

S = 1.074

6661 reflections

326 parameters

H atoms treated by a
mixture of independent
and constrained refinement $(\Delta/\sigma)_{\max} = 0.003$ $\Delta\rho_{\max} = 0.486 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.579 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)Table 1. *Selected geometric parameters* ($\text{\AA}$, $^\circ$)

Cu—O1	1.938 (2)	Cu—N1B	1.985 (2)
Cu—O2	1.947 (2)	Cu—O11	2.216 (2)
Cu—N1A	1.984 (2)		
O1—Cu—O2	83.95 (8)	N1A—Cu—N1B	81.65 (10)
O1—Cu—N1A	167.47 (10)	O1—Cu—O11	97.36 (9)
O2—Cu—N1A	96.18 (9)	O2—Cu—O11	99.16 (9)
O1—Cu—N1B	95.38 (9)	N1A—Cu—O11	94.99 (9)
O2—Cu—N1B	166.87 (10)	N1B—Cu—O11	93.94 (10)

Table 2. *Hydrogen-bonding geometry* ($\text{\AA}$, $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O11—H111...O4 ⁱ	0.79 (1)	2.35 (2)	2.947 (3)	134 (1)
O11—H111...O5 ⁱ	0.79 (1)	2.27 (2)	2.999 (3)	153 (1)
O11—H112...O4 ⁱⁱ	0.81 (1)	1.97 (2)	2.777 (3)	173 (2)
C3A—H3A...N1L ⁱⁱⁱ	0.93	2.42	3.349 (10)	176.9
C3B—H3B...N1L ⁱⁱⁱ	0.93	2.48	3.403 (11)	174.9
C5A—H5A...O42A ^{iv}	0.93	2.51	3.210 (4)	132.6
C6B—H6B...O1	0.93	2.58	3.082 (4)	114.5
C6B—H6B...C11 ^v	0.93	2.767	3.541 (4)	141.3
C51B—H51D...O11 ^{vi}	0.96	2.387	3.292 (5)	157.1

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, -y, 1-z$; (iii) $-x, -y, 1-z$; (iv) $-x, -1-y, 1-z$; (v) $1-x, 1-y, -z$; (vi) $-x, 1-y, -z$.

The three coordinating ligands were refined anisotropically and the positions of the H atoms were calculated and refined using a riding model. The water H atoms at O11 were located in a difference electron-density map and were refined with isotropic displacement parameters using O—H and H...H distance restraints of 0.82 (2) and 1.30 (2) $\text{\AA}$, respectively. The acetonitrile solvent molecule was located by interpreting two electron-density peaks near a centre of symmetry with a very short inter-peak distance of about 1.10 $\text{\AA}$. Application of the symmetry operation resulted in four atomic positions of which the central generated peak to peak distance was approximately 1.45 $\text{\AA}$. Thus, the peak near the centre was assigned to a C atom and a rigid model of acetonitrile was refined with distance restraints [N1L—C1LA = 1.140 (15) and C1LA—C1LB = 1.453 (15) $\text{\AA}$]. The positions of the H atoms of the methyl C1LB atom were calculated in a previous refinement with SHELXL97 (Sheldrick, 1997) using the HFIX 137 option and a dummy C atom. The H-atom coordinates were fixed in the final refinement cycles. All atoms of the acetonitrile solvent molecule were refined with a site occupancy factor of 0.5 and isotropic displacement parameters.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *PLATON* and *PLUTON* (Spek, 1990). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1187). Services for accessing these data are described at the back of the journal.

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A New Dinuclear Molybdenum Compound, (Bu₄N)[Mo₂(CO)₆(SPh)₂(CH₂CCH₃COO)]

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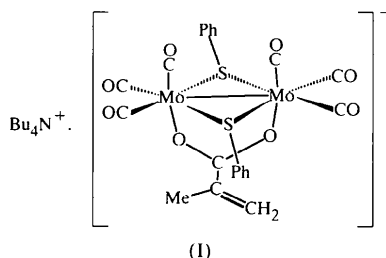
Abstract

The crystal structure of the title compound, tetrabutylammonium bis(μ -benzenethiolato-*S:S*)- μ -methacrylato-*O:O'*-bis(tricarbonylmolybdenum)(*Mo—Mo*), (C₁₆H₃₆N)[Mo₂(C₄H₅O₂)(C₆H₅S)₂(CO)₆], shows that it contains a Bu₄N⁺ cation and a dinuclear anion with three bridging ligands, *i.e.* [Mo₂(CO)₆(SPh)₂(CH₂CCH₃COO)][−]; the

α -methacrylate group acts as a bidentate bridging ligand and coordinates two Mo atoms to form a five-membered ring. The Mo—Mo bond distance is 2.9115 (5) Å and the O—C—O angle is 125.8 (4)°.

