Stepwise Conversion of $[Os(CF_3CO_2)_2(CO)_4]$ into $[Os(pyS)_2(CO)_2]$: *X*-Ray Crystal Structures of the Complexes $[Os(pyS)_2(CO)_x]$ where $x = 2$ or 3 and pyS is the Pyridine-2-thionato Ligand†

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The tetracarbonyl osmium(II) complex $[Os(CF_3CO_2)_2(CO)_4]$ or its decarbonylated derivative $[Os(CF_3CO_2)_2(CO)_3]$ reacts with pyridine-2-thione (pySH) in refluxing chloroform by substitution and addition respectively to give the compound *fac*-$[Os(CF_3CO_2)_2(pySH)(CO)_3]$ containing monodentate trifluoroacetate ligands and *S*-bonded pySH. This complex spontaneously eliminates trifluoroacetic acid in the same refluxing solvent to give *fac*-$[Os(CF_3CO_2)(pyS)(CO)_3]$ which has bidentate pyS and monodentate trifluoroacetate. The same reagents in refluxing toluene give $[Os(pyS)_2(CO)_3]$ but no further decarbonylation occurs unless this tricarbonyl complex is treated with Me_3NO at room temperature and then $[Os(pyS)_2(CO)_2]$ is formed. The single-crystal *X*-ray structures of the complexes $[Os(pyS)_2(CO)_3]$ and $[Os(pyS)_2(CO)_2]$ have been determined; the former contains non-interconverting monodentate and bidentate pyS but both ligands are chelating in the latter. Four intermediates in the overall conversion of $[Os(CF_3CO_2)_2(CO)_4]$ into $[Os(pyS)_2(CO)_2]$ are identified. This complex may also be synthesised by the direct reaction of pyridine-2-thione with $[Os_3(CO)_{12}]$.

We have already described the conversion of $[Os_3(CO)_{12}]$ into $[Os(CF_3CO_2)_2(CO)_4]$ by heating the parent carbonyl compound with trifluoroacetic acid in a sealed tube at 185 °C.[1] The yield is excellent so we considered the trifluoroacetato complex as a convenient source of a range of osmium(II) complexes since at least two CO ligands and the trifluoroacetato ligands ought to be replaceable. Here we describe the chemistry of $[Os(CF_3CO_2)_2(CO)_4]$ with pyridine-2-thione (pySH). We have been able to follow the stepwise conversion into $[Os(pyS)_2(CO)_2]$ (**4a**) *via* several intermediates which have been well characterised and have determined the single-crystal *X*-ray structures of (**4a**) and its immediate precursor $[Os(pyS)_2(CO)_3]$ (**3a**).

Results and Discussion

Syntheses.—The complex *cis*-$[Os(CF_3CO_2)_2(CO)_4]$ reacts with pySH in refluxing chloroform for 30 min to give initially the simple substitution compound *fac*-$[Os(CF_3CO_2)_2(pySH)(CO)_3]$ (**1**) (67%) and the compound *fac*-$[Os(CF_3CO_2)(pyS)(CO)_3]$ (**2**) (25%), which is formed by the loss of CF_3CO_2H from (**1**). These products are easily separated by t.l.c. on silica. A similar but longer reaction (2 h) gave only complex (**2**) so that it seems likely that (**1**) is formed initially by substitution of a CO ligand (one of the two that are mutually *trans* to each other) by the ligand pySH. Subsequently complex (**1**) eliminates CF_3CO_2H to give (**2**). The course of the initial substitution almost certainly involves a unimolecular loss of CO since we know that *cis*-$[Os(CF_3CO_2)_2(CO)_4]$ slowly but spontaneously loses CO in solution at room temperature to give *fac*-$[Os(CF_3CO_2)_2(CO)_3]$ containing mono- and bi-dentate trifluoroacetate ligands[1] and that this complex readily takes up monodentate ligands with chelate ring opening. We have been able to prepare complex (**1**) almost but not totally free from complex (**2**) since it is partially converted into (**2**) during the work-up procedure.

Reaction of *cis*-$[Os(CF_3CO_2)_2(CO)_4]$ with pySH for longer times and at higher temperatures (3.5 h in refluxing toluene) gave the complex $[Os(pyS)_2(CO)_3]$ (**3a**) in good yield (84%) with no evidence for (**1**) or (**2**) as a reaction product. At this temperature complex (**1**) is readily converted into (**2**) which reacts with pySH to eliminate CF_3CO_2H to give complex (**3a**), which is obtained as yellow needles. Complex (**3a**) was shown to be indefinitely stable in refluxing toluene.

