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Structures of the Mercuration Products of Dimethyl and Diethyl Malonate: $Hg[CH(COOCH_3)_2]_2$ (1) and $Hg[CH(COOC_2H_5)_2]_2$ (2)

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Abstract. (1): Bis[bis(methoxycarbonyl)methyl]mercury(II), $[Hg(C_5H_7O_4)_2]$, $M_r = 462{\cdot}80$, triclinic, $P\bar{1}$, $a = 10{\cdot}772$ (2), $b = 8{\cdot}502$ (4), $c = 8{\cdot}585$ (3) Å, $\alpha = 71{\cdot}28$ (3), $\beta = 64{\cdot}70$ (4), $\gamma = 78{\cdot}26$ (2)°, $V = 671{\cdot}2$ (5) Å^3, $Z = 2$, $D_x = 2{\cdot}290$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 96{\cdot}60$ cm^{-1}, $F(000) = 436$, $T = 293$ K, final $R = 0{\cdot}039$ for 3064 observed reflections. (2): Bis[bis(ethoxycarbonyl)methyl]mercury(II), $[Hg(C_7H_{11}O_4)_2]$, $M_r = 518{\cdot}91$, triclinic, $P\bar{1}$, $a = 9{\cdot}305$ (3), $b = 10{\cdot}579$ (3), $c = 10{\cdot}659$ (3) Å, $\alpha = 112{\cdot}51$ (4), $\beta = 65{\cdot}45$ (3), $\gamma = 98{\cdot}04$ (4)°, $V = 881{\cdot}5$ (6) Å^3, $Z = 2$, $D_x = 1{\cdot}955$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 84{\cdot}3$ cm^{-1}, $F(000) = 500$, $T = 293$ K, final $R = 0{\cdot}033$ for 3353 observed reflections. Two dimethyl or diethyl malonate moieties are linked by an Hg atom to give discrete molecules in which mercury is digonally coordinated. Hg–C bond lengths are in the range 2·127 (8)–2·153 (6) Å.

Introduction. As a part of our study of mercurated aliphatic compounds we investigated the mercuration products of the dimethyl and diethyl esters of malonic acid. It was of interest to obtain more data on the Hg–C bond lengths.

Experimental. Colorless crystals of (1) were obtained by mercuration of dimethyl malonate with mercury(II) oxide in water (Schrauth & Schoeller, 1908). Transparent crystals of (2) were obtained by an analogous procedure using diethyl malonate (Glidewell, 1977).

Intensities measured on a Philips PW 1100 diffractometer (Mo$K\alpha$ radiation, graphite monochromator) in the range $3 < \theta < 30°$, $\theta/2\theta$ scan mode, scan speed 0·04° s^{-1}, scan width 1·2° for both (1) and (2). Lattice parameters determined by least-squares procedure from 20 reflections, $6 < \theta < 11°$ (1) and $5 < \theta < 8°$ (2). Standard reflections monitored every 2 h showed a continuous drop in intensity amounting to 18% at the end of data collection for both compounds. The intensities were corrected accordingly. Lorentz, polarization and absorption corrections (Harkema, 1979) were applied. Additional information on data collection and structural refinement is given in Table 1. For both structures the position of the Hg atom was located by Patterson methods, remaining non-H and some H atoms (on the α-C atoms) from difference Fourier maps. Other H-atom positions were calculated geometrically (riding model, C–H 1·08 Å). Full-matrix least-squares refinement on F with anisotropic temperature factors for non-H atoms, grouped isotropic temperature factor for H, unit weights. Scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction. Calculations were made on an UNIVAC 1110 computer using *SHELX*76 (Sheldrick, 1976).

