A Vibrational Spectroscopic Study of $[Rh_4(CO)_{12}]$*

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The metal–metal stretching region of the i.r. and Raman spectra of $[Rh_4(CO)_{12}]$ is reported and analysed. The hitherto unpublished solution and ^{13}CO-enriched spectra suggest that the metal–metal region should be re-assigned, and these results are compared with those for $[Ir_4(CO)_{12}]$.

ALTHOUGH a large number of homo-[1,2] and hetero-metallic[1-3] carbonyl clusters are now known, information on metal–metal bond strengths in clusters is scarce. Thermochemical measurements have been made[4] in an attempt to obtain this information but problems arise in interpreting the data.[2,5] *X*-Ray measurements also provide a clue to the bonding within the metal framework, but more quantitative information should be possible from vibrational spectroscopic studies. However, apart from a few Raman/i.r. studies,[6] this area has been rather neglected. Infrared studies of carbonyl clusters in the region of the metal–metal vibrations are scarce, and Raman spectra are difficult to obtain because most of the clusters are intensely coloured. In addition, laser irradiation often produces decomposition, although this can sometimes be avoided by using long wavelength irradiation of samples in spinning cells.

The recent paper by Oxton[7] on metal–metal force constants in metal-cluster compounds prompts us to report our measurements on $[Rh_4(CO)_{12}]$. Previous measurements[8,9] on $[Rh_4(CO)_{12}]$ were made on solids, and metal–metal force constants were calculated from these data.[7] We have obtained Raman spectra of solutions of $[Rh_4(CO)_{12}]$ and i.r. spectra of $[Rh_4(CO)_{12}]$ (*ca.* 90% ^{13}CO) which suggest that the metal–metal region should be reassigned.

RESULTS AND DISCUSSION

The structure of $[Rh_4(CO)_{12}]$ (Figure 1) both in the crystal[10] and in solution[11] belongs to the point group C_{3v} whereas the homologous iridium compound is fully tetrahedral, T_d.[12] $[Co_4(CO)_{12}]$ also has C_{3v} symmetry[13] but, because it is intensely coloured, Raman spectra are difficult to obtain[14] and the results are somewhat dubious.

The M_4 cluster vibrations for $[Ir_4(CO)_{12}]$ are designated $\nu_1(a_1)$, $\nu_2(e)$, $\nu_3(t_2)$ and become $\nu_1(a_1)$, $\nu_2(e)$, $\nu_3(a_1)$, $\nu_3(e)$ for $[Rh_4(CO)_{12}]$ due to the formal splitting of the triply degenerate mode, ν_3, in the lower symmetry. All these vibrations are Raman-active for both symmetries whereas only ν_3 is i.r. active in T_d symmetry whilst all are formally active in C_{3v}.

The Raman spectrum of $[Ir_4(CO)_{12}]$ in the metal–metal region has been assigned previously.[15] Because $[Ir_4(CO)_{12}]$ is remarkably insoluble, solution Raman polarization data were not available to assist with this assignment, but the observed frequencies were placed approximately in the ratio $\nu_1 : \nu_3 : \nu_2 = 2 : \sqrt{2} : 1$ predicted[16] from a simple valence force-field (SVFF) calculation. This was supported by a more detailed force-constant analysis,[15] and was verified by measuring the far-i.r. spectrum,[17] which shows one band at 162 cm^{-1}, due to ν_3. We note here that further confirmation of this assignment comes from the relative intensities of the ν_2 and ν_3 bands in the Raman spectrum of $[Ir_4(CO)_{12}]$. It can be shown from a bond polarizability model[18] that, neglecting contributions to the polarizability derivatives from changes in bond orientations in the ν_2 and ν_3 modes, the intensities of the ν_1, ν_2, and ν_3 Raman bands of a tetrahedral cage for $x(z,x + z)y$ scattering geometry[19] are proportional to $80(\bar{\alpha}')^2$, $7(\gamma')^2$, and $42(\gamma')^2$, respectively, where $\bar{\alpha}'$ and γ' are respectively the mean value of $(\partial\alpha_{\parallel}/\partial r + 2\partial\alpha_{\perp}/\partial r)$ and the anisotropy $(\partial\alpha_{\parallel}/\partial r - \partial\alpha_{\perp}/\partial r)$ of the M–M bond polarizability derivative tensor.[18] The Raman intensity ratio of 1 : 6 thus predicted for $\nu_2 : \nu_3$ is very close to the observed peak height ratio of $I_{162}/I_{131} = 6.2$, and there can thus be no doubt that these assignments are correct for $[Ir_4(CO)_{12}]$.