Reaction of pySH with $[Os_3(CO)_{12}]$ in refluxing toluene gives the previously reported clusters $[Os_3H(pyS)(CO)_{10}]$ and $[Os_3H(pyS)(CO)_9]$ containing doubly and triply bridging pyS ligands respectively.[2] Related clusters from 2-pyridone and 2-aminopyridine are also known.[3] Reaction for 11 h gave these in 49 and 19% yields respectively. We were also able to isolate from this reaction the mononuclear complex $[Os(pyS)_2(CO)_2]$ (**4a**) (30%), which was not described in the original report.[2] Since we have shown that the tricarbonyl complex (**3a**) does not decarbonylate in refluxing toluene, it cannot be an intermediate in the formation of (**4a**). Almost certainly therefore $[Os_3H(pyS)(CO)_9]$ reacts with more pySH to give clusters with fewer than three CO per Os atom before breaking down into monomeric units. For example, cluster compounds such as $[Os_3H(pyS)(pySH)(CO)_8]$ and $[Os_3H_2(pyS)_2(CO)_7]$ could be formed by further substitition and oxidative addition but since such species were not observed they must readily break down into $[Os(pyS)_2(CO)_2]$ (**4a**). Displaced CO would be very rapidly degassed out of solution so that there would be insufficient CO in the system for (**3a**) to be formed.

In spite of the thermal stability of complex (**3a**) in refluxing toluene, we were able to decarbonylate it easily at room temperature to give the dicarbonyl (**4a**) by oxidising off one CO ligand by reaction with $Me_3NO\cdot 2H_2O$. The synthetic

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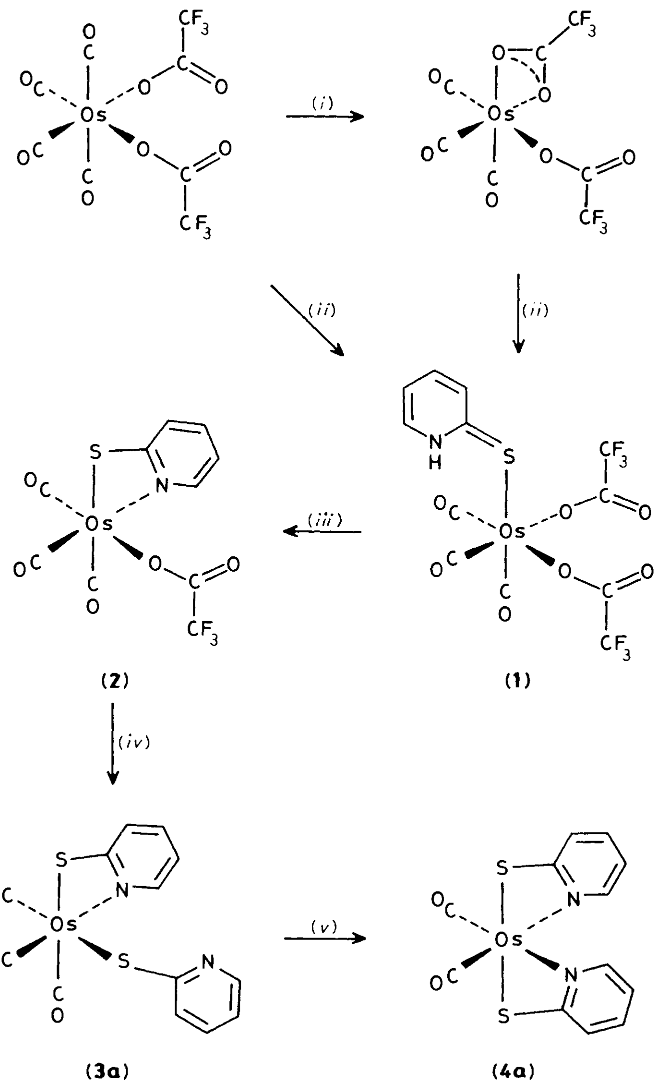
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. I.r. and ^{1}H n.m.r. data for the new complexes (**1**)—(**4**)

Complex	ν(CO)^a/cm^{-1}	δ(^{1}H n.m.r.)
(**1**) [Os(CF$_3$CO$_2$)$_2$(pySH)(CO)$_3$]^b	2 129vs, 2 055vs, 2 041vs^c	13.61 (s, br, NH), 7.88 (m, H^6), 7.82 (m, H^4), 7.76 (m, H^3), 7.28 (m, H^5)
(**2**) [Os(CF$_3$CO$_2$)(pyS)(CO)$_3$]^d	2 120vs, 2 048vs, 2 030vs^e	7.94 (m, H^6), 7.57 (m, H^4), 7.01 (m, H^5), 6.90 (m, H^3)
(**3a**) [Os(pyS)$_2$(CO)$_3$]^d	2 103vs, 2 033vs, 2 016vs	8.22 (m, H^6), 7.92 (m, H^6), 7.45 (m, H^4), 7.35 (m, H^3), 7.25 (m, H^4), 6.88 (m, H^5), 6.81 (m, H^5), 6.79 (m, H^3)
(**3b**) [Os(mpyS)$_2$(CO)$_3$]^f	2 102vs, 2 031vs, 2 013vs	
(**4a**) [Os(pyS)$_2$(CO)$_2$]^d	2 028vs, 1 958vs	8.23 (m, H^6), 7.41 (m, H^4), 6.82 (m, H^5), 6.76 (m, H^3)
(**4b**) [Os(mpyS)$_2$(CO)$_2$]^d	2 030vs, 1 959vs	7.24 (t, H^4), 6.55 (d, H^3, H^5),^{g} 2.56 (s, Me)

[a] Recorded in CHCl$_3$ solution. [b] Recorded in CDCl$_3$ at 200 MHz. [c] ν(CO$_2$) 1 725ms, 1 701ms, and 1 401m cm^{-1}. [d] Recorded in CD$_2$Cl$_2$ at 200 MHz. [e] ν(CO$_2$) 1 693s and 1 412m cm^{-1}. [f] N.m.r. spectrum not recorded. [g] H^3 and H^5 signals overlap.



