Both molecules have an $-S=CPh_2$ group attached to Os(2), are planar at C(2), and have short S(2)–C(2) distances of 1·659 (21) and 1·604 (17) Å for (III) and (IV). The Os(2)–S(2) distances [2·348 (5), 2·349 (5) Å] are slightly shorter than Os–S distances for the (μ-S) moieties, average values for which are 2·425 Å for (III) and 2·404 Å for (IV). Such Os–S distances are entirely in accord with those observed for (μ-S) in (VI) (Adams & Golembeski, 1979; Adams, Golembeski & Selegue, 1981) having an average value of 2·417 Å.

(VII) (Johnson, Lewis, Pippard & Raithby, 1980) also has a (μ-SCH_3) group with Os–S distances of 2·402 Å.

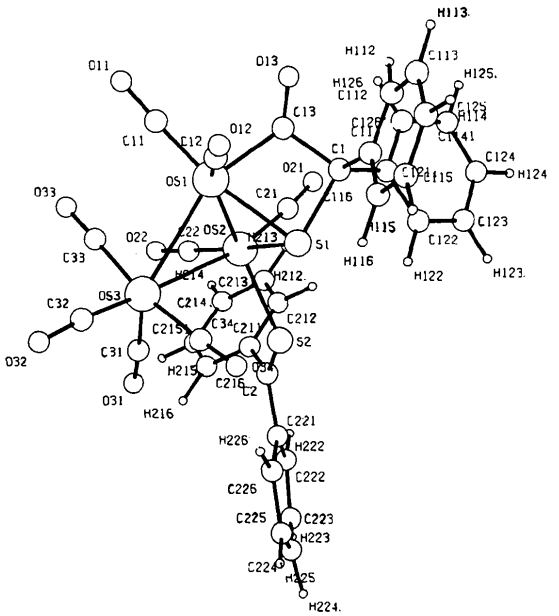

Fig. 1. Molecule (III) viewed perpendicular to the bridging carbonyl group.

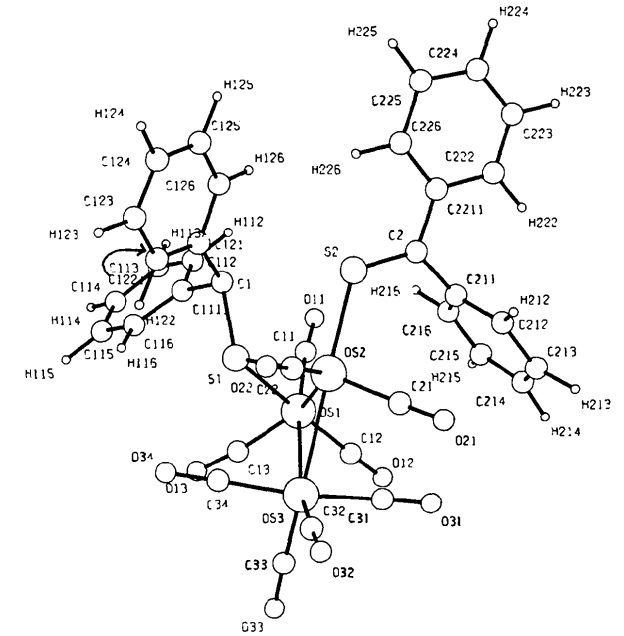

Fig. 2. A *PLUTO* drawing of molecule (IV).

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Structure of 1,1,1,2,2,2,3,3,3,3-Decacarbonyl-1,2-μ-diphenylmethylthiolato-1,2-μ-hydrido-*triangulo*-triosmium, $C_{23}H_{12}O_{10}Os_3S$

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(*Received* 17 *November* 1982; *accepted* 30 *March* 1983)

Abstract. $M_r = 1050·95$, triclinic, space group $P\bar{1}$, $a = 9·250$ (5), $b = 12·274$ (8), $c = 13·526$ (9) Å, $\alpha = 97·55$ (5), $\beta = 94·89$ (5), $\gamma = 117·96$ (4)°, $U = 1325·7$ (14) Å^3, $Z = 2$, $D_x = 2·63$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 14·45$ mm^{-1}, $F(000) = 924$, $T = 298$ K. The structure refined to a final R of 0·0453

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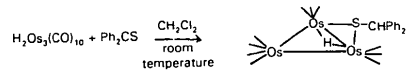
for 3872 observed reflections. The molecule is a *triangulo*-triosmium framework with an Os—Os edge bridged by (μ_2-H) and (μ_2-SCHPh$_2$).

