

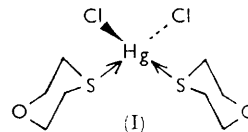
Complexes of Mercury. Part III.¹ X-Ray Analysis of Dichlorobis-(1,4-thioxan)mercury(II)

By R. S. McEwen* and G. A. Sim,† Department of Chemistry, University of Illinois, Urbana, Illinois, U.S.A.

Dichlorobis-(1,4-thioxan)mercury(II) crystallises in the orthorhombic system, space group $Pn2_1a$, with four molecules of $C_8H_{16}Cl_2HgO_2S_2$ in a cell of dimensions $a = 15.31$, $b = 19.69$, $c = 4.33$ Å. The mercury atom is co-ordinated 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 Cl-Hg-Cl 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 oxygen-bonded in the complexes.³ 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

* Present address: Bell Telephone Laboratories, Murray Hill, New Jersey, U.S.A.

† Present address: Chemical Laboratory, University of Sussex.

¹ Part II, W. R. Costello, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. (A)*, 1966, 1190.

² P. J. Hendra and D. B. Powell, *J. Chem. Soc.*, 1960, 5105.

³ R. A. Walton, *Inorg. Chem.*, 1966, **5**, 643.

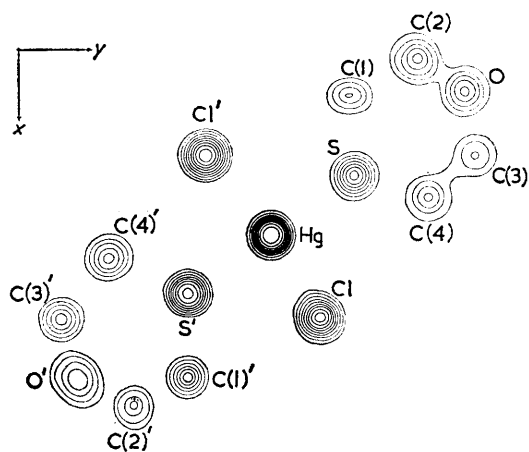


FIGURE 1 The final three-dimensional electron-density distribution shown by means of superimposed contour sections drawn parallel to (001). Contour interval $10 \text{ e}\text{\AA}^{-3}$ around the mercury atom, $2 \text{ e}\text{\AA}^{-3}$ around the chlorine and sulphur atoms, and $1 \text{ e}\text{\AA}^{-3}$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

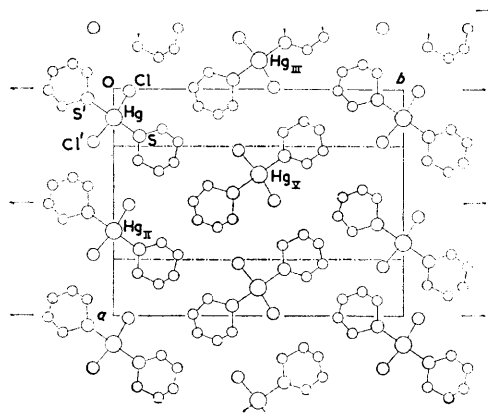


FIGURE 2 The crystal structure as viewed along the c axis

TABLE 1

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

	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	3.0	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	3.2	0.06	0.06	0.07
C(1)	0.3132	0.0833	0.1990	2.9	0.08	0.08	0.10
C(2)	0.3631	0.1562	0.2515	2.4	0.08	0.08	0.09
C(3)	0.2339	0.2238	0.2217	5.6	0.14	0.13	0.14
C(4)	0.1748	0.1672	0.1800	3.1	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	3.0	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

* For the mercury atom an anisotropic temperature factor was employed. This was of the form

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

with parameters

b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
0.0029	0.0021	0.0307	-0.0002	-0.0030	-0.0001

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

TABLE 2

Interatomic distances (\AA) and valency angles with standard deviations

Bond lengths					
	Dist.	S.d.		Dist.	S.d.
Hg-Cl	2.43	0.018	Hg-Cl'	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

Valency angles

S.d.					
	S.d.			S.d.	
Cl-Hg-Cl'	114°	0.6°	S-Hg-S'	115°	0.8°
Cl-Hg-S	112	0.6	Cl'-Hg-S'	103	0.6
Cl-Hg-S'	103	0.6	Cl'-Hg-S	110	0.6
Hg-S-C(1)	100	3.0	Hg-S'-C(1)'	107	2.2
Hg-S-C(4)	101	3.1	Hg-S'-C(4)'	107	2.4
C(1)-S-C(4)	95	4.1	C(1)'-S'-C(4)'	98	3.0
S-C(1)-C(2)	108	5.6	S'-C(1)'-C(2)'	112	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	9.5	O'-C(3)'-C(4)'	120	5.7
C(3)-C(4)-S	115	7.8	C(3)'-C(4)'-S'	112	4.7

