Spectroscopic Investigation of $W_2(CO)_{10}{}^{2-}$ and $HW_2(CO)_{10}{}^{-}$

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Abstract: A moderately intense band at 1680 cm^{-1} in the infrared spectrum of $[Et_4N][HW_2(CO)_{10}]$, observed prominently only at low temperature (93 K), is attributed to metal-hydrogen-metal asymmetric stretching. This band is absent in the ir spectrum of $[Et_4N][DW_2(CO)_{10}]$. Intense bands attributable to symmetric W-W and W-H-W stretching are observed at 109 and 101 cm^{-1} in the Raman spectra of $[Et_4N]_2[W_2(CO)_{10}]$ and $[Et_4N][HW_2(CO)_{10}]$, respectively. The $d\sigma W_2 \rightarrow d\sigma^* W_2$ electronic transition of $W_2(CO)_{10}{}^{2-}$ is assigned to an intense absorption band observed in solution at 28.5 kK. This band is not present in the solution electronic absorption spectrum of $HW_2(CO)_{10}{}^{-}$. Weaker peaks, at 26.8 and 30.3 kK, are tentatively assigned to $d\pi \rightarrow 2\sigma$ and $d\pi \rightarrow d_{x^2-y^2}$ transitions, respectively.

The nature of the metal-hydrogen-metal bond has attracted much attention.[1-8] The field has been stimulated recently by structural studies of complexes containing W-H-W units. Particularly interesting is the discovery that the W-H-W linkage is linear in $[Et_4N][HW_2(CO)_{10}]$,[7] whereas it is bent in $[(Ph_3P)_2N][HW_2(CO)_{10}]$.[7,8] Apparently, W-H-W deformation in $HW_2(CO)_{10}{}^{-}$ requires very little energy.

We have undertaken a comparative study of the vibrational and electronic spectroscopic properties of $HW_2(CO)_{10}{}^{-}$ and $W_2(CO)_{10}{}^{2-}$, in an effort to elucidate the bonding in the W-H-W bridging unit. In this paper we report the infrared and Raman spectra of solid samples of $[Et_4N][HW_2(CO)_{10}]$, $[Et_4N][DW_2(CO)_{10}]$, and $[Et_4N]_2[W_2(CO)_{10}]$, as well as solution electronic spectra of $HW_2(CO)_{10}{}^{-}$ and $W_2(CO)_{10}{}^{2-}$.

Experimental Section

General. Starting materials were of reagent grade or better. All reactions were carried out under an atmosphere of nitrogen. Solids were stored under N_2 at −20° in the dark. When slight water content was of no harm, solvents were deoxygenated by bubbling N_2 through or by several freeze-thaw cycles on a vacuum line. Otherwise, solvents were distilled from the following drying agents under N_2: ether and tetrahydrofuran-$LiAlH_4$; ethanol-$Mg(OEt)_2$ or CaH_2; isopropyl alcohol-CaH_2; dichloromethane and acetone-Linde 4A molecular sieves; benzene-Na/benzophenone; hydrocarbons-Na.

$[Et_4N][HW_2(CO)_{10}]$ and $[Et_4N][DW_2(CO)_{10}]$. These compounds were prepared by a slight modification of the procedure given by Hayter[4] using two times as much $NaBH_4$ in order that reaction with $W(CO)_6$ would be complete in 1-2 days. The compound $[Et_4N][DW_2(CO)_{10}]$ was synthesized using $NaBD_4$ in ordinary undeuterated solvents. Crystals of the protio and deuterio compounds are yellow and light orange, respectively, although visible spectra in ethanol solution are identical: Raman spectra $[Et_4N][HW_2(CO)_{10}]$ (solid, 70-2880 cm^{-1}) 101 (48), 380 (6), 415 sh (7), 436 (81), 487 (40), 672 (5), 1115 (4), 1296 (6), 1458 (8), 1851 (19), 1891 (3), 1963 (52), 2069 (18) (numbers in parentheses are relative intensities; sh = shoulder); $[Et_4N][DW_2(CO)_{10}]$ (solid, 70-2170 cm^{-1}) 101 (50), 378 (3), 436 (62), 486 (32), 1852 (12), 1963 (32), 2068 (12). Integration of the cation and hydride[9] ^{1}H NMR signals showed that our sample of $[Et_4N][DW_2(CO)_{10}]$ contained 80 ± 10% deuterium.

