Correspondence

Origin of the Structure in M–H–M Vibrational Modes of $HW_2(CO)_{10}^-$

Sir:

As with hydrogen-bonded compounds, it can be expected that vibrational studies of hydride-bridged metal complexes will be very informative on questions of structure, bonding, and dynamics. Analyses of band shapes, isotope shifts, and fine structure have been particularly rewarding for the hydrogen-bonded systems. Kaesz and co-workers have noted that room-temperature Raman spectra of some polymetallic hydride-bridged complexes usually exhibit broad features in the 900 ± 200 cm^{-1} region that can be assigned to the M–H–M array. They also note a correlation between the frequency of this broad feature and the M–H–M angle.[1] Fermi resonance was postulated as a possible source of the extreme broadening. More recently Cooper, Onaka, and Shriver reported low-temperature infrared and Raman spectra for a series of hydride-bridged compounds of the type $HM_2(CO)_{10}^-$, where M = Cr, Mo, and W.[2] They observed well-resolved features in the 900 ± 200 cm^{-1} region of the low-temperature Raman spectra, and in an interpretation similar to that of Kaesz, it was noted that Fermi resonance with the M–C stretches and M–C–O overtones might account for the observed structure. In the Fermi resonance mechanism, overtones and/or combination bands, which usually are weak, gain intensity by mixing with a fundamental.[3] This interaction may occur when the frequency of a combination or overtone falls near the frequency of a fundamental transition. In this paper we present isotopic data to test the postulate that Fermi resonance produces the structure around 900 cm^{-1} for $HW_2(CO)_{10}^-$.

Results and Discussion. To a first approximation, the vibrations associated with the M–H–M array in hydride-bridged transition-metal complexes may be explained on the basis of a triatomic model.[2] For the M–H–M angle of 137° characteristic of $[Et_4N][HW_2(CO)_{10}]$,[4] the ν_1 M–H–M mode, which primarily involves displacement of the metal atoms, is expected in the low-frequency region. A symmetric in-plane mode ν_2 (which may be described as either a symmetric M–H stretch or an M–H–M deformation) and possibly an out-of-plane mode occur around 900 cm^{-1}, and a high-frequency mode, the asymmetric stretch, occurs around 1700 cm^{-1}.[2] The asymmetric stretch for $[Et_4N][HW_2(CO)_{10}]$ occurs at 1683 cm^{-1} in the low-temperature infrared spectrum,[2] but as shown in Figure 1 four M–H–M features, rather than the expected one or two, are observed in the 900 cm^{-1} region. Of the several possible origins for these extra bands, Fermi resonance between ν_2 and the overtone or combination involving the M–C stretch or M–C–O deformation was an appealing explanation,[2] but this idea is ruled out by the ^{18}O experiments described here.

The substitution of ^{18}O for ^{16}O shifts the frequencies of the M–C stretch and M–C–O deformation fundamentals by 5–14 cm^{-1} (Table I, Figures 1 and 2). Thus, a shift of 10–28 cm^{-1} is expected for the overtone or combination involving these bands. A shift of this magnitude would be expected to significantly change features arising from Fermi resonance. As illustrated in the figures, however, the appearance of the ^{18}O and ^{16}O spectra in the M–H–M deformation region are nearly identical, and, as shown in Table I, the frequencies do not change significantly. On this basis, Fermi resonance between ν_2 and an overtone or combination of the M–C stretch or the M–C–O deformation can be discounted as the origin of the "extra" bands assigned to the W–H(D)–W deformation for $HW_2(CO)_{10}^-$. The generalization of this interpretation to the similar $HCr_2(CO)_{10}^-$ and $HMo_2(CO)_{10}^-$ ions also is reasonable. The systems studied by Kaesz and co-workers, which are mainly polynuclear rhenium hydrides with highly bent M–H–M arrays, are quite different from $HW_2(CO)_{10}^-$, so the possibility exists that the breadth and apparent structure observed by them in the ca. 950 cm^{-1} region may arise from Fermi resonance. The combination of low-temperature spectroscopy and isotopic substitution which have been applied here may be useful for checking other systems.

