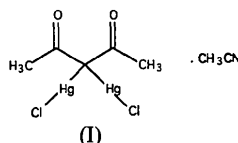Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement.* Univ. of Göttingen, Germany.

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A New Dimercurated Derivative of Acetylacetone, [Hg₂(C₅H₆O₂)Cl₂].CH₃CN

CHRISTIAN BONHOMME,* PAUL TOLEDANO AND JACQUES LIVAGE

Laboratoire de Chimie de la Matière Condensée, Université P. et M. Curie, 4 Place Jussieu, Tour 54, 75252 Paris CEDEX 05, France

Abstract

The unit cell of the title compound μ-diacetylmethylene-1:2κ^2C-bis[chloromercury(II)]–acetonitrile (1/1), [Hg₂(C₅H₆O₂)Cl₂].C₂H₃N, contains four discrete asymmetric units. Each unit contains one dimercurated acetylacetone moiety and one associated acetonitrile molecule. Hg—C bond lengths are 2.11 (1) Å and Hg—Cl bond lengths are in the range 2.306 (4)–2.326 (3) Å. C—Hg—Cl bond angles are in the range 172.5 (3)–174.5 (3)°, in agreement with the near linearity of the three atoms. Hg···O and Hg···N contacts in the range 2.844 (9)–3.12 (2) Å are also observed.

Comment

The mercurated derivatives of β-diketones and β-keto esters have been studied widely over the last two decades, especially by vibrational spectroscopic and solution-NMR techniques. However, the bonding of the Hg atoms remained unclear. Some authors have suggested that mercury should be bonded to the O atoms of β-diketone moieties, while others indicated that mercury was bound to the methylene C atom. Some compounds have been characterized by X-ray diffraction, *e.g.* bis(dipivaloylmethyl)mercury (Allmann, Flatau & Musso, 1972), dipivaloylmethylmercury acetate (Allmann & Musso, 1973) and 3,3-bis(chloromercury)-2,4-pentanedione (McCandlish & Macklin, 1975), and these show the formation of Hg—C bonds in all cases. More recently, two novel crystallographic structures involving monomercurated acetylacetone molecules and dimercurated ethyl

acetoacetate molecules were proposed (Toledano, Bonhomme, Henry & Livage, 1993).

The present paper describes the structure of a new dimercurated acetylacetone derivative (I), which is comparable with a similar structure published by McCandlish & Macklin (1975).

(I)

Figs. 1 and 2 show the molecular structure of the [Hg₂(C₅H₆O₂)Cl₂].CH₃CN asymmetric unit and a packing diagram, respectively.

The structure of this dimercurated compound consists of discrete entities having intermolecular interactions. Two Hg atoms replace the two H atoms on the C(3) atom of acetylacetone. Hg—Cl bond lengths are in the range 2.306 (4)–2.326 (3) Å. Such distances have been observed for similar compounds (Matković-Calogović, 1987; Matković-Calogović, Popović & Korpar-Colig, 1992). The C—Hg—Cl bond angles are 174.5 (3) and 172.5 (3)°. This deviation from linearity is significant and may be attributed to secondary interactions with electronegative atoms surrounding the Hg atoms. Actually, each Hg atom is connected to an O atom of a symmetry related molecule and two Hg···O contacts are observed: Hg(1)···O(1ⁱ) 2.88 (1) and Hg(2)···O(2ⁱⁱ) 2.844 (9) Å [symmetry codes: (i) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $-z$; (ii) $x - \frac{1}{2}$, $\frac{1}{2} - y$, z]. These distances are smaller than the sum of the van der Waals radii of Hg and O [≈2.94 Å (Grdenic & Bruvo, 1982)]. The Hg···O contacts link the different acetylacetone moieties and suggest a 'polymeric' structure in the *ab* plane. Acetonitrile molecules are then oriented along the *c* axis of the crystal. Two Hg···N contacts are observed: Hg(1)···N 3.07 (2) and Hg(2)···N
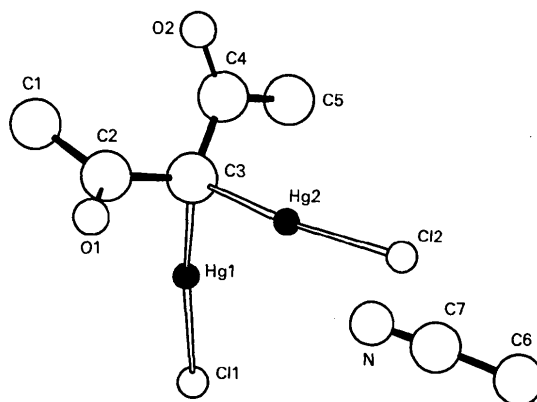

Fig. 1. *ORTEP* (Johnson, 1965) view of the structure of [Hg₂(C₅H₆O₂)Cl₂].CH₃CN, showing the atom-labelling scheme. H atoms are omitted.

