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Preliminary communication

THE INTERACTION OF HETEROCYCLIC THIOAMIDES WITH TRIOSMIUM CLUSTERS: THE X-RAY CRYSTAL STRUCTURE OF $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-SC=NCH}_2\text{CH}_2\text{S})$

A.M. BRODIE, H. DIANE HOLDEN, J. LEWIS and M.J. TAYLOR
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

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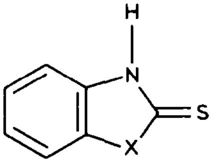
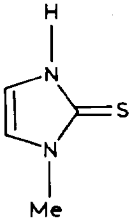
Summary

Heterocyclic thioamides react with $Os_3(CO)_{10}(MeCN)_2$ to yield complexes $HOs_3(CO)_{10}L$ of the deprotonated thioamide coordinated in the thiolate form via the exocyclic sulphur atom. Decarbonylation yields $HOS_3(CO)_9L$ with L coordinated via both sulphur and nitrogen: these can be desulphurised to yield sulphur-capped cluster species.

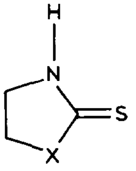
The affinity of cluster species for sulphur containing ligands is well established [1]. We have accordingly studied the interaction of the thioamides HL^{1-6} with triosmium clusters, where this property might be useful in stabilising the thiolate form of the thioamide (see later).



(HL^1, X = O;
HL^2, X = S;
HL^3, X = NH)



(HL^4)



(HL^5, X = S;
HL^6, X = NH)

The reaction of the thioamides HL^{1-6} with $Os_3(CO)_{10}(MeCN)_2$ in CH_2Cl_2 or benzene at room temperature results in the formation of the complexes HOs_3-

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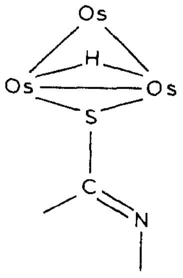
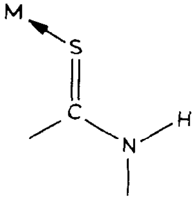
$(CO)_{10}L^*$. The ^1H NMR spectra of these complexes exhibit resonances at δ ca. −17 ppm due to the hydride ligand in addition to those due to the coordinated ligand. Their ^{13}C NMR spectra exhibit resonances of intensity 2/2/2/2/1/1 due to the carbonyl ligands, which are very similar to those observed for the thiolate complexes $HOs_3(CO)_{10}SR$ [2]. These data would suggest that the thioamides HL^{1-6} are coordinated in the thiolate form (I) rather than in the thione form (II).



(I)



(II)

This has been further confirmed for $HOs_3(CO)_{10}L^5$ by a single crystal X-ray crystallographic study**. The structure is shown in Fig. 1 together with bond lengths. The important feature of the structure is the C(1)—S(1) bond length of 1.790 Å, typical of a C—S single bond [3]. This is significantly longer than that found in free HL^5 (1.641 Å [4]) or in the complexed thione form (II) found in $W(CO)_5(HL^5)$ (1.68 Å [5]) or $PdCl_2(HL^5)_4$ (1.666 Å [4]).

The C(1)—N(1) bond length of 1.266 Å in $HOs_3(CO)_{10}L^5$ also indicates appreciable double bond character [3]. Although the hydride ligand was not located directly in the X-ray analysis, the observation of a single hydride to ^{187}Os coupling ($^1J(OsH)$ 33.8 Hz) in the ^1H NMR spectrum [6], indicates the hydride bridges the two equivalent osmium atoms also bridged by the sulphur atom, as in (1).