Comment

The structures of dinuclear molybdenum–carbonyl compounds containing thiolato bridges, [Mo₂(CO)₈(SPh)₂] [(II); Zhuang *et al.*, 1995] and [Mo₂(CO)₈(SCH₂COOCH₂CH₃)₂] (Zhuang *et al.*, 1987), have been determined previously. These compounds possess an interesting electrochemical behavior of a reversible two-electron transfer occurring in one step; also, the axial carbonyl of these compounds can be substituted by the coordinating solvent, *e.g.* CH₃CN, to afford the product [Mo₂(CO)₆(CH₃CN)₂(SPh)₂] (Zhuang *et al.*, 1989). We now extend our studies to include compounds where carboxylate ligands substitute the carbonyl ligands of (II) and report the structure of the title compound, (I).



The structure of the anion of (I) is shown in Fig. 1. Each Mo atom has a distorted octahedral geometry involving three carbonyl C atoms, two S atoms from bridging SPh groups and one O atom from an α -methacrylate ligand. Two *fac*-Mo(CO)₃ fragments are linked together by two SPh and one α -methacrylate ligand forming a hetero-tribridged dimer, which can be considered as an edge-sharing bi-octahedral structure.

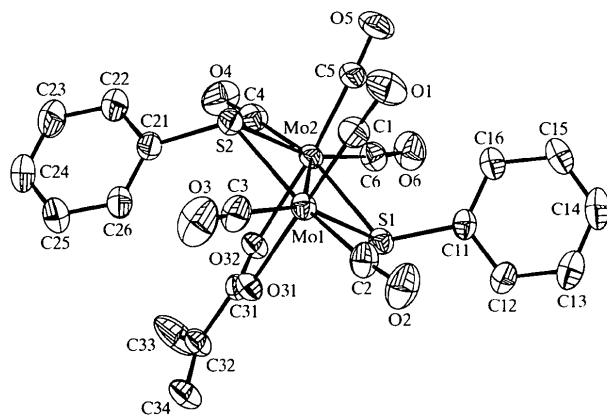


Fig. 1. View of the anion of the title compound with displacement ellipsoids shown at the 30% probability level and H atoms omitted for clarity.

The structure of the Mo₂S₂ unit in the title compound is similar to that in compound (II). On introduction of the α -methacrylate ligand, the Mo₂S₂ unit contracts slightly, resulting in smaller Mo—S—Mo angles and a shorter Mo—Mo distance. Interestingly, however, the Mo—S distances are essentially equal to those of (II). The *trans*-Mo—C distances are considerably shorter than those *cis* to the α -methacrylate ligand. The α -methacrylate ligand substitutes for two axial carbonyls of (II) to form an approximately planar Mo—O—C—O—Mo five-membered ring [Mo—Mo 2.9115 (5) Å]. As a result of this long Mo—Mo distance, the O—C—O angle [125.8 (4)°] is slightly wider than a normal *sp*² angle (120°).

Experimental

The title compound was synthesized by the reaction of [Mo₂(CO)₈(SPh)₂] with Bu₄NBr and CH₂C(CH₃)COONa (1:1:1) in acetone, and crystallized by allowing the filtrate, with added *i*-PrOH, to stand at a temperature below 273 K for several days.

Crystal data

(C₁₆H₃₆N)[Mo₂(C₄H₅O₂)-(C₆H₅S)₂(CO)₆]
 $M_r = 905.80$
 Monoclinic
 $P2_1/c$
 $a = 15.1675(4)$ Å
 $b = 11.9640(3)$ Å
 $c = 24.1413(4)$ Å
 $\beta = 103.156(1)^\circ$
 $V = 4265.8(2)$ Å³
 $Z = 4$
 $D_x = 1.410$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å
 Cell parameters from 7334 reflections
 $\theta = 1.38$ – 25.02°
 $\mu = 0.733$ mm⁻¹
 $T = 293(2)$ K
 Plate
 $0.70 \times 0.35 \times 0.26$ mm
 Green

Data collection

Siemens SMART CCD diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.664$, $T_{\max} = 0.868$
 14 825 measured reflections

