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A mixed tribridging dimolybdenum(I) compound, bis(μ-benzenethiolato-*S*:*S*)-hexacarbonyl-μ-iodo-dimolybdenum(I)-(*Mo—Mo*)

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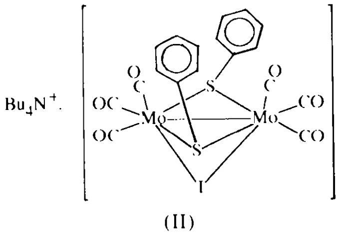
Abstract

In the structure of the complex anion of the title compound, $(C_{16}H_{36}N)[Mo_2I(C_6H_5S)_2(CO)_6]$, two Mo atoms are linked by three bridging ligands (one I and two benzenethiolate), forming an $Mo_2I(C_6H_5S)_2$ core. The Mo_2S_2 unit, with a mean Mo—S distance of 2.475 (2) Å and a mean Mo—S—Mo angle of 71.21 (4)°, is approximately planar. Relative to this Mo_2S_2 unit, the two benzene rings are in a *syn* configuration. The Mo—I distances are 2.9460 (6) and 2.9599 (6) Å, the Mo—Mo distance is 2.8824 (7) Å and the Mo—I—Mo angle is 58.43 (2)°.

Comment

Recent studies in our laboratory on Mo^I compounds revealed that halogen ions are capable of coordinating to the Mo^I atom by substituting for the axial CO in the parent compound $[Mo_2(C_6H_5S)_2(CO)_8]$, (I), forming tribridging Mo^I compounds (Pan *et al.*, 1998). The title compound, (II), is a new member of this series.



(II)

The structure of the anion of the title compound (Fig. 1) shows iodide acting as the third bridge coordinating the two Mo atoms, by substituting two axial CO of (I), forming a face-sharing bi-octahedron. The Mo_2S_2 unit in (II) adopts a planar configuration, which is similar to that in (I) (Zhuang *et al.*, 1995), except for a slight contraction of the Mo—S—Mo angle and the Mo—Mo distance. A difference between (I) and (II) is that, while the two phenyl rings in (I) are in an *anti* configuration, those in (II) are in a *syn* configuration, due to the steric hindrance of the I atom relative to the planar Mo_2S_2 unit. Furthermore, in contrast with (I), the axial Mo—C distances are shorter in (II) than the equatorial ones. This is an indication of the difficulty of further substitution of the axial CO in (II) to generate a tetrabridged compound.

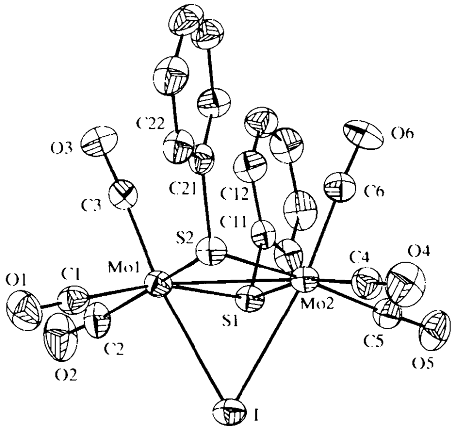


Fig. 1. View of the anion of (II), with displacement ellipsoids shown at the 30% probability level and H atoms omitted for clarity.

The Mo—I bond distances in (II) [2.9460 (6) and 2.9599 (6) Å] are quite long, and the Mo1—I—Mo2 angle [58.43 (2)°] is very acute, indicating the weak coordination between the Mo and I atoms. This suggests that (II) could be a good precursor for synthesizing new Mo^I compounds *via* substitution of the iodine bridge by other appropriate ligands.