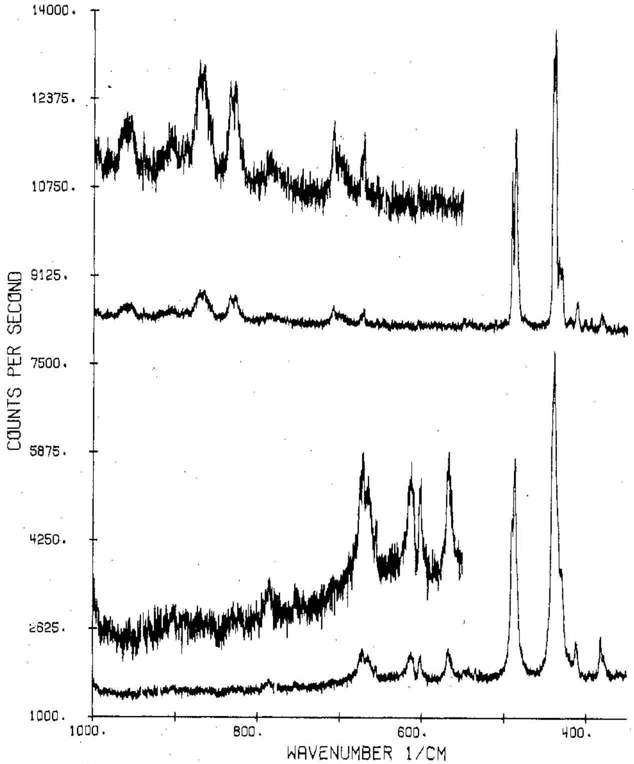

Figure 1. Low-temperature Raman spectra of naturally abundant $[Et_4N][HW_2(CO)_{10}]$ (upper two curves) and the heavy-hydrogen counterpart $[Et_4N][DW_2(CO)_{10}]$ (lower two curves).

Table I. Low-Temperature Raman Frequencies, cm^{-1}

compd	W–H(D)	WCO and W–C
$[Et_4N][HW_2(C^{NA}O)_{10}]$	960, 869, 832, 702	491, 486, 440, 434, 430
$[Et_4N][HW_2(C^{18}O)_{10}]$	958, 866, 827, 699	485, 470, 430, 425, 417
$[Et_4N][DW_2(C^{NA}O)_{10}]$	666, 612, 602, 568	490, 486, 440, 430
$[Et_4N][DW_2(C^{18}O)_{10}]$	660, 610, 597, 565	485, 472, 430, 425, 415

Now that Fermi resonance has been ruled out as an explanation of the structure for the ca. 900 cm^{-1} band system of $HW_2(CO)_{10}^-$, other alternatives, such as multiple-well potential minima and factor group coupling, bear investigation. The idea of multiple minima is attractive because diffraction results for many of the $HM_2(CO)_{10}^-$ compounds show that the hydride ligand is disordered over two or more positions.[4-7]

Experimental Section. Syntheses were carried out with rigorous air-free techniques. Tungsten hexacarbonyl, Et_4NBr, $NaBH_4$, and $NaBD_4$ were obtained from Strem Chemicals, Aldrich, Sigma Chemicals, and Alfa-Ventron, respectively,

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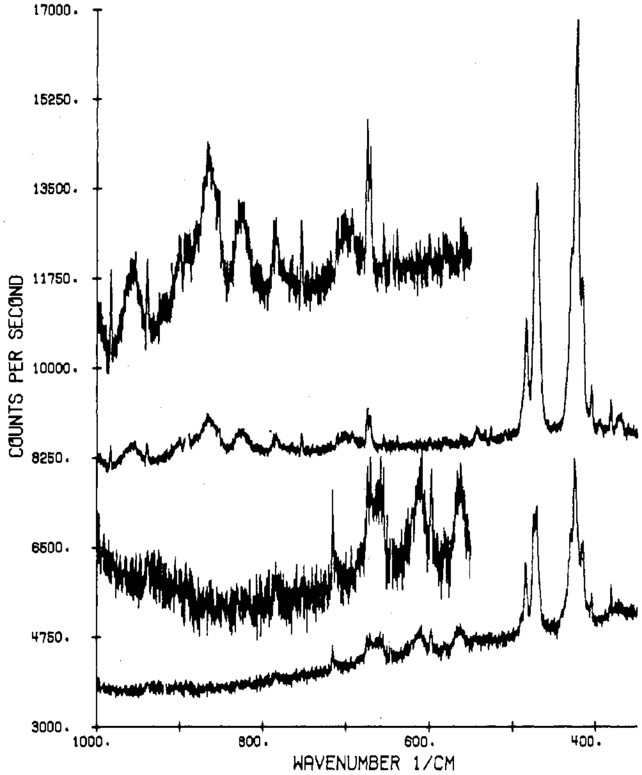