3.12 (2) Å. This packing arrangement is different from the one presented by McCandlish & Macklin (1975) for the compound [Hg₂(C₅H₆O₂)Cl₂] where a single Hg···O interaction binds the individual molecules into weakly linked chains along the *b* axis of the crystal.
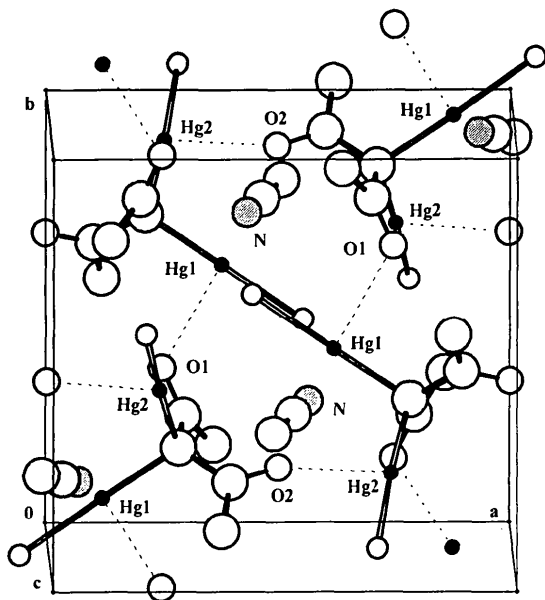

Fig. 2. Packing diagram of the structure of [Hg₂(C₅H₆O₂)-Cl₂].CH₃CN showing Hg···O contacts in the *ab* plane.

Experimental

Acetylacetone (2,4-pentanedione) (1 ml, 9.68 mmol) was added slowly, at room temperature and under stirring, to a saturated aqueous solution of mercuric chloride (20 ml, $[Hg^{2+}]$ = 0.25 mol l⁻¹) following a synthesis proposed by Bonati & Minghetti (1970). A white precipitate was immediately obtained and was filtered and washed with iced water, with no further treatment (0.8 g, 48% yield). Chemical analysis led to the formula [Hg(C₅H₇O₂)Cl]. This compound was recrystallized from acetonitrile at room temperature. Upon aging and after several days, single crystals were obtained. Crystals were insensitive to air moisture and were found to be suitable for X-ray structure determination.

Crystal data

[Hg₂(C₅H₆O₂)Cl₂].C₂H₃N
M_r = 611.24
Monoclinic
$P2_1/a$
a = 10.733 (1) Å
b = 10.089 (1) Å
c = 11.479 (2) Å
β = 91.09 (1)°
V = 1242.8 (4) Å³
Z = 4
D_x = 3.27 Mg m⁻³

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 13–14°
μ = 25.09 mm⁻¹
T = 293 K
Parallelepiped
0.3 × 0.2 × 0.1 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.54, T_{max} = 1.44
4891 measured reflections
2185 independent reflections
1671 observed reflections
$[I \geq 3\sigma(I)]$

R_{int} = 0.065
θ_{max} = 25°
h = −12 → 12
k = 0 → 11
l = 0 → 13
2 standard reflections monitored every 100 reflections frequency: 60 min intensity variation: 1%

Refinement

Refinement on F
R = 0.0279
wR = 0.0331
S = 2.36
1671 reflections
129 parameters
Only H-atom U's refined
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.003

$\Delta\rho_{max}$ = 0.8 e Å⁻³
$\Delta\rho_{min}$ = −1.1 e Å⁻³
Extinction correction: Larson (1970)
Extinction coefficient: primary, 17.5 (9)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hg(1)	0.12038 (5)	0.07846 (5)	0.12386 (4)	0.0311
Hg(2)	0.24090 (5)	0.34622 (5)	0.24407 (5)	0.0343
Cl(1)	−0.0574 (3)	−0.0512 (3)	0.1418 (3)	0.0377
Cl(2)	0.2095 (4)	0.4971 (5)	0.3916 (3)	0.0532
O(1)	0.251 (1)	0.354 (1)	−0.0274 (9)	0.0460
O(2)	0.4987 (8)	0.150 (1)	0.1394 (9)	0.0445
C(1)	0.362 (1)	0.167 (1)	−0.088 (1)	0.0365
C(2)	0.296 (1)	0.249 (1)	0.002 (1)	0.0250
C(3)	0.284 (1)	0.194 (1)	0.125 (1)	0.0227
C(4)	0.395 (1)	0.122 (1)	0.174 (1)	0.0328
C(5)	0.375 (2)	0.024 (2)	0.273 (2)	0.0548
N	0.060 (2)	0.158 (2)	0.375 (1)	0.0791
C(6)	−0.018 (3)	0.202 (3)	0.575 (2)	0.0910
C(7)	0.027 (2)	0.176 (2)	0.462 (1)	0.0541

