Without that correction the derived $2D/k_B$ is too large. Nevertheless, the magnetic ions in this crystal are so far apart that it should come as no surprise that the superexchange interactions are so very weak.

The observed g values are typical of those found with chromium(III). It is not clear what significance, if any, should be attached to the lack of an exchange correction to the fit of the perpendicular-susceptibility data. It was judged not worthwhile to extend the measurement of $\chi_\perp$ to lower temperatures.

In conclusion, the analysis of low-temperature magnetic susceptibility measurements has been shown to be a powerful technique for the precise determination of ground-state zero-field splittings of the magnitude commonly observed in chromium(III) complexes.

Acknowledgment. We thank Professor E. I. Solomon of MIT for generously providing the crystals, as well as for unpublished crystallographic information on this system. This research was supported by the National Science Foundation through Grants DMR-76-18963, DMR 77-13318, and DMR 7906119. We also thank Dr. Andries van der Bilt and Dr. Kyong O. Joung for their assistance in the early stages of this work and Dr. R. P. Hudson for his comments on the manuscript.

Registry No. $[Cr(NH_3)_6](ClO_4)_2Br{\cdot}CsBr$, 74346-15-9.

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Metal–Hydrogen Stretching Frequencies from μ_3-Bridged Metal Hydride Cluster Complexes and Hydrogen Adsorbed on Metal Surfaces

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Received January 17, 1980

Metal–hydrogen stretching frequencies of μ_3-bridging hydrogen ligands have been determined from the infrared spectra of a number of metal hydride cluster complexes. A vibrational model is described which suggests that the ratio of the antisymmetric and symmetric M–H stretching frequencies is related simply to the angular disposition of the three M–H bonds. This model is equally applicable to the study of hydrogen atoms adsorbed on metal surfaces.

Introduction

In recent papers the vibrational frequencies associated with the metal–hydrogen stretching modes of μ_2-bridging[1,2] and interstitial[3] hydrogen ligands in metal cluster complexes have been described. Of the various types of hydrogen ligand environment encountered in metal clusters, that which is least satisfactorily characterized by vibrational spectroscopy, or indeed by any technique, is the μ_3-bridged site. Here we report the infrared absorption frequencies corresponding to the vibrations of μ_3-bridging hydride ligands in a number of metal hydride cluster complexes, and a vibrational model is developed which leads to a simple relationship between the M–H stretching frequencies and the M_3H geometry.

Few hydrogen ligands in μ_3-bridged sites have been directly located by diffraction techniques. Of the complexes considered here only for $H_4Co_4(\pi\text{-}C_5H_5)_4$ have hydrogen positions been determined; the hydride ligands have been located by X-ray diffraction ca. 0.8 Å above the centers of the four Co_3 faces.[4] Although some early controversy surrounded their structures, it now seems likely that a similar hydrogen environment exists in the mixed-metal clusters $HMCo_3(CO)_{12}$ (M = Fe, Ru, and Os), by analogy with the structure of the phosphite derivative $HFeCo_3(CO)_9(P(OCH_3)_3)_3$, where the hydrogen ligand has been shown by the more accurate neutron diffraction study to be situated ca. 0.98 Å above the center of the Co_3 triangle.[5-8] Evidence for μ_3-bridged environments in the other complexes is less direct and derives from observations of enlarged M_3 faces and "swept-back" carbonyl ligands.[9,10]

Theory of the Vibrational Model

The three vibrational modes of a μ_3-bridging hydrogen ligand in a pyramidal C_{3v} environment comprise a nondegenerate symmetric M–H stretching mode, $\nu_{MH}{}^{sym}$, and a doubly degenerate antisymmetric M–H stretching mode, $\nu_{MH}{}^{asym}$. In the extreme case of the hydrogen atom lying in the plane of the three metal atoms, D_{3h} symmetry, the vibrations would become a nondegenerate out-of-plane deformation and a doubly degenerate M–H stretching mode. The observed vibrational frequencies are thus expected to be somewhat sensitive to the separation of the hydrogen ligand from the plane of the metal atoms. If we take the standard vibration equations for a pyramidal M_3H molecule (see, for example, ref 11a) using a central force field, and introduce the approximation that the M–M stretching frequencies are very much lower than the M–H stretching frequencies, we obtain expressions 1 and 2 for the two M–H stretching frequencies

$$\nu_{MH}{}^{sym} = [(1 + 3m_M \cos^2 \beta/m_H)(k_r/m_M)]^{1/2}/2\pi c \qquad (1)$$

$$\nu_{MH}{}^{asym} = [(1 + 3m_M \sin^2 \beta/2m_H)(k_r/m_M)]^{1/2}/2\pi c \qquad (2)$$

