Characterisation of Supported Trinuclear Osmium Clusters by Extended *X*-Ray Absorption Fine Structure (EXAFS) Spectroscopy

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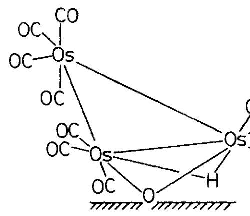
Trinuclear osmium clusters grafted on to alumina and tethered to thiolated silica have been characterised by analysis of the EXAFS of the Os L(III) edge spectra of these and related model complex samples.

Several attempts have been made to characterise the surface species formed by the interaction of osmium carbonyl clusters with inorganic oxide supports.[1-4] It has been established by a combination of infrared modelling, thermal desorption

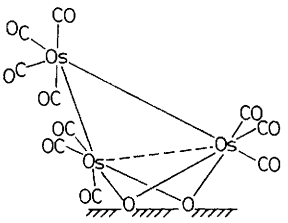
Table 1. EXAFS spectroscopy derived distances and Debye–Waller factors (σ^2) for compounds or models for supported species. *X*-Ray diffraction distances in parentheses.

Compound or model	Squared residual[a]	Distances/Å and σ^2/Å^2									
		Os–C	σ^2	Os · · · O[d]	σ^2	Os–X[e]	σ^2	Os–Os[f]	σ^2	Os–Os[g]	σ^2
(2)	0.105	1.89 (1.93)	0.008	2.86 (3.07)	0.016			2.78 (2.88)	0.008		
(3)	0.107	1.93 (1.92)	0.008	2.91 (3.05)	0.015			2.83 (2.82)	0.010	2.64 (2.68)	0.013
(4)[b]	0.113	1.91 (1.91)	0.008	2.91 (3.05)	0.018	2.24 (2.10)	0.016	2.81 (2.82)	0.012		
(5)[b]	0.062	1.90 (1.87)	0.010	2.90 (3.04)	0.016	2.24 (2.09)	0.019	2.82 (2.82)	0.009	3.08 (3.08)	0.011
(1c)	0.292	1.93	0.024	2.90	0.026			2.84	0.009		
(1a)[b]	0.187	1.91	0.016	2.89	0.026	2.25	0.006	2.84	0.009		
(1b)[b]	0.185	1.90	0.012	2.89	0.018	2.24	0.016	2.84	0.006	3.13	0.014
(6)[c]	0.217	1.91 (1.87)	0.009	2.89 (3.04)	0.019	2.31 (2.40)	0.012	2.82 (2.85)	0.007		
(7)[c]	0.070	1.92	0.013	2.90	0.022	2.36	0.005	2.84	0.010		

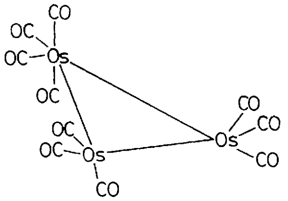
[a] On k^2 weighted EXAFS spectra. [b] X = O. [c] X = S. [d] Carbonyl oxygen. [e] Bridging atom. [f] Single bond. [g] Bridged bond.



(1a)



(1b)



(1c)

measurements, and EXAFS spectroscopy that at temperatures of between 100 and 150 °C a surface bound species of the form $HOs_3(CO)_{10}$(O-surface) (**1a**) is initially formed.[4]

The information obtained by EXAFS was restricted to an estimate for the osmium–osmium bond length of 2.68 Å for (**1a**) on silica, from inspection of a maximum in the Fourier transform.[4] The composite nature of this peak in osmium carbonyl complexes has been noted[5] and this makes such inspection difficult. We report that this surface species can in fact be characterised more completely by EXAFS spectroscopy, which also provides evidence for a bis-oxygen bridged structure (**1b**).

The recording and analysis of the osmium L(III) edge absorption spectra† was similar to that described previously,[5] with two exceptions. Firstly, a cubic smoothing procedure[7] was employed for the supported systems studied and for (μ-H)$Os_3(CO)_{10}$(μ-SPr^n). Secondly, analysis was entirely by curved wave methods[8] using the program EXCURVE which incorporates least squares routines.[9]

In addition to the grafted cluster on alumina (**1**), a series of model complexes of known molecular structure were investigated to establish the reliability of the parameters used *viz.* $Os_3(CO)_{12}$ (**2**),[10] (μ-H)$_2Os_3(CO)_{10}$ (**3**),[11] (μ-H)$Os_3(CO)_{10}$(μ-OMe) (**4**),[12] and $Os_3(CO)_{10}$(μ-OEt)$_2$ (**5**).[13] To demonstrate whether a bridging sulphur atom could be distinguished from a bridging oxygen, data from (μ-H)$Os_3(CO)_9$(μ-SPr^n) (**6**)[13] and (μ-H)$Os_3(CO)_{10}$\{μ-S[CH$_2$]$_3$Si(OMe)$_{3-n}$(O-silica)$_n$\} (**7**)[10,14] were analysed.