Scheme 1. (*i*) CHCl$_3$, 20 °C; (*ii*) CHCl$_3$, pySH, 62 °C; (*iii*) CHCl$_3$, 62 °C; (*iv*) toluene, pySH, 110 °C; (*v*) Me$_3$NO·2H$_2$O, CH$_2$Cl$_2$, 20 °C

results are represented in Scheme 1. The corresponding 6-methylpyridine-2-thione compounds [Os(mpyS)$_2$(CO)$_3$] (**3b**) and [Os(mpyS)$_2$(CO)$_2$] (**4b**) were prepared similarly.

Characterisation of Complexes (**1**)—(**4**).—Each of complexes (**1**)—(**3**) gives three strong i.r. absorptions around 2 000 cm^{-1} (Table 1) consistent with a *fac* configuration that is lacking three-fold symmetry. This is expected to be the most stable arrangement of three CO ligands. Both (**1**) and (**2**) give i.r. absorptions (Table 1) which characterise the trifluoroacetate ligands as monodentate; there is a greater separation of ν_{asym}(CO$_2$) and ν_{sym}(CO$_2$) for monodentate than for bidentate trifluoroacetate, for example the complex [Os(CF$_3$CO$_2$)$_2$(CO)$_3$] contains both kinds of ligand with absorptions at 1 698 and 1 410 cm^{-1} for monodentate and 1 653 and 1 434 cm^{-1} for bidentate trifluoroacetate.[1] Thus in complex (**2**) the pyS rather than the CF$_3$CO$_2$ ligand is chelating.

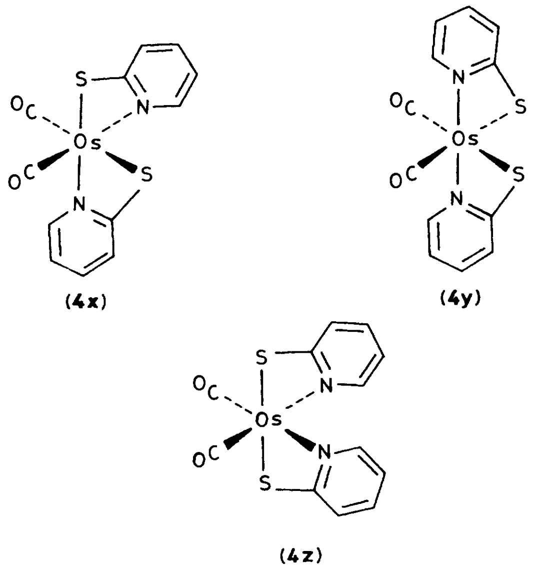


Figure 1. Three possible configurations of the complex (**4a**) containing *cis* carbonyl ligands

The ^{1}H n.m.r. spectra of these complexes are also consistent with the configurations given in Scheme 1. Compound (**1**) contains the pySH rather than the pyS ligand; a NH signal is observed at δ 13.61. Compound (**3a**) exhibits two sets of pyS signals assigned to the mono- and bi-dentate ligands respectively. The only gross structural features of these complexes not established spectroscopically are the configurations of the complexes (**4a**) and (**4b**). The i.r. spectra are only consistent with a *cis* dicarbonyl arrangement [two strong ν(CO) absorptions, Table 1], so there are three possible configurations (Figure 1). A simple loss of a CO ligand *cis* to the monodentate pyS allowing it to become bidentate would lead to structures (**4x**) and (**4y**), but since the pyS ligands in (**4a**) and mpyS ligands in (**4b**) are equivalent (n.m.r. evidence) we can rule out structure (**4x**). The structure (**4z**) with *cis* carbonyl ligands and *trans* sulphur atoms can only be formed from (**3**) by a rearrangement involving the sulphur atoms converting from *cis* to *trans*. Most other known octahedral complexes with two chelating pyS ligands have an arrangement with sulphur atoms *trans* and the nitrogen atoms *cis*. This is certainly so for [Ru(pyS)$_2$(PPh$_3$)$_2$],[4,5] which is of

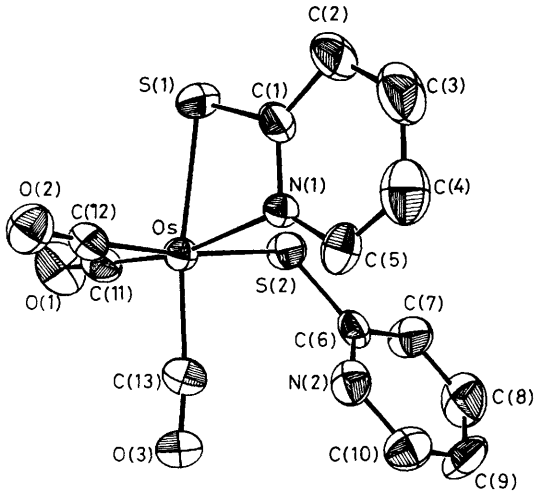


Figure 2. Molecular structure of the complex $[Os(pyS)_2(CO)_3]$, (**3a**)

