Ni(α-*rac*-1,7-CTH)(NCS)$_2$ > Ni(γ-*rac*-1,7-CTH)(NCS)$_2$ > Ni(β-*meso*-1,7-CTH)(NCS)$_2$. The values of the splitting of the ν(CN of NCS) bands of these isomers listed in Table V substantiate this expectation.

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Registry No. Ni(δ-*rac*-1,7-CTH)(ClO$_4$)$_2$, 102629-52-7; Ni(α-*rac*-1,7-CTH)(ClO$_4$)$_2$, 51372-01-1; Ni(ε-*rac*-1,7-CTH)(ClO$_4$)$_2$, 102629-54-9; Ni(α-*rac*-1,7-CTH)Cl$_2$, 102629-55-0; Ni(δ-*rac*-1,7-CTH)Cl$_2$, 102629-56-1; Ni(δ-*rac*-1,7-CTH)(NCS)$_2$, 102629-57-2; Ni(ε-*rac*-1,7-CTH)(NCS)$_2$, 102629-58-3; Ni(β-*meso*-1,7-CTH)(NCS)$_2$, 14409-17-7; Ni(α-*rac*-1,7-CTH)(NCS)$_2$, 26029-89-0; Ni(β-*rac*-1,7-CTH)(NCS)$_2$, 26029-90-3; Ni(γ-*rac*-1,7-CTH)(NCS)$_2$, 15557-17-2.

Supplementary Material Available: Figure 4, showing proton magnetic resonance spectra for (A) Ni(α-*rac*-1,7-CTH)Cl$_2$, (B) Ni(δ-*rac*-1,7-CTH)Cl$_2$, and (C) Ni(ε-*rac*-1,7-CTH)(NCS)$_2$ in CDCl$_3$ solution at 34 °C (signals labeled with an asterisk due to impurities) (1 page). Ordering information is given on any current masthead page.

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Vibrational Spectroscopic Studies of μ-Hydrido-Bridged Metal Clusters. 1. $H_3Mn_3(CO)_{12}$

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Infrared and Raman spectra of $H_3Mn_3(CO)_{12}$ and its partially and fully deuterated analogues are reported and assignments made to the bands associated with ν_{CO}, ν_{MnMn}, and hydrogenic $\nu^{as}_{MnH/MnD}$, $\nu^{s}_{MnH/MnD}$, and $\gamma_{MnH/MnD}$ vibrations. Multiple bands observed in the regions of metal–hydrogen stretching modes are in part attributed to unequal MnHMn interbond angles in $H_3Mn_3(CO)_{12}$.

Introduction

Identification of the vibrations of μ_2- and μ_3-bridging hydrogen atom ligands in transition-metal hydrides is complicated by the low intensities and broad nature of the bands in infrared and Raman spectra.[1] However, recording spectra at liquid-nitrogen temperature markedly sharpens up these bands and provides a diagnostic aid to their assignments.[2-4] We present here a vibrational spectroscopic study of the μ-hydrido triangulo metal cluster $H_3Mn_3(CO)_{12}$ and of its deuterium-substituted derivatives. An X-ray diffraction study by Kirtley, Olsen, and Bau[5] shows the $H_3Mn_3(CO)_{12}$ compound to crystallize in the triclinic system, space group $P\bar{1}$, with two molecules per unit cell. The hydrogen atoms were located by using Fourier difference techniques and were found to be within the plane of the Mn_3 triangle giving an approximate molecular symmetry of D_{3h}. In more detail it was found that one of the μ-bridging hydrogen atoms has a considerably larger MHM angle (ca. 149°) than the other two (ca. 126 and ca. 119°), giving a more detailed point group of C_1, with C_{2v} worth considering as an approximation.

Experimental Section

$H_3Mn_3(CO)_{12}$ and its deuterium-substituted analogues were prepared from literature methods.[6] Infrared spectra, in the range 4000–200 cm^{-1}, were recorded on Perkin-Elmer 325, Perkin-Elmer 577, and Digilab FTS-14 spectrophotometers; a Beckman RIIC 1R720M interferometer was used in the range 400–10 cm^{-1}. Raman spectra were recorded on a Spex Raman spectrophotometer Model 1401 equipped with a Spectra Physics Model 165 mixed-gas laser. A rotating laser beam device, similar in construction to that reported by Zimmer and Kiefer,[7] was used to obtain the Raman spectra of $H_3Mn_3(CO)_{12}$, which was found to be highly sensitive to laser radiation.

