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Application of Raman Spectroscopy to Bridged–Nonbridged Equilibria for Polynuclear Metal Carbonyl Derivatives. Metal–Metal Stretching Frequencies of $Co_2(CO)_8$, $Fe_2(CO)_8^{2-}$, $Co_4(CO)_{12}$, and $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$

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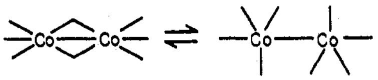
For dinuclear first transition series carbonyls, the M–M stretching frequency appears above 200 cm^{-1} when bridging carbonyls are present and between 190 and 140 cm^{-1} for single-bonded nonbridged species. These systematics were used to elucidate tautomeric equilibria for several dinuclear metal carbonyls. In the presence of a dipositive counterion, it was found that $Fe_2(CO)_8^{2-}$ exists in a bridged–nonbridged equilibrium mixture in DMF solution. Evidence for three tautomeric forms of $Co_2(CO)_8$ was obtained, and the presence of bridging carbonyls in $HFe_2(CO)_8^-$ was confirmed.

Raman spectra in the metal–metal stretching region have been reported for perhaps several dozens of polynuclear carbonyls, but the technique has not been applied to a significant extent as a tool for the structural eluciation of polynuclear carbonyls. This is partly because all of the metal–metal stretching vibrations predicated by molecular symmetry are not necessarily observed, and also because some of the metal–metal stretching vibrations expected around 100-cm^{-1} region are obscured by C–M–C deformations.[2] In the present paper, we explore the utility of Raman spectroscopy in the M–M stretching region for the study of bridged–nonbridged tautomeric equilibria of some dinuclear metal carbonyls.

The first well-documented case of tautomerism in a polynuclear carbonyl was provided by Noack[3] and Bor[4] in their solution infrared studies of $Co_2(CO)_8$, eq 1. Following this discovery, similar bridge–terminal carbonyl interchange equilibria were found for other polynuclear carbonyls,[5–9] and CO interchanges of this type have been invoked to explain carbonyl scrambling on the NMR time scale for polynuclear carbonyls.[10] The $Co_2(CO)_8$ system has recently been reinvestigated by Bor and Noack,[11] who confirmed that the principal species in solution are those depicted in the eq 1 and postulated the presence of a third form based on the observation of two otherwise unassignable features in the CO stretching region.



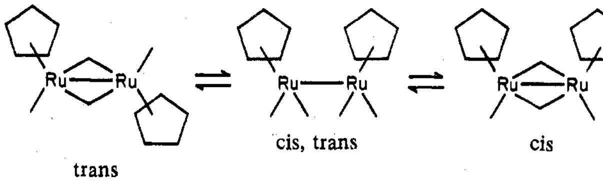
(1)

Experimental Section

Dicobalt octacarbonyl (Alfa Inorganics) was sublimed before use, and $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ was prepared by the literature method[12] and purified by sublimation after the recrystallization from ethyl acetate–*n*-hexane solutions. The purity of these compounds was checked by infrared spectra. $[Et_4N][HFe_2(CO)_8]$, $[Et_4N]_2[Fe_2(CO)_8]$, $[Bu_4N]_2[Fe_2(CO)_8]$, and $(DMTED)[Fe_2(CO)_8]$ (DMTED is *N,N'*-dimethyltriethylenediamine, $C_8H_{18}N_2$) were prepared by synthetic methods similar to those of Greenwood et al.[13] All of the solvents were dried over molecular sieves and purged with dry nitrogen. Fresh solutions under an inert atmosphere were contained in 12-mm o.d. sample tubes, and the laser Raman spectra were obtained using a back-scattering geometry on rotating samples. A description of this sampling technique and the means of temperature control is given elsewhere.[14] A Spex 1401 spectrometer was used with Spectra Physics Ar^+ or Kr^+ lasers. Unless otherwise stated, spectra were obtained with 514.5-nm excitation.

Results and Discussion

An indication that Raman spectroscopy might be applied as a tool for the study of bridged–nonbridged tautomeric equilibria is that solid $Co_2(CO)_8$, which has two bridging carbonyls, yields a strong peak at 229 cm^{-1}, whereas solid $Mn_2(CO)_{10}$, which has no bridging carbonyls, displays a peak at 160 cm^{-1}. A more convincing illustration of the frequency shift for the metal–metal stretch between bridged and nonbridged carbonyls is afforded by the low-frequency Raman spectrum of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$, which exists as a mixture of both bridged and nonbridged isomers in solution (eq 2).[5,9]



(2)

In the solid state, where this compound exists in the carbonyl-bridged form, one metal–metal stretch feature is observed at 217 cm^{-1}; however, in solution two polarized features are observed at 221 and 180 cm^{-1}, which are assigned to the M–M stretch in the bridged and nonbridged forms, respectively. As shown in Table I, the bridged form is favored at low temperatures, in harmony with McArdle and Manning's findings.[9] Small changes in peak position and shape were observed as a function of temperature, and these may reflect changes in the rotational conformation populations. However, this point was not explored in detail because sample decomposition precluded precise measurements.

