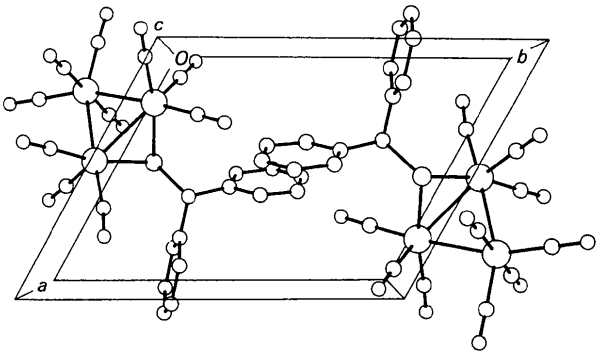

Fig. 2. The contents of the unit cell.

References

Adams, R. D. & Dawoodi, Z. (1981). *J. Am. Chem. Soc.* **103**, 6510–6512.

Adams, R. D., Golembeski, N. M. & Selegue, J. P. (1981). *J. Am. Chem. Soc.* **103**, 546–555.

Allen, V. F., Mason, R. & Hitchcock, P. B. (1977). *J. Organomet. Chem.* **140**, 297–307.

Holden, H. D., Johnson, B. F. G., Lewis, J., Raithby, P. R. & Uden, G. (1983). *Acta Cryst.* C**39**, 1197–1200.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, B. F. G., Lewis, J., Pippard, D., Raithby, P. R., Sheldrick, G. M. & Rouse, K. D. (1979). *J. Chem. Soc. Dalton Trans.* pp. 616–618.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Uden, G. (1982). PhD Thesis, Univ. of Cambridge, England.

Acta Cryst. (1983). C**39**, 1203–1205

Structure of *S*,*S*′-Trimethylenebis(1,1,1,2,2,2,3,3,3,3-decacarbonyl-1,2-*μ*-hydrido-1,2-*μ*-sulphido-*triangulo*-triosmium), $C_{23}H_8O_{20}Os_6S_2$

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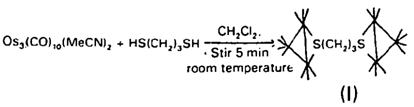
(*Received* 17 *November* 1982; *accepted* 2 *February* 1983)

Abstract. $M_r = 1809{\cdot}62$, monoclinic, $P2_1/c$, $a = 14{\cdot}765\ (5)$, $b = 14{\cdot}047\ (4)$, $c = 17{\cdot}840\ (3)$ Å, $\beta = 91{\cdot}98\ (2)°$, $U = 3697{\cdot}7\ (10)$ Å^3, $Z = 4$, $D_x = 3{\cdot}250$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 20{\cdot}71$ mm^{-1}, $F(000) = 3176$, $T = 298$ K. The structure refined to a final R of 0·0565 for 3582 observed reflections. The molecule consists of two $(\mu\text{-H})Os_3(CO)_{10}$ moieties linked by a $[(\mu\text{-S})CH_2]_2CH_2$ chain.

Introduction. The final part of the work† on the reactions of some osmium clusters with organic thiols is concerned with the crystal structure of the title compound (I). $Os_3(CO)_{10}(MeCN)_2$ reacts with $HS(CH_2)_3SH$ in methylene dichloride to give (I) as the sole identifiable product in 20% yield.



(I)

Experimental. After purification by TLC recrystallization from hexane gave crystals suitable for X-ray work (Uden, 1982); crystal size 0·07 × 0·38 × 0·42 mm. Syntex $P2_1$ automatic four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Lp and semi-empirical absorption corrections applied. Intensities of 4320 reflections in quadrant $+h$, $+k$, $\pm l$ with $3 \leq 2\theta \leq 50°$ measured; 3582 reflections $[I \geq 3\sigma(I)]$ used in analysis. Structure solution and refinement carried out using *SHELX76* (Sheldrick, 1976); E map, calculated using automatic centrosymmetric EEES option, showed six large peaks defining two triangles of Os atoms; following difference syntheses found positions for all other non-H atoms. With Os and S atoms given anisotropic, and C and O atoms isotropic thermal parameters during final cycles of blocked full-matrix least-squares refinement on F^2, R converged to 0·0565 and R_g to 0·0678; unit weights used throughout. All atoms given complex neutral-atom scattering factors (*International Tables for X-ray Crystallography* 1974).

Discussion. Fig. 1 shows a drawing of the molecule; atomic coordinates are in Table 1,‡ bond distances and angles in Table 2.

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† See two preceding papers (Holden, Johnson, Lewis, Raithby & Uden, 1983*a*, *b*).

‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38565 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional coordinates* ($\times 10^4$) *and isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}/U_{iso}
Os(1)	1619 (1)	3248 (1)	−8 (1)	37 (1)*
Os(2)	1640 (1)	1630 (1)	965 (1)	36 (1)*
Os(3)	3197 (1)	2809 (1)	897 (1)	35 (1)*
Os(4)	2729 (1)	8197 (1)	6447 (1)	33 (1)*
Os(5)	1928 (1)	7520 (1)	7786 (1)	36 (1)*
Os(6)	3182 (1)	9068 (1)	7848 (1)	31 (1)*
C(1)	3584 (25)	3410 (26)	−1007 (19)	46 (9)
C(2)	4511 (23)	2957 (24)	−1201 (17)	37 (8)
C(3)	4949 (22)	3594 (23)	−1805 (17)	35 (8)
S(1)	2992 (6)	2528 (7)	−426 (4)	40 (5)*
S(2)	5896 (6)	2948 (6)	−2199 (4)	32 (5)*
C(11)	1720 (28)	4331 (29)	−632 (21)	52 (10)
O(11)	1803 (23)	5027 (25)	−999 (18)	84 (10)
C(12)	734 (42)	2591 (45)	−741 (33)	107 (18)
O(12)	365 (27)	2140 (29)	−1107 (22)	95 (12)
C(13)	606 (32)	3814 (33)	401 (25)	65 (12)
O(13)	50 (22)	4185 (23)	784 (17)	80 (9)
C(21)	1241 (31)	2472 (33)	1706 (24)	67 (12)
O(21)	849 (23)	3035 (25)	2123 (19)	88 (10)
C(22)	1963 (35)	801 (37)	1734 (28)	82 (15)
O(22)	2480 (25)	419 (27)	2240 (20)	98 (11)
C(23)	544 (32)	1127 (32)	816 (24)	69 (12)
O(23)	−176 (23)	668 (24)	665 (17)	93 (10)
C(24)	2129 (32)	797 (34)	198 (25)	78 (12)
O(24)	2529 (20)	311 (21)	−171 (16)	73 (8)
C(31)	3042 (21)	2987 (21)	1935 (15)	25 (7)
O(31)	2958 (18)	3065 (18)	2548 (14)	54 (7)
C(32)	3952 (30)	1721 (33)	1034 (23)	61 (11)
O(32)	4364 (24)	1022 (26)	1144 (19)	89 (10)
C(33)	4147 (22)	3684 (22)	798 (16)	33 (7)
O(33)	4717 (20)	4276 (21)	780 (15)	70 (8)
C(41)	6756 (30)	3717 (31)	−581 (23)	59 (12)
O(41)	6418 (21)	4020 (23)	−57 (17)	76 (9)
C(42)	8381 (33)	3536 (33)	−1041 (24)	68 (12)
O(42)	9117 (20)	3840 (20)	−790 (15)	63 (8)
C(43)	7381 (29)	1944 (30)	−1080 (22)	56 (10)
O(43)	7492 (21)	1151 (23)	−892 (16)	79 (9)
C(51)	7042 (28)	1634 (30)	−2971 (22)	53 (10)
O(51)	6511 (20)	1063 (21)	−3149 (16)	67 (8)
C(52)	8376 (28)	2467 (29)	−3798 (22)	55 (10)
O(52)	8487 (21)	2488 (22)	−4457 (17)	74 (9)
C(53)	9023 (25)	3448 (25)	−2554 (18)	42 (9)
O(53)	9617 (21)	3991 (22)	−2428 (16)	73 (9)
C(54)	8821 (29)	1448 (29)	−2406 (22)	55 (10)
O(54)	9257 (21)	856 (23)	−2182 (16)	80 (9)
C(61)	5944 (26)	5001 (26)	−2809 (19)	46 (9)
O(61)	5363 (21)	5573 (22)	−2816 (16)	73 (8)
C(62)	6486 (30)	3707 (32)	−3830 (24)	68 (12)
O(62)	6293 (20)	3396 (21)	−4417 (16)	73 (8)
C(63)	7728 (26)	4882 (26)	−3147 (19)	43 (9)
O(63)	8322 (19)	5391 (20)	−3310 (14)	60 (7)

* $U_{eq} = \frac{1}{3}$ of the trace of the orthogonalized **U** matrix.

