The Vibrational Spectra of the Acetylene Ligand in $[Os_3(CO)_9(\mu_2\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C_2H_2)]$ and the Identification of a Similar Species from Acetylene adsorbed on Pt(111) and Pd(111)

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The i.r. and Raman spectra of the acetylenic ligand in $[Os_3(CO)_9(\mu_2\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C_2H_2)]$ have been analysed and close analogies with electron energy loss spectra obtained from acetylene chemisorbed on Pt(111) and Pd(111) crystal faces confirm that the adsorbed species have the same hydrocarbon structure as the ligand.

Recently we have reported substantial successes in the identification of species formed from the chemisorption of hydrocarbons on metal surfaces, by comparison of their vibrational spectra with those of metal clusters containing ligands of known structure.[1–3] In this paper we report the frequencies associated with the vibrational modes of the acetylene ligand in the cluster $[Os_3(CO)_9(\mu_2\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C_2H_2)]$ (**1**). It has been proposed[4] that the structure of this cluster is as shown in

Figure 1, and is of C_s symmetry. The acetylenic ligand is formally co-ordinated *via* σ-bonds to two osmium atoms and π-bonded to the third, as in the related cluster compound $[Os_3(CO)_{10}(PhC_2Ph)]$.[5] In (**1**) the bridging carbonyl frequency $\nu(CO)$ occurs at 1875 cm^{-1}. A combined *X*-ray/neutron diffraction study of the acetylene cluster is currently being undertaken to establish its precise geometry.

The cluster was prepared by the literature method;[4] the deuteriated cluster $[Os_3(CO)_{10}(C_2D_2)]$ was prepared using C_2D_2 in the place of C_2H_2. I.r. spectra of (**1**) and its C_2D_2 analogue in CsI discs were measured at 300 and 95 K on a Perkin-Elmer 577 spectrophotometer. The Raman spectrum of (**1**) was recorded using the 674.4 nm line of an Ar/Kr laser with a Spex 1401 double monochromator.

The i.r. spectrum of (**1**) is shown in Figure 2. Assignment of the 'acetylenic' modes of (**1**) has been made by taking into account both the isotope shifts of the absorptions on deuteriation and their intensities in the i.r. and Raman spectra, and by comparison with appropriate model compounds. The metal–carbon stretching modes fall in a region of the spectrum made complicated by 'carbonyl' modes. However, an absorption at 521 cm^{-1} shifts to 513 cm^{-1} on deuteriation; this has no counterpart in the Raman spectrum, and is assigned to the antisymmetric stretching mode of the Os–C σ-bonds. A pair of absorptions at 343 and 338 cm^{-1} shift to 321 cm^{-1} on deuteriation, and these are assigned to the stretching mode of the Os–$C_2$$\pi$-bond. The OsCO deformations totally obscure the i.r. spectrum in the region 600—530 cm^{-1}, but give rise to very weak bands in the Raman; hence the two bands of medium intensity at 570 and 551 cm^{-1} in the Raman can be attributed to the symmetric stretching mode of the Os–C σ-bonds. The assignment is summarised in Table 1.

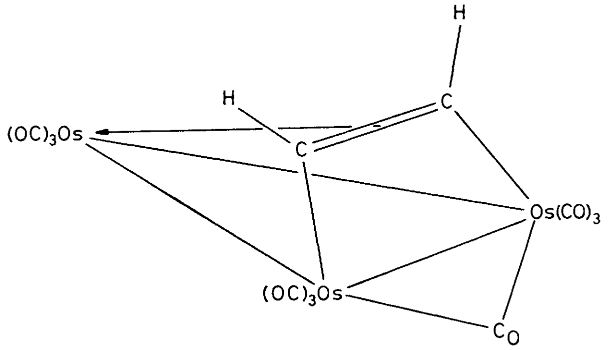

Figure 1. Proposed structure of cluster (**1**).

