

The Crystal Structure and Absolute Configuration of the 2:1 Complex Between Testosterone and Mercuric Chloride

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The 2:1 complex between testosterone and mercuric chloride, $(C_{19}H_{28}O_2)_2HgCl_2$, was prepared by dissolving testosterone and mercuric chloride together in the minimum quantity of hot benzene. Crystallization took place in a sealed container at a constant temperature of 50°C. The crystals are monoclinic, space group $C2$, with $a=21.339$, $b=7.784$, $c=12.640$ Å, $\beta=120.00^\circ$. The crystal structure was solved from the three-dimensional Patterson and Fourier syntheses and was refined by block-diagonal least squares to $R=0.064$. The steroid molecules are hydrogen bonded 'head-to-tail' through the 3-oxo and 17-hydroxyl oxygen atoms. The two 17-hydroxyl groups of two steroid molecules and the two chlorine atoms, form an extremely distorted tetrahedral configuration about the mercury atom with the angle Cl-Hg-Cl equal to 165° and Hg-OH equal to 2.48 Å.

Introduction

The complex between testosterone and mercuric chloride was prepared during an attempt to establish methods for forming complexes between steroids and amino acids, a project which has been in progress in this laboratory as a starting point in the study of the interaction between steroids and proteins. Testosterone is a powerful androgen formed by the interstitial cells of the adult testis and is responsible for the development and growth of the male primary and secondary sex characteristics. It circulates in the blood, loosely bound to carrier proteins, and is catabolized mainly by the liver to form 17-ketosteroids which are excreted in the urine. Testosterone has been used as a drug in the treatment of testicular failure due to primary disease of the gonad or to anterior pituitary insufficiency, in the treatment of patients with disseminated breast carcinoma, in osteoporosis, and for its ability to stimulate protein synthesis.

Experimental data

The complex was prepared by dissolving together testosterone and mercuric chloride in equal molar proportions in the minimum quantity of hot benzene. The container was sealed and maintained at a constant temperature of 50°C whereupon large, irregular, striated crystals were obtained.

Unit-cell parameters and space-group determinations were carried out on a General Electric single crystal orienter. The unit cell was found to be monoclinic and systematic X-ray extinctions were observed for all spectra with $h+k=2n+1$. The non-centro-

symmetric space-group $C2$ was chosen so as to be compatible with the asymmetry of the steroid molecules. Density measurements indicated one molecule of mercuric chloride per two molecules of steroid, with two such units per unit cell. The crystal data were: $(C_{19}H_{28}O_2)_2HgCl_2$, $M=848.3$, $a=21.339 \pm 0.003$, $b=7.84 \pm 0.002$, $c=12.640 \pm 0.006$ Å, $\beta=120.00 \pm 0.05^\circ$, $V_0=1818.8$ Å³, $D_m=1.539 \pm 0.011$ (by flotation), $Z=2$, $D_c=1.549$ g.cm⁻³, $F(000)=860$. Space group $C2$ (C_2^3 , no. 5). Cu $K\alpha$ single-crystal diffractometry. (The equivalent body-centered unit cell has space group $I2$ and cell dimensions $a=18.585$, $b=7.784$, $c=12.640$ Å, $\beta=96.1^\circ$.)

A roughly cubic crystal was selected for intensity measurements and this was ground into a sphere so that absorption of X-rays in the specimen would be uniform in all directions (no corrections were made for this absorption). The intensities of 1940 independent spectra with $2\theta \leq 140^\circ$ were measured on the single crystal orienter by the stationary crystal/stationary counter method, using balanced nickel/cobalt filters. The intensities were each counted for ten seconds with each filter.