Table 1. *Crystal data and experimental parameters*

	(1)	(2)
Crystal dimensions (mm from centroid)	(100), (1̄00), (010), (0$\bar{1}$0) 0·065; ($\bar{2}$0$\bar{1}$) 0·095; ($\bar{1}\bar{2}\bar{2}$) 0·088; (101), ($\bar{3}\bar{4}\bar{3}$) 0·092; (11$\bar{4}$) 0·094	(001), (00$\bar{1}$) 0·053; (0$\bar{1}$1), (01$\bar{1}$) 0·060; (010), (0$\bar{1}$0) 0·049; (101), ($\bar{1}$0$\bar{1}$) 0·075; (410), ($\bar{4}\bar{1}$0) 0·083;
Range of *hkl*	−13→14, −10→11, 0→10	−11→12, −14→13, 0→10
Standard reflections	$\bar{3}$1$\bar{1}$, $\bar{2}$20, 004	$2\bar{2}$0, 030, 02$\bar{3}$
Transmission-factor range	0·304–0·378	0·440–0·502
Total data	3116	3407
Unique data with $I > 3\sigma(I)$	3064	3353
Least-squares parameters	175	212
Final R, wR	0·039, 0·039	0·033, 0·033
$(\Delta\rho)_{max}$ (e Å^{-3})	3·5 (0·96 Å from Hg)	1·5 (0·88 Å from Hg)
Largest Δ/σ for non-H atoms in final cycle	0·071	0·025

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2 for (1) and Table 3 for (2). *ORTEP* drawings (Johnson, 1965) of the two molecules with the atom-numbering schemes are shown in Figs. 1 and 2. Interatomic distances and angles are listed in Table 4 for (1) and 5 for (2).*

In structure (1) the Hg atom links two dimethyl malonate moieties to form discrete molecules with a digonal coordination of mercury, the C–Hg–C angle

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43882 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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being 173·8 (4)°. The Hg–C bond lengths are 2·127 (8) and 2·131 (8) Å. The Hg atom is approached by two O atoms from the carbonyl groups of the adjacent molecule at Hg···O distances of 2·666 (7) and 2·823 (6) Å. These distances are shorter than the sum of the van der Waals radii (~2·94 Å) and are therefore within the effective coordination of mercury (Grdenić, 1965, 1981).

In (2) the two diethyl malonate moieties are linked by the Hg atom and the two Hg–C bonds thus formed have values of 2·135 (6) and 2·153 (6) Å. The C–Hg–C angle of 173·7 (3)° is similar to that in (1). Hg is

Table 2. *Atomic coordinates and equivalent isotropic thermal parameters* (Å²) *for* (1)

$U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2(U_{12}aba^*b^*\cos\gamma + U_{13}aca^*c^*\cos\beta + U_{23}bcb^*c^*\cos\alpha)]$.

	x	y	z	U_{eq}
Hg	0·19713 (3)	0·42967 (5)	0·24053 (4)	0·0411 (1)
C(1)	0·3037 (12)	0·0659 (15)	0·7118 (13)	0·077 (3)
C(2)	0·3853 (8)	0·2065 (12)	0·4068 (11)	0·049 (2)
C(3)	0·3583 (7)	0·2381 (11)	0·2422 (10)	0·045 (2)
C(4)	0·4802 (7)	0·2773 (10)	0·0669 (10)	0·044 (2)
C(5)	0·5608 (11)	0·2937 (18)	−0·2393 (13)	0·085 (4)
C(6)	0·0882 (16)	1·0314 (16)	0·2009 (19)	0·097 (4)
C(7)	0·0322 (8)	0·7525 (11)	0·2864 (10)	0·047 (2)
C(8)	0·0337 (7)	0·6125 (11)	0·2173 (9)	0·045 (2)
C(9)	−0·0983 (7)	0·5271 (11)	0·3100 (10)	0·045 (2)
C(10)	−0·2431 (11)	0·3730 (18)	0·2857 (14)	0·084 (4)
O(1)	0·3012 (7)	0·0921 (9)	0·5388 (8)	0·066 (2)
O(2)	0·4650 (6)	0·2701 (10)	0·4252 (8)	0·067 (2)
O(3)	0·4557 (6)	0·2490 (10)	−0·0602 (8)	0·063 (2)
O(4)	0·5857 (6)	0·3309 (9)	0·0406 (8)	0·059 (2)
O(5)	0·0837 (8)	0·8864 (9)	0·1523 (8)	0·070 (2)
O(6)	−0·0056 (7)	0·7545 (9)	0·4393 (8)	0·064 (2)
O(7)	−0·1155 (7)	0·4543 (11)	0·2064 (8)	0·076 (2)
O(8)	−0·1831 (6)	0·5278 (9)	0·4578 (7)	0·060 (2)

Table 3. *Atomic coordinates and equivalent isotropic thermal parameters* (Å²) *for* (2)