Non-bonded contacts ($< 3.8 \text{ \AA}$)

S' ····· Cl _I	3.25	S' ····· Hg _I	3.65
C(4)' ····· O _{VI}	3.26	S ····· Hg _I	3.65
C(1) ····· O' _{VI}	3.31	Hg ····· Cl' _I	3.67
C(4) ····· O' _{III}	3.31	C(3) ····· O' _{IV}	3.69
C(3) ····· O' _{III}	3.32	C(3) ····· O' _{IV}	3.70
S' ····· Cl' _I	3.32	C(3)' ····· C(2) _{VI}	3.71
Cl' ····· C(2)' _{II}	3.41	C(2) ····· Cl _{II}	3.72
S ····· Cl _I	3.51	Cl' ····· C(1)' _{II}	3.74
S ····· Cl' _I	3.54	C(1)' ····· Cl _I	3.76
Hg ····· Cl _I	3.62	C(2) ····· C(3)' _V	3.78

The subscripts refer to the positions

I: $x, y, 1+z$	IV: $-x, \frac{1}{2}+y, 1-z$
II: $\frac{1}{2}+x, y, \frac{1}{2}-z$	V: $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$
III: $-x, \frac{1}{2}+y, -z$	VI: $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}+z$

TABLE 3

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

Atoms included in derivation of plane	Atoms omitted	Atoms included in derivation of plane	Atoms 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-dithian⁴ and 1,3,5-trithian,¹ 98° in 1,4-dithian 1,4-dioxide,⁵ and 100° in 1,4-dithiin⁶ and thianthren.⁷ The average carbon-sulphur bond length

⁴ R. E. Marsh, *Acta Cryst.*, 1955, **8**, 91.

⁵ H. M. M. Shearer, *J. Chem. Soc.*, 1959, 1394.

⁶ P. A. Howell, R. M. Curtis, and W. N. Lipscomb, *Acta Cryst.*, 1954, **7**, 498.

