

refined with isotropic displacement parameters. A weighting scheme of type  $w = w_1.w_2$  with  $w_1 = k_1/(a + b|F_o|)^2$  and  $w_2 = k_2/(c + d\sin\theta/\lambda)$  was used to obtain flat dependence in  $\langle w\Delta^2F \rangle$  versus  $\langle F_o \rangle$  and versus  $\langle \sin\theta/\lambda \rangle$  (PESOS; Martínez-Ripoll & Cano, 1975); the coefficients used are  $k_1 = 0.582$ ;  $k_2 = 1.036$ ;  $a = 3.468$ ,  $b = 0.449$  for  $|F_o| \leq 1.28$ ;  $a = 4.098$ ,  $b = -0.177$  for  $1.28 < |F_o| \leq 5.47$ ;  $a = 2.551$ ,  $b = 0.092$  for  $5.47 < |F_o| \leq 10.92$ ;  $a = 5.082$ ,  $b = -0.1374$  for  $10.92 < |F_o| \leq 21.28$ ;  $a = 2.048$ ,  $b = 0.0094$  for  $21.28 < |F_o| \leq 66.45$ ;  $a = 1.049$ ,  $b = 0.028$  for  $|F_o| > 66.45$ ;  $c = 4.446$ ,  $d = -11.415$  for  $\sin\theta/\lambda \leq 0.33$ ;  $c = 0.216$ ,  $d = 1.792$  for  $0.33 < \sin\theta/\lambda \leq 0.44$ ;  $c = 2.253$ ,  $d = -2.904$  for  $0.44 < \sin\theta/\lambda \leq 0.51$ ;  $c = 0.071$ ,  $d = 1.556$  for  $\sin\theta/\lambda > 0.51$ . Non-H atoms were refined anisotropically. H atoms were calculated geometrically at their expected positions and included as fixed contributors. Most calculations were carried out using the XRAY76 system (Stewart *et al.*, 1976) running on a MicroVAX 3800 computer. Geometric calculations were performed using PARST (Nardelli, 1983).

PR, ASJ, AL and JMG-Z are grateful for financial assistance from UPV/EHU (grant No. 160.310-EA166/92). ASJ acknowledges financial support from the Departamento de Educación, Universidades e Investigación del Gobierno Vasco (grant No. BF190.134 Modalidad AE).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AL1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Abrahams, S. C. (1967). *J. Chem. Phys.* **46**, 2052–2063.  
 Abrahams, S. C., Bernstein, J. L. & Jamieson, P. B. (1968). *J. Chem. Phys.* **48**, 2619–2629.  
 Abrahams, S. C. & Reddy, J. M. (1965). *J. Chem. Phys.* **43**, 2533–2543.  
 Barakin, V. V., Klevtsova, R. F. & Gaponenko, L. A. (1982). *Kristallografiya*, **27**, 38–42.  
 Bensch, W., Hug, P., Emmenegger, R., Reller, A. & Oswald, H. R. (1987). *Mater. Res. Bull.* **22**, 447–454.  
 Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, Univ. of Nijmegen, The Netherlands.  
 Clearfield, A., Moini, A. & Rudolf, P. R. (1985). *Inorg. Chem.* **24**, 4606–4609.  
 Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.  
 Gatehouse, B. M. & Leverett, P. (1969). *J. Chem. Soc. A*, pp. 849–854.  
 Gonschorek, V. W. & Hahn, T. (1973). *Z. Kristallogr.* **138**, 167–176.  
 Hazen, R. M., Finger, L. W. & Mariathasan, J. W. E. (1985). *J. Phys. Chem. Solids*, **46**, 253–263.  
 Huyghe, P. M., Lee, M.-R., Quarton, M. & Robert, F. (1991). *Acta Cryst.* **C47**, 244–246, 1797–1799.  
 Jeitschko, W. (1972). *Acta Cryst.* **B28**, 60–76.  
 Jeitschko, W. (1973). *Acta Cryst.* **B29**, 2074–2081.  
 Klevtsova, R. F., Kozeva, L. P. & Klevtsov, P. V. (1976). *Sov. Phys. Crystallogr.* **20**, 571–574.