$U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2(U_{12}aba^*b^*\cos\gamma + U_{13}aca^*c^*\cos\beta + U_{23}bcb^*c^*\cos\alpha)]$.

	x	y	z	U_{eq}
Hg	0·54420 (3)	0·29628 (3)	0·53380 (3)	0·0379 (1)
C(1)	0·8005 (14)	−0·0081 (11)	0·7162 (12)	0·088 (3)
C(2)	0·7120 (12)	−0·0448 (9)	0·6171 (11)	0·067 (2)
C(3)	0·7060 (8)	0·0307 (7)	0·4356 (8)	0·045 (2)
C(4)	0·7353 (8)	0·1513 (6)	0·3911 (8)	0·043 (1)
C(5)	0·7635 (9)	0·1197 (7)	0·2331 (9)	0·052 (2)
C(6)	0·9159 (16)	0·1726 (12)	0·0196 (11)	0·097 (4)
C(7)	1·0079 (19)	0·2748 (14)	−0·0202 (13)	0·136 (5)
C(8)	−0·1170 (13)	0·4576 (13)	0·7079 (14)	0·109 (4)
C(9)	0·0058 (10)	0·3542 (10)	0·6069 (12)	0·073 (3)
C(10)	0·2463 (8)	0·4493 (6)	0·6327 (8)	0·043 (2)
C(11)	0·3594 (8)	0·4450 (6)	0·6971 (7)	0·041 (2)
C(12)	0·4370 (8)	0·5756 (7)	0·7458 (7)	0·040 (1)
C(13)	0·5407 (11)	0·7121 (8)	0·9253 (9)	0·059 (2)
C(14)	0·5338 (13)	0·7131 (9)	1·0673 (11)	0·077 (3)
O(1)	0·7439 (7)	0·0602 (5)	0·5528 (6)	0·055 (1)
O(2)	0·6578 (7)	−0·0776 (5)	0·3796 (6)	0·060 (1)
O(3)	0·8847 (7)	0·1907 (6)	0·1720 (6)	0·069 (2)
O(4)	0·6894 (8)	0·0415 (6)	0·1666 (7)	0·072 (2)
O(5)	0·1264 (6)	0·3650 (6)	0·6661 (7)	0·060 (1)
O(6)	0·2547 (6)	0·5147 (5)	0·5592 (6)	0·058 (1)
O(7)	0·4630 (7)	0·5882 (5)	0·8648 (6)	0·055 (1)
O(8)	0·4739 (7)	0·6652 (5)	0·6938 (6)	0·054 (1)

Table 4. *Interatomic distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *for* (1)

Hg–C(3)	2·127 (8)	C(3)–Hg–C(8)	173·8 (4)
Hg–C(8)	2·131 (8)	C(3)–C(2)–O(1)	108·7 (9)
C(1)–O(1)	1·44 (2)	C(3)–C(2)–O(2)	127·6 (7)
C(2)–C(3)	1·49 (1)	O(1)–C(2)–O(2)	123·8 (9)
C(2)–O(1)	1·35 (1)	Hg–C(3)–C(2)	109·9 (6)
C(2)–O(2)	1·19 (1)	Hg–C(3)–C(4)	109·7 (5)
C(3)–C(4)	1·51 (1)	C(2)–C(3)–C(4)	116·4 (7)
C(4)–O(3)	1·33 (1)	C(3)–C(4)–O(3)	110·2 (7)
C(4)–O(4)	1·22 (1)	C(3)–C(4)–O(4)	126·2 (8)
C(5)–O(3)	1·45 (1)	O(3)–C(4)–O(4)	123·5 (7)
C(6)–O(5)	1·44 (2)	C(2)–O(1)–C(1)	114·4 (10)
C(7)–C(8)	1·49 (2)	C(4)–O(3)–C(5)	116·0 (9)
C(7)–O(5)	1·34 (1)	C(8)–C(7)–O(5)	111·2 (7)
C(7)–O(6)	1·20 (1)	C(8)–C(7)–O(6)	128·0 (8)
C(8)–C(9)	1·51 (1)	O(5)–C(7)–O(6)	120·8 (10)
C(9)–O(7)	1·32 (2)	Hg–C(8)–C(7)	110·4 (6)
C(9)–O(8)	1·21 (1)	Hg–C(8)–C(9)	108·0 (5)
C(10)–O(7)	1·45 (2)	C(7)–C(8)–C(9)	114·1 (6)
		C(8)–C(9)–O(7)	111·8 (6)
		C(8)–C(9)–O(8)	125·8 (10)
		O(7)–C(9)–O(8)	122·4 (8)
Hg···O(6^i)	2·823 (6)	C(7)–O(5)–C(6)	116·9 (8)
Hg···O(8^i)	2·666 (7)	C(9)–O(7)–C(10)	114·8 (7)

