Crook, J. E., Elrington, M., Greenwood, N. N., Kennedy, J. D., Thornton-Pett, M. & Woollins, J. D. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2407–2414.
Crook, J. E., Elrington, M., Greenwood, N. N., Kennedy, J. D. & Woollins, J. D. (1984). *Polyhedron*, **3**, 901–904.
Elrington, M., Greenwood, N. N., Kennedy, J. D. & Thornton-Pett, M. (1984). *J. Chem. Soc. Chem. Commun.* pp. 1398–1399.
Kennedy, J. D. (1986). *Prog. Inorg. Chem.* **34**, 211–434.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1992). *TEXSAN. Crystal Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siedle, A. R. & Todd, L. J. (1976). *Inorg. Chem.* **15**, 2838–2842.
Ye, B.-H., Chen, X.-M., Zeng, T.-X. & Ji, L.-N. (1995). *Inorg. Chim. Acta*, **240**, 5–11.
Zsolnai, L. & Huttner, G. (1994). *ZORTEP. A Program for Molecular Graphics*. University of Heidelberg, Germany.

Acta Cryst. (1998). C**54**, 1815–1816

A Hetero-Tribridged Dinuclear Molybdenum Compound $[Bu_4N][Mo_2(CO)_6(p\text{-}Cl\text{-}C_6H_4S)_2Br]$

GUOHUA PAN, BOTAO ZHUANG* AND JIUTONG CHEN

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, State Key Laboratory of Structural Chemistry, Fuzhou, Fujian 350002, People's Republic of China. E-mail: zbt@ms.fjirsm.ac.cn

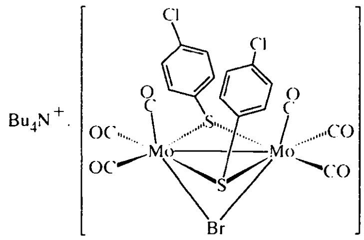
(Received 13 January 1998; accepted 29 May 1998)

Abstract

The title compound, tetra-*n*-butylammonium μ-bromo-bis(μ-*p*-chlorobenzenethiolato)bis(tricarbonylmolybdenum)(*Mo—Mo*), $(C_{16}H_{36}N)[Mo_2Br(C_6H_4ClS)_2(CO)_6]$, contains a Bu_4N^+ cation and an $[Mo_2(CO)_6(p\text{-}Cl\text{-}C_6H_4S)_2Br]^-$ anion. The structure of the anion can be viewed as a cofacial bi-octahedral dimer, in which two *fac*-$Mo(CO)_3$ fragments are bridged by two *p*-$Cl\text{-}C_6H_4S^-$ groups and one Br^- ligand. The mean Mo—Br distance is 2.765 (2) Å and the Mo—Br—Mo angle is 62.68 (4)°.

Comment

Low-valence dinuclear molybdenum–carbonyl complexes with thiolato bridges of the type $[Mo_2(CO)_8(SR)_2]$ were synthesized over a decade ago (Zhuang *et al.*, 1984; Smith *et al.*, 1987) by a convenient route. These complexes were found to undergo a reversible two-electron redox reaction in a single step, accompanied by formation/cleavage of a single metal–metal bond and significant rearrangement of the Mo_2S_2 core. The axial CO ligands of these complexes can be substituted by coordinating solvent molecules such as CH_3CN to afford solvent-substituted species, *i.e.* $[Mo_2(CO)_6(CH_3CN)_2(SR)_2]$. The structures of these complexes were subsequently determined (Zhuang *et al.*, 1989*a*,*b*, 1995). Herein, the title compound, $[Bu_4N][Mo_2(CO)_6(p\text{-}Cl\text{-}C_6H_4S)_2Br]$, (I), is taken account of as an additional member of this family.



(I)

The structure of the anion of the title compound is shown in Fig. 1. The geometry around each Mo atom is distorted octahedral, with one Br, three carbonyl C and two *p*-chlorobenzenethiolato S ligating atoms. Two *fac*-$Mo(CO)_3$ fragments are bridged by two *p*-$Cl\text{-}C_6H_4S$ ligands and one Br^- ion to form a hetero-tribridged cofacial bi-octahedral structure containing an approximately planar Mo_2S_2 unit. The two chlorobenzene groups are in a *syn* configuration relative to the Mo_2S_2 plane. The fact that the Mo—Mo distance [2.8761 (14) Å] is significantly shorter than that of

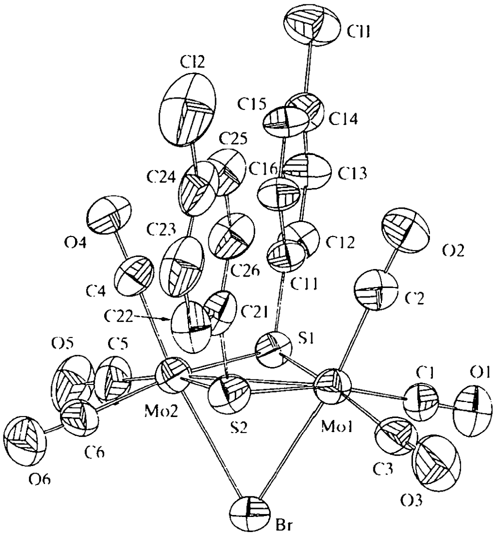


Fig. 1. View of the structure of the title complex anion with displacement ellipsoids shown at the 30% probability level.