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Table I. Metal-Hydrogen Stretching Frequencies (cm^{-1}) of Some μ_3-Bridging Hydride Ligands[a]

complex	$\nu_{MH}{}^{sym}$	$\nu_{MD}{}^{sym}$	$\nu_{MH}{}^{sym}/\nu_{MD}{}^{sym}$	$\nu_{MH}{}^{asym}$	$\nu_{MD}{}^{asym}$	$\nu_{MH}{}^{asym}/\nu_{MD}{}^{asym}$	T, K	ref
$H_2Ru_6(CO)_{18}$	708 m	(620)[b] w	(1.14)[b]	660, 652 s	462, 454 s	1.43	95	*d*
$[HOs_6(CO)_{18}]^-$ [c]	1020 w ?	690 w	1.52	1255 s	905 s	1.38	95	*d*
$H_4Co_4(\pi\text{-}C_5H_5)_4$	958 s	694 s	1.36	1050 m	772 sh	1.36	95	*d*
	950			1052			300	13
$HFeCo_3(CO)_{12}$	1118	817	1.37				300	16
$HRuCo_3(CO)_{12}$	1121	805	1.39				300	16
$HOsCo_3(CO)_{12}$	1109	809	1.37				300	16
Pt(111)	550	400	1.37	1230	900	1.37	90	19
W(110)	767							21

[a] Abbreviations: s = strong; m = medium; w = weak; sh = shoulder. [b] See discussion in the text. [c] $[n\text{-}Bu_4N]^+$ salt. [d] This work.

quencies (in wavenumbers), where β is the acute angle between the M-H bonds and the threefold axis, k_r is the M-H bond stretching force constant, c is the speed of light, and m_M and m_H are the masses of the metal and hydrogen atoms, respectively. On the further assumption that $m_M \gg m_H$, so that the angle-dependent terms of (1) and (2) are considerably greater than unity, the ratio of the two frequencies is given by relationship (3). This simple relationship is comparable

$$\nu_{MH}{}^{asym}/\nu_{MH}{}^{sym} = (\tan \beta)/2^{1/2} \tag{3}$$

with the relationship derived previously to describe μ_2-bridging metal-hydrogen stretching frequencies.[1]

It is pertinent to enquire as to what this model would predict in the event that the hydrogen ligand lies close to the plane of the three metal atoms, that is the environment approaches a planar, D_{3h} configuration. In this event $\beta \rightarrow 90°$ and an infinite $\nu_{MH}{}^{asym}/\nu_{MH}{}^{sym}$ ratio is obtained at this angle. If we consider the extreme case of a regular D_{3h} environment, the hydrogenic modes now comprise a doubly degenerate, antisymmetric stretch (symmetry e′) and an out-of-plane deformation (symmetry a_2''). A simple valence force field may then be defined where, making the approximations that $m_M \gg m_H$ and that $k_r \gg k_\delta$,[11b] where k_δ is the in-plane angle deformation force constant, we write

$$\nu_{MH}{}^{asym} = [3k_r/8\pi^2c^2m_H]^{1/2} \tag{4}$$

$$\nu_{MH}{}^{sym} = [3k_\Delta/4\pi^2c^2m_H]^{1/2} \tag{5}$$

where k_Δ is the angle bending force constant for the out-of-plane motion. One then obtains the limiting ratio