The complexes $HOs_3(CO)_{10}L$ can be decarbonylated by reaction with Me_3NO ($L = L^1$, L^2 or L^6) or thermally ($L = L^5$) to form $HOs_3(CO)_9L$. ^1H and ^{13}C NMR

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*Adequate microanalytical, IR, ^1H and ^{13}C NMR and mass spectral data have been obtained for all the complexes reported. Representative data are given below:

$HOs_3(CO)_{10}L^5$ (I): IR ν(CO) (cyclohexane): 2109w, 2071vs, 2061s, 2022s, 2015s, 2005m, 1987sh, 1984w cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.22(t, 2H), 3.56(t, 2H), −17.25(s, 1H), $^1J(OsH)$ 33.8 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ (rel. int.) 180.7(1), 179.9(1), 176.4(2), 173.7(2), 170.3(2), 170.3(2), 168.8(2) ($^2J(CH)$ 9.8 Hz) ppm; *m/e* (^{192}Os) 975.

$HOs_3(CO)_9L^5$ (IIa/IIb): IR ν(CO) (cyclohexane): 2090sh, 2087m, 2057s, 2034sh, 2031s, 2009w, 2004s, 1991s, 1968m, 1960w, 1954m cm^{-1}. ^1H NMR ($CDCl_3$): δ(IIa) 3.96 (t, 2H), 3.47 (t, 2H), −14.4 (s, 1H); δ(IIb) −12.3(s) ppm; Ratio IIa/IIb 3/1; *m/e* (^{192}Os) 947.

$HOs_3(CO)_9L^5$ (IVa/IVb): IR ν(CO) (cylcohexane): 2109m, 2078s, 2047s, 2040m, 2022s, 2009w, 2004s, 1985m, 1978m, 1969m cm^{-1}. ^1H NMR CD_2Cl_2 (room temperature): δ 4.06 (m, 2H), 2.82 (m, 2H), −16.76 (s, 1H) ppm; *m/e* (^{192}Os) 947.

**Crystal Data: $C_{13}H_5NO_{10}Os_3S_2$, *m* 969.90. Monoclinic $P2_1/c$, *a* 19.387(8), *b* 9.528(2), *c* 24.420(7) Å, β 111.20(2)°, *U* 4205 $Å^3$. $Z = 8$, D_c 3.06 g cm^{-3}, $F(000) = 3423$, Mo-K_α radiation (λ 0.71069 Å). μ (Mo-K_α) 183.10 cm^{-1}. 7403 unique intensity data were measured on a Stoe 4-Circle automatic diffractometer and the structure solved and refined for 5390 data having $F_0 \geqslant 5\sigma(F_0)$. $R = 0.0825$ and $R_g = 0.0973$.

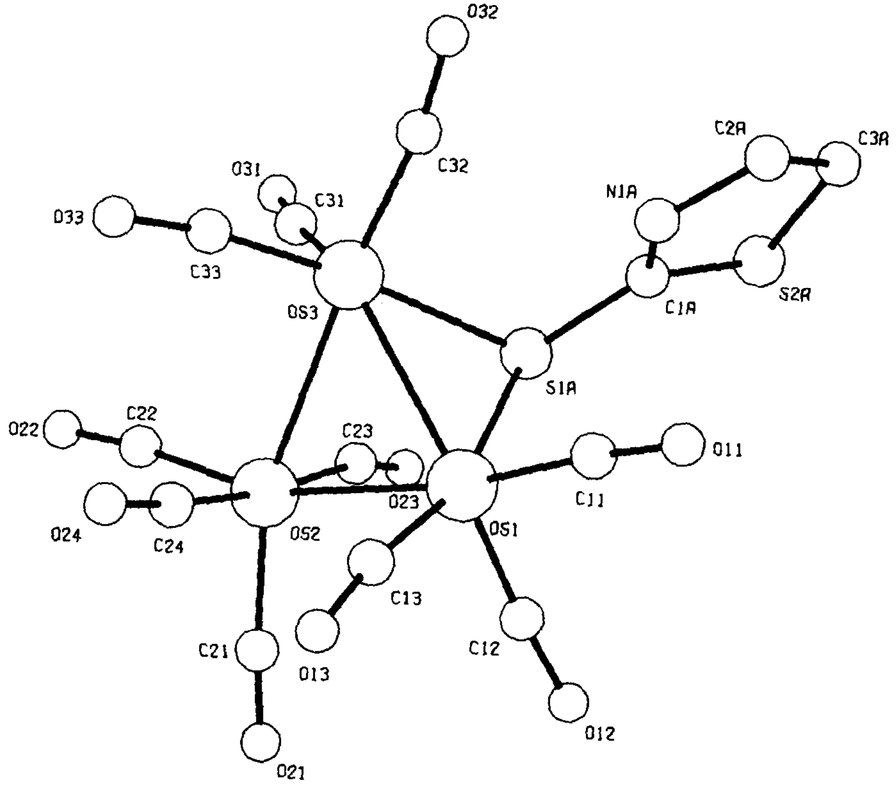
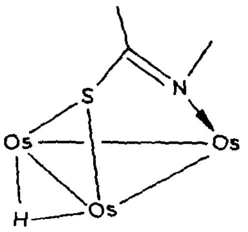
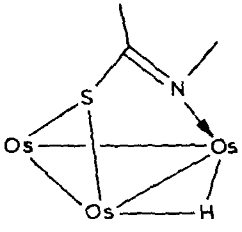