Introduction. As a continuation of a series of work* investigating the reaction of triosmium clusters with thioorganic compounds, the molecular structure for the title compound (I) is now reported. It was formed in low yield as the only product in the reaction of $H_2Os_3(CO)_{10}$ with thiobenzophenone.



(I)

Experimental. Bronze-coloured, shining crystals, suitable for X-ray work, obtained by slow crystallization from hexane (Uden, 1982); approximate crystal size 0·13 × 0·29 × 0·19 mm. Syntex $P2_1$ four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Lp and semi-empirical absorption corrections applied. Intensity data for 4688 reflections with $3 \le 2\theta \le 55°$ in hemisphere $+h, \pm k, \pm l$ collected in ω–2θ scan mode; 3872 unique data having $F_o \ge 6\sigma(F_o)$ used during subsequent structure solution and refinement. No systematic absences observable, thus indicating triclinic, $P1$ or $P\bar{1}$; solution of structure and its refinement entirely satisfactory in the latter. Structure solution by direct methods using *SHELX*76 (Sheldrick, 1976) revealed positions for the three Os atoms, and thereafter

* See preceding paper (Holden, Johnson, Lewis, Raithby & Uden, 1983).

Table 1. *Fractional coordinates* (×10⁴) *and isotropic temperature factors* (Å² × 10³)

	x	y	z	U_{eq}/U_{iso}
Os(1)	1628 (1)	8061 (1)	1608 (1)	55 (1)*
Os(2)	4664 (1)	9531 (1)	3014 (1)	54 (1)*
Os(3)	2181 (1)	10303 (1)	2886 (1)	55 (1)*
S(1)	4719 (4)	11180 (3)	2205 (3)	46 (2)*
C(111)	5763 (18)	13738 (14)	2662 (11)	40 (3)
C(112)	5198 (24)	13709 (19)	1650 (15)	65 (5)
C(113)	4979 (26)	14687 (20)	1397 (17)	74 (6)
C(114)	5337 (25)	15666 (19)	2118 (15)	69 (5)
C(115)	5947 (23)	15774 (18)	3084 (15)	62 (5)
C(116)	6097 (21)	14764 (16)	3355 (13)	53 (4)
C(121)	7952 (18)	13126 (14)	2897 (11)	39 (3)
C(122)	9115 (22)	13580 (16)	3786 (14)	56 (4)
C(123)	10751 (31)	13940 (22)	3751 (19)	88 (7)
C(124)	11239 (29)	13870 (20)	2802 (17)	78 (6)
C(125)	10185 (30)	13474 (22)	1931 (19)	87 (7)
C(126)	8436 (24)	13080 (18)	1992 (15)	64 (5)
C(11)	−535 (23)	7573 (17)	938 (14)	58 (4)
O(11)	−1829 (21)	7314 (15)	516 (12)	93 (5)
C(12)	696 (23)	7200 (17)	2686 (14)	58 (4)
O(12)	227 (18)	6701 (13)	3346 (11)	77 (4)
C(13)	1956 (24)	6771 (18)	1004 (14)	62 (5)
O(13)	2152 (21)	5940 (16)	580 (13)	99 (5)
C(14)	2613 (22)	9014 (17)	584 (14)	56 (4)
O(14)	3117 (17)	9547 (13)	−39 (10)	71 (4)
C(21)	4143 (23)	8150 (18)	3634 (14)	60 (5)
O(21)	3880 (18)	7351 (14)	4088 (11)	80 (4)
C(22)	5748 (22)	9037 (16)	2109 (13)	54 (4)
O(22)	6365 (19)	8692 (14)	1529 (12)	85 (4)
C(23)	6644 (22)	10568 (16)	3971 (13)	54 (4)
O(23)	7822 (19)	11057 (14)	4578 (11)	82 (4)
C(31)	255 (24)	9376 (18)	3414 (14)	61 (5)
O(31)	−903 (20)	8854 (15)	3795 (12)	87 (4)
C(32)	1033 (22)	10573 (16)	1849 (13)	52 (4)
O(32)	283 (19)	10720 (14)	1206 (12)	87 (4)
C(33)	2700 (23)	11758 (18)	3827 (14)	59 (5)
O(33)	3051 (18)	12657 (14)	4446 (11)	77 (4)
C(1)	6169 (18)	12738 (14)	2979 (12)	40 (3)

* U_{eq} = ⅓ of the trace of the orthogonalized **U** matrix.

