

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.

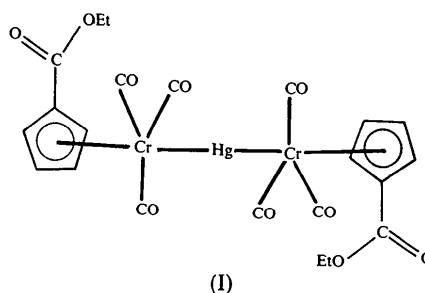
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[Cr₂Hg(CO)₆(C₅H₉O₂)₂]} lies on a crystallographic inversion centre so that the Cr—Hg—Cr skeleton is exactly linear. The coordination polyhedron around each Cr atom approximates to a square-based pyramid with the substituted cyclopentadienyl ring occupying 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



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-ethoxycarbonylcyclopentadienyl)chromio]mercury

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Abstract

The central Hg atom of the title compound {hexacarbonyl-1κ³C,2κ³C-bis[1,2(η⁵-ethoxycarbonylcyclopentadienyl)]dichromiummercury(2 Cr—Hg),

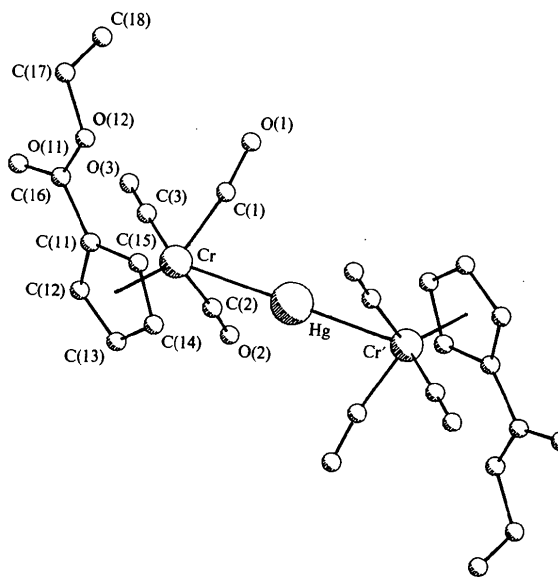


Fig. 1. A perspective drawing of the title compound with atom numbering.

174 (2)°, respectively] and Hg—Cr—C(1) and Hg—Cr—C(2) [72.6 (4) and 70.2 (3)°, respectively] indicate that the C(1) and C(2) carbonyl ligands are semi-bridging. To the best of our knowledge, this is the first example of semi-bridging carbonyls in a system containing a non-multiple Hg—Cr bond. Since the average Cr—C and Hg—C distances, D_1 and D_2 , are 1.86 (1) and 2.739 (9) Å, the bridge asymmetry parameter $\alpha [(D_2 - D_1)/D_1]$ is 0.47 (Curtis & Butler, 1978; Klinger, Butler & Curtis, 1978; Song, Wang, Hu, Wang & Wang, 1993).

Experimental

The title compound was prepared according to the method of Song, Dong & Hu (1992). Crystals were obtained by evaporation from 50% (v/v) CH₂Cl₂/petroleum ether solution.

Crystal data

[Cr₂Hg(CO)₆(C₈H₉O₂)₂]