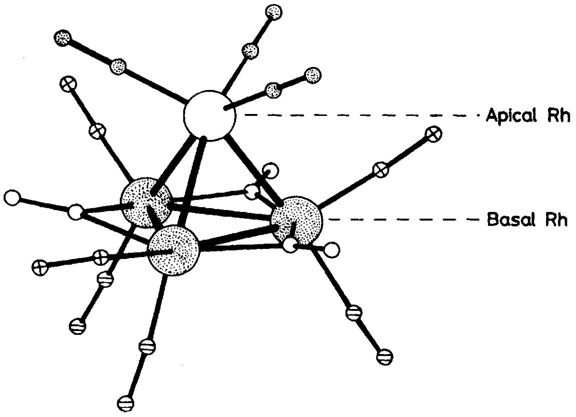

FIGURE 1 The structure of $[Rh_4(CO)_{12}]$

The metal–metal stretching region of the Raman spectrum of $[Rh_4(CO)_{12}]$ in CH_2Cl_2 (Figure 2) is very similar to that of $[Ir_4(CO)_{12}]$, but in the far-i.r. spectrum two bands are observed, at 198 and 176 cm^{-1}.[8] These have previously been assigned[8] to the e and a_1 components respectively of ν_3, split into two components in the lower symmetry, the higher frequency component being assigned to e on account of its greater intensity. This satisfactorily accounts for the i.r. spectrum, since it is generally found that for fairly small symmetry perturbations the e and a_1 components approximately retain the 2 : 1 intensity ratio expected from their respective

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* 2,3; 2,4; 3,4-Tri-μ-carbonyl-1,1,1,2,2,3,3,4,4,-nonacarbonyl-*tetrahedro*-tetrarhodium.

degeneracies. However, it is not consistent with the Raman spectrum, in which we find there is a prominent band at 170 cm^{-1} but *no band* in the region 190—200 cm^{-1} detectable above the noise level in our spectra (3% of ν_1). A band at 200 cm^{-1} reported previously[8] to have *ca.* 10% of the intensity of ν_1 in the Raman spectrum of $[Rh_4(CO)_{12}]$ is evidently due to an impurity, probably $[Rh_6(CO)_{16}]$, which we find to have a strong Raman band at this frequency and which is the likely product of laser irradiation of $[Rh_4(CO)_{12}]$.

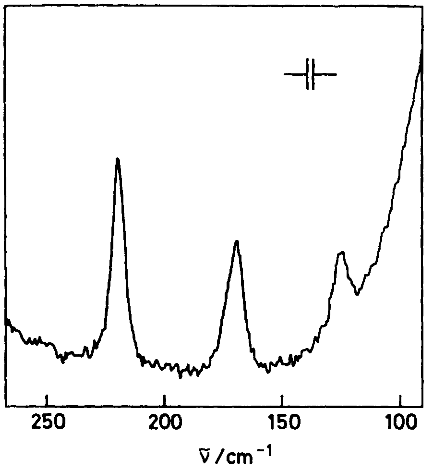

FIGURE 2 The Raman spectrum of $[Rh_4(CO)_{12}]$ in solution in CH_2Cl_2; 647.1 nm excitation, 2 cm^{-1} bandpass

TABLE 1

Low-frequency vibrational spectra ($\tilde{\nu}/cm^{-1}$) of $[Rh_4(CO)_{12}]$ and $[Ir_4(CO)_{12}]$

$[Rh_4(CO)_{12}]$			$[Ir_4(CO)_{12}]$		
	Raman				
I.r. (solid) [a]	(CH_2Cl_2 solution) [b]	(solid)	I.r. (solid)	Raman (solid) [b]	Assignment
	125(3.2) $\rho > 0.65$	127m		131 [c](1.6)	*e*, ν(M–M)
176w	170(6.5) $\rho > 0.70$	166m 172s	162 [d]	162 [c](10)	t_2, ν(M–M)
198m					a_1, δ(M–M–CO)
	219(10) $\rho < 0.03$	219.5s		209 [c](8)	a_1, ν(M–M)

[a] $[Rh_4(^{13}CO)_{12}]$ absorbs at 175 and 196 cm^{-1}. [b] Relative intensities in parentheses. [c] This work and ref. 15. [d] This work and ref. 17.

