The Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with Heterocyclic Thioamides. The Crystal and Molecular Structure of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}S\overline{C{=}NCH_2CH_2S})]$†

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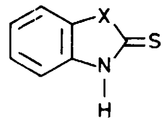
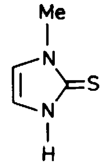
The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with the heterocyclic thioamides HL yields products which are formulated as $[Os_3H(CO)_{10}L]$ (L being the deprotonated thioamide co-ordinated *via* the exocyclic sulphur atom). The structure of $[Os_3H(CO)_{10}(S\overline{C{=}NCH_2CH_2S})]$ has been established by an *X*-ray analysis. The crystals are monoclinic, space group $P2_1/c$, $a = 19.387(8)$, $b = 9.528(2)$, $c = 24.420(7)$ Å, $\beta = 111.20(2)°$, and $Z = 8$. The structure was refined to $R = 0.0825$ for 5 390 unique diffractometer data. The osmium atoms define a triangle with the thioamido ligand bridging one edge *via* the exocyclic sulphur atom. Spectroscopic data on the complexes, supported by the *X*-ray structure of $[Os_3H(CO)_{10}(S\overline{C{=}NCH_2CH_2S})]$, indicate the thioamido ligands are binding in the thiolate form. The $[Os_3H(CO)_{10}L]$ complexes are decarbonylated to yield $[Os_3H(CO)_9L]$ complexes upon reaction with trimethylamine oxide or by refluxing in octane. Further thermolysis of $[Os_3H(CO)_9(S\overline{C{=}NCH_2CH_2S})]$ affords the sulphur capped species $[Os_3H(CO)_9(\mu_3\text{-}S)L]$ (L = thiazolinyl ligand formed from the desulphurization of $(S\overline{C{=}NCH_2CH_2S})$.

Triosmium clusters exhibit a marked propensity to react with a range of organosulphur compounds.[1-4] Although their interaction with thioamides has not been studied previously it was recently reported[4] that thioformamido complexes of the type $[Os_3(\mu\text{-}H)(CO)_{10}L]$ are obtained when organoisothiocyanates add to $[Os_3H_2(CO)_{10}]$. Thioamido complexes are obtained[5,6] when $[Ru_3(CO)_{12}]$ reacts with the heterocyclic thioamide, benzothiazoline-2-thione (2-mercaptobenzothiazole), HL^1; *e.g.* $[Ru_2(CO)_6L^1{}_2]$ and $[Ru_3(\mu\text{-}H)(CO)_9L^1]$. In contrast[7] the reaction of HL^1 with $[Fe_3(CO)_{12}]$ affords $[Fe_3(CO)_9S_2]$. Desulphurization of thioamide ligands also occurs when $[Co_2(CO)_8]$ reacts with the primary thioamides $R^1C(S)NHR^2$ ($R^1 = CH_3$ or C_6H_5, $R^2 = C_6H_{11}$), but in this case the organic moiety remains co-ordinated in the product complexes, which are of the type $[Co_3(CO)_7(\mu_3\text{-}S)(\mu\text{-}R^1C{=}NR^2)]$.[8]

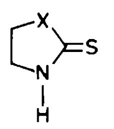
In this paper we report that the heterocyclic thioamides HL^1—HL^6 react readily with $[Os_3(CO)_{10}(MeCN)_2]$ to yield the complexes $[Os_3H(CO)_{10}L]$. Decarbonylation of these complexes, either thermally ($L = L^5$) or by reaction with trimethylamine oxide ($L = L^1$, L^2, or L^6), gives the complexes $[Os_3H(CO)_9L]$. In the case where $L = L^5$, further thermal reaction causes the desulphurization of the thioamido ligand, resulting in the complex $[Os_3H(CO)_9(\mu_3\text{-}S)L^7]$ (for L^7 see Figure 2). Carbon-13 and hydrogen-1 (including ^{187}Os–^1H coupling) n.m.r. data have been used extensively to provide structural information on the new compounds, and for $[Os_3H(CO)_{10}L^5]$ an *X*-ray structural analysis has been carried out. A preliminary report of this work has appeared.[9]



HL^1 X = S
HL^2 X = O
HL^3 X = NH



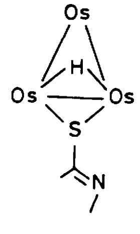
HL^4



HL^5 X = S
HL^6 X = NH

Results and Discussion

The Complexes $[Os_3H(CO)_{10}L]$ ($L = L^1$—L^6).—Analytical, mass spectral, and ν(CO) i.r. data for these complexes, obtained from the reaction of the thioamides HL^1—HL^6 with the cluster complex $[Os_3(CO)_{10}(MeCN)_2]$, are listed in Table 1. N.m.r. spectral data (Tables 2 and 3) and the *X*-ray structure of $[Os_3H(CO)_{10}L^5]$ indicate that the thioamide ligand should be regarded as binding in the thiolate form as depicted in (**1**), rather than in the thione form found for the free thioamides.



(**1**)

The structure of $[Os_3H(CO)_{10}L^5]$ is shown in Figure 1 and selected bond parameters are presented in Table 4. There are two crystallographically independent molecules which are chemically similar. The osmium atoms define a triangle with the Os–Os distances [2.837(2)—2.865(2) Å] being slightly shorter than the average metal–metal distance of 2.877(3) Å found in $[Os_3(CO)_{12}]$.[10] The thioamido ligand bridges an edge of the cluster *via* the exocyclic sulphur atom. The Os–S distances [2.416(11)—2.419(8) Å] are similar to those found in other (μ-SR) osmium clusters.[2-4,11] Within the thioamido ligand, the exocyclic C(1a,b)–S(1a,b) bond at 1.79(4) Å is as expected[12] for a single bond (*ca.* 1.80 Å). It is longer than that observed[13,14] for free HL^5 [1.641(7)—1.680(7) Å] or for the complexed thione form (1.67—1.68 Å) in $[PdCl_2(HL^5)_4]$[14] and $[W(CO)_5$-

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† 1,1,1,2,2,2,3,3,3,3-Decacarbonyl-1,2-μ-hydrido-1,2-μ-(thiazoline-2-thiolato)-*triangulo*-triosmium.

