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1,7-Dioxa-4,10-dimercuracyclododecane, a Redetermination of the Structure

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Abstract. $C_8H_{16}Hg_2O_2$, monoclinic, $C2/c$, a = 19·273 (8), b = 4·461 (2), c = 14·667 (8) Å, β = 120·4 (4)°, V = 1087·5 Å^3, Z = 4, D_x = 3·33, D_m = 3·30 Mg m^{-3}. The structure was refined to R = 0·067 for 659 independent reflexions measured with an automatic single-crystal diffractometer. The 12-membered-ring molecule has $\bar{1}$ point symmetry, not 2 as previously reported. The C—Hg—C bond angle is 176 (2)° with bond lengths of 2·12 (6) and 2·13 (6) Å.

Introduction. The crystal structure of the title compound needed a redetermination by means of modern methods since the results reported formerly (Grdenić, 1952) were obtained from the (010) projection based upon 139 zero-layer $h0l$ reflexions recorded photographically with an oscillation camera.

The three-dimensional data of a plate-shaped crystal with the dimensions 0·02 × 0·10 × 0·15 mm were recorded on a Philips PW 1100 four-circle automatic diffractometer (graphite-monochromatized Mo $K\alpha$ radiation, λ = 0·7107 Å) within the range 3° < 2θ < 70°. The intensities of 659 independent reflexions with $I > 3\sigma(I)$, corrected for absorption [μ = 27·13 mm^{-1} (Harkema, 1979)], polarization and Lorentz effects, were used for the structure determination by the heavy-atom method. Unit weights were allotted to all reflexions. Full-matrix least-squares refinement with anisotropic thermal parameters, carried out with XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), led to a final R of 0·067. The structure in the alternative space group $C2$ could be less satisfactorily refined with an R of 0·072. Neutral-atom scattering factors for Hg, C, O, and anomalous-dispersion corrections for Hg were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on the Univac 1110 of the Zagreb University Computing Centre (SRCE). The final atomic coordinates with their standard deviations are given in Table 1.* Interatomic distances and bond angles are listed in Table 2, while conformational data are given in Table 3.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^3)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
Hg	−0·0253 (1)	0·2860 (4)	0·1156 (1)	47 (5)
C(1)	0·087 (3)	0·501 (12)	0·164 (4)	68 (14)
C(2)	0·148 (2)	0·326 (11)	0·159 (3)	52 (11)
C(3)	0·174 (2)	0·057 (11)	0·041 (4)	61 (13)
C(4)	0·133 (3)	−0·055 (12)	−0·077 (4)	67 (14)
O	0·112 (1)	0·217 (7)	0·053 (2)	47 (7)

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Hg—C(1)	2·13 (6)	C(1)—Hg—C(4^{i})	176·0 (1·9)
Hg—C(4^{i})	2·12 (6)	Hg—C(1)—C(2)	117·2 (3·4)
C(1)—C(2)	1·45 (8)	C(1)—C(2)—O	106·1 (2·9)
C(2)—O	1·43 (5)	C(2)—O—C(3)	108·7 (2·6)
O—C(3)	1·47 (6)	O—C(3)—C(4)	107·7 (3·1)
C(3)—C(4)	1·57 (7)	C(3)—C(4)—Hg	108·9 (4·2)

Hg···Hg^{ii}	3·550 (3)	Hg···C(1^{v})	3·99 (5)
C(1)···Hg^{ii}	4·07 (7)	C(2)···C(1^{v})	3·88 (7)
C(4^{i})···C(1^{ii})	3·97 (8)	C(3)···C(1^{v})	3·91 (8)
C(4^{i})···C(2^{ii})	4·20 (8)	C(3)···C(2^{v})	3·84 (7)
C(2)···C(2^{iii})	4·11 (5)	C(4)···C(3^{v})	4·24 (7)
C(2)···C(3^{iii})	4·11 (5)	C(4)···O^{v}	3·89 (7)
C(1)···C(4^{iv})	4·23 (8)	O···C(1^{v})	3·73 (7)
		Hg···O^{vi}	3·11 (3)

Symmetry code: (i) $-x,-y,-z$; (ii) $-x, y, \frac{1}{2} - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $-x, 1 + y, \frac{1}{2} - z$; (v) $x, 1 + y, z$; (vi) $-x, -y + 1, -z$.

