Figure 3 compares rates for *N*-methyldihydrophenazine with those for $Ru(NH_3)_6^{2+}$, a prototype outer-sphere metal-center reductant. Here the correlation has been eroded, nor is it restored if specific rates pertaining to other metal ion reducing centers are substituted for those of $Ru(NH_3)_6^{2+}$ or if rates for another dihydro species replace those for the methylphenazine derivative. The severity of scatter in these cases serves to remain us that Marcusian proportionalities between redox rates are generally to be expected only if the reagents being compared have closely related structures.[30]

An earlier report,[10b] however, describes a group of oxidants that conform particularly closely to the Marcus picture. These are $(NH_3)_5Co^{III}$ derivatives of N-donor ligands, the structures of which dictate outer-sphere reduction. Within this series, rates of reduction by a number of pyridine-derived radicals have been found to be proportional to rates for metal ion reductants, provided that the former do not lie too close to the diffusion-controlled limit. If oxidants of this type, which are designated in Figure 3 as solid circles, are considered to establish a "normal" pattern,[31] then the $Ru(NH_3)_6^{2+}$ reductions of the pyruvato (pyruv) and phenylglyoxylato (Phg) complexes, and most especially, the chloro complex,[32] may be presumed to enjoy an extra kinetic advantage over the corresponding reductions by the dihydro reductant. Since this advantage cannot be attributed to the intervention of an inner-sphere component, we suspect that it reflects a directionally favorable path for $Ru(NH_3)_6^{2+}$, in which the positive metal center approaches the oxidant through the chloride ligand or, in the case of the keto–acid complexes, through the negative end of the C=O dipole. With aromatic reductants, an analogous path may be presumed to be much less favorable due to electrostatic repulsion between the negative end of the dipole (which faces

outward) and the π-electron regions shielding the ring.

Finally, this work bears upon the question, already considered by others,[3a,33] as to how drastically the flavin system may be modified without affecting its electron-transfer behavior. We have seen that replacement of the 1-N in riboflavin (V) with C–H (yielding the 1-deaza compound, VI) desta-

V   VI

VII

R = ribosyl

bilizes the semiquinone (radical) state of the flavin perceptibly but does not significantly alter the reactivity pattern of the dihydro species. In contrast, replacement of the 5-N yields the 5-deaza compound, VII, which undergoes reduction with much greater difficulty than its isosteres V and VI in strongly acidic media; only a small steady-state concentration of its radical is formed under conditions where reductions of V and VI are virtually complete. This is not at all surprising, for in the 5-deaza compound the pyrazine-like system comprising the central ring has been disrupted. It is the second nitrogen, a strongly electron-attracting center being in the same ring as N-1 and conjugated with the latter, which, more than any other feature, may be held responsible for the ease with which the flavin system is reduced.[34]

(30) This statement implies also that the members of any reaction series used to establish such proportionalities should be of related structural types.
(31) Rates for these five oxidants, indicated by solid circles, conform to the relationship

$$\log k(\text{PhMeH}) = 0.88 \log k(\text{Ru}) + 2.85$$

with a correlation coefficient of 0.960.
(32) Similarly striking departures from linearity involving reactions of $(NH_3)_5CoCl^{2+}$ have been observed in earlier comparisons[10c,11b] of $Ru(NH_3)_6^{2+}$ rates with those for aromatic reductants.

(33) Spencer, R.; Fisher, J.; Walsh, C. *Biochemistry* **1977**, *16*, 3586.
(34) See, for example: Fanchiang, Y.-T.; Thomas, J. C.; Neff, V. D.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1942.

An Assignment of the ν(CO) Spectra of $H_4M_4(CO)_{12}$ (M = Ru, Os)

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The *P*Ī space group in which they crystallize enables an assignment of the ν(CO) vibrational spectra of the title compounds. Correlation with a tetrahedral $M_4(CO)_{12}$ molecule together with qualitative intensity and interaction considerations is invoked.