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

Os(2)–Os(1)	2·863 (2)	Os(3)–Os(1)	2·847 (2)
C(11)–Os(1)	1·899 (19)	C(12)–Os(1)	1·935 (19)
C(13)–Os(1)	1·850 (20)	C(14)–Os(1)	1·939 (18)
Os(3)–Os(2)	2·867 (2)	S(1)–Os(2)	2·406 (3)
C(21)–Os(2)	1·866 (19)	C(22)–Os(2)	1·859 (19)
C(23)–Os(2)	1·905 (18)	S(1)–Os(3)	2·404 (4)
C(31)–Os(3)	1·873 (20)	C(32)–Os(3)	1·844 (17)
C(33)–Os(3)	1·880 (19)	C(1)–S(1)	1·839 (15)
H(1)–C(1)	0·853 (100)	C(111)–C(1)	1·541 (20)
C(121)–C(1)	1·506 (20)	C(112)–C(111)	1·413 (23)
C(116)–C(111)	1·356 (22)	C(113)–C(112)	1·387 (26)
C(114)–C(113)	1·331 (26)	C(115)–C(114)	1·343 (25)
C(116)–C(115)	1·401 (24)	C(122)–C(121)	1·398 (22)
C(126)–C(121)	1·342 (23)	C(123)–C(122)	1·371 (28)
C(124)–C(123)	1·402 (30)	C(125)–C(124)	1·335 (29)
C(126)–C(125)	1·469 (29)	O(11)–C(11)	1·158 (21)
O(12)–C(12)	1·150 (20)	O(13)–C(13)	1·200 (22)
O(14)–C(14)	1·132 (20)	O(21)–C(21)	1·166 (21)
O(22)–C(22)	1·156 (21)	O(23)–C(23)	1·151 (20)
O(31)–C(31)	1·166 (22)	O(32)–C(32)	1·152 (20)
O(33)–C(33)	1·183 (21)		
Os(3)–Os(1)–Os(2)	60·3 (1)	C(11)–Os(1)–Os(2)	157·8 (6)
C(11)–Os(1)–Os(3)	97·6 (6)	C(12)–Os(1)–Os(2)	87·2 (5)
C(12)–Os(1)–Os(3)	86·8 (5)	C(12)–Os(1)–C(11)	90·4 (8)
C(13)–Os(1)–Os(2)	100·8 (6)	C(13)–Os(1)–Os(3)	161·1 (6)
C(13)–Os(1)–C(11)	101·3 (8)	C(13)–Os(1)–C(12)	92·8 (8)
C(14)–Os(1)–Os(2)	90·6 (5)	C(14)–Os(1)–Os(3)	90·0 (5)
C(14)–Os(1)–C(11)	90·8 (8)	C(14)–Os(1)–C(12)	176·7 (8)
C(14)–Os(1)–C(13)	89·9 (8)	Os(3)–Os(2)–Os(1)	59·6 (1)
S(1)–Os(2)–Os(1)	81·8 (1)	S(1)–Os(2)–Os(3)	53·4 (1)
C(21)–Os(2)–Os(1)	89·2 (6)	C(21)–Os(2)–Os(3)	114·8 (6)
C(21)–Os(2)–S(1)	167·8 (6)	C(22)–Os(2)–Os(1)	89·1 (5)
C(22)–Os(2)–Os(3)	136·2 (5)	C(22)–Os(2)–S(1)	95·6 (5)
C(22)–Os(2)–C(21)	92·5 (8)	C(23)–Os(2)–Os(1)	177·0 (5)
C(23)–Os(2)–Os(3)	117·5 (5)	C(23)–Os(2)–S(1)	96·4 (5)
C(23)–Os(2)–C(21)	92·3 (8)	C(23)–Os(2)–C(22)	93·4 (8)
Os(2)–Os(3)–Os(1)	60·1 (1)	S(1)–Os(3)–Os(1)	82·2 (1)
S(1)–Os(3)–Os(2)	53·4 (1)	C(31)–Os(3)–Os(1)	89·9 (6)
C(31)–Os(3)–Os(2)	117·2 (6)	C(31)–Os(3)–S(1)	170·0 (6)
C(32)–Os(3)–Os(1)	88·8 (5)	C(32)–Os(3)–Os(2)	134·7 (5)
C(32)–Os(3)–S(1)	93·1 (5)	C(32)–Os(3)–C(31)	92·8 (8)
C(33)–Os(3)–Os(1)	173·8 (6)	C(33)–Os(3)–Os(2)	114·3 (6)
C(33)–Os(3)–S(1)	96·5 (6)	C(33)–Os(3)–C(31)	90·7 (8)
C(33)–Os(3)–C(32)	97·4 (8)	Os(3)–S(1)–Os(2)	73·2 (1)
C(1)–S(1)–Os(2)	111·1 (5)	C(1)–S(1)–Os(3)	109·0 (5)
C(111)–C(1)–S(1)	110·3 (10)	C(121)–C(1)–S(1)	112·3 (11)
C(121)–C(1)–C(111)	108·9 (12)	C(112)–C(111)–C(1)	123·1 (15)
C(116)–C(111)–C(1)	119·6 (14)	C(116)–C(111)–C(112)	117·0 (15)
C(113)–C(112)–C(111)	120·6 (18)	C(114)–C(113)–C(112)	119·1 (20)
C(115)–C(114)–C(113)	123·1 (21)	C(116)–C(115)–C(114)	118·1 (19)
C(115)–C(116)–C(111)	122·0 (16)	C(122)–C(121)–C(1)	118·6 (14)
C(126)–C(121)–C(1)	121·1 (15)	C(126)–C(121)–C(122)	120·2 (16)
C(123)–C(122)–C(121)	120·8 (18)	C(124)–C(123)–C(122)	118·4 (22)
C(125)–C(124)–C(123)	123·0 (24)	C(126)–C(125)–C(124)	117·3 (22)
C(125)–C(126)–C(121)	120·1 (18)	O(11)–C(11)–Os(1)	177·6 (17)
O(12)–C(12)–Os(1)	176·3 (17)	O(13)–C(13)–Os(1)	177·7 (17)
O(14)–C(14)–Os(1)	176·8 (16)	O(21)–C(21)–Os(2)	174·9 (17)
O(22)–C(22)–Os(2)	177·4 (17)	O(23)–C(23)–Os(2)	171·5 (16)
O(31)–C(31)–Os(3)	175·9 (17)	O(32)–C(32)–Os(3)	178·4 (16)
O(33)–C(33)–Os(3)	177·5 (16)		

