## Complexes of Mercury. Part III.1 X-Ray Analysis of Dichlorobis-(1,4-thioxan)mercury(II)

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Dichlorobis-(1,4-thioxan)mercury(II) crystallises in the orthorhombic system, space group Pn2<sub>1</sub>a, with four molecules of  $C_8H_{16}Cl_2HgO_2S_2$  in a cell of dimensions  $a=15\cdot31,\,b=19\cdot69,\,c=4\cdot33\,\text{Å}$ . The mercury atom is coordinated in a distorted tetrahedral manner by two sulphur atoms at an average distance of 2.57 Å and two chlorine atoms at an average distance of 2.48 Å. The angles S-Hg-S and CI-Hg-CI are 115 and 114°, respectively. Each thioxan molecule is in the chair conformation with the S-Hg bond oriented equatorially.

The saturated heterocycle 1,4-thioxan forms complexes with a number of metal halides.2,3 From infrared spectroscopy Hendra and Powell deduced that the heterocycle retains the chair conformation in most of them; 2 Walton has agreed with this and concluded that thioxan is sulphur-bonded rather than oxygenbonded in the complexes.<sup>3</sup> We have determined the crystal structure of dichlorobis-(1,4-thioxan)mercury(II) and find that the complex contains discrete molecules (I) in which the mercury atom is co-ordinated in a distorted tetrahedral manner by two chlorine and two sulphur atoms. The thioxan molecules adopt the chair conformation and the S-Hg bonds are oriented equatorially.

The final three-dimensional electron-density distribution is shown in Figure 1 by means of superimposed contour sections drawn parallel to (001). The arrangement of atoms in the crystal as viewed in projection

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Part II, W. R. Costello, A. T. McPhail, and G. A. Sim, J. Chem. Soc. (A), 1966, 1190.
 P. J. Hendra and D. B. Powell, J. Chem. Soc., 1960, 5105.

<sup>&</sup>lt;sup>3</sup> R. A. Walton, Inorg. Chem., 1966, 5, 643.

Dis.

· · · · Cl<sub>II</sub> ......

3.76

 $C(1)' \cdots Cl_1 \cdots C(2) \cdots C(3)'_{V} \cdots \cdots$ 

S.d.

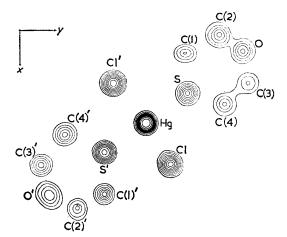


FIGURE 1 The final three-dimensional electron-density distribution shown by means of superimposed contour sections drawn parallel to (001). Contour interval 10 eÅ-3 around the mercury atom, 2 eÅ-3 around the chlorine and sulphur atoms, and 1 eÅ-3 around the carbon atoms

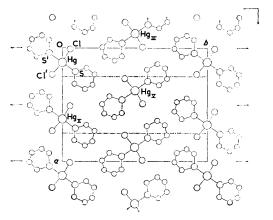


FIGURE 2 The crystal structure as viewed along the c axis

## TABLE 1

Atomic co-ordinates (as fractions of the cell edges), temperature factors, and positional standard deviations (Å)

	x/a	y/b	z/c	B	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Hg	0.1248	0.0000	0.0627	*	0.003	0	0.003
Cl	0.0088	0.0507	-0.2449	1.8	0.017	0.018	0.019
Cl′	0.2313	-0.0702	-0.2465	1.3	0.015	0.016	0.017
S	0.2059	0.0886	0.3803	2.8	0.020	0.020	0.026
S'	0.0432	-0.0906	0.3858	$3 \cdot 0$	0.020	0.020	0.027
O	0.3208	0.2059	0.1054	3.5	0.06	0.06	0.07
O'	-0.0756	-0.2100	0.2067	$3 \cdot 2$	0.06	0.06	0.07
C(1)	0.3132	0.0833	0.1990	$2 \cdot 9$	0.08	0.08	0.10
C(2)	0.3631	0.1562	0.2515	$2 \cdot 4$	0.08	0.08	0.09
C(3)	0.2339	0.2238	0.2217	$5 \cdot 6$	0.14	0.13	0.14
C(4)	0.1748	0.1672	0.1800	$3 \cdot 1$	0.08	0.09	0.11
C(1)'	-0.0706	-0.0918	0.2497	1.0	0.06	0.06	0.07
C(2')	-0.1109	-0.1494	0.3242	$3 \cdot 0$	0.08	0.09	0.11
C(3)'	0.0066	-0.2261	0.2659	1.5	0.06	0.06	0.07
C(4)'	-0.0767	-0.1740	0.2346	1.6	0.07	0.06	0.08

 $\mbox{*}$  For the mercury atom an anisotropic temperature factor was employed. This was of the form

 $T = \exp[-(b_{11}h^2 + b_{22}h^2 + b_{33}l^2 + b_{12}hh + b_{23}hl + b_{13}hl)]$ with parameters

 $b_{11}$  $b_{23}$ -0.0002-0.0030 -0.00010.0029 0.00210.0307

along the c axis is shown in Figure 2. The atomic coordinates and their standard deviations are in Table 1 and the interatomic distances and valency angles in Table 2.

TABLE 2

Interatomic distances (Å) and valency angles with standard deviations

Bond		

S.d.

Dist.

