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Structure of 1,3-μ_2-Acetato-2-(acetonitrile)-μ_3-sulfido-tris[(diethyl dithiophosphate-S,S')-μ_2-sulfido-molybdenum(IV)](3 Mo–Mo)

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Abstract. [Mo$_3$S$_4$(C$_2$H$_3$N)(C$_2$H$_3$O$_2$)(C$_4$H$_{10}$O$_2$PS$_2$)$_3$], $M_r = 1072$, triclinic, $P\bar{1}$, $a = 12\cdot877$ (3), $b = 12\cdot954$ (3), $c = 12\cdot807$ (3) Å, $\alpha = 108\cdot70$ (2), $\beta = 102\cdot05$ (2), $\gamma = 71\cdot62$ (2)°, $V = 1906\cdot5$ Å^3, $Z = 2$, $D_x = 1\cdot87$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 16\cdot4$ cm^{-1}, $F(000) = 1068$, $R = 0\cdot045$ for 3148 unique observed reflections [$I \geq 3\sigma(I)$]. The Mo atoms are all octahedrally coordinated by two μ_2-S atoms (Mo—μ_2-S av. 2·284 Å), a μ_3-S atom (Mo—μ_3-S av. 2·334 Å) and a chelating S$_2$P(OC$_2$H$_5$)$_2$ terminal ligand [Mo—S, 2·537 Å]. In addition, Mo(1) and Mo(3) are coordinated by a bridging CH$_3$COO ligand (Mo—O$_b$ 2·197 Å), while Mo(2) is coordinated by a CH$_3$CN molecule (Mo—N 2·232 Å). There are three Mo—Mo bonds [Mo(1)—Mo(2) 2·763, Mo(1)—Mo(3) 2·682, Mo(2)—Mo(3) 2·743 Å] in the [Mo$_3$S$_4$]$^{4+}$ cluster core, which has an incomplete cubane-like structure.

Experimental. Crystals of the title compound were prepared by the method described by Wu, Lu, Zhu, Wu & Lu (1987). Crystal 0·25 × 0·20 × 0·25 mm. Data were collected using an AFC four-circle diffractometer and Mo $K\alpha$ radiation at *ca* 296 K. $\omega/2\theta$
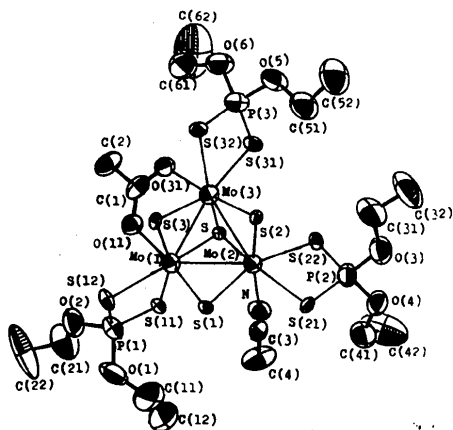
scan, scan speed varied from 3 to 5° min^{-1} (in ω); the scan width was (0·60 + 0·35tanθ)°. Cell constants were obtained by least-squares analysis of 25 diffraction maxima with $26 \leq \theta \leq 27°$. A total of 7080 intensities up to a maximum 2θ of 50° ($0 < h < 12$, $-12 < k < 12$, $-12 < l < 12$) were measured. Max. (sinθ)/$\lambda = 0\cdot59$ Å^{-1}; 3832 reflections with $I < 3\sigma(I)$ were considered unobserved. 3148 reflections with $I \geq 3\sigma(I)$ used in the refinement. Three standard reflections were measured periodically, no random