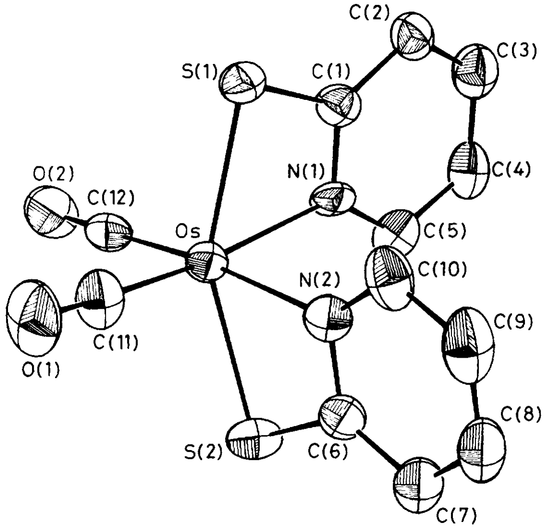


Figure 3. Molecular structure of the complex $[Os(pyS)_2(CO)_2]$, (**4a**)

known *X*-ray structure, and probably so for $[Os(pyS)_2(PPh_3)_2]$ (although the *cis* isomer appears to be in equilibrium in solution with the *trans* isomer),[6] $[Ru(pyS)_2(diene)]$ (diene = cyclo-octa-1,5-diene or norbornadiene),[7,8] $[Ru(pyS)_2(CO)(PPh_3)]$,[9] and $[Rh(pyS)_3(pySH)]$.[10] This geometry is not always found since $[Rh(pyS)_2(pySH)_2]Cl$ has the two chelating pyS ligands in a plane with sulphur atoms *cis*. In this case the monodentate ligands (pySH) are mutually *trans*. Certainly structures (**4y**) and (**4z**) must be considered as possibilities. In the absence of satisfactory evidence for the structure of complexes (**4**), the single-crystal *X*-ray structure of (**4a**) was determined. Also the structure of (**3a**) was determined similarly to see whether there are any structural features indicating which CO ligand would be most susceptible to nucleophilic attack by the oxidant, Me_3NO. The CO ligand with the longest M–C bond and the shortest CO bond should be that with the lowest orbital energies at carbon and hence the most reactive towards nucleophiles at this atom. We thought that if the CO ligand *trans* to monodentate pyS were attacked by Me_3NO, then the rearrangement to structure (**4z**) might be understood.

Table 2. Selected bond lengths (Å) and angles (°) for $[Os(pyS)_2(CO)_3]$ (**3a**)

Os–C(11)	1.89(1)	C(2)–C(3)	1.42(2)
Os–C(12)	1.90(1)	C(3)–C(4)	1.40(2)
Os–C(13)	1.927(9)	C(4)–C(5)	1.39(2)
Os–N(1)	2.129(8)	C(5)–N(1)	1.34(1)
Os–S(1)	2.446(3)	C(6)–N(2)	1.35(1)
Os–S(2)	2.424(3)	C(6)–S(2)	1.72(1)
C(11)–O(1)	1.14(1)	C(6)–C(7)	1.39(2)
C(12)–O(2)	1.14(1)	C(7)–C(8)	1.39(2)
C(13)–O(3)	1.13(1)	C(8)–C(9)	1.39(2)
C(1)–N(1)	1.34(1)	C(9)–C(10)	1.35(2)
C(1)–S(1)	1.76(1)	C(10)–N(2)	1.37(1)
C(1)–C(2)	1.40(1)		
N(1)–Os–S(1)	67.4(2)	C(11)–Os–C(13)	91.4(4)
N(1)–Os–S(2)	86.6(2)	C(12)–Os–C(13)	92.4(5)
N(1)–Os–C(12)	91.1(4)	Os–C(11)–O(1)	177(1)
N(1)–Os–C(13)	101.9(4)	Os–C(12)–O(2)	177(1)
S(1)–Os–S(2)	84.1(1)	Os–C(13)–O(3)	173(1)
S(1)–Os–C(11)	99.3(3)	Os–N(1)–C(1)	102.4(6)
S(1)–Os–C(12)	88.7(3)	Os–S(1)–C(1)	79.9(4)
S(2)–Os–C(12)	172.8(3)	Os–S(2)–C(6)	109.7(4)
S(2)–Os–C(13)	94.8(3)	N(1)–C(1)–S(1)	110.3(7)
C(11)–Os–C(12)	90.7(5)	N(2)–C(6)–S(2)	119.8(9)

Table 3. Selected bond lengths (Å) and angles (°) for $[Os(pyS)_2(CO)_2]$ (**4a**)