Hg-Cl	$2 \cdot 43$	0.018	HgCl'	2.52	0.016
Hg-S	2.54	0.022	Hg-S'	2.59	0.022
C(1)-S	1.82	0.09	C(1)'-S'	1.84	0.06
C(4)-S	1.84	0.09	C(4)'-S'	1.84	0.07
C(2)-O	1.33	0.10	C(2)'-O'	1.40	0.10
C(3)-O	1.47	0.15	C(3)'-O'	1.32	0.09
C(1)-C(2)	1.64	0.11	C(1)'-C(2)'	1.33	0.10
C(3)-C(4)	1.45	0.16	C(3)'-C(4)'	1.49	0.09
		Valence	y angles		
		S.d.	y ungles		S.d.
Cl-Hg-Cl'	114°	0.6°	S-Hg-S'	115°	0.8°
Cl-Hg-S		0.6	Cl'-Hg-S'		0.6
Cl-Hg-S'		0.6	Cl'-Hg-S		0.6
Hg-S-C(1)		3.0	Hg-S'-C(1)'		$2 \cdot 2$
Hg-S-C(4)		3.1	Hg-S'-C(4)'		$2.\overline{4}$
C(1)-S- $C(4)$		4.1	C(1)'-S'-C(4)'		3.0
S-C(1)-C(2)	108	5.6	S'-C(1)'-C(2)'		5.3
C(1)- $C(2)$ - $O$	110	6.8	C(1)'-C(2)'-O'	117	7.5
C(2)-O- $C(3)$	117	8.1	C(2)'-O'-C(3)'	120	6.4
O-C(3)-C(4)	110	$9.\overline{5}$	O'-C(3)'-C(4)'	120	5.7
C(3)-C(4)-S	115	7.8	C(3)'-C(4)'-S'		4.7
	Non-bo	onded co	ntacts (<3.8 Å)		
$S' \cdot \cdot \cdot \cdot \cdot Cl_{\mathbf{I}} \dots$		3.25			3.65
$C(4)' \cdots O_{VI} \dots$		3.26			3.65
$C(3) \cdots O'_{v_1} \dots$		3.31			3.67
$C(4) \cdots O'_{III} \ldots$		3.31			3.69
$C(3) \cdots O'_{III} \dots$		$3.31 \\ 3.32$	$C(3) \cdot \cdot \cdot \cdot O'_{IV}$		3.70
C(3) · · · O m · ·		0.02	C(3) O IV	• • • • • • • • • •	3.10

The subscripts refer to the positions

3.41

3.51

3.54

3.62

 $\cdots \cdot C(\bar{2})'_{\mathbf{II}} \quad \ldots \ldots$ 

 $\cdots \cdot \operatorname{Cl}^{\bar{r}_{\mathbf{I}}} \ldots \ldots$ 

 $Hg \cdot \cdot \cdot \cdot Cl_{\mathbf{I}}$  .....

 $\cdots c i_r \cdot \dots \cdot$ 

## TABLE 3

Displacements (Å) of the atoms from planes through the carbon atoms of the thioxan molecules

Atoms	included			Atoms	included		
in derivation		Atoms		in derivation		Atoms	
of plane		omitted		of plane		omitted	
C(1)	0.01	s	-0.95	C(1)'	0.06	S'	-0.77
C(2)	-0.02	O	0.63	C(2)'	-0.07	O	0.45
C(3)	0.01			C(3)'	0.06		
C(4)	-0.01			C(4)'	-0.05		

In the thioxan rings the average value of the C-S-C valency angle is 97°, in good agreement with the angles in other six-membered rings containing sulphur atoms, e.g., 99° in 1,4-dithian 4 and 1,3,5-trithian, 1 98° in 1,4dithian 1,4-dioxide,5 and 100° in 1,4-dithiin6 and thianthren.<sup>7</sup> The average carbon-sulphur bond length

<sup>4</sup> R. E. Marsh, Acta Cryst., 1955, 8, 91.

 H. M. M. Shearer, J. Chem. Soc., 1959, 1394.
 P. A. Howell, R. M. Curtis, and W. N. Lipscomb, Acta Cryst., 1954, 7, 498.

<sup>7</sup> H. Lynton and E. G. Cox, J. Chem. Soc., 1956, 4886; I. Rowe and B. Post, Acta Cryst., 1958, 11, 372.