Supplementary data available: See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Table 1. Analytical, mass spectral, and i.r. data for the complexes

Compound	Analysis (%)[a] C	H	N	m/z $[M^+(^{192}Os)]$	$\tilde{\nu}$(CO)/cm^{-1} (cyclohexane solution)
$[Os_3H(CO)_{10}L^1]$	20.1 (20.1)	0.4 (0.5)	1.2 (1.4)	1 023	2 100m, 2 071vs, 2 061s, 2 023s, 2 015s, 2 008s, 1 989 (sh), 1 985m
$[Os_3H(CO)_{10}L^2]$	20.5 (20.4)	0.45 (0.5)	1.5 (1.4)	1.007	2 112m, 2 074vs, 2 063s, 2 024s, 2 016s, 2 009s, 1 990 (sh), 1 986m
$[Os_3H(CO)_{10}L^3]$	20.6 (20.4)	0.5 (0.6)	2.7 (2.8)	1 006	2 108m, 2 072vs, 2 061s, 2 021s, 2 011s, 1 982m[b]
$[Os_3H(CO)_{10}L^4]$	17.7 (17.4)	0.7 (0.6)	3.15 (2.9)	970	2 109m, 2 072vs, 2 061s, 2 022vs, 2 012s, 2 005 (sh), 1 987 (sh), 1 984m
$[Os_3H(CO)_{10}L^5]$	16.2 (16.1)	0.5 (0.5)	1.5 (1.4)	975	2 109m, 2 071vs, 2 061s, 2 022s, 2 015s, 2 005m, 1 987 (sh), 1 984w
$[Os_3H(CO)_{10}L^6]$[c]	17.8 (17.9)	0.9 (1.0)	2.95 (2.9)	958	2 110m, 2 072vs, 2 062s, 2 023vs, 2 014s, 2 007m, 1 990 (sh), 1 986m
$[Os_3H(CO)_9L^1]$	19.3 (19.4)	0.5 (0.5)	1.4 (1.4)	995	2 091 (sh), 2 088m, 2 059s, 2 035m, 2 032s, 2 010w, 2 006s, 1 994s, 1 968m, 1 962w, 1 957m
$[Os_3H(CO)_9L^2]$	19.9 (19.7)	0.55 (0.5)	1.3 (1.4)	979	2 093w, 2 090m, 2 062 (sh), 2 059s, 2 037 (sh), 2 034s, 2 013m, 2 007s, 1 994s, 1 970m, 1 963w, 1 960m
$[Os_3H(CO)_9L^5]$	15.2 (15.3)	0.5 (0.5)	1.5 (1.5)	947	2 090w, 2 087m, 2 057s, 2 034 (sh), 2 031s, 2 009m, 2 004s, 1 991s, 1 968m, 1 960w, 1 954m
$[Os_3H(CO)_9L^6]$	15.6 (15.6)	0.7 (0.65)	3.0 (3.0)	930	2 090w, 2 086m, 2 058m, 2 054s, 2 032 (sh), 2 030s, 2 007m, 2 001s, 1 987s, 1 964m, 1 956w, 1 952m[d]
$[Os_3H(CO)_9(\mu_3\text{-}S)L^7]$	15.3 (15.3)	0.5 (0.5)	1.4 (1.5)	947	2 109m, 2 078vs, 2 047vs, 2 040m, 2 022s, 2 009w, 2 004s, 1 985m, 1 978m, 1 969m

[a] Required values given in parentheses. [b] ν(NH) at 3 365 cm^{-1}. [c] Contains 0.25 molecule hexane. [d] ν(NH) at 3 461 cm^{-1}.

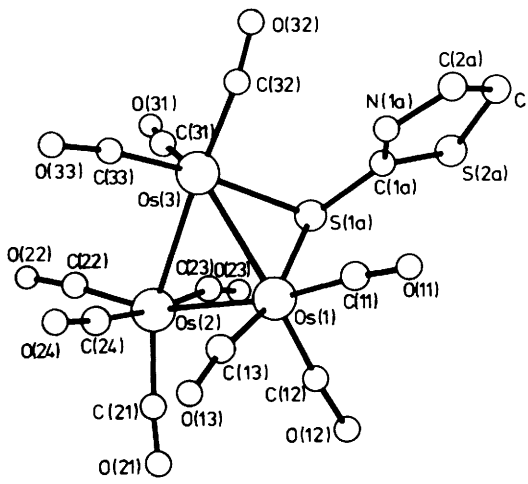


Figure 1. Molecular structure of $[Os_3H(CO)_{10}L^5]$

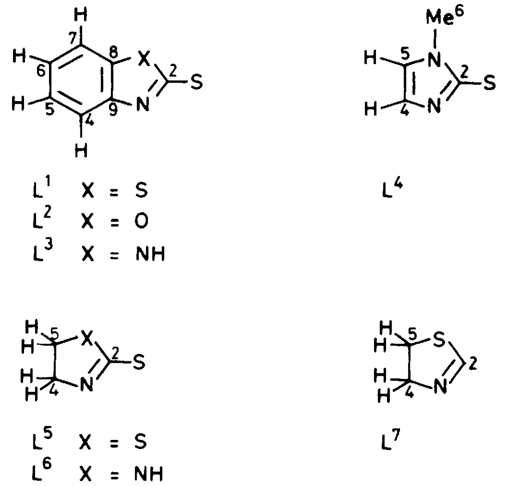
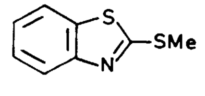


