Di-μ-phenylmethanethiolato-μ-sulfido-bis[carbonyl(η^5^-cyclopentadienyl)molybdenum(III)]

Richard Chee Seng Wong, Mei Lee Ooi and Seik Weng Ng
Di-µ-phenylmethanethiolato-µ-sulfido-bis[carbonyl(η⁵-cyclopentadienyl)-molybdenum(III)]

The reaction of bis[cyclopentadienyliatetrafulvalenyl]molybdenum(I) with dibenzyl trisulfide affords the title compound, \([\text{Mo}_2\text{S}_3\text{C}_5\text{H}_5\text{S}_2\text{C}_6\text{H}_5\text{S}_2\text{CO}]_2\], as one of the products. Three independent molecules exist in the asymmetric unit of the triclinic unit cell; one is related to another by a false inversion center and is related to the third by a false translation. In each dinuclear entity, each Mo atom is bonded to a cyclopentadienyl anion and a carbon monoxide molecule; the phenylmethanethiolate groups bridge a pair of Mo atoms, as does the sulfide atom.

**Comment**

The previous study reported the isolation of several compounds from the reaction of cyclopentadienyliatetrafulvalenylmolybdenum(I) with dibenzyl trisulfide (Wong et al., 2004). Also present in the products of the reaction is \([\eta^5\text{C}_5\text{H}_5\text{S}_2\text{CO}]\text{Mo}^{III}\)_2S, (I) (Fig. 1), which differs from \([\eta^5\text{C}_5\text{H}_5\text{S}_2\text{CO}]\text{Mo}^{II}\)_2 in having a sulfide linkage in addition to the two phenylmethanethiolate linkages. In the related reaction of \([\eta^5\text{C}_5\text{H}_5\text{S}_2\text{CO}]\text{Cr}^{III}\)_2 with diphenyl disulfide, one of the products is \([\eta^5\text{C}_5\text{H}_5\text{S}_2\text{CO}]\text{Cr}^{III}\)_2S, but the carbonyl ligands are cleaved in the reaction (Goh et al., 1992). In the present structure, if the cyclopentadienyl ring is considered to occupy three sites, the geometry of the Mo atom is pseudo-pentagonal bipyramidal.

### Experimental

The isolation of the title compound is described in the previous report (Wong et al., 2004).

**Crystal data**

\[
\begin{align*}
\text{Mo}_2\text{S}_3\text{C}_5\text{H}_5\text{S}_2\text{C}_6\text{H}_5\text{S}_2\text{CO}]_2 & : \\
Z & = 6 \\
D_x & = 1.752 \text{ Mg m}^{-3} \\
\text{Mo Kα radiation} & \\
\text{Cell parameters from 6754 reflections} & \\
\theta & = 2.6-29.2^\circ \\
\mu & = 1.28 \text{ mm}^{-1} \\
T & = 223 (2) \text{ K} \\
\text{Block, red} & \\
V & = 3732.9 (4) \text{ Å}^3 \\
0.38 & \times 0.30 \times 0.28 \text{ mm}
\end{align*}
\]