We have therefore considered the possibility that the splitting of ν_3 is very small, and have shown that this is confirmed by a normal co-ordinate analysis (see below). The i.r. band, at 198 cm^{-1}, which has no counterpart in the spectra of $[Ir_4(CO)_{12}]$, is therefore attributed to a δ(M–M–CO) vibration of the bridging carbonyl ligands. There are two modes of this type, of a_1 and *e* symmetry, and the i.r. band at 198 cm^{-1} is assigned to the a_1 mode, which from a bond-dipole model is expected to have the greater i.r. intensity, but very low Raman intensity on account of the near coplanarity of the basal $Rh_3(\mu\text{-}CO)_3$ unit. A simple calculation shows that such a δ(M–M–CO) mode at 198 cm^{-1} may be expected to shift to 196.5 cm^{-1} upon substitution of ^{12}CO by ^{13}CO, in good agreement with the measured frequency (196 cm^{-1}) in the i.r. spectrum of $[Rh_4(CO)_{12}]$ (90% ^{13}CO).

The assignment of the vibrations of the Rh_4 cluster (Table 1) follows by analogy with that for $[Ir_4(CO)_{12}]$, and the very low depolarization ratio of the Raman band at 219 cm^{-1} of $[Rh_4(CO)_{12}]$ confirms the assignment of this band to ν_1 (a_1). It is clear from the Raman spectrum of $[Rh_4(CO)_{12}]$ in CH_2Cl_2 solution that the splitting of ν_3 is less than 2 cm^{-1}, since the ν_3 band recorded with this spectral resolution is quite symmetrical (Figure 2), although there is a poorly resolved splitting of this band (*ca.* 5 cm^{-1}) in the Raman spectrum of the crystalline solid.

The absence of a detectable splitting of ν_3 in the solution spectrum of $[Rh_4(CO)_{12}]$ is an interesting vibrational problem which we have investigated using a SVFF approximation in which only the four rhodium atoms and the $Rh_{ap.}$–$Rh_{bas.}$ and $Rh_{bas.}$–$Rh_{bas.}$ (ap. = apical, bas. = basal) force constants (f_a and f_b respectively) were included. For most structures of high symmetry the splitting of degenerate vibrations as a result of a force-constant perturbation to a lower symmetry is a linear function of the differences in the force constants,[20] and the vibrational spectrum is thus sensitive to asymmetry. For a tetrahedral cage, however, we find[21] that for $f_a \neq f_b$ there is *no first order splitting of* ν_3. It is only as a consequence of the coupling of $\nu_3(a_1)$ with ν_1, and of $\nu_3(e)$ with ν_2 induced by the perturbation, that there is a second-order splitting of ν_3. Correct to second-order terms in the force constants, this splitting is given by the expression below, where $(\nu_3)_0$ and f_0 are the frequency and

$$\frac{\nu_3(a_1) - \nu_3(e)}{(\nu_3)_0} = -\tfrac{3}{8}\left(\frac{f_a - f_b}{f_0}\right)^2$$

force constant for the unperturbed cluster. For a 10% difference in f_a and f_b the splitting of ν_3 is thus calculated to be less than 0.7 cm^{-1}, and we can only conclude that, in $[Rh_4(CO)_{12}]$, f_a differs from f_b by less than *ca.* 20%. It is therefore clear that, in this special case of a C_{3v} force constant perturbation of a M_4 tetrahedron, vibrational spectroscopy in the ν(M–M) region is a very insensitive method of detecting the difference between apical and basal M–M bonds.

In addition to the absence of a detectable splitting of ν_3 in the solution spectra of $[Rh_4(CO)_{12}]$, the very small Raman depolarization ratio of ν_1 and the absence of ν_1 and ν_2 in the i.r. spectrum are also consistent with the selection rules of a fully tetrahedral molecule. It is thus probable that the coupling of $\nu_3(a_1)$ with ν_1 and of $\nu_3(e)$ with ν_2, which would induce i.r. intensity in ν_1 and ν_2, is small. It is only in the Raman intensity ratio $I(\nu_2) : I(\nu_3)$ that a substantial departure from tetrahedral behaviour is observed (expected ratio $I(\nu_2) : I(\nu_3) = 1 : 6$). This could be due to significant coupling of $\nu_3(e)$ with ν_2, but in view of the other evidence above that this coupling is small it is more likely due to a difference between the anisotropies ($\partial\alpha_{\parallel}/\partial r - \partial\alpha_{\perp}/\partial r$) of the apical and basal M–M bonds.