Figure 2. Ligand atom-numbering scheme for n.m.r. assignments in Table 2

$(HL^5)]$.[15] The C(1a,b)–N(1a,b) bond distance of 1.29(7) Å indicates appreciable double-bond character.[12] The hydride ligand was not located directly by the *X*-ray analysis, but the observation in the ^{1}H n.m.r. spectrum of a resonance at -17.25 p.p.m. indicated its presence (Table 2). Moreover, since a single satellite peak due to ^{187}Os–^{1}H coupling is seen on either side of this resonance [^1J(OsH) = 33.8 Hz], the hydride must bridge equivalent osmium atoms as shown in (1). Similar ^{187}Os–^{1}H couplings are exhibited by the other $[Os_3H(CO)_{10}L]$ complexes.[16]

Full carbon-13 and hydrogen-1 n.m.r. data for the complexed thioamido ligands are listed in Table 2 and resonances have been assigned following the numbering scheme in Figure 2. Proton resonances have been assigned in the normal manner using decoupling techniques and in the case of $[Os_3H(CO)_{10}L^1]$ confirmed by computer simulation to extract the coupling constants. Carbon-13 resonances have been assigned on the basis of their relative intensities and gated-decoupling experiments, including selective proton–carbon decoupling. Chemical shifts were also compared with data available for the parent thioamides, HL,[17–22] and their 2-methylthio derivatives[20–24] (*e.g.* MeL^1). The carbon-13 chemical shifts lie closer to the values observed for the 2-methylthio compounds than for the thioamides, which is a further pointer to the thiolate mode of bonding. For example, the C^2 resonance, which occurs at 189.9



MeL^1

Table 2. Hydrogen-1 and thioamido ligand ^{13}C n.m.r. data for the complexes

	^{13}C (δ[a]/p.p.m.)							^1H (δ[a]/p.p.m.)				
Compound	C^2	C^4	C^5	C^6	C^7	C^8	C^9	H^4	H^5	H^6	H^7	Os–H
$[Os_3H(CO)_{10}L^1]$	171.6	123.1 [^1J(CH) 163.6]	126.7 [^1J(CH) 160.6]	126.1 [^1J(CH) 160.8]	121.6 [^1J(CH) 164.6]	138.3	151.1	7.90 (d)[b]	7.45 (t)	7.37 (t)	7.76 (d)	−16.81 [^1J(OsH) 34.0]
$[Os_3H(CO)_9L^1]$	190.7	125.5 [^1J(CH) 165.9]	129.0 [^1J(CH) 163.9]	126.6 [^1J(CH) 163.1]	122.2 [^1J(CH) 166.8]	132.9	151.7	7.89 [d, J(HH) 8.9]	*ca.* 7.72	7.47 (t)	*ca.* 7.73	−14.59 [7,[c] ^1J(OsH) 34.2] −12.25 (1)
$[Ru_3H(CO)_9L^1]$[d]	*e*	123.7	128.9	126.5	122.6	134.7	152.3	7.77 [d, J(HH) 8.3]	7.62 [t, J(HH) 7.7]	7.40 [t, J(HH) 7.6]	7.71 [d, J(HH) 8.0]	−12.90 (12)[f] −13.71 (1)[f]
$[Os_3H(CO)_{10}L^2]$	169.1	120.0 [^1J(CH) 165.6]	126.0 [^1J(CH) 162.6]	125.2 [^1J(CH) 161.2]	110.4 [^1J(CH) 166.3]	152.0	141.3	*ca.* 7.69 (m)	*ca.* 7.30 (m)[g]	*ca.* 7.31 (m)[g]	*ca.* 7.38 (m)	−16.94 [^1J(OsH) 34.1]
$[Os_3H(CO)_9L^2]$[h]								*i*				−14.30 [5, ^1J(OsH) 34.4] −12.31 [3, ^1J(OsH) 30.8, 32.9]
$[Os_3H(CO)_{10}L^3]$	155.3	119.8 [^1J(CH) 163.9]	124.3 [^1J(CH) 161.1]	122.9 [^1J(CH) 164.1]	110.4 [^1J(CH) 163.1]	142.2[g]	135.5[g]	7.64 (d)[j]	*ca.* 7.30 (m)	*ca.* 7.30 (m)	7.33 (d)	−16.67 [^1J(OsH) 33.9]
$[Os_3H(CO)_{10}L^4]$	148.5	127.5 [^1J(CH) 192.1]	124.1 [^1J(CH) 189.0]	34.1 [^1J(CH) 140.4]				6.93 [d, J(HH) 1.2][g]	6.91 [d, J(HH) 1.2][g]	3.79 (s)		−16.75 [^1J(OsH) 33.6]
$[Os_3H(CO)_{10}L^5]$	172.5	62.7 [^1J(CH) 143.9]	39.2 [^1J(CH) 144.2]					4.22 [t, J(HH) 8.4]	3.56 [t, J(HH) 8.4]			−17.25 [^1J(OsH) 33.8]
$[Os_3H(CO)_9L^5]$	198.1	70.1 (3)[c] 69.6 (1)	37.6 (3) 37.1 (1)					3.96 [t, J(HH) 8.3][k]	3.47 [t, J(HH) 8.3][k]			−14.41 [3, ^1J(OsH) 34.1] −11.97 (1)
$[Os_3H(CO)_{10}L^6]$[h]								3.73[l]	3.73			−17.15
$[Os_3H(CO)_9L^6]$	*e*	60.0[m]	48.4[m]					3.2—3.6[n]				−14.59 [5, ^1J(OsH) 34.2] −12.53 [4, ^1J(OsH) 30.5, 33.5]
$[Os_3H(CO)_9(\mu_3\text{-}S)L^7]$[o]	212.3	72.8 (2) 71.6 (1)	33.4					4.06 (m)	2.82 (m)			−16.76 (br) −17.24 (2), −15.90 (1)[p]