$M_r = 746.96$

Triclinic

$P\bar{1}$

$a = 6.390$ (3) Å

$b = 7.521$ (4) Å

$c = 13.842$ (4) Å

$\alpha = 94.37$ (5)°

$\beta = 99.82$ (3)°

$\gamma = 112.22$ (5)°

$V = 600$ (1) Å³

$Z = 1$

$D_x = 2.07$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 10$ – 15°

$\mu = 7.31$ mm⁻¹

$T = 296$ (1) K

Block

$0.3 \times 0.2 \times 0.2$ mm

Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer

ω - 2θ scans

Absorption correction: empirical

$T_{\min} = 0.326$, $T_{\max} = 1.427$

2318 measured reflections

2108 independent reflections

1606 observed reflections

$[I \geq 3\sigma(I)]$

$R_{\text{int}} = 0.064$

$\theta_{\max} = 25^\circ$

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = 0 \rightarrow 16$

3 standard reflections frequency: 60 min

intensity variation: -15.7%

Refinement

Refinement on F

$R = 0.080$

$wR = 0.088$

$S = 3.02$

1606 reflections

163 parameters

H-atom parameters not refined

Unit weights applied

$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 2.10$ e Å⁻³

$\Delta\rho_{\min} = -3.07$ e Å⁻³

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Hg				3.92 (2)
Cr	1.1697 (4)	0.1250 (3)	0.8410 (2)	2.54 (5)
O(1)	0.869 (3)	0.345 (2)	0.871 (1)	6.2 (4)
O(2)	1.571 (2)	0.243 (2)	1.015 (1)	6.3 (4)
O(3)	1.462 (2)	0.516 (2)	0.801 (1)	5.4 (4)
O(11)	1.132 (3)	0.231 (2)	0.568 (1)	6.2 (4)
O(12)	0.779 (2)	0.126 (2)	0.600 (1)	5.6 (4)
C(1)	0.986 (3)	0.253 (2)	0.866 (2)	4.4 (4)
C(2)	1.412 (3)	0.194 (2)	0.952 (2)	4.3 (4)
C(3)	1.350 (3)	0.365 (2)	0.816 (1)	3.1 (4)
C(11)	1.048 (3)	0.012 (3)	0.681 (1)	3.7 (4)
C(12)	1.263 (3)	0.009 (2)	0.719 (1)	3.5 (4)
C(13)	1.243 (4)	-0.121 (2)	0.784 (2)	4.9 (5)
C(14)	1.011 (3)	-0.195 (2)	0.795 (1)	4.0 (4)
C(15)	0.890 (3)	-0.112 (3)	0.734 (1)	4.3 (4)
C(16)	0.996 (3)	0.139 (2)	0.612 (1)	3.8 (4)
C(17)	0.709 (5)	0.250 (3)	0.539 (2)	7.2 (7)
C(18)	0.772 (4)	0.437 (3)	0.597 (2)	6.0 (6)

Table 2. Selected geometric parameters (Å, °)

Cp(1) is the centroid of the cyclopentadienyl ring.

Hg—Cr	2.695 (1)	Cr—C(3)	1.838 (9)
Hg—C(1)	2.769 (9)	Cr—Cp(1)	1.83 (2)
Hg—C(2)	2.709 (9)	O(1)—C(1)	1.20 (1)
Cr—C(1)	1.83 (1)	O(2)—C(2)	1.13 (2)
Cr—C(2)	1.88 (1)	O(3)—C(3)	1.14 (2)
Cr—Hg—Cr ¹	180.0	C(2)—Cr—C(3)	81.9 (4)
Cr—Hg—C(1)	39.2 (4)	C(2)—Cr—Cp(1)	124.5 (5)
Cr—Hg—C(2)	40.5 (4)	C(3)—Cr—Cp(1)	116.6 (5)
C(1)—Hg—C(2)	66.0 (4)	Hg—C(1)—Cr	68.2 (8)
Hg—Cr—C(1)	72.6 (4)	Hg—C(1)—O(1)	120 (1)
Hg—Cr—C(2)	70.2 (3)	Cr—C(1)—O(1)	172 (1)
Hg—Cr—C(3)	133.3 (4)	Hg—C(2)—Cr	69.4 (8)
Hg—Cr—Cp(1)	110.0 (3)	Hg—C(2)—O(2)	116 (1)
C(1)—Cr—C(2)	107.4 (6)	Cr—C(2)—O(2)	174 (2)
C(1)—Cr—C(3)	81.7 (4)	Cr—C(3)—O(3)	180 (2)
C(1)—Cr—Cp(1)	126.1 (5)		

Symmetry code: (i) $2 - x, -y, 2 - z$.

The structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and from subsequent difference syntheses. The large residual peaks (> 1 e Å⁻³) and holes (< -1 e Å⁻³) in the final difference synthesis were located near the Hg and Cr atoms. The high values of T_{\max} and R are thought to arise from the poor quality of the crystal. Calculations were carried out on a PDP11/44 computer with the *SDP-Plus* package (B. A. Frenz & Associates, Inc., 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(1,3-benzothiazole-2-thiolato-*N,S'*)-(2,2'-bipyridine-*N,N'*)cadmium(II)

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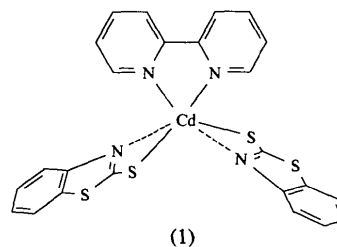
Abstract

The title tris-chelate complex [Cd(C₇H₄NS₂)₂-(C₁₀H₈N₂)] is monomeric, with a coordination sphere of the type N₄S₂. The Cd atom is linked to two thiazole N atoms and two exocyclic S atoms from two bidentate 1,3-benzothiazole-2-thiolate anions and two bipyridine N atoms. The Cd-atom coordination geometry is trigonal prismatic.

Comment

The 1,3-benzothiazole-2-thiolate (mbt⁻) anion, C₇H₄NS₂⁻, is a versatile ligand with more than one donor

atom potentially available for coordination to one or more metal centres in a variety of ways (Raper, 1985). Although extensively studied by spectroscopic methods, crystallographic investigations of zinc and cadmium complexes of this ligand have been limited (McCleverty *et al.*, 1982; Hursthouse, Khan, Mazid, Motevalli & O'Brien, 1990). We have recently reported the synthesis of the complexes [M(C₇H₄NS₂)₂(py)₂], [M(C₇H₄NS₂)₂(2,2'-bpy)] and [M(C₇H₄NS₂)₂(phen)] (py = pyridine, phen = phenanthroline, bpy = bipyridine, M = Zn or Cd) and the single-crystal structures of [Zn(C₇H₄NS₂)₂(py)₂], [Zn(C₇H₄NS₂)₂(2,2'-bpy)] and [Cd(C₇H₄NS₂)₂(py)₂] (Baggio, Garland & Perek, 1993). The three adducts were found to be monomeric, with distorted tetrahedral ZnN₂S₂ and distorted octahedral CdN₄S₂ cores, respectively.



This report presents results of the crystal structure determination of the tris-chelate complex [Cd(C₇H₄NS₂)₂-(2,2'-bpy)], (1). Fig. 1 presents the structural diagram and the atomic numbering scheme. The Cd atom lies on the twofold axis and its environment can be adequately described as trigonal prismatic, with no appreciable rotation (<1°) from the regular geometry of the two basal planes defined by N1, N2', S1 and N1', N2, S1', respectively (primes denote atoms generated by the twofold rotation). The intrachelate angles S—Cd—N and N—Cd—N are in the narrow range 62.5 (1)–69.2 (3)° and reflect the rigid chelate geometry in (1). In the complex [Cd(C₇H₄NS₂)₂(py)₂] already noted, the average intrachelate angle S—Cd—N is 62.1 (1)° and the N(py)—Cd—N(py) angle is 94.9 (2)°. Thus, substitution of the two pyridine N atoms by the bpy N atoms of the bidentate ligand leads to a configuration of three almost equivalent 'bites', with a mean normalized value of 1.05 (Kepert, 1977). Kepert's rules predict for this case a rather undistorted trigonal prismatic geometry as the most stable configuration, in accordance with the present results. Comparison of complex (1) with [Zn(C₇H₄NS₂)₂(2,2'-bpy)] noted above reveals that in the latter, the mbt⁻ ligands are bonded through the exocyclic S atom only, resulting in a distorted tetrahedral ZnN₂S₂ geometry. The larger size of the Cd atom allows S,N-bidentate bonding of the two mbt⁻ ligands. These structures illustrate the differences in coordination that can result in zinc(II) and cadmium(II) thiolates and may be relevant to their different biological activity (Reddy, Zhang, Schlemper & Schrauzer, 1992).