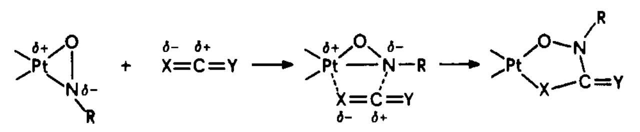
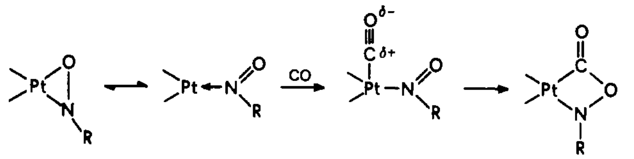
Scheme I



Scheme II



caused by the CF_3 and CH_3 substituents are different from those occurring in the aromatic derivatives (e.g. PhNO), where the excess of charge back-donated to the π^*_{NO} MO can be effectively delocalized because of a strong conjugative effect.

It is important to note that the carbon atom of the CF_3 or CH_3 group in the η^2 complexes does not belong to the Pt-N-O plane, being characterized by a torsion angle (C-N-O-Pt) of about 120° (see Figures 2 and 3). On the contrary, the planarity is a characteristic of the η^1 coordination. This means that the N atom has a hybridization close to sp^3, which is consistent with the single-bond character of the N-O bond. The small ligand perturbation caused by the η^1 coordination does not appreciably alter the sp^2 hybridization of the N atom and the N-O bond, which still has double-bond character.

The identification of the electronic structure internal to the coordinated ligands that has been clarified by our theoretical results can also serve to rationalize the mechanism of the reaction of the nitroso complexes with alkenes, CO_2, or CO_2-like molecules to give stable compounds in which the entering molecule inserts into the Pt-N bond, with formation of a C-N bond.[2,28,30]

The attack of the electrophilic carbon atom of the entering molecule takes place according to Scheme I (X = S, Y = S, NPh; X = O, NPh, Y = O), which is based on the assumption that the reactants can lead to a dipolar addition to the platinum and nitrogen atoms of the complex. Our results confirm that the nitrogen atom in η^2-coordinated nitroso ligands increases substantially its negative charge with respect to the free molecule, and therefore its nucleophilic character. The hypothesis of a dipolar mechanism seems to be consistent also with theoretical evidence.

The reaction of CO with coordinated nitroso ligands is particularly interesting because it could correspond to the final step of the catalytic deoxygenation of nitro compounds. As discussed in detail in refs 1 and 2, in the case of $Pt(PPh_3)_2(PhNO)$ this reaction leads to the formation of nonstoichiometric quantities of CO_2. A possible reaction intermediate has been postulated according to Scheme II. The cyclic intermediate due to the insertion of CO into a Pt-O bond is not completely consistent with the experimental results.[2,29] The existence of the cyclic species could be postulated by assuming that an equilibrium between η^2 and η^1 coordination modes takes place. Our results do not agree with this view, especially in the case of the CF_3NO ligand, since the two coordination modes I and II differ in stability by about 160 kJ·mol^{-1}. However, one cannot exclude the idea that the η^1 coordination of RNO is favored in the presence of a coordinated CO group, which can be competitive with RNO in the back-donation mechanism. Further theoretical studies would be in order to elucidate such a hypothesis.

Acknowledgment. This work has been supported by the Italian CNR and by the Italian Ministry of Education. We thank Prof. S. Cenini for stimulating discussions.

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Vibrational Spectra of the μ_2-Hydride Ligands in $[H_4M_4(CO)_{12}]$ (M = Os, Ru)

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Received March 27, 1990

The vibrational spectra of the hydride ligands in the title compounds are interpreted in terms of D_{2d} molecular symmetry. The pseudo-D_{4h} symmetry of the four hydrides (if the rest of the cluster is neglected) and the spherical symmetry of the hydride 1s orbital are shown to have a profound effect on the Raman intensities of some of the hydride modes.