- Lii, K. H., Wang, C. C., Chiang, R. K. & Wang, S. L. (1989). *J. Solid State Chem.* **80**, 144–148.  
 Martínez-Ripoll, M. & Cano, F. H. (1975). *PESOS. Program for the Automatic Treatment of Weighting Schemes for Least-Squares Refinement*. Instituto Rocasolano, Madrid, Spain.  
 Matsumoto, K., Kobayashi, A. & Sasaki, Y. (1975). *Bull. Chem. Soc. Jpn.*, **48**, 1009–1013.  
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.  
 Ozeki, T., Ichida, H. & Sasaki, Y. (1987). *Acta Cryst.* **C43**, 2220–2221.  
 Román, P., San José, A., Aranzabe, A. & Luque, A. (1992). *Thermochim. Acta*, **206**, 137–147.  
 Román, P., San José, A., Luque, A. & Gutiérrez-Zorrilla, J. M. (1993). *Z. Kristallogr.* **204**, 179–191.  
 Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.  
 Steiner, T. & Saenger, W. (1993). *J. Am. Chem. Soc.* **115**, 4540–4547.  
 Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY76 System*. Technical Report TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.  
 Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.  
 Thiele, A. & Fuchs, J. (1979). *Z. Naturforsch. Teil B*, **34**, 145–154.  
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1994). **C50**, 1191–1193

## A Pyridine-2-thiolato Molybdenum Complex

PEIHUA YU, LIANGREN HUANG AND BOTAO ZHUANG\*

*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*

(Received 10 June 1993; accepted 3 December 1993)

### Abstract

The coordination polyhedra of the two molybdenum(0) atoms in tetraethylammonium nonacarbonyl- $1\kappa^5C_2\kappa^4C-\mu$ -(pyridine-2-thiolato-1:2 $\kappa^2S$ ,-2 $\kappa^1N$ )-dimolybdate,  $(C_8H_{20}N)[Mo_2(\mu-C_5H_4NS)(CO)_9]$  are distorted octahedra which share an S atom from a pyridine-2-thiolato ligand. The Mo...Mo distance is 4.5609 (7) Å.

### Comment

Molybdenum complexes containing Mo—S and Mo—N bonds are of special interest because of their relevance to a variety of molybdenum-containing enzymes (Cramer, Hodgson, Gillum & Mortenson, 1978) and hydrodesulfurization catalysts (Anzenhofer & de Boer, 1969). To our knowledge,

molybdenum complexes containing Mo—S and Mo—N bonds involving a pyridine-2-thiolato (pyS) moiety as a mixed bidentate (*N,S*) ligand have not been reported in the literature, although many Group VII and Group VIII metal complexes with pyS ligands are known (Demming, Meah, Bates & Hursthouse, 1988; Oro, Ciriano, Viguri, Tiripicchio, Tiripicchio-Camellini & Lahoz, 1986). During our studies of molybdenum-sulfur complexes with molybdenum in a low oxidation state, we obtained several complexes with pyS in different coordination modes. Here we report the synthesis and X-ray crystal structure of the title compound, (I), in which pyS is in a bridging five-electron-donating mode of coordination.

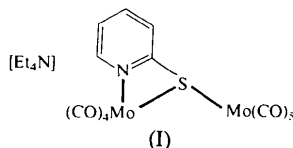


Fig. 1 shows an ORTEP (Johnson, 1965) drawing with the atom-labelling scheme for the anion of the title compound. Both Mo atoms are in an oxidation state of zero with distorted octahedral coordination and are bridged by one S atom. Mo(1) is coordinated by an N and an S atom from the ligand pyS and by four CO ligands, Mo(2) is coordinated by an S atom and five CO ligands; the Mo...Mo distance is 4.5609 (7) Å, indicating no significant metal-metal interaction. The bond distance Mo(1)—S [2.617 (1) Å] is longer than Mo(2)—S [2.582 (1) Å], implying a lower electron density at the Mo(2) atom. This is obviously due to the unequal electron contribution of the five-electron-donor pyS ligand to the two Mo atoms, and a somewhat greater electron back-donation to the  $\pi^*$  orbitals of the CO ligands from Mo(2) because of their greater number.