Using these data, a three-dimensional Patterson synthesis was computed in which the $|F^2|$ terms were modified by the factor $1/f_{Hg}^2$. The mercury atom, which lies on the twofold symmetry axis, was assigned the coordinates (000), and the chlorine atom was easily located. Owing to the domination of the phases of the structure factors by the mercury atom, and to the relatively heavy vectors between this atom and lighter ones, the Patterson synthesis could be regarded as being equivalent to the Fourier synthesis obtained using the phases due to the mercury atom at the origin, and so the thirty-two large Patterson vectors represented tentative atomic locations. By examining the distances between these 'atoms' and allowing for known

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stereochemical features of the steroid molecule, only seven atomic positions could be confirmed. A Fourier synthesis phased on the mercury, chlorine and seven atoms which were assigned carbon form factors, showed a pseudo-mirror plane at $y = \frac{1}{2}$, but the outline of the steroid molecule could be seen lying roughly parallel to (100) and straddling the pseudo-mirror plane. Once again using the known stereochemistry of the steroid molecule, all the remaining atoms were placed, but with some uncertainty over the positions of C(8), C(14) and C(16) which lay close to the 'mirror plane' and over the positions of atoms C(7), C(9) and C(6), C(10),

the members of each pair being closely related in position by the 'mirror plane'. A set of structure factors calculated for these atoms, with an overall isotropic temperature factor of 4 \AA^2 gave an R value of 0.23, compared with 0.31 for the mercury and chlorine atoms alone. Four cycles of block-diagonal least-squares refinement of the positional and isotropic thermal parameters (holding the mercury atom fixed at the origin) yielded an R value of 0.18. After examination of the interatomic distances it was found that C(8) and C(14) had each been placed on the wrong side of the 'mirror plane'; however, even with all the scattering matter in

Table 1. *Positional and thermal parameters*

Standard deviations, which refer to the last two digits of each number, are given in parentheses.

	x/a	y/b	z/c	$B(\text{iso})$
C(1)	0.1714 (10)	0.7806 (28)	0.7981 (17)	4.56 (31)
C(2)	0.1976 (11)	0.7595 (33)	0.9358 (20)	5.32 (32)
C(3)	0.1620 (10)	0.6079 (27)	0.9526 (17)	4.43 (31)
C(4)	0.1415 (8)	0.4559 (21)	0.8631 (14)	4.00 (27)
C(5)	0.1585 (7)	0.4631 (20)	0.7751 (12)	3.47 (24)
C(6)	0.1540 (10)	0.3048 (26)	0.7077 (16)	4.16 (29)
C(7)	0.1097 (11)	0.3295 (27)	0.5681 (18)	4.18 (32)
C(8)	0.1367 (5)	0.4818 (29)	0.5285 (9)	2.84 (19)
C(9)	0.1372 (9)	0.6472 (21)	0.5954 (14)	3.10 (24)
C(10)	0.1852 (8)	0.6277 (22)	0.7394 (14)	3.26 (23)
C(11)	0.1597 (10)	0.8028 (30)	0.5507 (19)	5.00 (32)
C(12)	0.1135 (9)	0.8269 (26)	0.4142 (16)	4.23 (28)
C(13)	0.1171 (7)	0.6692 (21)	0.3464 (13)	3.18 (22)
C(14)	0.0913 (5)	0.5124 (28)	0.3911 (10)	2.78 (21)
C(15)	0.0819 (9)	0.3712 (28)	0.3027 (17)	4.57 (33)
C(16)	0.0542 (9)	0.4653 (30)	0.1794 (16)	5.01 (33)
C(17)	0.0618 (8)	0.6574 (23)	0.2090 (14)	3.58 (24)
C(18)	0.1940 (10)	0.6361 (28)	0.3675 (17)	4.41 (29)
C(19)	0.2643 (10)	0.6078 (29)	0.7807 (18)	4.74 (32)
O(3)	0.1507 (9)	0.5863 (27)	1.0413 (17)	6.40 (36)
O(17)	0.0799 (7)	0.7698 (20)	0.1359 (12)	4.88 (24)
Cl	0.0588 (3)	1.0399 (6)	-0.1083 (5)	8.34 (—)*
Hg	0.0000 (—)	1.0000 (—)	0.0000 (—)	5.26 (—)*

* Equivalent $B(\text{iso})$. The anisotropic thermal parameters for the thermal motion of these atoms, in the form

$$T = \exp - [(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}kl + 2b_{23}hl) \times 10^{-5}]$$

are:

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Hg	355 (2)	1110 (10)	790 (6)	0 (—)	149 (6)	0 (—)
Cl	433 (14)	2018 (99)	1228 (43)	-101 (27)	305 (22)	902 (49)