Introduction

It is now usually relatively easy to identify those bands in the vibrational spectra of metal clusters that are associated with modes involving bridging hydride ligands. Such features shift to lower frequency on deuteration and sharpen markedly on cooling. However, in many cases the detailed interpretation of the spectra themselves is far from clear. The present communication deals with one such case, that of the clusters $[H_4M_4(CO)_{12}]$ (M = Ru, Os).

X-ray diffraction analyses[1] indicate that the clusters have very similar D_{2d} molecular symmetry; the four metal atoms define a tetrahedron elongated along one 2-fold axis, resulting in four long and two short metal-metal bonds. Neutron diffraction studies[2] of phosphite derivatives show the same bond length pattern for the metal skeleton, with the hydrides each bridging one of the longer bonds; average MHM angles are 112.2° (Os) and 114.2° (Ru).

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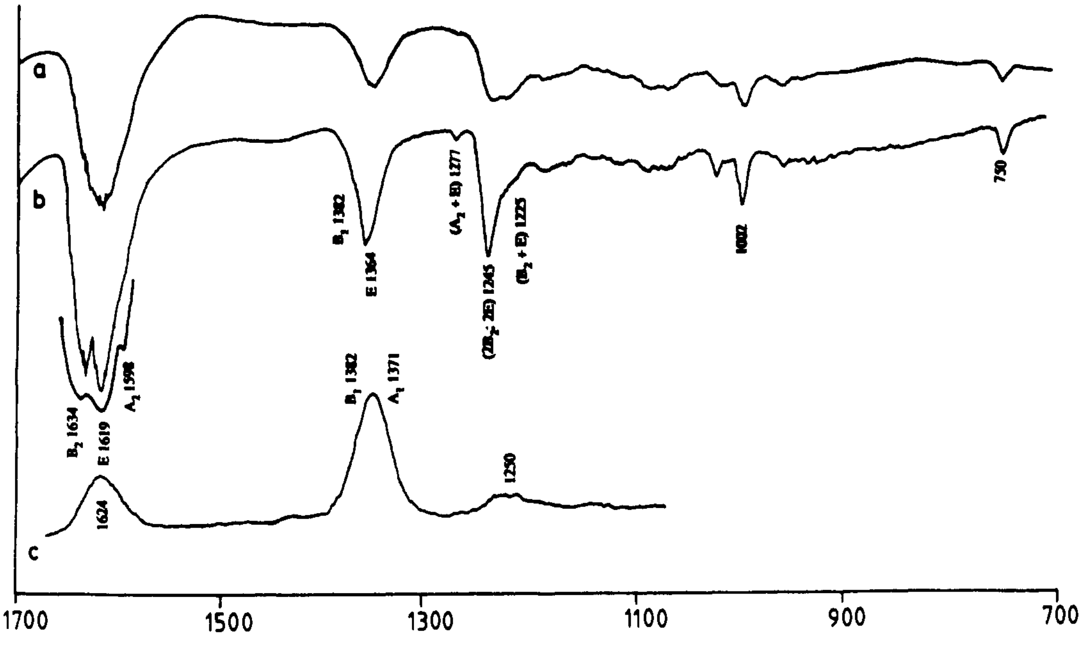

Figure 1. Solid-state infrared [(a) 300 K and (b) 100 K] and Raman [(c) 300 K] spectra in the metal-hydrogen stretching region of $[H_4Os_4(CO)_{12}]$. The insert shows the 100 K infrared spectrum of a more concentrated CsI disk.