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Mo(1)	0·2937 (1)	0·2709 (1)	0·9489 (1)	3·27 (3)
Mo(2)	0·1427 (1)	0·2770 (1)	1·0772 (1)	3·09 (2)
Mo(3)	0·2419 (1)	0·4485 (1)	1·1258 (1)	3·20 (3)
S	0·3299 (3)	0·2637 (2)	1·1336 (2)	1·40 (7)
S(1)	0·1251 (3)	0·2353 (3)	0·8879 (3)	1·86 (8)
S(2)	0·0574 (3)	0·4653 (2)	1·1132 (3)	1·52 (7)
S(3)	0·2282 (3)	0·4558 (3)	0·9474 (3)	1·78 (8)
S(11)	0·4177 (3)	0·0705 (3)	0·9021 (3)	2·19 (8)
S(12)	0·3187 (3)	0·2357 (3)	0·7463 (3)	3·03 (9)
S(21)	−0·0488 (3)	0·2452 (3)	1·0550 (3)	2·34 (8)
S(22)	0·1307 (3)	0·2640 (3)	1·2686 (3)	2·50 (9)
S(31)	0·2835 (3)	0·5000 (3)	1·3339 (3)	2·69 (9)
S(32)	0·1996 (3)	0·6632 (3)	1·1752 (3)	2·66 (9)
N	0·2014 (9)	0·0900 (8)	1·0508 (8)	4·6 (3)
O(11)	0·4569 (6)	0·3081 (6)	0·9866 (7)	4·1 (2)
O(31)	0·4089 (6)	0·4596 (6)	1·1385 (6)	4·0 (2)
P(1)	0·4061 (3)	0·0807 (3)	0·7483 (3)	4·6 (1)
P(2)	−1·0217 (3)	0·2487 (3)	1·2144 (3)	4·25 (9)
P(3)	0·2413 (3)	0·6620 (3)	1·3332 (3)	4·6 (1)
O(1)	0·364 (1)	−0·0167 (8)	0·6605 (7)	7·4 (3)
O(2)	0·5191 (8)	0·0613 (8)	0·7065 (8)	6·9 (3)
O(3)	−0·1090 (8)	0·3423 (8)	1·2881 (8)	6·5 (3)
O(4)	−0·0453 (8)	0·1470 (7)	1·2372 (7)	5·9 (2)
O(5)	0·1490 (8)	0·7373 (7)	1·4092 (7)	5·7 (3)
O(6)	0·3316 (8)	0·7233 (8)	1·3965 (8)	6·3 (3)
C(1)	0·475 (1)	0·3912 (9)	1·069 (1)	4·4 (3)
C(2)	0·592 (1)	0·411 (1)	1·084 (1)	6·0 (4)
C(3)	0·242 (1)	−0·003 (1)	1·035 (1)	5·3 (4)
C(4)	0·299 (1)	−0·131 (1)	1·018 (2)	7·8 (6)
C(11)	0·270 (1)	−0·054 (2)	0·671 (2)	9·2 (6)
C(12)	0·311 (2)	−0·169 (1)	0·689 (2)	10·2 (6)
C(21)	0·604 (2)	−0·047 (2)	0·684 (2)	9·3 (6)
C(22)	0·651 (2)	−0·056 (2)	0·587 (2)	16 (1)
C(31)	−0·118 (2)	0·466 (1)	1·314 (1)	8·2 (5)
C(32)	−0·176 (2)	0·522 (2)	1·404 (2)	12·0 (7)
C(41)	0·013 (2)	0·027 (1)	1·184 (1)	7·6 (5)
C(42)	0·058 (2)	−0·029 (2)	1·270 (2)	13 (1)
C(51)	0·041 (1)	0·710 (1)	1·385 (1)	7·7 (6)
C(52)	−0·034 (2)	0·802 (2)	1·460 (2)	9·7 (7)
C(61)	0·440 (1)	0·691 (2)	1·356 (2)	8·7 (6)
C(62)	0·524 (2)	0·664 (3)	1·451 (2)	17 (1)

Fig. 1. Drawing of the title compound with thermal ellipsoids.