Table 4
Structure amplitudes and phase

Structure amplitudes and phases									
h $k$	$l  F_o   F_c                                  $	h $k$	$l  F_{\rm o}   F_{\rm c}  \propto$	h $k$	$l  F_{ m o}   F_{ m c}  \propto$	h $k$	$l  F_{\rm o}   F_{\rm c}  \propto$	h	$k \mid F_{\rm o} \mid F_{\rm c} \mid \alpha$
0 2	0 327 344 358 2 195 141 8	٤. 1	0 25 330 90 1 18 11 359	3 7	1 166 1/0 E1 2 107 109 285	4 17	2 123 92 168 0 13 15 152		2 46 34 251 3 168 174 <b>3</b> 59
0 3	1 143 59 <b>254</b> 3 250 192 84		2 145 104 88 3 14 22 192	3 8	3 26 32 128 1 172 153 200	4 1	1 78 73 232 3 83 65 292	6	7 0 222 247 268 2 126 104 277
0 4	0 232 217 360 2 210 154 356	5 5	0 90 88 275 1 160 115 184		2 104 101 153 3 37 37 150	4 13	0 90 89 200 2 99 74 165	6	8 1 51 42 12 3 147 136 354
0 5	1 186 120 82 3 120 94 95		2 33 28 288 3 140 174 178	3 9		4 19	3 28 23 269 0 12 14 153	6	9 0 208 203 264 2 91 76 285
0 6	0 128 122 15 2 239 178 3	2 3	1 185 125 349	3 10	3 44 50 122 1 107 111 188	ĺ	1 60 .52 .247 3 56 46 280	6	10 0 58 61 <b>2</b> 42 1 47 45 19
0 7	1 139 89 72 3 96 78 <b>101</b>	2 4	2 161 140 96 0 114 97 73		2 58 69 164 3 36 35 182	4 20	0 93 80 188 2 52 39 175		2 45 49 53 3 78 86 349
0 8	0 111 118 26 2 260 197 348		1 135 95 182 2 110 92 255	3 11	2 68 7 <b>0 25</b> 8	4 21	3 24 26 229 0 17 24 158	6	11. 0 125 128 265 1 41 34 144
0 9	1 244 169 76 3 144 94 93	2 5	3 134 126 177 0 237 217 89 3 45 43 173	3 12	3 23 30 99 1 112 110 174	4 22	1 21 17 268 0 49 48 165	6	2 92 77 287 12 0 22 38 214 1 34 27 11
0 10	0 220 224 5 2 218 153 356 1 197 137 72	2 6	3 45 43 173 0 50 47 59 1 144 91 177	2 12	2 75 75 188 3 23 30 207	4 23	2 38 40 204 0 -7 10 29 0 49 56 152		2 20 29 37
0 12	1 197 137 72 3 157 117 100 0 255 224 1		2 47 35 240 3 129 108 174	3 13	1 93 99 102 2 63 65 248 3 23 26 99	4 24 5 0	0 49 56 152 1 181 204 180 2 118 153 0	6	3 67 66 350 13 0 105 93 267 1 48 54 139
0 13	2 13h 91 h 1 124 91 91	2 7	0 250 225 88 2 185 135 96	3 14	1 76 80 169 2 56 60 195	5 1	1 170 192 268 2 110 136 277		2 104 92 277 3 37 44 320
0 14	3 120 100 83 0 189 188 352	2 8	3 49 42 148 0 143 114 83	3 <b>1</b> 5	3 22 33 211 1 76 81 102	5 2	3 21 27 283 1 145 163 190	6	14 0 18 28 221 1 76 61 345
0 15	2 72 65 24 1 10 29 197		1 121 93 165 2 26 - 19 266	3 2)	2 52 53 236 3 27 25 93	, -	2 72 104 350 3 30 40 167	6	3 83 68 2 15 0 104 126 274
0 1/	3 139 109 76 0 87 87 339	2 9	3 142 121 188 0 235 193 94	3 16		5 3	1 133 136 260 2 64 97 286	6	2 93 78 271 16 1 95 76 344
0 17	2 82 77 32 1 37 42 202		1 125 73 164 2 187 135 94	3 17	3 16 25 216	5 4	3 35 49 277 1 135 141 186	6	3 88 69 7 17 0 140 111 281
0 18	3 93 77 62 0 101 102 341	2 10	3 13 14 233 0 28 23 203	3 18	2 48 55 263		2 63 77 343 3 34 43 166	6	2 83 70 259 13 1 61 44 337
0 19	a 46 51 45 1 34 31 121		1 129 82 177 2 51 35 70	3 19	2 38 42 156 1 42 52 79	5 5	1 110 124 267 2 62 71 274	6	3 81 66 1 19 0 95 82 279 1 24 30 306
0 20	3 73 61 70 0 83 86 357 1 45 37 87	2 11	3 147 121 176 0 271 219 92 1 67 53 144		3 14 22 129	5 6	3 <b>3</b> 6 46 282 1 82 103 180		2 63 50 <b>261</b>
0 22	1 45 37 87 3 51 51 79 0 75 82 9		1 67 53 144 2 139 107 84 3 40 38 324	3 20	2 24 35 151		2 37 62 3 3 43 60 195	6	20 0 14 26 22 1 17 21 326 21 0 65 55 270
0 23	1 53 59 50 0 48 £2 13	2 12	0 70 71 233 1 123 83 171	3 21	1 37 44 83	5 7	1 103 108 280 2 32 45 248	6	21. 0 65 55 270 2 38 29 289 23 0 53 44 260
1 1	2 48 72 94 3 2 49 86		2 49 48 38 3 151 118 177	3 22	1 32 39 184	5 8	3 40 44 267 1 106 114 171	7	1 12 21 294 0 1 134 162 0
1 2	1 177 168 8 2 70 78 175	2 13	0 186 162 89 1 29 40 112	3 23	2 20 27 166 1 24 34 98 2 12 24 254		2 60 69 12 3 30 42 203	,	2 84 109 0 3 13 29 0
1 3	3 36 54 353 1 207 1:4 77		2 125 98 98 3 53 49 322	3 24 4 0	1 18 27 168	5 9	1 132 129 274 2 83 97 256	7	1 1 135 162 261 2 84 114 98
