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## Structure of $\mu$ -Diethyldithiophosphinato-tris(diethyldithiophosphinato)-tri- $\mu$ -thio- $\mu_3$ -thio-triangulo-trimolybdenum(IV)

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**Abstract.** [Mo<sub>3</sub>S<sub>4</sub>{(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>PS<sub>2</sub>]<sub>4</sub>],  $M_r = 1028.9$ , monoclinic,  $P2_1/n$ ,  $a = 11.791$  (2),  $b = 20.721$  (3),  $c = 16.100$  (3) Å,  $\beta = 107.50$  (1)°,  $V = 3752$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.79$ ,  $D_x = 1.82$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 1.79$  mm<sup>-1</sup>,  $F(000) = 2056$ , 6483 observed unique reflections (room temperature),  $R = 0.037$  (316 parameters). The three Mo atoms together with four bridging S atoms form a trinuclear cluster with local symmetry close to  $C_{3v}$ . Each of the Mo atoms is chelated by a bidentate diethyldithiophosphinato ligand; two Mo atoms are bridged in addition by the remaining diethyldithiophosphinato residue. Preliminary results have been reported [Keck, Kuchen, Mathow & Wunderlich (1982). *Angew. Chem.* **94**, 927–928; *Angew. Chem. Int. Ed. Engl.* **21**, 929].

**Introduction.** Trinuclear complexes of transition metals containing sulfur ligands are of well known importance in bioinorganic chemistry (Müller, Diemann, Jostes & Bögge, 1981). A classification of different trinuclear clusters containing no (type A), one (type B) or two (type C) capping  $\mu_3$ -ligands has been reported by Müller, Jostes & Cotton (1980). Mo clusters of type B are documented in two forms: in type B1 three single  $\mu$ -S atoms are bridging each side of the Mo triangle as in the cation [Mo<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>S<sub>4</sub>]<sup>+</sup> (Vergamini, Vahrenkamp & Dahl, 1971), while in type B2 these three S atoms are replaced by S<sub>2</sub> groups as in Mo<sub>3</sub>S<sub>7</sub>Cl<sub>4</sub> (Marcoll, Rabenau, Mootz & Wunderlich, 1974). In these two as well as in all structures of type B reported thereafter the three Mo atoms have equal coordination numbers. In the compound under study the bridging of the three Mo–Mo bonds was under debate: There was either a cluster of type B1 containing one dithio-

phosphinato ligand as an additional bridge (thus unequal coordination numbers of the Mo atoms) or one of type C with two Mo–Mo bonds bridged by a single S atom while the third side of the triangle is bridged by the dithiophosphinato group.

**Experimental.** The preparation of the title compound is reported by Keck, Kuchen & Mathow (1986) and yielded black opaque well shaped crystals of monoclinic habit. A crystal of approximately 0.3 × 0.3 × 0.4 mm was used for the refinement of the lattice parameters (15 reflections,  $33 < 2\theta < 40^\circ$ , Mo  $K\alpha$  radiation, crystal monochromator, Syntex P2<sub>1</sub>) as well as for the data collection. From systematic absences the space group  $P2_1/n$  (cell choice 1 with fully reduced mesh, *International Tables for Crystallography*, 1983) has been determined. Density, determined by flotation, yielded  $Z = 4$  formula units per cell. The intensities of 7955 reflections [Mo  $K\alpha$ ,  $(\sin\theta)/\lambda < 0.6168$  Å<sup>-1</sup>] were measured using an  $\omega$  scan with variable speeds and a scan width of 0.6°. Because of the large amount of data measurement was performed at an average rate of 115 reflections per hour. Compared with usual data collection (*ca* 40 refl. h<sup>-1</sup>) this should not increase the positional e.s.d.'s by more than about 20% (Hope & Nichols, 1981). The indices ranged from 0 to  $h = 14$ ,  $k = 25$  and from  $l = -19$  to  $l = 18$ , the intensities of three standard reflections (7,9,11, 783, 4,13,4) did not show significant variations. Seven low-order reflections with too high intensities, systematically absent reflections, and symmetry-equivalent ones have been eliminated. 456 reflections showed background imbalances of more than 2:1 of which in general the higher value was in error (probably multiple reflec-

tions) and was replaced by the lower value (Wunderlich, 1986). In a later stage of the refinement 28 weak reflections showed  $F_o \gg F_c$  and were eliminated. The final set of data contained 7341 reflections (6483 observed and 858 unobserved,  $I < 1.96\sigma$ ). No absorption correction was applied ( $\mu = 1.79 \text{ mm}^{-1}$ ).

