

Table 3. *Least-squares planes*

(a) Deviations ( $\text{\AA}$ ) of the atoms from some least-squares planes in the molecule, with their dihedral angles. (\* denotes the atoms not used in the plane calculations.)

Plane 1		Plane 2		Plane 3	
C(1)	-0.688*	C(2)	0.187*	C(3)	-0.048*
C(2)	-0.036	O(2)	0.001	O(3)	-0.002
C(3)	0.035	O(7)	0.002	O(8)	-0.003
C(4)	0.641*	C(10)	-0.005	C(12)	0.008
C(5)	-0.037	C(11)	0.001	C(13)	-0.002
O(5)	0.038				

Plane 4		Plane 5	
C(4)	0.063*	O(1)	-0.006
O(4)	0.002	C(5)	-0.127*
O(9)	0.002	C(6)	0.024
C(14)	-0.006	O(6)	-0.031
C(15)	0.002	C(7)	-0.005
		C(8)	0.018

$\angle$ (Plane 1) (Plane 2) 62.8°     $\angle$ (Plane 1) (Plane 4) 95.7°  
 $\angle$ (Plane 1) (Plane 3) 126.0     $\angle$ (Plane 1) (Plane 5) 18.7

(b) Main torsional angles around the bond defined by the central atoms

Pyranose ring		Conformation
C(1)-C(2)-C(3)-C(4)	-50.3°	-sc
C(2)-C(3)-C(4)-C(5)	49.3	sc
C(3)-C(4)-C(5)-O(5)	-55.3	-sc
C(4)-C(5)-O(5)-C(1)	65.0	sc
C(5)-O(5)-C(1)-C(2)	-64.1	-sc
O(5)-C(1)-C(2)-C(3)	56.8	sc

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## The Structure of $[\text{CH}_3\text{S}(\text{CH}_2)_2\text{SCH}_3\text{Mo}(\text{CO})_3(\text{SnCl}_3)\text{Cl}](\text{CH}_2\text{Cl}_2)$

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**Abstract.** Triclinic,  $P\bar{1}$ ,  $a=9.835$  (3),  $b=11.068$  (3),  $c=9.006$  (2)  $\text{\AA}$ ,  $\alpha=92.04$  (2),  $\beta=119.28$  (2),  $\gamma=96.36$  (2)°,  $V=845.4$   $\text{\AA}^3$ ,  $Z=2$ ,  $D_c=2.21$   $\text{g cm}^{-3}$ ,  $D_m=2.17$   $\text{g cm}^{-3}$  (by flotation in an iodomethane-chloroform mixture).  $\text{Mo } K\alpha_1$  radiation,  $\lambda=0.70926$   $\text{\AA}$ ,  $\mu(\text{Mo } K\alpha)=30.1$   $\text{cm}^{-1}$ ,  $T=21$  (1)°C, final  $R=0.086$  for 2192 observed reflexions. An irregular capped octahedral geometry exists about Mo; Sn (which occupies the capped position) has an irregular trigonal bipyramidal arrangement. One Cl atom is bonded to both Mo and Sn with bond lengths 2.535 (5) and 2.781 (4)  $\text{\AA}$  respectively. The Sn-Mo distance is 2.688 (2)  $\text{\AA}$ .

**Introduction.** Small red air-stable crystals of the title compound were obtained by crystallization from  $\text{CH}_2\text{Cl}_2$ . Weissenberg and precession photographs of

Lateral angles

C(2)-O(2)-C(10)-O(7)	63.7°
C(3)-O(3)-C(12)-O(8)	-1.0
C(4)-O(4)-C(14)-O(9)	-1.9
C(5)-C(6)-O(6)-C(7)	-175.7
C(6)-O(6)-C(7)-O(1)	3.7
H(5)-C(5)-C(6)-H(6a)	-61.9
H(5)-C(5)-C(6)-H(6b)	177.5

Table 3 (cont.)

Conformation

sc  
-sp  
-sp  
-ap  
sp  
-sc  
ap

We wish to record our thanks to Dr Martin-Lomas and Dr Chacon-Fuertes, CSIC (Madrid), for the crystals. We also thank the Centro de Proceso de Datos del Ministerio de Educación y Ciencia (Madrid) for allowing us to use the 1108 UNIVAC computer. All calculations were performed with the X-RAY System of Crystallographic Programs.