<table>
<thead>
<tr>
<th>Selected geometric parameters (Å, °).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cl1—Mo1—Cl2a</strong> 35.2 (1) C7a—Mo2a—S1a 147.5 (1) C1a—Mo1a—Cl1a 2.360 (5) Mo2b—C6b 2.360 (5) Mo2a—C7b 2.350 (6) Mo2b—C8b 2.303 (5) Mo2a—C9a 2.266 (5) Mo2b—Cl10b 2.320 (6) Mo2a—Cl18b 1.952 (8) Mo2b—Cl12b 1.967 (8) Mo2a—S1a 2.460 (2) Mo2b—S1b 2.435 (2) Mo2a—S2a 2.452 (2) Mo2b—S2b 2.449 (2) Mo2a—S3a 2.437 (2) Mo2b—S3b 2.440 (2) Mo2a—S12a 1.965 (9) Mo1c—C1c 2.362 (5) C8a—Mo1c—Clc 2.351 (6) C9—Mo1c—C2c 2.322 (5) C7a—Mo1c—C3c 2.278 (6) C8a—Mo1c—C4c 2.292 (5) Mo1b—C1b 2.286 (5) Mo1c—C5c 2.344 (5) Mo1a—Cl10a 2.329 (5) Mo1c—C11c 2.007 (8) Mo2a—S1a 2.454 (2) Mo1c—S1c 2.463 (2) Mo2a—S2a 2.462 (2) Mo1c—S2c 2.455 (2) Mo2a—S3a 2.443 (2) Mo1c—S3c 2.438 (2) Mo1b—C1b 2.236 (6) Mo1c—S5c 2.356 (6) Mo1b—C2b 2.318 (6) Mo1c—C7c 2.322 (6) Mo1b—C3b 2.231 (6) Mo2c—C8c 2.287 (5) Mo1b—C4b 2.313 (6) Mo2c—C9c 2.300 (6) Mo1b—C11b 2.197 (8) Mo12c—C12c 2.001 (7) Mo1b—S1b 2.461 (2) Mo1c—S1c 2.457 (2) Mo1b—S2b 2.471 (2) Mo1c—S2c 2.461 (2) Mo1b—S3b 2.439 (2) Mo1c—S3c 2.438 (2)</td>
</tr>
<tr>
<td><strong>C1a—Mo1—C4a</strong> 59.1 (1) C7a—Mo2a—S1a 147.5 (1) C1a—Mo1a—Cl1a 2.360 (5) Mo2b—C6b 2.360 (5) Mo2a—C7b 2.350 (6) Mo2b—C8b 2.303 (5) Mo2a—C9a 2.266 (5) Mo2b—Cl10b 2.320 (6) Mo2a—Cl18b 1.952 (8) Mo2b—Cl12b 1.967 (8) Mo2a—S1a 2.460 (2) Mo2b—S1b 2.435 (2) Mo2a—S2a 2.452 (2) Mo2b—S2b 2.449 (2) Mo2a—S3a 2.437 (2) Mo2b—S3b 2.440 (2) Mo2a—S12a 1.965 (9) Mo1c—C1c 2.362 (5) C8a—Mo1c—Clc 2.351 (6) C9—Mo1c—C2c 2.322 (5) C7a—Mo1c—C3c 2.278 (6) C8a—Mo1c—C4c 2.292 (5) Mo1b—C1b 2.236 (6) Mo1c—S5c 2.356 (6) Mo1b—C2b 2.318 (6) Mo1c—C7c 2.322 (6) Mo1b—C3b 2.231 (6) Mo2c—C8c 2.287 (5) Mo1b—C4b 2.313 (6) Mo2c—C9c 2.300 (6) Mo1b—C11b 2.197 (8) Mo12c—C12c 2.001 (7) Mo1b—S1b 2.461 (2) Mo1c—S1c 2.457 (2) Mo1b—S2b 2.471 (2) Mo1c—S2c 2.461 (2) Mo1b—S3b 2.439 (2) Mo1c—S3c 2.438 (2)</td>
</tr>
<tr>
<td><strong>Cl1—Mo1—Cl2a</strong> 35.2 (1) C7a—Mo2a—S1a 147.5 (1) C1a—Mo1a—Cl1a 2.360 (5) Mo2b—C6b 2.360 (5) Mo2a—C7b 2.350 (6) Mo2b—C8b 2.303 (5) Mo2a—C9a 2.266 (5) Mo2b—Cl10b 2.320 (6) Mo2a—Cl18b 1.952 (8) Mo2b—Cl12b 1.967 (8) Mo2a—S1a 2.460 (2) Mo2b—S1b 2.435 (2) Mo2a—S2a 2.452 (2) Mo2b—S2b 2.449 (2) Mo2a—S3a 2.437 (2) Mo2b—S3b 2.440 (2) Mo2a—S12a 1.965 (9) Mo1c—C1c 2.362 (5) C8a—Mo1c—Clc 2.351 (6) C9—Mo1c—C2c 2.322 (5) C7a—Mo1c—C3c 2.278 (6) C8a—Mo1c—C4c 2.292 (5) Mo1b—C1b 2.236 (6) Mo1c—S5c 2.356 (6) Mo1b—C2b 2.318 (6) Mo1c—C7c 2.322 (6) Mo1b—C3b 2.231 (6) Mo2c—C8c 2.287 (5) Mo1b—C4b 2.313 (6) Mo2c—C9c 2.300 (6) Mo1b—C11b 2.197 (8) Mo12c—C12c 2.001 (7) Mo1b—S1b 2.461 (2) Mo1c—S1c 2.457 (2) Mo1b—S2b 2.471 (2) Mo1c—S2c 2.461 (2) Mo1b—S3b 2.439 (2) Mo1c—S3c 2.438 (2)</td>
</tr>
<tr>
<td><strong>Cl1—Mo1—Cl2a</strong> 35.2 (1) C7a—Mo2a—S1a 147.5 (1) C1a—Mo1a—Cl1a 2.360 (5) Mo2b—C6b 2.360 (5) Mo2a—C7b 2.350 (6) Mo2b—C8b 2.303 (5) Mo2a—C9a 2.266 (5) Mo2b—Cl10b 2.320 (6) Mo2a—Cl18b 1.952 (8) Mo2b—Cl12b 1.967 (8) Mo2a—S1a 2.460 (2) Mo2b—S1b 2.435 (2) Mo2a—S2a 2.452 (2) Mo2b—S2b 2.449 (2) Mo2a—S3a 2.437 (2) Mo2b—S3b 2.440 (2) Mo2a—S12a 1.965 (9) Mo1c—C1c 2.362 (5) C8a—Mo1c—Clc 2.351 (6) C9—Mo1c—C2c 2.322 (5) C7a—Mo1c—C3c 2.278 (6) C8a—Mo1c—C4c 2.292 (5) Mo1b—C1b 2.236 (6) Mo1c—S5c 2.356 (6) Mo1b—C2b 2.318 (6) Mo1c—C7c 2.322 (6) Mo1b—C3b 2.231 (6) Mo2c—C8c 2.287 (5) Mo1b—C4b 2.313 (6) Mo2c—C9c 2.300 (6) Mo1b—C11b 2.197 (8) Mo12c—C12c 2.001 (7) Mo1b—S1b 2.461 (2) Mo1c—S1c 2.457 (2) Mo1b—S2b 2.471 (2) Mo1c—S2c 2.461 (2) Mo1b—S3b 2.439 (2) Mo1c—S3c 2.438 (2)</td>
</tr>
</tbody>
</table>
Data collection