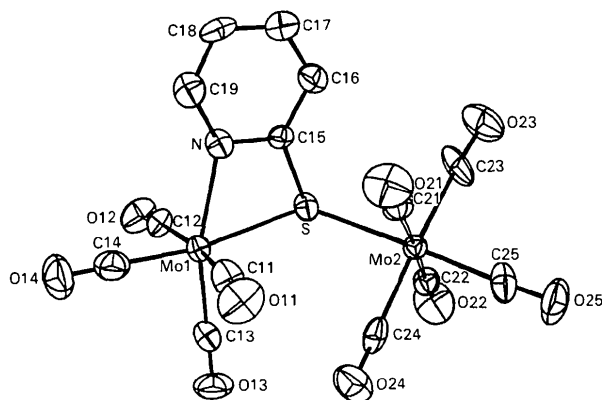


Fig. 1. ORTEP (Johnson, 1965) drawing of  $[Mo_2(CO)_9(C_5H_4NS)]^-$ . H atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

## Experimental

The title complex was prepared by the reaction of  $Mo(CO)_6$  with pySH, NaOMe and  $Et_4NCl$  (in 1:1:1:1 molar ratio) in tetrahydrofuran at 318–323 K under a nitrogen atmosphere. Single crystals suitable for X-ray diffraction were obtained by recrystallization from tetrahydrofuran-ethanol solution.

### Crystal data

$(C_8H_{20}N)-$   
 $[Mo_2(C_5H_4NS)(CO)_9]$   
 $M_r = 684.39$   
Monoclinic  
 $C2/c$   
 $a = 23.571$  (5) Å  
 $b = 7.868$  (1) Å  
 $c = 30.518$  (9) Å  
 $\beta = 97.33$  (2)°  
 $V = 5613.4$  Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.62$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069$  Å  
Cell parameters from 20 reflections  
 $\theta = 5-15^\circ$   
 $\mu = 0.99$  mm<sup>-1</sup>  
 $T = 296$  K  
Plate  
 $0.70 \times 0.60 \times 0.40$  mm  
Reddish orange

### Data collection

MSC/Rigaku diffractometer  
 $\omega/2\theta$  scans [speed  
 $16^\circ$  min<sup>-1</sup>, width  
 $(1.80 + 0.35 \tan \theta)^\circ$ ]  
Absorption correction:  
DIFABS (Walker &  
Stuart, 1983)  
 $T_{min} = 0.70$ ,  $T_{max} = 1.19$   
5488 measured reflections  
5343 independent reflections  
3715 observed reflections  
 $[I > 3.0\sigma(I)]$

$R_{int} = 0.029$   
 $\theta_{max} = 25^\circ$   
 $h = 0 \rightarrow 28$   
 $k = 0 \rightarrow 9$   
 $l = -36 \rightarrow 35$   
3 standard reflections  
monitored every 250  
reflections  
intensity variation: 3.0%

### Refinement

Refinement on  $F$   
 $R = 0.056$   
 $wR = 0.059$   
 $S = 2.73$   
3715 reflections  
325 parameters  
H-atom parameters not  
refined  
 $w = 1/[\sigma^2(F_o^2) + (0.01F_o)^2 + 1.0]$

$(\Delta/\sigma)_{max} = 0.18$   
 $\Delta\rho_{max} = 1.04$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -1.14$  e Å<sup>-3</sup>  
Atomic scattering factors  
from *International Tables*  
for X-ray Crystallography  
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

	$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			$B_{eq}$
	x	y	z	
Mo(1)	0.63359 (3)	-0.09923 (9)	0.56231 (2)	2.76 (1)
Mo(2)	0.61653 (3)	0.13521 (9)	0.69668 (2)	2.58 (1)
S	0.60637 (8)	-0.1188 (3)	0.64266 (5)	3.05 (4)
O(11)	0.7219 (3)	0.2050 (9)	0.5768 (2)	5.8 (2)
O(12)	0.5469 (3)	-0.3941 (9)	0.5275 (2)	5.4 (2)
O(13)	0.5420 (3)	0.1679 (9)	0.5246 (2)	5.7 (2)
O(14)	0.6779 (3)	-0.124 (1)	0.4708 (2)	6.2 (2)
O(21)	0.7512 (2)	0.125 (1)	0.6952 (2)	6.5 (2)
O(22)	0.4814 (3)	0.148 (1)	0.6942 (2)	7.0 (2)
O(23)	0.6239 (3)	-0.099 (1)	0.7808 (2)	6.0 (2)
O(24)	0.6016 (3)	0.3951 (9)	0.6152 (2)	5.8 (2)
O(25)	0.6256 (3)	0.4440 (9)	0.7613 (2)	6.9 (2)