$$\nu_{MH}{}^{asym}/\nu_{MH}{}^{sym} = [k_r/2k_\Delta]^{1/2} \tag{6}$$

Experimental Section

The complexes $H_2Ru_6(CO)_{18}$,[9] $[n\text{-}Bu_4N][HOs_6(CO)_{18}]$[12] and $H_4Co_4(\pi\text{-}C_5H_5)_4$[13] and their deuterated analogues were prepared by reported methods. Infrared spectra of the complexes were measured as KBr disks, at 300 and 95 K, using Perkin-Elmer 325 and Digilab FTS-14 spectrophotometers. Assigned vibrational frequencies of $\nu_{MH}{}^{asym}$ and $\nu_{MH}{}^{sym}$ in the complexes studied, together with previous data, are given in Table I. Peak absorption intensities arising from these modes were found to be temperature-dependent, peak heights increasing upon cooling as previously found for other nonterminal hydride ligands.[1,3] This behavior, shown for the case of $H_4Co_4(\pi\text{-}C_5H_5)_4$ in Figure 1, provides an important experimental criterion for identifying metal-hydrogen stretching modes. The absorption frequencies appeared to be almost independent of temperature.

Results and Discussion

The 600-1200-cm^{-1} region of the infrared spectra of $H_4Co_4(\pi\text{-}C_5H_5)_4$ and $D_4Co_4(\pi\text{-}C_5H_5)_4$, at 95 K, is shown in Figure 2. The behavior of the more intense Co-H stretching mode on deuteration is plainly seen. The position of the weaker absorption in the spectrum of the deuterated species is less obvious; this absorption is tentatively ascribed to a shoulder, at 772 cm^{-1}, on the intense band near 800 cm^{-1}. The spectrum

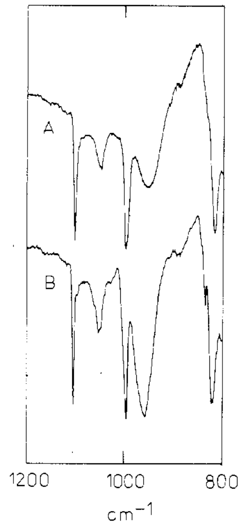

Figure 1. Infrared spectra of $H_4Co_4(\pi\text{-}C_5H_5)_4$ measured at 300 K (A) and 95 K (B).

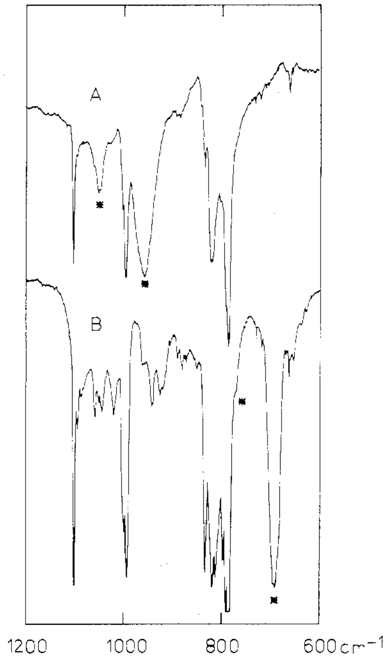

Figure 2. Infrared spectra of $H_4Co_4(\pi\text{-}C_5H_5)_4$ (A) and $D_4Co_4(\pi\text{-}C_5H_5)_4$ (B), at 95 K. Absorptions marked with an asterisk are assigned to hydrogenic modes. The spectrum of $D_4Co_4(\pi\text{-}C_5H_5)_4$ was obtained with a considerably greater amount of sample than was the case for $H_4Co_4(\pi\text{-}C_5H_5)_4$.

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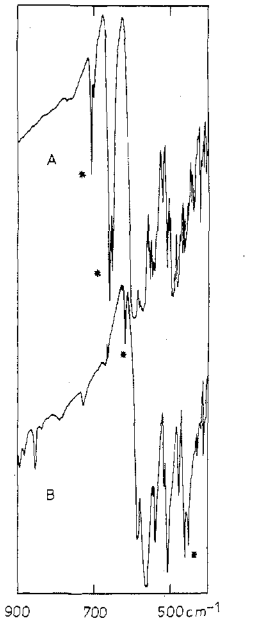