[a] Unless otherwise stated, in $CDCl_3$, at 25 °C; J values in Hz. For atom numbering see Figure 2. [b] The H^4—H^7 resonances are further split as result of longer-range coupling. Calculated coupling constants: $J(H^4H^5)$ 6.20, $J(H^4H^6)$ 0.58, $J(H^4H^7)$ 2.39, $J(H^5H^6)$ 7.50, $J(H^5H^7)$ 1.24, and $J(H^6H^7)$ 7.68 Hz. [c] Relative intensity. [d] Proton n.m.r. data in CD_2Cl_2. [e] Not observed. [f] At −35 °C. [g] Assignments may be interchanged. [h] Carbon-13 n.m.r. data not recorded. [i] $\delta(H^4$—$H^7)$ complex multiplet *ca.* 7.45 p.p.m. [j] δ(NH) 9.33 p.p.m. [k] Major resonance. Weaker resonances not listed, assigned to unsymmetrical isomer also observed. [l] At −10 °C. δ(NH) not observed. At −30 °C, two broad resonances observed for H^4,H^5. [m] Broad. [n] Complex multiplets for H^4 and H^5. [o] In CD_2Cl_2; ^{13}C at −20 °C, ^1H at 0 °C. [p] At −60 °C.

Table 3. Carbonyl carbon-13 n.m.r. data (δ/p.p.m.)[a] for the complexes

Compound	A,B	C	D,E	F[b]
$[Os_3H(CO)_{10}L^1]$	180.9, 179.8	173.7	176.3, 170.2	168.9 (10.6)
$[Os_3H(CO)_{10}L^2]$	180.5, 179.5	173.3	176.1, 169.6	168.3 (11.3)
$[Os_3H(CO)_{10}L^3]$	181.5, 179.8	173.7	176.2, 169.8	169.1 (10.0)
$[Os_3H(CO)_{10}L^4]$	181.7, 180.0	174.0	176.4, 169.7	169.5 (11.7)
$[Os_3H(CO)_{10}L^5]$	180.7, 179.9	173.7	176.4, 170.3	168.8 (9.8)

	A	B	C,D	E
$[Os_3H(CO)_9L^1]$[c]	187.2	181.3	179.0, 174.8	174.2 (9.2)
$[Os_3H(CO)_9L^5]$[c]	187.1	181.5	178.8, 175.5	174.9
$[Os_3H(CO)_9L^6]$[c]	186.3	182.6	179.3, 175.9	175.8
$[Os_3H(CO)_9(\mu_3\text{-}S)L^7]$[d]	184.1, 181.2, 178.2, 175.5, 174.8, 174.2, 173.1, 169.2, 165.3			

[a] In $CDCl_3$ at 25 °C. For carbonyl labelling see Figure 3. Relative intensities: for $[Os_3H(CO)_{10}L]$ A,B = 1; C,D,E,F = 2; for $[Os_3H(CO)_9L]$ B = 1; A,C,D,E = 2. [b] ^2J(CH)/Hz in parentheses. [c] Only resonances for symmetrical form are listed. [d] In CD_2Cl_2 at −20 °C. Only nine most intense resonances are listed; all of approximately same intensity.

Table 4. Selected bond distances (Å) and angles (°) for $[Os_3H(CO)_{10}L^5]$ with estimated standard deviations in parentheses

Molecule 1		Molecule 2	
Os(1)–Os(2)	2.864(2)	Os(4)–Os(6)	2.854(2)
Os(1)–Os(3)	2.842(2)	Os(4)–Os(5)	2.865(2)
Os(2)–Os(3)	2.855(2)	Os(6)–Os(5)	2.837(2)
Os(1)–S(1a)	2.418(11)	Os(4)–S(1b)	2.417(9)
Os(3)–S(1a)	2.416(11)	Os(5)–S(1b)	2.419(8)
C(1a)–S(1a)	1.79(4)	C(1b)–S(1b)	1.79(5)
C(1a)–S(2a)	1.73(6)	C(1b)–S(2b)	1.75(4)
C(1a)–N(1a)	1.27(7)	C(1b)–N(1b)	1.31(6)
S(2a)–C(3a)	1.85(7)	S(2b)–C(3b)	1.83(7)
C(2a)–C(3a)	1.57(11)	C(2b)–C(3b)	1.49(10)
N(1a)–C(2a)	1.41(7)	N(1b)–C(2b)	1.46(10)
Os(1)–Os(2)–Os(3)	59.6(1)	Os(4)–Os(6)–Os(5)	60.5(1)
Os(2)–Os(1)–Os(3)	60.0(1)	Os(6)–Os(4)–Os(5)	59.5(1)
Os(1)–Os(3)–Os(2)	60.4(1)	Os(4)–Os(5)–Os(6)	60.1(1)
Os(1)–S(1a)–Os(3)	72.0(3)	Os(4)–S(1b)–Os(5)	72.7(2)
Os(1)–S(1a)–C(1a)	106.4(17)	Os(4)–S(1b)–C(1b)	108.3(15)
Os(3)–S(1a)–C(1a)	109.4(17)	Os(5)–S(1b)–C(1b)	107.7(12)
S(1a)–C(1a)–S(2a)	116.5(28)	S(1b)–C(1b)–S(2b)	115.9(25)
S(1a)–C(1a)–N(1a)	126.4(43)	S(1b)–C(1b)–N(1b)	128.3(29)
S(2a)–C(1a)–N(1a)	116.8(37)	S(2b)–C(1b)–N(1b)	115.8(33)