The ability to qualitatively interpret the ν(CO) vibrational spectra of simple transition-metal carbonyls has been of considerable utility.[1] It is therefore unfortunate that it has so far not proved to be possible to generally extend this method to the ν(CO) vibrations of carbonyl cluster compounds, although recent detailed analyses of the ν(CO) spectra of some species of relatively high symmetry provide insight into both

the general problem and its solution.[2–4] Such analyses are rather exceptional since the number of symmetry-distinct interaction constants exceeds the number of observables and thus

(1) P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, New York, 1975; S. F. A. Kettle, *Top. Curr. Chem.*, **71**, 111 (1977).
(2) G. Bor, G. Sbrignadello, and F. Marcati, *J. Organomet. Chem.*, **46**, 357 (1972).
(3) G. Bor, G. Sbrignadello, and K. Noack, *Helv. Chim. Acta*, **55**, 815 (1975).
(4) G. A. Battison, G. Bor, U. K. Dietler, S. F. A. Kettle, R. Rossetti, G. Sbrignadello, and P. L. Stanghellini, *Inorg. Chem.*, **19**, 1961 (1980).

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inhibits band assignment. In the present paper, we present assignments of the vibrational spectra of two species for which only frequency data have been available. We do this in the light of the detailed analyses mentioned above. In addition, we exploit both insights gained through correlation methods and a favourable aspect of the crystal structure.

The compounds $H_4M_4(CO)_{12}$ (M = Ru, Os), which are the object of the present study, have D_{2d} symmetry and are poorly soluble. They therefore represent a much more difficult problem than the soluble T_d species $M_4(CO)_{12}X_4$ (M = Mn, Re; X = SR, SeR), which have been the subject of previous studies.[5,6] We shall proceed by exploring the source of the difficulties in some detail before describing the way we have attempted to overcome them.

The compound $H_4Ru_4(CO)_{12}$ crystallizes in the $P\bar{1}$ space group with Z = 2.[7] The existence of a center of symmetry in the unit cell means that there will be a mutual exclusion between the infrared and Raman spectra of crystalline samples, provided that intermolecular vibrational coupling occurs. There is no doubt that such coupling is general for species containing a high proportion of terminal carbonyl groups and is certainly to be expected for the present species. However, some $\nu(CO)$ modes may not be involved in intermolecular vibrational coupling, in which case spectral coincidences will occur. Such coincidences may be accidental but would then be unlikely to generally persist when more than one isomorphous isostructural compound is studied. The crystal structure of $H_4Os_4(CO)_{12}$ has recently been determined, and it has been found to be isomorphous with the ruthenium compound.[8] We are therefore able to discuss the vibrational spectra of both species because similar considerations apply. In the event, the spectra of the two species serve to illuminate each other. The fact that Z = 2 in a $P\bar{1}$ unit cell means that the infrared and the Raman spectra of crystalline samples will individually be interpretable on a molecular basis (modified by the recognition of the C_1 site symmetry in the lattice). However, if both spectra are considered together, it will be clear that a molecular interpretation is not appropriate unless correlation effects are absent. These considerations are important for $H_4M_4(CO)_{12}$ (M = Ru, Os) because of their low solubility, which precludes solution Raman measurements and solution infrared overtone measurements. In this paper we report the infrared spectra of solution and crystalline materials and the Raman spectra of polycrystalline samples in the 2000-cm^{-1} region.

Detailed analyses of the $\nu(CO)$ vibrational spectra of carbonyl cluster compounds containing two metal atoms have shown the necessity of including vibrational coupling between terminal CO groups on different metal atoms. The generality of this necessity is also evident in the spectra of large cluster species—there are too many bands to be interpreted on a local molecular site-symmetry basis. The idealized molecular symmetry of $H_4M_4(CO)_{12}$ species is D_{2d}, there being three carbonyl groups on each metal atom and a hydrogen atom briding each of the four "equatorial" M–M bonds. From this geometry it follows that 14 different $\nu(CO)$ bond stretching and interaction force constants would be involved in a full $\nu(CO)$-only vibrational analysis. The CO stretching vibrations of the carbon monoxide group subtend a representation that has the direct sum $2 A_1 (R) + A_2 + B_1 (R) + 2 B_2 (R, IR) + 3 B (R, IR)$, spectral activities being given in parentheses. That is, there are, in principle, only eight observable frequencies in the fundamental region. The molecular vibrational