⁷ 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 phases

h	k	l	$ F_o $	$ F_c $	α	h	k	l	$ F_o $	$ F_c $	α	h	k	l	$ F_o $	$ F_c $	α	h	k	l	$ F_o $	$ F_c $	α	h	k	l	$ F_o $	$ F_c $	α
0	2	0	327	344	358	2	1	0	267	330	90	3	7	1	166	170	81	4	17	0	123	92	168	6	6	2	46	34	251
0	2	1	195	141	8	2	1	1	18	151	359	3	7	2	107	109	285	4	17	1	13	15	152	6	7	3	168	174	359
0	3	1	143	59	254	2	2	0	145	14	88	3	8	3	21	32	128	4	17	2	78	73	232	6	8	0	222	247	268
0	3	2	250	192	84	2	2	1	11	22	192	3	8	4	172	153	200	4	13	0	83	65	292	6	9	1	126	184	277
0	4	0	232	217	360	2	3	0	90	68	275	3	9	1	104	101	153	4	13	1	99	89	200	6	10	2	51	42	12
0	4	1	210	154	386	2	3	1	160	115	184	3	9	2	37	37	150	4	13	2	74	99	165	6	10	3	147	136	354
0	5	1	116	120	82	2	3	2	33	28	288	3	10	1	127	121	76	4	19	0	28	23	269	6	9	0	208	203	264
0	5	2	120	94	95	2	3	3	140	174	178	3	10	2	80	84	297	4	19	1	12	14	153	6	10	1	58	61	242
0	6	0	128	122	15	2	3	4	349	330	89	3	10	3	44	50	122	4	20	2	56	46	280	6	10	2	47	45	19
0	6	1	239	178	3	2	4	1	185	125	349	3	11	1	107	111	188	4	20	3	93	80	188	6	11	3	78	86	349
0	7	1	139	89	72	2	4	2	161	140	9	3	11	2	58	69	164	4	20	4	160	52	247	6	11	4	45	49	53
0	7	2	96	78	101	2	4	3	114	97	73	3	11	3	36	35	182	4	21	0	17	24	158	6	12	1	92	77	287
0	8	0	111	118	26	2	5	1	135	95	182	3	12	1	109	110	92	4	21	1	21	17	268	6	12	2	41	34	144
0	8	1	260	197	348	2	5	2	110	92	255	3	12	2	68	70	258	4	22	0	49	48	165	6	12	3	22	38	214
0	9	1	244	169	76	2	6	0	134	126	177	3	13	0	23	30	99	4	22	1	21	17	268	6	13	0	92	77	287
0	10	0	220	224	5	2	6	1	237	217	89	3	13	1	112	110	174	4	22	2	38	40	204	6	13	1	34	27	11
0	10	1	218	153	356	2	6	2	45	47	59	3	13	2	75	75	188	4	23	0	7	10	29	6	14	2	20	29	37
0	11	1	197	137	72	2	7	0	144	91	177	3	14	0	93	99	102	4	23	1	49	56	152	6	14	3	67	66	350
0	12	0	255	224	1	2	7	1	129	108	174	3	14	1	63	65	248	4	24	0	181	204	180	6	15	0	105	93	267
0	12	1	134	91	4	2	7	2	185	135	9	3	15	0	76	80	169	4	24	1	118	153	0	6	15	1	48	54	139
0	12	2	124	91	91	2	8	0	250	225	88	3	15	1	112	110	174	4	25	0	170	192	268	6	16	0	104	92	277
0	13	0	120	100	83	2	8	1	185	135	9	3	16	0	110	136	277	4	25	1	110	136	277	6	16	1	37	44	320
0	14	0	189	158	352	2	9	0	49	42	148	3	16	1	76	80	169	4	25	2	21	27	283	6	16	2	18	28	221
0	14	1	72	65	24	2	9	1	121	93	165	3	16	2	52	53	236	4	26	0	145	163	190	6	17	0	76	61	345
0	15	1	17	20	197	2	9	2	26	19	266	3	17	0	27	25	93	4	26	1	72	104	350	6	17	1	83	68	2
0	15	2	139	109	76	2	10	0	142	121	188	3	17	1	61	74	171	4	26	2	133	136	260	6	17	2	104	126	274
0	16	0	87	77	339	2	10	1	235	193	94	3	17	2	50	52	183	4	27	0	64	97	286	6	18	0	93	78	271
0	17	1	82	77	32	2	10	2	125	73	164	3	18	0	159	25	216	4	27	1	35	49	277	6	18	1	88	69	7
0	17	2	93	77	62	2	11	0	187	135	94	3	18	1	135	141	186	4	27	2	135	141	186	6	18	2	140	111	281
0	18	0	101	102	341	2	11	1	13	14	233	3	19	0	67	65	192	4	28	0	63	77	343	6	19	0	83	70	259
0	19	1	34	31	121	2	11	2	28	23	203	3	19	1	57	65	192	4	28	1	34	43	166	6	19	1	61	44	337
0	19	2	73	61	70	2	12	0	129	82	177	3	20	0	38	42	156	4	29	0	110	124	267	6	20	0	91	66	1
0	20	0	83	86	357	2	12	1	147	121	176	3	20	1	42	52	79	4	29	1	62	71	274	6	20	1	55	82	279
0	21	1	45	37	87	2	12	2	271	219	92	3	21	0	35	40	288	4	30	0	82	103	180	6	21	0	24	30	306
0	22	0	51	51	79	2	12	3	67	53	144	3	21	1	39	47	196	4	30	1	37	62	3	6	22	0	14	26	22
0	22	1	75	82	9	2	13	0	139	107	84	3	22	0	24	35	151	4	30	2	43	60	195	6	22	1	17	21	326
0	23	1	53	59	50	2	13	1	40	38	324	3	22	1	31	18	176	4	31	0	103	108	280	6	23	0	65	55	270
0	24	0	48	42	13	2	14	0	70	71	233	3	23	0	37	44	83	4	31	1	32	45	248	6	23	1	38	29	289
1	1	2	48	72	94	2	14	1	123	83	171	3	23	1	27	30	280	4	32	0	106	114	171	6	24	0	53	44	260
1	2	1	177	163	8	2	15	0	49	48	38	3	24	0	20	27	166	4	32	1	12	60	112	7	0	1	134	162	0
1	2	2	70	78	175	2	15	1	185	162	89	3	24	1	24	34	98	4	33	0	132	129	274	7	1	0	84	109	0
1	3	1	36	54	353	2	15	2	29	40	112	3	25	0	18	24	254	4	33	1	83	97	256	7	2	0	13	29	0
1	3	2	207	144	77	2	16	0	125	98	98	3	25	1	18	27	168	4	34	0	132	129	274	7	3	0	135	162	261
1	3	3	118	118	103	2	16	1	53	49	322	3	26	0	152	158	180	4	34	1	83	97	256	7	4	0	84	114	98
1	4	1	43	55	110	2	17	0	93	92	244	3	26	1	191	203	180	4	35	0	134	141	177	7	5	0	145	155	7
1	4	2	226	204	7	2	17	1	30	25	173	3	27	0	205	234	179	4	35	1	91	95	359	7	6	0	85	112	345
1	5	1	137	133	165	2	18	0	53	46	53	3	27	1	65	81	270	4	36	0	112	122	271	7	7	0	23	25	327
1	5	2	34	29	352	2	18	1	119	96	178	3	28	0	166	184	181	4	37	0	75	92	266	7	8	0	137	139	266
1	6	1	231	216	90	2	19	0	113	114	91	3	29	0	62	45	105	4	38	0	99	107	184	7	9	0	67	87	95
1	6	2	146	145	86	2	19	1	34	24	39	3	30	0	12	20	64	4	39	0	63	79	353	7	10	0	30	39	290
1	6	3	23	27	102	2	20	0	21	23	322	3	31	0	195	187	180	4	40	0	63	67	271	7	11	0	46	62	1
1	7	1	216	196	355	2	20	1	13	21	231	3	32	0	21	38	5	4	41	0	176	186	188	7	12	0	38	47	0
1	7	2	143	143	188	2	21	0	54	45	187	3	33	0	132	107	265	4	42	0	52	60	342	7	13	0	86	90	271
1	7	3	21	28	30	2	21	1	75	61	165	3	34	0	126	129	271	4	43	0	27	21	183	7	14	0	27	45	90
1	8	1	192	155	97	2	22	0	112	122	85	3	35	0	205	234	179	4	44	0	56	67	264	7	15	0	40	48	272
1	8	2	129	121	80	2	22	1	55	45	110	3	36	0	71	52	81	4	45	0	43	47	281	7	16	0	88	95	2
1	8	3	28	29	90	2	23	0	30	43	53	3	37	0															

