Skeletal Characterisation of High Nuclearity Osmium Carbonyl Clusters by Extended *X*-Ray Absorption Fine Structure (EXAFS) Spectroscopy

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Non-bonded osmium–osmium distances have been identified from the EXAFS of the Os L(III) edge spectra of $Os_6(CO)_{18}$, $[N(PPh_3)_2]_2[Os_6(CO)_{18}]$, and $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ and can be used to characterise the cluster skeleton.

Extended *X*-ray absorption fine structure (EXAFS) studies have been widely used to probe local geometries at metal centres,[1] but attempts to establish metal skeletons in discrete cluster compounds have been limited.[2] Sole observation of a neighbouring metal within a bonding distance is insufficient for a skeletal identification which requires the location of any more remote separations. We report that such non-bonded distances can be observed in cluster complexes of osmium.

$Os_3(CO)_{12}$ (1)

$Os_6(CO)_{18}$ (2)

$[N(PPh_3)_2]_2[Os_6(CO)_{18}]$ (3)

$[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (4)

Osmium L(III) edge *X*-ray absorption spectra were recorded for $Os_3(CO)_{12}$ (1),[3] $Os_6(CO)_{18}$ (2),[4] $[N(PPh_3)_2]_2[Os_6(CO)_{18}]$ (3),[5] and $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (4)[6] (complexes of known structure) on the Synchrotron Radiation Source at the Daresbury Laboratory.† Using routines in the SRS Program Library,[8] the background-subtracted EXAFS portions of the spectra were analysed, without any further manipulations on the experimental data, using plane and curved wave methods.[9] Procedures based on the program EXAFS[10] were employed, with *ab initio* atomic phase shifts and back scattering factors taken from the EXAFS database.[7] The curved wave method yielded good fits of the experimental data over an energy range of *ca.* 40 to *ca.* 840 eV above the absorption edge. The experimental and theoretical scattering curves for (4) are shown in Figure 1; the fits for the other three samples were closer than this one. Neighbouring shell radii used to provide these fits are given in Table 1. Osmium–carbon distances were close to the averaged *X*-ray diffraction values. The standard deviation on the diffraction-derived bond length in the $[Os_6(CO)_{18}]^{2-}$ anion is 0.05 Å, and this may partly account for the discrepancy for complex (3). In the analysis of the anion in (4), $[Os_{10}C(CO)_{24}]^{2-}$, the carbido carbon was consolidated

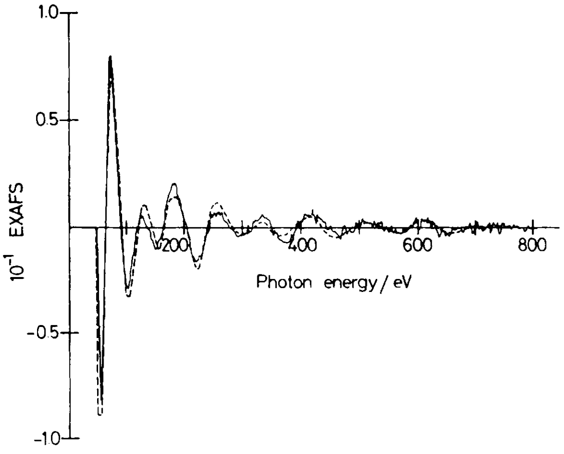

Figure 1. Experimental (——) and theoretical (- - -) EXAFS of the Os L(III) edge absorption spectrum of $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (4).

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† The data will be deposited with the EXAFS data bank at the Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.[7]

Table 1. EXAFS-derived distances for the first three shells (mean X-ray diffraction values in parentheses).

		Distances/Å		
Compound	Normalised squared residuals	Os–C	Os–Os	Os - - - O
(**1**)	0.0099	1.94(1.93)	2.79(2.88)	2.93(3.07)
(**2**)	0.0310	1.91(1.89)	2.78(2.78)	2.82(3.03)
(**3**)	0.0209	1.90(1.83)	2.82(2.86)	2.87(2.93)
(**4**)	0.0344	1.94(1.90)	2.81(2.84)	2.89(3.0)

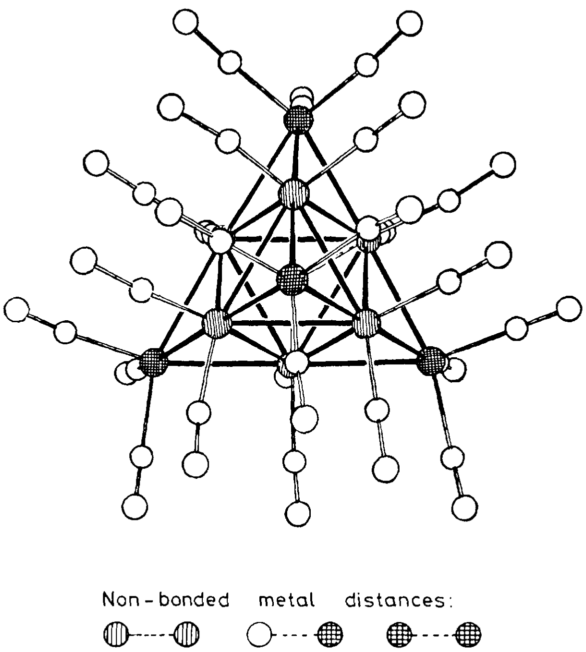

Figure 2. Structure of the $[Os_{10}C(CO)_{24}]^{2-}$ anion. The three non-bonded metal distances are indicated by shading.