problem is seriously underdetermined. In the present study, we largely circumvent these problems by a combination of symmetry correlations and inequality relations and by setting ourselves a lower goal: the assignment of symmetry labels to the spectral features. It is helpful toward this goal to first discuss the $\nu(CO)$ spectrum of an isolated $M_4(CO)_{12}$ unit of T_d symmetry.

Each $M(CO)_3$ unit in a tetrahedral $M_4(CO)_{12}$ molecule has C_{3v} symmetry, and the local A_1 and E vibrations provide convenient bases for a discussion of the $\nu(CO)$ vibrations of the entire molecule. In T_d the $A_1(C_{3v})$ functions give rise to $A_1 + T_2$ molecular vibrations and the $E(C_{3v})$ to $E + T_1 + T_2$. Of these, only the T_2 are infrared active. Because for molecules containing $M(CO)_3$ units it is commonly found that the vibration of $E(C_{3v})$ symmetry has approximately twice the infrared intensity of the $A_1(C_{3v})$, we would expect $T_2(E)$ to be somewhat more intense than $T_2(A_1)$, the species in parentheses indicating the C_{3v} basis. Mixing between these T_2 symmetry coordinates would be indicated by a depature from this simple intensity inequality. Because in C_{3v} it is invariably true that $\nu(A_1) > \nu(E)$ and because the noncrossing rule is applicable, we can safely correlate the higher frequency T_2 mode as $T_2(A_1)$ and the lower as $T_2(E)$. Nonetheless, it is important to recognize that what by correlation is labeled the $T_2(A_1)$ normal coordinate may contain more of the $E(C_{3v})$ coordinate than it does $A_1(C_{3v})$!

In the Raman spectra of $M(CO)_3$ units it is commonly found that $I(E) > I(A_1)$, and so we might expect arguments analogous to those developed above for the infrared spectra to be applicable to the Raman. However, it is necessary to recognize that the intensity parallel between infrared and Raman intensities is *unlikely* to persist on further mixing (i.e., on passing from C_{3v} to T_d). This ascent in symmetry leads to a vector sum of local components in the case of the infrared spectra but a tensor sum for the Raman. Whereas the local infrared vector is defined by a single quantity (the derived dipole; its direction is symmetry determined), three quantities are needed to define the Raman tensor. Further, these derived polarizabilities may well differ in sign.[9] It follows that a "molecular" vibration that has high infrared activity may or may not have a strong band in the Raman spectrum.[10] That is, it is entirely possible that, even if there is a sharing of infrared intensity between the $T_2(A_1)$ and $T_2(E)$ coordinates, there could be a corresponding localization of Raman intensity. Finally, we note that in $M_4(CO)_{12}$ species the $\nu(CO)$ E vibration is Raman active but can make no general comment on its intensity.

Because the coupling between the intervening internal vibrational coordinates, M–C, M–M, and M–C, is small, it seems likely that the coupling between terminal CO groups on different metal atoms in a cluster is in large measure mediated by a "through-space" mechanism. That is, intramolecular vibrational coupling between $M(CO)_n$ units may well occur by a mechanism similar to the intermolecular vibrational coupling often found between different carbonyl molecules in the same lattice. The observation that molecular $\nu(CO)$ E_g modes—which do not subtend a dipole—are intermolecularly coupled in crystalline metal hexacarbonyls[11] indicates the inadequacy of a simple transition dipole–transition dipole coupling model. While it would be unwise to place great faith in it in the intramolecular case, it may, nonetheless, give

(5) P. S. Braterman, *J. Chem. Soc. A.* 907 (1968).