TABLE 2

ν(CO) vibrational spectroscopic data ($\tilde{\nu}$/cm^{-1}) for $[Rh_4(CO)_{12}]$ in solution

Raman (CH_2Cl_2)	I.r. (heptane)	Assignment	
	1 880vs	e	$\nu(\mu\text{-CO})$
1 918w	1 920w	a_1	
2 027w (sh), ρ *ca.* 0.75	2 035.0(sh)	e	$\nu(CO_t)$ *
2 044vs, br, $\rho = 0.74$	2 042.0	e	
	2 044.6	a_1	
2 070m, $\rho = 0.7$	2 069.5	e	
	2 074.9	a_1	
2 108vs, $\rho < 0.05$	2 106.6	a_1	

* Data from ref. 22; CO_t = terminal carbonyl.

The observed M_4 stretching frequencies may be used to calculate the *mean* M–M stretching force constant, $(f_a + f_b)/2$, of $[Rh_4(CO)_{12}]$ by assuming these to be the frequencies for a bare Rh_4 cluster without ligands, as done previously by Oxton.[7] The value 87.5 N m^{-1} thus obtained is considerably less than that similarly obtained [7] for $[Ir_4(CO)_{12}]$ (159 N m^{-1}). It should be noted that the bare-cluster approximation underestimates the effective masses of the metal atoms in metal carbonyl clusters, and therefore leads to M–M force constants which are somewhat too small (see for example the data in ref. 7). Thus a full calculation [15] for $[Ir_4(CO)_{12}]$, including ligand deformation modes, gives f(Ir–Ir) = 169 N m^{-1}. For $[Rh_4(CO)_{12}]$ the far-i.r. spectrum shows that the region of δ(M–M–CO) vibrations overlaps that of the Rh_4 cluster modes, and the bare-cluster approximation may be less satisfactory for this molecule than it is for $[Ir_4(CO)_{12}]$. However, there can be little doubt that the substantial difference between the M–M force constant of $[Ir_4(CO)_{12}]$ and the *mean* M–M force constant for $[Rh_4(CO)_{12}]$ is qualitatively significant.

Though not the primary objective of this study, the Raman spectrum of $[Rh_4(CO)_{12}]$ in CH_2Cl_2 was also recorded in the ν(CO) region (Table 2). These measurements complement the published solution infrared data, and are entirely consistent with the assignment of the frequencies in the terminal ν(CO) region by Bor *et al.*[22] Thus the band at *ca.* 2 030 cm^{-1} is confirmed as a fundamental, but the choice between the proposed assignments (I and II) remains open since the depolarization ratio of the Raman band at 2 070 cm^{-1} is consistent with either a_1 or e.

It is of note that although it has been shown here that the vibrational spectra of $[Rh_4(CO)_{12}]$ in the ν(M–M) region are insensitive to differences in the force constants f_a and f_b so that we are unable to determine from the vibrational data whether or not $f_a - f_b$ is small, the difference in the $Rh_{ap.}$–$Rh_{bas.}$ and $Rh_{bas.}$–$Rh_{bas.}$ bond lengths in $[Rh_4(CO)_{12}]$, and in all its derivatives so far examined by X-ray analysis, have been found to be rather small.[23]

EXPERIMENTAL

Raman spectra were recorded initially using excitation at 752.5 nm (100 mW) from a krypton ion laser, with stationary samples using a Coderg PH1 spectrometer. Equally satisfactory spectra were subsequently obtained using 647.1 nm excitation with spinning sample cells containing dichloromethane solutions of $[Rh_4(CO)_{12}]$, or the solid substance, under an atmosphere of CO. Calibration was by superposition of neon emission lines. Far-i.r. spectra (40—400 cm^{-1}) were recorded from thick vaseline mulls, using a Beckmann R.I.I.C. FS 720/FTC 100 interferometer with internal calibration.

The compound $[Rh_4(CO)_{12}]$ was prepared using the procedure described by Martinengo *et al.*[24] and recrystallisation was carried out twice from heptane solution under an atmosphere of CO at $\leqslant$25 °C in order to prevent the formation of any $[Rh_6(CO)_{16}]$. Isotopic enrichment was carried out by repeatedly exposing a dichloromethane solution of $[Rh_4(CO)_{12}]$ to ^{13}CO (Prochem 95% ^{13}CO) using standard vacuum-line techniques. The final enrichment was established by thermal decomposition followed by high-resolution mass spectrometry on the evolved gas.

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