

## Metal-Hydrogen Stretching Frequencies in Metal Cluster Complexes. The First Reported $\nu_{\text{MH}}$ for an Interstitial Hydrogen Ligand

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**Summary** Metal-hydrogen stretching absorptions have been observed in the i.r. spectra of the ions  $[\text{HRu}_6(\text{CO})_{18}]^-$  and  $[\text{DRu}_6(\text{CO})_{18}]^-$  near 825 and 600  $\text{cm}^{-1}$ , respectively, constituting the first reported observation of  $\nu_{\text{MH}}$  for an interstitial hydrogen ligand.

ALTHOUGH hydride ligands in metal cluster complexes may be terminal,  $\mu_2$ -bridging,  $\mu_3$ -bridging, or interstitial, metal-hydrogen stretching absorptions have been definitely established for only the former two environments. The existence of a correlation between the M-H stretching frequencies and the M-H-M interbond angle has been recently demonstrated in the case of some  $\mu_2$ -bridged metal hydrides.<sup>1</sup> Few metal clusters containing an interstitial H ligand are known.<sup>2-4</sup> The first example in which this was found to occur was the  $[\text{HRu}_6(\text{CO})_{18}]^-$  ion, as characterised by an X-ray diffraction study, together with <sup>1</sup>H n.m.r. and solution i.r. spectroscopic data.<sup>3</sup> A recent single-crystal neutron diffraction investigation of the complex  $[(\text{Ph}_3\text{P})_2\text{N}][\text{HCo}_6(\text{CO})_{15}]$  has shown that this anion also contains an interstitial H ligand.<sup>4</sup> We have studied the i.r. spectrum of the  $[\text{HRu}_6(\text{CO})_{18}]^-$  ion, and that of its deuterium analogue, in the polycrystalline tetramethylammonium salt.

I.r. spectra of the salts were measured, as KBr discs, at 298 and *ca.* 95 K using a Digilab FTS-14 spectrophotometer. Spectra of  $[\text{Me}_4\text{N}][\text{HRu}_6(\text{CO})_{18}]$  and  $[\text{Me}_4\text{N}][\text{DRu}_6(\text{CO})_{18}]$  measured at the lower temperature are shown in the Figure.

Absorptions having no counterparts in the spectrum of the other isotopic species are found near 825 (H complex) and 600  $\text{cm}^{-1}$  (D complex). The intensity of each such absorption is strongly temperature-dependent, the bands becoming pronouncedly sharper on cooling from room temperature to low temperature. The  $\nu_{\text{RuH}}$  absorption appears to consist of a broad doublet at 298 K but gives rise to two sharp bands of almost equal integrated intensity, at 806 and 845  $\text{cm}^{-1}$ , in the 95 K spectrum of the  $[\text{HRu}_6(\text{CO})_{18}]^-$  ion. Absorption due to  $\nu_{\text{RuD}}$ , apparent at 298 K only as a slight shoulder on the intense band associated with a Ru-CO angle-bending vibration occurring just below 600  $\text{cm}^{-1}$ , appears as a single, sharp band at 608  $\text{cm}^{-1}$  upon cooling. Subtraction of i.r. absorbance spectra of the H and D species, using  $[\text{Me}_4\text{N}]^+$  bands for scaling purposes, performed on the Digilab Nova 1200 computer, virtually eliminated absorption arising from the Ru-CO angle-bending mode in the region where a second component of  $\nu_{\text{RuD}}$  would be expected. However, no absorption arising from a second component of  $\nu_{\text{RuD}}$  could be observed. Two weak bands in the spectrum of  $[\text{DRu}_6(\text{CO})_{18}]^-$  at 95 K, at 812 and 851  $\text{cm}^{-1}$ , are attributed to  $\nu_{\text{RuH}}$  of isotopically dilute  $[\text{HRu}_6(\text{CO})_{18}]^-$ , present as a result of incomplete deuteration. From a comparison of the intensities of these bands with those in pure  $[\text{HRu}_6(\text{CO})_{18}]^-$ , with reference to selected  $[\text{Me}_4\text{N}]^+$  absorptions, the degree of deuteration was estimated to be *ca.* 95%.