	2 118 118 103 3 43 55 110	2 14	0 93 92 244 1 30 25 173	4 1	2 191 203 180	5 10 5 11	1 134 141 177 2 91 95 359 1 112 122 271	7	2 1 145 155 7 2 · 85 112 345
1 l	1 226 204 7 2 137 133 165	_	2 53 46 53 3 119 96 178	4 2	3 65 81 270	5 12	2 75 92 266 1 99 107 184	7	3 23 25 327 3 1 137 139 266
1 5	3 34 29 <b>3</b> 52 1 231 216 90	2 15	0 113 114 91		1 62 45 105 2 195 187 180	5 13	2 63 79 353	í	2 67 87 95 3 30 39 290
•	2 146 145 86 3 23 27 102	2 16	2 98 71 95 3 21 23 322 0 13 21 231	4 3		,	1 93 96 264 2 63 67 271 3 18 21 292	7	4 1 98 109 4 2 46 62 1
1 6	1 216 196 355 2 143 143 188	2 10	1 54 45 187 3 75 61 165		1 132 107 265 2 46 44 350	5 14	1 76 86 188 2 52 60 342	7	3 38 47 <b>0</b> 5 1 86 90 <b>271</b> 2 27 <b>45</b> 90
1 7	3 21 28 30 1 192 165 97	2 17	0 112 122 85 2 55 45 110	4 4		5 15	3 27 21 183 1 56 67 264		3 40 48 <b>272</b>
1 8	2 129 121 80 3 28 29 90 1 147 145 359	2 18	0 30 43 53 1 42 37 170		1 71 52 81 2 188 168 182 3 32 23 112	5 16	2 43 47 281 3 30 29 297 1 41 56 195	7	6 1 88 95 2 2 39 5 <b>3 357</b> 3 40 46 <b>35</b> 9
1 (	2 93 91 178 3 41 42 6	2 19	3 68 52 <b>1</b> 77 0 75 72 82	4 5		5 17	3 31 28 176 1 36 45 275	7	3 40 46 359 7 1 102 110 273 2 56 61 78
1 9	1 124 124 92 2 80 75 83		2 59 60 108 3 38 34 139		2 42 32 352 3 158 168 268	5 18	3 27 28 280 1 37 45 174	7	3 30 36 281 8 1 104 105 353
1 10	3 46 46 99 1 107 101 355	2 20	0 35 47 45 1 24 20 165 2 20 29 202	4 6	2 94 79 197	ŕ	2 23 28 2 3 20 26 206	•	2 63 78 6 3 30 36 25
	2 60 61 184 3 44 43 16	2 21	3 65 57 176	4 7	3 31 25 270 0 44 38 158	5 19 ·	1 45 51 279 2 25 35 239	7	9 1 97 112 279
1 11	1 102 93 99 2 52 55 74	2 22			2 62 68 290 2 18 27 238 3 156 162 263	5 20	1 39 47 174 2 25 35 3	7	2 63 75 74 3 23 24 275 10 1 99 112 356 2 63 75 3
1 12	3 45 41 95 1 90 88 <b>3</b> 2 44 49 <b>1</b> 68		1 39 36-172 2 18 31 195	4 8	0 290 273 173 2 99 81 200	5 21 5 22	1 36 46 275 2 26 34 259 1 34 43 181		3 18 25 <b>2</b> 9
1 13	3 40 43 16 1 92 89 83	2 23	2 35 33 90	4 9	3 40 34 258	5 22 5 23	2 21 31 349 1 27 38 264	7 7	2 63 87 86
, , , ,	2 /3 53 102 3 32 31 118	2 24	0 11 19 280 1 18 21 167		1 32 33 21 2 27 26 150	5 24 6 0	1 17 34 185	7	12 1 89 103 1 2 68 77 353 13 1 76 91 269
1 · 14	1 88 90 10 2 -0 65 163	2 25 3 0	0 28 39 101 1 126 154 180 2 71 100 180	4 10	3 169 161 258 0 194 200 172	6 1	1 75 69 0 3 76 84 0 0 127 133 273		2 51 64 92 14 1 58 71 7
1 .15	3 22 28 6 1 82 9 <b>3 88</b>	3 1	3 28 51 180 1 127 173 9		1 63 42 272 2 98 82 200	6 2	2 166 158 271 0 128 119 85		2 33 49 <b>3</b> 42 3 16 24 6
1 16	2 65 65 93 1 81 92 0	, I	2 72 105 253 3 26 45 82	4 11	1 44 37 281		1 119 109 351 2 64 65 255	7	15 1 44 57 264 2 31 37 99
1 17	2 67 63 <b>1</b> 73 1 69 79 90 2 61 65 82	3 2	1 153 186 165 2 88 121 194	4 12		6 3	3 77 93 9 0 236 250 274 1 47 40 348	7	3 23 26 <b>3</b> 00 16 1 39 50 5
1. 18	1 63 74 <b>3</b> 58 2 55 53 <b>17</b> 7	3 3	3 33 52 202 1 160 179 105	4 13	3 23 26 49		2 143 127 265 3 18 24 185	7	2 24 29 342 3 18 23 12 17 1 34 46 277
1 19	1 51 62 97 2 36 42 74	3 L	2 92 118 251 3 34 43 75 1 149 161 168	رــ -	1 76 57 257 2 20 16 133	6 4	0 49 48 65 1 150 116 354	ı	2 16 23 74 3 20 23 285
1 20	1 40 45 <b>3</b> 54 2 25 <b>33 19</b> 1	3 4	1 149 161 168 2 84 98 199 3 37 48 215	14 14	3 91 78 271 0 121 122 193		2 63 49 253 3 152 148 1	7	18 1 26 41 355 2 20 26 11
1 21	1 29 36 101 1 23 31 7	3 5	1 143 154 98 2 76 101 253		1 17 18 115 2 130 97 171	6 5	0 <b>2</b> 46 292 272 1· 96 82 347	7	19 1 34 42 281 2 18 26 68
1 23 1 24 2 0	1 19 27 85 1 18 28 10 1 74 65 180	3 6	3 40 46 80 1 171 156 178	4 15	3 37 29 80 1 103 83 245	, .	2 147 127 268 3 44 49 162	7	20 1 33 44 355 2 27 33 359
	3 132 190 180		2 97 104 175 3 25 33 196	4 16	3 84 65 282 0 99 103 197	6 6	0 51 57 77 1 98 67 355	7	21 1 33 45 273 2 26 33 73

