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Raman Frequencies of Transition Metal Complexes[1]

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Raman spectra are reported for several series of relatively simple homonuclear transition metal complexes that contain metal to metal bonds. The low-frequency region of these spectra is generally characterized by an intense, sharp band assignable to the metal-metal stretching vibration. The utility of Raman spectroscopy in structural investigations of systems that contain transition metal to transition metal bonds is discussed briefly.

Compounds containing metal-metal bonds are ubiquitous[2] and although X-ray crystallography is well established as a useful technique in the structural investigations of these substances, the length of a bond between two metal centers is a sensitive function of a variety of parameters, including oxidation states, the nature of additional ligands, and other aspects of molecular geometry. It is apparent, therefore, that the use of interatomic distances to infer information about chemical bonding requires measured caution. Our interest in the area of metal-metal bonds[3] has prompted us to examine an alternative spectroscopic approach that would constitute a valuable addition to the range of techniques applicable to the examination of these substances.

Vibrational spectroscopy, particularly Raman spectroscopy, is theoretically capable of supplying a wealth of information about metal-metal bonds.[4] However, experimental barriers, *viz.*, the decomposition of colored samples due to the intense radiation of the exciting line, have severely limited the usefulness of Raman spectroscopy in the study of this broad class of compounds. The advent of low-frequency laser excitation and defocusing techniques have vastly increased the flexibility of Raman spectroscopy in recent years. Here we wish to report the results of an investigation emphasizing the qualitative utility of Raman spectroscopy as a technique for the study of metal-metal bonds between transition metals and, in particular, for complexes containing strong metal-metal bonds.

The reasons for emphasizing compounds that contain strong metal-metal bonds are twofold. First, simple theory predicts that the intensity of a Raman vibrational band can be related to the relative order of the bond under investigation.[5] Thus, the assignment of metal-metal stretching frequencies is aided considerably in such systems. Second, several theoretical treatments of the bonding in such systems have been presented. Since the metal-metal stretching frequency can be used to calculate a valence force constant, which can be correlated empirically with bond strength, and band intensity is apparently a function of bond order,[5] an analysis of the Raman spectra of these systems should ultimately provide a means of experimentally probing the nature of the bonding in such systems.

Experimental Section

Di- and Trinuclear Rhenium Complexes. $[(n\text{-}C_4H_9)_4N]_2[Re_2X_8]$ (X = Cl, Br),[6] $Re_2(O_2CCH_3)_2X_4\cdot 2H_2O$ (X = Cl, Br),[7] $Re_2(O_2CCH_3)_4X_2$ (X = Cl, Br),[7] $Re_2Cl_6[P(n\text{-}C_3H_7)_3]_2$,[3] $Re_2Cl_6(tmtu)_2$,[7] $Re_2Cl_5(DTH)_2$,[7] $Re_2OCl_5(O_2CCH_2CH_3)[P(C_6H_5)_3]_2$,[8] and $Re_2OCl_3(O_2CCH_2CH_3)_2[P(C_6H_5)_3]_2$[9] were all prepared by literature procedures.

The procedure described by Cotton[7] for the preparation of $Re_2(O_2CCH_3)_3Cl_3\cdot H_2O$ was attempted repeatedly. The materials produced had variable compositions. A typical analysis is given. *Anal.* Calcd for $Re_2(O_2CCH_3)_3Cl_3\cdot H_2O$: C, 10.69; H, 1.65; Cl, 15.78. Found: C, 14.20; H, 2.11; Cl, 10.84.

Rhenium trichloride and rhenium tribromide were purchased from Var-lac-oid Chemical Co. and used as received. The preparation of $Re_3Cl_9[P(C_6H_5)_3]_3$ and $Re_3Cl_9(C_5H_5N)_3$ was achieved using previously described procedures.[10]

Dinuclear Molybdenum Complexes. The molybdenum complexes $(NH_4)_5Mo_2Cl_9\cdot H_2O$,[11] $Mo_2Cl_4L_4$[3] (L = $(n\text{-}C_4H_9)_3P$, $(CH_3O)_3P$), $Mo_2(O_2CCH_3)_4$,[12] $Mo_2(O_2CCF_3)_4$,[13] and $Mo_2(O_2CCF_3)_4(C_5H_5N)_2$[14] were synthesized by established procedures.

Dinuclear Complexes of Ruthenium, Rhodium, and Copper. Tetra-*n*-butyratodiruthenium chloride[15] and rhodium(II) acetate methanolate[16] were prepared by known methods. Copper(II) acetate dihydrate was obtained from Alfa Inorganics and used as received.

Complexes with Fe-Fe Bonds. Diiron nonacarbonyl, triiron dodecacarbonyl, and bis(cyclopentadienyliron dicarbonyl) were purchased from Alfa Inorganics. Each was rinsed with copious amounts of pentane and dried under reduced pressure in a nitrogen atmosphere. Tetrakis(cyclopentadienyliron carbonyl) was prepared as reported by King.[17]

Spectra. Raman spectra were recorded on a Cary Model 82 laser Raman spectrometer equipped with rotating-sample cells similar to those described elsewhere.[18] Unless otherwise noted, a slit width of 3 cm^{-1} and a scanning rate equal to the ratio of the slit width to time constant were employed. Blue (4880 Å) or green (5145 Å) excitation was provided by a Coherent Radiation Laboratory Model 52 argon ion laser. Repeated scanning of all samples revealed no evidence of irradiation-induced decomposition. Reported frequencies are accurate to ± 1 cm^{-1}. Infrared spectra were recorded

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[1] Supported by the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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on a Perkin-Elmer 225 spectrophotometer employing Nujol mulls supported on polyethylene plates. Frequencies are accurate to ±1 cm^{-1}.

Results

Di- and Trinuclear Complexes of Rhenium. Several dinuclear rhenium(III) complexes are known.[19] Most of these fall into one of several structural patterns.[19] The exceptionally short Re-Re distances (2.22-2.24 Å) found in these complexes are consistent with the existence of a strong metal-metal bond and an eight-electron quadrupole bond is supposed.[19]

The Raman spectra of crystalline bis(tetra-*n*-butylammonium) octachloro- and octabromodirhenate(III) and hexachlorobis(tri-*n*-propylphosphine)dirhenium(III) (**1**, **2**, **7**) are shown in Figure 1. The spectral data for these and the related complexes $Re_2(O_2CCH_3)_2X_4 \cdot 2H_2O$ (X = Cl, Br; **3** and **4**), $Re_2(O_2CCH_3)_4X_2$ (X = Cl, Br; **5** and **6**), and $Re_2Cl_6L_2$ (L = tmtu (tetramethylthiourea); **8**) are collected in Table I.