Figure 2. Low-temperature Raman spectra of oxygen-18-containing $[Et_4N][HW_2(CO)_{10}]$ (upper two curves) and $[Et_4N][DW_2(CO)_{10}]$ (lower two curves).

and used as obtained. The isotopic $W(C^{18}O)_6$ was prepared by oxygen-exchange techniques.[8] $[Et_4N][H$(and D)$W_2(CO)_{10}]$ were synthesized by a slightly modified version of Hayter's procedure.[9] The compounds were recrystallized once, and the purity was checked by infrared and Raman spectra.

The Raman spectrometer was a Spex 1401. Raman samples were cooled in an Air Products Displex unit, and spectra were recorded either on pressed pellets attached to the cold finger with a thin layer of Apiezon N grease or on samples deposited on the cold finger from a THF solution. Either the 676.4-nm Kr-ion laser line or the 514.5-nm Ar-ion laser line was used to irradiate the samples, with 10-mW maximum power at the sample. The temperature was measured just above the sample block, but the actual temperature in the region being irradiated is considerably above the measured temperature. For example, in one run a temperature of 80 K was calculated from the Stokes and anti-Stokes Raman spectra for the pellet in contact with the cold finger cooled to 10 K.

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Registry No. $[Et_4N][HW_2(CO)_{10}]$, 12083-01-1; $[Et_4N][HW_2(C^{18}O)_{10}]$, 69551-87-7; $[Et_4N][DW_2(CO)_{10}]$, 55971-52-3; $[Et_4N][DW_2(C^{18}O)_{10}]$, 69551-89-9.

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Comments on the Description of Dioxygen Bound End-On to Transition Metals

Sir:

Considerable discussion has occurred regarding the nature of the binding of dioxygen to first-row transition-metal complexes.[1-6] Unrecognized difficulties in interpreting infrared results have led to the rejection of our position[2] on the nature of the bound dioxygen. Attempts to translate our arguments into an oxidation state description have led to a misquoting of our position. In this communication, we clarify these problems.

Our interest in the binding of dioxygen to cobalt(II) complexes began with the interpretation of their EPR spectra. The original interpretations[7] were based on a Fermi contact analysis, and the cobalt hyperfine splitting was rationalized in terms of direct delocalization of the unpaired electron on the metal. On the basis of the information available at the time, this was a viable rationalization of the spectral results. In our first publication[8] on this subject, we stated that the data did not conclusively prove an essentially ionic $Co(III)-O_2^-$ formulation but could be rationalized equally well with a Fermi contact interpretation by utilizing a coordinated singlet O_2 formulation. Since neither interpretation was conclusive nor able to explain all of the spectral results, information regarding ^{17}O anisotropic hyperfine coupling parameters was considered essential. In the course of making preparations to carry out this experiment, a publication appeared in which the key results were presented[9] but not properly interpreted. We concluded from the results[2b] that the cobalt hyperfine coupling must be arising via an indirect mechanism and could not be attributed to the unpaired electron being delocalized on cobalt.[10] The earlier interpretations[7,8] of the EPR spectra based on direct delocalization of the electron cannot be correct, for the summation of the cobalt and ^{17}O anisotropic hyperfine coupling parameters would suggest more than one unpaired electron in a system which contains only one unpaired electron. A new interpretation of the EPR results was offered and a spin-pairing model[2b] was employed to describe the interaction of the metal center with O_2. This spin-pairing model is an extension, which accommodates a wide range of electron transfer into O_2, of the molecular orbital description of these adducts proposed by Wayland et al.[11] Contrary to earlier interpretations, the spin-pairing model and our EPR interpretation[2b] lead to the conclusion that regardless of whether the charge on the bound O_2 were slightly positive, neutral, or negative, the unpaired