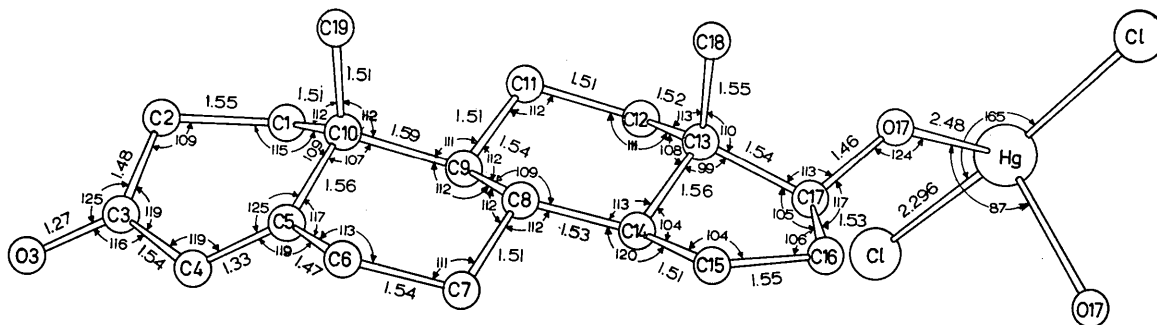


Fig. 1. A perspective view of the complex, in the correct absolute configuration. The atoms are numbered according to the standard scheme for steroids. Interatomic distances (Å) and angles (°) have standard deviations in the ranges 0.02–0.03 Å and 1–2° respectively.

Table 2. Comparison between the observed structure amplitudes and those calculated with use of the final atomic parameters as obtained in this analysis

The hkl indices listed here are for the correct absolute configuration of the molecule. The listed values of $FOBS$ and $FCAL$ are ten times absolute scale.