Two observations are immediately apparent from these results. First, an intense band at 285 ± 10 cm^{-1} appears in the spectra of all these compounds. The invariance in frequency of this band and its relative intensity suggests strongly that it is the totally symmetric (A_1) Re-Re stretching vibration. Second, those complexes that contain radially disposed chlorine atoms (**1**, **3**, **7**, **8**) all display a moderately intense band at approximately 365 cm^{-1} while those complexes which contain similarly arranged bromine atoms (**2**, **4**) show a strong to very intense band at approximately 210 cm^{-1}. These two bands are of appropriate frequency[20] and relative intensity (*i.e.*, Cl < Br) to be the totally symmetric Re-Cl and Re-Br stretching modes, respectively.

The structure of pentachlorobis(2,5-dithiahexane)dirhenium (**9**) has been determined by single-crystal X-ray crystallography.[21] The short Re-Re bond distance (2.293 Å) suggests a strong metal-metal bond is present. The formulation of this compound as a mixed-valence complex of rhenium(II) and rhenium(III) as suggested by Cotton[7] is consistent with its magnetic characteristics and further implies that the Re-Re bond has a multiplicity of 3.

As a consequence of the strong dissimilarity between the environments experienced by adjacent rhenium centers in **9**, which can be anticipated to result in a reduction of the induced dipole moment of this molecule, the metal-metal stretching vibration in pentachlorobis(2,5-dithiahexane)dirhenium should have reduced Raman but increased infrared activity. In fact, **9** exhibits a relatively weak Raman band at 267 cm^{-1} but a moderately intense infrared band at 265 cm^{-1}. In view of their similar and appropriate frequencies as well as their relative intensities, these bands are assigned as arising principally from the Re-Re stretching vibration.

The dinuclear rhenium complexes oxopentachloropropionatobis(triphenylphosphine)dirhenium(IV) (**10**) and μ-oxo-μ-chloro-di-μ-propionato-bis(chlorotriphenylphosphine-rhenium) (**11**) have been structurally characterized by single-crystal X-ray crystallography studies.[8,9] A meaningful description of the bonding in these compounds is not presently available and the presence of bridging atoms undoubtedly imposes constraints on the metal-metal bond distances precluding an empirical evaluation of bond order based on bond order-bond length relationships;[22] nontheless, the short rhenium-rhenium bond distances in these compounds (2.522 and 2.514 Å, respectively) imply the existence of appreciable metal-metal interaction and a bond order of ~2 seems reasonable.[8,9]

Table I. Solid-State Raman Frequencies (cm^{-1}) Observed for Some Di- and Trinuclear Rhenium Complexes[a]

$[(C_4H_9)_4N]_2$-Re_2Cl_8[b,e]	$[(C_4H_9)_4N]_2$-Re_2Br_8[c]	$Re_2(O_2$-$CCH_3)_2Cl_4 \cdot 2H_2O$[c,e]	$Re_2(O_2$-$CCH_3)_2Br_4 \cdot 2H_2O$[c]
363 m	278 s	962 w	405 w
336 w	240 w	883 w	380 w
301 w	212 vs	550 w (ν_2)	373 w
275 vs	157 w	370 w	277 vs
250 w	143 w	279 vs	232 s
192 m		160 w	209 m
156 m		145 m	138 w
120 m			

Re_2Cl_5-$(DTH)_2$[c]	Re_3Cl_9[c]	Re_3Br_9[c]	Re_3Cl_9-$[P(C_6H_5)_3]_3$[c]
267 w	998 w (ν_4)	254 vs	358 w
	745 m (ν_3)	206 m	340 w
	495 m (ν_2)		231 vs
	250 vs		200 w

$Re_2(O_2C$-$CH_3)_4Cl_2$[c]	$Re_2(O_2C$-$CH_3)_4Br_2$[c]	Re_2Cl_6-$[P(C_3H_7)_3]_2$[c,e]	Re_2Cl_6 $(tmtu)_2$[c]
960 m	842 w (ν_3)	363 m	357 m
955 m, sh	715 w	278 vs	276 vs
716 w	700 w	206 w, sh	
700 m	612 w	195 m	
615 w	562 m (ν_2)	183 w	
575 w	391 m	158 m	
395 m	284 vs	120 m	
289 vs	189 m		
277 w	135 m		
238 w			
196 m			

Re_3Cl_9-$(C_5H_5N)_3$[b]	Re_2OCl_5-$(O_2CCH_2CH_3)$-$[P(C_6H_5)_3]_2$[c]	$Re_2OCl_3(O_2C$-$CH_2CH_3)_2[P$-$(C_6H_5)_3]_2$[c]	Re_2-$(CO)_{10}$[d]
353 m	432 m (ν_2)	216 vs	122 s
223 vs	360 m		
	340 w		
	310 w		
	216 vs		
	210 m, sh		

[a] Qualitative intensities: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. ν_2, ν_3, and ν_4 are respectively the first, second, and third overtone bands. [b] Obtained using 4880-Å exciting radiation. [c] Obtained using 5145-Å exciting radiation. [d] Taken from C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, 8, 2363 (1969). [e] Essentially equivalent solution (CH_2Cl_2 or CH_3CN) and solid-state values of ν(Re-Re) were observed.

The low-frequency Raman spectrum of crystalline **10** is seen in Figure 2. The most prominent feature in both this spectrum and that of the related complex **11** is a strong spike at 216 cm^{-1} which we assign as consisting principally of the Re-Re stretching mode.