Os–C(11)	1.885(6)	C(2)–C(3)	1.377(9)
Os–C(12)	1.863(6)	C(3)–C(4)	1.38(1)
Os–N(1)	2.149(4)	C(4)–C(5)	1.392(9)
Os–N(2)	2.120(5)	C(5)–N(1)	1.342(7)
Os–S(1)	2.441(1)	C(6)–N(2)	1.365(8)
Os–S(2)	2.419(2)	C(6)–S(2)	1.730(6)
C(11)–O(1)	1.121(7)	C(6)–C(7)	1.390(9)
C(12)–O(2)	1.148(7)	C(7)–C(8)	1.37(1)
C(1)–N(1)	1.304(7)	C(8)–C(9)	1.40(1)
C(1)–S(1)	1.745(6)	C(9)–C(10)	1.40(1)
C(1)–C(2)	1.419(8)	C(10)–N(2)	1.348(8)
N(1)–Os–S(1)	66.7(1)	S(2)–Os–C(12)	103.9(2)
N(1)–Os–S(2)	94.6(1)	C(11)–Os–C(12)	91.4(3)
N(1)–Os–N(2)	85.2(2)	Os–C(11)–O(1)	177.9(7)
N(1)–Os–C(12)	93.5(2)	Os–C(12)–O(2)	178.2(5)
N(2)–Os–S(1)	93.5(1)	Os–N(1)–C(1)	102.1(4)
N(2)–Os–S(2)	67.5(1)	Os–S(1)–C(1)	80.7(2)
N(2)–Os–C(11)	91.5(2)	Os–N(2)–C(6)	102.0(4)
S(1)–Os–C(11)	103.3(2)	Os–S(2)–C(6)	81.2(2)
S(1)–Os–C(12)	94.1(2)	N(1)–C(1)–S(1)	110.5(4)
S(2)–Os–C(11)	93.6(2)	N(2)–C(6)–S(2)	109.4(4)

The molecular structures of complexes (**3a**) and (**4a**) are shown in Figures 2 and 3 respectively. Selected bond lengths and angles for (**3a**) are in Table 2 while those for (**4a**) are in Table 3. The overall geometry of (**3a**) is as expected from its spectra and that of (**4a**) corresponds to structure (**4z**), that is there has been a *cis* to *trans* rearrangement of the S atoms in the final decarbonylation step in Scheme 1. The structures of (**3a**) and (**4a**) correspond with those of $[Ru(pyS)_2(CO)_2(PPh_3)]$ and $[Ru(pyS)_2(CO)(PPh_3)]$.[9] The geometries of (**3a**) and (**4a**) are essentially octahedral with distortions as a result of the small bite angles of the chelating pyS ligands; 67.4° in (**3a**) and 66.7 and 67.5° in (**4a**). Figure 4 shows the three chelating pyS ligands together with the ligands *trans* to them projected into the plane of the four-membered chelate rings. These geometries are clearly very similar. Using the positions of the atoms of the *trans* ligands bonded to osmium to define idealised octahedral co-ordination axes, these are shown to pass outside the positions of the S and N atoms of the chelates. The angles between the *trans* ligands projected into this plane (92.1, 93.5, and 91.3°) are only slightly expanded from 90° as a result of the very small bite angle opposite. It seems that there is no reason for the *trans*

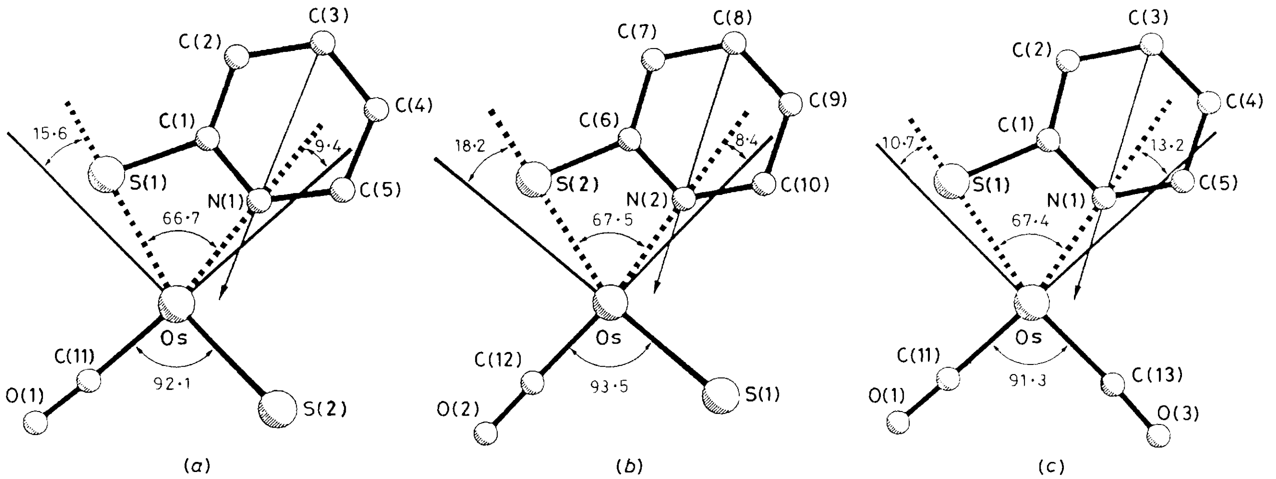
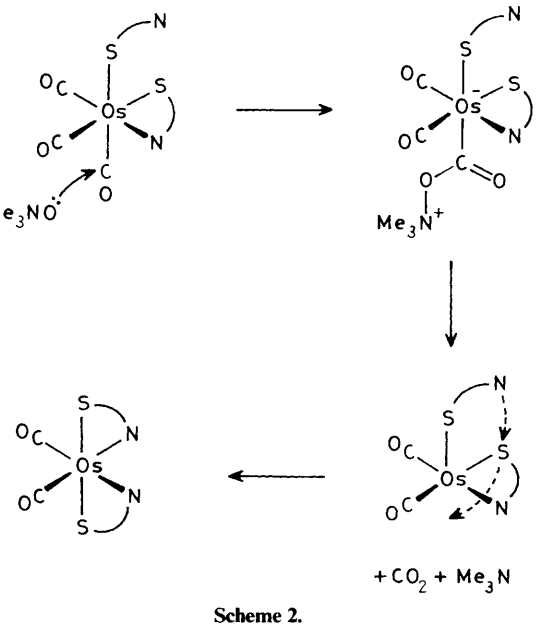