Table 3. *Molecular geometry and conformation*

Plane defined by the Hg and O atoms and the origin

$$1{\cdot}2115x - 2{\cdot}8717y + 9{\cdot}1838z - 0$$

(x,y,z are fractional coordinates relative to the monoclinic axes)

Distances (Å) of the C atoms from the plane (invariant)

C(1)	−0·032	C(2)	0·600
C(3)	0·525	C(4)	−0·175

Distances (Å) between the Hg and O atoms

Hg···Hg^{i}	4·724 (4)	Hg···O	3·22 (3)
O···O^{i}	4·24 (4)	Hg···O^{i}	3·12 (3)

Torsion angles (°)

Hg—C(1)—C(2)—O	54·1 (5·2)
C(1)—C(2)—O—C(3)	176·2 (4·2)
C(2)—O—C(3)—C(4)	−178·2 (4·0)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36162 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. The compound was known as 'mercury diethylene oxide' (Sand, 1901). A six-membered-ring structure assigned to it was inconsistent with the stereochemistry of the covalently bound mercury. Later, a dimeric structure, $O(CH_2CH_2HgCH_2CH_2)_2O$ was suggested by a two-dimensional analysis (Grdenić, 1952). In the redetermination of the structure reported here, the dimeric ring was confirmed but not the molecular symmetry, which is $\bar{1}$ instead of 2. In the trial-and-error location of the Hg atom at $x \sim \frac{1}{40}$, $z \sim \frac{1}{8}$, it was overlooked that $z + \frac{1}{4}$ was as good a solution as z, but with a shift of the molecule centre from 2 to $\bar{1}$. In fact, a two-dimensional analysis of the $h0l$ data could not distinguish between the two possibilities.

The geometry of the ring (Fig. 1) is best described by reference to the plane defined by the Hg and O atom positions and the origin (Table 3). The C(1) and C(4) atoms deviate only slightly from the plane but C(2) and C(3) are > 0·5 Å away. Since the Hg—C bonds are almost collinear, the C(1)—Hg—C(4^i) angle being 176 (2)°, this particular arrangement of the C and O atoms is essential for the ring formation. Its conformation may be visualized by means of two parallel planar zig-zag $CH_2CH_2OCH_2CH_2$ chains in an *anti* position to each other with their ends connected by the Hg atoms. The torsion angles are given in Table 3. All bond lengths have the expected values (within the relatively large e.s.d.'s of 0·05 to 0·08 Å due to the small number of reflexions obtainable in the given experimental conditions). The Hg—C(1) and Hg—C(4^i) bonds of 2·13 (6) and 2·12 (6) Å, practically equal in length, are slightly longer than the average of those observed recently in non-mixed organomercurials, *e.g.* 2·085 (7) in $Hg(C_6H_5)_2$ (Grdenić, Kamenar & Nagl, 1977), 2·053 (3) in $C(HgCN)_4.H_2O$ (Grdenić, Sikirica & Korpar-Čolig, 1978), 2·07 (5)–2·13 (4) in orthorhombic $C_{18}H_{12}Hg_3$ (Brown, Massey & Wickens, 1978), 2·07 (2) in $Hg(C_6H_5CH_2)_2$ (Hitchcock, 1979), 2·061 (18) in $Hg(C_4H_3S)_2$ (Grdenić, Kamenar & Žeželj, 1979), 2·096 (16) in $Hg(C_6HF_4)_2$ (Brown, Massey & Wickens, 1980*a*), 2·04 (2)–2·16 (5) in $C_{18}H_{12}Hg_3$ (Brown, Massey & Wickens, 1980*b*), 2·09 (1) in $Hg(o\text{-}C_6H_4CH_3)_2$ (Liptak, Ilsley, Glick & Oliver, 1980), 2·077 (6) and 2·083 (6) Å in $[(tert\text{-}C_4H_9)_3C_6H_2]_2Hg$ (Huffman, Nugent & Kochi, 1980), as well as of those published earlier and reviewed by Grdenić (1977). There is no appreciable interaction between the Hg and O atoms within the molecule since the Hg···O, Hg···O^i and Hg···O^{vi} distances of 3·22 (3), 3·12 (3) and 3·11 (3) Å are larger than the sum of the van der Waals radii (Grdenić, 1965) and the ring is not deformed by such an interaction. The intermolecular Hg···Hg^{ii} contact of 3·550 (3) Å is close to the second interatomic contact in the solid α-Hg, while the intermolecular C···Hg distances are too large to be considered as contacts, even with the methylene radius of 2·0 Å (Pauling, 1960). In the same way only the C···C intermolecular distances less than about 4·2 Å can be considered as packing contacts. The closest ones are between the molecules related by translation along the b axis, *e.g.* C(2)···C(1^v), C(3)···C(1^v) and C(3)···C(2^v) (Table 2) are even less than 4·0 Å. The molecules are stacked into columns along the **b** direction with a stronger interaction within columns than between them. The physical evidence of such packing is perfect cleavage by which the slightly pressed crystal is transformed into fibres.