The structures of the rhenium(III) halides Re_3X_9 (X = Cl, Br, I) and several of their derivatives, $Re_3X_9L_3$, have been established.[23,24] These compounds share several structural features in common (*cf.* Figure 3). In particular, they all contain a triangular cluster of rhenium atoms, the distance between rhenium centers being nearly the same (~2.48 Å)

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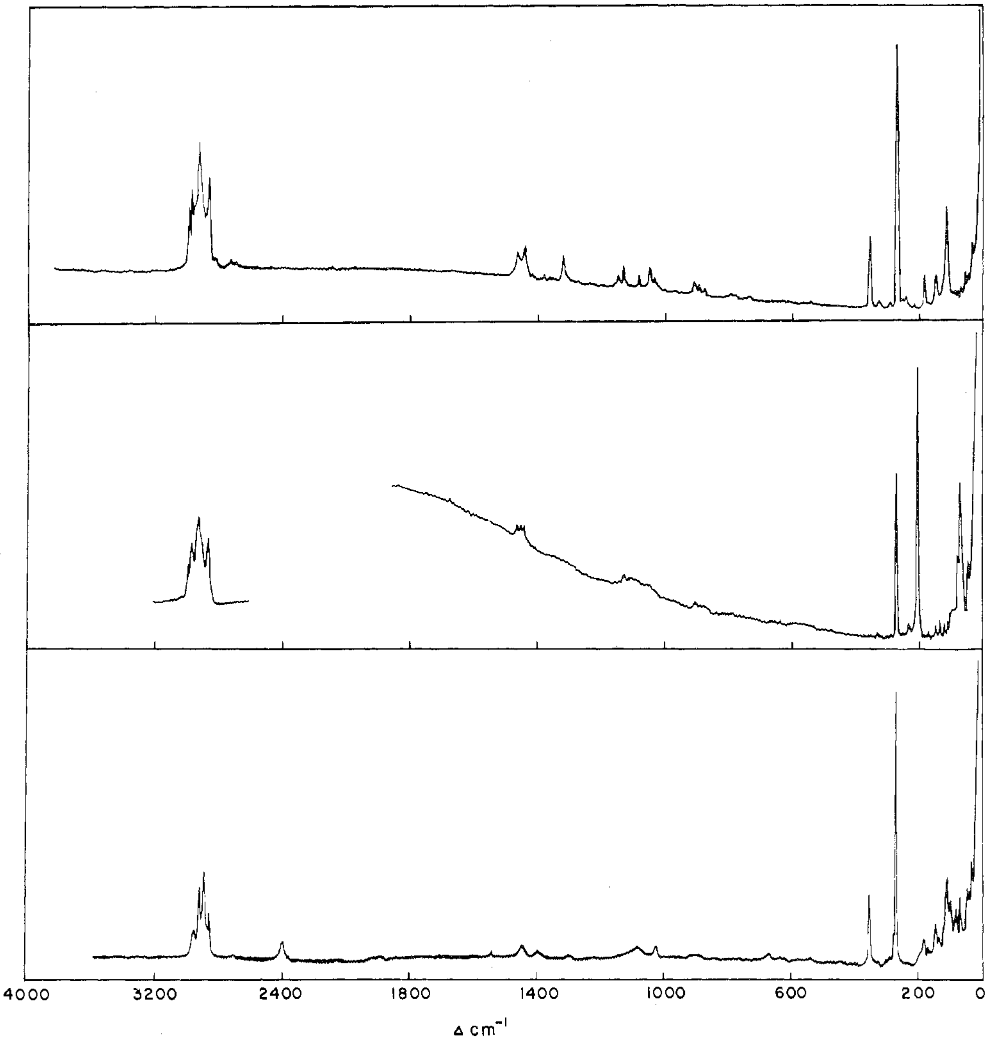

Figure 1. Raman spectra of crystalline $[(C_4H_9)_4N]_2Re_2Cl_8$ (top), $[(C_4H_9)_4N]_2Re_2Br_8$ (middle), and $Re_2Cl_6[P(C_3H_7)_3]_2$ (bottom). Experimental conditions are given in Table I.

in each. The bonding between rhenium atoms in these trinuclear complexes has been described in both valence bond[25] and molecular orbital terms.[26] Both descriptions suggest that each rhenium atom forms two double bonds, one to each of its neighbors, implying a Re-Re bond order of 2.

Figure 2 shows the low-frequency solid-state Raman spectra of Re_3Cl_9 and $Re_3Cl_9[P(C_6H_5)_3]_3$. These data and those of the related complexes Re_3Br_9 and $Re_3Cl_9(C_5H_5N)_3$ are collected in Table I. Comparison of these results reveals that an intense band falling between 255 and 220 cm^{-1} is common to the spectrum of each of these complexes. This band is assumed to be the A_1' breathing mode of the trinuclear rhenium cluster.

Two metal-metal vibration modes (A_1' and E' symmetries) are predicted for the trinuclear complexes Re_3X_9 and $Re_3X_9L_3$ (idealized point group, D_{3h}). Both are Raman active and by the simple cluster approximation[27] a ratio of $\nu_{A_1'}/\nu_{E'} = \sqrt{2}$ is predicted with the E′ stretching mode expected to occur at the lower frequency. Indeed, a weak band appears at ~200 cm^{-1} in most of these spectra and may in fact be the E′ cage mode. The deviations from the predicted value are not significantly greater than those previously observed[27] for the symmetry-related systems $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ and presumably result from the mixing of metal-ligand modes into the E′ metal-metal mode.

The Re-X stretching mode is conspicuously absent from the spectra of all but one of these related complexes. The fact that it appears as a moderately intense band in the spectrum of $Re_3Cl_9(C_5H_5N)_3$, a light green complex, but is absent in the spectra of Re_3Cl_9, Re_3Br_9, and $Re_3Cl_9[P(C_6H_5)_3]_3$, all of which are dark red, suggests that this failure may reflect the preferred intensity enhancement of certain bands, a common phenomenon in spectra where strong resonance Raman effects prevail (*vide infra*).

Dinuclear Complexes of Molybdenum. Molybdenum(II) forms a number of dinuclear compounds which bear strong structural similarities to the isoelectronic complexes of rhenium(III) (**1**, **2**, **5**, **7**). Here, too, the metal-metal bond distances are exceedingly short (2.09-2.14 Å), suggesting the presence of a strong metal-metal interaction. By analogy to the Re(III) complexes, an eight-electron quadruple bond is suggested for these compounds.[3,19]

Figure 3 shows the Raman spectra of crystalline pentaammonium nonachlorodimolybdate(II) monohydrate, $(NH_4)_5$-$Mo_2Cl_9 \cdot H_2O$, and tetrachlorotetrakis(tri-*n*-butylphosphine)dimolybdenum(II), $Mo_2Cl_4[P(C_4H_9)_3]_4$. The data for these