Table I. Symmetry Classifications of the ν_{CO} and ν_{MnMn} Modes in $H_3Mn_3(CO)_{12}$ or $D_3Mn_3(CO)_{12}$, Assuming D_{3h} Skeletal Symmetry[a-c]

description[c]	symmetry	activity
$\nu_{CO(ax)}$	a'_1	Ra only
$\nu_{CO(eq)}$		
ν_{MnMn}		
$\nu_{CO(eq)}$	a'_2	inactive
$\nu_{CO(ax)}$	e'	IR and Ra
$\nu_{CO(eq)}$		
$\nu_{CO(eq)}$		
ν_{MnMn}		
$\nu_{CO(ax)}$	a''_2	IR only
$\nu_{CO(ax)}$	e''	Ra only

[a] For reasons cited in the text the hydrogenic modes are not suitably described by D_{3h} symmetry. [b] IR = infrared; Ra = Raman. [c] (ax) and (eq) refer to modes involving axial and equatorial carbonyl ligands, respectively.

Results and Discussion

To a first approximation it is convenient to divide the molecular vibrations into three main groups: the CO stretching modes, ν_{CO}; the metal–metal stretches, ν_{MM}; and the metal–hydrogen vibrations, ν^{as}_{MH}, ν^{s}_{MH}, and γ_{MHM}, where the first two MH modes involve MH bond stretching and the latter hydrogen deformation out of the MHM plane (as and s denote asymmetric and symmetric with respect to planes that approximately bisect the MHM angles). The metal–carbon stretching and the metal–carbon–oxygen bending vibrations will not be considered in great detail due to the complexity of the spectrum in the 650–350-cm^{-1} region, where these vibrations are typically observed. A description of ν_{CO} and ν_{MM} vibrations is listed in Table I, based on the approximate molecular symmetry of D_{3h}.

The CO Stretching Vibrations, ν_{CO}. Assuming a molecular symmetry of D_{3h} for the solution state (vide infra), four infrared-active fundamentals (a_2'' + 3e′) are predicted and observed (Figure 1). $H_3Mn_3(CO)_{12}$ shows bands at 2078 (m), 2032 (ms), 2008 (m), and 1982 (m) cm^{-1} in hexane solution. The following

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Table II. Observed Infrared and Raman Bands of $H_2Mn_3(CO)_{12}$ and $D_3Mn_3(CO)_{12}$ and Their Assignments to ν_{CO}, ν_{MnMn}, ν_{MnHMn}, and γ_{MnHMn} Fundamentals[a–c]

obsd freq, cm^{-1}				
$H_3Mn_3(CO)_{12}$		$D_3Mn_3(CO)_{12}$		
IR	Raman	IR	Raman	assignt
	2117 vs			ν_{CO}; a_1'
2078 vs	2085 s			ν_{CO}; e'
	2076 s			
	2049 s			ν_{CO}; a_1'
2032 vs	2000 w			ν_{CO}; a_2''
2008 vs	2025 s			ν_{CO}; e'
	2013 vs			
1985 vs	1991 vs			ν_{CO}; e'
	1977 vs			
	1963 s			ν_{CO}; e''
	1956 m			
	1931 m			ν_{CO}; a_2'
1710 w	1720 w			
1690 vw	1694 vw			
1660 m	*1665 m*			ν^{as}_{MnHMn}
1605 m	*1605 m*			
			1246 vw	
			1227 vw	
		1245 mw	*1205 m*	ν^{as}_{MnDMn}
1198 mw		1211 mw		
1155 vw		*1162 mw*	*1159 m*	ν^{as}_{MnDMn}
1118 vw				
1100 vw		1080 vw		
1072 vw				
1060 vw		1050 vw		
1045 w				
1025 vw		1020 vw		
996 vw	981 vw	990 vw		
962 w	961 w	965 vw	954 w	
925 vw	939 w			
	920 vw			
900 wm	*903 wm*			ν^{s}_{MnHMn}
	884 vw	890 vw	890 vw	
862 m	*870 wm*			ν^{s}_{MnHMn}
		847 vw	840 vw	
825 m	*832 wm*			ν^{s}_{MnHMn}
	810 vw		820 vw	
799 vw	800 m	795 vw	742 vw	
			717 vw	
		700 w	*702 m*	ν^{s}_{MnDMn}
			692 vw	
		690 w sh	*679 m*	ν^{s}_{MnDMn}
660 w sh	675 wm	660 w sh		
		650 vs	*652 m*	ν^{s}_{MnDMn}
650 vs	645 wm			
640 s		632 s	638 vw	
608 s				γ_{MnHMn}
588 vw		590 ms	592 vw	
548 w	556 m	569 w	557 m	
		543 w	545 vw	
			531 vw	
		518 ms		γ_{MnDMn}
		500 vw		
	487 w sh			
	478 vs	457 vw		
460 ms		*445 s*		ν_{MC}; a_2''
	450 m			
	411 m			
	307 w			
	214 w			
	(198)[d]			ν_{MnMn}; a_1'
	165 s			ν_{MnMn}; e'
144 w db		144 w db		
	80 s			