Table 2. *Selected geometric parameters* (Å, °)

Hg(1)—Cl(1)	2.326 (3)	Hg(2)—N	3.12 (2)
Hg(1)—O(1ⁱ)	2.88 (1)	Hg(2)—C(3)	2.11 (1)
Hg(1)—C(3)	2.11 (1)	C(2)—O(1)	1.21 (2)
Hg(1)—N	3.07 (2)	C(4)—O(2)	1.22 (2)
Hg(2)—Cl(2)	2.306 (4)	C(7)—N	1.09 (2)
Hg(2)—O(2ⁱⁱ)	2.844 (9)	C(6)—C(7)	1.42 (3)
C(3)—Hg(1)—Cl(1)	174.5 (3)	C(6)—C(7)—N	179.0 (23)
C(3)—Hg(2)—Cl(2)	172.5 (3)		

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, -z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

Direct methods were used for the location of the Hg atoms. Full-matrix least-square refinements were carried out including anisotropic displacement parameters in the last cycles for all non-H atoms. H-atom positions were calculated and one overall refined U_{iso} was used [0.10 (2) Å²]. After subsequent refinement, a *DIFABS* (Walker & Stuart, 1983) correction was applied. The *SHELXS*86 (Sheldrick, 1985) system of computer programs was used for the direct methods. Refinement was

performed with the *CRYSTALS* program (Watkin, Carruthers & Betteridge, 1988). All calculations were carried out on a DELL 333D (33 MHz) computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including H-atom geometry, have been deposited with the IUCr (Reference: DU1077). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[Cr₂Hg(CO)₆(C₈H₉O₂)₂]} lies on a crystallographic inversion centre so that the Cr—Hg—Cr skeleton is exactly linear. The coordination polyhedron around each Cr atom approximates to a square-based pyramid with the substituted cyclopentadienyl ring occupying the apical position. The average Cr—Hg bond length is 2.695 (1) Å.

Comment

The title compound (I) is centrosymmetric and thus has a *trans* configuration of the cyclopentadienyl rings with respect to the linear Cr—Hg—Cr axis; this is also the case for the ethoxycarbonylcyclopentadienyl molybdenum analogue (Song, Dong & Hu, 1992). However, the tungsten analogue containing

(I)
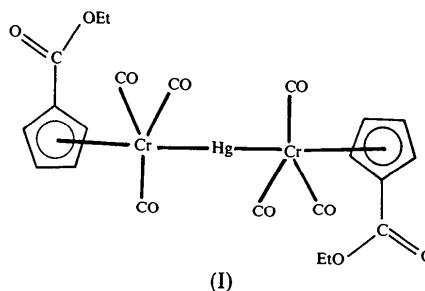
unsubstituted cyclopentadienyl rings is non-centrosymmetric and has a *cis* configuration of cyclopentadienyl ligands with respect to the W—Hg—W axis (Song, Yang, Dong & Hu, 1991). The bond angles Cr—C(1)—O(1) and Cr—C(2)—O(2) [172 (1) and

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Bis[(tricarbonyl)(η⁵-ethoxycarbonylcyclo-pentadienyl)chromio]mercury

Li-Cheng Song* and Qing-Mei Hu

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Ru-Ji Wang and Hong-Gen Wang

Central Laboratory, Nankai University, Tianjin 300071, People's Republic of China

Abstract

The central Hg atom of the title compound {hexacarbonyl-1κ³C,2κ³C-bis[1,2(η⁵)-ethoxycarbonylcyclopentadienyl]dichromiummercury(2   *Cr—Hg*),
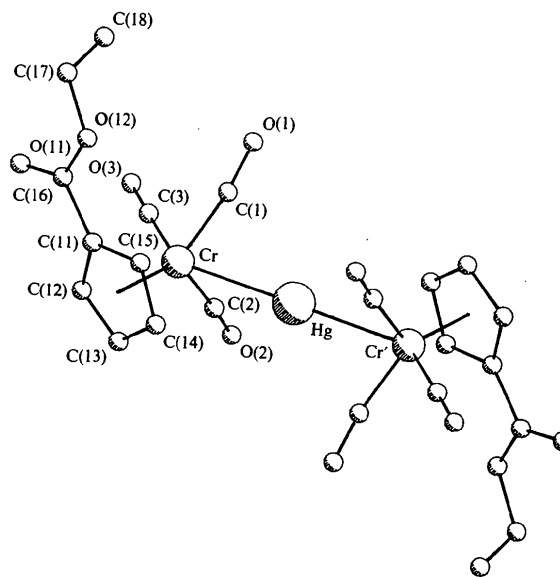
Fig. 1. A perspective drawing of the title compound with atom numbering.