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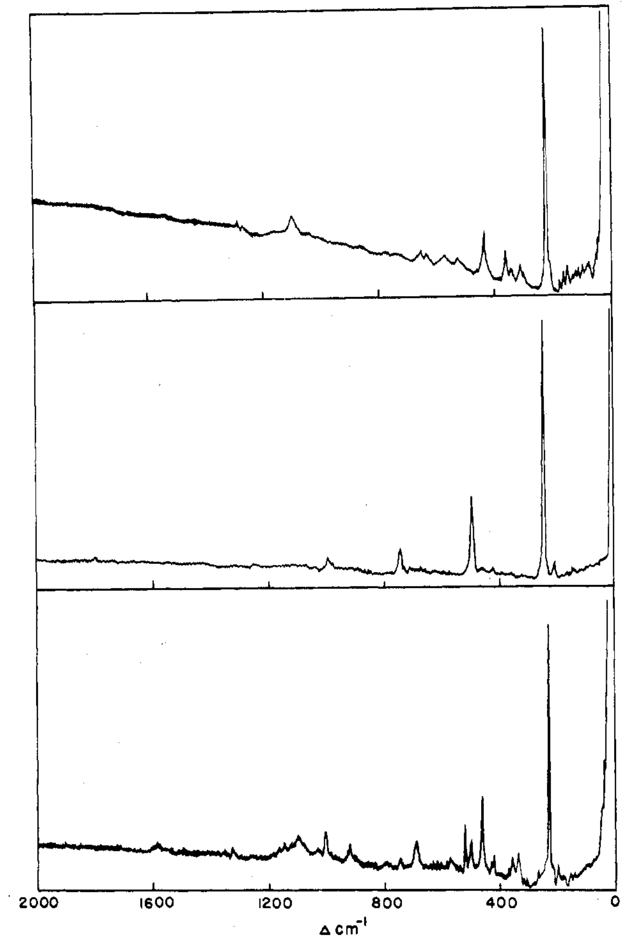

Figure 2. The solid-state Raman spectra of $Re_2OCl_5(O_2CCH_2CH_3)[P(C_6H_5)_3]_2$ (top), Re_3Cl_9 (middle), and $Re_3Cl_9[P(C_6H_5)_3]_3$ (bottom) obtained using 5145-Å exciting radiation.

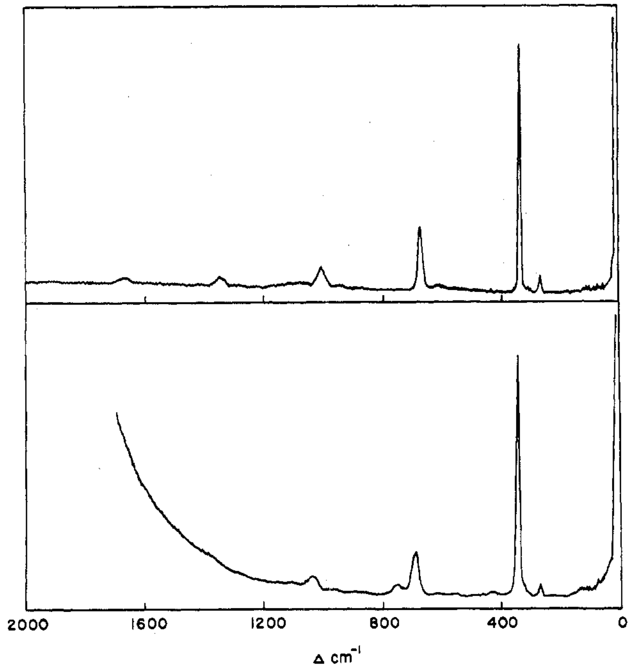

Figure 3. Low-frequency solid-state Raman spectra of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ (upper) and $Mo_2Cl_4[P(C_4H_9)_3]_4$ (lower) observed with 4880- and 5145-Å exciting radiation, respectively.

compounds and the related derivative $Mo_2Cl_4[P(OCH_3)_3]_4$ are presented in Table II. All these complexes display an intense single band centered at 345 ± 10 cm^{-1}, which is assumed to be the (A_1) Mo–Mo stretching mode. A weak band at 282 ± 10 cm^{-1} also occurs in these spectra and is attributed to the (A_1) Mo–Cl stretching mode.

The structures of several dinuclear molybdenum(II) carboxylates have been determined by single-crystal X-ray crystallography.[14,28,29] The Mo-Mo distance in all of these compounds is virtually equivalent (~2.10 Å). The Raman spectrum of crystalline molybdenum(II) acetate has been reported by Cotton, who assigned the strong band at 406 cm^{-1} to the Mo-Mo stretching mode.[30] Although our findings support this assignment, other aspects of their data urged reexamination. Figure 4 shows the solid-state Raman spectra of $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCF_3)_4$.

A comparison between the data for dinuclear rhenium(III) and dinuclear molybdenum(II) compounds reveals several differences. First, consonant with the considerable difference between the approximate reduced masses of these two isoelectronic systems, the Mo-Mo stretching mode occurs at a significantly higher frequency than does the corresponding Re-Re stretch. Second, it is apparent that the nature of neither axial nor radial ligands significantly affects the solid-state or solution values of ν(Re-Re). By way of contrast, the solid-state values of ν(Mo-Mo) span a range of ~70 cm^{-1}. As previously noted,[14] significant differences occur in most solvents between the solid-state and solution values of ν(Mo-Mo) observed for $Mo_2(O_2CCF_3)_4$. This difference increases as the ligand donor properties of the solvent become substantial. Thus, for example, in pyridine ν(Mo-Mo) occurs at ~60 cm^{-1} below the solid-state value. In view of the fact that the magnitude of this shift has been interpreted[14] as indicating decreased metal-metal interaction, it should be noted that in such solvents the frequencies of virtually *all* the bands in the spectrum of $Mo_2(O_2CCF_3)_4$ show a solvent dependence. Thus, for example the very intense band which appears at 1468 cm^{-1} in the solid state and in most solvents is shifted to 1454 cm^{-1} in pyridine solution.

Third, the relative intensity of the Mo-Cl stretching band is seen to be significantly less than that observed for the corresponding Re-Cl band. Although this difference may reflect the relative differences in the covalency and hence polarizability of the two bonds, it may also result from inherent differences between the excitation profiles of these two classes of compounds.[31] Finally, it is noteworthy that, contrary to the report[14,30] that the Mo-Mo stretching modes constitute the strongest bands in the Raman spectra of both $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCF_3)_4$, the data presented in Figure 4 and Table II indicate that there are in these spectra a number of bands of similar or greater intensity than ν(Mo-Mo).