Figure 3. Infrared spectra of $H_2Ru_6(CO)_{18}$ (A) and $D_2Ru_6(CO)_{18}$ (B), at 95 K. Weak bands arising from a small proportion of $[(Ph_3P)_2N][DRu_6(CO)_{18}]$ impurity are present in the 700–900-cm^{-1} region of the spectrum of the deuterated complex. Asterisks: hydrogenic modes.

of $D_4Co_4(\pi\text{-}C_5H_5)_4$, in addition to showing the changes caused by the isotopic shifts of the M–H stretching modes, displays multiple absorptions which presumably arise from the $HD_3Co_4(\pi\text{-}C_5H_5)_4$ isotopic impurity. The four hydrido ligands are crystallographically inequivalent, and this seems to be reflected in the complexity of the weak absorptions near 1050 and 950 cm^{-1}.

The most straightforward assignment of the observed infrared absorptions to the symmetric and antisymmetric M–H stretching modes occurs in the case of $H_2Ru_6(CO)_{18}$. The infrared spectra of $H_2Ru_6(CO)_{18}$ and $D_2Ru_6(CO)_{18}$, in the region 400–900 cm^{-1}, are shown in Figure 3. The most obvious effect of deuteration is to shift to lower frequency the two absorptions which occur near 710 and 650 cm^{-1} in the spectrum of the H complex. In the $H_2Ru_6(CO)_{18}$ crystal the Ru_6 cluster occupies a site of C_i symmetry, and geometric considerations suggest that two opposite Ru_3 faces are bridged by hydrogen ligands.[9,14] Group theory would thus predict a single IR-active component of $\nu_{RuH}{}^{sym}$ and two IR-active components of $\nu_{RuH}{}^{asym}$. This prediction leads us to assign (Figure 2) the single band near 710 cm^{-1} to $\nu_{RuH}{}^{sym}$ and the doublet near 650 cm^{-1} to $\nu_{RuH}{}^{asym}$. The corresponding modes in the spectrum of $D_2Ru_6(CO)_{18}$ are less readily assigned. One plausible interpretation places $\nu_{RuD}{}^{sym}$ at 620 cm^{-1} and a doublet arising from $\nu_{RuD}{}^{asym}$ near 450 cm^{-1}. The isotopic ratio for the antisymmetric modes would then be 1.43, close to the expected value of ca. $2^{1/2}$. The isotope ratio $\nu_{RuH}{}^{sym}/\nu_{RuD}{}^{sym}$ under this assignment would be 1.14, considerably less than the expected value, and this would imply that considerable coupling exists between the symmetric mode and the Ru–CO deformation modes of the same symmetry which occur just below 600 cm^{-1}. That coupling of this type does, in fact, exist is supported by the rather extensive changes which are apparent in the 500–600-cm^{-1} region upon deuteration. Mechanical coupling between the lower frequency carbonyl modes and the metal–hydrogen stretching modes is not too surprising in view of the distortion of the carbonyl coordination geometry caused by the presence of the hydrogen ligand in the μ_3-bridged site.[9a] An alternative assignment of $\nu_{RuD}{}^{sym}$, which gives an isotope ratio closer to the expected value, is to the sharp, intense band near 500 cm^{-1} in the spectrum of $D_2Ru_6(CO)_{18}$.

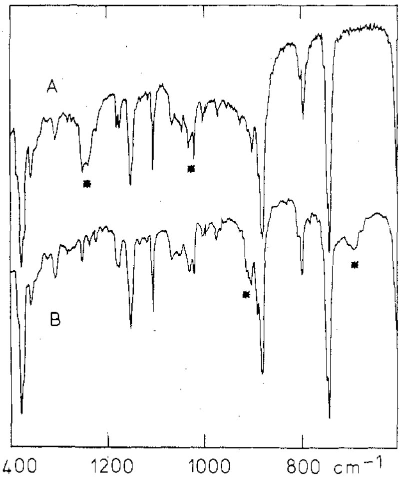

Figure 4. Infrared spectra of $[n\text{-}Bu_4N][HOs_6(CO)_{18}]$ (A) and $[n\text{-}Bu_4N][DOs_6(CO)_{18}]$ (B), at 95 K. Asterisks: hydrogenic modes.

