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Di-μ-phenylmethanethiolatobis[dicarbonyl-(η^5-cyclopentadienyl)molydenum(II)]

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The reaction of bis[cyclopentadienyltricarbonylmolybdenum(I)] with dibenzyl trisulfide affords the dinuclear title compound, $[Mo_2^{II}(C_5H_5)_2(C_7H_7S)_2(CO)_4]$, as one of the products. The two benzylthiolate anions function as bridges to the Mo atoms. The geometry of the Mo atom is described as pseudo-pentagonal bipyramidal if the cyclopentadienyl ring is assumed to occupy three sites.

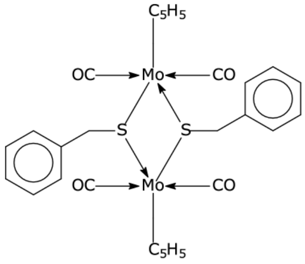
Key indicators

Single-crystal X-ray study
T = 163 K
Mean σ(C–C) = 0.004 Å
R factor = 0.025
wR factor = 0.050
Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The reaction of dimeric cyclopentadienyltricarbonylchromium(I) with diphenyl disulfide affords one Cr^{III} and two Cr^{II} products in which the phenylmethanethiolate group engages in bridging two Cr atoms (Goh *et al.*, 1992). A similar reaction of $[(C_5H_5)(CO)_3Mo]_2$ with the disulfide yielded $[(C_5H_5)(C_6H_5S)(CO)_2Mo^{II}]_2$ as a 2:1 cocrystal with $[(C_5H_5)(C_6H_5S)(O)Mo^{V}]_2O$ (Benson *et al.*, 1980); $[(C_5H_5)(C_6H_5S)(CO)_2Mo^{II}]_2$ itself could be synthesized by reacting the $[(C_5H_5)(CO)_3Mo]^-$ anion with phenylsulfonyl chloride (Adams *et al.*, 1978). In our hands, the reaction of this molybdenum reagent with dibenzyl trisulfide also yielded several compounds, one of which is (I) (Fig. 1). The two phenylmethanethiolate anions function as bridges to the Mo atoms, which are each coordinated by two carbonyl ligands. The bond dimensions of the metal atom are similar to those found in the phenyl homolog (Adams *et al.*, 1978).



(I)

Experimental

Bis(cyclopentadienyltricarbonylmolybdenum(I) (0.2 g, 0.4 mmol), which was synthesized from hexacarbonylmolybdenum(0) (Birdwhistell *et al.*, 1978), was dissolved in toluene (20 ml). The solution reacted with solid dibenzyl trisulfide, a commercial compound, under a nitrogen atmosphere at 333 K for 3.5 h. The solution was concentrated to a small volume before being loaded on to a 1.5 × 10 cm silica-gel column that was prepared in n-hexane. The first fraction was eluted as a red–brown fraction with 2:1 n-hexane–toluene. Single crystals were obtained by recrystallization from the same solvent system at 245 K. The compound was identified as the title compound by X-ray diffraction. The second fraction was eluted as a pink fraction

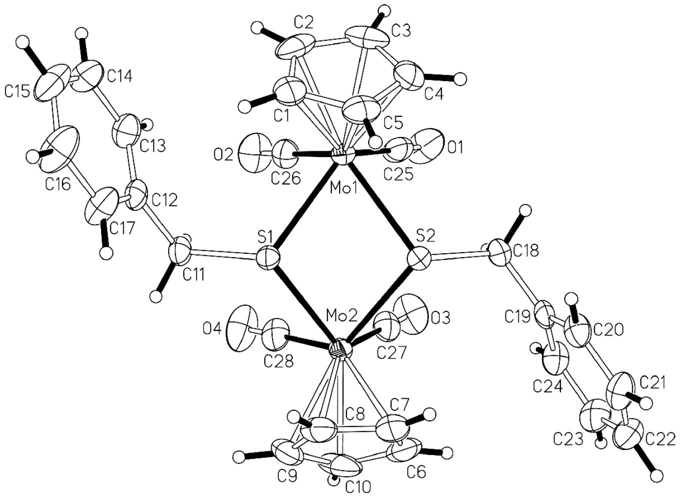


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

with 1:1 *n*-hexane–toluene. The crystals that were obtained by recrystallization were identified by spectroscopic measurements as $[(\eta^5\text{-}C_5H_5)(C_7H_7S)(S)Mo^{II}]_2$. The third fraction was eluted as a brown–pink fraction with 2:1 toluene–ether, and the solid compound was identified as a polymorphic form of $[(\eta^5\text{-}C_5H_5)(C_7H_7S)(S)Mo^{II}]_2$. The final fraction was eluted as a red–brown fraction with ether alone. Crystals were obtained by using ether as the solvent for recrystallization. The structure of this compound, $[(\eta^5\text{-}C_5H_5)(C_7H_7S)(CO)Mo^{III}]_2S$, is described in the following report (Wong *et al.*, 2004).