Figure 4. Projections in the planes of the chelating pyS ligands in the complexes (**4a**), (*a*) and (*b*), and (**3a**), (*c*). These show the relation between the heteroatom positions of the chelates and the co-ordination axes as defined by the positions of the *trans* ligands. The angles S(2)–Os–C(11), S(1)–Os–C(12), and C(11)–Os–C(15) are not those given in Tables 2 and 3 but are the angles projected in the plane of the Os–pyS system

ligands to align directly opposite the S and N atoms of the chelates but rather they maintain octahedral or closely octahedral geometries. It is probable that the octahedral axes as drawn in Figure 4 relate to the positions of the pyS ligands even though the heteroatoms are well away from the axes as shown. The points of intersection of the directions of the idealised lone pair of the nitrogen atoms and the octahedral axes are probably close to the position of maximum electron density of the N–Os bonds. Likewise if, as seems likely, the directions of the orbitals on sulphur used for S–Os bonding are at 90° with respect to the S–C bonds as expected if only *p* orbitals on sulphur are used, or rather greater than this if there is some *s*-orbital contribution to this bonding, the positions of greatest electron density in the Os–S bonds will be close to the intersections of these directions and the octahedral axes.

One reason for our determining the structure of complex (**3a**) was to see if there are any significant differences in the Os–CO distances. The distance *trans* to the chelating S atom is the longest which would imply this is the most electrophilic carbon atom and this CO ligand should be the one oxidised to CO_2. Simple chelate ring closure would then lead to structure (**4x**) (Figure 1) which is not observed. However, the differences in the Os–CO distances are not very big and of little significance in view of the estimated standard deviations (e.s.d.s). Thus we have developed no clear picture of the reason for the structure adopted by complex (**4a**). Considering the relative *trans* effects of the S and N atoms in (**3a**), one would expect S to have a larger effect than nitrogen, and of the two Os–S distances that to the monodentate pyS ligand is significantly shorter. Assuming that this monodentate ligand has a stronger Os–S bond than the other pyS ligand we might expect it to have the larger *trans* effect. If C(12)O(2) is the one that is displaced, we could imagine the process in Scheme 2 as the route to complex (**4a**). Clearly this evidence does not rule out an alternative route to another isomer, (**4x**) or (**4y**), which rapidly isomerises to (**4z**) (Figure 1). We view this as unlikely since only one isomeric product was observed during the course of the reaction even though this was carried out at room temperature.



Scheme 2.

Experimental

The complex $[Os(CF_3CO_2)_2(CO)_4]$ was synthesised quantitatively from $[Os_3(CO)_{12}]$ and trifluoroacetic acid as described previously.[1] The tetracarbonyl complex readily decarbonylates to the tricarbonyl $[Os(CF_3CO_2)_2(CO)_3]$ in solution and this complex may be used alternatively as the starting material. Generally we have used the tetracarbonyl compound. Pyridine-2-thione was used as purchased (Aldrich plc). Chromatography was on 2 mm thick preparative t.l.c. plates using SiO_2.

Syntheses.—*fac*-$[Os(CF_3CO_2)(pyS)(CO)_3]$. A solution of the complex $[Os(CF_3CO_2)_2(CO)_4]$ (0.050 g) and pySH (0.018 g, 2 mol per mol Os) in chloroform (20 cm^3) was heated under reflux for 2 h. The solvent was removed under reduced pressure and the residue separated by t.l.c. [eluant: light petroleum (b.p. 30—40 °C)–CH_2Cl_2 (1:4, v/v)] to give one main colourless band yielding *fac*-$[Os(CF_3CO_2)(pyS)(CO)_3]$ (**2**) as colourless crystals (0.037 g, 81%) from dichloromethane–hexane mixtures (Found: C, 23.8; H, 0.85; N, 2.65. $C_{10}H_4F_3NO_5OsS$ requires C, 24.15; H, 0.8; N, 2.8%).

fac-$[Os(CF_3CO_2)_2(pySH)(CO)_3]$ (**1**). An identical treatment to that above except for a reflux time of 30 min instead of 2 h gave complex (**2**) (0.012 g, 25%) and colourless crystals of *fac*-$[Os(CF_3CO_2)_2(pySH)(CO)_3]$ (**1**) (0.38 g, 67%). Crystals of (**1**) were contaminated with a small amount of (**2**) and could not be obtained analytically pure.

