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Microwave Spectrum and Molecular Structure for Manganese Pentacarbonyl Hydride

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Microwave rotational transitions for $HMn(CO)_5$ with ^{13}C isotopic substitution in the axial and in one equatorial site were measured using a Flygare–Balle-type pulsed-beam spectrometer. Rotational constants obtained are $A = B = 903.433(1)$ MHz for the axial ^{13}CO isotopomer and $A = 902.278(3)$ MHz and $B = 907.761(3)$ MHz for the isotopomer with one equatorial ^{13}C substitution. The new data are combined with previous data on $HMn(CO)_5$ and $DMn(CO)_5$ to obtain structural parameters for this complex. The Mn–H bond length obtained is r(Mn–H) = 1.65(2) Å and $\angle C_{ax}$–Mn–C_{eq} = 97.0(5)°.

Introduction

There has been considerable interest in transition metal hydrides because they are involved in many important reactions. They are often quite reactive and may function as reactants, as key intermediates, or as catalysts.[1,2]

$HMn(CO)_5$ has been extensively studied since it was first reported in 1931[3] and is apparently the most stable "first-row" transition metal hydride. Structural data for this complex have been obtained using X-ray diffraction,[4] neutron diffraction,[5] and electron diffraction.[6] The results of the crystal structure work and the gas-phase electron diffraction measurements agree to within a few hundredths of an angstrom for the bond lengths. The agreement is not quite as good for interbond angles, but they would be expected to be affected more by crystal packing forces, as was seen in earlier work.[7]

The rotational constants and Mn quadrupole coupling strengths for $HMn(CO)_5$ and $DMn(CO)_5$ were reported in a previous communication.[8]

Experimental Section

The ^{13}C-substituted isotopomers of $HMn(CO)_5$ were prepared using ^{13}C-enriched $Mn_2(CO)_{10}$. Studies of ^{13}CO substitution in $Mn_2(CO)_{10}$ were reported by Muetterties *et al.*[9] The ^{13}CO-exchange reactions were carried out by heating 1.5 g of $Mn_2(CO)_{10}$ (Strem) in a 200-mL closed flask with 1 atm of ^{13}CO and 50 mL of solvent for 18 h at 120 °C. Exchange was obtained using either octane or tetraglyme as the solvent. Neither of these solvents was entirely satisfactory, however, since the octane was difficult to remove completely from the $Mn_2(CO)_{10}$ using vacuum distillation. For the tetraglyme, some decomposition of the tetraglyme resulted in a lower boiling impurity.

$HMn(CO)_5$ was prepared by following the general methods of King[10] and Edgell and Risen,[11] except that tetraglyme (Aldrich) was used as the solvent and $NaK_{2.8}$ to supply the alkali metal. An excess of $NaK_{2.8}$ was added to 1.5 g of $Mn_2(CO)_{10}$ in 60 mL of tetraglyme, and the mixture was stirred and shaken occasionally for 18 h to produce $NaMn(CO)_5$ and $KMn(CO)_5$. The mixture was then acidified by adding 40 mL of deoxygenated 85% phosphoric and the product collected at 77 K under 10–50-Torr vacuum. The tetraglyme was used in place of tetrahydrofuran, which would be more difficult to separate from the product and caused interference in the spectrum. The water was removed from the collected $HMn(CO)_5$ sample by two passes through supported P_2O_5 columns (Fluka No. 79610) under vacuum. The estimated ^{13}C enrichment was 10–15% ^{13}CO ligands on the $HMn(CO)_5$.

Table 1. Measured and Calculated $K = 0$ Transition Frequencies for $J = 3 \rightarrow 4$ Transitions for $HMn(CO)_5$ with One ^{13}CO Substitution in the Axial Site[a]

J	J'	$2F$	$2F'$	measd	calcd	measd – calcd
3	4	5	7	7226.071	7226.070	0.001
3	4	11	13	7227.795	7227.790	0.005
3	4	9	11	7228.049	7228.055	–0.006

[a] The calculated frequencies were obtained from a least-squares fit to the measured frequencies. The rotational constant obtained in this fit is $A = B = 903.4334(5)$ MHz. The fixed parameters are listed in Table 3. The total angular momentum is $\vec{F} = \vec{I} + \vec{J}$. Values are given in MHz, and the standard deviation for the fit is 5.4 kHz.

Microwave Spectra

The $J = 3 \rightarrow 4$ transitions near 7200 MHz were measured for $HMn(CO)_4$ ^{13}CO isotopomers with axial ^{13}CO substitution and a single ^{13}CO equatorial substitution using a modified Flygare-Balle pulsed-beam spectrometer.[12] If 10% of the CO ligands are ^{13}CO, and these are randomly distributed, then calculating the probabilities of the major isotopomers gives 36.0% unsubstituted, 26.2% monosubstituted with ^{13}CO in an equatorial position, 6.6% substituted in the axial position, 2.9% equatorial disubstituted *trans*, and 1.5% disubstituted *cis*. We expected fairly weak resonances from molecules with one ^{13}CO in the axial position (6.6% of the total $HMn(CO)_5$) and even weaker ones from more highly substituted forms.