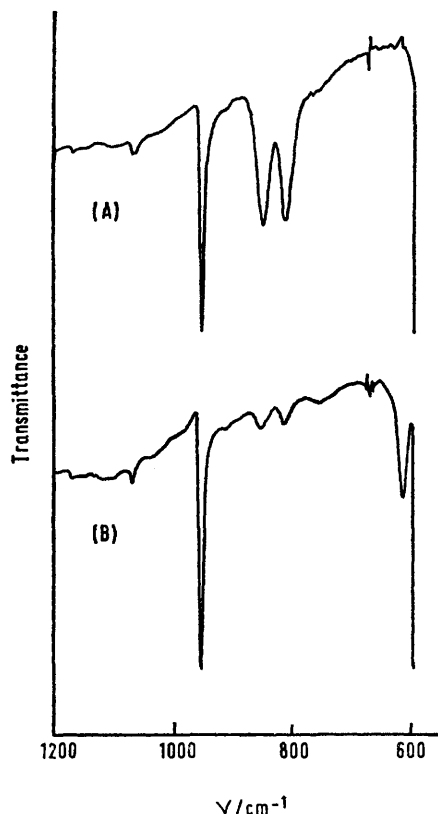


FIGURE. I.r. spectra of  $[\text{Me}_4\text{N}][\text{HRu}_6(\text{CO})_{18}]$  (A) and  $[\text{Me}_4\text{N}][\text{DRu}_6(\text{CO})_{18}]$  (B), at 95 K.

The two bands of approximately equal intensity exhibited at 95 K by  $\nu_{\text{RuH}}$  of  $[\text{Me}_4\text{N}][\text{HRu}_6(\text{CO})_{18}]$  are somewhat intriguing since, if hydrogen is sited at the centre of a regular octahedron, a single, triply-degenerate, i.r.-active mode might be expected. The two bands observed are

unlikely to arise from a site-group effect, where a splitting would be expected to give two components with an intensity ratio close to 2:1, while factor-group coupling is made improbable by the observation that two bands of approximately equal intensity are also present in the spectrum of the isotopically dilute  $[\text{HRu}_6(\text{CO})_{18}]^-$  ion in the deuteriated complex. The most probable origin of the observed splitting would therefore seem to lie in Fermi resonance of an overtone (provided the H ligand does not occupy a centre of inversion in the crystal) or a combination mode with  $\nu_{\text{RuH}}$ . The isotope ratio,  $\nu_{\text{RuH}}/\nu_{\text{RuD}}$ , is then estimated to be 1.36.

We have also examined the i.r. spectrum of the  $[\text{HRu}_6(\text{CO})_{18}]^-$  ion in the  $[\text{Ph}_4\text{As}]^+$  and  $[(\text{Ph}_3\text{P})_2\text{N}]^+$  salts. In the former salt two bands of approximately equal intensity are again observed at low temperature, at 817 and 842  $\text{cm}^{-1}$ , and are assigned to  $\nu_{\text{RuH}}$ . The corresponding region of the i.r. spectrum of  $[(\text{Ph}_3\text{P})_2\text{N}][\text{HRu}_6(\text{CO})_{18}]$  is complicated by the presence of cation absorptions and no firm assignment is given in this case.

Simple harmonic force constant calculations, treating the  $[\text{HRu}_6]$  octahedron as a set of linear symmetric Ru-H-Ru oscillators and the metal mass as effectively infinite, yield a Ru-H stretching force constant,  $k_{\text{r}}$ , of 21  $\text{N m}^{-1}$ . This is ca. 20% of the values of force constants derived in a similar manner for the  $\mu_2$ -bridged metal hydride cluster complexes discussed in ref. 1, where a typical value of  $k_{\text{r}}$  was 108  $\text{N m}^{-1}$ . The very low value of  $k_{\text{r}}$  in the  $[\text{HRu}_6]$  complex undoubtedly reflects the fact that the H to Ru bonding is equally shared between six metal atoms. It is also consistent with the rather long Ru-H bond which is present in this ion, 2.03 (1) Å,<sup>3</sup> which may be compared with a more usual range of ca. 1.7–1.9 Å for  $\mu_2$ -bridged Ru-H bonds.<sup>5</sup>

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<sup>5</sup> See, for example, A. J. P. Domingos, B. F. G. Johnson, J. Lewis, and G. M. Sheldrick, *J.C.S. Chem. Comm.*, 1973, 912; G. M. Sheldrick and J. P. Yesinowski, *J.C.S. Dalton*, 1975, 873.