Published on 01 January 1967. Downloaded by Michigan State University on 25/01/2016 16:51:43.

(1.84 Å) is not significantly different from values reported for such bonds in 1,4-dithian (1.81 Å),⁴ 1,4-dithian 1,4-dioxide (1.81 Å),⁵ methanethiol (1.82 Å),⁸ and 1,3,5-trithian (1.80 Å).¹ 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,⁹ 2.51 Å in 1,6-dithiacyclodeca-*cis*-3,*cis*-8-dienebis(mercuric chloride),¹⁰ and 2.44 Å in dichloro-(1,3,5-trithian)mercury.¹ The average Hg-S distance of 2.57 Å is close to values of 2.53 Å in 1,6-dithiacyclodeca-*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.¹ 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-(1,3,5-trithian)mercury.¹

EXPERIMENTAL

Crystal Data.—Dichlorobis-(1,4-thioxan)mercury(II), C₈H₁₆Cl₂HgO₂S₂, *M* = 479.9. Orthorhombic, *a* = 15.31, *b* = 19.69, *c* = 4.33 Å, *U* = 1305 Å³, *Z* = 4, *D*_c = 2.44 g. cm.⁻³. Space group *Pn*2₁*a*. *F*(000) = 904. Absorption coefficient for X-rays (λ = 1.5418 Å), μ = 291 cm.⁻¹.

Crystallographic Measurements.—Oscillation, rotation, and Weissenberg photographs were taken with Cu-*K*_α radiation; precession photographs were taken with Mo-*K*_α radiation. The lattice parameters were obtained from precession photographs. The *h**k*0—3 reflexions were recorded photographically by means of an equi-inclination Weissenberg instrument and the intensities were estimated visually.

⁸ R. W. Kilb, *J. Chem. Phys.*, 1955, **23**, 1736; N. Solimene and B. P. Dailey, *ibid.*, p. 124.

⁹ 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. (B)*, 1966, 454.

Absorption corrections appropriate to a cylindrical crystal were applied.¹² In all, 974 independent structure amplitudes ($|F_o|$) 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 *Pn*2₁*a*.

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. least-squares 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]

¹⁰ K. K. Cheung and G. A. Sim, *J. Chem. Soc.*, 1965, 5988.

¹¹ H. Scouloudi, *Acta Cryst.*, 1953, **6**, 651.

¹² "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, 1959, vol. II; 1962, vol. III.