(6) E. W. Abel, P. J. Hendra, R. A. N. McLean, and M. M. Qurashi, *Inorg. Chim. Acta*, 3, 77 (1969).

(7) R. D. Wilson, S. M. Wu, R. G. Lane, and R. Bau, *Inorg. Chem.*, 17, 1271 (1978).

(8) B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *Acta Crystallogr., Sect. B*, B37, 1728 (1981).

(9) S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc., Dalton Trans.*, 2413 (1972).

(10) The force of this argument is easy to demonstrate in a simple case. The $\nu(CO)$ vibration of a single coordinate CO group is both infrared and Rama active. However, when six are octahedrally coordinated to a single metal atom, the molecular $\nu(CO)$ vibrations are either infrared or Raman active, never both.

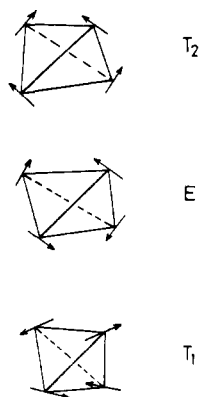(11) D. N. Kariuki and S. F. A. Kettle, *Inorg. Chem.*, 17, 141 (1978).

Figure 1. Dipolar patterns associated with π-type vibrations in a tetrahedral species.

some guidance. In Figure 1 we show, schematically, representative T_2, E, and T_1 modes derived from $E(C_{3v})$, depicted in terms of dipole moment changes. Of these, in the T_1 mode the interactions between any pair of dipoles is either attractive—the "head" of one dipole being close to the "tail" of another—or zero, suggesting that this T_1 mode will have the lowest frequency. For both the T_2 and E vibrations the "top" pair of dipoles in the tetrahedra of Figure 1—and also the "bottom" pair—are in phase. The two vibrations differ in the phase relationship between "top" and "bottom" pairs. This "top"–"bottom" interaction is probably attractive for the E vibration but repulsive for the T_2. This is best seen in Figure 1 by comparing the relative orientations of dipoles at either end of arms of the of the central X (one arm is dotted) in each diagram, although it is to be recognized that these diagrams effectively show projections. These arguments suggest a frequency order

$$\nu(T_2) > \nu(E) > \nu(T_1)$$

which is consistent with our interpretation of the spectral data we present.

Turning now to the $A_1(C_{3v})$-derived modes, we note that is seems invariably true that the highest frequency mode in metal clusters is totally symmetric; dipole arguments corresponding to those presented above for the $E(C_{3v})$-derived features lead to the same conclusion. We therefore have

$$\nu(A_1) > \nu(T_2)$$

These arguments are summarized in Figure 2a. The juxtaposition of two T_2 modes in Figure 2a suggests that mixing will occur between them. Such a mixing is indicated in Figure 2b, which shows the descent in symmetry from T_d to D_{2d} and the consequent spectral activities. Because the T_1 mode is silent in T_d, the derived E mode in D_{2d} will only gain infrared and Raman intensities by mixing with the E modes derived from the active T_2 modes. It seems likely that one E mode will be much weaker than the other two.

In Figure 2b we have placed the B_2 components of the T_2 modes at higher frequency than the E. There is a simple reason for this. The vibrations are shown for the $A_1(C_{3v})$ derived modes in Figure 3. If the bond (f) and interaction (f_s, short M–M bond; f_l, long M–M bond) force constants are as defined in Figure 3, then the F matrix element for the B_2 vibration is

$$f + f_s - 2f_l$$

whereas that for the E vibrations is

$$f - f_s$$

Because, surely, $f_s > f_l$, we have $\nu(B_2) > \nu(E)$. Entirely similar arguments apply to the $E(C_{3v})$-derived modes.
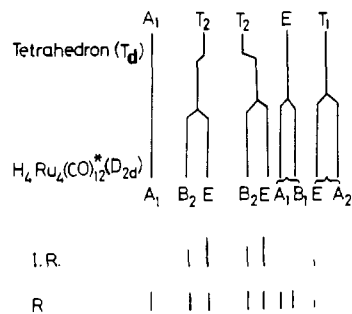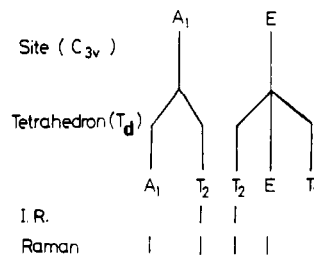
* for the modifications appropriate to H₄Os₄(CO)₁₂ see the text.