[a] vs = very strong; ms = medium strong; m = medium; mw = medium weak; w = weak; vw = very weak; sh = shoulder; db = doublet. [b] Solid-state data in the IR region were from KBr disks except for the ν_{CO} region, which was measured in *n*-hexane solution. Raman data were measured on polycrystalline samples. All solid-state spectra were run at liquid-nitrogen temperatures. [c] All assignments given for the hydridic vibrations are for the most likely frequencies while recognizing the presence of extensive coupling with δ_{MnCO} and ν_{MnC} in the case of the out-of-plane hydride deformation and of the strong Fermi resonance phenomena with the hydride stretches (see text). [d] See text.

is an assignment of these vibrational modes by comparison with the assignments reported for the complexes $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ of D_{3h} symmetry. Two expectations are utilized in making our assignments:[8-10]

(1) Axial ν_{CO} frequencies will be greater than equatorial ν_{CO} frequencies, where axial refers to those six carbonyl ligands out of the plane of the metal triangle and equatorial refers to the remaining six carbonyl ligands in the plane of the metal triangle.

(2) Those modes involving vibrating dipoles opposing each other will have higher frequencies than those modes with dipoles pointing in the same direction for the axial ligands on the same metal atom, while the reverse order will be true for the equatorial ligands.[8-10]

One of the e′ modes and the a_2'' mode involve axial CO ligands; hence, these will therefore be expected to have higher frequencies than the two remaining infrared-active e′ modes, which involve equatorial CO ligands, although account must be taken of the fact that, in the case of the ruthenium and osmium clusters mentioned above, those axial and equatorial e′ modes that arise from the a_1 modes of an isolated $M(CO)_4$ unit of C_{2v} local symmetry are strongly coupled together.[10] The e′ axial mode involves CO groups on the same metal atom vibrating against each other (dipoles opposed; a_1 under local C_{2v} symmetry) and is therefore assigned to the highest frequency infrared band (i.e. at 2078 cm^{-1}) with the axial a_2'' mode assigned to the next lower band at 2032 cm^{-1}.

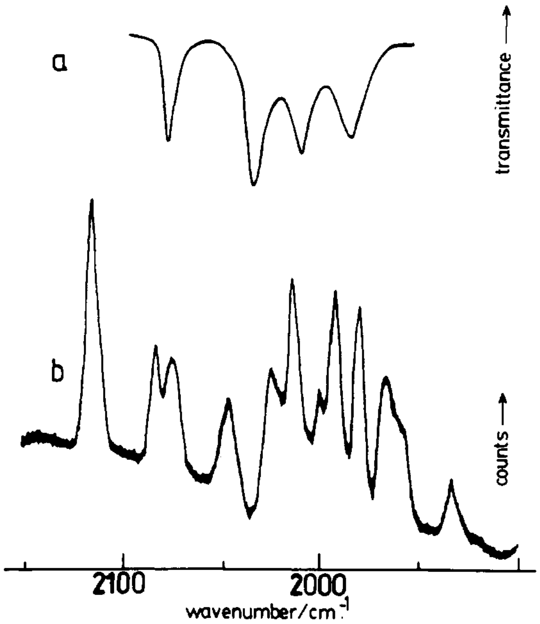

Figure 1. (a) Infrared (*n*-hexane solution) and (b) Raman (polycrystalline sample at liquid-nitrogen temperatures) spectra in the carbonyl stretching region of $H_3Mn_3(CO)_{12}$. The 568-nm laser line was used.