N	0.6879 (3)	-0.2770 (8)	0.6097 (2)	2.8 (1)
C(11)	0.6905 (3)	0.097 (1)	0.5747 (3)	3.8 (2)
C(12)	0.5772 (3)	-0.300 (1)	0.5415 (2)	3.6 (2)
C(13)	0.5760 (4)	0.069 (1)	0.5378 (2)	4.4 (2)
C(14)	0.6619 (4)	-0.121 (1)	0.5058 (3)	4.4 (2)
C(15)	0.6677 (3)	-0.250 (1)	0.6490 (2)	3.0 (2)
C(16)	0.6934 (3)	-0.321 (1)	0.6873 (2)	3.4 (2)
C(17)	0.7379 (4)	-0.431 (1)	0.6849 (3)	4.6 (2)
C(18)	0.7568 (4)	-0.466 (1)	0.6447 (3)	4.3 (2)
C(19)	0.7316 (3)	-0.383 (1)	0.6084 (3)	3.3 (2)
C(21)	0.7031 (3)	0.127 (1)	0.6960 (2)	3.0 (1)
C(22)	0.5304 (3)	0.139 (1)	0.6953 (2)	3.7 (2)
C(23)	0.6212 (4)	-0.026 (1)	0.7495 (2)	4.7 (2)
C(24)	0.6083 (3)	0.304 (1)	0.6433 (3)	3.6 (2)
C(25)	0.6218 (4)	0.332 (1)	0.7381 (3)	4.7 (2)
N(3)	0.4101 (3)	0.3603 (9)	0.1050 (2)	3.4 (1)
C(31)	0.3606 (3)	0.426 (1)	0.1280 (3)	4.7 (2)
C(32)	0.3580 (5)	0.620 (1)	0.1301 (3)	6.9 (3)
C(33)	0.4058 (4)	0.166 (1)	0.1067 (3)	4.7 (2)
C(34)	0.4515 (4)	0.066 (1)	0.0870 (3)	5.5 (3)
C(35)	0.4680 (4)	0.419 (1)	0.1274 (3)	5.0 (2)
C(36)	0.4825 (4)	0.378 (1)	0.1756 (3)	4.9 (2)
C(37)	0.4050 (4)	0.420 (1)	0.0575 (3)	4.7 (2)
C(38)	0.3483 (4)	0.380 (2)	0.0290 (3)	6.4 (3)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Mo(1)···Mo(2)	4.5609 (7)	O(21)—C(21)	1.136 (6)
Mo(1)—S	2.617 (1)	O(14)—C(14)	1.180 (6)
Mo(1)—N	2.284 (4)	O(13)—C(13)	1.153 (8)
Mo(1)—C(11)	2.052 (6)	O(12)—C(12)	1.079 (6)
Mo(1)—C(12)	2.109 (6)	O(22)—C(22)	1.153 (6)
Mo(1)—C(13)	1.974 (7)	O(23)—C(23)	1.111 (6)
Mo(1)—C(14)	1.934 (5)	O(24)—C(24)	1.110 (7)
Mo(2)—S	2.582 (1)	O(25)—C(25)	1.128 (7)
Mo(2)—C(21)	2.046 (6)	N—C(15)	1.361 (6)
Mo(2)—C(22)	2.025 (6)	N—C(19)	1.330 (6)
Mo(2)—C(23)	2.043 (6)	C(15)—C(16)	1.367 (7)
Mo(2)—C(24)	2.094 (7)	C(16)—C(17)	1.370 (7)
Mo(2)—C(25)	1.991 (6)	C(17)—C(18)	1.387 (8)
S—C(15)	1.765 (5)	C(18)—C(19)	1.353 (7)
O(11)—C(11)	1.121 (6)		
S—Mo(1)—N	63.6 (1)	C(22)—Mo(2)—C(25)	89.1 (2)
S—Mo(1)—C(11)	96.1 (1)	C(23)—Mo(2)—C(24)	177.5 (2)
S—Mo(1)—C(12)	91.0 (1)	C(23)—Mo(2)—C(25)	89.3 (3)
S—Mo(1)—C(13)	99.0 (1)	C(24)—Mo(2)—C(25)	89.6 (2)
S—Mo(1)—C(14)	169.6 (2)	Mo(1)—S—Mo(2)	122.59 (6)
N—Mo(1)—C(11)	92.5 (2)	Mo(1)—S—C(15)	80.9 (1)
N—Mo(1)—C(12)	90.8 (2)	Mo(2)—S—C(15)	112.0 (2)
N—Mo(1)—C(13)	162.5 (2)	Mo(1)—N—C(15)	103.3 (4)
N—Mo(1)—C(14)	106.3 (3)	Mo(1)—N—C(19)	137.7 (3)
C(11)—Mo(1)—C(12)	173.0 (2)	C(15)—N—C(19)	119.0 (5)
C(11)—Mo(1)—C(13)	88.1 (2)	Mo(1)—C(11)—O(11)	172.7 (5)
C(11)—Mo(1)—C(14)	86.6 (2)	Mo(1)—C(12)—O(12)	173.4 (6)
C(12)—Mo(1)—C(13)	90.7 (2)	Mo(1)—C(13)—O(13)	178.2 (5)
C(12)—Mo(1)—C(14)	86.2 (2)	Mo(1)—C(14)—O(14)	175.5 (7)
C(13)—Mo(1)—C(14)	91.2 (2)	S—C(15)—N	111.8 (3)
S—Mo(2)—C(21)	89.0 (1)	S—C(15)—C(16)	126.9 (4)
S—Mo(2)—C(22)	89.2 (2)	N—C(15)—C(16)	121.4 (5)
S—Mo(2)—C(23)	90.9 (2)	C(15)—C(16)—C(17)	118.2 (5)
S—Mo(2)—C(24)	90.2 (1)	C(16)—C(17)—C(18)	120.4 (5)
S—Mo(2)—C(25)	178.4 (2)	C(17)—C(18)—C(19)	118.3 (5)
C(21)—Mo(2)—C(22)	178.0 (2)	N—C(19)—C(18)	122.5 (5)
C(21)—Mo(2)—C(23)	92.1 (3)	Mo(2)—C(21)—O(21)	179.1 (4)
C(21)—Mo(2)—C(24)	90.2 (2)	Mo(2)—C(22)—O(22)	177.1 (6)
C(21)—Mo(2)—C(25)	92.7 (2)	Mo(2)—C(23)—O(23)	173.1 (6)
C(22)—Mo(2)—C(23)	88.8 (2)	Mo(2)—C(24)—O(24)	176.9 (6)
C(22)—Mo(2)—C(24)	89.0 (3)	Mo(2)—C(25)—O(25)	178.9 (5)