Figure 2. Correlations between (a, top) C_{3v} and T_d and between (b, bottom) T_d and D_{2d} $\nu(CO)$ coordinates, together with the corresponding associated spectral patterns expected.
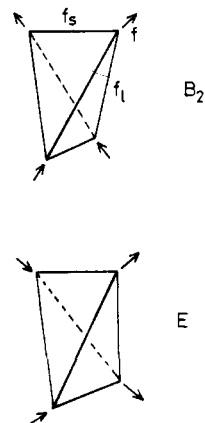

Figure 3. Schematic B_2 and E symmetry coordinates in a D_{2d} species.

Finally, we expect each B_2/E pair in the infrared spectrum to have an approximate 1:2 intensity ratio because of their common T_2 parentage. The solution infrared spectrum of the ruthenium compound is in excellent accord with these expectations (Figure 4a), with two sets of B_2/E pairs. The lowest frequency, relatively weak, band is assigned to the E mode of $T_1(T_d)$ parentage.

The solution infrared spectrum of the osmium compound is shown in Figure 4b and may be interpreted similarly. The lower frequency B_2 mode appears to be absent, but we believe that it is coincident with its E partner at 2022 cm⁻¹. This conclusion is supported by intensity arguments. The 2022-cm⁻¹ peak (Os) has an appreciably higher relative intensity than the 2025-cm⁻¹ peak in the ruthenium compound. Further, the higher intensity of the 1999-cm⁻¹ (E) band (Os) relative to its ruthenium counterpart would lead us to expect a lower, not higher, relative intensity for the 2025-cm⁻¹ band since it is from this latter band that the majority of its intensity may be regarded as being derived.
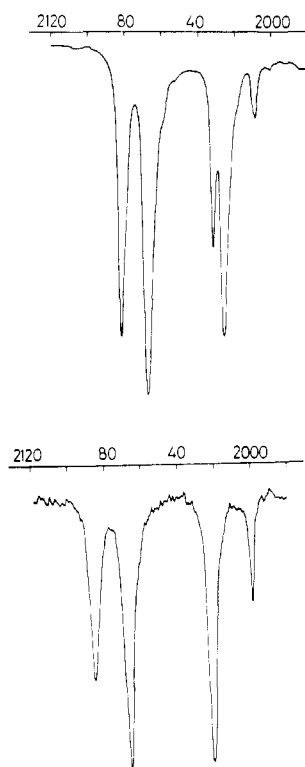
Figure 4. Infrared spectra of *n*-heptane solutions with background subtracted: (a, top) $H_4Ru_4(CO)_{12}$; (b, bottom) $H_4Os_4(CO)_{12}$.
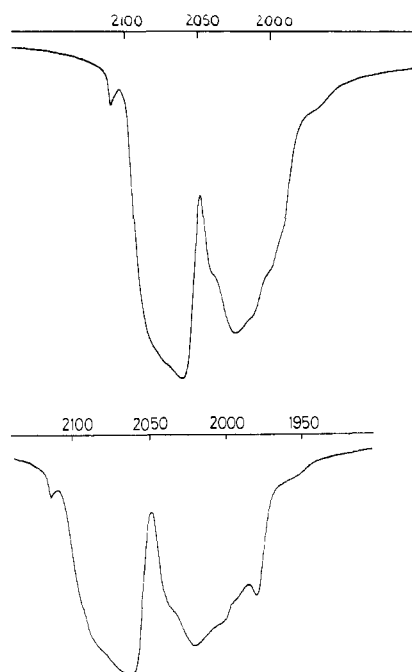
Figure 5. Infrared spectra of crystalline species: (a, top) $H_4Ru_4(CO)_{12}$; (b, bottom) $H_4Os_4(CO)_{12}$.