Dinuclear Complexes of Ruthenium, Rhodium, and Copper. In addition to rhenium and molybdenum, a number of other transition metal ions are known to form dinuclear carboxylates. The metal-metal interactions in these compounds range from strong multiple bonds to weak antiferromagnetic spin-spin coupling. Thus, the very short Ru-Ru distance (2.281 Å) in tetra-*n*-butyratodiruthenium chloride suggests a strong metal-metal interaction. The Raman

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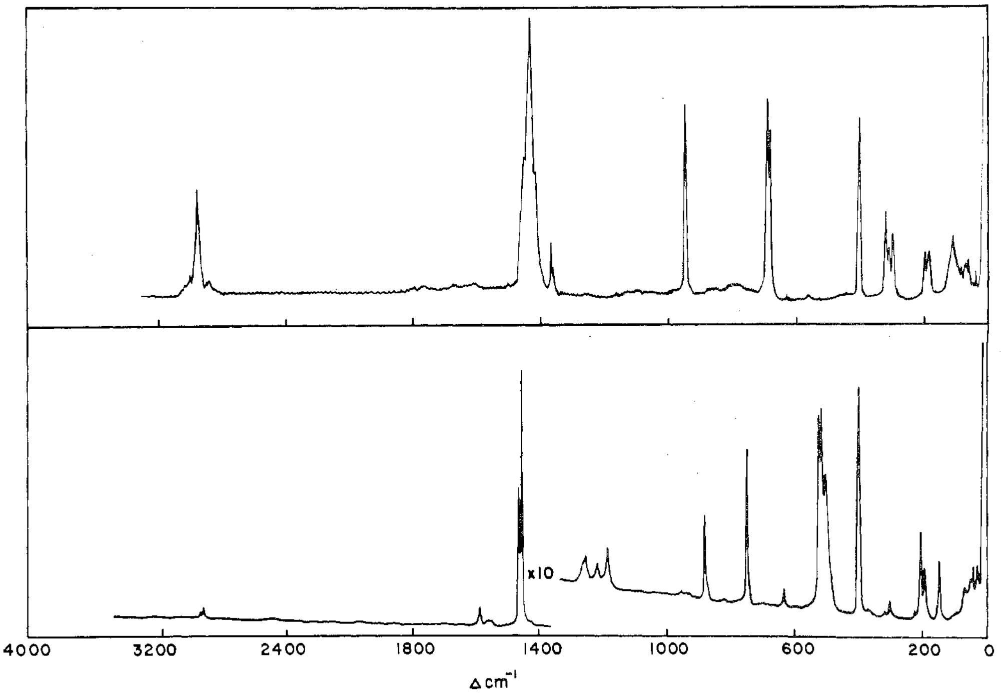

Figure 4. Raman spectra of crystalline $Mo_2(O_2CCH_3)_4$ (upper) and $Mo_2(O_2CCF_3)_4$ (lower) recorded using 4880-Å exciting radiation.

Table II. Summary of Selected Solid-State Raman Frequencies (cm^{-1}) Observed for Some Dinuclear Molybdenum Complexes

$(NH_4)_5Mo_2Cl_9\cdot H_2O$[a]	$Mo_2Cl_4[P(C_4H_9)_3]_4$[b]	$Mo_2Cl_4[P(OCH_3)_3]_4$[b]	$Mo_2(O_2CCH_3)_4$[a]	$Mo_2(O_2CCF_3)_4$[a]	$Mo_2(O_2CCF_3)_4$-$(C_5H_5N)_2$[a]
1340 w (ν_4)	1042 w (ν_3)	1038 w (ν_3)	1438 vs	1462 vs	1466 vs
1000 w (ν_3)	760 w	785 w	1367 m	1458 vs	1455 vs
666 m (ν_2)	698 m (ν_2)	760 w	1360 w	1242 w	1030 w
339 vs	440 w	691 w (ν_2)	950 s	1228 w	1000 m
274 w	350 vs	528 w	692 s	1178 w	733 w
	277 w	458 w	685 s	872 w	509 m
		387 m	406 s	742 m	368 m
		347 vs	322 m	517 m	
		290 w	313 m	509 m	
			300 m	455 w	
			290 m	395 m	
			200 m	200 w	
			110 m	142 w	

[a] Obtained using 4880-Å exciting radiation. [b] Obtained using 5145-Å exciting radiation.

spectrum of $Ru_2[O_2C(CH_2)_2CH_3]_4Cl$ is shown in Figure 5. The intense absorption at 337 cm^{-1} is assigned to the Ru-Ru stretching mode. The remaining bands at 667 and 995 cm^{-1} represent, respectively, the first and second overtones of this fundamental.

The isostructural dinuclear acetates of rhodium(II) and copper(II) have been structurally characterized.[32,33] The Rh-Rh bond length in $Rh_2(O_2CCH_3)_4\cdot 2H_2O$ is sufficiently short (2.386 Å) that moderate metal-metal interaction is indicated and a multiple bond has been proposed.[34]

Dinuclear, carboxylato-bridged compounds of copper(II) represent one of several classes of compounds in which the Cu-Cu distances are short enough to indicate possible metal-metal interaction. Although a detailed explanation of the nature of this interaction is lacking, it is now generally agreed that the interaction is principally one between orbitals of σ symmetry, but the question remains unanswered as to whether this interaction is transmitted through the π orbitals of the bridging carboxy groups (superexchange) or results instead from a direct interaction between $d_{x^2-y^2}$ orbitals.[35] The demonstrated sensitivity of Raman spectroscopy to weak metal-metal interactions[4a] suggested a possible means of probing this question.