Three transitions were observed in the quadrupole hyperfine pattern for $J = 3 \rightarrow 5$ transitions in $HMn(CO)_5$ with one ^{13}CO in the axial site. The frequencies are given in Table 1. If we only consider the fraction of substituted molecules, we might expect that intensities should be stronger for a single ^{13}CO equatorial substitution in 26% of the molecules. The single equatorial ^{13}CO molecules, however, have lost the C_4 symmetry axis, so all K states are now possible, and they are now asymmetric tops, further complicating the spectrum. These effects result in rather weak resonance signals for the single ^{13}CO equatorial substitution lines listed in Table 2. There are 10 transitions listed with at least one line for each possible value of K_{oblate}.

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Table 2. Measured and Calculated Transition Frequencies for $J = 3 \rightarrow 4$ Transitions in $HMn(CO)_5$ with One ^{13}CO Substitution in an Equatorial Site[a]

J	K	$2F$	J'	K'	$2F'$	measd	calcd	measd – calcd
3	1	9	4	1	11	7229.453	7229.457	–0.004
3	1	11	4	1	13	7230.033	7230.041	–0.008
3	–2	9	4	–2	11	7237.627	7237.610	0.017
3	2	9	4	2	11	7238.671	7238.686	–0.015
3	–2	11	4	–2	13	7240.772	7240.755	0.018
3	0	11	4	0	13	7241.530	7241.542	–0.012
3	3	11	4	–3	13	7243.119	7243.112	0.007
3	–1	7	4	–1	9	7250.576	7250.577	–0.001
3	–1	9	4	–1	11	7251.374	7251.381	–0.007
3	–1	11	4	–1	13	7251.971	7251.966	0.005

[a] The rotational constants obtained in this fit are $A = 907.761(3)$ and $B = 902.278(3)$ MHz. Fixed parameters for this fit are listed in Table 3. K is the value of K_{oblate} for the basis state rotational wave functions. Frequencies are in MHz, and the standard deviation for the fit is 12.0 kHz.

Table 3. Values for Parameters Which Were Fixed at Previously Obtained Values[8] in Fitting the New ^{13}CO Data for $HMn(CO)_5$

param	value	param	value
eqQ(Mn)	–44.22 MHz	C_{cc}	5.0 kHz
D_J	0.09 kHz	C	697 MHz
D_{JK}	0.05 kHz		

Data Analysis and Parameter Values

The measured rotational transitions were analyzed using an iterative, nonlinear least-squares-fit procedure to adjust parameters in the Hamiltonian to obtain the lowest standard deviation of the calculated from experimental transition frequencies. Terms included in the Hamiltonian are rotational constants, one or two centrifugal distortion constants, the quadrupole coupling, and spin-rotational interaction strengths. The details of the matrix elements were discussed previously.[8,13,14] The total angular momentum is $\vec{F} = \vec{I} + \vec{J}$, where $\vec{I}$ is the manganese nuclear spin and $\vec{J}$ the rotational angular momentum. Since relatively few transitions were measured for the ^{13}CO isotopomers, all parameters except the rotational constants were fixed at values obtained in fitting the previous[8] $HMn(CO)_5$ data, and the values are listed in Table 3.

The results for fitting the measured $J = 3 \rightarrow 4$, $k = 0$ transitions for manganese pentacarbonyl hydride with ^{13}CO in the axial site are given in Table 1. Since this isotopomer is still a symmetric top, the only adjustable parameter was $A = B = 903.4334(5)$ MHz.

The isotopomer with one ^{13}CO substitution in an equatorial site is a slightly asymmetric top. The transition frequencies are fairly insensitive to the C rotational constant so that parameter was fixed at the value $C = 697$ MHz calculated from the structure. The A and B rotational constants were adjustable parameters and values obtained are $A = 907.761(3)$ and $B = 902.278(3)$ MHz. The results of this fit are given in Table 2.

Structure and Mn–H Bond Length

The present measurements provide three new rotational constants and two more are available from previous work[8] on $HMn(CO)_5$ and $DMn(CO)_5$, giving a total of five rotational constants for the various isotopomers. Since only one isotope of manganese is available, bond lengths cannot be obtained directly from a Kraitchman analysis. Therefore, the measured rotational constants were used in a least-squares-fit procedure to determine the various structural parameters. Some of the bond lengths of (C–O or Mn–C) were fixed to previous values obtained from the neutron diffraction[5] or electron diffraction[6] data. In all of the fits, the interbond angles C_{ax}–Mn–C_{eq} and Mn–C_{eq}–O and the bond length r(Mn–H) were adjustable parameters. Only four parameter fits were used so that uncertainties in the parameters could be readily obtained.