The two remaining infrared bands are assigned to the equatorial e′ modes with now the higher frequency mode involving vibrating dipoles pointing in the same direction (Table II). A confirmation of this assignment is provided by the resonance Raman spectrum

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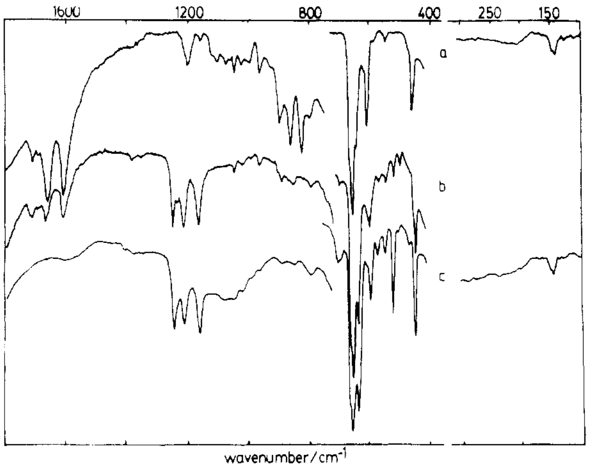

Figure 2. Infrared spectra (KBr disks) of (a) $H_3Mn_3(CO)_{12}$, (b) partially deuterated $H_3Mn_3(CO)_{12}$, and (c) $D_3Mn_3(CO)_{12}$ at liquid-nitrogen temperatures.

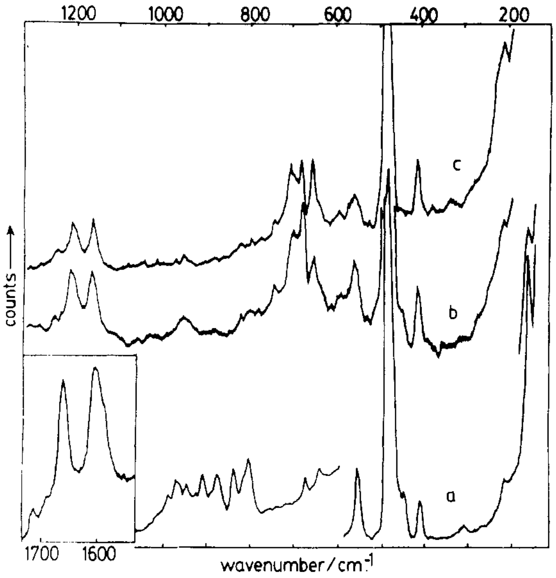

Figure 3. Raman spectra of polycrystalline samples at liquid-nitrogen temperatures of (a) $H_3Mn_3(CO)_{12}$, (b) partially deuterated $H_3Mn_3(CO)_{12}$, and (c) $D_3Mn_3(CO)_{12}$. The 568-nm laser line was used.

of $H_3Mn_3(CO)_{12}$ reported in ref 14.

Figure 1 shows the solution-state infrared and solid-state Raman spectra in the CO stretching region. The crystal structure of this compound is quite a favorable one, as there are two molecules per primitive unit cell in sites of symmetry C_1 related to each other by a center of symmetry. Under the site symmetry all molecular vibrations are infrared and Raman active, but the factor group imposes a center of symmetry, which makes the in-phase combinations of these molecular vibrations Raman active only and the out-of-phase combinations infrared active only. Therefore, the pattern of bands in the infrared spectrum or the Raman spectrum alone should be explicable in terms of an isolated molecular model of C_1 symmetry with the correlation field effects appearing as a separation between infrared and Raman frequencies.

The solid-state infrared spectrum has broad overlapping bands, as is very often observed for the carbonyl complexes in this region. This makes assignments in this infrared region of the solid state very difficult. However, the solid-state Raman spectrum in this region is of good quality (Figure 1) and a peak count immediately gives the expected 12 bands. The following is a tentative assignment for this region of the Raman spectrum. The highest frequency band at 2117 cm^{-1} is clearly the totally symmetric breathing mode of the CO bonds, a′ under D_{3h} symmetry as in the solution state. The e′ mode assigned in solution to the band at 2078 cm^{-1} is clearly split in the solid, giving a doublet at 2085 and 2076 cm^{-1}. A comparison with the spectra of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ would suggest[9] the lowest frequency weak band at 1931 cm^{-1} to be probably the a_2' mode, which is inactive under D_{3h} symmetry. The next higher frequency doublet at 1956 and 1963 cm^{-1} is probably the split e″ mode under D_{3h}. The 1991- and 1977-cm^{-1} peaks appear like another split e′ while the remaining e′ mode is assignable to the doublet at 2013 and 2025 cm^{-1}. Strongly infrared-active a_2'' (ca. 2032 cm^{-1} in the solution IR spectrum) is probably the very weak peak at 2000 cm^{-1}, which leaves the 2046-cm^{-1} peak to be assigned to the other Raman-active a_1' mode.