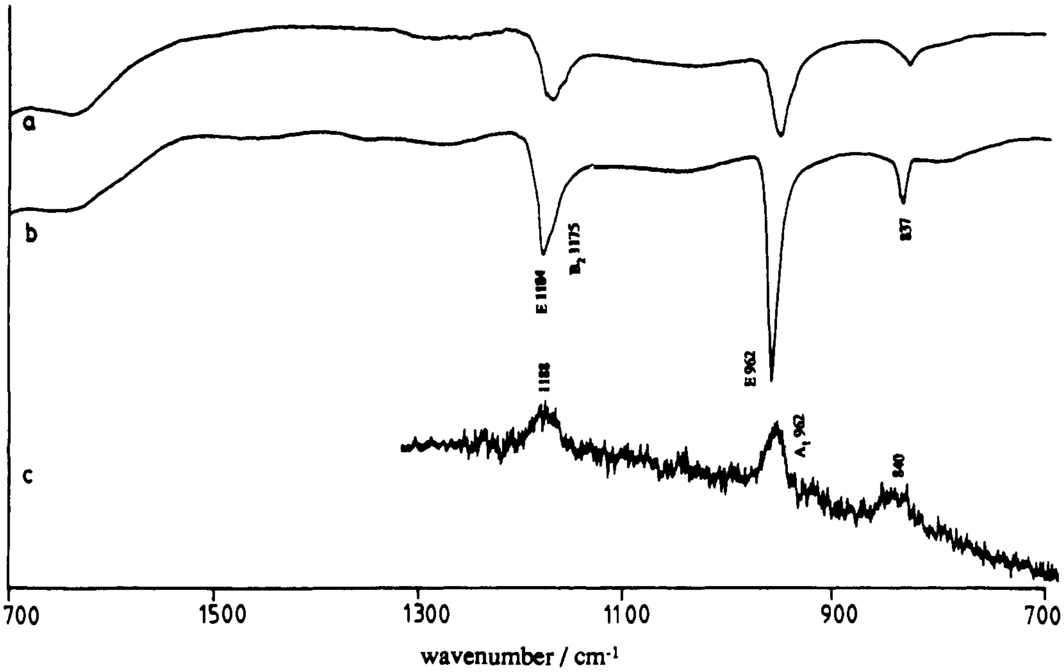

Figure 2. Solid-state infrared [(a) 300 K and (b) 100 K] and Raman [(c) 300 K] spectra in the metal-deuterium stretching region of $[D_4Os_4(CO)_{12}]$.

The infrared and Raman spectra[3] of the H_4, D_4, and H_2D_2 isotopomers of the ruthenium cluster have previously been discussed by Andrews, Kirtley, and Kaesz[4] (AKK). They were unable to reconcile the available spectra with models that involved either all four hydride vibrators coupled over the D_{2d} molecular symmetry or individual uncoupled hydrides on C_2 sites. In the present paper, we show first that the data of AKK were incomplete, since they did not identify a third band in the ν_{MH} region of the spectra. Second, we show that our spectra are indeed consistent with D_{2d} molecular symmetry, provided one considers some additional correlation with the D_{4h} symmetry of the four hydride ligands taken in the absence of the remainder of the cluster. The coupling between the M_2H units, although sufficient to necessitate a D_{2d} molecular model, is however comparatively weak, as AKK had concluded.

Results

Infrared (recorded at 300 and 100 K) and Raman spectra of the clusters $[X_4Os_4(CO)_{12}]$ (X = H, D) in the ν_{M_2H} or ν_{M_2D} regions are shown in Figures 1 and 2. Infrared spectra (100 K) over the 700–400-cm^{-1} region are shown in Figure 3. Frequencies are collected in Table I.

Discussion

The Pseudo-D_{4h} Model. Before proceeding to assign the spectra of the clusters, we propose a model which is of use in predicting the relative intensities of some of the modes. We first recognize that the four hydride ligands lie, essentially, at the corners of a

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[3] Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

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Table I

$[H_4Os_4(CO)_{12}]$		$[D_4Os_4(Co)_{12}]$		$[H_4Ru_4(CO)_{12}]$		$[D_4Ru_4(CO)_{12}]$		assignt[a]	
IR	R	IR	R	IR	R	IR	R		
1634 mw	1624 v br	1175 w, sh	1188 vw, br	ca. 1590 vw, sh	1585 w, br	ca. 1170 vw	1160 m	B_2	ν_{M_2H}(asym)
1619 m		1184 mw		1607 vw, br				E	
1598 vw, sh								A_2	
1382 vw, sh	1385 w, sh			1295 w, sh				B_1	ν_{M_2H}(sym)
n.o.	1371		962 m, br		1290 m		912 m	A_1	
1364 mw		962 m		1290 mw		907 mw		E	
1277 vw				1161 w				$E(A_2 + E)$	$2\gamma_{M_2H}$
1245 mw	1250 w, br				ca. 1190 vw, br			$A_1(2B_2, 2E)$	
1225 w, sh				1194 mw				$E(B_2 + E)$	
645 w, sh				608 vw, sh				A_2	γ_{M_2H}
638 vs	641 vw	(542/540) m		614 vs	618 w	(508/506) m		E	
632 vs		516 m		620 ms		489 m		B_2	