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one of these crystals (mounted about  $\mathbf{a}$  and  $\mathbf{a}^*$  respectively) indicated triclinic Laue symmetry. Cell dimensions were obtained from 12 strong reflexions ( $2\theta > 24^\circ$ ) centred on the Mo  $K\alpha_1$  peak ( $\lambda=0.70926$   $\text{\AA}$ ) without the use of a monochromator. Intensities were collected in two shells  $0^\circ < 2\theta < 30^\circ$  and  $30^\circ < 2\theta < 50^\circ$  with a  $\theta$ ,  $2\theta$  scan and monochromatized  $K\alpha_1$  radiation. Otherwise the data were collected as reported by Einstein & Jones (1972). The variation of standard reflexions was approximately  $\pm 5\%$ .

The data set consisted of 3000 unique reflexions of which 2192 were classed as observed  $\{I > 2.35\sigma(I)$ ,  $\sigma(I) = [(T) + (ts/tb)^2(B_1 + B_2) + (KI)^2]^{1/2}$  where  $T$  = total count,  $ts$  = scan time,  $tb$  = total background count time,  $B_1$  and  $B_2$  are the background counts,  $K$  is a constant equal to 0.03, and  $I$  is the net count}. The intensities

were corrected for the monochromator polarization and for Lorentz polarization effects, but not for absorption. The last could introduce an extreme error of  $\pm 5\%$  in  $F$ . The structure was solved by Patterson and Fourier methods.

Full-matrix least-squares refinement of data ( $2\theta < 30^\circ$ ) gave an  $R$  of 0.069 ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ). At this stage anisotropic temperature factors were needed to describe the Sn, Mo, and Cl atoms. After this most H atoms were located from a difference synthesis, but where peaks were not found their positions were

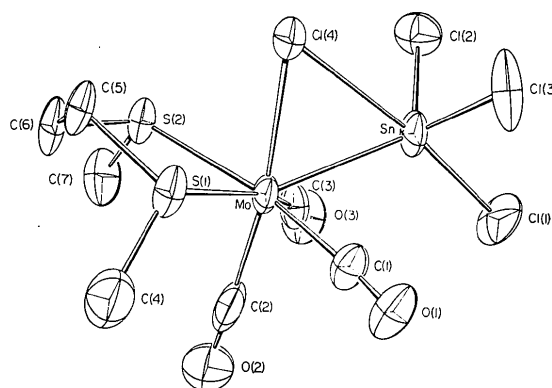


Fig. 1. Molecular structure of [CH<sub>3</sub>S(CH<sub>2</sub>)<sub>2</sub>SCH<sub>3</sub>Mo(CO)<sub>3</sub>(SnCl<sub>3</sub>)Cl](CH<sub>2</sub>Cl<sub>2</sub>). (The thermal ellipsoids shown represent a probability of 50% electron density.)

Table 1. *Coordinates and thermal parameters*

(a) Fractional atomic coordinates with e.s.d.'s ( $\times 10^4$ ) for Sn, Mo, Cl, S, ( $\times 10^3$ ) for remaining atoms

	x	y	z
Sn	2676 (2)	2667 (1)	2575 (2)
Mo	-168 (2)	2264 (2)	2347 (2)
Cl(1)	2860 (7)	2053 (6)	126 (8)
Cl(2)	3793 (6)	4676 (4)	2870 (6)
Cl(3)	4648 (6)	1674 (5)	4545 (8)
Cl(4)	2085 (5)	3231 (4)	5221 (5)
S(1)	-909 (5)	1299 (4)	4411 (6)
S(2)	-1371 (5)	4009 (4)	2952 (6)
O(1)	74 (2)	-31 (1)	197 (2)
O(2)	-330 (2)	106 (2)	-86 (2)
O(3)	-54 (2)	366 (1)	-75 (2)
C(1)	48 (2)	62 (2)	209 (2)
C(2)	-215 (3)	147 (2)	32 (3)
C(3)	-32 (2)	318 (2)	42 (2)
C(4)	-275 (3)	33 (2)	329 (3)
C(5)	-132 (2)	258 (2)	537 (2)
C(6)	-232 (2)	337 (2)	410 (2)
C(7)	-307 (2)	436 (2)	109 (3)
H(71)	-380	356	51
H(72)	-361	492	136
H(73)	-278	471	28
H(61)	-256	402	464
H(62)	-332	287	328
H(51)	-181	229	602
H(52)	-32	309	619
H(41)	-312	4	406
H(42)	-268	-40	269
H(43)	-353	78	244

generated. H atomic parameters were not refined. Following this all the data were employed for full-matrix least-squares refinement which gave a final  $R$  of 0.086. Weights determined from counter statistics  $(1/\sigma_F)^2$  were used.

Programs used were those described by Einstein & Jones (1972). Scattering factors were from Cromer & Waber (1965) except for H which was from Stewart, Davidson & Simpson (1965). Sn and Mo were corrected for anomalous dispersion with values listed in *International Tables for X-ray Crystallography* (1962).