The Metal–Metal Stretching Vibrations, ν_{MM}. The totally symmetric metal–metal stretching vibration (a_1' symmetry) of the $H_3Mn_3(CO)_{12}$ complex, which is only Raman active under strict D_{3h} molecular symmetry, has been assigned by Onaka and Shriver[11] to a band at 163 cm^{-1}, observed in a Raman spectrum run at liquid-helium temperatures. We have also observed this band in our liquid-nitrogen-temperature spectra (Figure 3). Energy losses have been observed[12] in incoherent inelastic neutron-scattering (IINS) spectra at 146 and 96 cm^{-1} and have been assigned to the ν_{MM} a_1' and e′ modes, respectively. There are no formal selection rules in IINS, so two energy losses are predicted for the ν_{MM}, showing intensity from hydrogen motions involved in the normal modes, so the assignment appears to be correct on that basis. However, the possibility of hydrogen motion in other vibrations appearing in this region, like those involving predominantly deformation of CMC angles, should not be ignored. The far-infrared spectra of $H_3Mn_3(CO)_{12}$ and $D_3Mn_3(CO)_{12}$ (Figure 2) show a partially resolved doublet at ca. 144 cm^{-1}. This infrared band and the 146-cm^{-1} IINS loss almost certainly belong to the same vibration and thus cannot be the a_1' mode because of the infrared activity especially because this is the only infrared band seen in this region (Figure 2). It is tempting at this juncture to assign this band to the e′ mode. From this assignment, i.e. 163 cm^{-1} (a_1') and 146 cm^{-1} (e′), the principal force constant for metal–metal stretching in the case of $H_3Mn_3(CO)_{12}$, k_r, has been calculated to be 37 N m^{-1}, assuming the stretch–stretch interaction force constant, f_{rr}, to be $-0.08k_r$.[13]

This value of k_r is about 37% of the value of k_r in $Mn_2(CO)_{10}$, 59 N m^{-1}, and has been rationalized[13] as a consequence of the expected[5] weakening of the MnMn bonds due to the presence of the μ-bridging hydride ligands. Force constant k_r has an even lower value of 23 N m^{-1} when the frequencies 146 and 96 cm^{-1} are used for the a_1' and e′ modes, respectively.

In a following publication[14] resonance Raman spectroscopic evidence is provided for an alternative assignment of 198 cm^{-1} (a_1') and 165 cm^{-1} (e′) for these metal–metal stretching modes. The main problem with this revised assignment is the lack of a strong feature in the normal Raman spectrum at 198 cm^{-1} for the a_1' mode. This implies a rather large change in the electron density associated with the MM bond due to the introduction of a bridging hydride. This possibly finds support in the photoelectron spectroscopic results in the closely related complex $H_3Re_3(CO)_{12}$ reported by Green et al.[15] and the neutron diffraction investigations of bridging hydrides by Bau et al.[16] These workers have deduced a three-center bond, similar to that found in boranes,[17] with an appreciable amount of electron density localized on the hydrogen atom rather than on the metal–metal bond.

A calculation using this revised assignment, neglecting all ligands, and assuming independent principal and interaction force constants now gives the result $k_r = 53.3$ N m^{-1} and $f_{rr} = -5.5$ N

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m^{-1}, which more satisfactorily shows a lowering of only about 9.5% from the value of the principal force constant obtained for $Mn_2(CO)_{10}$. The calculated interaction force constant, f_{rr}, is ca. −10.3% of the principal force constant, k_r, to be compared with the value of −8% recommended for approximate normal-coordinate analysis.[13]

The Metal–Hydrogen Vibrations, ν_{MH}. The frequency regions for asymmetric (ν^{as}) and symmetric (ν^{s}) hydrogen–metal stretching vibrations of μ-hydrides in a range of carbonyl compounds have previously been identified[3] as 1700–1300 cm^{-1} for ν^{as} and 1300–800 cm^{-1} for ν^{s}. The infrared and Raman spectra, Figures 2 and 3, at 298 and 100 K, of $H_3Mn_3(CO)_{12}$ show energy transfers in the above frequency regions assignable to the ν^{as} and ν^{s} modes, respectively.