h	k	l	$FOBS$	$FCAL$	h	k	l	$FOBS$	$FCAL$	h	k	l	$FOBS$	$FCAL$	h	k	l	$FOBS$	$FCAL$
1	0	1	1428	1738	1	0	1	1428	1738	1	0	1	1428	1738	1	0	1	1428	1738
1	0	2	1153	1216	1	0	2	1153	1216	1	0	2	1153	1216	1	0	2	1153	1216
1	0	3	871	871	1	0	3	871	871	1	0	3	871	871	1	0	3	871	871
1	0	4	656	656	1	0	4	656	656	1	0	4	656	656	1	0	4	656	656
1	0	5	484	484	1	0	5	484	484	1	0	5	484	484	1	0	5	484	484
1	0	6	359	359	1	0	6	359	359	1	0	6	359	359	1	0	6	359	359
1	0	7	282	282	1	0	7	282	282	1	0	7	282	282	1	0	7	282	282
1	0	8	229	229	1	0	8	229	229	1	0	8	229	229	1	0	8	229	229
1	0	9	191	191	1	0	9	191	191	1	0	9	191	191	1	0	9	191	191
1	0	10	158	158	1	0	10	158	158	1	0	10	158	158	1	0	10	158	158
1	0	11	131	131	1	0	11	131	131	1	0	11	131	131	1	0	11	131	131
1	0	12	107	107	1	0	12	107	107	1	0	12	107	107	1	0	12	107	107
1	0	13	87	87	1	0	13	87	87	1	0	13	87	87	1	0	13	87	87
1	0	14	70	70	1	0	14	70	70	1	0	14	70	70	1	0	14	70	70
1	0	15	56	56	1	0	15	56	56	1	0	15	56	56	1	0	15	56	56
1	0	16	45	45	1	0	16	45	45	1	0	16	45	45	1	0	16	45	45
1	0	17	36	36	1	0	17	36	36	1	0	17	36	36	1	0	17	36	36
1	0	18	29	29	1	0	18	29	29	1	0	18	29	29	1	0	18	29	29
1	0	19	23	23	1	0	19	23	23	1	0	19	23	23	1	0	19	23	23
1	0	20	18	18	1	0	20	18	18	1	0	20	18	18	1	0	20	18	18
1	0	21	14	14	1	0	21	14	14	1	0	21	14	14	1	0	21	14	14
1	0	22	11	11	1	0	22	11	11	1	0	22	11	11	1	0	22	11	11
1	0	23	9	9	1	0	23	9	9	1	0	23	9	9	1	0	23	9	9
1	0	24	7	7	1	0	24	7	7	1	0	24	7	7	1	0	24	7	7
1	0	25	6	6	1	0	25	6	6	1	0	25	6	6	1	0	25	6	6
1	0	26	5	5	1	0	26	5	5	1	0	26	5	5	1	0	26	5	5
1	0	27	4	4	1	0	27	4	4	1	0	27	4	4	1	0	27	4	4
1	0	28	3	3	1	0	28	3	3	1	0	28	3	3	1	0	28	3	3
1	0	29	3	3	1	0	29	3	3	1	0	29	3	3	1	0	29	3	3
1	0	30	2	2	1	0	30	2	2	1	0	30	2	2	1	0	30	2	2
1	0	31	2	2	1	0	31	2	2	1	0	31	2	2	1	0	31	2	2
1	0	32	1	1	1	0	32	1	1	1	0	32	1	1	1	0	32	1	1
1	0	33	1	1	1	0	33	1	1	1	0	33	1	1	1	0	33	1	1
1	0	34	1	1	1	0	34	1	1	1	0	34	1	1	1	0	34	1	1
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1	0	38	1	1	1	0	38	1	1	1	0	38	1	1	1	0	38	1	1
1	0	39	1	1	1	0	39	1	1	1	0	39	1	1	1	0	39	1	1
1	0	40	1	1	1	0	40	1	1	1	0	40	1	1	1	0	40	1	1
1	0	41	1	1	1	0	41	1	1	1	0	41	1	1	1	0	41	1	1
1	0	42	1	1	1	0	42	1	1	1	0	42	1	1	1	0	42	1	1
1	0	43	1	1	1	0	43	1	1	1	0	43	1	1	1	0	43	1	1
1	0	44	1	1	1	0	44	1	1	1	0	44	1	1	1	0	44	1	1
1	0	45	1	1	1	0	45	1	1	1	0	45	1	1	1	0	45	1	1
1	0	46	1	1	1	0	46	1	1	1	0	46	1	1	1	0	46	1	1
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1	0	48	1	1	1	0	48	1	1	1	0	48	1	1	1	0	48	1	1
1	0	49	1	1	1	0	49	1	1	1	0	49	1	1	1	0	49	1	1
1	0	50	1	1	1	0	50	1	1	1	0	50	1	1	1	0	50	1	1
1	0	51	1	1	1	0	51	1	1	1	0	51	1	1	1	0	51	1	1
1	0	52	1	1	1	0	52	1	1	1	0	52	1	1	1	0	52	1	1
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1	0	60	1	1	1	0	60	1	1	1	0	60	1	1	1	0	60	1	1
1	0	61	1	1	1	0	61	1	1	1	0	61	1	1	1	0	61	1	1
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1	0	67	1	1	1	0	67	1	1	1	0	67	1	1	1	0	67	1	1
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1	0	71	1	1	1	0	71	1	1	1	0	71	1	1	1	0	71	1	1
1	0	72	1	1	1	0	72	1	1	1	0	72	1	1	1	0	72	1	1
1	0	73	1	1	1	0	73	1	1	1	0	73	1	1	1	0	73	1	1
1	0	74	1	1	1	0	74	1	1	1	0	74	1	1	1	0	74	1	1
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1	0	80	1	1	1	0	80	1	1	1	0	80	1	1	1	0	80	1	1
1	0	81	1	1	1	0	81	1	1	1	0	81	1	1	1	0	81	1	1
1	0	82	1	1	1	0	82	1	1	1	0	82	1	1	1	0	82	1	1
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1	0	86	1	1	1	0	86	1	1	1	0	86	1	1	1	0	86	1	1
1	0	87	1	1	1	0	87	1	1	1	0	87	1	1	1	0	87	1	1
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1	0	89	1	1	1	0	89	1	1	1	0	89	1	1	1	0	89	1	1
1	0	90	1	1	1	0	90	1	1	1	0	90	1	1	1	0	90	1	1
1	0	91																	

altered indexing $h\bar{k}l$. The configuration so obtained agrees with that normally found in naturally occurring steroids. A perspective view of the complex in the correct configuration is given in Fig. 1.

