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_3-$Mn_3(CO)_{12}$ 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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Vibrational Spectroscopic Studies of μ-Hydrido-Bridged Metal Clusters. 2. Resonance Raman Spectrum of H₃Mn₃(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

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		assignt
$H_3Mn_3(CO)_{12}$	$D_3Mn_3(CO)_{12}$	
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	$\nu_{MC(eq)}$

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

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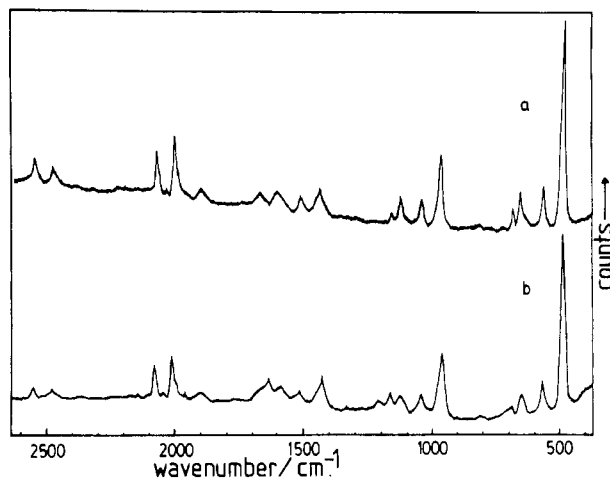†Present address: Esso Chemical Research Centre, Abingdon, Oxon OX13 6BB, U.K.

Figure 1. Resonance Raman spectra run by using the 488-nm excitation of polycrystalline samples of (a) $H_3Mn_3(CO)_{12}$ and (b) $D_3Mn_3(CO)_{12}$ at ca. 100 K.

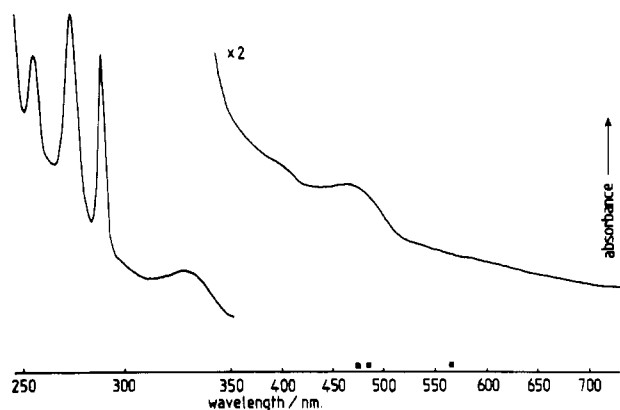**Figure 2.** Electronic spectrum of $H_3Mn_3(CO)_{12}$, at ca. 10 K, isolated in an argon matrix. The laser frequencies used for the Raman experiments are indicated with asterisks.

fundamental (2982 cm^{-1} + 478 cm^{-1} = 2560 cm^{-1} and 2014 cm^{-1} + 478 cm^{-1} = 2492 cm^{-1}). The electronic spectrum is given in Figure 2 together with the exciting lines used for the Raman experiments.

The X-ray diffraction study by Kirtley, Olsen, and Bau[6] 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. This gives the molecule a site symmetry of C_1. However, a close examination of the structural parameters indicates a structure approximating C_{2v} symmetry. The following is an explanation of the relatively complicated resonance Raman spectrum of this compound, based on the latter molecular symmetry. From the X-ray crystallographic data[6] we can safely assume the ground electronic state to be nondengenerate. Therefore, the condition necessary for the observation[7] of the resonance Raman effect is that the electronic transition involved should be dipole-allowed (i.e. large transition moment, high extinction coefficient). The excited-state molecular geometry will normally show a distortion with respect to the ground-state molecular geometry. Those normal modes that show progressions or are enhanced are usually the ones whose normal coordinates relate to the distortion of the excited state from the ground-state geometry. It can easily be shown[7] that these shifts of equilibrium position take place only along totally symmetric coordinates.

In looking for an explanation of the observed resonance Raman spectrum, we start with the carbonyl stretching region. The following is a correlation between the irreducible representations spanned by the carbonyl stretching vibrations under D_{3h} idealized
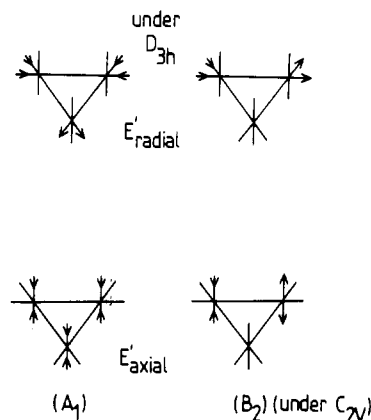

Figure 3. Unique pair of resonance-enhanced carbonyl stretching vibrations of A_1 symmetry under the C_{2v} molecular point group and their parentage in the E' modes under the idealized D_{3h} molecular point group.

molecular symmetry and the more realistic molecular symmetry of point group C_{2v}.