[a] Symmetry species in parentheses refer to the combinations and overtones of the deformation fundamental modes giving rise to the observed features.

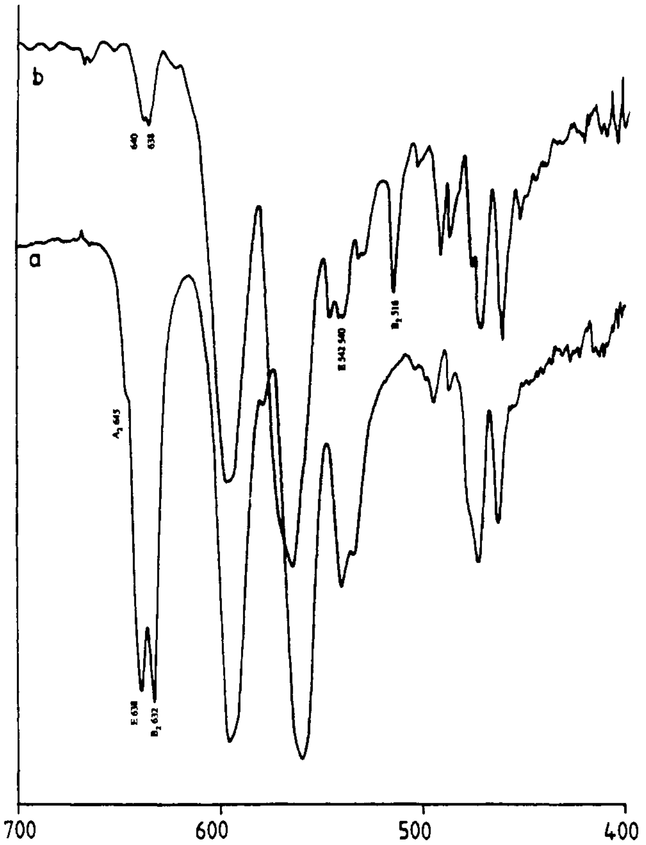

Figure 3. Solid-state infrared spectra at 100 K in the 700–400-cm^{-1} region of (a) $[H_4Os_4(CO)_{12}]$ and (b) $[D_4Os_4(CO)_{12}]$.

square;[2] the H_4 unit thus has D_{4h} symmetry if the rest of the cluster is neglected. In particular, the physical forms of the ν_{MH}(sym) modes under this pseudo-D_{4h} symmetry closely resemble those under D_{2d} as far as the hydrogen motion is concerned. The group-theoretical selection rules under D_{4h} are more stringent than for D_{2d}, and we will show that the observed spectra are explicable if the D_{4h} rules retain some applicability in D_{2d}.

The situation is less clear-cut for the ν_{M_2H}(asym) and γ_{M_2H} modes; they transform isomorphically under D_{2h} (as $A_2 + B_2 + E$), but their symmetry coordinates do not correspond directly with any in the D_{4h} model. It is necessary to decompose these modes into components parallel to the molecular $C_2(2)$ axis (C_4 axis in D_{4h}) and tangential to it. These parallel and tangential coordinates span $A_{2u}(IR) + B_{2u}(-) + E_g(R)$ and $A_{2g}(-) + B_{2g}(R) + E_u(IR)$, respectively, under D_{4h}, correlating with $B_2(IR,R) + A_2(-) + E(IR,R)$ under D_{2d}. It is clear that if the $A_2 + B_2 + E$ modes spanned by, e.g., ν_{M_2H}(asym) were close to those appropriate to D_{4h}, then, although both B_2 and E modes are formally both infrared and Raman active in D_{2d}, the actual activity would be in the form of a complementary pair, with one showing only infrared activity and the other only Raman. If, however, the D_{2d} modes do not approach the D_{4h} limits, then the B_2 and E modes are likely each to have appreciable Raman and infrared intensities.