The final atomic parameters for the correct absolute configuration, in a right-handed coordinate system, are given in Table 1, along with standard deviations obtained from the inverses of the full least-squares normal equations blocks for each atom. Table 2 lists the comparison between the observed and calculated structure amplitudes for all measured reflections (all reflections were used in the least-squares refinement, irrespective of the observed magnitudes of their intensities). In this Table, the signs of the indices hkl have been changed as described above, so that the correct absolute configuration of the molecule is given thereby.

Description of the steroid molecules

With the exception of the Hg-Cl bond, the standard deviations of all interatomic distances and angles lie in the ranges 0.02–0.03 Å and 1–2° respectively. With these observed errors, none of the bond distances differ significantly from their normally expected values. The distances found for bonds C(4)–C(5) and C(3)–O(3) are consistent with their chemically established double bond characters. The bond angles in rings *A*, *B* and *C* are generally larger than expected for tetrahedral carbon atoms, but are in accord with similar angles found in other steroids (Norton, 1965). The enlargement of the angle C(2)–C(1)–C(10) to 115° assists in relieving the strain imposed on ring *A* by the $\Delta^{4,5}$ bond. The bond distances and angles are summarized in Fig. 1.

Rings *B*, *C* and *D* are *trans* fused. Rings *B* and *C* have normal configurations and are chair shaped, but ring *A* is distorted by the double bond between atoms C(4) and C(5), which also affects the *A/B* ring junction. The dihedral angles at the junctions of rings *B*, *C* and *D* are in the region of 130° whereas that at the *A/B* junction is 125°; however, the *A/B* junction itself retains its planarity [see Table 3(b)]. The conjugated

system O(3)=C(3)–C(4)=C(5)–C(6) is, with the exception of C(4) which lies 0.15 Å out of the plane, planar to within 0.04 Å. Atom C(10) also lies in this plane. Ring *D* is a β -envelope and has normal configuration with atoms C(14), C(15), C(16) and C(17) planar to within 0.04 Å. The 17-hydroxyl group has the β -configuration with a torsional angle C(18)–C(13)–C(17)–OH of 54°.

Table 3(b). *Interplanar angles*

Planes	Angle
<i>A/B</i>	134°
<i>B/C</i>	177
<i>C/D</i>	174
<i>A1/A2</i>	161
<i>A2/A3B1</i>	153
<i>B2/A3B1</i>	125
<i>B2/B3C1</i>	131
<i>C2/B3C1</i>	129
<i>C2/C3D1</i>	133
<i>D2/C3D1</i>	134
C(1)–C(17)/(100)	19
C(1)–C(17)/(010)	100
C(1)–C(17)/(001)	74

The steroid nucleus has been analysed in terms of the usual least-squares planes and interplanar angles and these are summarized in Table 3. The torsional angles in the steroid nucleus are summarized in Table 4.

Coordination of the mercury atoms

The mercury atom is positioned on a twofold symmetry axis with the Hg-Cl bond at 82.5° to this axis. That is, the mercuric chloride molecule, instead of being linear, is bent to give a Cl–Hg–Cl angle of 165°. The 17-hydroxy oxygen atom is 2.48 Å from the mercury atom with an OH–Hg–OH angle of 87°. The plane of these last three atoms is nearly perpendicular to the Cl–Hg–Cl plane (92°), so that the hydroxyl groups from two steroid molecules and the two chlorine atoms form a very distorted tetrahedral configuration about the mercury atom (Figs. 1, 2 and 3). This