7172 independent reflections
 5177 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 25.02^\circ$
 $h = -11 \rightarrow 18$
 $k = -14 \rightarrow 10$
 $l = -28 \rightarrow 28$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.098$
 $S = 1.090$
 7172 reflections
 460 parameters
 H atoms: riding model
 $w = 1/[\sigma^2(F_o^2) + (0.0245P)^2 + 4.4211P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.387$ e Å⁻³
 $\Delta\rho_{\min} = -0.394$ e Å⁻³
 Extinction correction: none
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Mo1—C1	1.938 (5)	Mo2—C5	1.942 (5)
Mo1—C2	1.995 (5)	Mo2—C6	1.992 (6)
Mo1—C3	2.026 (6)	Mo2—C4	2.006 (5)
Mo1—O31	2.228 (3)	Mo2—O32	2.245 (3)
Mo1—S1	2.4527 (12)	Mo2—S1	2.4774 (12)
Mo1—S2	2.4809 (12)	Mo2—S2	2.4950 (13)
Mo1—Mo2	2.9115 (5)		
C1—Mo1—O31	175.5 (2)	C6—Mo2—S1	85.38 (14)
C2—Mo1—O31	100.5 (2)	C4—Mo2—S1	157.50 (14)
C3—Mo1—O31	87.8 (2)	O32—Mo2—S1	77.83 (8)
C1—Mo1—S1	98.9 (2)	C5—Mo2—S2	83.9 (2)
C2—Mo1—S1	82.72 (15)	C6—Mo2—S2	163.33 (15)
C3—Mo1—S1	158.9 (2)	C4—Mo2—S2	86.6 (2)
O31—Mo1—S1	77.95 (8)	O32—Mo2—S2	90.09 (8)
C1—Mo1—S2	85.99 (15)	S1—Mo2—S2	107.36 (4)
C2—Mo1—S2	164.8 (2)	C5—Mo2—Mo1	96.84 (15)
C3—Mo1—S2	87.12 (15)	C6—Mo2—Mo1	137.27 (14)
O31—Mo1—S2	92.01 (8)	C4—Mo2—Mo1	137.5 (2)
S1—Mo1—S2	108.60 (4)	O32—Mo2—Mo1	80.69 (8)
C1—Mo1—Mo2	93.22 (15)	S1—Mo2—Mo1	53.41 (3)
C2—Mo1—Mo2	135.55 (15)	S2—Mo2—Mo1	53.96 (3)
C3—Mo1—Mo2	139.60 (14)	C11—S1—Mo1	113.97 (15)
O31—Mo1—Mo2	82.34 (8)	C11—S1—Mo2	120.3 (2)
S1—Mo1—Mo2	54.20 (3)	Mo1—S1—Mo2	72.39 (3)
S2—Mo1—Mo2	54.41 (3)	C12—S2—Mo1	117.2 (2)
C5—Mo2—O32	173.9 (2)	C21—S2—Mo2	113.3 (2)
C6—Mo2—O32	103.4 (2)	Mo1—S2—Mo2	71.62 (3)
C4—Mo2—O32	84.8 (2)	C31—O31—Mo1	124.9 (3)
C5—Mo2—S1	105.29 (14)	C31—O32—Mo2	126.2 (3)

H atoms were all located theoretically and refined. Structure solution and refinement were carried out on an Indy workstation of a Silicon Graphics instrument with *SHELXTL/PC* (Sheldrick, 1994).

Data collection: *SMART* (Siemens, 1996). Cell refinement: local programs. Data reduction: *SAINT* (Siemens, 1994). Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXTL/PC* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1087). Services for accessing these data are described at the back of the journal.

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(–)-Sparteine Copper(II) Dinitrite†

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Abstract

The title complex, [Cu(NO₂)₂(C₁₅H₂₆N₂)], has been prepared and its crystal structure determined. The chiral nitrogen-chelating alkaloid (–)-sparteine acts as a bidentate ligand, reacting with one Cu^{II} ion in ethanol to form the title complex, with two nitrite groups occupying the remaining coordination sites to produce a distorted five-coordinate square-pyramidal structure. One nitrite is bound through one O atom and the other nitrite acts as a η²-chelating group.

Comment

Over the past two decades, several studies of transition metal complexes of the neutral alkaloid (–)-sparteine (C₁₅H₂₆N₂) have been reported (Boschmann *et al.*, 1974, 1978; Fraencel *et al.*, 1974; Childers *et al.*, 1975; Wroblewski & Long, 1977), and the crystal and molecular structures of some sparteine metal complexes of the type [MX₂(C₁₅H₂₆N₂)] have been determined (Togni *et al.*, 1990; Choi *et al.*, 1995).

Previously, we determined the crystal structure of (–)-sparteine copper(II) dinitrate, and found that molecules of this compound are mixed four- and five-coordinate in one crystalline phase and only four-coordinate in the other (Choi *et al.*, 1995). These results indicate the near electronic energy equivalence of four- and five-coordinate about Cu^{II} in this compound. This is a rare example of a pure compound which displays two different coordination numbers in the same crystalline structure.

The nitrite ion, like the nitrate ion, can coordinate to a metal in either a mono- or bidentate fashion, and we expected that (–)-sparteine copper(II) dinitrite, (I), might also exhibit similar structural features. However, the Cu^{II} ion in this complex is exclusively five-coordinate, with a highly distorted square-pyramidal geometry in

† Alternative name: {1,3,4,7,8,9,10,11,13,14,14a-dodecahydro-7,14-methano-2*H*,6*H*-dipyrido[1,2-*a*:1',2'-*e*][1,5]diazocine-*N,N'*}-dinitrito-*O,O'*-copper(II).