The observation of three fairly intense features in the M–M stretching region for $Co_2(CO)_8$ presents a more subtle problem, because only two would be expected for the two predominant isomers which are thought to exist in solution.[3,4] Furthermore one of these features (185 cm^{-1}) occurs at the same frequency as the most intense Co–Co stretching mode of $Co_4(CO)_{12}$. However this band does not arise from the presence of $Co_4(CO)_{12}$ impurity because the solution spectra do not display a second medium-intensity feature at 250 cm^{-1}, which also is characteristic of $Co_4(CO)_{12}$ (Figure 1). Furthermore, removal of the solvent leads to a solid with the typical Raman spectrum of $Co_2(CO)_8$.

Another possibility is that either the 185- or 159-cm^{-1} peak arises from an unspecified photolysis product present in solution in a photostationary state resulting from the laser irradiation. Several types of experiments were performed to test this hypothesis. In one series of experiments, the laser power was steadily increased and the relative intensities of the three bands were noted. As may be seen in Table II, the relative intensities are substantially unchanged with a nearly threefold increase in laser power, indicating that a photostationary state is not involved. Similarly it was found that the initial spectrum is relatively unaffected when sample spinning is stopped (prolonged irradiation of the stationary sample does lead to the buildup of $Co_4(CO)_{12}$, as judged by the appearance of a 250-cm^{-1} band).

Table I. Observed Metal–Metal Stretching Frequencies and Their Relative Intensities (Peak Height Intensities)

Compd	ν(M–M), cm^{-1}		[ν(M–M), cm^{-1}] rel intens															
	Solid	Soln [ρ]^c																
			Acetone soln				THF soln			CH$_2$Cl$_2$ soln				*n*-Pentane soln				
				22 °C	−15 °C	−55 °C		22 °C	−11 °C		22 °C	−24 °C	−70 °C		22 °C	−37 °C	−92 °C	
$Co_2(CO)_8$	229	235 [~0]^a	[235]	0.3	0.5	0.5	[235]	0.4	0.7	[239]	0.3	0.4	0.7	[236]	0.1	0.3	0.5	
		185 [0.3$_2$]^a	[185]	1.0	1.0	1.0	[186]	1.0	1.0	[186]	1.0	1.0	1.0	[185]	1.0	1.0	1.0	
		159 [0.3$_4$]^a	[159]	0.5	0.4	0.3	[158]	0.7	0.4	[159]	0.6	0.5	0.4	[157]	0.5	0.5	~0	
			Acetone soln				THF soln			CH$_3$CN soln								
				22 °C	−19 °C	−78 °C		22 °C	−51 °C		22 °C	−51 °C						
$[(\pi\text{-Cp})Ru(CO)_2]_2$	217	221 [~0]^a	[221]	1.0	1.0	1.0	[221]	1.0	1.0	[221]	1.0	1.0						
		180 [0.2$_3$]^a	[180]	0.8	0.4	0.3	[178]	0.7	~0	[178]	0.7	~0						
$(Et_4N)[HFe_2(CO)_8]$	255																	
$(Et_4N)_2[Fe_2(CO)_8]$	161	168 [0.3$_3$]^b																
$(Bu_4N)_2[Fe_2(CO)_8]$	172	168 [0.3$_0$]^b																
			DMF soln															
				22 °C	−27 °C	−51 °C												
$(DMTED)[Fe_2(CO)_8]$	178	222 [0.3$_5$]^b	[222]	1.0	1.0	1.0												
		167 [0.4$_0$]^b	[167]	1.1	0.6	0.5												

[a] Acetone solution. [b] DMF (*N,N*-dimethylformamide) solution. [c] ρ is depolarization ratio.