We now turn to the vibrational spectra of the crystalline materials and recall that we expect both infrared and Raman spectra to be interpretable on a molecular basis (but with a lack of agreement on frequencies). Because of the C_1 site symmetry, we must expect each E mode to be split into two components.

The infrared spectra (Figure 5) consist of broad bands (particularly for the osmium compound), but they are sufficiently well resolved for it to be clear that the above discussion permits a complete assignment. There is little evidence for intensity stealing by otherwise infrared-silent modes resulting
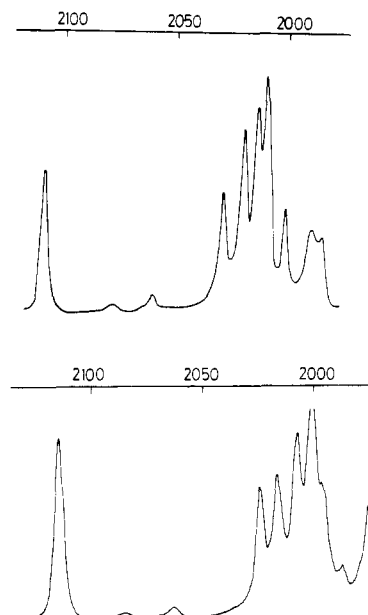
Figure 6. Raman spectra of crystalline species; (a, top) $H_4Ru_4(CO)_{12}$; (b, bottom) $H_4Os_4(CO)_{12}$.

from site-symmetry effects because the spectra of the crystalline materials have intensity patterns that follow from the solution spectra. The highest frequency A_1 mode appears weakly. Those modes that we have assigned in the solution spectra as E modes often split into components separated by ca. 10 cm⁻¹; the mean position of these components is within a few wavenumbers of the solution frequencies of the E modes. The lowest frequency $E(T_1)$ mode can be seen weakly resolved into two components in the ruthenium compound, but is clearly stronger in the osmium, in accord with the solution data; one component is rather sharp.

There is rather little difference between the two spectra in the ca. 2020-cm⁻¹ region, supporting the argument for coincidence of B_2 and E features in the solution osmium spectrum. The separation of these peaks in the solution infrared spectrum of the ruthenium compound is only 6 cm⁻¹ compared with the ca. 20-cm⁻¹ spread of features in the corresponding infrared spectrum of the solid; the frequency change of the B_2 mode on changing state is 8 cm⁻¹. If these quantities are approximately transferable to the osmium compound, then it is evident that there should be some correspondence between the infrared spectra of the two crystalline materials provided that the B_2 mode in osmium is not of negligible intensity but, rather, is coincident with the E peak.

We now turn to the Raman spectra of the polycrystalline materials (Figure 6) with only one additional comment: that in the absence of additional solid-state induced mixing we expect site-symmetry effects to split molecular E modes into two proximate bands of similar intensities. This comment is relevant because of the much sharper bands obtained in the Raman spectra compared to the infrared.

The assignment of the highest frequency A_1 mode is unambiguous. Almost as unambiguous is the appearance of only very weak features at frequencies approximating the very intense $T_2(A_1)$-derived peaks in the infrared spectra. Clearly, Raman intensity has been transferred to the lower frequency region, indicating mixing between the two $T_2(T_d)$ symmetry coordinates. Next, we note that, if a T_2 mode is split into three components, as here by a combination of molecular and site effects, we might expect, as a first approximation, three bands of equal intensity. This expectation is entirely consistent with the spectra in the 2020-cm⁻¹ region. The similarity between the ruthenium and osmium spectra in this region is striking and supports the conclusion derived from the infrared spectra