The ν^{as} vibrations are easily assigned in the Raman spectrum to the temperature-sensitive bands at ca. 1665 and 1605 cm^{-1} moving down to ca. 1205 and 1159 cm^{-1}, respectively, on deuterium isotopic substitution (Figure 3). The corresponding infrared bands (Figure 2) are at ca. 1660 and 1608 cm^{-1} with some very weak deuterium-sensitive features at ca. 1710 and 1690 cm^{-1} (also found in the Raman spectrum) of the protonated compounds. There are three bands in the infrared spectrum of the deuterio complex at ca. 1250, 1211, and 1162 cm^{-1} assignable to $\nu^{as}{}_{MnD}$. An examination of the partially deuterated spectrum shows the very weak features at ca. 1700 cm^{-1} to behave independently of the other bands in this region at 1660 and 1605 cm^{-1} and are therefore probably due to Fermi resonance with combinations of the bands around 850 cm^{-1}. Of the three bands at ca. 1200 cm^{-1} in the deuterio complex those at 1245 and 1162 cm^{-1} seem to grow with deuteration relative to that at ca. 1211 cm^{-1}. There is already a band of comparable intensity at ca. 1200 cm^{-1} in the case of the $H_3Mn_3(CO)_{12}$ complex, which is most probably a multiphonon band. Therefore, it is likely that these three bands have $\nu^{as}{}_{MnD}$ character with probably the bands at 1245 and 1162 cm^{-1} having a major share. The above frequencies for the $\nu^{as}{}_{MnH}$ and $\nu^{as}{}_{MnD}$ vibrations give a deuterium isotopic shift ratio of ca. 1.38, thus confirming the assignment.

In the ν^{s} region of the manganese hydride there are six medium to weak bands at 962, 925, 900, 862, 825, and 799 cm^{-1} in the infrared spectrum. Multiple, often analogous, features are also found in the Raman spectrum at 981, 961, 939, 920, 903, 884, 870, 832, 810, and 800 cm^{-1} (Figure 3). Infrared bands at 900, 862, and 825 cm^{-1} virtually disappear on the replacement of H by D, although some much weaker residual bands occur at 965, 890, 847, and 795 cm^{-1}. Similar residual bands left over in the Raman are at ca. 954, 890, 840, and 820 cm^{-1}. In the search for the analogous vibrations in the deuterium complex, it is easier to assign the Raman spectrum first as the frequency region where these bands are expected to appear on deuteration is rather bare in the protonated complex, except for a couple of weak to medium bands at 675 and 645 cm^{-1}. In contrast, the infrared spectrum shows a very intense set of bands in this region due to δ_{MCO} and ν_{MC} modes. The frequency region of the new set of bands that appears in the Raman spectrum on deuterium substitution could be fairly accurately predicted by an isotopic shift ratio of ca. 1.38 when applied to the bands from the hydrogen-containing species. The $\nu^{s}{}_{MnD}$ bands in the Raman epectrum are found at ca. 742, 702, 679, 652, and 592 cm^{-1}. The weak peaks at 676 and 645 cm^{-1} in the protonated complex, which are probably the δ_{MCO} vibrations, have disappeared on deuteration, and they could probably underlie the bands at 679 and 652 cm^{-1}.

From the Raman results, a careful inspection of the infrared spectrum produces the following frequencies for this type of vibration. These are at 700, 690, 660, 632, 590, and 569 cm^{-1}, respectively.

The incoherent inelastic neutron-scattering spectrum of $H_3Mn_3(CO)_{12}$ shows[12,18] a strong energy-transfer region with main peaks near 610 and 320 cm^{-1}. The neutron-scattering technique strongly favors the observation of vibrations containing appreciable hydrogen motion[12] and in other cases has readily shown the presence of coupled δ_{MH} and δ_{MCO} modes as in[18] $HCo(CO)_4$. However, for the $H_3Mn_3(CO)_{12}$ compound there is a third type of metal–hydrogen vibration, the out-of-plane deformation mode, γ_{MHM}. In several μ-hydrido species this has been shown[19] to occur in the vicinity of ca. 700 cm^{-1}. In the infrared spectrum of $H_3Mn_3(CO)_{12}$ a mass- and temperature-sensitive band at ca. 608 cm^{-1} disappears from this region, and a similar band appears at ca. 518 cm^{-1} in the spectrum of $D_3Mn_3(CO)_{12}$ and is probably to be assigned to γ_{MnHMn}. There is also a medium intense band at ca. 460 cm^{-1} in $H_3Mn_3(CO)_{12}$ that moves down to ca. 444 cm^{-1} in $D_3Mn_3(CO)_{12}$. This is probably the a_2'' ν_{MC} mode of the axial ligands mixing with γ_{MnHMn}, similar to what is found in the case of the rhenium complexes;[20] vide infra. This explains the low deuterium substitution frequency shift ratio of ca. 1.17 observed for the γ_{MnHMn} assignment. This infrared feature at 608 cm^{-1} clearly corresponds to the neutron-scattering feature at ca. 610 cm^{-1}. It is interesting to note that there is no band in the Raman spectrum corresponding to this frequency, in agreement with the expectation of a very small polarizability change for such a vibration.