Table II. Intensity of $Co_2(CO)_8$ (Mineral Oil Solution) Bands vs. Laser Power

Laser power, mW	Rel intens at 159 cm^{-1}	185 cm^{-1}	235 cm^{-1}
300	0.37	1.0	0.17
600	0.36	1.0	0.14
840	0.28	1.0	0.19

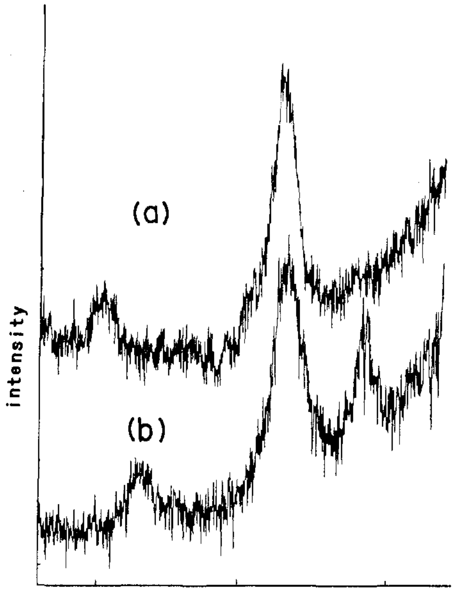


Figure 1. Raman spectra of (a) $Co_4(CO)_{12}$ and (b) $Co_2(CO)_8$ in acetone at room temperature.

In another series of experiments, the relative intensities of the three peaks were noted as the exciting laser wavelength was changed from 676.4 to 457.9 nm. If the intensities of the 185- or 159-cm^{-1} line relative to the 235-cm^{-1} line were constant or decreased as the near-uv absorption bands of $Co_2(CO)_8$ are approached, this experiment would indicate that the 185- or 159-cm^{-1} peaks are not associated with a photolysis product. The results were ambiguous, however, because an

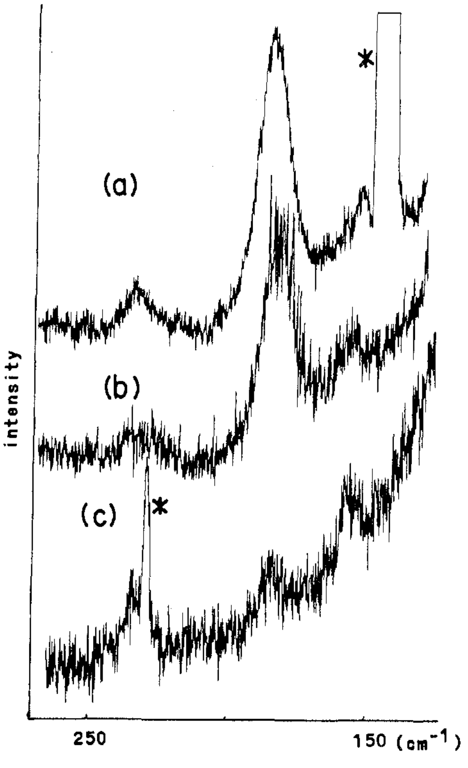


Figure 2. Raman spectra of $Co_2(CO)_8$ in acetone at room temperature using laser exciting lines at (a) 457.9 nm, (b) 488.0 nm, and (c) 676.4 nm. Asterisks denote laser plasma lines.

increase in the 185-cm^{-1} band was noted (Figure 2). This result is subject to two simple interpretations: the 185-cm^{-1} feature arises from a photolysis product or this feature displays greater preresonance excitation in the available wavelength range than do the species responsible for the 235- and 159-cm^{-1} peaks.

The general conclusion drawn from these experiments on $Co_2(CO)_8$ solutions is that the three bands at 235, 185, and 159 cm^{-1} appear to represent three discrete tautomers of $Co_2(CO)_8$. In line with this interpretation, it was found that the 235-cm^{-1} peak is favored at the expense of those at 185

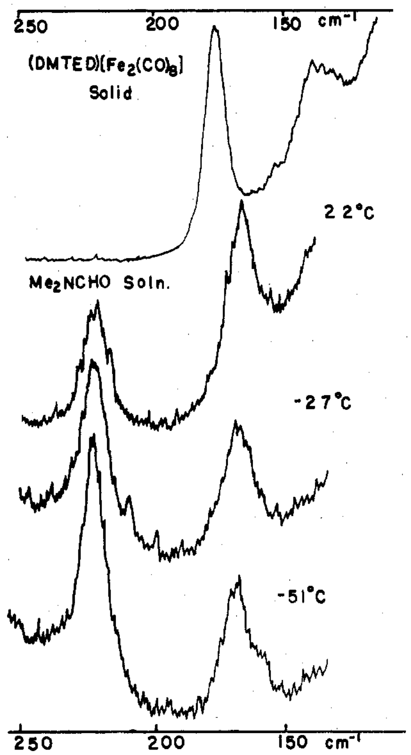
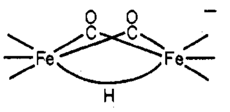


Figure 3. Temperature-dependent Raman spectra of (DMTED)-$[Fe_2(CO)_8]$ in the solid state and at various temperatures in DMF solution.