Fig. 1. The X-ray structure of $HOs_3(CO)_{10}L^5$. Bond lengths: Os(1)—Os(2) 2.864(3), Os(1)—Os(3) 2.842(3), Os(2)—Os(3) 2.855(3), Os(1)—S(1A) 2.418(11), Os(3)—S(1A) 2.416(11), S(1A)—C(1A) 1.790(41), C(1A)—N(1A) 1.266(71), C(1A)—S(2A) 1.731(55).

data for these complexes are in full agreement with the coordination of L via both sulphur and nitrogen as shown in IIIa and IIIb. In addition, a single crystal X-ray study of $HRu_3(CO)_9L^2$ has also revealed this mode of coordination [7], and spectral data for this complex are very similar to those of its osmium analogue.



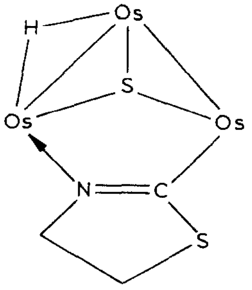
(III a)



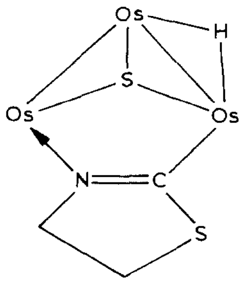
(III b)

Detailed examination of the IR, ^1H and ^{13}C NMR spectra of $HOs_3(CO)_9L$ (L = L^1, L^2, L^5, L^6) reveal the presence of two isomers IIIa and IIIb, differing only in the location of the hydride ligand. ^1H NMR studies show that the relative populations of IIIa and IIIb are dependent on the nature of L. For $HOs_3(CO)_9L^1$ it was possible to resolve $^1H—^{187}Os$ coupling for both isomers: the more abundant isomer exhibiting a resonance at δ −14 ppm with $^1J(OsH)$ 34.1 Hz can be assigned to the symmetrical hydride bridged isomer IIIa, whereas the other isomer exhibits a resonance at δ −12.3 ppm with $^1J(OsH)$ 30.8 and 32.9 Hz, consistent with structure IIIb.

If $HOs_3(CO)_9L^5$ is heated to reflux in octane the ligand expells a sulphur atom to form a sulphur-capped species of the same stoichiometry, which also exists in two isomeric forms IVa and IVb. These isomers interconvert rapidly on the NMR time-scale at room temperature, and cooling of the sample is required to resolve their hydride resonances. Similar observations have been made for a related thioformamido complex which forms an analogues sulphur-capped species on heating [8].



(IVa)



(IVb)

The affinity of osmium clusters for sulphur and hydride ligands results in the binding of thioamides in the thiolate form. This is particularly noteworthy for ethylene thiourea which normally prefers the thione form [9]. The consequent lengthening of the exocyclic C—S bond facilitates its cleavage and the formation of sulphur-capped species. Full preparative and spectroscopic details for all the complexes reported here, together with X-ray crystallographic studies on $HOs_3(CO)_9L$, will be published shortly.

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