From direct methods (*EXTL*, *MULTAN*) 12 heavy atoms were localized; the structure was completed and refined in the usual way. 29 H atoms could be located from difference electron densities, the remaining 11 H atoms were constructed. All H atoms were added as fixed-atom contributions. The final refinement (316 parameters) on  $F$  converged with all  $\Delta/\sigma < 0.1$ ,  $R = 0.037$  (0.043), and  $wR = 0.062$  (0.063) for the observed (all) data at a minimum of  $S = 2.1$ . The weighting scheme was  $w = 1/(\sigma_F^2 + 0.0004F^2)$ , scattering factors were taken from Cromer & Waber (1974) and corrections for anomalous dispersion (Cromer & Liberman, 1974) of Mo, S, and P were included. Residual electron densities ranged from  $-0.6$  to  $+0.8 \text{ e \AA}^{-3}$ . The final parameters of the non-H atoms are listed in Table 1.\* The anisotropic displacement parameters are in the expected range except those of the ethyl groups at P(1) which show a tendency to disorder compensated by enlarged displacement parameters. All calculations were carried out with a local modified version of the program system *EXTL* (Syntax, 1976).

**Discussion.** Fig. 1 shows one molecule with bond lengths. The bond angles of the three Mo atoms are given in Table 2, whilst the angles at the remaining non-H atoms have been deposited. The molecule forms a cluster of type B1 with a dithiophosphinato residue bridging the bond Mo(1)–Mo(2). This residue squeezes the  $\text{Mo}_3\text{S}_4$  core by shortening the bond Mo(1)–Mo(2) to 2.735 (1) Å which is significantly shorter (though between the Mo atoms of higher coordination number) than the bonds Mo(1)–Mo(3) with 2.758 (1), Mo(2)–Mo(3) with 2.760 (1) Å, and all Mo–Mo bonds reported for a trinuclear cluster containing the same core (Müller, Jostes & Cotton, 1980). The squeezing is paralleled by enlarged bond angles within the five-membered ring [108.4 (1), 114.0 (1), and 107.0 (1)° at atoms S(41), P(4), and S(42), respectively] as well as by a reduction of bond angles Mo(1)–S–Mo(2). To minimize this squeezing the five-membered ring adopts an envelope conformation [atoms Mo(1), Mo(2), S(41), and S(42) planar within 0.01 Å, atom P(4) 0.72 Å out