ν_{CO}'s under D_{3h}	ν_{CO}'s under C_{2v} ($\sigma_h \rightarrow \sigma_{yz}$)
$2A_1'$	$2A_1$
A_2'	B_2
$3E'$	$3(A_1 + B_2)$
A_2''	B_1
E''	$A_2 + B_1$

Therefore, there are five totally symmetric vibrations predicted under C_{2v} molecular symmetry as candidates for enhancement in the ν_{CO} region. Only two are observed to do so (Figure 1).

In clusters of similar geometry reported in the literature, there has never been any doubt as to the assignment of the highest ν_{CO} mode: this is the totally symmetric mode (A_1' or A_1), with an in-phase coupling of the axial and equatorial vibrations.[8] Equatorial and axial are in reference respectively to carbonyl groups that are approximately in the plane of the metal triangle and perpendicular to that plane. Therefore, one could safely assume a similar normal mode for the highest frequency ν_{CO} (ca. 2117 cm^{-1}) of $H_3Mn_3(CO)_{12}$. Unexpectedly, this vibration is not enhanced in the resonance Raman spectrum of this cluster (Figure 1). However, a closer inspection of the appropriate symmetry coordinates does enable the identification of a unique pair of A_1 vibrations related to a pair of E' modes under D_{3h} symmetry as the possible candidates for the two observed peaks (Figure 3). One of these is an in-phase vibration of the axial CO's on one metal atom (the unique metal atom under C_{2v} molecular symmetry) but $2\pi/3$ out-of-phase with respect to the other two metal centers. The other symmetry coordinate relates to similar motions involving the equatorial CO's. It is interesting to note that these two symmetry coordinates have been found to be thoroughly mixed in the case of structurally similar clusters like $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$, where a number of investigations are reported in the literature.[8] Therefore, this observation of enhancement of these two modes would indicate the excited-state geometry to be a distortion along either one or both of these symmetry coordinates.

In the light of these considerations we can consider the vibrational mode at 478 cm^{-1}, which gives the strongest progression in the spectrum. The origin of this should clearly be sought among the ν_{MC} modes that are symmetry-related to the above-mentioned resonance-enhanced ν_{CO} modes. The assignments for this region of the carbonyl compounds in the literature are much less thorough compared to those of the ν_{CO} region. Considering the cluster compounds of similar geometry, $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$, there are four reports in the literature concerned with this frequency region.[9-12] They all agree in one respect, that δ_{MCO} vibrations

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(7) Clark, R. J. H.; Stewart, B. *Struct. Bonding (Berlin)* **1979**, *36*, 1.

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(9) Huggins, D. K.; Flitcroft, N.; Kaesz, H. D. *Inorg. Chem.* **1965**, *4*, 166.
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are at higher frequencies (ca. 650–500 cm^{-1}) than the ν_{MC} vibrations (ca. 500–350 cm^{-1}), with some overlap between the two regions. However, only two reports, the earliest by Huggins, Flitcroft, and Kaesz[9] and the latest by Adams and Taylor,[10] give an indication as to the relative frequency ordering for the axial and equatorial M–C vibrations. The former group argues that because the axial CO bonds are believed to be of higher bond order than the equatorial CO bonds, the reverse should be true for the M–C bonds and predicts equatorial M–C stretches to be of higher frequency than their axial counterparts. Adams and Taylor[10] have used the reverse order without providing an explanation. The very reasonable arguments that Huggins et al.[9] have used are the ones we prefer for the $H_3Mn_3(CO)_{12}$ cluster, and we assign the resonance-enhanced ν_{MC} (ca. 478 cm^{-1}) mode, which is at the top of the frequency range characteristic of M–C stretching vibrations (ca. 500–350 cm^{-1}), to be due to the equatorial M–C bonds. We find that this choice produces a very reasonable assignment of the observed resonance Raman spectrum (vide infra). The fact that only one mode is enhanced in the ν_{MC} region (unlike the pair of modes in the ν_{CO} region) could be explained if one were to assume negligible coupling between the axial and equatorial M–C stretching modes. This is a reasonable assumption considering the heavy mass of the interconnecting manganese atom and the low polarity of the M–C bond. The much greater coupling between C–O bond stretching modes is predominantly dipolar through space rather than through bond.[11] It is significant that, to explain the ν_{CO} region of the vibrational spectra of these compounds, one needs to consider all the vibrational interactions, intramolecular and intermolecular, while the ν_{MC} and δ_{MCO} region can be explained, to a good first approximation, by using an isolated-metal model, where only the groups attached to one metal atom are considered.[11]

Our identification of the vibrational modes that are resonance-enhanced makes it possible to deduce the largest distortion in the excited-state geometry compared to that of the ground state. This should involve an extension (or contraction) of both equatorial M–C bonds on one metal atom with respect to those on the other two metal atoms. A lesser distortion is predicted for the C–O bonds, and from valence bonding considerations, this would probably be opposite in sign to that of the M–C bonds. We conclude that the electronic transition involved is probably of a metal–ligand charge-transfer character.