Table I

| $H_4Ru_4(CO)_{12}$ | | | Molecular Mode | $H_4Os_4(CO)_{12}$ | | |
Infrared Solution	Infrared Crystal	Raman Crystal		Raman Crystal	Infrared Crystal	Infrared Solution
	2111	2108	A₁	2115	2114	
2081	2083	2078	B₂	ca 2083	ca 2085	2086
2066.5	ca 2073 / 2061	2065 / 2060	E	ca 2063	ca 2069 / ca 2063	2067.5
2031	2039	2029	B₂	2024	ca 2035	
2025	ca 2025 / 2014	2020 / 2014	E	2017 / 2008	2020 / ca 2006	2022
		2010 / 2001	A₁ / B₁	2001 / 1976		
2009	ca 2000 / ca 1994	ca 1989 / 1985	E	ca 1993 / 1997 / 1987	1980	1999
			A₂			

that the B₂/split-E pattern is essentially the same for both species in the solid state.

There seems little doubt that peaks at 2010 (Ru) and 2002 cm⁻¹ (Os) should be assigned as one component of the E(T_d) mode, which splits in D_{2d} into A₁ + B₁. In the limiting E(T_d) mode both of these features would be of the same intensity (and degenerate). The distortion to D_{2d} will destroy this equality. These modes are Raman active and, because of the correlation shown in Figure 3, are expected to have appreciable intensity while being silent in the infrared spectra. For the same reason, to a first approximation we would expect the A₁ and B₁ modes to be of comparable intensities. This expectation seems to be born out in the ruthenium case where peaks at 2010 and 2001 cm⁻¹ may be assigned to this pair, the lower frequency band being the weaker. The rather broad peaks at ca. 1989 and 1985 cm⁻¹ are then assigned to the E(T₁) mode. If similar arguments are applied to the osmium case, then the A₁/B₁ splitting has to be rather larger, peaks at 2001 and 1976 cm⁻¹ being assigned to these modes on intensity grounds. The

weak peaks at 1997 and 1987 cm⁻¹ then become components of the splite E(T₁) mode. Alternative assignments of this lower frequency region are possible but that given above is the one which we prefer. The silent (in D_{2d}) A₂ mode may acquire some intensity because of the C_1 molecular site; we note that its frequency is expected to fall in this region. Its appearance may account for the triple-headed nature of the ca. 1990-cm⁻¹ peak in Figure 6b, but there is no corresponding feature in Figure 6a.

The assignments that arise from the above arguments are collected in Table I. Frequencies for the infrared spectra of the crystalline materials are, of course, rather approximate.

Conclusion

This paper is somewhat unusual in that it has taken detailed discussion of a variety of different pieces of evidence to lead to reasonably firm conclusions about the frequency order of the spectrally active ν(CO) modes of a cluster compound. For a simpler molecule, a paragraph would have sufficed. It is to be noted that the existence of two similar molecules that showed some significant differences in their spectra was important to the development of the argument. Without the dual data our conclusion would have been much more tentative. Perhaps of particular significance is the qualitative model associated with Figure 1. If this approach were of general applicability, some considerable progress in the understanding of the ν(CO) spectra of metal clusters becomes possible.

Experimental Section

H₄Ru₄(CO)₁₂ was prepared by reacting a toluene solution of Ru₃(CO)₁₂ with H₂ (ca. 1 atm) at 80 °C for 1 day. A sample of H₄Os₄(CO)₁₂ was kindly supplied by Dr. B. F. G. Johnson (University of Cambridge).

IR spectra were obtained by using a Perkin-Elmer PE580 spectrometer with Data Station. Particular care was required for the solution spectrum of the poorly soluble H₄Os₄(CO)₁₂. The spectrum shown in Figure 4b is the average of several scans, solvent subtracted, amplified, and smoothed. Raman spectra were recorded with a Spex 1401 spectrometer and a Spectra Physics 165 Ar/Kr laser. The exciting line was 6471 Å and the power incident on the sample ca. 30 mW. The resultion was ca. 1 cm⁻¹. Infrared and Raman data have previously been reported for H₄Ru₄(CO)₁₂,[12] but without assignment. The agreement with our data is good.

(12) S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, 97, 3942 (1972).