The Raman spectrum of copper(II) acetate dihydrate is seen in Figure 5. A close similarity between the high-frequency (3200-600 cm^{-1}) region of the spectrum of $Rh_2(O_2CCH_3)_4\cdot 2CH_3OH$ and that of $Cu_2(O_2CCH_3)_4\cdot 2H_2O$ is apparent. These bands arise principally from modes localized in the acetato groups. The low-frequency regions of both spectra are rich in detail with the most intense bands in both spectra occurring in this region. Indeed, the strong spike at 170 cm^{-1} in the spectrum of $Rh_2(O_2CCH_3)_4\cdot 2CH_3OH$ may, in fact, be ν(Rh-Rh). Unfortunately, the considerable complexity of this region in both spectra, combined with the decreased intensity expected for a band resulting from the stretching mode of these significantly weaker metal-metal interactions prevents a ready, unambiguous assignment of ν(M-M) in these compounds. Nonetheless,

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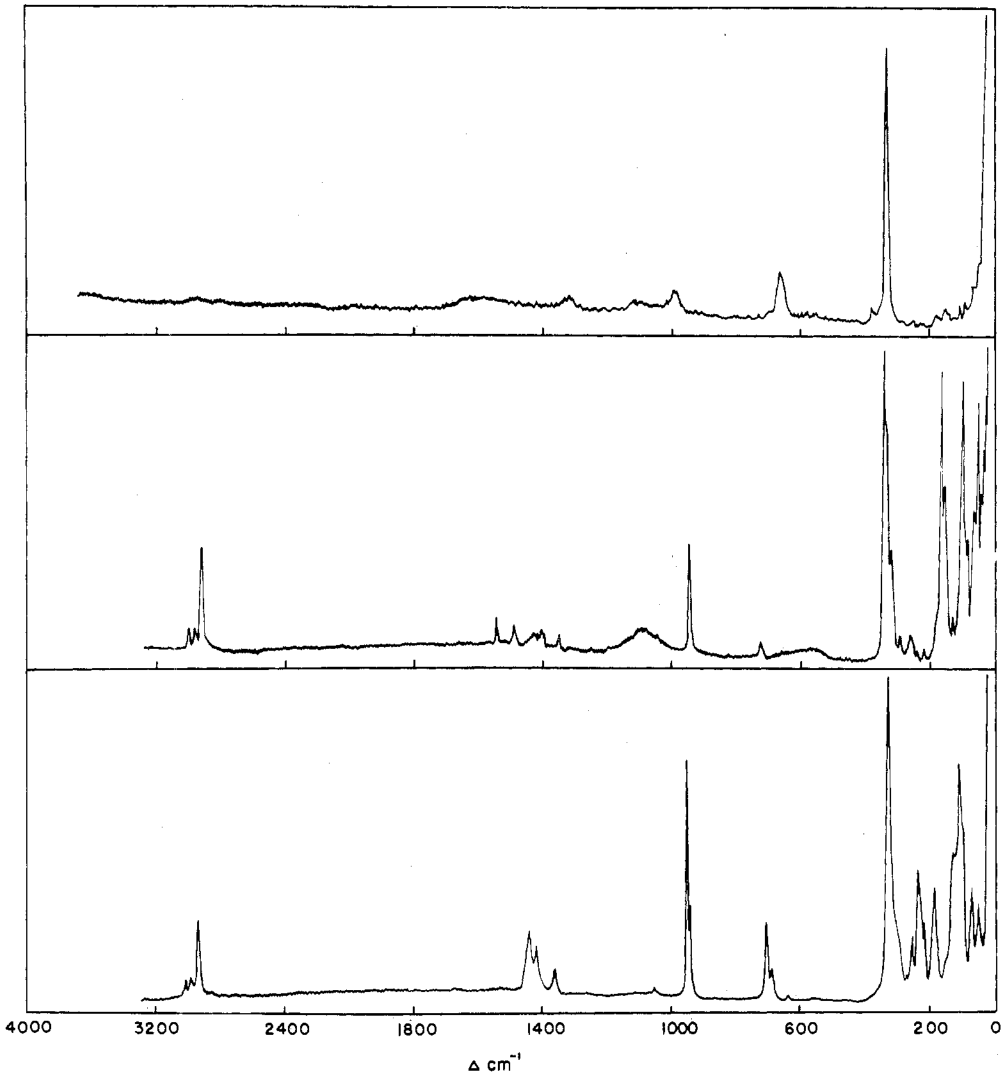

Figure 5. Solid-state Raman spectra of $Ru_2[O_2C(CH_2)_2CH_3]_4Cl$ (top), $Rh_2(O_2CCH_3)_4 \cdot 2CH_3OH$ (middle), and $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$ (bottom). Experimental conditions are given in Table IV.

the detailed nature of these spectra serves to underline the value of Raman spectroscopy as a qualitative technique for the "fingerprint" characterization of compounds that display undistinguished high-frequency vibrational spectra. A summary of the Raman frequencies observed for $Ru_2[O_2C(CH_2)_2CH_3]_4Cl$, $Rh_2[O_2CCH_3]_4 \cdot 2CH_3OH$, and $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$ is presented in Table III.

Compounds with Fe-Fe Bonds. Iron forms a number of homonuclear complexes that contain metal-metal bonds. Among the structurally simplest of these are diiron nonacarbonyl, $Fe_2(CO)_9$, and triiron dodecacarbonyl, $Fe_3(CO)_{12}$, the structures of which are well known,[36,37] as is also the structure of bis(cyclopentadienyliron dicarbonyl),[38] $[C_5H_5Fe(CO)_2]_2$, and tetrakis(cyclopentadienyliron carbonyl),[39] $[C_5H_5Fe(CO)]_4$.

The solid-state spectra of $Fe_2(CO)_9$ and $[C_5H_5Fe(CO)]_4$ are shown in Figure 6. These data and those for the related complexes $Fe_3(CO)_{12}$ and $[C_5H_5Fe(CO)_2]_2$ are summarized in Table IV. The common feature in all these spectra is an intense band centered at 220 ± 10 cm⁻¹ which we assign as arising primarily from the Fe-Fe stretching mode in these compounds. These assignments are in agreement with that made by Terzis and Spiro, who examined the Raman spectrum of $[C_5H_5Fe(CO)]_4$ in chloroform solution and observed a single band at 214 cm⁻¹ which they attributed to the (A_1) Fe-Fe stretching mode.[40]

Table III. Selected Raman Frequencies (cm⁻¹) Observed for Crystalline $Ru_2[O_2C(CH_2)_2CH_3]_4Cl$, $Rh_2(O_2CCH_3)_4 \cdot 2CH_3OH$, and $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$

$Ru_2[O_2C(CH_2)_2CH_3]_4Cl$[a]	$Rh_2(O_2CCH_3)_4 \cdot 2CH_3OH$[a]	$Cu_2(O_2CCH_3)_4 \cdot 2H_2O$[b]
995 w (ν_3)	948 m	960 s
667 m (ν_2)	725 w	955 m
383 w	355 vs	710 m
337 vs	330 sh	690 m
180 w	310 m	325 vs
155 w	294 w	250 m
	250 w	230 m
	180 m	177 m
	170 vs	110 m
	167 s	100 s

[a] Obtained using 5145-Å exciting line. [b] Obtained using 4880-Å exciting line.