So far we have avoided the use of specific symmetry labels when assigning the hydrogen-sensitive ν^{as}, ν^{s}, and γ modes of the MnHMn group. Because of the different observed MnHMn angles,[5] ca. 149 (9), 126 (7), and 119 (6)°, where the figures in parentheses indicate the estimated errors, the possibility must be considered of relatively independent frequencies for the three MHM groups.

Under the D_{3h} point group MHM would have the vibrational symmetries

$\nu^{as}{}_{MnHMn}$	a_2' and e′
$\nu^{s}{}_{MnHMn}$	a_1' and e′
γ_{MnHMn}	a_2'' and e″

On this basis, only three infrared-active bands are predicted overall (2e′ and a_2''), but in practice at least seven H–D-sensitive bands are observed. In the $\nu^{as}{}_{MnHMn}$ region one e′ mode is expected under D_{3h} symmetry, but in fact two bands are found at ca. 1660 and 1605 cm^{-1}. The frequency separation seems too large for a split degeneracy of the e′ mode. It seems more reasonable to assign the ca. 1605-cm^{-1} band to overlapping ν^{as} absorptions from the groups with the not-dissimilar MnHMn angles of 126 and 119° and the ca. 1660-cm^{-1} band to the group with a considerably greater MHM angle of ca. 149°.[3] In any case relatively small frequency splittings due to coupling are to be expected between the hydrogenic modes of the different MnHMn groups because of the heavy mass of the interconnecting Mn atoms.

On this basis there should be three absorptions in the $\nu^{s}{}_{MnHMn}$ region, two high frequencies now being rather close together. In fact, up to about 10 are found. However, unexplained multiplicities of bands in the ν^{s} region are not uncommon in other cases.[19,21] It has been concluded[21] that they are not caused by Fermi resonance between $\nu^{s}{}_{MHM}$ and overtone or combination bands of ν_{MC} or δ_{MCO} in an earlier study of the $[HW_2(CO)_{10}]^-$ ion. But we shall provide strong evidence in a following publication[20] that this is indeed the case for the compound $H_3Re_3(CO)_{12}$. Considering the close structural similarities between the latter compound and $H_3Mn_3(CO)_{12}$, we favor the Fermi resonance explanation as the cause of this multiplicity of bands sensitive to deuterium substitution. Finally, in the γ_{MnHMn} region only one band has been found (at 608 cm^{-1}), but this is in a region heavily overlapped by bands from the δ_{MnCO} and ν_{MC} modes.

Further evidence for the relative independence of the hydrogenic modes associated with different MHM groups comes from a consideration of the residual ν^{as} and ν^{s} regions in the spectrum from the only partially deuterium-substituted compound (Figure

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3). Although the principal species expected is still $D_3Mn_3(CO)_{12}$, others such as $D_2HMn_3(CO)_{12}$ and $DH_2Mn_3(CO)_{12}$ would be expected to be present. Given coupling between adjacent H or D vibrations, overall complex absorption regions would hence be expected in the regions involving vibrations of the residual hydrogens. In fact, in both the ν^{as} and ν^{s} regions the residual H features are very similar in shape to those of the original $H_3Mn_3(CO)_{12}$ compound. This is just what would be expected of the residual MHM vibrators if they are independent of each other in $H_3Mn_3(CO)_{12}$. Therefore, the modes from the partially deuterium-substituted species coincide to give the same pattern. The frequencies of the relevant infrared and Raman spectra and their assignments as discussed above are summarized in Table II.

Conclusion. The ν_{CO} and ν_{MnMn} modes of $H_3Mn_3(CO)_{12}$ and $D_3Mn_3(CO)_{12}$ have been assigned on the basis of approximately D_{3h} symmetry for the heavy-atom skeleton. For the $H_3Mn_3(CO)_{12}$ compound characteristic frequency regions have been identified for ν^{as}_{MnHMn}, ν^{s}_{MnHMn}, and γ_{MnHMn} modes, although complexities in the first two regions indicate that different MnHMn angles give different frequencies. For this reason an assumption of D_{3h} symmetry is not appropriate for the hydrogenic modes.