Table 4. Summary of crystal and intensity data*

	Compound (**3a**)	Compound (**4a**)
Formula	$C_{13}H_8N_2O_3OsS_2$	$C_{12}H_8N_2O_2OsS_2$
M/g mol^{-1}	494.55	466.54
Description	Colourless rod	Colourless prism
System	Orthorhombic	Monoclinic
a/Å	9.414(1)	7.576(1)
b/Å	11.852(2)	16.693(3)
c/Å	26.797(4)	11.903(2)
β/°		113.93(3)
U/Å^3	2 989.6	1375.9
Space group	*Pbca*	$P2_1/c$
Z	8	4
F(000)	1 856	872
D_c/g cm^{-3}	2.20	2.25
Crystal size/mm	0.15 × 0.15 × 0.38	0.24 × 0.18 × 0.45
μ(Mo-K_α)/cm^{-1}	88.2	95.7
No. of unique reflections	4 887	3 422
No. data with $I_o > 3\sigma(I_o)$	1 282	2 475
No. parameters refined	191	173
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.023	0.039
$R' = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.029	0.051
Largest shift e.s.d.	0.01	0.00

* Details common to both compounds: X(Mo-K_α) 0.710 73 Å (graphite monochromator); temperature 25(1) °C; weighting scheme $1/\sigma(F_o)^2$.

Table 5. Fractional atomic co-ordinates for $[Os(pyS)_2(CO)_3]$, compound (**3a**)

Atom	x	y	z
Os	0.111 11(3)	0.243 53(3)	0.063 36(1)
S(1)	−0.140 2(3)	0.293 7(2)	0.069 8(1)
S(2)	0.134 9(3)	0.356 5(2)	0.138 3(1)
O(1)	0.213(1)	0.443 8(7)	0.003 1(4)
O(2)	0.035 3(9)	0.110 7(7)	−0.029 8(3)
O(3)	0.409 6(8)	0.143 0(7)	0.064 2(3)
N(1)	−0.006 4(9)	0.127 5(8)	0.107 8(3)
N(2)	0.308(1)	0.190 8(8)	0.167 2(4)
C(1)	−0.139(1)	0.169(1)	0.104 9(4)
C(2)	−0.256(2)	0.118(1)	0.127 4(5)
C(3)	−0.225(1)	0.016(1)	0.153 1(5)
C(4)	−0.087(2)	−0.028(1)	0.155 2(5)
C(5)	0.022(1)	0.031(1)	0.132 2(4)
C(6)	0.252(1)	0.292 6(9)	0.178 8(3)
C(7)	0.286(1)	0.347(1)	0.223 1(5)
C(8)	0.381(2)	0.295(1)	0.255 4(5)
C(9)	0.440(2)	0.191(1)	0.243 5(5)
C(10)	0.401(1)	0.142(1)	0.199 8(5)
C(11)	0.176(1)	0.367(1)	0.024 5(4)
C(12)	0.068(1)	0.161(1)	0.004 7(4)
C(13)	0.300(1)	0.181 8(8)	0.066 9(4)

fac-$[Os(pyS)_2(CO)_3]$ (**3a**). A colourless solution of $[Os(CF_3CO_2)_2(CO)_4]$ (0.050 g) and pySH (0.027 g, 3 mol per mol Os) in toluene (25 cm^3) was heated under reflux for 3.5 h to give a yellow solution. Removal of the solvent under vacuum and t.l.c. separation [eluant: dichloromethane–diethyl ether (9:1, v/v)] gave one major band which afforded complex (**3a**) as pale yellow needles (0.037 g, 84%) from dichloromethane–hexane mixtures (Found: C, 31.95; H, 1.85; N, 5.55. $C_{13}H_8N_2O_3OsS_2$ requires C, 31.55; H, 1.65; N, 5.65%).

cis-$[Os(pyS)_2(CO)_2]$ (**4a**). Trimethylamine oxide hydrate (0.018 g, 1.5 mol per mol Os) was added to a solution of $[Os(pyS)_2(CO)_3]$ (**3a**) (0.050 g) in dichloromethane (20 cm^3). The i.r. spectrum showed complete reaction after 15 min. The solution was filtered through silica, the solvent removed, and the residue separated by t.l.c. [eluant: light petroleum (b.p. 30—40 °C)–dichloromethane (3:7, v/v)]. The yellow band gave yellow crystals which were recrystallised from dichloromethane–hexane mixtures to give (**4a**) as yellow crystals almost quantitatively (Found: C, 30.8; H, 1.85; N, 6.0. $C_{12}H_8N_2O_2OsS_2$ requires C, 30.9; H, 1.7; N, 6.0%).

cis-$[Os(mpyS)_2(CO)_2]$ (**4b**). A solution of $[Os(CF_3CO_2)_2(CO)_4]$ (0.050 g) and 6-methylpyridine-2-thione (mpySH) (0.031 g, 3 mol per mol Os) in toluene (25 cm^3) was heated under reflux for 3.5 h and the reaction worked-up as for (**3a**) to give pale yellow crystals of *fac*-$[Os(mpyS)_2(CO)_3]$ (**3b**) (0.036 g, 77%). This sample was treated with trimethylamine oxide as above to give (**4b**) as yellow crystals (92%) (Found: C, 34.05; H, 2.45; N, 5.6. $C_{14}H_{12}N_2O_2OsS_2$ requires C, 34.0; H, 2.45; N, 5.65%).