Table 1. Parameters of the non-H atoms with e.s.d.'s in parentheses

The equivalent isotropic temperature factors ( $\text{\AA}^2$ ) have been calculated by  $U_{eq} = 1/24\pi^2(B_{11}a^{*2}a^2 + B_{12}a^*b^*abc\cos\gamma + \dots)$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
Mo(1)	0.01551 (3)	0.43435 (2)	0.18179 (3)	0.0255
Mo(2)	0.02644 (3)	0.32099 (2)	0.09748 (3)	0.0255
Mo(3)	0.20344 (3)	0.41198 (2)	0.11693 (3)	0.0258
S(1)	-0.13077 (10)	0.39196 (6)	0.06542 (8)	0.0312
S(2)	0.09351 (11)	0.50194 (6)	0.09676 (8)	0.0320
S(3)	0.10989 (11)	0.35833 (7)	-0.00639 (8)	0.0344
S(4)	0.16062 (10)	0.35446 (6)	0.22944 (8)	0.0276
S(11)	-0.12595 (11)	0.52934 (6)	0.18481 (9)	0.0350
S(12)	0.13103 (13)	0.49555 (7)	0.32111 (9)	0.0418
S(21)	-0.09877 (12)	0.24708 (7)	-0.02565 (9)	0.0389
S(22)	0.15780 (12)	0.21862 (7)	0.11752 (10)	0.0415
S(31)	0.33199 (11)	0.45833 (8)	0.02810 (9)	0.0401
S(32)	0.40074 (12)	0.40985 (9)	0.22352 (10)	0.0512
S(41)	-0.09554 (12)	0.38807 (6)	0.28639 (9)	0.0369
S(42)	-0.08647 (13)	0.24838 (6)	0.17903 (9)	0.0377
P(1)	0.00374 (14)	0.56301 (7)	0.28783 (11)	0.0472
P(2)	0.03279 (12)	0.18144 (7)	0.01445 (9)	0.0350
P(3)	0.46868 (12)	0.45701 (8)	0.13807 (10)	0.0395
P(4)	-0.07128 (12)	0.29122 (6)	0.29433 (9)	0.0317
C(11)	0.0768 (8)	0.6367 (4)	0.2558 (8)	0.118
C(12)	0.0225 (10)	0.6956 (6)	0.2421 (7)	0.110
C(13)	-0.0509 (8)	0.5843 (5)	0.3757 (6)	0.091
C(14)	-0.1186 (13)	0.5410 (6)	0.4002 (8)	0.134
C(21)	0.0956 (6)	0.1626 (3)	-0.0725 (4)	0.048
C(22)	0.1940 (8)	0.1123 (4)	-0.0495 (7)	0.087
C(23)	-0.0220 (6)	0.1060 (3)	0.0448 (4)	0.051
C(24)	-0.1173 (8)	0.0747 (4)	-0.0303 (6)	0.079
C(31)	0.5180 (7)	0.5372 (4)	0.1777 (5)	0.067
C(32)	0.4198 (10)	0.5787 (4)	0.1921 (7)	0.100
C(33)	0.5985 (5)	0.4169 (3)	0.1264 (5)	0.058
C(34)	0.5772 (7)	0.3476 (4)	0.0985 (7)	0.084
C(41)	-0.1883 (5)	0.2588 (3)	0.3350 (4)	0.046
C(42)	-0.1862 (7)	0.1852 (3)	0.3449 (6)	0.066
C(43)	0.0666 (5)	0.2684 (3)	0.3780 (4)	0.043
C(44)	0.0854 (7)	0.3026 (4)	0.4643 (5)	0.071

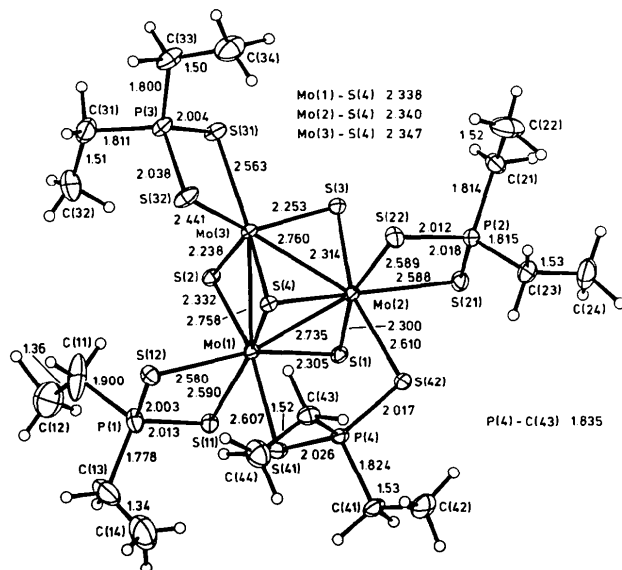


Fig. 1. The molecule of  $[\text{Mo}_3\text{S}_4(\text{C}_2\text{H}_5)_2\text{PSi}]_n$  in arbitrary crystallographic orientation with bond lengths (Å). The e.s.d.'s are: Mo–Mo 0.001, Mo–S 0.001–0.002, S–P 0.002, P–C 0.006–0.010, and C–C 0.01–0.02 Å. The non-H atoms are represented by thermal ellipsoids of 50% probability (*ORTEPII*, Johnson, 1976); the radius of the H atoms was set to  $B = 1.5 \text{ \AA}^2$ .

\* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, and additional bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43294 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond angles (°) at the Mo atoms; *e.s.d.*'s are 0.01° for Mo—Mo—Mo, 0.03–0.04° for Mo—Mo—S, and 0.04–0.05° for S—Mo—S

Mo(1)	Mo(2)	Mo(3)	S(1)	S(2)	S(4)	S(11)	S(12)
Mo(3)	60.31						
S(1)	53.47	96.79					
S(2)	97.97	51.33	94.74				
S(4)	54.26	54.07	106.97	103.82			
S(11)	142.06	136.90	88.63	85.67	160.70		
S(12)	139.65	97.90	164.64	90.96	85.40	77.57	
S(41)	96.46	143.09	89.22	164.46	89.30	79.40	81.70
Mo(2)	Mo(1)	Mo(3)	S(1)	S(3)	S(4)	S(21)	S(22)
Mo(3)	60.26						
S(1)	53.64	96.87					
S(3)	99.51	51.83	96.50				
S(4)	54.19	54.04	107.07	103.81			
S(21)	141.94	136.81	88.33	85.00	160.95		
S(22)	139.24	98.16	164.47	89.74	85.06	78.03	
S(42)	97.94	145.04	89.02	161.54	91.26	77.55	80.88
Mo(3)	Mo(1)	Mo(2)	S(2)	S(3)	S(4)	S(31)	
Mo(2)	59.43						
S(2)	54.46	99.63					
S(3)	100.39	53.84	100.04				
S(4)	53.79	53.82	106.58	105.53			
S(31)	145.64	138.30	91.19	84.73	157.18		
S(32)	116.18	126.57	120.34	136.15	80.15	78.50	

of this plane] with the following torsion angles: Mo(1)—[1°]—Mo(2)—[−23°]—S(42)—[43°]—P(4)—[−43°]—S(41)—[21°]—Mo(1). The bridging residue reduces the maximal possible symmetry from C<sub>3v</sub> to C<sub>s</sub> [mirror plane through Mo(3), S(4), and S(1)] which is approximately fulfilled within the Mo<sub>3</sub>S<sub>4</sub> core but clearly disturbed by the organic ligands. The S atoms can be grouped into four structurally different kinds with averaged bond angles of 71.95 (4) (μ<sub>3</sub>-S), 73.81 (4) (μ-S), 87.62 (7) (bidentate ligand) and 107.71 (7)° (bridging ligand). The four dialkyldithiophosphinato ligands show the expected geometry as in

similar Mo complexes {e.g. [(Et<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>Mo<sub>3</sub>-S(S<sub>2</sub>)<sub>3</sub>]<sup>+</sup>·(Et<sub>2</sub>PS<sub>2</sub>)<sup>-</sup>, Meyer & Wunderlich (1982)}; this includes the tendency to disorder within these ligands {as in [Cd(Et<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>], Wunderlich (1986)} which cannot be excluded for the ligand involving P(1) of the present structure.

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## Structure of the Antitumour Agent Di-μ-acetato-(O)-bis[(2-pyridinecarbaldehyde thiosemicarbazono)copper(II)]

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**Abstract.** [Cu<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>7</sub>H<sub>7</sub>N<sub>4</sub>S)<sub>2</sub>], *M<sub>r</sub>* = 603.62, triclinic, *P* $\bar{1}$ , *a* = 8.834 (1), *b* = 8.989 (1), *c* = 8.801 (1) Å,  $\alpha$  = 117.48 (1),  $\beta$  = 91.77 (1),  $\gamma$  = 110.94 (1)°, *V* = 562.7 (3) Å<sup>3</sup>, *Z* = 1, *D<sub>x</sub>* = 1.78 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71069 Å,  $\mu$  = 21.17 cm<sup>-1</sup>, *F*(000) = 306, room temperature, final *R* = 0.0291 for 2052 observed reflections. This crystal structure reveals that the title compound is in a dimeric form with the

two Cu<sup>2+</sup> ions in an unusual distorted square-pyramidal coordination. There is no direct metal–metal bond. The two metallic atoms are linked by two bridging acetate groups.

**Introduction.** The tridentate ligand 2-(2-pyridine-methylene)hydrazinecarbothioamide (more commonly called 2-pyridinecarbaldehyde thiosemicarbazone