full-matrix least-squares refinement on F^2 and difference syntheses found positions for all non-H atoms. With Os and S refined anisotropically, C, O and H(1) isotropically, and phenyl H atoms in calculated positions, R converged to 0·0453 and R_g to 0·0502; unit weights used throughout. All atoms had complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974).

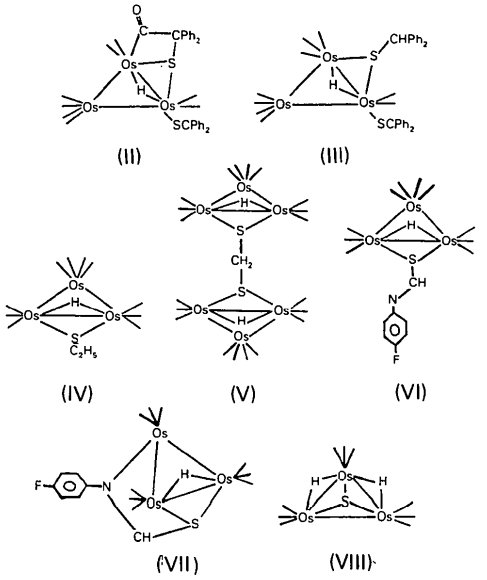
Discussion. Table 1* shows fractional atomic coordinates and isotropic thermal parameters, Table 2 bond lengths and angles. A drawing of the molecule is presented in Fig. 1 and unit-cell contents are shown in Fig. 2.

In contrast with the products of the reaction of thiobenzophenone with $H_2Os_3(CO)_9(NMe_3)$ (II, III), reported in the previous paper, the organic thiol reacts with $H_2Os_3(CO)_{10}$ to give the title compound (I). Only one mole of Ph_2CS reacts. The three Os atoms lie in an almost equilateral triangle, with Os(1)–Os(2) 2·863 (2) and Os(1)–Os(3) 2·847 (2) Å. The (μ-SCHPh$_2$) moiety lies across the Os(2)–Os(3) edge [2·867 (2) Å]. The large angles for the *cis* carbonyl ligands [Os(3)–Os(2)–C(21) 114·8 (6), Os(2)–Os(3)–C(31) 117·2 (6)°] indicate that there is also a bridging hydride across this Os–Os bond. The S(1)–C(1) distance of 1·839 (15) Å and the tetrahedral geometry at C(1) show the second H atom to be located on C(1).