TABLE ·	4	(Continued)
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		THE T (Committee)		
$h  k  l   F_{\rm o}  \  F_{\rm c}   \alpha$	$h  k  l \mid F_{\rm o} \mid \mid F_{\rm c} \mid  \alpha$	$h  k  l \mid F_{\rm o} \mid F_{\rm c} \mid  \alpha$	$h  k  l \mid F_{\rm o} \mid \mid F_{\rm c} \mid \mid \alpha$	$h  k  l \mid F_{\rm o} \mid \mid F_{\rm c} \mid  \alpha$
7 22 1 27 40 357	2 63 71 102	3 34 30 172	2 27 34 277	15 8 1 43 53 11
7 23 1 17 34 273	3 22 25 117	11 3 2 53 64 281	3 41, 34 281	2 32 36 336
8 0 0 186 196 .0	9 10 1 82 95 Il	3 28 27 105 11 4 1 100 104 183	13 2 1 69 74 185 2 42 49 346	15 9 1 41 52 258 2 27 35 107
2 81 78 0 8 1 0 33 36 343	2 52 60 161 3 12 21 349	2 63 73 173	3 26 26 173	15 10 1 37 46 9°
3 120 141 65	9 11 1 68 78 86	11 5 1 100 105 90	13 3 1 75 82 267	2 25 33 340
8 2 0 212 230 0	. 2 47 58 92 3 12 26 109	2 62 77 276 11 6 1 89 97 181	2 56 61 275 13 5 1 74 82 268	15 11 1 31 43 273 2 21 27 91
1 87 70 95 2 96 92 354	9 12 1 63 72 354	2 62 76 179	13 5 1 74 82 268 2 54 64 266	15 12 1 29 37 352
8 3 1 76 61 84	2 42 49 184 3 19 28 32	11 7 1 82 96 95 2 51 61 257	13 6 1 73 87 179	2 22 27 11 15 13 1 27 42 284
2 43 38 357 3 132 134 90	3 19 28 32 9 13 1 62 72 104	11 8 1 72 82 167	2 50 60 355 13 7 1 84 79 271	2 21 27 62
8 4 0 249 228 2	2 36 49 60	2 47 60 189 11 9 1 63 73 100	2 49 59 267	15 14 1 26 37 344 15 15 1 22 37 283
1 77 57 79 2 117 99 3	3 15 20 82. 9 14 1 60 66 348	2 33 54 246	13 8 1 59 71 180 2 34 49 7	16 0 0 123 102 0
8 5 1 154 104 78	2 35 46 198	11 10 1 50 64 176 2 26 37 186	13 9 1 46 58 278	2 51 36 0 16 1 1 33 32 <b>7</b> 4
2 28 30 331 3 107 106 96	9 15 1 46 59 99 2 <b>28</b> 42 76	11 11 1 43 53 94	2 23 35 265 3 8 17 267	3 46 51 100
8 6 0 220 193 4	9 16 1 44 54 1	2 18 28 269 3 19 30 102	13 10 1 · 33 48 179	16 2 0 100 85 8 2 67 49 <b>353</b>
1 40 35 47 2 144 123 354	2 30 34 176 9 17 1 36 48 88 2 24 31 90	11 12 1 39 50 187	3 17 23 197 13 11 1 32 43 269	3 24 29 272
3 23 28 228		2 17 29 172	3 18 23 276	16 3 0 5 <b>3</b> 53 178 1 26 25 60
8 7 0 44 51 163 1 175 131 81	9 18 1 33 44 8 2 17 29 162	3 18 22 180 11 13 1 40 54 87	13 12 1 30 43 186 3 16 21 192	2 26 29 351
3 88 87 93		2 22 33 269	13 13 1 28 42 266	3 49 61 98
8 8 0 187 161 9 1 53 41 283	2 20 28 103	11 14 1 43 59 186 2 29 42 164	2 '18 26 273 3 11 19 292	16 4 0 97 93 10 2 68 50 345 3 16 21 266
2 141 116 354	9 20 1 27 40 16 2 19 29 147	11 15 1 45 57 84	13 14 1 29 44 188	3 16 21 266
3 13 14 231	9 21 1 22 33 78	2 30 42 275 11 16 1 39 53 186	2 22 30 340 13 15 1 30 45 264	16 5 0 50 46 164 1 38 37 59
8 9 0 28 23 154 1 107 89 73	9 22 1 13 30 7 10 0 1 63 45 180	2 30 41 168	2 29 34 268	2 30 34 338 3 38 61 102
3 58 63 107	3 150 141 180	11 17 1 35 49 94 2 28 34 262	13 16 1 33 48 183	2 30 34 338 3 38 61 102 3 38 61 102 16 6 0 92 84 8
8 10 0 60 71 10 1 30 24 251	10 1 0 225 234 88 2 69 65 104	11 18 1 31 41 171	2 24 36 349 13 17 1 28 44 270	16 6 0 92 84 8
2 145 122 359	3 30 31 160 10 2 0 57 61 81	2 25 32 188	13 18 1 20 38 18ა	1 21 24 66 2 71 51 353
8 11 0 34 36 333 1 34 30 73 2 20 26 150	3 30 31 160 10 2 0 57 61 81 1 44 35 190	11 19 1 25 39 102 11 20 1 15 29 171	14 0 1 102 78 0 3 94 59 0 14 1 0 109 89 272	16 7 0 21 16 32
2 20 26 150	3 118 121 178	12 0 0 148 131 180 2 128 119 180		1 31 26 77 16 8 0 80 70 6
3 77 74 91 8 12 0 94 97 5 1 17 27 237 2 103 89 360	10 3 0 166 186 84 2 80 76 100	12 1 1 117 88 281	2,127 102 268 14 2 0 12 16 66	1 30 27 74
1 17 27 237	3 39 36 168	3 122 91 259	1 102 77 352	2 63 47 352 16 9 0 44 38 355
2 103 89 360 3 35 32 71		12 2 0 171 154 180 1 24 27 100	3 67 51 8 14 3 0 109 102 276	1 37 33 89
8 13 0 34 41 326	2 45 39 255	1 24 27 100 2 110 89 178	<b>2</b> 97 70 265	16 10 0 71 59 351 2 51 45 13
1 51 45 103 3 76 68 77	3 87 89 171	3 24 25 268	3 28 26 142 14 4 0 33 36 84	
8 14 0 111 125 352	10 5 0 119 128 67 2 113 112 %	12 3 0 41 47 175 1 82 71 276	1. 39 34 345	16 11 1 27 30 97 16 12 0 58 50 350 1 25 32 243 16 13 1 25 33 99 16 14 0 56 50 347 17 0 1 60 56 0
2 66 53 23 3 27 28 41	3 29 29 172	2 28 29 6	3 68 60 7 14 5 0 <b>107</b> 98 273	1 25 32 243 16 13 1 25 33 99 16 14 0 56 50 347
8 15 0 35 45 335	10 6 1 48 41 177 3 84 80 181	3 89 68 265 12 4 0 94 99 170	2 62 50 268	16 14 0 56 50 347 17 0 1 60 56 0
1 28 32 117 3 99 80 73	10 7 0 57 64 105	1 51 43 77	3 15 17 200 14 6 3 83 72 357	2 35 3 <b>9 180</b>
8 16 0 112 127 346	1 48 · 38 353 2 145 133 87	2 109 86 194 3 38 40 258	14 7 0 117 115 265	2 35 39 180 17 1 1 60 54 88 2 35 40 98
2 56 50 32 8 17 1 38 36 114	10 8 0 39 35 256	12 5 3 75 68 260	·1 21 18 6 2 44 32 291	17 2 1 60 55 7
3 82 72 74	1 100 83 171 3 60 55 180	12 6 0 102 105 175 1 41 40 63	14 8 2 15 25 300	2 34 37 170
8 18 0 99 108 347 2 38 43 45	10 9 0 160 145 98	2 76 59 189	3 79 79 351 14 9 0 128 123 262	17 3 1 47 47 81 2 33 34 104