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Registry No. $H_3Mn_3(CO)_{12}$, 51160-01-1; $D_3Mn_3(CO)_{12}$, 12170-84-2; D_2, 7782-39-0.

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Vibrational Spectroscopic Studies of μ-Hydrido-Bridged Metal Clusters. 2. Resonance Raman Spectrum of $H_3Mn_3(CO)_{12}$ and Likely Excited-State Geometry

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The resonance Raman spectrum of $H_3Mn_3(CO)_{12}$ is reported and used to provide assignments of several vibrational modes. The identification of the modes that are resonance-enhanced suggests a probable geometry for the electronic excited state involved.

Resonance Raman spectroscopy has been widely used for the investigation of biologically important cluster compounds like the iron–sulfur clusters.[1] Also, many examples of its use in the investigation of bimetallic clusters are reported in the literature where the metal–metal modes of vibration appear to show the most enhancement.[2] However, this technique does not appear to have been applied to polymetallic clusters with metal–metal bonds. Here we report the resonance Raman spectroscopic investigation of a trimetal cluster hydride, $H_3Mn_3(CO)_{12}$, which provides some interesting insight into its geometry in the electronically excited state.

Experimental Section

$H_3Mn_3(CO)_{12}$ and its deuterated analogues were prepared by using literature methods.[3] Raman spectra were recorded on a Spex Raman spectrophotometer Model 1401 equipped with a Spectra Physics Model 165 ion laser. A rotating laser beam device similar in construction to that reported by Zimmer and Kiefer[4] was used. This provides heat dissipation by the relative motion between the sample and the laser beam and also allows easy sample cooling, which was done with liquid nitrogen. These elaborate measures were necessary as this compound was found to be very sensitive to laser radiation.

Results and Discussion

The normal Raman spectrum obtainable with the 568-nm laser exciting line has been dealt with in a previous publication.[5] However, when the 488-nm or the 476-nm laser line is used for excitation, a completely different spectral pattern is obtained (Figure 1), which is recognizable as due to the resonance Raman effect. This shows a strong progression up to about three overtones of a fundamental of frequency of ca. 478 cm^{-1}, which we label ν, together with three other vibrational modes producing progressions ($n\nu + \nu_1$) with ν as a basis. The average values of the frequencies of these latter modes are 79, 164, and 198 cm^{-1}. Further, probably slightly enhanced bands are visible in the metal–hydrogen stretching regions. There are two greatly enhanced bands found in the carbonyl stretching region, at ca. 2082 and 2014 cm^{-1}. These are accompanied by a pair of bands at 2558 and 2490 cm^{-1} due probably to combinations with the 478-cm^{-1}

Table I. Frequencies of Observed Bands in the Resonance Raman Spectra of $H_3Mn_3(CO)_{12}$ and $D_3Mn_3(CO)_{12}$ and Their Assignments

obsd freq, cm^{-1}		
$H_3Mn_3(CO)_{12}$	$D_3Mn_3(CO)_{12}$	assignt
2558	2560	$\nu_{1CO} + \nu_{MC(eq)}$
2490	2488	$\nu_{2CO} + \nu_{MC(eq)}$
2082	2082	ν_{1CO}
2014	2013	ν_{2CO}
2000	2000	
1910	1910	$4\nu_{MC(eq)}$
1663	1637	ν^{as}_{MH}
1599	1587	ν^{as}_{MH}
1516	1514	$3\nu_{MC(eq)} + \delta_{CMC}$
1434	1434	$3\nu_{MC(eq)}$
	1202	ν^{as}_{MD}
	1154	ν^{as}_{MD}
1149		$2\nu_{MC(eq)} + \nu^{s}_{MnMn}$
1112	1112	$2\nu_{MC(eq)} + \nu^{as}_{MnMn}$
1035	1037	$2\nu_{MC(eq)} + \delta_{CMC}$
958	958	$2\nu_{MC(eq)}$
675	675	$\nu_{MC(eq)} + \nu^{s}_{MnMn}$
642	640	$\nu_{MC(eq)} + \nu^{as}_{MnMn}$
556	558	$\nu_{MC(eq)} + \delta_{CMC}$
477	478	$\nu_{MC(eq)}$

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