$[Mo_2(CO)_8(SPh)_2]$, (II) [2.9624 (7) Å], and that the Mo—S—Mo angles are smaller than those of (II) [73.56 (3)°], indicate that the Mo_2S_2 unit contracts along the Mo—Mo bond direction on the introduction of a Br bridge. Interestingly, the Mo—S bonds are not influenced by the Br bridge and the electron-withdrawing character of the Cl substituent; the mean Mo—S distance [2.471 (3) Å] of (I) is very similar to that of (II) [2.474 (1) Å]. In contrast with (II), the axial Mo—C distances in (I) are shorter than the equatorial Mo—C distances due to different *trans* effects. The mean Mo—Br distance is longer than the sum of the respective covalent radii (Br 1.14 and Mo 1.32 Å; Aylward & Findly, 1974), and the Mo—Br—Mo angle is markedly acute [62.68 (4)°]. This suggests weak coordination between Mo and Br.

Experimental

The title compound was synthesized by the reaction of $[Mo_2(CO)_8(p\text{-}Cl\text{-}C_6H_4S)_2]$ with Bu_4NBr (1:1) in acetone, and was crystallized from ^{i}PrOH on standing for several days below a temperature of 273 K.

Crystal data

$(C_{16}H_{36}N)[Mo_2Br(C_6H_4ClS)_2(CO)_6]$
$M_r = 969.55$
Monoclinic
$P2_1/c$
$a = 9.5700 (3)$ Å
$b = 20.2292 (7)$ Å
$c = 22.1484 (5)$ Å
$\beta = 100.122 (1)°$
$V = 4221.0 (2)$ Å^3
$Z = 4$
$D_x = 1.526$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3782 reflections
$\theta = 1.37–25.04°$
$\mu = 1.806$ mm^{-1}
$T = 293 (2)$ K
Needle
0.80 × 0.09 × 0.07 mm
Black

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.456$, $T_{max} = 0.908$
14 180 measured reflections

7399 independent reflections
2630 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$
$\theta_{max} = 25.04°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 24$
$l = -13 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.250$
$S = 0.886$
7377 reflections
433 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1218P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.006$
$\Delta\rho_{max} = 0.856$ e Å^{-3}
$\Delta\rho_{min} = -0.791$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Mo1—C2	1.894 (14)	Mo2—C4	1.881 (14)
Mo1—C3	1.966 (13)	Mo2—C5	1.98 (2)
Mo1—C1	1.994 (15)	Mo2—C6	2.00 (2)
Mo1—S1	2.475 (3)	Mo2—S1	2.454 (3)
Mo1—S2	2.486 (3)	Mo2—S2	2.468 (3)
Mo1—Br	2.7604 (15)	Mo2—Br	2.769 (2)
Mo1—Mo2	2.8761 (14)		
S1—Mo1—S2	107.62 (11)	S1—Mo2—Mo1	54.65 (7)
S1—Mo1—Br	75.74 (8)	S2—Mo2—Mo1	54.82 (8)
S2—Mo1—Br	75.68 (8)	Br—Mo2—Mo1	58.51 (4)
Br—Mo1—Mo2	58.80 (4)	Mo1—Br—Mo2	62.68 (4)
S1—Mo2—S2	108.92 (11)	Mo2—S1—Mo1	71.40 (9)
S1—Mo2—Br	75.91 (8)	Mo2—S2—Mo1	70.98 (9)
S2—Mo2—Br	75.81 (8)		

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. The large crystal could not wholly dip in the homogeneous area of the X-ray beam. The inhomogeneous irradiation and the empirical nature of the absorption correction probably led to the high $wR(F^2)$ value. H atoms were located theoretically and refined.

Data collection: *SMART* (Siemens, 1996). Cell refinement: local programs. Data reduction: *SAINT* (Siemens, 1994). Programs used to solve structure: *SHELXTL* (Sheldrick, 1990). Programs used to refine structure: *SHELXTL*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXTL* and local programs.

We are grateful to NNSF and SKLSC for financial support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1177). Services for accessing these data are described at the back of the journal.

References

Aylward, G. H. & Findly, T. J. V. (1974). In *SI Chemical Data*, 2nd ed. New York: John Wiley.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1990). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994). *SAINT Software Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART Software Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Smith, D. A., Zhuang, B., Newton, W. E., McDonald, J. W. & Schultz, F. A. (1987). *Inorg. Chem.* **26**, 2524–2531.
Zhuang, B., Huang, L. & He, L. (1995). *Chin. J. Struct. Chem.* **14**, 359–363.
Zhuang, B., Huang, L., He, L., Yang, Y. & Lu, J. (1989*a*). *Inorg. Chim. Acta*, **157**, 85–90.
Zhuang, B., Huang, L., He, L., Yang, Y. & Lu, J. (1989*b*). *Acta Chim. Sin.* **47**, 25–30.
Zhuang, B., McDonald, J. W., Schultz, F. A. & Newton, W. E. (1984). *Organometallics*, **3**, 943–945.