into a mean Os–C shell; the weighted mean of the carbido and carbonyl distances derived from X-ray diffraction is 1.93 Å, very close to the EXAFS value. Agreement is generally good for osmium–osmium bonding distances, with $Os_3(CO)_{12}$ affording the largest discrepancy. However, the non-bonded osmium–oxygen separations were consistently underestimated, perhaps owing to multiple scattering effects.

The value of EXAFS in cluster chemistry, however, depends upon the ability to locate non-bonded metal–metal distances. In the anion $[Os_{10}C(CO)_{24}]^{2-}$, there are three such separations with $r_{Os---Os}/r_{Os-Os}$ ratios of 1.414, 1.732, and 2.000 for an idealised geometry (Figure 2). The averaged X-ray diffraction values give similar ratios. The Fourier transform (incorporating the phase and backscattering factor of the first-carbon-shell) of the experimental and theoretical scattering curves of (**4**) are shown in Figure 3. Five peaks are evident, due at increasing apparent shell radius, to the Os–C distance (*ca.* 1.96 Å), composite Os–Os and Os - - - O separations (*ca.* 3.01 Å) and three Os - - - Os distances (*ca.* 4.34, 5.08, and 5.98 Å). The distances used to give the theoretical scattering curve (Figure 1) and its Fourier transform (Figure 3) are given in Table 2.

Table 2. Estimation of non-bonded metal–metal distances (diffraction values in parentheses).

Compound	Distances/Å
(**2**)	4.58(4.57), 5.06(4.78)
(**3**)	4.12(4.05)
(**4**)	4.05(4.01), 4.86(4.91), 5.74(5.67)

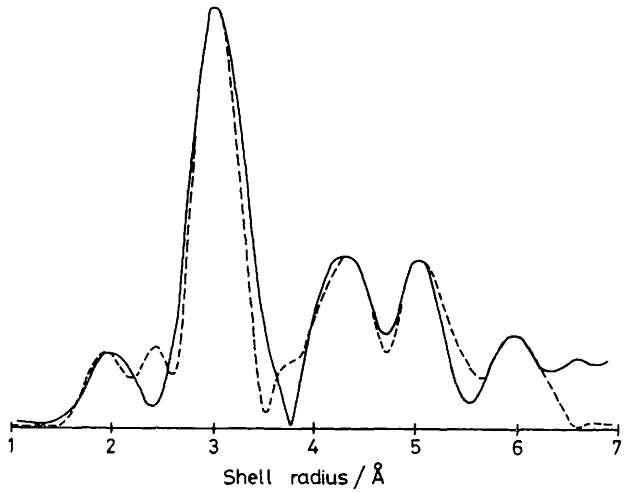

Figure 3. Fourier transform of experimental (——) and theoretical (- - -) scattering curves of (**4**) shown in Figure 1.

Observed $r_{Os---Os}/r_{Os-Os}$ ratios of 1.44, 1.73, and 2.05 were obtained, and these values are close to the idealised skeleton ones. Similar analyses have been carried out for the octahedral cluster $[Os_6(CO)_{18}]^{2-}$ (**3**) and the capped trigonal bipyramidal $Os_6(CO)_{18}$ (**2**). For complex (**3**), the single non-bonded metal–metal distance was evident in the Fourier transform. However in complex (**2**), only the shorter of the two non-bonded separations, *viz.* across the trigonal bipyramids, was clearly observed. The separation between the two atoms capping the central metal tetrahedron has a very low average occupancy (0.33) (the average shell occupancy of bonded osmium atoms is 4 in this complex) so it would be difficult to locate. However its position was estimated by minimising the squared residuals and using a narrow Gaussian window for the Fourier transform.

The distances so determined are given in Table 2. Agreement between the mean X-ray diffraction and EXAFS distances is within 0.1 Å for all but the outermost shell in $Os_6(CO)_{18}$ discussed above. Even if the evidence for the outermost metal–metal separation in (**2**) is discarded, then the skeletons of (**2**) and (**3**) can be distinguished by the $r_{Os---Os}/r_{Os-Os}$ ratio for the first non-bonded shell. These ratios are 1.63 and 1.414 for the idealised geometries of (**2**) and (**3**) respectively; the observed ratios are 1.65 and 1.46.

These results demonstrate that, for highly backscattering metals at least, EXAFS can provide strong evidence about the skeletal geometry of a high nuclearity cluster. This information is easiest to obtain on species of high symmetry with a restricted number of non-bonded shells and relatively high shell occupancies. We are extending this survey to lighter elements and are applying the techniques to less well characterised solution and supported species.

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