There are three more vibrational modes showing distinct enhancement. These are at average frequencies of 79, 164, and 198 cm^{-1}. The vibrational modes expected in this frequency region are the metal–metal stretching modes, the CMC metal–carbon deformations, and lattice modes. Resonance enhancement of lattice modes is not commonly encountered.[7]

The δ_{CMC} modes give the following vibrations under idealized D_{3h} symmetry:

$$2A_1' + 2A_2' + 4E' + 2A_1'' + 2A_2'' + 4E''$$

Again the vibrations that transform as A_1 under C_{2v} but correlate to E' under D_{3h} are the probable candidates for enhancement. Using a similar course of reasoning to that used in the assignment of the ν_{MC} mode, we would expect only one δ_{MC} mode, the one that is confined to the deformation of the equatorial M–C bonds, to be enhanced, and we assign this to the 79-cm^{-1} band. This leaves the other two bands at ca. 164 and 198 cm^{-1} to be assigned to the metal–metal stretches. Here the two modes of A_1 symmetry under C_{2v} would be well mixed because of strong mechanical and electronic coupling within the metal triangle.

It should be noted that the latter assignments are at variance with those found in the literature and are discussed in detail in a previous paper.[5]

These three vibrations, at 79, 164, and 198 cm^{-1}, appearing in secondary progressions show no enhancement of their fundamental

bands. Such secondary progressions could be understood in terms of the so-called Duschinsky effect,[7] where the excited-state normal coordinates are generally some linear combination of the ground-state coordinates. Thus, a vibrational level corresponding to one of the excited-state coordinates may have overlaps with the levels of both ground-state coordinates. The observation that these secondary progressions, $n\nu + n_1\nu_1$ with ν as a basis, having $n_1 = 1$ only, suggests a small component of geometric change on resonant excitation, along Q_1, the normal coordinate with frequency ν_1, and is confirmed by the absence of overtones of ν_1 or any apparent enhancement of its fundamental.

An alternate explanation of the appearance of progressions of the above type is provided by a Herzberg–Teller vibronic coupling with a nearby transition of the same symmetry as the resonant electronic transition, even when the geometric change on resonant excitation may be zero along normal coordinate Q_1.[7]

A comparison of the resonance Raman spectra of $H_3Mn_3(CO)_{12}$ and $D_3Mn_3(CO)_{12}$ (Figure 1) shows some enhancement of the bands assignable to the asymmetric stretching of the MHM and MDM bridges and not their symmetric stretching modes. This observation is again in excellent agreement with the excited-state geometry deduced from the rest of the resonance Raman spectrum. An electronic transition involving one metal center more than the other two would bring about an asymmetry in the MHM bridge.

Because of the sensitive nature of $H_3Mn_3(CO)_{12}$, it is necessary to consider the possibility of the reported spectra being due to a photodecomposition product and not due to $H_3Mn_3(CO)_{12}$ itself. The following are the observations that argue against such a conclusion.

First, attempts to run Raman spectra of $H_3Mn_3(CO)_{12}$ at ambient temperatures, even with the aid of a spinning-sample arrangement, resulted in sample decomposition, producing a Raman spectrum identical with that of $Mn_2(CO)_{10}$, and the latter compound does not show resonance enhancement with the exciting frequencies used in these experiments.

Second, the electronic spectrum of $H_3Mn_3(CO)_{12}$ (Figure 2) and the frequencies of the exciting lines used are compatible with the observation of a normal Raman spectrum with the 568-nm line and resonance effects with the 488- and 476-nm excitations. Detailed resonance excitation profiles on some of the vibrational bands would certainly be of utility in confirming these observations. However, a lack of the necessary instrumentation has prevented us from performing such measurements.

Last, the fact that these spectra, the Raman and the resonance Raman, are found to be reproducible when the same sample is used and the exciting lines are cycled between these three laser frequencies would argue very strongly for the thesis of this paper.

Conclusion

The resonance Raman spectrum of $H_3Mn_3(CO)_{12}$ can be rationalized in terms of an electronic charge-transfer transition involving one metal center to a greater extent than the other two and confined to the plane defined by the triangle of metal atoms. An excited-state geometry where the largest distortion with respect to the ground state is in the equatorial M–C bonds attached to this unique metal center is inferred. Further distortions of a lesser extent are indicated for the other features associated with this metal center, the equatorial C–O bonds, the equatorial C–M–C angle, the metal–metal bonds, and the M–H bonds, respectively. This study also provides several definitive assignments of the vibrational modes and a better understanding of vibrational coupling in these systems.

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