 \cdot 2H_2O$,[8] and Hg(I) *o*-phthalate.[10] In the perchlorate and nitrate the group is part of a discrete unit $H_2O-Hg-Hg-H_2O$ whereas in the bromate the characteristic unit is the molecule $BrO_3-Hg-Hg-BrO_3$. The *o*-phthalate and the present structure both contain infinite chains. That the dimensions of the O—Hg—Hg—O group are independent of the anion is also shown by the shortest Hg—O distances. They are accordant within standard deviations although there are small deviations in the Hg—Hg—O angle. These are likely to be due to the shape and dimensions of the various anions.

Concerning the Hg—O bond the structure of $Hg_2(phen)(NO_3)_2$ should also be considered. In this structure a linear Hg—Hg—O bond appears only at one end of the doublet whereas at the other end there is a somewhat more complex arrangement of mercury-nitrogen bonds. In spite of this the Hg—O distance (2.24 ± 4 Å) as well as the Hg—Hg distance are in agreement with those in the present structure.

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REFERENCES

1. Dorm, E. and Lindh, B. *Acta Chem. Scand.* **21** (1967) 1661.
2. Dorm, E. *Acta Chem. Scand.* **21** (1967) 2834.
3. Werner, P.-E. *Univ. Stockholm, Inorg. Chem.*, DIS, No. 4 (1964).
4. Werner, P.-E. *Z. Krist.* **120** (1964) 375.
5. de Schulten, A. *Bull. Soc. Franc. Minéral.* **26** (1903) 113.
6. *IUCr World List of Crystallographic Computer Programs,* Accession No. 384.
7. *Ibid.* 363.
8. Grdenić, D. *J. Chem. Soc.* **1956** 1312.
9. Johansson, G. *Acta Chem. Scand.* **20** (1966) 553.
10. Lindh, B. *Acta Chem. Scand.* **21** (1967) 2745.
11. Potts, R. A. and Allred, A. L. *Inorg. Chem.* **5** (1966) 1066.
12. Elder, R. C., Halpern, J. and Pond, J. S. *J. Am. Chem. Soc.* **89** (1967) 6877.

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