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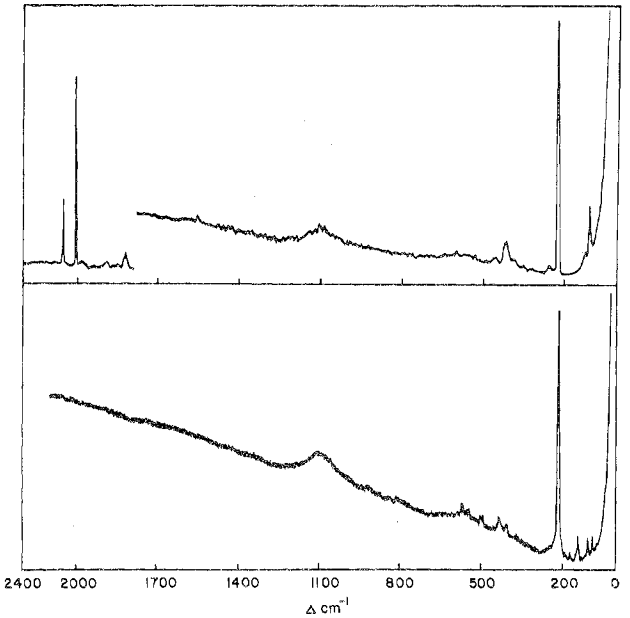

Figure 6. Raman spectra of crystalline $Fe_2(CO)_9$ (upper) and $[C_5H_5Fe(CO)]_4$ (lower) obtained using 5145-Å exciting radiation.

Table IV. Summary of the Solid-State Raman Frequencies Observed for Several Dinuclear and Cluster Compounds with Fe-Fe Bonds[a]

$Fe_2(CO)_9$	$Fe_3(CO)_{12}$	$[C_5H_5Fe(CO)_2]_2$	$[C_5H_5Fe(CO)]_4$
2108 m	219 vs	453 m	440 w
2017 s		413 m	413 w
1825 w		365 m	221 vs
445 w		226 vs	145 w
405 w			
385 w			
355 w			
275 w			
225 vs			
98 m			

[a] Obtained using 5145-Å exciting radiation.

It is apparent from these results that the nature of the coordinating ligands in these complexes has little influence on the value of ν(Fe-Fe). Indeed, the essential structural characteristic common to each of these complexes is that they are all presumed to contain Fe-Fe single bonds. It is not surprising, therefore, that despite the fact that $Fe_3(CO)_{12}$ contains two structurally unique Fe-Fe bonds differing by ~0.12 Å, this difference is insufficient to produce two distinct Fe-Fe stretching frequencies for this compound. By comparison, the considerable influence which bond order and hence bond strength has on ν(Fe-Fe) is apparent in the spectrum of tetracarbonyldi-μ-2,2,5,5-tetramethylhex-3-yne-diiron, the resonance Raman spectrum of which has recently been obtained by Spiro.[41] This complex, which is purported to contain an Fe-Fe double bond,[42] exhibits an intense Fe-Fe stretching band at 284 cm^{-1}.

The Raman spectra of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have been examined in detail.[27] Below 200 cm^{-1} both spectra are characterized by the appearance of sharp, relatively intense bands at 185 and 158 cm^{-1}, respectively, assigned to the A_1 cluster vibration. Triiron dodecacarbonyl is, of course, not isostructural with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$; however, in light of the relative insensitivity of ν(Fe-Fe) to the nature of substituent ligands, it is reasonable to conclude that the differences among ν(Fe-Fe), ν(Ru-Ru), and ν(Os-Os) in these three complexes are principally a reflection of the significant differences between the reduced masses of the basic trinuclear metal skeleton. This suggestion is supported by the similar values observed for the metal-metal stretching force constants in $Os_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $[C_5H_5Fe(CO)]_4$ (0.91, 0.82, and 1.3 mdyn/Å, respectively).[27,40]

Discussion

The principal aim of this study was to determine to what extent bands attributable to the stretching of metal-metal bonds can be identified in the Raman spectra of relatively simple homonuclear transition metal complexes. It is apparent from the results obtained that in those complexes where relatively strong metal-metal interactions are involved, the most prominent feature in the low-frequency region of the Raman spectra of these compounds is frequently a strong spike assignable to the metal-metal stretching mode.

The complexes presented in this paper are all deeply colored compounds with electronic profiles that extend well into the visible region and, in some cases, beyond. Their Raman spectra, therefore, are not ordinary spectra, since under such conditions the exciting frequency approaches or enters the region of the electronic absorption of the molecule, producing a resonance Raman effect.[43] Although there has recently been increased interest in resonance Raman spectroscopy, only scattered quantitative experimental data have appeared. Nonetheless, from a combination of these results and the present study, several qualitative observations can be made which, from a practical point of view, deserve brief comment.

First, both the absolute and relative intensities of resonance Raman bands are strongly dependent on the frequency of the exciting radiation.[43,44] The variation of relative intensities with exciting wavelength (excitation profile) can be considerable. An unexceptional example of this effect is illustrated by the spectrum of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ in which a greater than twofold change in the relative intensity of ν(Mo-Cl) and ν(Mo-Mo) is observed in going from 4880- to 5145-Å exciting radiation. The intense carbonyl stretching bands observed in the spectrum of $Fe_2(CO)_9$, contrasted by the failure to observe any high-frequency band in the spectra of $Fe_3(CO)_{12}$, $[C_5H_5Fe(CO)_2]_2$, and $[C_5H_5Fe(CO)]_4$, is an illustration of how strongly enhanced the intensities of some resonance Raman bands can be. The absence of a band in a resonance Raman spectrum does not, therefore, preclude its existence since a preferential intensity enhancement of some bands may preclude the observation of less intense emissions. Second, resonance Raman spectra are frequently characterized by the appearance of strong overtones the half-widths of which increase linearly with vibrational quantum number (*cf.* Figure 3).[44,45]

A recognized, albeit empirical, relationship exists between bond stretching force constant and bond order; however, rigorous calculation of the stretching force constants for structures of the complexity presented in this study is computationally unrealistic and although incisive simplications

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(44) W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, 52, 399 (1970).