The geometry of the carbonyls about Os(1) is also noteworthy. p_π–d_π backbonding from carbon to osmium bonds takes place into the same *d*-orbital for the –C(12)–O(12) and –C(14)–O(14) carbonyls. This manifests itself as a noticeable lengthening of Os–C distances [Os(1)–C(12) 1·935 (19), Os(1)–C(14) 1·939 (18) Å], compared to those where the carbonyls are not competing for electron back-donation into the same *d*-orbital. Thus Os(1)–C(11) 1·899 (19) and Os(1)–C(13) 1·850 (20) Å are shorter.

The Os–S distances are comparable to those reported in other (μ-S*R*) compounds. Average Os–S distances in (IV) [2·40 (1) Å (Allen, Mason & Hitchcock, 1977)], (V) [2·422 (4) Å (Adams, Golembeski & Selegue, 1981)], (VI) [2·423 (3) Å (Adams & Dawoodi, 1981)] and the compound reported in this work [Os(2)–S(1) 2·406 (3), Os(3)–S(1) 2·404 (4) Å] are all similar. Slightly longer Os–S bond lengths have been noted by Adams & Dawoodi (1981) for (VII), a decarbonylated decomposition product of (VI) [average Os–S 2·453 (4) Å].

Reaction of $H_2Os_3(CO)_{10}$ with COS (Uden, 1982) gives rise to the previously characterized μ_3-sulphido compound, (VIII) (Johnson, Lewis, Pippard, Raithby, Sheldrick & Rouse, 1979).



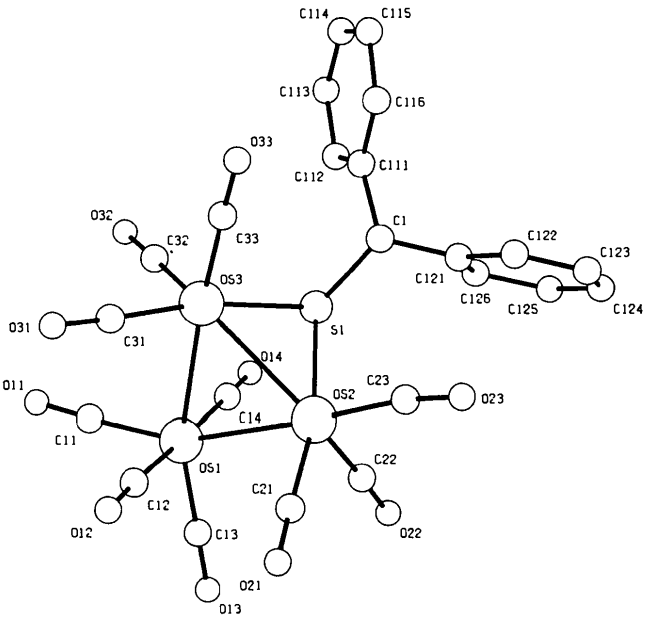


Fig. 1. The molecule showing the atom-numbering scheme.

* Lists of structure factors, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38564 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

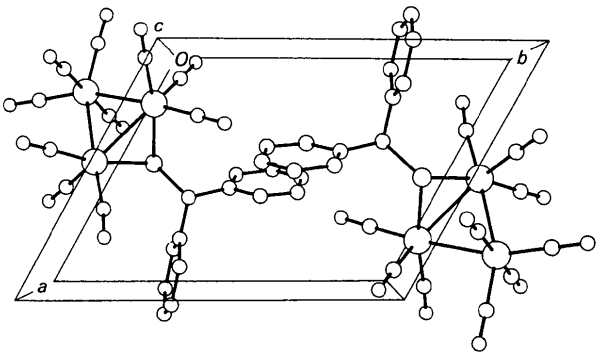


Fig. 2. The contents of the unit cell.

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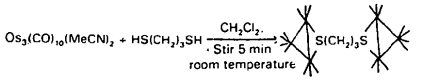
(*Received* 17 *November* 1982; *accepted* 2 *February* 1983)

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}, λ(Mo $K\alpha$) = 0·71069 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 (μ-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 $3 \le 2\theta \le 50°$ measured; 3582 reflections [$I \ge 3\sigma(I)$] 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.

* To whom correspondence should be addressed.

† 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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