Reaction of $[Os_3(CO)_{12}]$ *with Pyridine-2-thione.*—A solution of $[Os_3(CO)_{12}]$ (0.1004 g, 0.111 mmol) and pySH (0.0384 g, 0.345 mmol) in toluene (sulphur-free, 30 cm^3) was degassed and refluxed under nitrogen for 11 h. Removal of the solvent under vacuum and t.l.c. of the residue [SiO_2; eluant, light petroleum (b.p. 30—40 °C)] gave three bands yielding $[Os_3H(pyS)(CO)_{10}]$ as a yellow solid (0.053 g, 49%) (Found: C, 18.7; H, 0.55; N, 1.55. $C_{15}H_5NO_{10}Os_3S$ requires C, 18.7; H, 0.5; N, 1.4%), $[Os_3H(pyS)(CO)_9]$ as a pale yellow solid (0.020 g, 19%), and $[Os(pyS)_2(CO)_2]$, compound (**4a**), as yellow crystals (0.047 g, 30%). The trinuclear clusters gave similar spectra to those reported and the identity of (**4a**) was confirmed spectroscopically by comparison with data for an authentic sample. Mass spectra are totally consistent with the formulations of these compounds.

Crystal-structure Determinations.—Suitable crystals of each compound, (**3a**) and (**4a**), were examined using similar procedures. The crystal was attached to a glass fibre mounted on a brass pin in a goniometer head and optically centred on an Enraf-Nonius CAD4 diffractometer. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of 25 reflections ($6 \leqslant \theta \leqslant 9°$) for (**3a**) and 24 reflections ($5 \leqslant \theta \leqslant 11°$) for (**4a**). Details of the crystal data for both compounds are given in Table 1. Systematic absences $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$ and $hk0$, $h = 2n + 1$ for (**3a**) and $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$ for (**4a**) and subsequent least-squares refinement confirmed the choices of the respective space groups as *Pbca* and $P2_1/c$.

Data for each compound were collected using the ω—2θ scan technique with variable scan rates of 1.7—8.3° min^{-1} in omega to a maximum 2θ angle of 60° for (**3a**) and 56° for (**4a**), and variable scan ranges calculated by theta scan width = 0.8 + 0.350 tanθ°. Background measurements using the moving crystal–moving counter technique were made at the beginning and end of each scan. Three standard reflections monitored every 120 min during the data collection showed little loss of intensity; a small decay correction was applied as was an empirical absorption correction based on a series of psi scans. Lorentz and polarisation corrections were also applied to each data set.

The structures were solved by standard Patterson[11] and difference Fourier techniques. Final refinement for each structure was fully anisotropic, full-matrix, least squares using only those reflections with $I_o > 3\sigma I_o$. Scattering factors were taken from Cromer and Waber,[12] and anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[13] The highest peaks in the final difference Fourier were 1.12(13) and 1.05(22) e Å^{-3} for (**3a**) and (**4a**) respectively, and were positioned near to the osmium atoms. No attempt was made to locate hdyrogen atoms on the pyridinethionato rings. Final refinement parameters are given in Table 4 and positional parameters in Tables 5 and 6.

All calculations were carried out on a DEC MicroVAX II computer using the SDP/VAX system of programs.[14]

Table 6. Fractional atomic co-ordinates for [Os(pyS)$_2$(CO)$_2$], compound (**4a**)

Atom	*x*	*y*	*z*
Os	0.808 14(4)	0.181 69(2)	0.691 94(2)
S(1)	0.852 0(3)	0.276 6(1)	0.853 8(2)
S(2)	0.912 8(3)	0.083 2(1)	0.582 9(2)
O(1)	0.473 0(9)	0.083 2(4)	0.687 0(7)
O(2)	0.543(1)	0.290 9(4)	0.494 0(6)
N(1)	1.054 1(8)	0.258 4(3)	0.732 0(5)
N(2)	1.009 4(8)	0.099 2(4)	0.812 0(6)
C(1)	1.050(1)	0.302 2(4)	0.821 6(7)
C(2)	1.190(1)	0.362 6(5)	0.877 6(8)
C(3)	1.332(1)	0.372 2(6)	0.834 4(8)
C(4)	1.335(1)	0.324 2(6)	0.740 9(9)
C(5)	1.193(1)	0.265 9(5)	0.690 0(7)
C(6)	1.048(1)	0.051 6(5)	0.731 7(8)
C(7)	1.179(1)	−0.011 6(6)	0.773(1)
C(8)	1.264(1)	−0.025 9(5)	0.897(1)
C(9)	1.224(1)	0.023 1(6)	0.979(1)
C(10)	1.095(1)	0.087 2(6)	0.934 4(8)
C(11)	0.599(1)	0.118 9(5)	0.687 3(8)
C(12)	0.644(1)	0.248 3(4)	0.568 1(7)

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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