Details of the relevant parameters obtained from the curve fitting of the experimental EXAFS spectra and a comparison of the interatomic distances with those from *X*-ray diffraction are given in Table 1. Generally good estimates of Os–C and Os–Os bond distances were obtained. As observed previously,[5] carbonyl Os · · · O distances were underestimated (by 5%). A series of noncrystallographic models were also employed to establish the sensitivity of the technique towards the weaker scattering aspects of the structural models *i.e.* the bridging atoms and the odd bond length in isosceles osmium triangles. For example, six models of increasing complexity and number of shells were used for (**5**): (i) a three shell Os–C, Os–Os, and Os · · · O model, (ii) an additional fourth shell due to an Os–O (one or two bridges per cluster) or Os · · · Os distance, and (iii) five shell models involving Os–C, Os–O (one or two bridges per cluster), Os–Os, Os · · · O, and Os · · · Os. The weak back scattering of the bridging oxygen atoms to the nonadjacent metal atom was ignored. Three of the models (the two 5 shell models and the 4 shell mono-oxygen bridged version) gave similar low residuals, but the models with a single oxygen per cluster required anomalously small Debye–Waller factors for this shell (*ca.* 0.008). Attempts to introduce an extra oxygen bridge in (**4**) and dummy bridges in (**2**) yielded, as expected, large damping factors for the Os–O shell (0.03 and 0.05 respectively). It seems clear that the presence of the bridging oxygen atoms can be established (giving a σ^2 value of *ca.* 0.018 Å^2) and the estimation of unequal bond lengths in isosceles metal triangles is accurate.

The EXAFS spectrum of the alumina supported species (**1**) was fitted approximately equally well by models (**1a**), (μ-H)-$Os_3(CO)_{10}$(μ-O-), and (**1b**), $Os_3(CO)_{10}$(μ-O-)$_2$, with metal–metal distances similar to the appropriate model complex; the poorer fit obtained for model (**1c**), $Os_3(CO)_{10}$, which has no oxygen bridges, indicates that these atoms contribute significantly to the EXAFS pattern. In the mono-oxygen bridged model (**1a**), the Debye–Waller type factor (0.006) is very small, whilst that for the doubly bridged model (**1b**) is consistent with those observed for (**4**) and (**5**). It seems unlikely that static disorder and/or the mean correlated vibrational motion of osmium and oxygen atoms are reduced on changing from a crystalline environment to the surface of an amorphous oxide. So the model (**1b**) appears more probable. Evidence against this model has relied principally on the absence of evolved hydrogen during the reaction of $Os_3(CO)_{12}$ and oxides to form (**1**). Sample history may alter the proportions of (**1a**) and (**1b**) in a particular case.‡

From attempts to construct a model of the $HOs_3(CO)_{10}$-

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† The data will be deposited with the EXAFS data bank at the Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K. (ref. 6).

‡ The sample in this study was prepared by the reaction of (**2**) and Aluminium Oxide C in n-heptane for 2 h and stored at —25 °C for several months.

(O-surface) on the (100) plane of a disordered spinel-type lattice (preferentially exposed by γ-alumina[15]), the following became apparent: (i) that if the carbonyl ligands were not to penetrate the surface then the bridging oxide must at least also be bound to an aluminium adatom possibly as an [=$Al(OH)_2$] unit, occupying a tetrahedral site, and (ii) this being so, it is clear that the bis-oxygen bridged species can also be formed without the carbonyl ligands contacting the surface. It is interesting to note that attempts at this laboratory to form surface species on hydrated single crystals of corundum were not successful, possibly for the reasons outlined above.

$Os_3(CO)_{12}$ **(2)** $(\mu\text{-}H)_2Os_3(CO)_{10}$ **(3)** $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OMe)$ **(4)**

$Os_3(CO)_{10}(\mu\text{-}OEt)_2$ **(5)** $(\mu\text{-}H)Os_3(CO)_9(\mu\text{-}SPr^n)$ **(6)**

$(\mu\text{-}H)Os_3(CO)_{10}\{\mu\text{-}S[CH_2]_3Si(OMe)_{3-n}(O\text{-silica})_n\}$ **(7)**

It was evident from analysis of the spectra of **(6)** and **(7)**, that the bridging atom could be detected in these sulphur bridged materials. Estimates of the Os–S distance were short, but attempts to model these spectra with a bridging oxygen instead, gave an anomalously large Os–O distance (2.30 Å). It is also clear that the Debye–Waller factor (Os–S) of the supported species is again low. However the i.r. spectrum of the sample showed some deterioration, perhaps to a species with a higher average co-ordination number of the bridging atom.

These results demonstrate that EXAFS spectroscopy can provide much more detailed information about the local structures of supported clusters than noted previously. Future work will be directed towards understanding the larger deviations of bonded and non-bonded distances and also the Debye–Waller factors. Complications due to multiple scattering and the chemical dependence of back scattering factors are being investigated.

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