Table 3(c). *Deviations (Å) from the least-squares planes*

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>A2</i>	<i>A3B1</i>	<i>B2</i>	<i>B3C1</i>	<i>C2</i>	<i>C3D1</i>	<i>D2</i>	<i>D3</i>	C(1)–C(17)
C(1)	–0.34				–0.18	0.07							–0.10
C(2)	0.26				0.17								0.06
C(3)	–0.03				–0.23								–0.52
C(4)	–0.13				–0.21								–0.48
C(5)	0.08	–0.21			0.22	0.08	0.59						0.12
C(6)		0.20				–0.07	0.01						0.43
C(7)		–0.22					–0.01	–0.02					–0.09
C(8)		0.25	0.22				–0.66	0.02	0.01				0.38
C(9)		–0.25	–0.21				0.01	0.02	0.64				–0.02
C(10)	0.16	0.22			0.45	0.06	–0.01						0.55
C(11)			0.23					–0.02	–0.01	–0.07			0.37
C(12)			–0.25						0.01	0.08			–0.20
C(13)			0.26	0.29					–0.72	0.07	–0.07	0.69	0.28
C(14)			–0.25	–0.27					–0.01	–0.07	0.63	–0.04	–0.18
C(15)				0.14							0.07	0.06	0.07
C(16)				0.04							–0.12	–0.06	–0.24
				–0.19							0.12	0.04	–0.42

Table 4. *Torsional angles in the rings*

φ_{A-B} is the torsional angle about the A-B bond, in which the other two atoms required to define the angle are those attached to either end of the bond and are in the ring in question.

A ring		B ring		C ring		D ring	
Bond	φ_{A-B}^*	Bond	φ_{A-B}	Bond	φ_{A-B}	Bond	φ_{A-B}
C(1)—C(2)	-58	C(5)—C(6)	-52	C(8)—C(9)	-52	C(13)—C(14)	+47
C(2)—C(3)	+31	C(6)—C(7)	+52	C(9)—C(11)	+55	C(14)—C(15)	-35
C(3)—C(4)	+2	C(7)—C(8)	-55	C(11)—C(12)	-58	C(15)—C(16)	+9
C(4)—C(5)	-12	C(8)—C(9)	+58	C(12)—C(13)	+58	C(16)—C(17)	+20
C(5)—C(10)	-13	C(9)—C(10)	-52	C(13)—C(14)	-59	C(13)—C(17)	-40
C(10)—C(1)	+49	C(10)—C(5)	+52	C(8)—C(14)	+56		

* The sign convention for the direction of the torsional angle is that of Klyne & Prelog (1960).

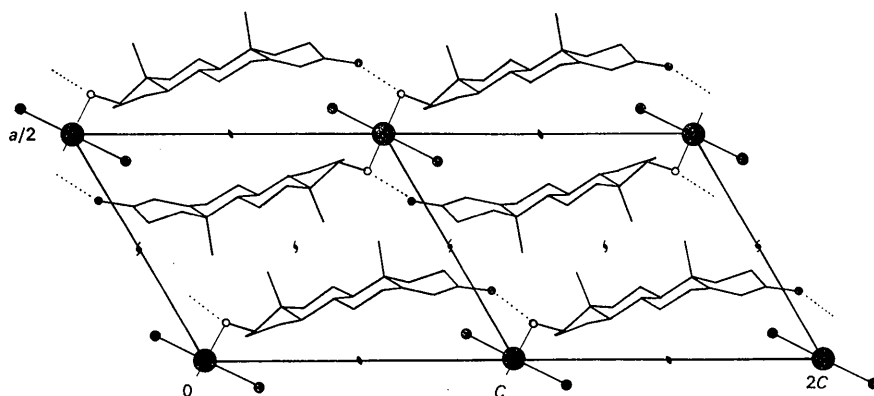


Fig. 2. Projection onto the plane (010) of the unit cell. The hydrogen bonding between the steroid molecules is indicated by the dotted lines between the 17-hydroxyl oxygen (○) and the 3-one oxygen (●) atoms.