Assignment of the Spectra. For the sake of clarity, the discussion will refer mainly to the spectra of the osmium clusters, except where the spectra of the ruthenium clusters differ significantly.

Consideration of Figure 1 shows that there are three regions of infrared and Raman activity in the frequency range associated with metal–bridging hydride stretching modes, at ca. 1625, ca. 1370, and ca. 1245 cm^{-1}. All these show significant sharpening on cooling and shift to lower frequencies on deuteration. Since the bond angles at the hydride ligands are significantly greater than 90°,[2] it is reasonable to assign the bands at ca. 1625 cm^{-1} to the antisymmetric Os–H stretching modes.[5] The splitting between the remaining two sets of bands (ca. 120 cm^{-1}) is much too large to result from site splitting of the E component of ν_{Os_2H}(sym); no such splitting could be resolved for ν_{Os_2H}(asym) and γ_{Os_2H} (vide infra). Since the relative intensities of the bands are the same for independently prepared (and analytically pure) samples, neither band can be explained as resulting from an impurity. The out-of-plane deformation modes of the hydride ligands are expected at ca. 700 cm^{-1},[6] and it thus appears likely that one of the bands results from enhancement of the overtone of the deformation mode by Fermi resonance with ν_{Os_2H}(sym). AKK appear not to have identified the counterpart of the lowest frequency band in the spectra of $[H_4Ru_4(CO)_{12}]$. Before making any detailed analysis of the ν_{Os_2H} modes, it is clearly necessary first to assign the deformation modes at lower frequency.

The Out-of-Plane Deformation Mode (γ_{M_2H}). Figure 3 shows the infrared spectra of $[H_4Os_4(CO)_{12}]$ and $[D_4Os_4(CO)_{12}]$ in the 700–400-cm^{-1} region. It is clear that the very strong bands at 638 and 632 cm^{-1} shift on deuteration and can be assigned to the hydride deformation modes. At first sight, it seems reasonable to assign the bands to the split E component of the D_{2d}-coupled modes. However, the 638-cm^{-1} band is significantly broader, and in the ruthenium cluster the two bands are of dissimilar relative intensities. We therefore assign the broader 638-cm^{-1} band to the E mode and the 632-cm^{-1} band to the B_2 component. This is consistent with the D_{4h} model. Consideration of the cluster geometry shows that the vectors corresponding to γ_{M_2H} and ν_{M_2H}(asym) for an M_2H unit subtend angles of ca. 48 and ca. 42°, respectively (i.e. close to 45°), with the molecular 2-fold axis.[2]

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Hence, the parallel and tangential components of each mode are of comparable magnitude, and neither D_{4h} limit is approached. The B_2 and E γ_{Os_2H} modes might then be expected to have basically comparable intensities; certainly it is very unlikely that the E mode should be very strong and the B_2 weak or unobserved. The spectrum of the deuterated cluster shows two weak bands at 638 cm^{-1}, corresponding to the γ_{Os_2H} mode of the $[HD_3Os_4(CO)_{12}]$ isotopic impurity; the slight splitting reflects the crystallographically distinct sites for the hydrides. It is to be expected that the center of gravity of the γ_{Os_2H} modes in the H_4 cluster will approximate to these frequencies of vibrationally isolated hydride vibrators; accordingly, the vibrationally silent (under strict D_{2h} symmetry) A_2 mode might be expected in the 640–645-cm^{-1} region. A reproducible shoulder is observed at 645 cm^{-1} and is tentatively assigned to the A_2 mode. In the Raman spectrum, a very weak band can just be observed at 641 cm^{-1}. Although it is intermediate in frequency between the IR features assigned to the E (638 cm^{-1}) and A_2 (645 cm^{-1}) modes, we assign it to the E mode, since it is unlikely that the formally inactive A_2 mode would have observable Raman intensity while the B_2 and E modes do not.