Identification of the hydrogenic modes in the spectra of $[n\text{-}Bu_4N][HOs_6(CO)_{18}]$ and $[n\text{-}Bu_4N][DOs_6(CO)_{18}]$ is complicated by the absorptions of the cation, Figure 4; however, one such mode may be seen to shift from near 1250 cm^{-1} to near 900 cm^{-1} upon deuteration. A weaker isotope-sensitive absorption appears to shift on deuteration from among a group of cation absorptions at 1020 cm^{-1} to ca. 690 cm^{-1}.

Inspection of the general range of isotope ratios in Table I shows that in the complexes other than $H_2Ru_6(CO)_{18}$ these are much as expected. In these cases a greater frequency separation exists betwen the M–H stretching modes and the low-frequency carbonyl modes than is the case for the unusually low frequency of the former in the ruthenium cluster.

In the spectra of those complexes where no splitting of the $\nu_{MH}{}^{asym}$ absorption may be seen and used as a clue to assignment, we may use eq 3 as a guide to the correct assignment of the metal–hydrogen stretching modes. This approach is instructive in the case of $HMCo_3(CO)_{12}$ (M = Fe, Ru, and Os) where a single M–H stretching absorption has been observed for each complex.[15,16] If we assume that the site occupied by the hydrogen atom in these complexes is unaffected by the introduction of phosphite ligands, as in $HFeCo_3(CO)_9(P(OCH_3)_3)_3$, the angle β between the Co–H bonds and the threefold axis is estimated to be 55.7°. By use of eq 3 the predicted frequency ratio $\nu_{MH}{}^{asym}/\nu_{MH}{}^{sym}$ is 1.036, and we conclude that the single, asymmetric absorption observed in the spectrum of each of these complexes probably represents a near coincidence between the symmetric and antisymmetric Co–H stretching modes. Use of eq 3 is less conclusive in the case of $H_4Co_4(\pi\text{-}C_5H_5)_4$ where again the closeness of the frequency ratio to unity, 1.096, means that physically reasonable Co–H distances are obtained with either possible assignment; the crystallographically determined hydrogen positions in this case must be used with caution since they were found by using X-ray diffraction and almost certainly represent shorter Co–H bonds than actually occur.[17] Assignment of the higher frequency absorption to $\nu_{CoH}{}^{asym}$ leads to a calculated Co–H distance of 1.69 Å and a separation of the hydrogen atom from the Co_3 plane, $r(Co_3\cdots H)$, of 0.92 Å, compared with

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(14) The site symmetry of the Ru_6 cluster was stated incorrectly in ref 9a as C_1.

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(17) The X-ray[6] and neutron[7] diffraction structure determinations of $HFeCo_3(CO)_9(P(OCH_3)_3)_3$ placed the hydrogen ligand 0.75 Å and 0.98 Å from the plane of the cobalt atoms, respectively.

Table II. Estimated Structural Parameters for Hydrogen in μ_3-Bridging Sites

complex	$\nu_{MH}^{asym}/\nu_{MH}^{sym}$	β_{obsd}, deg	β_{theor}, deg	$\bar{r}$(M-M),[a] Å	r(M-H),[b] Å	$r(M_3\cdots H)$,[b,c] Å
$H_2Ru_6(CO)_{18}$	0.926		52.6	2.954[d]	2.15	1.30
$[HOs_6(CO)_{18}]^-$	1.195		59.4	2.973[e]	1.99	1.01
$H_4Co_4(\pi\text{-}C_5H_5)_4$	1.096	60.7	57.2	2.467[f]	1.69	0.92
$HFeCo_3(CO)_{12}$	~1	55.7[g]	~54.7	2.488[g]	~1.76	~1.01
$HRuCo_3(CO)_{12}$	~1	55.7[g]	~54.7	2.488[g]	~1.76	~1.01
$HOsCo_3(CO)_{12}$	~1	55.7[g]	~54.7	2.488[g]	~1.76	~1.01
Pt(111)	2.236		72.4	2.79[h]	1.69	0.51

[a] Mean metal-metal bond length. [b] Calculated assuming C_{3v} symmetry. [c] $r(M_3\cdots H)$ represents the separation of the hydrogen ligand from the plane of the three metal atoms. [d] Reference 9a. [e] Reference 10. [f] Reference 4. [g] Reference 7, see text. [h] Reference 19.