In 1978 Ibach and Lehwald[6] adsorbed acetylene onto a Pt(111) face at temperatures below 300 K. On the basis of electron energy loss spectroscopy (EELS), they postulated that the surface species formed had the same type of structure as the acetylene ligand in (**1**). Taking into account the 'metal surface selection rule' which states that, at specular angles of electron reflection, the EEL spectrum should be dominated by losses resulting from vibrations with a component of their dynamic dipoles perpendicular to the surface,[7] they concluded that the plane of the acetylenic species could not be perpendicular to the surface. More recently, EEL spectra have been obtained for C_2H_2 and C_2D_2 on Pd(111) at 150 K,[8] which show similar patterns of frequencies and intensities to those from Pt(111) and have been interpreted in an analogous manner. Less clear-cut EEL spectra below 270 K on Rh(111)[9] probably arise from the same surface species.

For a species on a metal surface that is of C_s symmetry, only those vibrational modes that are of a′ symmetry are expected to be EEL-active. Table 1 compares the data for the a′ modes of (**1**) and of its C_2D_2 analogue with the EELS data for C_2H_2/C_2D_2 on Pt(111); the two C_2H_2 spectra are illustrated in Figure 2. The agreement between the i.r. and EELS data is remarkably good, whether one considers frequencies, the intensity patterns, or the shifts on deuteriation. The main discrepancy concerns the frequency of the γ(CH)(sym) mode. However, this mode is also the most variable in frequency in the EEL spectra for C_2H_2 on Pt(111), Pd(111), and Rh(111); the very strong bands occur at 770, 706, and 673 cm^{-1}, respectively, on these three surfaces.

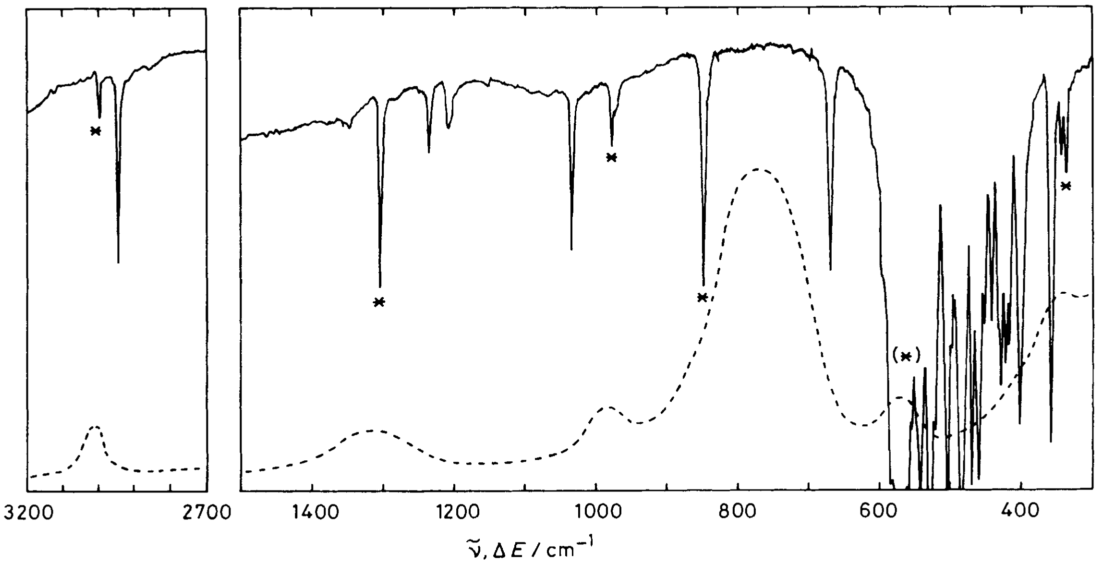

Figure 2. The transmission i.r. spectrum of $Os_3(CO)_{10}(C_2H_2)$ (solid line) measured at 95 K compared with the electron energy loss spectrum for C_2H_2 adsorbed on Pt(111) below 300 K (dashed line); the EEL spectrum is redrawn, with permission, from ref. 6. The bands from the a′ modes of the C_2H_2 ligand in the metal cluster compound, which correspond to the EEL-active bands, are indicated with asterisks. The asterisk in parentheses denotes a Raman frequency obscured in the i.r. spectrum by the multiplicity of absorptions between 580 and 350 cm^{-1}. These and the isolated band near 670 cm^{-1} (bridging CO) arise from δ(MCO) and ν(MC) modes of the multiple carbonyl ligands; all other i.r. bands are from the C_2H_2 ligand.