O(1)–C(2)–C(3)–Hg	88 (1)	C(3)–Hg–C(8)–C(7)	−160 (3)
O(2)–C(2)–C(3)–Hg	−91 (1)	C(3)–Hg–C(8)–C(9)	75 (3)
O(3)–C(4)–C(3)–Hg	−75 (1)	Hg–C(8)–C(7)–O(5)	104 (1)
O(4)–C(4)–C(3)–Hg	104 (1)	Hg–C(8)–C(7)–O(6)	−75 (1)
C(2)–C(3)–Hg–C(8)	−163 (3)	Hg–C(8)–C(9)–O(7)	−82 (1)
C(4)–C(3)–Hg–C(8)	68 (3)	Hg–C(8)–C(9)–O(8)	101 (1)

Symmetry code: (i) $-x$, $1-y$, $1-z$

Table 5. *Interatomic distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *for* (2)

Hg–C(4)	2·135 (6)	C(4)–Hg–C(11)	173·7 (3)
Hg–C(11)	2·153 (6)	C(1)–C(2)–O(1)	107·1 (8)
C(1)–C(2)	1·51 (2)	C(4)–C(3)–O(1)	109·2 (6)
C(2)–O(1)	1·45 (1)	C(4)–C(3)–O(2)	127·4 (9)
C(3)–C(4)	1·48 (1)	O(1)–C(3)–O(2)	123·4 (9)
C(3)–O(1)	1·35 (1)	Hg–C(4)–C(3)	109·8 (4)
C(3)–O(2)	1·19 (1)	Hg–C(4)–C(5)	109·9 (6)
C(4)–C(5)	1·50 (1)	C(3)–C(4)–C(5)	114·8 (6)
C(5)–O(3)	1·34 (1)	C(4)–C(5)–O(3)	110·7 (7)
C(5)–O(4)	1·21 (1)	C(4)–C(5)–O(4)	126·2 (7)
C(6)–C(7)	1·37 (2)	O(3)–C(5)–O(4)	123·1 (9)
C(6)–O(3)	1·47 (1)	C(7)–C(6)–O(3)	111·1 (11)
C(8)–C(9)	1·45 (1)	C(2)–O(1)–C(3)	116·3 (7)
C(9)–O(5)	1·47 (2)	C(5)–O(3)–C(6)	114·8 (8)
C(10)–C(11)	1·48 (1)	C(8)–C(9)–O(5)	110·4 (9)
C(10)–O(5)	1·34 (1)	C(11)–C(10)–O(5)	110·1 (8)
C(10)–O(6)	1·20 (1)	C(11)–C(10)–O(6)	128·0 (6)
C(11)–C(12)	1·49 (1)	O(5)–C(10)–O(6)	121·9 (9)
C(12)–O(7)	1·34 (1)	Hg–C(11)–C(10)	109·0 (4)
C(12)–O(8)	1·22 (1)	Hg–C(11)–C(12)	106·9 (4)
C(13)–C(14)	1·48 (2)	C(10)–C(11)–C(12)	115·1 (7)
C(13)–O(7)	1·46 (1)	C(11)–C(12)–O(7)	110·4 (7)
		C(11)–C(12)–O(8)	128·6 (8)
		O(7)–C(12)–O(8)	121·0 (7)
Hg···O(6^i)	2·723 (5)	C(14)–C(13)–O(7)	106·9 (7)
Hg···O(8^i)	2·682 (8)	C(9)–O(5)–C(10)	117·0 (9)
		C(12)–O(7)–C(13)	116·9 (7)