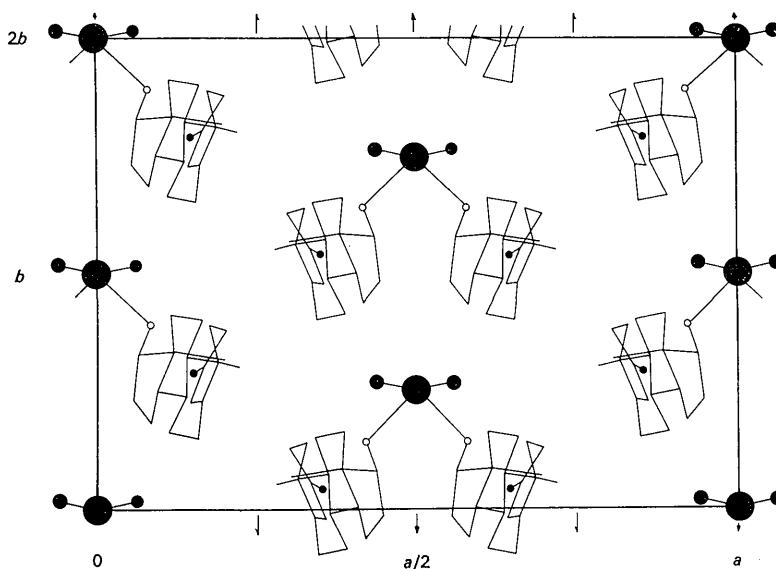


Fig. 3. Projection onto the plane (001) of the unit cell, showing the distorted tetrahedral environment of the mercury atoms and the staggered bilayer packing of the steroid molecules.

tetrahedral coordination to the mercury atom is more distorted than that found in other similar examples (e.g. bis(triphenylarsine oxide)mercuric chloride, in which the angles Cl-Hg-Cl and O-Hg-O are 147° and 93° and the distance Hg-O is 2.35 Å) (Brändén, 1963).

The Hg-Cl bond length of 2.296 ± 0.006 Å falls within the range of distances observed by other investigators between these two atoms (2.20–2.34 Å) but the Hg-O distance of 2.48 ± 0.02 Å is significantly greater than the range of observed covalent bond lengths for mercury and oxygen (2.03–2.28 Å), (Grdenic, 1965). The observed distance is however, significantly less than the sum of the van der Waals radii of these two atoms (2.9 Å), which indicates that some form of bonding exists between them.

Packing of the molecules

The steroid molecules are hydrogen bonded 'head-to-tail' via the 3-keto and 17-hydroxyl groups, the OH...O distance and the C(17)-OH...O(3) angle

being 2.75 Å and 110° respectively. A very interesting point is that the angle Hg-OH...O is 113°, indicating that the environment of the hydroxyl oxygen atom is almost tetrahedral, as for example, in ice (Peterson & Levy, 1957). The steroid molecules are approximately planar and lie almost parallel to the (100) face of the crystal, with the hydrogen bonded molecules stacked in pairs 'bottom-to-bottom' along the twofold symmetry axes. The layers, which include the mercuric chloride molecules, are propagated through the unit cells by means of the 2_1 axes which translate them so as to minimize interference between adjacent methyl groups (Fig. 3). This packing is similar to that found in 4-bromoestrone (Norton, Kartha & Lu, 1963).

Apart from the hydrogen bonding, there are only thirteen intermolecular distances less than 4.0 Å (Table 5). Eleven of these are between chlorine atoms and rings *A* and *D*, and between O(3) and ring *D*. There are, in addition, twenty-seven longer 'contacts' in the range 4.0–4.5 Å between molecules related by the twofold axes and between methyl groups of one molecule and the ring system of the 2_1 related molecules.

Table 5. Intermolecular distances less than 4.0 Å

Contact	Position*	Distance
Cl—C(1)	1/00 $\bar{1}$	3.75 Å
Cl—C(2)	1/00 $\bar{1}$	3.49
Cl—C(3)	1/00 $\bar{1}$	3.88
Cl—C(4)	1/01 $\bar{1}$	3.79
Cl—C(15)	2/010	3.79
Cl—C(16)	2/010	3.93
O(1)—C(3)	1/00 $\bar{1}$	3.75
O(1)—O(2)	1/00 $\bar{1}$	2.75
O(2)—C(16)	1/001	3.43
O(2)—C(17)	1/001	3.53
O(2)—C(18)	1/001	3.77
C(4)—C(16)	2/001	3.94
C(11)—C(18)	3/001	3.78

* Equivalent position nomenclature: the symbol 1/01 $\bar{1}$ is taken to mean that the second atom mentioned in the contact is in the molecule at equivalent position 1, translated 0, 1 and -1 unit cells in the *a*, *b* and *c* directions respectively. The equivalent positions are $1=(x, y, z)$; $2=(\bar{x}, y, \bar{z})$; $3=(\frac{1}{2}-x, \frac{1}{2}+y, \bar{z})$.

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