Vibrational Frequencies associated with the Interstitial Atom in [M₆(CO)₁₅C]²⁻ and [M₆(CO)₁₅N]⁻ (M = Co or Rh)

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Isotopic labelling of the interstitial atom in [M₆(CO)₁₅C]²⁻ and [M₆(CO)₁₅N]⁻ enabled the metal–interstitial atom frequencies to be assigned and the associated force constants, f_{ax} and f_{eq}, are found to be very similar for the M₆–C and M₆–N groups, with the values for M = Rh being significantly smaller than when M = Co.

Transition metal carbonyl clusters containing a variety of interstitial atoms are now known but, apart from a few studies,[1-4] the vibrational frequencies associated with the interstitial atoms have not been determined and little is known about the nature of their bonding within the metallic skeleton.

We now describe i.r. studies on the isoelectronic, isostructural, trigonal prismatic clusters [M₆(CO)₁₅C]²⁻ and [M₆(CO)₁₅N]⁻ (M = Co and Rh),[5,6] which enabled the metal–interstitial atom frequencies to be assigned. The i.r. spectra of ¹⁴N- and ¹⁵N-labelled (PPh₄)[M₆(CO)₁₅N] (M = Co, Rh) have been measured in Nujol on a Perkin-Elmer 683 spectrometer equipped with a data handling station and the bands associated with the interstitial atom–metal vibrations are summarised in Table 1; it was not possible to obtain i.r. spectra for the cobalt and rhodium carbide anions with the same counterion and, in this case, i.r. spectra of the ¹²C- and ¹³C-labelled clusters, (PPN)₂[Co₆(CO)₁₅C] {PPN = [(Ph₃P)₂N]⁺} and K₂[Rh₆(CO)₁₅C], were measured as Nujol mulls.

For these cluster anions there are two interstitial atom vibrations ν_{ax} (a₂″) and ν_{eq} (e′) which involve motion respec-

tively along and perpendicular to the 3-fold symmetry axis of the clusters (point group D_{3h}). The bands associated with these vibrations were clearly identified from differences between the spectra of the isotopomers, and the assignment of the lower frequency to the e′ mode follows from the greater intensity expected for this doubly degenerate vibration.

In order to relate the frequencies to force constants a simple valence force field (SVFF) approximation has been used, in which also the vibrations in question are regarded as motions of the interstitial atom within an infinitely heavy M₆-cage. These assumptions set to zero the coupling of the interstitial atom modes with ν(M–M) vibrations and with CO stretching and deformation modes relative to the M₆-cage. Since the valence p-orbitals of the interstitial atom also separate into axial (a₂″) and transverse (e′) components it seems appropriate to formulate the interstitial atom force field in terms of axial and equatorial force constants f_{ax} and f_{eq} rather than with force constants for bonds linking the interstitial atom with each of the metal atoms. The internal co-ordinates associated with f_{ax} and f_{eq} are the changes in the distances of the interstitial atom from the triangular and rectangular faces of the cluster, respectively. The bonding is thus envisaged as the multicentre overlap of the interstitial atom axial p-orbital with the a₂″ combination of metal orbitals centred on each triangular face of the cluster, and the overlap of sp² hybrid orbitals of the interstitial atom with metal orbital combinations at the centre of each rectangular face. The alternative picture of equivalent bonds between the interstitial and six metal atoms does not satisfactorily account for the observed frequencies. Thus if a and b denote the M–M distances within a triangular face and between triangular faces of the cluster it may be shown that in a SVFF approximation the ratio ν_{ax}/ν_{eq} for this bonding picture is equal to $(1.5)^{\frac{1}{2}}b/a$. The distances a and b

Table 1. I.r. frequencies associated with ν(M₆–E) in [M₆(CO)₁₅E]$^{n-}$ (E = C, n = 2; E = N, n = 1).

Compound	ν(a₂″)/cm⁻¹ [a]	ν(e′)/cm⁻¹ [a]
[Co₆(CO)₁₅C]²⁻	772 (745)	719 (692)
[Rh₆(CO)₁₅C]²⁻	689 (664)	653 (631)
[Co₆(CO)₁₅N]⁻	722 (700)	698 (678)
[Rh₆(CO)₁₅N]⁻	645 (627)	622 (605)

[a] Figures in parentheses refer to the ¹³C- or ¹⁵N-enriched (90%) isotopomer.

are approximately equal for these clusters,[5,6] and the observed frequency ratio, which is much closer to unity than the SVFF calculated ratio, thus requires that an interaction force constant between stretching of M–C or M–N bonds lying in the same σ_v symmetry plane of the cluster is introduced into the force field, whose value however (ca. 25—35 N m^{-1}) appears to us to be unacceptably large.

With the axial–equatorial bonding model it follows in the aforementioned approximations that $f_{ax} = 2\pi^2 v_{ax}^2 c^2 m$ and $f_{eq} = 8\pi^2 v_{eq}^2 c^2 m/3$ where m is the mass of the interstitial atom. The isotope shifts calculated from these formulae are less by ca. 4 cm^{-1} than the observed shifts, owing to the small degree of coupling of the interstitial atom vibrations with other motions which is ignored in this simple treatment. The force constants given in Table 2 are thus the mean of the values obtained for each pair of isotopomers.

The force constants show that there is little difference between the M_6–C and M_6–N groups, with f_{eq} being always slightly bigger than f_{ax}. However, there is a significant decrease in both f_{eq} and f_{ax} on going from Co_6–C/Co_6–N to Rh_6–C/Rh_6–N clusters and this is in keeping with the increase in d(M–C/N),[5,6] which is greater than expected on the basis of covalent radii.

It is also of interest to compare our data on $[Co_6(CO)_{15}C]^{2-}$ with those obtained on $[Co_6(CO)_{12}C(\mu_3\text{-S})_2]$.[1] In the latter

Table 2. Force constants associated with $v(M_6\text{–E})$ in $[M_6(CO)_{15}E]^{n-}$ (E = C, $n = 2$; E = N, $n = 1$).

Compound	f_{ax}/N m^{-1}	f_{eq}/N m^{-1}
$[Co_6(CO)_{15}C]^{2-}$	204	235
$[Rh_6(CO)_{15}C]^{2-}$	162	195
$[Co_6(CO)_{15}N]^{-}$	209	261
$[Rh_6(CO)_{15}N]^{-}$	167	207

case, we calculate f_{ax} and f_{eq} to be 229 and 138 N m^{-1}, respectively. It appears that the low value of f_{eq} in $[Co_6(CO)_{12}C(\mu_3\text{-S})_2]$ results in extensive mixing of $v(e')$-$(Co_6\text{–C})$ with Co–C–O bending vibrations,[1] and the approximations made here do not therefore give an accurate value for this force constant. Nevertheless it is clear that f_{eq} in $[Co_6(CO)_{12}C(\mu_3\text{-S})_2]$ is significantly less than in $[Co_6(CO)_{15}\text{-}C]^{2-}$. The vibrations $v(a_2'')(Co_6\text{–C})$ in either $[Co_6(CO)_{12}C(\mu_3\text{-S})_2]$ or $[Co_6(CO)_{15}C]^{2-}$ are not significantly mixed with Co–C–O bending vibrations however, as judged from the isotope vibration frequency ratios,[1] and f_{ax} is similar in both compounds.

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