O(1)–C(3)–C(4)–Hg	−80 (1)	C(4)–Hg–C(11)–C(10)	−169 (2)
O(2)–C(3)–C(4)–Hg	101 (1)	C(4)–Hg–C(11)–C(12)	66 (2)
O(3)–C(5)–C(4)–Hg	100 (1)	Hg–C(11)–C(10)–O(5)	94 (1)
O(4)–C(5)–C(4)–Hg	−81 (1)	Hg–C(11)–C(10)–O(6)	−86 (1)
C(3)–C(4)–Hg–C(11)	65 (2)	Hg–C(11)–C(12)–O(7)	−92 (1)
C(5)–C(4)–Hg–C(11)	−168 (2)	Hg–C(11)–C(12)–O(8)	89 (1)

Symmetry code: (i) $1-x$, $1-y$, $1-z$

approached by two O atoms at distances of 2·723 (5) and 2·682 (8) Å. These short contacts cause deviation of the C–Hg–C angle from collinearity.

Hg–C bond lengths in these two structures are in agreement with those in some other mercurated aliphatic compounds, *e.g.* 2·13 (6) and 2·12 (6) Å in $C_8H_{16}Hg_2O_2$ (Grdenić & Bruvo, 1982) and 2·13 (3) and 2·18 (3) Å in $C_{22}H_{38}HgO_4$ (Allmann, Flatau & Musso, 1972).

Other bond lengths and angles in both compounds are within expected ranges. The difference in size of the methyl and ethyl groups results in different packing of the molecules in the two unit cells [see Fig. 3 for (1) and Fig. 4 for (2)] and in different geometry of the molecules, as can be seen from the torsion angles.

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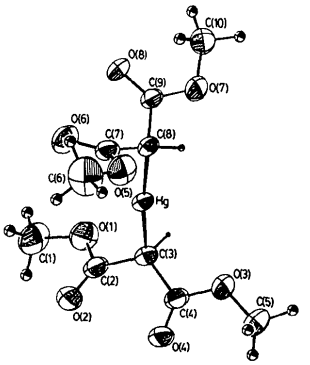

Fig. 1. *ORTEP* plot with the atom-numbering scheme for compound (1).

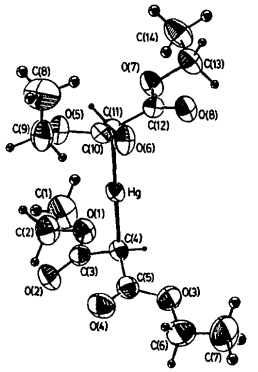

Fig. 2. *ORTEP* plot with the atom-numbering scheme for compound (2).

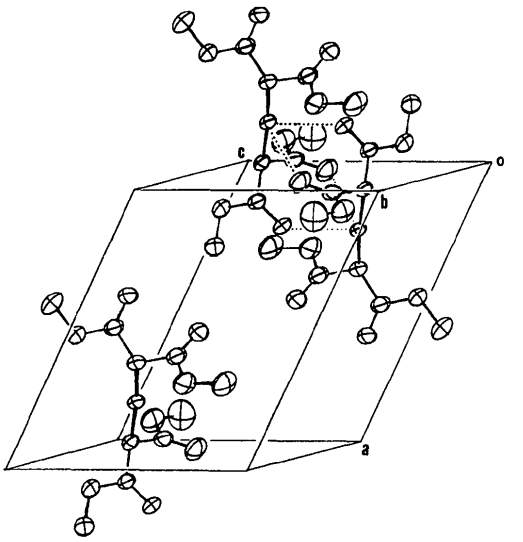

Fig. 3. A view of the molecular packing of compound (1) in the unit cell. Hg···O contacts are shown by dotted lines.

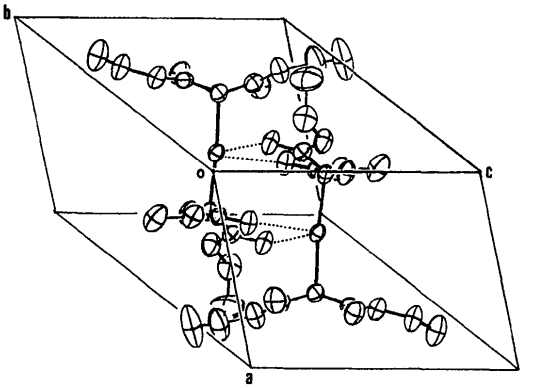

Fig. 4. A view of the molecular packing of compound (2) in the unit cell. Hg···O contacts are shown by dotted lines.

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