The crystal was mounted on a glass fibre in a random orientation for preliminary examination. The structure was solved by direct methods. Three atoms (two Mo atoms and an S atom) were located from an *E* map and the remaining atoms were found in the succeeding difference Fourier syntheses. H atoms were located and were included in the structure-factor calculations, but their positions were not refined. The

structure was refined using a full-matrix least-squares method in which the function minimized was  $\sum w(|F_o| - |F_c|)^2$  and the weight *w* was defined as per Killean & Lawrence (1969) with terms of 0.010 and 1.0. Scattering factors were taken from Cromer & Waber (1974). Calculations were performed on a VAX computer using *SDP/VAX* (Frenz, 1978).

The financial support of NNSF and NSFCAS is greatly acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: L11070). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Anzenhofer, K. & de Boer, J. J. (1969). *Acta Cryst.* **B25**, 1419–1420.
- Cramer, S. P., Hodgson, K. O., Gillum, W. O. & Mortenson, L. E. (1978). *J. Am. Chem. Soc.* **100**, 3398–3407.
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Demming, A., Meah, M. N., Bates, P. A. & Hursthouse, M. B. (1988). *J. Chem. Soc. Dalton Trans.* pp. 235–238.
- Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 SDP - A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* **B25**, 1750–1752.
- Oro, L. A., Ciriano, M. A., Viguri, F., Tiripicchio, A., Tiripicchio-Camellini, M. & Lahoz, F. J. (1986). *Nouv. J. Chem.* **10**, 75–78.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1994). **C50**, 1193–1196

## A Pseudo-Octahedral Tungsten Oxo Compound, $[\text{WO}(\text{C}_{18}\text{H}_{12}\text{O})(\text{C}_{13}\text{H}_{13}\text{P})_3]\cdot\text{C}_7\text{H}_8$

JUDITH L. KERSCHNER, CHARLES E. KRILEY,  
PHILLIP E. FANWICK AND IAN P. ROTHWELL\*

*Department of Chemistry, 1393 Brown Building,  
Purdue University, West Lafayette, IN 47907-1393,  
USA*

(Received 24 February 1993; accepted 6 January 1994)

### Abstract

The compound tris(diphenylmethylphosphine)oxo-[1,1':3',1''-terphenyl-2'-olato(2-)- $\text{C}^2\text{O}$ ]tungsten(IV) toluene solvate contains one cyclometallated 2',6-di-