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

Mo(1)—Mo(2)	2·7632 (8)	S(31)—P(3)	1·998 (3)
Mo(1)—Mo(3)	2·6817 (9)	S(32)—P(3)	1·987 (3)
Mo(1)—S	2·340 (2)	N—C(3)	1·12 (1)
Mo(1)—S(1)	2·286 (3)	O(11)—C(1)	1·28 (1)
Mo(1)—S(3)	2·280 (2)	O(31)—C(1)	1·283 (9)
Mo(1)—S(11)	2·537 (2)	P(1)—O(1)	1·553 (6)
Mo(1)—S(12)	2·560 (2)	P(1)—O(2)	1·574 (7)
Mo(1)—O(11)	2·225 (5)	P(2)—O(3)	1·572 (5)
Mo(2)—Mo(3)	2·7425 (8)	P(2)—O(4)	1·565 (5)
Mo(2)—S	2·336 (2)	P(3)—O(5)	1·566 (5)
Mo(2)—S(1)	2·286 (2)	P(3)—O(6)	1·554 (6)
Mo(2)—S(2)	2·273 (2)	O(1)—C(11)	1·49 (1)
Mo(2)—S(21)	2·571 (3)	O(2)—C(21)	1·47 (2)
Mo(2)—S(22)	2·549 (2)	O(3)—C(31)	1·49 (1)
Mo(2)—N	2·232 (6)	O(4)—C(41)	1·49 (2)
Mo(3)—S	2·327 (2)	O(5)—C(51)	1·49 (2)
Mo(3)—S(2)	2·293 (2)	O(6)—C(61)	1·47 (1)
Mo(3)—S(3)	2·285 (2)	C(1)—C(2)	1·57 (2)
Mo(3)—S(31)	2·514 (3)	C(3)—C(4)	1·56 (1)
Mo(3)—S(32)	2·549 (2)	C(11)—C(12)	1·48 (2)
Mo(3)—O(31)	2·169 (5)	C(21)—C(22)	1·46 (1)
S(11)—P(1)	1·989 (3)	C(31)—C(32)	1·38 (1)
S(12)—P(1)	1·974 (3)	C(41)—C(42)	1·45 (1)
S(21)—P(2)	1·987 (3)	C(51)—C(52)	1·47 (1)
S(22)—P(2)	1·990 (3)	C(61)—C(62)	1·50 (2)

Mo(2)—Mo(1)—Mo(3)	60·47 (2)	Mo(1)—S—Mo(3)	70·15 (5)
S—Mo(1)—S(1)	104·60 (7)	Mo(2)—S—Mo(3)	72·05 (5)
S—Mo(1)—S(3)	108·38 (7)	Mo(1)—S(1)—Mo(2)	74·36 (6)
S—Mo(1)—S(11)	86·55 (6)	Mo(2)—S(2)—Mo(3)	73·84 (6)
S—Mo(1)—S(12)	161·05 (7)	Mo(1)—S(3)—Mo(3)	71·96 (6)
S—Mo(1)—O(11)	82·8 (1)	Mo(1)—S(11)—P(1)	87·85 (9)
S(1)—Mo(1)—S(3)	93·55 (8)	Mo(1)—S(12)—P(1)	87·55 (9)
S(1)—Mo(1)—S(11)	100·01 (8)	Mo(2)—S(21)—P(2)	87·81 (9)
S(1)—Mo(1)—S(12)	88·23 (7)	Mo(2)—S(22)—P(2)	88·34 (9)
S(1)—Mo(1)—O(11)	172·6 (1)	Mo(3)—S(31)—P(3)	88·18 (9)
S(3)—Mo(1)—S(11)	156·70 (8)	Mo(3)—S(32)—P(3)	87·45 (9)
S(3)—Mo(1)—S(12)	84·23 (7)	Mo(2)—N—C(3)	171·5 (6)
S(3)—Mo(1)—O(11)	83·7 (1)	Mo(1)—O(11)—C(1)	120·6 (5)
S(11)—Mo(1)—S(12)	77·39 (7)	Mo(3)—O(31)—C(1)	121·6 (5)
S(11)—Mo(1)—O(11)	80·5 (1)	S(11)—P(1)—S(12)	107·0 (1)
S(12)—Mo(1)—O(11)	84·7 (1)	S(11)—P(1)—O(1)	112·0 (3)
Mo(1)—Mo(2)—Mo(3)	58·30 (2)	S(11)—P(1)—O(2)	115·0 (3)
S—Mo(2)—S(1)	104·76 (7)	S(12)—P(1)—O(1)	116·1 (3)
S—Mo(2)—S(2)	105·59 (7)	S(12)—P(1)—O(2)	106·7 (3)
S—Mo(2)—S(21)	160·66 (7)	O(1)—P(1)—O(2)	100·1 (4)
S—Mo(2)—S(22)	87·37 (7)	S(21)—P(2)—S(22)	106·6 (1)
S—Mo(2)—N	82·2 (2)	S(21)—P(2)—O(3)	114·5 (3)
S(1)—Mo(2)—S(2)	98·12 (7)	S(21)—P(2)—O(4)	113·6 (2)
S(1)—Mo(2)—S(21)	87·16 (7)	S(22)—P(2)—O(3)	112·2 (3)
S(1)—Mo(2)—S(22)	159·10 (7)	S(22)—P(2)—O(4)	114·9 (3)
S(1)—Mo(2)—N	85·3 (2)	O(3)—P(2)—O(4)	95·1 (3)
S(2)—Mo(2)—S(21)	87·33 (7)	S(31)—P(3)—S(32)	106·3 (1)
S(2)—Mo(2)—S(22)	94·80 (7)	S(31)—P(3)—O(5)	112·3 (3)
S(2)—Mo(2)—N	170·3 (2)	S(31)—P(3)—O(6)	112·9 (3)
S(21)—Mo(2)—S(22)	77·07 (7)	S(32)—P(3)—O(5)	113·8 (2)
S(21)—Mo(2)—N	83·7 (2)	S(32)—P(3)—O(6)	114·6 (3)
S(22)—Mo(2)—N	79·6 (2)	O(5)—P(3)—O(6)	97·0 (4)
Mo(1)—Mo(3)—Mo(2)	61·24 (2)	P(1)—O(1)—C(11)	124·0 (6)
S—Mo(3)—S(2)	105·25 (7)	P(1)—O(2)—C(21)	124·5 (6)
S—Mo(3)—S(3)	108·65 (7)	P(2)—O(3)—C(31)	122·4 (6)
S—Mo(3)—S(31)	85·19 (7)	P(2)—O(4)—C(41)	121·5 (5)
S—Mo(3)—S(32)	159·29 (8)	P(3)—O(5)—C(51)	119·0 (5)
S—Mo(3)—O(31)	83·5 (1)	P(3)—O(6)—C(61)	121·3 (5)
S(2)—Mo(3)—S(3)	92·70 (7)	O(11)—C(1)—O(31)	127·7 (7)
S(2)—Mo(3)—S(31)	98·31 (7)	O(11)—C(1)—C(2)	115·7 (8)
S(2)—Mo(3)—S(32)	89·30 (7)	O(31)—C(1)—C(2)	116·5 (8)
S(2)—Mo(3)—O(31)	171·3 (1)	N—C(3)—C(4)	177·1 (8)
S(3)—Mo(3)—S(31)	159·45 (7)	O(1)—C(11)—C(12)	109·5 (9)
S(3)—Mo(3)—S(32)	84·8 (1)	O(2)—C(21)—C(22)	107 (1)
S(3)—Mo(3)—O(31)	84·82 (7)	O(3)—C(31)—C(32)	108·3 (8)
S(31)—Mo(3)—S(32)	78·05 (7)	O(4)—C(41)—C(42)	107·6 (9)
S(31)—Mo(3)—O(31)	81·7 (1)	O(5)—C(51)—C(52)	107·2 (9)
S(32)—Mo(3)—O(31)	82·1 (1)	O(6)—C(61)—C(62)	107 (1)
Mo(1)—S—Mo(2)	72·46 (5)		