Table 2. *Bond lengths* (Å) *and angles* (°)

Os(2)—Os(1)	2·860 (3)	Os(3)—Os(1)	2·856 (3)
S(1)—Os(1)	2·406 (9)	C(11)—Os(1)	1·894 (40)
C(12)—Os(1)	2·037 (60)	C(13)—Os(1)	1·866 (47)
Os(3)—Os(2)	2·840 (3)	C(21)—Os(2)	1·884 (45)
C(22)—Os(2)	1·849 (50)	C(23)—Os(2)	1·777 (47)
C(24)—Os(2)	1·957 (46)	S(1)—Os(3)	2·403 (8)
C(31)—Os(3)	1·889 (28)	C(32)—Os(3)	1·902 (45)
C(33)—Os(3)	1·878 (32)	Os(5)—Os(4)	2·864 (3)
Os(6)—Os(4)	2·841 (3)	Os(6)—Os(5)	2·855 (3)
S(2)—Os(6)	2·403 (10)	S(2)—Os(4)	2·419 (9)
C(2)—C(1)	1·560 (50)	S(1)—C(1)	1·853 (37)
C(3)—C(2)	1·557 (45)	S(2)—C(3)	1·828 (34)
Os(4)—C(41)	1·892 (50)	Os(4)—C(42)	1·832 (40)
Os(4)—C(43)	1·883 (45)	Os(5)—C(51)	1·984 (30)
Os(5)—C(52)	1·877 (50)	Os(5)—C(53)	1·949 (48)
Os(5)—C(54)	1·975 (35)	Os(6)—C(61)	1·842 (40)
Os(6)—C(62)	1·872 (38)	Os(6)—C(63)	1·856 (42)
O(11)—C(11)	1·186 (53)	O(12)—C(12)	1·050 (72)
O(13)—C(13)	1·204 (56)	O(21)—C(21)	1·243 (57)
O(22)—C(22)	1·280 (62)	O(23)—C(23)	1·264 (57)
O(24)—C(24)	1·129 (56)	O(31)—C(31)	1·111 (37)
O(32)—C(32)	1·169 (58)	O(33)—C(33)	1·184 (44)
O(41)—C(41)	1·155 (53)	O(42)—C(42)	1·237 (55)
O(43)—C(43)	1·173 (52)	O(51)—C(51)	1·159 (51)
O(52)—C(52)	1·193 (49)	O(53)—C(53)	1·178 (47)
O(54)—C(54)	1·116 (52)	O(61)—C(61)	1·175 (49)
O(62)—C(62)	1·161 (51)	O(63)—C(63)	1·177 (47)

Table 2 (*cont.*)

Os(3)—Os(1)—Os(2)	59·6 (1)	S(1)—Os(1)—Os(2)	82·1 (2)
S(1)—Os(1)—Os(3)	53·5 (2)	C(11)—Os(1)—Os(2)	174·8 (12)
C(11)—Os(1)—Os(3)	115·2 (12)	C(11)—Os(1)—S(1)	94·1 (13)
C(12)—Os(1)—Os(2)	91·3 (17)	C(12)—Os(1)—Os(3)	139·3 (18)
C(12)—Os(1)—S(1)	98·0 (18)	C(12)—Os(1)—C(11)	92·8 (21)
C(13)—Os(1)—Os(2)	95·4 (14)	C(13)—Os(1)—Os(3)	121·4 (13)
C(13)—Os(1)—S(1)	174·9 (14)	C(13)—Os(1)—C(11)	88·1 (19)
C(13)—Os(1)—C(12)	86·5 (22)	Os(3)—Os(2)—Os(1)	60·1 (1)
C(21)—Os(2)—Os(1)	86·0 (14)	C(21)—Os(2)—Os(3)	86·4 (14)
C(22)—Os(2)—Os(1)	161·4 (16)	C(22)—Os(2)—Os(3)	102·2 (16)
C(22)—Os(2)—C(21)	87·4 (21)	C(23)—Os(2)—Os(1)	103·5 (14)
C(23)—Os(2)—Os(3)	163·7 (14)	C(23)—Os(2)—C(21)	92·8 (20)
C(23)—Os(2)—C(22)	94·1 (21)	C(24)—Os(2)—Os(1)	92·7 (14)
C(24)—Os(2)—Os(3)	90·0 (14)	C(24)—Os(2)—C(21)	176·3 (20)
C(24)—Os(2)—C(22)	92·9 (21)	C(24)—Os(2)—C(23)	90·8 (20)
Os(2)—Os(3)—Os(1)	60·3 (1)	S(1)—Os(3)—Os(1)	53·6 (2)
S(1)—Os(3)—Os(2)	82·6 (2)	C(31)—Os(3)—Os(1)	113·7 (9)
C(31)—Os(3)—Os(2)	84·8 (9)	C(31)—Os(3)—S(1)	165·7 (9)
C(32)—Os(3)—Os(1)	135·1 (13)	C(32)—Os(3)—Os(2)	89·8 (13)
C(32)—Os(3)—S(1)	92·7 (12)	C(32)—Os(3)—C(31)	94·0 (15)
C(33)—Os(3)—Os(1)	113·8 (9)	C(33)—Os(3)—Os(2)	173·9 (10)
C(33)—Os(3)—S(1)	94·8 (9)	C(33)—Os(3)—C(31)	97·0 (13)
C(33)—Os(3)—C(32)	95·8 (17)	Os(6)—Os(4)—Os(5)	60·1 (1)
Os(6)—Os(5)—Os(4)	59·6 (1)	Os(5)—Os(6)—Os(4)	60·4 (1)
S(1)—C(1)—C(2)	106·6 (23)	C(3)—C(2)—C(1)	107·9 (26)
S(2)—C(3)—C(2)	108·8 (22)	Os(3)—S(1)—Os(1)	72·9 (2)
C(1)—S(1)—Os(1)	108·1 (12)	C(1)—S(1)—Os(3)	113·2 (11)
O(11)—C(11)—Os(1)	177·3 (34)	O(12)—C(12)—Os(1)	168·9 (56)
O(13)—C(13)—Os(1)	167·9 (37)	O(21)—C(21)—Os(2)	169·6 (37)
O(22)—C(22)—Os(2)	156·8 (42)	O(23)—C(23)—Os(2)	171·5 (38)
O(24)—C(24)—Os(2)	169·1 (39)	O(31)—C(31)—Os(3)	178·0 (27)
O(32)—C(32)—Os(3)	175·1 (39)	O(33)—C(33)—Os(3)	174·8 (28)