Experimental

The title compound was synthesized by the reaction of $[Mo_2(C_6H_5S)_2(CO)_8]$ (Zhuang *et al.*, 1984; Smith *et al.*, 1987) with Bu_4NI (1:1) in acetone, and crystallized by allowing the filtrate, to which ^{i}PrOH had been added, to stand at a temperature below 273 K for several days. Analysis calculated for $C_{34}H_{46}IMo_2NO_6S_2$: C 42.90, H 4.87, N 1.47%; found: C 43.08, H 4.81, N 1.45%; IR (KBr, cm^{-1}): 2962.2 (*m*), 2933.2 (*w*), 2873.5 (*w*), 1996.0 (*s*), 1957.4 (*s*), 1945.8 (*s*), 1909.2 (*s*), 1849.4 (*s*), 1573.6 (*m*), 1475.3 (*m*), 1457.9 (*w*), 1436.7 (*m*), 1373.1 (*m*), 1299.8 (*w*), 1274.7 (*w*), 1174.5 (*w*), 1151.3 (*w*), 1105.0 (*w*), 1064.5 (*w*), 1022.1 (*m*), 999.0 (*w*), 877.5 (*m*), 800.3 (*w*), 750.2 (*s*), 742.5 (*s*), 688.5 (*s*), 615.2 (*m*), 582.4 (*m*), 528.4 (*w*), 511.1 (*w*), 497.6 (*m*), 476.3 (*m*), 468.6 (*m*), 422.3 (*m*); FT-IR (CsI, cm^{-1}): 582.4, 528.4, 511.1, 499.5, 484.1, 478.3,

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433.4, 422.2, 358.7, 337.5, 283.5, 239.1, 223.7, 198.3, 177.4, 150.4; UV-vis [CH_3COCH_3, λ (nm)]: 444, 402, 340, 315; ^{1}H NMR [CD_3COCD_3, δ (p.p.m.)]: 7.20–7.60 (*m*, 10H, SPh), 3.46 (*t*, 8^aH, $C^aH_2CH_2CH_2CH_3$), 1.83 (*m*, 8^bH, $CH_2C^bH_2CH_2CH_3$), 1.47 (*m*, 8^cH, $CH_2CH_2C^cH_2CH_3$), 1.01 (*t*, 12^dH, $CH_2CH_2CH_2C^dH_3$).

Crystal data

$(C_{16}H_{36}N)[Mo_2I(C_6H_5S)_2(CO)_6]$
$M_r = 947.62$
Monoclinic
$P2_1/n$
$a = 9.8951\ (4)$ Å
$b = 16.2430\ (7)$ Å
$c = 25.0787\ (10)$ Å
$\beta = 90.444\ (1)°$
$V = 4030.7\ (3)$ Å^3
$Z = 4$
$D_x = 1.562$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6187 reflections
$\theta = 1.49–25.02°$
$\mu = 1.531$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.40 × 0.15 × 0.10 mm
Black

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.698$, $T_{max} = 0.894$
13 287 measured reflections
6816 independent reflections

4719 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 25.02°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 29$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.089$
$S = 1.054$
6816 reflections
415 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2 + 2.8450P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.384$ e Å^{-3}
$\Delta\rho_{min} = -0.428$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

I—Mo1	2.9460 (6)	Mo1—Mo2	2.8824 (7)
I—Mo2	2.9599 (6)	Mo2—C6	1.947 (7)
Mo1—C3	1.919 (7)	Mo2—C5	1.992 (6)
Mo1—C1	2.004 (7)	Mo2—C4	2.000 (7)
Mo1—C2	2.017 (7)	Mo2—S1	2.4783 (15)
Mo1—S1	2.4675 (15)	Mo2—S2	2.4836 (15)
Mo1—S2	2.4714 (15)		
Mo1—I—Mo2	58.43 (2)	Mo1—S1—Mo2	71.29 (4)
S1—Mo1—S2	108.84 (5)	Mo1—S2—Mo2	71.14 (4)
S1—Mo2—S2	108.10 (5)		

Data were collected over a hemisphere of reciprocal space by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 4.95 cm. Coverage of the unique set was over 99% complete to at least 25° in θ. Crystal decay was monitored by measurement of duplicate reflections. H atoms were all located theoretically and not refined.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SMART* and *SAINT* (Siemens, 1994*b*). Data reduction: *XPREP* in *SHELXTL* (Siemens, 1994*a*). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1215). Services for accessing these data are described at the back of the journal.

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A dimolybdenum(I) carbonyl compound with thiolate and carboxylate bridges: tetrabutylammonium bis(μ-benzenethiolato-*S*:*S*)hexacarbonyl-μ-pivalate-*O*:*O*′-dimolybdenum(*Mo*—*Mo*)

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Abstract

In the anion of the title compound, $(C_{16}H_{36}N)[Mo_2(C_5H_9O_2)(C_6H_5S)_2(CO)_6]$, each Mo atom and three terminal carbonyl groups form a *fac*-Mo(CO)$_3$ fragment, and two Mo atoms and two benzenethiolate bridging

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