deviations. The intensities were corrected for absorption using empirical scan data (maximum and minimum transmission factors 1·22 and 0·86, respectively) and Lorentz and polarization factors.

The structure was solved by direct methods using *MULTAN*11/82 (Main *et al.*, 1982). Seven heavy atoms (Mo, S) were located in the *E* map. The remaining non-H atoms were located in the succeeding difference Fourier syntheses (H atoms were placed in geometrically calculated positions with C—H 0·95 Å, but not included in the refinement). The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-H atoms (370 variables). Final $R = 0·045$, $wR = 0·052$ and $S = 3·33$, the function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [\sigma_o^2(F_o^2) + (0·04F_o^2)^2]$ where $\sigma_o^2(F_o^2)$ is the standard deviation based on counting statistics. $(\Delta/\sigma)_{max} = 0·50$. In final difference electron density synthesis max. height less than 0·63 e Å^{-3}. All calculations were performed on a VAX 785 computer using *SDP* (Frenz, 1978), the scattering factors were taken from Cromer & Waber (1974). *ORTEP*II (Johnson, 1976) was used to produce the molecular configuration shown in Fig. 1. The atom coordinates and equivalent isotropic thermal parameters are listed in Table 1, important bond lengths and bond angles are given in Table 2.*

Related literature. A derivative of the title compound, [CuMo$_3$S$_4${S$_2$P(OC$_2$H$_5$)$_2$}$_3$(μ_2-CH$_3$COO)-{HCON(CH$_3$)$_2$}], has been reported (Wu *et al.*, 1987).

* Lists of H-atom coordinates, bond lengths and angles, structure factors, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51972 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A, 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
FRENZ, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination.* In *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. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
WU, X. T., LU, L. F., ZHU, L. Y., WU, Q. J. & LU, J. X. (1987). *Inorg. Chim. Acta*, **113**, 43–47.