$[(Ph_3P)_2N]_2[W_2(CO)_{10}]\cdot CH_2Cl_2$. A mixture containing 2.5 g (7.1 mmol) of $W(CO)_6$, 70 ml of THF, and 10 ml of sodium amalgam (1 g of Na (40 mmol)/10 ml of Hg) was stirred and irradiated with a 130-W, 366-nm uv lamp for 60 hr until no further change occurred in the carbonyl stretching region of the ir spectrum. The red liquid was removed and centrifuged and the supernatant was transferred to a fresh flask. The flask was left overnight at −78° to deposit dirty yellow crystals of $Na_2W_2(CO)_{10}$, which were washed with ether and dried in vacuo. $Na_2W_2(CO)_{10}$ (0.785 g, 1.13 mmol) was dissolved in 7 ml of acetone and centrifuged to remove a small amount of insoluble residue. The liquid phase was added to a well-stirred solution of 1.30 g (2.26 mmol) of $[(Ph_3P)_2N]Cl$[10] in 10 ml of dichloromethane. The red mixture was centrifuged to remove NaCl and added to 25 ml of well-stirred ether to precipitate yellow product (1.36 g or 70% based on $Na_2W_2(CO)_{10}$). This crude product was washed three times with 15-ml portions of isopropyl alcohol to remove $[(Ph_3P)_2N]Cl$ and crystallized from 4 ml of dichloromethane-1.5 ml of ether at 0° overnight. (Addition of the ether initiates crystallization at room temperature immediately.) The yellow prisms were washed with ether and dried in vacuo. Anal. Calcd for $C_{83}H_{62}P_4N_2W_2O_{10}Cl_2$: C, 55.08; H, 3.45; P, 6.85; W, 20.32; Cl, 3.92. Found: C, 54.71; H, 3.50; P, 7.04; W, 20.05; Cl, 3.69.

$[Et_4N]_2[W_2(CO)_{10}]$. This compound was prepared as described by Hayter.[4] Raman spectrum (solid, 90-600 and 1750-2150 cm^{-1}) 109 (54), 199 (2), 399 (35), 421 (18), 451 (84), 494 (14), 536 (4), 593 (22), 1790 (9), 1839 (3), 1876 sh (6), 1894 (16), 2020 (8).

Measurements. Infrared spectra were obtained with a Perkin-Elmer 225 spectrometer. Low-temperature ir spectra were measured using a modified Beckman RIIC VLT-2 unit. Electronic spectra were recorded on a Cary 17 instrument equipped with a quartz dewar for low-temperature measurements. For Raman spectra, a Cary 81 instrument fitted with a 6328 Å He-Ne laser was employed.

Results and Discussion

Vibrational Spectra. The ir spectrum of $[Et_4N][HW_2(CO)_{10}]$ at low temperature (93 K) exhibits a reasonably sharp, medium intensity band at 1680 cm^{-1} (Figure 1). As this peak is absent in the low-temperature spectra of the tetraethylammonium salts of $DW_2(CO)_{10}{}^{-}$ and $W_2(CO)_{10}{}^{2-}$, it is reasonable to attribute it to the asymmetric W-H-W stretch, which involves significant motion of the hydrogen atom.[11,12] No corresponding, isotopically shifted band could be found in the spectrum of the deuterio compound, even at low temperature. We assign an intense band at 109 cm^{-1} in the Raman spectrum of $W_2(CO)_{10}{}^{2-}$ (Figure 2) to the W-W stretching mode. Intense bands at 101 cm^{-1} in the spectra of both $HW_2(CO)_{10}{}^{-}$ and $DW_2(CO)_{10}{}^{-}$ (Figure 2) are assigned to the symmetric W-H(D)-W stretching mode, which rigorously involves no hydrogen (or deuterium) motion in a D_{4h} structure. Thus, our Raman data accord well with the crystal structure determined for $[Et_4N][HW_2(CO)_{10}]$.[7]

Extensive experimental studies of the asymmetric stretching bands in a variety of complexes containing triatomic bridging units (MXM) have shown red shifts and intensity enhancements with decreasing temperature in all

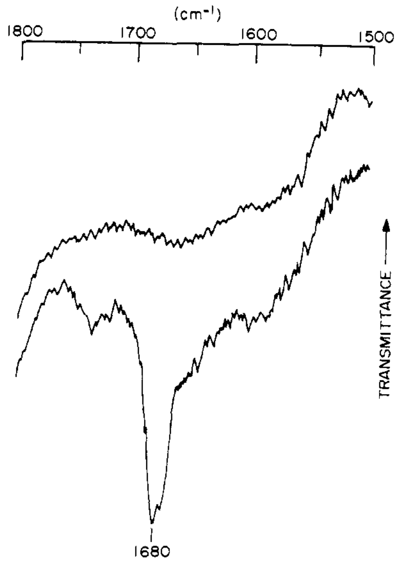

Figure 1. KBr pellet infrared spectra of $[Et_4N][HW_2(CO)_{10}]$: upper curve, 300 K; lower curve, 93 K.