Table 1. A comparison of the vibrational spectra of C_2H_2 and C_2D_2, in the cluster compound [$Os_3(CO)_{10}(C_2H_2)$], and chemisorbed on Pt(111) below 300 K.[a,b]

Mode	Symmetry[c]	$Os_3(CO)_{10}(C_2H_2)$		C_2H_2/Pt(111)[a]	$Os_3(CO)_{10}(C_2D_2)$	C_2D_2/Pt(111)[a]	$\tilde{\nu}(H)/\tilde{\nu}(D)$(cluster)	$\tilde{\nu}(H)/\tilde{\nu}(D)$(ads.)
		I.r.	Raman	EELS	I.r.	EELS		
ν[CH(D)](sym)	a′	2996 (w)	2996 (m)	3010 (m)	2180 (w,sh)[d]	2240 (w)	1.37	1.34
ν[CH(D)](asym)	a″	2945 (m)	2946 (m)	n.o.	2140 (w,sh)[d]	n.o.	1.38	—
ν(CC)	a′	1301 (m)	1303 (w)	1310 (w)	1282 (m)	1260 (w)	1.01	1.04
δ[CH(D)](asym)	a″	1035 (m)	1037 (vw)	n.o.	760 (m)	n.o.	1.36	—
δ[CH(D)](sym)	a′	978 (w)	n.o.	985 (w)	742 (w)	730 (w)	1.32	1.35
γ[CH(D)](sym)	a′	848 (s)	848 (vw)	770 (vs)	605 (s)	570 (vs)	1.40	1.35
γ[CH(D)](asym)	a″	n.o.	n.o.	n.o.	n.o.	n.o.	—	—
ν(MC)(sym)	a′	n.o.	570 (m) 551 (m)	570 (w)	n.o.	n.o.	—	—
ν(MC)(asym)	a″	521 (m)	n.o.	n.o.	513 (w)	n.o.	1.02	—
ν(MC_2)	a′	343 (w) 338 (w)	338 (mw)	340 (m)	321 (mw)	310 (m)	1.06	1.10
Combination Bands		1234 (w) 1208 (w)	n.o.	—	998 (vw) 986 (vw)	—	1.24 1.23	—

[a] Ref. 6. [b] All wavenumbers in cm^{-1}; ν, δ, and γ denote bond-stretching, in-plane angle-bending, and out-of-plane angle-bending modes, respectively; s = strong, m = medium, w = weak, v = very, sh = shoulder, n.o. = not observed. [c] According to formal C_s symmetry. [d] These bands constitute weak shoulders on the high-wavenumber wing of the very strong ν(CO) absorptions.

Bertolini and Rousseau[10] have observed a very different spectrum for acetylene on Ni(111), with a dominant ν(CC) band at 1200 cm^{-1} and a lower ν(CH)(sym) frequency of *ca.* 2930 cm^{-1}, which they assigned to the same surface species as above. However, their spectrum correlates very poorly with the i.r. data for (**1**). Lehwald and Ibach[11] also obtained similar spectra on Ni(111), but postulated the presence of a different acetylenic species, possibly π-bonded to two metal atoms.

There seems no doubt that the surface species formed by adsorption of acetylene on Pt(111) and Pd(111), and possibly on Rh(111), is very similar to the acetylenic ligand in (**1**), bonded to three metal atoms by two σ-bonds and a π-bond. It is encouraging that the same type of adsorbed species can be recognised by the 'family resemblance' of spectra even when individual wavenumbers of bands may differ by up to 15%.

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