On deuteration, most of the bands in this region are shifted in frequency and show small changes in intensity, indicating some weak coupling between γ_{Os_2H}, γ_{Os_2D} and the δ_{OsCO} and δ_{OsC} modes. However, the band at 560 cm^{-1}, which shifts to 565 cm^{-1} and gains relative intensity on deuteration, is clearly more strongly coupled to one of the hydride (deuteride) modes. The B_2 mode appears to have shifted to 516 cm^{-1}, giving rise to a sharp band of medium intensity. The E mode appears to have shifted into the cluster of bands at 546–532 cm^{-1}; although formally assigned to the doublet at 541 cm^{-1} in Table I, some of the E vibration has probably been mixed into the neighboring carbonyl modes.

The γ_{Ru_2H} modes can be similarly assigned. It is interesting that the frequency order $B_2 > E > A_2$ is the reverse of that found in the osmium cluster. The low Raman intensities of these modes is also of note. This may be a consequence of the spherical symmetry of the hydrogen 1s orbital. As the hydride rotates about the metal–metal vector (as opposed to stretching the M–H bonds), the change in polarizability in any direction is likely to be low.

The Symmetric Metal–Hydride Stretch (ν_{M_2H}(sym)). If the four M_2H coordinates are coupled over D_{2d} molecular symmetry, the modes span the $A_1(R) + E(R,IR) + B_1(R)$ irreducible representations. As noted by AKK, both the infrared and Raman intensities are concentrated in single, noncoincident, bands, which seem to be inconsistent with either the D_{2d} or the local C_2 model. These noncoincidences can be explained with the use of the pseudo-D_{4h} model.

Under D_{4h}, the modes span $A_{1g}(R) + E_u(IR) + B_{1g}(R)$. By comparison with the D_{2d} activities given earlier, it is likely that under D_{2d} the Raman activity of the E mode will be negligible, since the physical motion of the hydrides is essentially the same as in D_{4h}, where the Raman activity is identically zero. Further, we must expect the intensity of $B_1(R)$ (and of $B_{1g}(R)$ in D_{4h}) to be low. Because of the spherical symmetry of the hydrogen 1s orbital, the derived polarizability tensor associated with each ν_{M_2H}(sym) local coordinate is likely to be relatively symmetrical. Consider the case in which it is of circular cross section in the σ_h plane (in D_{4h}). In this case simple tensor addition gives $B_1(D_{2d})$ (and, of course, $B_{1g}(D_{4h})$) zero Raman activity. Most, if not all, of the Raman intensity then resides in the $A_1(D_{2d})/A_{1g}(D_{4h})$ mode. Only if the derived polarizability tensor has a nodality pattern akin to that of a $d_z{}^2$ orbital could this argument be reversed and the observed Raman band at 1371 cm^{-1} assigned as B_1. This situation is highly improbable, and we assign the band as A_1.

If the Raman spectrum is recorded at 100 K, a weak shoulder at 1382 cm^{-1} is observed, and we assign this to the B_1 mode. The infrared band at 1364 cm^{-1} is obviously assigned to the E mode; a very weak shoulder at 1382 cm^{-1} can presumably also be assigned to the B_1 mode. Since the γ_{Os_2H} modes are all at ca. 640 cm^{-1}, we recognize that overtones will occur at ca. 1280 cm^{-1}. Noting that under local site symmetry (C_2) both ν_{Os_2H}(sym) and the overtone of γ_{Os_2H} are of the same (totally symmetric) symmetry species, we must recognize the possibility of Fermi resonance. Since ν_{Os_2H}(sym) is expected to be of significant intensity in the Raman spectrum, we assign the bands at ca. 1370 cm^{-1} largely to ν_{Os_2H}(sym) modes and those at ca. 1245 cm^{-1} largely to the overtone of the deformation.