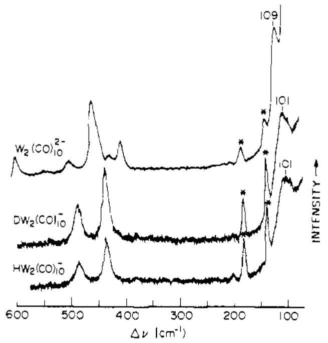

Figure 2. Raman spectra of solid samples of the tetraethylammonium salts of $W_2(CO)_{10}^{2-}$, $HW_2(CO)_{10}^{-}$, and $DW_2(CO)_{10}^{-}$. Samples were protected from the air and the spectra showed no changes over several hours. Bands near 135 and 180 cm^{-1} marked by asterisks are laser emissions.

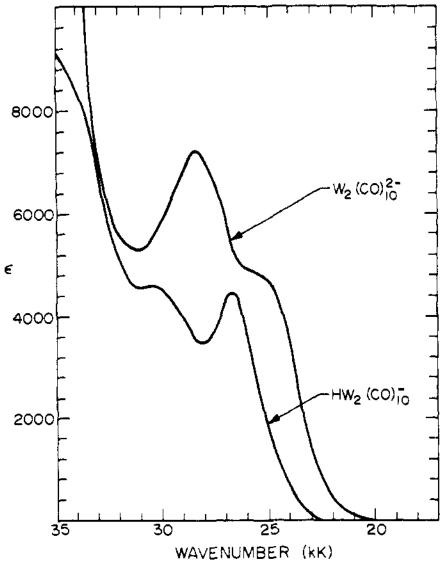

Figure 3. Electronic spectra at 300 K: $[(Ph_3P)_2N][W_2(CO)_{10}]$ in CH_2Cl_2 solution; $[Et_4N][HW_2(CO)_{10}]$ in tetrahydrofuran solution.

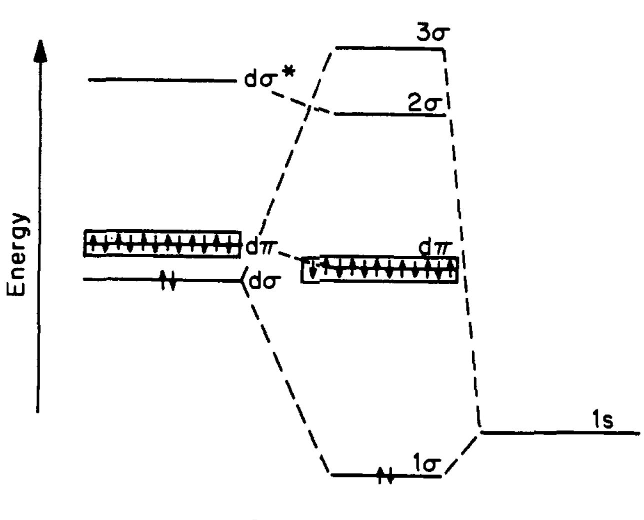

Figure 4. Schematic molecular orbital energy level scheme for $HW_2(CO)_{10}^{-}$.

cases,[13] although not so dramatic as for $HW_2(CO)_{10}^{-}$ (Figure 1). We are presently developing a mathematical model to account for the temperature dependence of the band shapes and intensities in both linear and bent MXM systems. A double-minimum potential in the linear case, as discussed previously for M-H-M interactions,[3-5] appears to account satisfactorily for the observed temperature behavior. A subsequent paper will be concerned in detail with experimental and theoretical aspects of this problem.[13]