Table 4. Results of the Fit To Determine Structural Parameters for $HMn(CO)_5$ Using the Measured Rotational Constants and Neutron Diffraction Data[6,a]

rotational constants	isotopomer	measd	calcd	measd – calcd
$A = B$	$HMn(CO)_5$	907.9841	907.9810	0.0031
$A = B$	$DMn(CO)_5$	902.7682	902.7682	0.0000
$A = B$	^{13}C(ax)	903.4334	903.4340	–0.0006
B	^{13}C(eq)	902.2783	902.2826	–0.0043
A	^{13}C(eq)	907.7613	907.7596	0.0017

[a] The listed rotational constants are in MHz. The standard deviation for the fit is 5.6 kHz.

Table 5. Results of the Fit To Determine Structural Parameters for $HMn(CO)_5$ Using the Measured Rotational Constants and Electron Diffraction Data[5,a]

rotational constants	isotopomer	measd	calcd	measd – calcd
$A = B$	$HMn(CO_5)$	907.9841	907.9922	–0.0081
$A = B$	$DMn(CO)_5$	902.7682	902.7681	0.0001
$A = B$	^{13}C(ax)	903.4334	903.4286	0.0048
B	^{13}C(eq)	902.2783	902.2744	0.0039
A	^{13}C(eq)	907.7613	907.7621	–0.0008

[a] The listed rotational constants are in MHz. The standard deviation for the fit is 10.2 kHz.

Table 6. $HMn(CO)_5$ Structural Parameters Obtained from Fits to the Measured Rotational Constants (Tables 4 and 5)[a]

param	ND	ED
r(Mn–H), Å	1.645(4)	1.65(2)
θ ($\angle C_{ax}$–Mn–C_{eq}), deg	97.0(4)	97.3(1.1)
ϕ ($\angle C_{ax}$–Mn–C_{eq}), deg	176.3(1.5)	177.0(2.2)
r(C_{eq}–O), Å	1.148(2)	1.142 (F)
r(Mn–C_{eq}), Å	1.822 (F)	1.822(20)
r(Mn–C_{ax}), Å	1.853 (F)	1.856 (F)
r(C_{ax}–O), Å	1.143 (F)	1.142 (F)

[a] The subscript eq refers to the equatorial CO groups and ax to the axial CO. F indicates that the parameter was fixed to neutron diffraction (ND)[5] or Electron Diffraction (ED)[6] Data. The indicated error limits are 2σ.

The best standard deviation for a four parameter fit was obtained using neutron diffraction (ND) data to fix r(Mn–C_{eq}) = 1.853 Å, r(Mn–C_{ax}) = 1.822 Å, and r(C_{ax}–O) = 1.143 Å. The values for the adjustable parameters are r(Mn–H) = 1.645(4) Å, θ (=$\angle C_{ax}$–Mn–C_{eq}) = 97.0(4)°, ϕ (=$\angle$Mn–C_{eq}–O) = 176.3(1.5)°, and r(C_{eq}–O) = 1.148(2) Å with a standard deviation for the fit of 5.6 kHz. Increases in θ, above 90°, will move the C_{ax} atoms closer to the H atom. The fit results are given in Table 4. The angle ϕ is measured on the H atom side of the plane containing the equatorial carbon atoms, so that decreases in ϕ to values less than 180° result in a bending (or geniculation) of Mn–C–O bonds to move the O atom closer to the H atom.

A reasonably small standard deviation of 10 kHz was obtained using electron diffraction (ED) data with r(Mn–C_{ax}) as an adjustable parameter, in addition to r(Mn–H), θ, and ϕ. The "best fit" value obtained of r(Mn–C_{ax}) = 1.822(20) Å is in excellent agreement with the value obtained in the neutron diffraction work. The results of this fit are shown in Table 5. The "best fit" value of r(Mn–H) = 1.65(2) Å is in excellent agreement with the value obtained using the neutron data. The values for θ and ϕ are also reasonably consistent. The values for the parameters obtained in these fits are listed in Table 6.

The Mn–H bond length of 1.65 Å is longer than both the neutron diffraction value at 1.60 Å and the electron diffraction value at 1.58 Å by about twice our estimated error limits of 0.02

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Å for this parameter. It would not be too surprising if the solid-state, crystal value differed from the gas-phase value by this much, but we would expect a longer bond length in the solid, if hydrogen-bonding effects played a role. There have been other cases where electron diffraction bond lengths were a few hundredths of an angstrom shorter than microwave values, so the deviation from the electron diffraction value is not unreasonable. If we use the manganese center-of-mass coordinate obtained from the above structure fits and carry out a Kraitchman analysis with the $HMn(CO)_5$ and $DMn(CO)_5$ data, we obtain r_s(Mn–H) = 1.647 Å. This value agrees well with our values obtained above. The Kraitchman-derived value is slightly shorter than the fit results, as we would expect, since it should be closer to the equilibrium bond length.

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