The infrared band found at 1245 cm^{-1} is assigned to the γ_{Os_2H} combination mode $(B_2 + E) = E$, enhanced by strong Fermi resonance with the E component of ν_{Os_2H}(sym) found at 1364 cm^{-1}. The strength of the resonance interaction is indicated by the comparable intensities of the two bands and by the significant frequency shift of the combination band from the sum of the frequencies of the two fundamentals (1270 cm^{-1}). The weaker band at 1277 cm^{-1} can be assigned to the $A_2 + E$ combination mode. The frequency order of the two combination bands in the infrared spectrum of $[H_4Ru_4(CO)_{12}]$ reflects the inverted order of the fundamentals (vide supra). Consideration of the Raman intensities indicates that Fermi resonance between γ_{M_2H}(sym) (A_1) and the overtones of the γ_{M_2H} modes is much weaker than that observed in the infrared spectrum, as is generally the case.

On deuteration, γ_{Os_2D}(sym) appears at 962 cm^{-1} in the infrared spectrum. The weak band at 837 cm^{-1} is probably too low in frequency to result from combinations of hydride deformation modes and is assigned to a combination or overtone of a carbonyl deformation mode. Since the deuteride deformation symmetry coordinates are mixed into a number of normal modes in the 550–510-cm^{-1} region, anharmonics of these modes might be expected to give rise to a number of weak bands, forming a broad unresolved envelope, rather than the individual well-resolved bands found for the H_4 clusters.

A very weak and broad feature at 1440–1470 cm^{-1} in the Raman spectrum of $[H_4Ru_4(CO)_{12}]$ can be assigned to the combination of γ_{Ru_2H}(sym) and the two ν_{RuRu} modes of A_1 symmetry at 199 and 146 cm^{-1}.[7]

The Antisymmetric Metal–Hydride Stretch. Coupling of γ_{M_2H}(sym) over D_{2d} symmetry gives rise to modes of symmetries $A_2(-) + B_2(IR,R) + E(IR,R)$, the same as did γ_{M_2H}. As was the case with the deformation modes (vide supra), both the B_2 and E modes are predicted to have significant intensity in the infrared and Raman spectra.

The infrared band at 1620 cm^{-1} in the spectrum of $[H_4Os_4(CO)_{12}]$ splits into components at 100 K, at 1634 and 1619 cm^{-1}. Rather than assign these to the split E mode, we prefer to assign them to the B_2 and E modes, respectively. The 1619-cm^{-1} band is significantly the broader, and no site splitting was noted on the other hydride modes. The weak shoulder at 1598 cm^{-1} is resolved into a reproducible peak in very concentrated KBr disks and is assigned to the A_2 mode. The Raman band at 1624 cm^{-1} is broad and probably contains intensity from both the E and B_2 modes. On deuteration, the B_2 mode is only visible as a shoulder. For the ruthenium cluster, ν_{Ru_2H}(asym) is weak and the B_2 mode is only visible in the infrared spectrum as a slight asymmetry on the low-frequency side of the E mode at 1607 cm^{-1}. On the deuteration, ν_{Ru_2D}(asym) is only just visible on the infrared spectrum but can be observed clearly in the Raman spectrum.

Conclusions

This detailed study of the hydride modes in $[H_4M_4(CO)_{12}]$ (M = Ru, Os) has shown that vibrational coupling between the hydride vibrations is weak but sufficient for a description of the modes under molecular D_{2d} symmetry to be necessary. For some of the modes, the Raman and infrared intensities were found to correlate with those predicted by a model in which the hydrogens are considered in isolation from the rest of the cluster. The spherical symmetry of the hydrogen 1s orbital also has an effect on some Raman intensities, which facilitates assignment of the Raman spectra.

It is clear that a normal-coordinate analysis of the hydridic modes is unlikely to yield any useful results. Both γ_{M_2H}(sym) and γ_{M_2H} are strongly perturbed—the former by strong Fermi resonance with combinations and overtones of the hydride deformation

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modes and the latter through strong coupling to carbonyl modes (particularly in the D_4 clusters)—and only ν_{M_2H}(asym) is likely to be a "pure" mode.