Crystal data

$[Mo_2(C_5H_5)_2(C_7H_7S)_2(CO)_4]$
$M_r = 680.47$
Monoclinic, $P2_1/n$
$a = 8.6302$ (6) Å
$b = 24.801$ (2) Å
$c = 13.2751$ (9) Å
$\beta = 108.702$ (1)°
$V = 2691.3$ (3) Å^3
$Z = 4$
$D_x = 1.679$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5707 reflections
$\theta = 2.6$–$26.4°$
$\mu = 1.12$ mm^{-1}
$T = 163$ (2) K
Plate, red
0.33 × 0.14 × 0.04 mm

Data collection

Siemens *P*4/CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{\min} = 0.709$, $T_{\max} = 0.957$
34532 measured reflections
5537 independent reflections
4169 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\max} = 26.5°$
$h = -10 \rightarrow 10$
$k = -31 \rightarrow 31$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.050$
$S = 0.90$
5537 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—C1	2.389 (2)	Mo2—C6	2.321 (3)
Mo1—C2	2.334 (3)	Mo2—C7	2.407 (3)
Mo1—C3	2.304 (3)	Mo2—C8	2.405 (3)
Mo1—C4	2.321 (2)	Mo2—C9	2.315 (3)
Mo1—C5	2.373 (2)	Mo2—C10	2.282 (3)
Mo1—C25	1.951 (3)	Mo2—C27	1.944 (3)
Mo1—C26	1.947 (3)	Mo2—C28	1.959 (3)
Mo1—S1	2.5209 (7)	Mo2—S1	2.5217 (6)
Mo1—S2	2.5115 (7)	Mo2—S2	2.5161 (6)
C1—Mo1—C2	34.5 (1)	C6—Mo2—C8	57.1 (1)
C1—Mo1—C3	57.8 (1)	C6—Mo2—C9	58.6 (1)
C1—Mo1—C4	57.5 (1)	C6—Mo2—C10	35.7 (1)
C1—Mo1—C5	34.0 (1)	C6—Mo2—C27	94.0 (1)
C1—Mo1—C25	148.1 (1)	C6—Mo2—C28	126.4 (1)
C1—Mo1—C26	112.2 (1)	C6—Mo2—C7	34.4 (1)
C1—Mo1—S2	116.9 (1)	C6—Mo2—S1	142.3 (1)
C1—Mo1—S1	85.9 (1)	C6—Mo2—S2	101.5 (1)
C2—Mo1—C3	35.3 (1)	C7—Mo2—C8	33.5 (1)
C2—Mo1—C4	58.3 (1)	C7—Mo2—C9	57.1 (1)
C2—Mo1—C5	57.3 (1)	C7—Mo2—C10	58.0 (1)
C2—Mo1—C25	116.7 (1)	C7—Mo2—C27	121.5 (1)
C2—Mo1—C26	91.7 (1)	C7—Mo2—C28	149.1 (1)
C2—Mo1—S1	111.3 (1)	C7—Mo2—S1	108.2 (1)
C2—Mo1—S2	146.8 (1)	C7—Mo2—S2	84.2 (1)
C3—Mo1—C25	90.4 (1)	C8—Mo2—C9	34.4 (1)
C3—Mo1—C26	105.9 (1)	C8—Mo2—C10	58.1 (1)
C3—Mo1—C4	35.3 (1)	C8—Mo2—C27	151.1 (1)
C3—Mo1—C5	57.9 (1)	C8—Mo2—C28	122.5 (1)
C3—Mo1—S1	143.5 (1)	C8—Mo2—S1	88.0 (1)
C3—Mo1—S2	127.2 (1)	C8—Mo2—S2	101.9 (1)
C4—Mo1—C5	34.8 (1)	C9—Mo2—C10	35.8 (1)
C4—Mo1—S2	94.1 (1)	C9—Mo2—C27	132.0 (1)
C4—Mo1—C25	98.8 (1)	C9—Mo2—C28	92.7 (1)
C4—Mo1—C26	141.0 (1)	C9—Mo2—S1	101.7 (1)
C4—Mo1—S1	128.3 (1)	C9—Mo2—S2	136.3 (1)
C5—Mo1—C25	132.4 (1)	C10—Mo2—C27	98.6 (1)
C5—Mo1—C26	146.0 (1)	C10—Mo2—C28	94.0 (1)
C5—Mo1—S1	94.5 (1)	C10—Mo2—S1	137.4 (1)
C5—Mo1—S2	89.5 (1)	C10—Mo2—S2	137.1 (1)
C25—Mo1—C26	71.3 (1)	C27—Mo2—C28	71.9 (1)
C25—Mo1—S1	125.6 (1)	C27—Mo2—S1	120.1 (1)
C25—Mo1—S2	83.0 (1)	C27—Mo2—S2	83.6 (1)
C26—Mo1—S1	83.5 (1)	C28—Mo2—S1	82.7 (1)
C26—Mo1—S2	120.8 (1)	C28—Mo2—S2	126.5 (1)
S1—Mo1—S2	69.7 (1)	S1—Mo2—S2	69.6 (1)

H atoms were placed at calculated positions in the riding-model approximation [aromatic C—H = 0.95 Å and aliphatic C—H = 0.99 Å; $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$].

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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