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are helpful, such results are frequently of limited value.[46] Stretching frequencies, in general, are not, of course, monotonically related to bond order. It is reasonable to expect, however, that within a homologous series in which the stretching frequencies are relatively pure (unmixed) and reduced masses remain relatively constant such a relationship will prevail since, in fact, under these conditions the observed stretching frequency becomes a sole function of the stretching force constant. The persistence of such a relationship in the present study is suggested by the fact that, in general, the metal-metal frequencies observed within a related series of complexes display little variation with respect to the nature of the coordinated ligands but do show considerable dependence on the order of the metal-metal bond. The monotonic relationship between bond order and ν(M-M) for a series of related complexes is clearly evident in Figure 7.

The slight effect which the nature of coordinating ligands has on ν(M-M) is noteworthy. This behavior appeared to be general within all series of complexes examined except that of the dinuclear molybdenum(II) carboxylates, the metal-metal stretching frequencies of which fell considerably above those of other dinuclear molybdenum(II) compounds. Even in those instances where the metal-ligand and metal-metal symmetry coordinates are such that significant mixing might be expected to occur[47] (*e.g.*, $Re_3Cl_9L_3$), the variation of ν(M-M) within a series remained relatively narrow. Although subject to further experimental verification, this pattern suggests that characteristic frequencies may be associated with specific metal-metal groups.

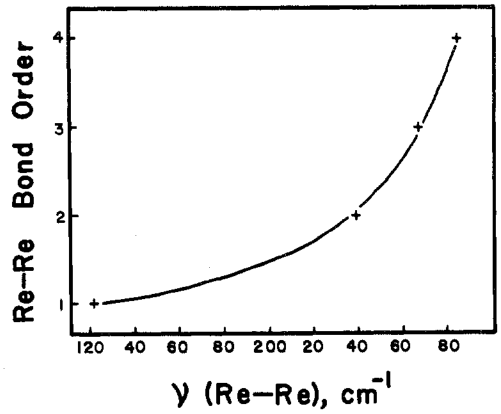

Figure 7. A plot of Re–Re bond order[19] against the average Re–Re stretching frequencies observed for a number of di- and trinuclear rhenium complexes of similar bond order.

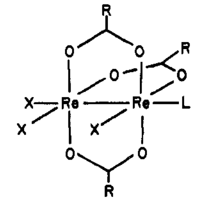

Figure 8. The proposed[7,22] structure for $Re_2(O_2CCH_3)_3X_3 \cdot H_2O$.

During the course of this and related studies we have noted a number of instances where the qualitative information gained from the Raman spectrum of a substance has aided considerably in its structural elucidation. One such example was provided by the investigation of a compound of the reported general formulation $Re_2(O_2CCH_3)_3X_3 \cdot H_2O$ (X = Cl, Br; **12**), which is a purportedly isolable intermediate in the controlled conversion of **3** and **4** to **5** and **6**, respectively.[7] This complex is proposed[7,22] to have the dinuclear structure shown in Figure 8. As formulated, **12** represents a mixed-valence compound with rhenium in the formal oxidation states of 3.5 and 2.5. The solid-state Raman spectrum of this material (X = Cl) showed two intense bands (289 and 279 cm^{-1}). The relative intensities of these bands were very much a function of reaction conditions. The intensity of the 289-cm^{-1} band increased regularly at the expense of the 279-cm^{-1} band as the reaction time increased. In addition, the spectrum of this substance isolated at different times appeared in virtually every respect to be a composite of the spectra of **3** and **5**. Based on these observations it would appear that the material formulated as $Re_2(O_2CCH_3)_3Cl_3 \cdot H_2O$ is, in fact, a mixture of variable proportions of compounds of **3** and **5** (X = Cl). Analytical data support this conclusion.

The applicability of Raman spectroscopy to the study of metal-metal bonds, although generally recognized, has been limited, except for isolated instances, to complexes that contain either post transition metal-post transition metal or transition metal-post transition metal bonds. The results presented here demonstrate the utility which Raman spectroscopy holds for the characterization and study of the increasingly large and important class of compounds that contain transition metal-transition metal bonds. Detailed analysis of such spectra can be expected to provide quantitative insight into the nature of such bonds.

Acknowledgments. We are indebted to our colleague George Bird for helpful discussions concerning the interpretation of the data reported in this paper.

Registry No. $[(C_4H_9)_4N]_2Re_2Cl_8$, 14023-10-0; $[(C_4H_9)_4N]_2Re_2Br_8$, 14049-60-6; $Re_2(O_2CCH_3)_2Cl_4 \cdot 2H_2O$, 14705-94-3; $Re_2(O_2CCH_3)_2Br_4 \cdot 2H_2O$, 40902-36-1; $Re_2Cl_5(DTH)_2$, 39322-81-1; Re_3Cl_9, 14973-59-2; Re_3Br_9, 33517-16-7; $Re_3Cl_9[P(C_6H_5)_3]_3$, 19696-45-8; $Re_2(O_2CCH_3)_4Cl_2$, 33612-87-2; $Re_2(O_2CCH_3)_4Br_2$, 33791-69-4; $Re_2Cl_6[P(C_3H_7)_3]_2$, 41021-44-7; $Re_2Cl_6(tmtu)_2$, 41021-43-6; $Re_3Cl_9(C_5H_5N)_3$, 12088-01-6; $Re_2OCl_5(O_2CCH_2CH_3)[P(C_6H_5)_3]_2$, 41007-92-5; $Re_2OCl_3(O_2CCH_2CH_3)_2[P(C_6H_5)_3]_2$, 39322-87-7; $(NH_4)_5Mo_2Cl_9$, 40902-25-8; $Mo_2Cl_4[P(C_4H_9)_3]_4$, 39306-31-5; $Mo_2Cl_4[P(OCH_3)_3]_4$, 39322-83-3; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $Mo_2(O_2CCF_3)_4$, 40902-26-9; $Mo_2(O_2CCF_3)_4(C_5H_5N)_2$, 39176-71-1; $Ru_2[O_2C(CH_2)_2CH_3]_4Cl$, 39322-85-5; $Rh_2(O_2CCH_3)_4$, 15956-28-2; $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$, 15523-07-6; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 33727-76-3; $[C_5H_5Fe(CO)_2]_2$, 12154-95-9; $[C_5H_5Fe(CO)]_4$, 12203-87-1.

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(46) Using limited and occasionally incorrect Raman data, Cotton has carried out an approximate normal-coordinate analysis of $Re_2X_8{}^{2-}$ and $Mo_2(O_2CCH_3)_4$, obtaining M-M stretching force constant values for both systems that range between 3.0 and 4.5 mdyn/Å.[30]

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