Atomic coordinates and thermal motion parameters are listed in Table 1, interatomic distances and angles in Table 2. Fig. 1 shows the labelling of the atoms.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31358 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 (cont.)

(b) Anisotropic vibrational amplitudes in the form  $\exp[-2\pi^2(h^2a^*U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$  ( $\times 10^3 \text{ \AA}^2$ ;  $\times 10^4 \text{ \AA}^2$  for Sn and Mo)

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Sn	437 (8)	498 (8)	626 (9)	93 (6)	433 (7)	78 (6)
Mo	350 (8)	405 (9)	397 (8)	88 (7)	281 (7)	25 (6)
Cl(1)	105 (5)	96 (5)	106 (5)	-6 (4)	92 (4)	-22 (4)
Cl(2)	61 (3)	59 (3)	55 (3)	-6 (3)	30 (3)	6 (2)
Cl(3)	62 (3)	106 (5)	119 (5)	50 (3)	70 (4)	55 (4)
Cl(4)	39 (2)	64 (3)	47 (3)	7 (2)	27 (2)	-6 (2)
S(1)	54 (3)	41 (3)	53 (3)	17 (2)	42 (2)	12 (2)
S(2)	45 (3)	44 (3)	51 (3)	18 (2)	35 (2)	9 (2)
O(1)	90 (10)	50 (8)	77 (9)	25 (8)	54 (8)	6 (7)
O(2)	66 (10)	91 (10)	64 (10)	7 (9)	23 (8)	-8 (8)
O(3)	88 (10)	85 (10)	63 (9)	27 (8)	50 (8)	30 (8)
C(1)	55 (11)	34 (10)	53 (11)	14 (9)	35 (9)	9 (8)
C(2)	62 (13)	79 (15)	59 (13)	28 (11)	40 (11)	-9 (11)
C(3)	41 (10)	44 (10)	55 (11)	24 (8)	29 (9)	22 (9)
C(4)	86 (16)	61 (13)	90 (16)	7 (12)	63 (14)	1 (12)
C(5)	57 (11)	51 (11)	46 (10)	20 (9)	45 (9)	13 (8)
C(6)	68 (12)	55 (11)	75 (13)	22 (10)	64 (11)	18 (10)
C(7)	65 (14)	88 (16)	83 (15)	36 (12)	48 (12)	26 (12)

Table 2. Distances (Å) and angles (°)

## (I) Bonded contacts

Mo—Cl(4)	2.535 (5)	Sn—Mo	2.688 (2)
Mo—S(1)	2.533 (4)	Sn—Cl(1)	2.381 (5)
Mo—S(2)	2.547 (4)	Sn—Cl(2)	2.314 (5)
Mo—C(1)	2.04 (2)	Sn—Cl(3)	2.316 (5)
Mo—C(2)	1.98 (2)	Sn—Cl(4)	2.781 (4)
Mo—C(3)	1.99 (2)	S(1)—C(4)	1.78 (2)
C(1)—O(1)	1.10 (2)	S(1)—C(5)	1.82 (2)
C(2)—O(2)	1.14 (2)	S(2)—C(7)	1.79 (2)
C(3)—O(3)	1.13 (2)	S(2)—C(6)	1.81 (2)
		C(6)—C(5)	1.49 (2)