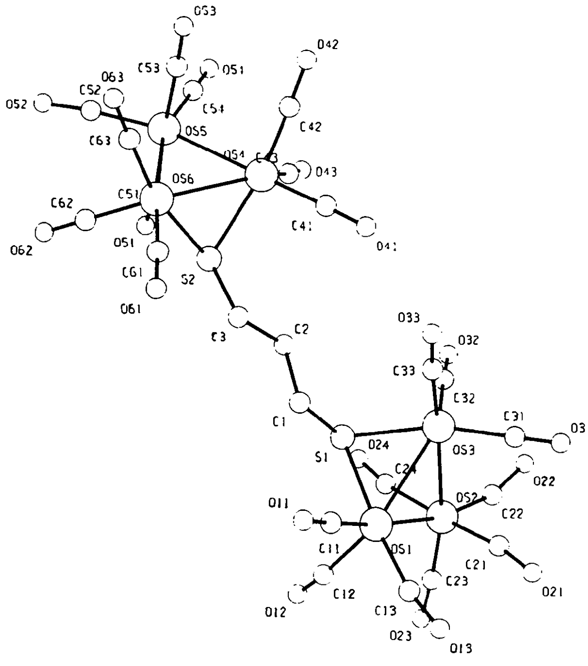
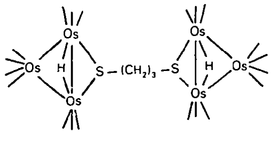


Fig. 1. Molecule (I), showing the numbering scheme.

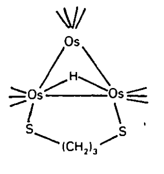
The propanedithiol chain has linked two $Os_3(CO)_{10}$ moieties giving a dimer with *triangulo*-triosmium frameworks which form approximately equilateral triangles. One side of each triangle is (μ-H) (μ-S)-bridged with Os(1)—Os(3) 2·856 (3) and Os(4)—Os(6) 2·841 (3) Å. Large angles for *cis* carbonyl groups [*e.g.* Os(3)—Os(1)—C(11) 115·2 (12), Os(1)—Os(3)—C(33) 113·8 (9)°] are taken as evidence for (μ-H) ligands, although the X-ray work did not locate the H atoms directly.

Geometries about the S atoms are unexceptional, the Os—S bond lengths of S(1)—Os(1) 2·406 (9), S(1)—Os(3) 2·403 (8), S(2)—Os(4) 2·419 (9), S(2)—Os(6) 2·403 (10) Å being entirely similar to those in compounds reviewed briefly in the preceding paper (Holden *et al.*, 1983*b*). S(1) lies 1·88 (2) Å below the plane of Os(1)Os(2)Os(3), and S(2) 1·90 (2) Å from that described by Os(4)Os(5)Os(6). The dihedral angle between these two planes of Os atoms is 78·9 (10)° (see Table 3). The —(C_3H_6)— link showed no evidence for conformational disorder in the crystal.