Bruker SMART CCD area-detector diffractometer
\( \phi \) and \( \omega \) scans
Absorption correction: multi-scan
(SADABS; Bruker, 2001)
\( T_{\text{min}} = 0.680, T_{\text{max}} = 0.715 \)
36947 measured reflections
17028 independent reflections
11206 reflections with \( I > 2\sigma(I) \)
\( R_{\text{int}} = 0.041 \)
\( \theta_{\text{max}} = 27.5^\circ \)
\( h = -14 \rightarrow 14 \)
\( k = -20 \rightarrow 19 \)
\( l = -29 \rightarrow 29 \)

Refinement

Refinement on \( F^2 \)
\( R[F^2 > 2\sigma(F^2)] = 0.066 \)
\( wR(F^2) = 0.216 \)
\( S = 1.07 \)
17028 reflections
766 parameters
H-atom parameters constrained

Molecule \( a \) is related to molecule \( b \) by a false inversion at approximately \((2/3, 2/3, 2/3)\); it is also related to molecule \( c \) by an approximate translation of \((1/3, 1/3, 1/3)\). The false symmetry/translational symmetry necessitated constraining the five-membered rings to be refined as regular pentagons \((C-C = 1.42 \text{Å})\) and the six-membered rings as regular hexagons \((C-C = 1.39 \text{Å})\). H atoms were placed at calculated positions in the riding-model approximation \([\text{aromatic C-H = 0.94 Å and aliphatic C-H = 0.98 Å; } U_{\text{iso}}(H) = 1.2U_{eq}(C)]\). The final difference Fourier had a large peak at about 1.5 Å from atom Mo1a and the deepest hole at about 1.5 Å from atom C11a.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

We thank the National University of Singapore for the diffraction measurements, and the University of Malaya (PJP FP005/2003A) for generously supporting this work.

References