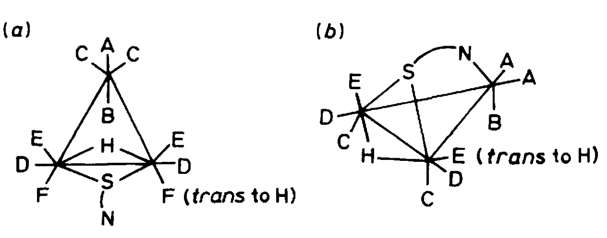


Figure 3. Carbonyl labelling scheme for n.m.r. assignments in Table 3: (*a*) $[Os_3H(CO)_{10}L]$ complexes; (*b*) $[Os_3H(CO)_9L]$ complexes

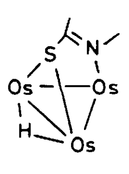
Table 5. I.r. spectra (1 600—700 cm^{-1}) of HL^1 and its complexes

HL^1[a]	$[Os_3H(CO)_{10}L^1]$[b]	$[Os_3H(CO)_9L^1]$[b]	$[Ru_3H(CO)_9L^1]$[a]
1 604m			
	1 590vw	1 567w	1 565w
1 505vs			
	1 470m		
1 464m	1 457m	1 457s	1 458vs
1 433vs	1 426s	1 414s	1 417s
1 328vs	1 311ms	1 321s	1 321m
1 251m	1 235m	1 237s	1 240s
1 080s	1 079m	1 096s	1 092vs
1 040vs		1 038s	1 035vs
1 019s	1 017m	1 019s	1 018s
	990m		
	975vs		
	940ms		
753vs	760vs	762vs	760vs
720 (sh)	727s	730ms	730s
709 (sh)	708vw	710m	708s

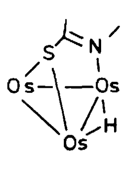
[a] From ref. 26, as KBr pellets. [b] This work, as hexachlorobutadiene and Nujol mulls.

p.p.m. for HL^1,[17,22] moves upfield to 171.6 p.p.m. in $[Os_3H(CO)_{10}L^1]$, nearer to the value of 167.6 p.p.m. for MeL^1.[22,24] Typically carbon atoms double bonded to a nitrogen are more shielded than those double bonded to a sulphur. Hence the upfield shift of C^2 on co-ordination reflects the change in the bonding pattern from S=C–N to S–C=N. Similar chemical shift correlations exist for the other $[Os_3H(CO)_{10}L]$ complexes and the 2-methylthio compounds. Carbon-13 chemical shifts for the carbonyl groups are listed in Table 3. Six resonances are observed with a relative intensity pattern of 1:1:2:2:2:2 as expected for the symmetrical structure (see Figure 3). The shifts are remarkably similar to those observed for the thiolato complexes $[Os_3H(CO)_{10}(SR)]$ (R = Et or Ph)[25] and may be assigned accordingly (*e.g.* for R = Et, δ 180.0, 179.8, 176.3, 173.7, 170.4, and 169.5 p.p.m.).

The Complexes $[Os_3H(CO)_9L]$ (L = L^1, L^2, L^5, *or* L^6).—The $[Os_3H(CO)_{10}L]$ complexes lose 1 mol of carbon monoxide upon reaction with trimethylamine oxide (L = L^1, L^2, or L^6) or when refluxed in octane (L = L^5) to give $[Os_3H(CO)_9L]$. These complexes are formulated as depicted in (**2**) where the thioamido ligand serves as a triple bridge with the sulphur bound to two osmium atoms and the nitrogen bound to the



(**2a**)



(**2b**)

third. Analytical and spectroscopic data (Tables 1—3) are consistent with this formulation and the ruthenium analogue of $[Os_3H(CO)_9L^1]$, *viz.* $[Ru_3H(CO)_9L^1]$, has been shown[6] to have such a structure by *X*-ray crystallography. Moreover, the i.r. spectra (Table 5) of these two complexes, in the 1 600—700 cm^{-1} range which contains bands due to the thioamido ligand, are virtually identical. The i.r. spectrum of L^1 is very sensitive to its mode of co-ordination. For example a band at 1 433 cm^{-1} for free HL^1 has been assigned[26] to a vibration involving the benzene ring and a contribution from ν(CN) (C belonging to the benzene ring). This band remains virtually unchanged on S co-ordination, occurring at 1 426 cm^{-1} for $[Os_3H(CO)_{10}L^1]$, but shifts to lower frequencies on NS co-ordination. For $[Os_3H(CO)_9L^1]$ it appears at 1 414 cm^{-1} and for $[Ru_3H(CO)_9L^1]$ at 1 417 cm^{-1}.