Electronic Spectra. The low energy portions of the electronic spectra of $W_2(CO)_{10}^{2-}$ and $HW_2(CO)_{10}^{-}$ are shown in Figure 3. All electronic spectral data are set out in Table I. By analogy to the assignment of the spectrum of $Mn_2(CO)_{10}$,[14,15] the intense band at 28.5 kK in $W_2(CO)_{10}^{2-}$ is attributed to the $d\sigma W_2 \rightarrow d\sigma^* W_2$ transition. Upon W-H-W bridge formation we would expect the metal-metal σ bonding electron pair to be greatly stabilized, as indicated in the molecular orbital scheme for $HW_2(CO)_{10}^{-}$ shown in Figure 4.[16] As the diagonal energy element H_{5dW} is expected to be much less negative than H_{1sH}, the three-center bonding σMO, $\varphi(1\sigma) = c_1 d\sigma W_2 + c_2 1sH$, would be expected to have very much more 1sH than metal $d\sigma W_2$ character ($c_2 > c_1$). The ground state of $HW_2(CO)_{10}^{-}$, therefore, could reasonably be viewed as containing two low-spin d^6, square pyramidal $W(CO)_5$ units bridged by a hydride ion. In this model the *difference* in the energies of the molecular orbitals of $HW_2(CO)_{10}^{-}$ derived from $d\sigma^* W_2$ and $d\pi$ levels of $W_2(CO)_{10}^{2-}$ would not be significantly affected, as both $d\sigma^* W_2$ and $d\pi$ are nonbonding with respect to the 1sH orbital. The former orbital is denoted 2σ in the level scheme for $HW_2(CO)_{10}^{-}$. Finally, the three-center antibonding σMO, $\psi(3\sigma) = c_3 d\sigma W_2 - c_4 1sH$, would have $c_3 > c_4$ and be more energetic than 2σ.

From the qualitative discussion presented above, we would not expect a low-energy absorption band attributable to a $d\sigma W_2 \rightarrow d\sigma^* W_2$ transition in the protonated binuclear complex. Examination of the electronic spectrum of $HW_2(CO)_{10}^{-}$ in Figure 3 reveals that the intense $d\sigma W_2 \rightarrow d\sigma^* W_2$ band is replaced by two weaker absorption peaks, one very close in energy and intensity to the low-energy shoulder in $W_2(CO)_{10}^{2-}$. It seems reasonable to propose that the 26.8 kK band represents the spin-allowed $d\pi \rightarrow 2\sigma$ transitions in $HW_2(CO)_{10}^{-}$, and that the weak shoulder (24.7 kK) observed at 80 K (Table I) is due to the corresponding singlet → triplet[17] absorptions. The band at 30.3

Table I. Electronic Spectra of $W_2(CO)_{10}^{2-}$ and $HW_2(CO)_{10}^{-}$[a]

$[Et_4N]_2[W_2(CO)_{10}]$[b]	$[(Ph_3P)_2N]_2[W_2(CO)_{10}]$[c]	$[Et_4N][HW_2(CO)_{10}]$[b]	$[Et_4N][HW_2(CO)_{10}]$[d]
...	...	...	24.7 sh
25.5 sh	25.5 sh (4840)	26.8 (4470)	26.9
28.5	28.5 (7210)	...	...
...		30.3 (4630)	30.5
...		...	~32.3 sh
...		~34.5 sh (8700)	34.7
40 sh		~39 sh (28,000)	~38.8 sh
...		...	44.7

[a] Band positions in kK; ϵ values in parentheses; sh = shoulder. [b] In THF solution at 300 K. [c] In CH_2Cl_2 solution at 300 K; spectral peaks are not given above 35 kK as $[(Ph_3P)_2N]Cl$ in ethanol absorbs strongly in the ultraviolet region [37 (ϵ 4300) and 44 kK (ϵ 64,000 sh)]. [d] In EPA solution at 80 K (EPA is ether:isopentane:ethanol 5:5:2 by volume).

kK could possibly be assigned to allowed $d\pi \rightarrow 3\sigma$ transitions, but more likely it is related to $[W(CO)_5]$-localized $d\pi \rightarrow d_{x^2-y^2}$ excitation, as $W(CO)_6$ has its lowest d-d bands in the 30 kK energy region.[18] Most importantly, however, there is no sign of a $d\sigma W_2 \rightarrow d\sigma^* W_2$ band in the protonated species, $HW_2(CO)_{10}^{-}$, strongly supporting the main features of the electronic structural scheme sketched in Figure 4.

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Supplementary Material Available. A listing of the KBr pellet infrared spectra of $[Et_4N][HW_2(CO)_{10}]$, $[Et_4N][DW_2(CO)_{10}]$, $[Et_4N]_2[W_2(CO)_{10}]$, $[(Ph_3P)_2N]_2[W_2(CO)_{10}]$, and $[(Ph_3P)_2N]Cl$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3073.

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