2 38 43 45 8 19 0 29 37 153	1 38 34 30 2 110 84 79	3 16 25 230 12 7 0 22 30 144	2 41 35 303	17 4 1 33 42 8
1 21 21 103	10 10 0 41 40 249	1 33 32 287	3 17 19 315 14 10 0 11 15 223	2 20 26 160 17 5 1 26 37 88
8 20 0 63 63 357	1 120 98 163 2 27 20 47	3 84 67 259 12 8 0 <b>133 13</b> 6 172	1 33 29 31	2 17 21 90
2 36 34 × 14 8 21 0 7 23 113	3 68 64 196	1 29 26 288	3 67 73 346	17 6 1 31 37 358 2 16 21 18 <b>2</b>
1 18 15 76	10 11 0 120 122 98 1 29 24 140	2 58 52 204 12 9 1 28 22 265	14 11 0 117 104 261 2 49 44 292	17 7 1 28 37 97
8 22 0 38 40 16 9 0 1 99 123 0	2 93 78 86	3 107 91 268	14 12 1 36 32 10	2 19 26 78 17 8 1 29 40 357 2 16 25 185
<b>2</b> 56 71 180	10 12 1 40 35 156 3 81 78 182	12 10 0 12 <b>9</b> 134 178 1 16 16 240	14 .13 0 70 60 271 2 72 56. 273	2 16 25 185 17 9 1 27 40 96
3 23 35 0 9 1 1 99 115 93	10 13 0 123 119 89	2 66 56 187	14 14 1 30 39 345	2 17 29 78
2 56 75 86	1 51 44 150 2 62 48 92	12 11 0 21 39 343 1 53 38 261	2 12 15 86 14 15 0 44 45 288	17 10 1 28 41 357 17 11 1 26 41 90
3 23 31 87 9 2 1 103 118 352				
9 2 1 103 118 352 2 59 79 194 3 19 27 19 9 3 1 109 120 104	10 14 1 38 29 173 3 82 69 175 10 15 0 101 110 78 1 25 23 161 2 45 43 131 10 16 3 57 65 168 10 17 0 68 64 77 2 47 45 116 10 19 0 62 59 79 1 22 26 313 2 36 40 108 10 20 1 20 29 186 10 21 0 57 49 88 10 21 0 57 49 88 11 0 1 76 84 180 2 36 46 180 3 31 33 180 11 1 82 84 82	2 28 33 156 88 268 12 12 0 122 126 182 1 30 32 226 2 65 50 180 12 13 1, 44 35 253 2 14 26 136 3 68 66 271 12 14 0 92 82 194 2 60 47 164	14 16 1: 28 40 324 14 17 0 33 35 305 15 0 1 67 59 0 2 54 49 0 3 14 20 0 15 1 1 67 64 278 2 44 40 72 3 16 17 260 15 2 1 67 6 346 2 44 41 22 3 21 21 27 15 3 1 66 59 282 2 43 43 63	17 12 1 19 40 4 18 0 1 13 15 0 18 1 0 81 72 87 2 29 22 97 18 3 0 86 77 90 2 34 33 92 18 4 1 42 34 190 18 5 0 87 77 90
9 3 1 109 120 104	1 25 23 161	1 30 32 226	2 54 49 0	2 29 22 97 18 3 0 86 77 90
9 3 1 109 120 104 2 71 85 66 3 23 30 69 9 4 1 104 117 348 2 69 77 199 3 27 32 29 9 5 1 91 102 94 2 56 70 83 3 27 30 91 9 6 1 87 98 8	1 25 23 161 2 45 43 131 10 16 3 57 65 168 10 17 0 <b>6</b> 8 64 77 2 47 45 116	2 65 50 180 12 13 1 44 35 253	3 14 20 0 15 1 1 67 64 278	18 3 0 86 77 90 2 34 33 92
2 71 85 66 3 23 30 69 9 4 1 104 117 348 2 69 77 199 3 27 32 29 9 5 1 91 102 94	10 17 0 68 64 77	12 13 1 44 35 253 2 14 26 136 3 68 66 271	15 1 1 67 64 278 2 44 40 72	18 4 1 42 34 190
2 69 77 199	2 47 45 116	3 68 66 271 12 14 0 92 82 194 2 60 47 164	3 16 17 260 15 2 1 67 60 346	18 5 0 87 77 90
3 27 32 29 9 5 1 91 102 94	10 19 0 62 59 79 79 1 22 26 313 2 36 40 108 10 20 1 20 29 186 10 21 0 57 49 88 1 10 176 84 180 2 36 46 180	2 60 47 164	2 44 41 22	18 6 1 111 55 172 18 7 0 71 56 94 18 8 0 6 13 123
2 56 70 83 3 27 30 91	2 36 40 108	12 15 1 32 31 249 2 59 21 118 12 16 0 36 48 193 12 17 1 17 25 221	3 21 21 27 15 3 1 66 59 282 2 43 43 63	18 7 0 71 56 94 18 8 0 6 13 123
9 6 1 87 98 8	10 20 1 20 29 186 10 21 0 57 49 88	12 16 0 36 48 193	2 43 43 63	1 38 46 161
2 60 66 1 <b>65</b> ·	1 10 18 306 11 0 1 76 84 180	12 17 1 17 25 221 12 18 0 26 30 197	3 20 23 254 15 4 1 65 61 351	19 1 1 34 45 91
2 71 85 66 3 23 30 69 9 4 1 104 117 348 2 69 77 199 3 27 32 29 9 5 1 91 102 94 2 56 70 83 3 27 30 91 9 6 1 87 98 8 2 60 66 165 3 26 37 358 9 7 1 88 99 79 2 60 60 103	11 0 1 76 84 180 2 36 46 180	12 19 0 11 23 129	2 43 44 13	18 9 0 32 29 111 19 1 1 34 45 91 19 2 1 27 38 180 19 3 1 21 35 86 19 4 1 17 30 186
2 60 60 103	3 31 33 180 11 1 1 82 84 82	1 18 25 259 12 20 0 44 48 178	3 20 23 254 15 4 1 65 61 351 2 43 44 13 15 5 1 64 64 275 2 42 43 82	18 9 0 32 29 111 19 1 1 34 45 91 19 2 1 27 38 180 19 3 1 21 35 86 19 4 1 17 30 186 19 5 1 14 29 92 13 4 1 80 87 183
3 26 37 358 9 7 1 88 99 79 2 60 60 103 3 29 34 112 9 8 1 89 94 11 2 60 69 160	11 1 1 82 84 82 2 40 51 286	13 0 1 53 55 180 2 27 26 0	15 6 1 54 59 4	18 8 0 6 13 123 1 38 46 161 18 9 0 32 29 111 19 1 1 34 45 91 19 2 1 27 38 180 19 3 1 21 35 86 19 4 1 17 30 186 19 5 1 14 29 92 13 4 1 80 87 183
3 29 34 112 9 8 1 88 94 11 2 60 69 160 3 26 29 356 9 9 1 82 90 61	3 31 33 180 11 1 1 82 84 82 2 40 51 286 3 34 34 105 11 2 1 82 85 190 2 49 56 160	13 0 1 53 55 180 2 27 26 0 3 39 41 180 13 1 1 58 61 262	15 3 1 66 59 282 2 43 43 63 3 20 23 254 15 4 1 65 61 351 2 43 44 13 15 5 1 64 64 275 2 2 42 43 82 15 6 1 54 59 4 26 25 15 7 1 51 54 264 26 31 38 99	17 12 1 19 40 4 18 0 1 13 15 0 18 1 0 81 72 87 2 29 22 97 18 3 0 86 77 90 2 34 33 92 18 4 1 42 34 190 18 5 0 87 77 90 18 6 1 111 55 172 18 7 0 71 56 94 18 8 0 6 13 123 1 88 9 0 32 29 111 19 1 1 34 45 91 19 2 1 27 38 180 19 3 1 21 35 86 19 4 1 17 30 186 19 5 1 14 29 92 13 4 1 80 87 183 2 155 61 357 2 1 194 116 349 2 179 133 89
3 26 29 356 9 9 1 82 90 81	11 2 1 82 85 190 2 49 58 160	3 39 41 180 13 1 1 58 61 262	2 31 38 99	2 ·55 61 357 2 5 1 194 116 349 2 179 133 89
				•