In solution at room temperature, the $[Os_3H(CO)_9L]$ complexes all exhibit two resonances in their proton n.m.r. spectra (Table 2), assignable to bridging hydride ligands, and pointing to the presence of two isomers, (**2a**) and (**2b**). Although their relative intensity varies from one complex to another, the most intense resonance at *ca.* −14 p.p.m. always shows only one set of ^{187}Os satellites and is therefore assigned to the symmetrical form, (**2a**). In the case of $[Os_3H(CO)_9L^2]$ the other isomer was in sufficient abundance to enable the resolution of two sets of satellite peaks [$\delta = -12.31$ p.p.m., $^1J(OsH) = 30.8$ and 32.9 Hz], indicating the hydride is bridging two non-equivalent osmium atoms[16] as in (**2b**). In the i.r. spectra (Table 1), the splittings of the ν(CO) absorptions confirm the presence of two isomers; in particular, the highest-frequency band at *ca.* 2 090 cm^{-1} always exhibits two components whose relative intensities parallel the n.m.r. observations. An earlier report[6] of the n.m.r. spectrum of $[Ru_3H(CO)_9L^1]$, which from *X*-ray crystallography appears to have the symmetric structure [as in (**2a**)] in the solid state, indicated only one hydride resonance was observed. A re-examination of this spectrum shows in fact that there are two broad hydride resonances at room temperature which as the sample is cooled to −35 °C appear as two sharp lines of relative intensity 12:1 (Table 2). That there are two isomers of $[Ru_3H(CO)_9L^1]$, interconverting at room temperature, is confirmed from the aromatic proton resonances. The room-temperature spectrum shows the expected multiplicity pattern *viz.* H^4(d), H^5(t), H^6(t), and H^7(d) (see Table 2 and Figure 4). On cooling to −35 °C, the resonance of H^4 moves sufficiently upfield to allow the observation of a second weak resonance, assignable to H^4 of the minor isomer (Figure 4). Other weak resonances are also seen.

The carbon-13 spectra of the $[Os_3H(CO)_9L]$ complexes also show that in each case the major isomer is the symmetrical one since in the carbonyl region five signals are seen, with a relative intensity pattern of 1:2:2:2:2 (Table 3) as expected for the case where the hydride bridges the same edge of the osmium triangle as the thioamido sulphur atom. If the hydride bridges a different edge, each CO group is unique and nine resonances should be observed. This accounts for other weak signals, often hardly discernible above the noise level, seen in the spectra. In the case of $[Os_3H(CO)_9L^5]$ the C^4 and C^5 resonances of the thioamido ligand are each resolved into two peaks with a relative intensity 3:1, as is the osmium hydride signal (Table 2). It is noted that the chemical shift of the carbon bound to the exocyclic sulphur atom (C^2) is the most sensitive to a change in co-ordination mode of the thioamido ligand. It shifts upfield by about 20 p.p.m. on going from μ-S-co-ordinated in $[Os_3H(CO)_{10}L]$ ($L = L^1$ or L^5) to μ-S,N-co-ordinated in $[Os_3H(CO)_9L]$. The fact that the value of the C^2 resonance for the latter complexes is close to those of free HL (189.9 p.p.m. for HL^1 [17,22] and 198.3 p.p.m. for HL^5 [18]) does not imply a return to the thione form of the ligand since the *X*-ray crystal structures of $[Ru_3H(CO)_9L^1]$[6] and a related osmium thioformamido[4] complex show the thiolate form to prevail.

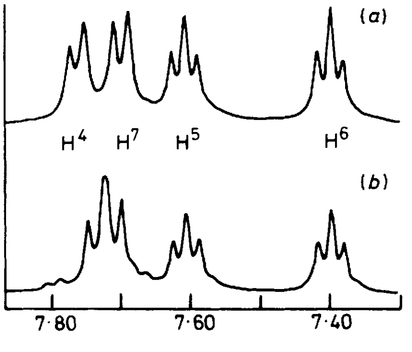
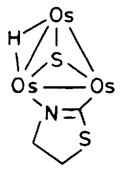


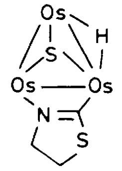
Figure 4. Aromatic proton resonances for $[Ru_3H(CO)_9L^1]$ in CD_2Cl_2: (*a*) at 25 °C; (*b*) at −35 °C

It is of interest that HL^6 is formally a thiourea (commonly known as ethylenethiourea), and normally is found bound to transition metals in the thione form.[27] The fact that it is found in the unusual deprotonated thiolate form in $[Os_3H(CO)_9L^6]$ and $[Os_3H(CO)_{10}L^6]$ must be a result of the affinity of the triosmium clusters for both thiolato and hydride ligands.

The Complex $[Os_3H(CO)_9(\mu_3\text{-}S)L^7]$.—Refluxing $[Os_3H(CO)_9L^5]$ in octane yields a complex, $[Os_3H(CO)_9(\mu_3\text{-}S)L^7]$, which is formulated as in (**3**), on the basis of analytical and spectroscopic data (Tables 1—3), and the fact that the structure is likely to be similar to that of $[Os_3H(CO)_9(\mu_3\text{-}S)(\mu\text{-}HC{=}NC_6H_4F\text{-}p)]$ formed from the desulphurization of a thioformamido ligand.[4] The thiazolinyl ligand L^7 has arisen from the desulphurization of the μ_3-thiazoline-2-thiolate ligand, L^5. The proton n.m.r. spectrum of the complex $[Os_3H(CO)_9(\mu_3\text{-}S)L^7]$ shows a broad hydride resonance at 0 °C, which in cooling to −60 °C resolves into two. This observation is consistent with hydride-ligand migration across two edges of the osmium triangle, which at lower temperatures is suppressed, giving the two forms, (**3a**) and (**3b**). One of the carbon-13 resonances of the organic ligand, C^4, also is split (Table 2). The reasonably facile desulphurization of thioamido[7,8] and related molecules[4] to give μ-S species would appear to be a general reaction for carbonyl clusters, although the intermediate species such as $[Os_3H(CO)_{10}L^5]$ and $[Os_3H(CO)_9L^5]$ are not always observed.



(**3a**)



(**3b**)

Experimental

Infrared spectra were recorded on solutions in 0.5-mm NaCl cells on a Perkin-Elmer 257 spectrometer with CO as calibrant. Mass spectra were obtained using an A.E.I. MS12 spectrometer. Hydrogen-1 and carbon-13 n.m.r. spectra were recorded using a Bruker WH400 instrument.