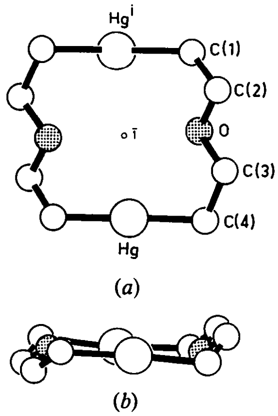

Fig. 1. Molecular structure of 1,7-dioxa-4,10-dimercuracyclododecane (H atoms omitted): (*a*) projected on the plane defined by the Hg and O atoms and the origin (equation of the plane is given in Table 3); (*b*) viewed approximately along the Hg···Hg^i direction.

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Hexacarbonyl(triphenylphosphineaurio)vanadium

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Abstract. $C_{24}H_{15}AuO_6PV$, rhombohedral, $a = 11{\cdot}088\,(10)$ Å, $\alpha = 75{\cdot}4\,(2)°$, $U = 1247{\cdot}2$ Å^3, $D_m = 1{\cdot}80$, $D_c = 1{\cdot}78$ Mg m^{-3}, $F(000) = 512$, $Z = 2$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 6{\cdot}52$ mm^{-1}, space group $R\bar{3}$ from the successful structure determination. 888 independent reflections have been refined to $R = 0{\cdot}059$. The molecule has crystallographically imposed 3 symmetry and the V atom is seven-coordinate and in a capped octahedral environment. The Au atom is in the capping position [V—Au 2·690 (3) Å] and the carbonyl groups are in the capped face [V—CO 2·002 (17) Å] and uncapped face [V—CO 1·932 (33) Å].

Introduction. There are very few examples of seven-coordinate molecules in which all the ligands are monodentate (Drew, 1977). Most of these have pentagonal-bipyramidal structures. However, in our view this was not likely to be the case for $V(CO)_6(AuPPh_3)$. This compound had been prepared many years ago (Kasenally, Nyholm, O'Brien & Stiddard, 1964) and contains one very bulky group, namely $AuPPh_3$, and we anticipated that this would need to keep well away from the other ligands. This could of course be achieved in a pentagonal bipyramid but a pentagonal girdle of five carbonyl groups seemed unlikely. In order to investigate further the structure of this molecule, and to continue our studies of seven-coordinate geometries, we have carried out a structure determination.

The crystals were prepared using the published method. Crystals of approximate size 0·3 × 0·4 × 0·5 mm were mounted on a Stoe Stadi-2 diffractometer. 3378 reflections with a 2θ maximum of 45° were measured by ω scan with a scan speed of 30 s deg^{-1} and a background count of 20 s. Of these, 888 independent reflections with $I > 2\sigma(I)$ were used in subsequent calculations. An absorption correction was applied (Stewart, 1972) but no extinction correction was made.

The positions of the Au and V atoms were obtained from the Patterson function and the positions of the remaining non-H atoms were obtained from Fourier maps. Atoms were refined anisotropically. H atoms were fixed in trigonal positions at 1·08 Å from the C atoms. Their thermal parameters were set equivalent to those of the C atoms to which they were bonded. The final R value was 0·059. Calculations were carried out using the *SHELX* 76 system (Sheldrick, 1976) at the University of Manchester Computer Centre. Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974).

Table 1. *Atomic coordinates* (×10^5 *for* Au, ×10^4 *for other atoms*) *and isotropic thermal parameters* (×10^3) *with e.s.d.'s in parentheses*

	x	y	z	U(Å^2)
Au(1)	24800 (1)	24800 (1)	24800 (1)	61 (1)
V(1)	1337 (2)	1337 (2)	1337 (2)	72 (3)
P(1)	3439 (2)	3439 (2)	3439 (2)	52 (3)
C(1)	4768 (11)	4117 (11)	2380 (12)	54 (15)
C(2)	5522 (15)	3457 (13)	1489 (14)	84 (20)
C(3)	6599 (16)	3876 (17)	674 (16)	100 (24)
C(4)	6885 (15)	4975 (18)	838 (17)	97 (23)
C(5)	6144 (16)	5619 (18)	1699 (16)	88 (25)
C(6)	5048 (15)	5217 (16)	2503 (15)	76 (22)
C(7)	3176 (16)	1362 (12)	571 (13)	66 (18)
O(7)	4190 (13)	1371 (11)	18 (10)	99 (17)
C(8)	1087 (28)	1851 (32)	−401 (30)	148 (57)
O(8)	928 (24)	2222 (28)	1418 (18)	217 (50)

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