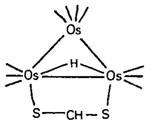
The structure determination shows the compound is (I) rather than (II), which had been strongly suggested on the basis of mass-spectral evidence. Adams & Selegue (1980) have reported the structural investigations of (III) and (IV) which have the bidentate dithioformato ligands chelating to give monomers. In (III), the (μ-H) Os—Os distance is 2·973 (1) Å (average) whilst the corresponding (μ-S_2CH) Os—Os in (IV) is 2·854 (1) Å.



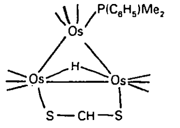
(I)



(II)



(III)



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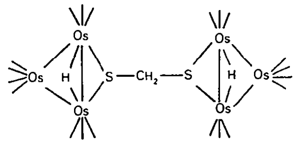
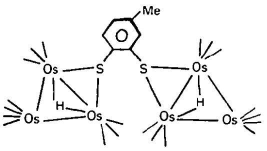


(V)



(VI)

Table 3. *Least-squares planes and atom distances from plane* (Å × 10^2)

Plane (1): Os(1), Os(2), Os(3)

$$-5{\cdot}453x + 7{\cdot}961y + 13{\cdot}358z - 1{\cdot}692 = 0$$

S(1)	−188 (2)	C(3)	−394 (4)
S(2)	−550 (2)	Os(4)	−504 (1)
C(1)	−228 (4)	Os(5)	−781 (1)
C(2)	−340 (4)	Os(6)	−598 (1)

Plane (2): Os(4), Os(5), Os(6)

$$11{\cdot}084x + 9{\cdot}067y + 2{\cdot}046z + 10{\cdot}662 = 0$$

S(2)	−190 (2)	C(3)	−227 (4)
S(1)	−515 (2)	Os(1)	−592 (1)
C(1)	−379 (4)	Os(2)	−717 (1)
C(2)	−324 (4)	Os(3)	−439 (1)

The dihedral angle between the planes is 78·9 (10)°.

Other examples of dimerization have been noted. (V) is formed by reaction of $H_2Os_3(CO)_{10}$ with CS_2 (Adams & Golembseki, 1979; Adams, Golembeski & Selegue, 1981), and our work has shown that 3,4-toluenedithiol reacts with $Os_3(CO)_{10}(MeCN)_2$ to give the analogous dimer (VI) (Holden & Uden, 1982, unpublished results). This compound crystallizes in the orthorhombic space group *Pbca*; all non-H atoms have been located, but the refinement converged at the high *R* value of *ca* 0·100, presumably because of problems with absorption corrections.

References

Adams, R. D. & Golembeski, N. M. (1979). *J. Am. Chem. Soc.* **101**, 1306–1307.

Adams, R. D., Golembeski, N. M. & Selegue, J. P. (1981). *J. Am. Chem. Soc.* **103**, 546–555.

Adams, R. D. & Selegue, J. P. (1980). *J. Organomet. Chem.* **195**, 223–238.

Holden, H. D., Johnson, B. F. G., Lewis, J., Raithby, P. R. & Uden, G. (1983*a*). *Acta Cryst.* C**39**, 1197–1200.

Holden, H. D., Johnson, B. F. G., Lewis, J., Raithby, P. R. & Uden, G. (1983*b*). *Acta Cryst.* C**39**, 1200–1203.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Uden, G. (1982). PhD Thesis, Univ. of Cambridge, England.

Acta Cryst. (1983). C**39**, 1205–1207

The Structure of (1,4-Dioxane)thallium(I) Tetrabromothallate(III), $Tl(C_4H_8O_2)^+.TlBr_4^-$

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Abstract. $M_r = 816{\cdot}4$, orthorhombic, $Cmc2_1$, $a = 10{\cdot}31$ (1), $b = 8{\cdot}560$ (5), $c = 15{\cdot}55$ (2) Å, $V = 1372{\cdot}3$ Å^3, $Z = 4$, $D_x = 3{\cdot}95$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 33{\cdot}98$ mm^{-1}, $F(000) = 1400$, $T = 293$ K, $R = 0{\cdot}057$ for 604 reflections. The structure consists of tetrahedral $TlBr_4^-$ ions and chains of Tl^+ ions bridged by 1,4-dioxane molecules; the geometry around eight-coordinate Tl^+ is a distorted dodecahedron.

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