Solvents were purified and dried in the usual manner, and reactions were performed under dinitrogen. A literature preparation[28] was used for $[Os_3(CO)_{10}(MeCN)_2]$ and the heterocyclic thioamides HL^2—HL^6 were all obtained from Aldrich Chemical Co. Trimethylamine oxide was sublimed *in vacuo*. Product purification was achieved using thin-layer chromatography (t.l.c.) with plates coated with Merck Kieselgel 60 PF_{254} to a thickness of 2 mm. All compounds were routinely recrystallized from CH_2Cl_2–hexane solution and dried *in vacuo*. Microanalyses (Table 1) were performed by the University Chemical Laboratory microanalytical department.

Syntheses.—$[Os_3H(CO)_{10}L^5]$. The complex $[Os_3(CO)_{10}(MeCN)_2]$ (200 mg, 0.21 mmol) and thiazolidine-2-thione (26 mg, 0.22 mmol) were stirred in benzene (30 cm^3) under gentle reflux for 10 min. Removal of the solvent under reduced pressure and t.l.c. [CH_2Cl_2–hexane (1:1) as eluant] gave the product as yellow crystals. Yield 164 mg (79%).

$[Os_3H(CO)_{10}L]$ ($L = L^1$—L^4 *or* L^6). These were prepared from $[Os_3(CO)_{10}(MeCN)_2]$ and the appropriate thione, in a manner similar to that described above for $[Os_3H(CO)_{10}L^5]$, except that for $L = L^4$ the t.l.c. eluant was CH_2Cl_2–hexane (3:1). For $L = L^6$ both the reaction solvent and t.l.c. eluant were neat CH_2Cl_2. The $[Os_3H(CO)_{10}L^6]$ was always obtained in low yield ($< 5\%$) as it tended to decompose on work up.

$[Os_3H(CO)_9L^1]$. To a solution of $[Os_3H(CO)_{10}L^1]$ (180 mg, 0.18 mmol) dissolved in CH_2Cl_2 (30 cm^3) was added dropwise trimethylamine oxide (27 mg, 0.36 mmol) in the same solvent (5 cm^3). The colour of the solution changed from yellow to orange. After gentle reflux for 1.5 h the solvent was removed under reduced pressure and the product purified by t.l.c. [CH_2Cl_2–hexane (1:3) as eluant]. It was obtained as orange crystals. Yield 61 mg (36%). The complex was also prepared in low yield by refluxing $[Os_3H(CO)_{10}L^1]$ in hexane for 24 h.

$[Os_3H(CO)_9L^2]$. This complex was prepared from $[Os_3H(CO)_{10}L^2]$ in a manner similar to that described above, except that the t.l.c. eluant was CH_2Cl_2–hexane (3:1).

$[Os_3H(CO)_9L^5]$. The complex $[Os_3H(CO)_{10}L^5]$ (72 mg, 0.074 mmol) was refluxed in octane (50 cm^3) for 15 min. Removal of the solvent under reduced pressure and t.l.c. [CH_2Cl_2–hexane (1:3) as eluant] gave the product as orange crystals. Yield 48 mg (69%). A faster moving yellow band yielded a trace amount (*ca.* 3 mg) of the compound $[Os_3H(CO)_9(\mu_3\text{-}S)L^7]$.

$[Os_3H(CO)_9L^6]$. The complex $[Os_3H(CO)_{10}L^6]$ was prepared *in situ* by stirring $[Os_3(CO)_{10}(MeCN)_2]$ (100 mg, 0.11 mmol) and imidazolidine-2-thione, HL^6 (11 mg, 0.11 mmol), in CH_2Cl_2 (40 cm^3) at 40 °C for 5 min. To the resulting yellow solution, trimethylamine oxide (16 mg, 0.21 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added dropwise. Stirring was continued for 15 min while the reaction was refluxed gently. Removal of the solvent under reduced pressure and t.l.c. [CH_2Cl_2–hexane (3:1) as eluant] gave the product as an orange-yellow solid. Yield 26 mg (26%).

$[Os_3H(CO)_9(\mu_3\text{-}S)L^7]$. The complex $[Os_3H(CO)_9L^5]$ (100 mg, 0.11 mmol) was refluxed in octane (50 cm^3) for 3 h. Removal of the solvent under reduced pressure and t.l.c. [CH_2Cl_2–hexane (1:3) as eluant] gave two main bands. The first band (yellow) yielded the product $[Os_3H(CO)_9(\mu_3\text{-}S)L^7]$ (66 mg, 66%) and the second (orange) yielded unreacted $[Os_3H(CO)_9L^5]$ (29 mg).

$[Ru_3H(CO)_9L^1]$. This complex was prepared following a modification of a literature method.[6] The compound $[Ru_3(CO)_{12}]$ (320 mg, 0.50 mmol) and benzothiazoline-2-thione, HL^1 (84 mg, 0.50 mmol), were gently refluxed in benzene (20 cm^3) for 1 h. Removal of the solvent under reduced pressure and t.l.c. [diethyl ether–hexane (1:4) as eluant] gave the product as red-brown crystals. Yield 100 mg (28%) [Found: C, 26.8; H, 0.6; N, 1.9%; M^+(^{104}Ru) 731. Calc. for $C_{16}H_5NO_9RuS_2$: C, 26.6; H, 0.7; N, 1.9%; *M*, 731].