## (II) Intermolecular non-bonded contacts (&lt; 3.4 Å) not involving hydrogen atoms

		Symmetry code		
	(i)	-x,	-y,	-z
	(ii)	1-x,	1-y,	1-z
	(iii)	x,	y,	-1+z
Cl(1)—O(1) <sup>i</sup>	3.392	O(1)—C(1) <sup>i</sup>		3.229
Cl(2)—Cl(2) <sup>ii</sup>	3.375	O(1)—C(2) <sup>i</sup>		3.285
O(1)—O(1) <sup>i</sup>	3.243	O(3)—O(3)		3.056
O(1)—O(2) <sup>i</sup>	3.302	O(3)—C(5) <sup>iii</sup>		3.336
Cl(4)—Mo—Sn	64.3 (1)	Mo—Sn—Cl(1)	117.9 (2)	
Cl(4)—Mo—S(1)	78.0 (2)	Mo—Sn—Cl(2)	117.6 (2)	
Cl(4)—Mo—S(2)	79.0 (2)	Mo—Sn—Cl(3)	117.8 (1)	
Cl(4)—Mo—C(1)	102.9 (5)	Mo—Sn—Cl(4)	55.2 (1)	
Cl(4)—Mo—C(2)	169.8 (5)	Cl(1)—Sn—Cl(2)	95.4 (2)	
Cl(4)—Mo—C(3)	112.5 (5)	Cl(1)—Sn—Cl(3)	97.9 (2)	
S(1)—Mo—Sn	128.7 (1)	Cl(1)—Sn—Cl(4)	172.9 (2)	
S(1)—Mo—C(1)	85.3 (4)	Cl(2)—Sn—Cl(3)	106.5 (2)	
S(1)—Mo—C(2)	92.7 (6)	Cl(2)—Sn—Cl(4)	89.6 (2)	
S(1)—Mo—C(3)	160.4 (4)	Cl(3)—Sn—Cl(4)	85.5 (2)	
S(2)—Mo—Sn	121.0 (1)	Mo—Cl(4)—Sn	60.5 (1)	
S(2)—Mo—C(1)	165.6 (4)	Mo—S(1)—C(4)	111.0 (7)	
S(2)—Mo—C(2)	95.5 (5)	Mo—S(1)—C(5)	103.4 (5)	
S(2)—Mo—C(3)	84.6 (5)	C(4)—S(1)—C(5)	103.9 (8)	
S(2)—Mo—S(1)	81.2 (2)	Mo—S(2)—C(6)	105.1 (6)	
C(1)—Mo—Sn	71.7 (5)	Mo—S(2)—C(7)	113.2 (7)	
C(1)—Mo—C(2)	80.2 (7)	C(6)—S(2)—C(7)	99.3 (9)	
C(1)—Mo—C(3)	107.3 (6)	Mo—C(1)—O(1)	175 (2)	
C(2)—Mo—Sn	125.7 (5)	Mo—C(2)—O(2)	177 (2)	
C(2)—Mo—C(3)	75.3 (8)	Mo—C(3)—O(3)	174 (2)	
C(3)—Mo—Sn	70.4 (4)	S(1)—C(5)—C(6)	113 (1)	
		S(2)—C(6)—C(5)	111 (1)	

**Discussion.** The compound DTH  $\text{Mo}(\text{CO})_3(\text{SnCl}_3)\text{Cl}$  (I) (DTH = 2,5-dithiahexane) was chosen for study as one of a series of organometallic compounds containing metal-metal bonds. In all these compounds seven-coordinate Mo or W has been found with a capped octahedral environment about the central metal atom. For (I) the Mo—Sn, Mo—Cl and Sn—Cl lengths are all considerably shorter than those reported for bipy(CO)<sub>3</sub>ClMoSnCH<sub>3</sub>Cl<sub>2</sub> (II) (bipy = 2,2'-bipyridyl) (Elder & Hall, 1968).

In (I) and (II) an irregular capped octahedral geometry exists about Mo, with the -SnCl<sub>3</sub> or -SnCl<sub>2</sub>CH<sub>3</sub> group in the unique capping position. Coordination of Sn is irregular trigonal bipyramidal and Cl(4) is bonded to both Sn and Mo, leading to the 'trigonal' axis being offset as was found in (II). The environment of Sn is quite asymmetric and Mössbauer studies showed very

low values for the isomer shift and quadrupole splitting (Cullen, Pomeroy, Sams & Tsin, 1976).

In addition an approximate non-crystallographic mirror plane extends through Mo, Sn, Cl(1) and Cl(4).

To explain the shortened Sn—Mo and Sn—Cl lengths of (I) relative to (II), we may use Bent's rule, that is, more electropositive substituents prefer hybrid orbitals having more *s* character. (I) has only one electropositive group (Mo) whereas (II) has two (Mo and CH<sub>3</sub>). One can visualize that in (II), both Mo and CH<sub>3</sub> compete for *s* character whereas in (I) only Mo has preference for *s* electrons. Then the Sn—Cl bonds of (II) can be expected to have more *p* character than in (I), and so it follows that in (II) they are longer. The Sn—Mo bond in (II) also has more *p* character than in (I) and so is longer in (II).

Increased competition for *dπ* electron density on the transition metal atom in (II) *vs* (I) due to the bipy group (compared to the DTH group) may also shorten the Sn—Mo bond in (II). However, since the electronegativities of S and N in these species are not very different, this effect is probably unimportant. Furthermore, in (I) the better *π* acceptor properties of the -SnCl<sub>3</sub> group compared to -SnCl<sub>2</sub>CH<sub>3</sub> in (II) may contribute to the short Mo—Sn length in (I).

In the DTH ligand the S(1)···S(2) bite is 3.306 compared with an S···S bite of 3.10 Å reported by Eisenberg (1970). The increased S···S distance would allow an angle nearer 90° to be subtended in keeping with the octahedral geometry. The covalent radii of Mo and S are 1.61 (Wilson & Shoemaker, 1957) and 1.04 Å (Pauling, 1960) respectively. This S—Mo length of 2.65 Å can be compared with the observed values of 2.533 (4) and 2.547 (4) Å indicating the possibility of some *π* character in these bonds.

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