1.80 and 1.10 Å, respectively, for the reverse assignment. The former assignment is thus somewhat preferred on the basis of the $r(Co_3\cdots H)$ value in the phosphite complex.[7,17] For the $[HOs_6(CO)_{18}]^-$ ion reasonable Os–H distances are obtained only when the antisymmetric Os–H stretching mode is assigned to the higher frequency absorption.

The present data are inadequate for a general statement to be made regarding the relative intensities of the symmetric and antisymmetric metal–hydrogen stretching modes in the infrared spectra of μ_3-bridged hydride complexes. In the case of μ_2-bridged hydride clusters it has been found that the antisymmetric mode gives rise to the more intense absorption in the infrared spectrum,[1,2] but our assignment of ν_{MH}^{asym} to the weaker absorption in the spectrum of $H_4Co_4(\pi\text{-}C_5H_5)_4$ suggests that this may not be a reliable criterion for assignment in μ_3-bridged systems.

The existence of μ_3-bridging hydrogen atoms chemisorbed on metal surfaces has been suggested.[18-20] Theoretical studies have suggested that hydrogen atoms adsorbed on the Pd(111) face occupy threefold bridging sites[18] and a similar situation on the Pt(111) face has been deduced from electron-energy-loss spectroscopy, where frequencies of 1230 and 550 cm^{-1} were determined for ν_{MH}^{asym} and ν_{MH}^{sym} respectively. In the latter study an angle β of 65.9° was estimated by using a simple vibrational model, but the expression used for the frequency ratio would appear to be in error. An angle of 72.4° is derived by the use of eq 3. This revised value of β leads to a calculated Pt–H bond length of 1.69 Å compared with the original estimate of 1.76 Å. A third example of triply bridging hydrogen atoms on metal surfaces has been suggested to occur on the W(110) face[20] for which a W–H symmetric stretching frequency of 767 cm^{-1} has been measured by electron-energy-loss spectroscopy.[21] The metal surface selection rule applicable to electron-energy-loss spectroscopy identifies the symmetric metal-hydrogen stretching mode as giving rise to the stronger band in cases of this type.

Structural parameters of the various μ_3-bridged sites considered here, obtained from eq 3 and the mean observed M–M bond lengths, are shown in Table II. The two extreme situations would appear to be $H_2Ru_6(CO)_{18}$, where the hydrogen atom is calculated to reside a rather large distance out of the plane of the ruthenium triangle, and hydrogen adsorbed on Pt(111), where the hydrogen atom is very close to the metal surface. The latter conclusion is entirely reasonable on steric grounds—that is, the "naked" metal surface contains no ligands which might provide an electrostatic or steric barrier to the close approach of the hydrogen atom to the plane of the metal atoms. A manifestation of such a barrier in metal cluster complexes is provided by the distortion of carbonyl ligand geometry which usually results from the presence of a μ_3-bridging hydrogen ligand.

Acknowledgment. We thank the S.R.C. for financial support and Professor S. F. A. Kettle for helpful discussions.

Registry No. $H_2Ru_6(CO)_{18}$, 12568-51-3; $[n\text{-}Bu_4N][HOs_6(CO)_{18}]$, 74096-97-2; $H_4Co_4(\pi\text{-}C_5H_5)_4$, 51831-76-6; $D_4Co_4(\pi\text{-}C_5H_5)_4$, 74113-02-3; $D_2Ru_6(CO)_{18}$, 74185-23-2; $[n\text{-}Bu_4N][DOs_6(CO)_{18}]$, 74113-04-5; $HFeCo_3(CO)_{12}$, 21750-96-9; $HRuCo_3(CO)_{12}$, 24013-40-9; $HOsCo_3(CO)_{12}$, 12560-42-8; Pt, 7440-06-4.

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