Molecular Structure Determination of $[Os_3H(CO)_{10}L^5]$.—*Crystal data.* $C_{13}H_5NO_{10}Os_3S_2$, $M = 969.90$, monoclinic, $a =$

Table 6. Atom co-ordinates (× 10^4) for $[Os_3H(CO)_{10}L^5]$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	5 048(1)	2 216(1)	4 075(1)	Os(4)	−10(1)	−2 118(2)	4 045(1)
Os(2)	3 799(1)	1 976(1)	3 014(1)	Os(5)	810(1)	289(1)	3 924(1)
Os(3)	4 278(1)	4 668(1)	3 514(1)	Os(6)	1 223(1)	−2 428(1)	3 769(1)
S(1a)	5 437(5)	3 831(9)	3 479(4)	S(1b)	−391(5)	−443(10)	3 248(4)
S(2a)	6 938(6)	5 113(16)	3 773(6)	S(2b)	−1 832(6)	1 090(14)	2 719(5)
C(1a)	6 182(24)	4 833(49)	3 976(19)	C(1b)	−1 071(22)	698(44)	3 350(17)
N(1a)	6 184(25)	5 457(51)	4 435(20)	N(1b)	−1 054(23)	1 320(45)	3 832(18)
C(2a)	6 825(34)	6 218(66)	4 761(26)	C(2b)	−1 768(45)	1 971(89)	3 740(35)
C(3a)	7 360(37)	6 287(73)	4 407(29)	C(3b)	−2 104(31)	2 472(61)	3 121(24)
C(11)	5 826(24)	2 649(47)	4 772(19)	C(41)	−743(18)	−1 537(35)	4 324(14)
O(11)	6 334(20)	2 821(40)	5 224(16)	O(41)	−1 245(22)	−1 395(42)	4 479(17)
C(12)	5 470(18)	630(36)	3 896(14)	C(42)	−518(23)	−3 675(45)	3 580(18)
O(12)	5 795(22)	−404(44)	3 784(17)	O(42)	−797(21)	−4 627(42)	3 301(16)
C(13)	4 514(20)	1 342(40)	4 450(16)	C(43)	467(20)	−3 338(40)	4 680(16)
O(13)	4 220(18)	573(37)	4 694(14)	O(43)	722(18)	−4 068(36)	5 075(14)
C(21)	3 769(24)	19(48)	2 943(18)	C(51)	489(21)	1 974(43)	4 149(17)
O(21)	3 805(21)	−1 147(43)	2 873(17)	O(51)	357(19)	3 127(37)	4 264(15)
C(22)	2 914(24)	2 469(48)	2 364(19)	C(52)	1 146(18)	1 017(36)	3 341(14)
O(22)	2 357(21)	2 634(40)	1 975(16)	O(52)	1 328(15)	1 415(29)	2 968(12)
C(23)	4 355(20)	2 359(40)	2 522(16)	C(53)	1 749(20)	418(40)	4 461(16)
O(23)	4 673(18)	2 299(35)	2 204(14)	O(53)	2 360(20)	564(40)	4 850(16)
C(24)	3 242(26)	1 844(51)	3 533(20)	C(61)	2 014(17)	−1 799(34)	3 482(13)
O(24)	2 879(18)	1 845(35)	3 825(14)	O(61)	2 569(18)	−1 496(35)	3 413(14)
C(31)	3 880(20)	5 446(40)	2 726(16)	C(62)	1 220(22)	−4 412(44)	3 590(17)
O(31)	3 732(16)	5 774(32)	2 257(13)	O(62)	1 236(19)	−5 668(38)	3 531(15)
C(32)	4 682(20)	6 373(38)	3 926(15)	C(63)	558(21)	−2 058(42)	2 850(17)
O(32)	4 836(20)	7 469(39)	4 142(15)	O(63)	266(17)	−1 950(33)	2 371(13)
C(33)	3 417(22)	5 086(43)	3 636(17)	C(64)	1 868(31)	−2 559(61)	4 525(25)
O(33)	2 850(19)	5 181(39)	3 702(15)	O(64)	2 148(21)	−2 653(41)	4 997(17)

19.387(8), $b = 9.528(2)$, $c = 24.420(7)$ Å, $\beta = 111.20(2)°$, $U = 4\,205$ Å^3, $Z = 8$, $D_c = 3.06$ g cm^{-3}, $F(000) = 3\,423$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 183.10 cm^{-1}, space group $P2_1/c$.

Data collection and structure solution. The complex [$Os_3H(CO)_{10}L^5$] was obtained as yellow block-shaped crystals by slow evaporation of a CH_2Cl_2–hexane solution. The intensities of 7 403 unique intensity data lying in the quadrant $+h$, $-k$, $\pm l$ with $5 \leqslant 2\theta \leqslant 50°$ were measured on a Stoe four-circle automatic dffractometer using graphite-monochromatized Mo-K_α radiation. All dimensions were derived from the angular measurements of 50 strong reflections lying in the shell $20 \leqslant 2\theta \leqslant 25°$. The peaks were scanned through ω and the data were profile fitted.[29] Lorentz polarization corrections and semiempirical absorption corrections based on a pseudo-ellipsoid model were applied to the data. Three standard reflections (8,0,0; 0,−4,0; 0,0,10) were measured after every 100 intensity data.

The structure was solved by direct methods using the SHELX program system [30] to give positions for the six osmium atoms in the asymmetric unit. There are two chemically similar, but not crystallographically identical molecules in this unit. Thereafter, all other non-hydrogen atoms were located for both of the molecules, from the ensuing difference syntheses. The structure was then refined by blocked-cascade least squares using complex neutral-atom scattering factors.[31] A unit weighting scheme was employed throughout all calculations and reflections (−2,0,4; 0,0,4; −1,1,2) with high Δ/σ deviations were omitted from the data set. The final values for $R(=\Sigma\Delta/\Sigma F_o, \Delta = |F_o - F_c|)$ and $R'[=(\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}]$ were 0.0825 and 0.0973 respectively for 5 390 reflections having $F_o \geqslant 5\sigma(F_o)$. The atomic co-ordinates are listed in Table 6.

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