(1.84 Å) is not significantly different from values reported for such bonds in 1,4-dithian (1.81 Å),4 1,4-dithian 1,4dioxide (1.81 Å), methanethiol (1.82 Å), and 1,3,5trithian (1.80 Å). The chair conformation of each thioxan molecule is clearly established by the displacements of the sulphur and oxygen atoms from the plane through the four carbon atoms (see Table 3).

The average Hg-Cl distance of 2.48 Å is close to values (for 4-co-ordinated mercury) of 2.50 Å in perloline tetrachloromercurate, <sup>9</sup> 2.51 Å in 1,6-dithiacyclodecacis-3,cis-8-dienebis(mercuric chloride),10 and 2.44 Å in dichloro-(1,3,5-trithian)mercury. The average Hg-S distance of 2.57 Å is close to values of 2.53 Å in 1,6dithiacyclodeca-cis-3,cis-8-dienebis(mercuric chloride),10 2.55 Å in bis(ethylenediamine)copper(II) tetrathiocyanatomercurate, 11 and 2.61 Å in dichloro-(1,3,5-trithian)mercury.<sup>1</sup> The valency angles S-Hg-S and Cl-Hg-Cl are enlarged beyond 109° 28' and the co-ordination tetrahedron around the mercury atom is therefore slightly distorted in the same manner as that in dichloro-(1,3,5trithian)mercury.1