It is to be hoped that the principles we have used in this study may enable the spectra of other clusters with multiple hydride ligands to be interpreted satisfactorily.

Experimental Section

$[H_4Ru_4(CO)_{12}]$ and $[D_4Ru_4(CO)_{12}]$ were prepared by the literature method.[3] Samples of $[H_4Os_4(CO)_{12}]$ and $[D_4Os_4(CO)_{12}]$ were kindly provided by Dr. B. F. G. Johnson, University of Cambridge. Infrared spectra of samples in KBr disks were measured on a Digilab FTS-20 FT-IR spectrophotometer; an RIIC low-temperature cell with liquid N_2 as coolant was used for the low-temperature (ca. 100 K) spectra. The Raman spectra were recorded on a Model 1401 Spex Raman spectrophotometer, equipped with a Spectra Physics Model 165 Kr ion laser (exciting line 647.1 nm) with incident power of ca. 250 mW.

Acknowledgment. P.L.S. and S.F.A.K. are indebted to NATO for financial support. The Italian Ministero delle Pubblica Istruzione is thanked for a grant (to R.R.). We are grateful to the SERC for assistance toward the purchase of a replacement laser tube.

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Investigation of the Redox States of $[Ru(bpy)_2CN]_2CN^+$: Evidence for Valence Delocalization of the Singly Oxidized Complex

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A spectroelectrochemical study of both the oxidized and reduced forms of $[Ru(bpy)_2CN]_2CN^+$ is reported. Th UV–vis spectra of the parent and reduced species indicate that the complex consists of two identical chromophores, which are nearly identical with the $Ru(bpy)_2(CN)_2$ chromophore, even though one ruthenium is bound to the carbon of the bridging CN while the other is nitrogen bound. Only the shift in the bridging CN stretching frequency with reduction offers any distinction between the two metal centers. The one-electron oxidation product of the bimetallic species is assigned as valence delocalized on the basis of the following observations: (1) only two CN stretches are observed in the oxidized form, (2) the shift to higher energy of the terminal CN stretches for the bimetallic species is half of that observed upon oxidation of the monometallic complex, (3) the sharpness and solvent independence of the near-IR band is not consistent with Hush predictions for the IVT band, and (4) the separation of the oxidation waves implies a comproportionation constant for the bimetallic species of 1.38×10^{10} (assuming no difference in metal centers) comparable in magnitude to other delocalized systems.

Introduction

Recently, there has been a great deal of interest in the synthesis of new coordination compounds in which a photosensitizer center is bound to a reactive center that acts as an electron donor, electron acceptor, or energy acceptor.[1] The presence of both moieties in the same complex alleviates the need for long photosensitizer lifetimes as well as high concentrations of the reactive moiety. These multimetallic coordination compounds are also being suggested as possible multielectron donors or acceptors, a necessary requirement for artificial photosynthesis.[1,2] Another application is the design of supramolecular photochemical devices using these coordination compounds as building blocks.[2] Central to the design of all of these schemes is the requirement of efficient electron or energy transfer between the two centers. Since there is usually no direct overlap between two metal centers, the transfer pathway is mediated by the bridging ligand. Several methods for evaluating the degree of communication between the centers exist in the literature.[3–17] With the synthesis and subsequent investigations of the Creutz–Taube ion, a great deal of controversy has arisen concerning strongly interacting systems approaching a delocalized limit in terms of the valence shell.[3–17] Theoretical treatments of these systems have contributed much to the basic understanding of electron-transfer theory.[4,11–13,15,18–30] The complex $[Ru(bpy)_2CN]_2CN^+$, thus, has multifold aspects of interest. It not only meets the requirements of a photosensitizer strongly absorbing in the visible region and possessing a long-lived emission (τ = 90 ns)[14] but also possesses additional coordination sites (CN) so that supramolecular species can be made. Indeed, such systems based on a $[Ru(bpy)_2CN]_2CN^+$ building block have already been reported.[2] In addition, the mixed-valence species offers the op-

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