## EXPERIMENTAL

Crystal Data.—Dichlorobis-(1,4-thioxan)mercury(II),  $C_8H_{16}Cl_2HgO_2S_2$ , M = 479.9. Orthorhombic, a = 15.31, b = 19.69, c = 4.33 Å, U = 1305 Å<sup>3</sup>, Z = 4,  $D_c = 2.44$ g. cm.<sup>-3</sup>. Space group  $Pn2_1a$ . F(000) = 904. Absorption coefficient for X-rays ( $\lambda = 1.5418 \text{ Å}$ ),  $\mu = 291 \text{ cm.}^{-1}$ .

Crystallographic Measurements.—Oscillation, rotation, and Weissenberg photographs were taken with Cu- $K_{\alpha}$  radiation; precession photographs were taken with Mo- $K_{\alpha}$  radiation. The lattice parameters were obtained from precession photographs. The hk0-3 reflexions were recorded photographically by means of an equi-inclination Weissenberg instrument and the intensities were estimated visually.

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 J. A. D. Jeffreys, G. A. Sim, R. H. Burnell, W. I. Taylor, R. E. Corbett, J. Murray, and B. J. Sweetman, Proc. Chem. Soc., 1963, 171; G. Ferguson, J. A. D. Jeffreys, and G. A. Sim, J. Chem. Soc. (R) 1966, 454 Chem. Soc. (B), 1966, 454.

Absorption corrections appropriate to a cylindrical crystal were applied.12 In all, 974 independent structure amplitudes ( $|F_0|$ ) were evaluated.

Structure Analysis.—From the three-dimensional Patterson function the position of the mercury atom was determined to be (0.125, 0, 0.075). All the vectors between the mercury and the chlorine, sulphur, carbon, and oxygen atoms were located, and detailed consideration of these demonstrated that the space group could not be Pnma but had to be  $Pn2_1a$ .

The co-ordinates and isotropic temperature factors of the mercury, chlorine, and sulphur atoms were adjusted by a round of least-squares calculations, using a modified version of the Gantzel, Sparks, and Trueblood U.C.L.A. leastsquares programme. A three-dimensional electron-density distribution was computed and the carbon and oxygen atoms located unambiguously. The least-squares programme was then used to adjust the positional and thermal parameters of the mercury, chlorine, sulphur, oxygen, and carbon atoms; an anisotropic temperature factor was assigned to the mercury atom, but isotropic parameters were retained for the other atoms. When the calculations were terminated the value of R was 16.4%.

The theoretical atomic scattering factors used in all the structure-factor calculations were taken from "International Tables." 12 The final values of the structure amplitudes and phase angles are in Table 4. The standard deviations of the final atomic co-ordinates were derived from the least-squares residuals by means of the equation

$$\sigma^2(u_i) = \sum_j w_j (\Delta F_j)^2 / [(n-s) \sum_j w_j (\partial f_j / \partial u_i)^2]$$

The results are in Table 1.

The calculations were performed on the IBM 7094 computer of the University of Illinois. We thank the U.S. National Science Foundation, Eli Lilly and Company, and the Hoffmann-LaRoche Foundation for financial support.

[6/971 Received, August 1st, 1966]

<sup>10</sup> K. K. Cheung and G. A. Sim, J. Chem. Soc., 1965, 5988.
<sup>11</sup> H. Scouloudi, Acta Cryst., 1953, 6, 651.
<sup>12</sup> "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, 1959, vol. II; 1962, vol. III.