and 159 cm^{-1}, when an acetone solution of $Co_2(CO)_8$ is cooled (Table I). The resulting interpretation that the bridged form of $Co_2(CO)_8$ is favored at low temperatures, which was confirmed in several solvents (Table I), agrees with the findings of Bor and Noack.[3,4]

The $Fe_2(CO)_8{}^{2-}$ ion, which is isoelectronic with $Co_2(CO)_8$, presents another interesting case of bridged–nonbridged equilibrium. X-ray structural data[15] and CO stretching frequencies for certain salts of this ion demonstrate the lack of bridging carbonyls in the solid state. In line with this, the Raman spectrum of solid $[Et_4N]_2[Fe_2(CO)_8]$ displays a band at 160 cm^{-1}, characteristic of a simple metal–metal bond. As shown in Table I, the exact position of this band is sensitive to the nature of the cation, but in all cases which we investigated, this feature clearly is in the nonbridged M–M stretching region. In DMF solution, both the tetraethylammonium and tetrabutylammonium salts display a single Raman line in the nonbridged M–M stretching region; however the DMF solution of a salt with a dipositive cation, DMTED = *N,N'*-dimethyltriethylenediamine, displays two Raman features in the metal–metal stretch region: one at 222 cm^{-1}, characteristic of a bridged form, and one at 167 cm^{-1}, characteristic of the nonbridged form. Apparently ion pairing with the dipositive cation promotes carbonyl bridging in this solvent. Temperature dependence of the intensities (Table I and Figure 3) demonstrates that the bridged form is favored at lower temperatures.

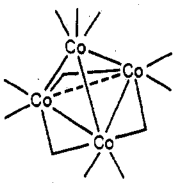
From infrared data it has been inferred that $HFe_2(CO)_8{}^-$ exists in a carbonyl-bridged form, I.[13] Since this system



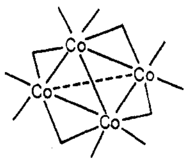
I

contains both the carbonyl bridge and the bridging hydride, it was of interest to compare its Raman spectrum with that of the parent nonbridged $Fe_2(CO)_8{}^{2-}$. Owing to instability of the hydride in solution, Raman spectroscopy was confined to the solid state, where a single mode was observed at 255 cm^{-1}. This feature is in the region of the other carbonyl-bridged systems and indicates that the systematics may also be extended to the elucidation of carbonyl bridging in hydride-bridged carbonyls.

The structure of $Co_4(CO)_{12}$ in solution has been the subject of some dispute, with the most recent ^{13}C and ^{59}Co NMR data indicating that the idealized C_{3v} symmetry found for the solid by x-ray diffraction, II,[16] persists in solution.[17] This finding



II (C_{3v})



III (D_{2d})

also is supported by new infrared data in the CO stretching region[17] and counters earlier suggestions that the structure has D_{2d} symmetry, III.[18] As already mentioned, our Raman data on this molecule in heptane solution show the presence of two polarized bands of 250 and 185 cm^{-1}, which are temperature independent and are assigned as preresonance-enhanced symmetric stretching frequencies for the carbonyl-bridged and the simple metal–metal bonded Co–Co linkages in the molecule. This observation agrees with either structure II or III since two symmetric skeletal bands are expected in either case; however, II is preferred owing to the infrared and NMR data of Cohen, Kidd, and Brown. In acetone solution the relative intensity ratio of the 250- to 185-cm^{-1} band does appear to vary with temperature. In view of the above-cited evidence this intensity variation probably arises from specific solvent interactions rather than changes in concentrations of tautomers.

Even though the increase in M–M stretching frequency is a useful diagnostic feature for carbonyl bridge formation, the origin of this increase is not easy to elucidate. The increase is consistent with the apparent shortening of M–M distances in the presence of bridging carbonyls,[19] but whether these effects arise from a strengthening of the M–M bond or from the bridging carbonyl bonds cannot be answered with the available data, owing to redundancy in the M–M and M–C–M linkages. Stated differently, bonds with bridging groups may provide the restoring force, so that the observation of an M–M stretch does not prove the existence of an M–M bond. According to a recent theoretical interpretation of carbonyl bridging, the metal–metal bond is actually weakened by the presence of the bridging carbonyls, and the primary force between metals arises from both metal–metal interactions and indirect metal–carbon–metal three-center interactions.[20]

The region from 130 to 290 cm^{-1} is free of serious interfering bands in simple carbonyls, and therefore Raman spectroscopy is a useful tool for the study of tautomeric equilibria in first-row and many second-row carbonyls. In the third row the metal–metal stretching modes frequently encroach on the C–M–C deformation region, so for these species more care is necessary in the use of Raman spectroscopy. It is worth noting that the η^5-C_5H_5 group sometimes displays a feature around the 120–140-cm^{-1} region. Halide ligands and monosubstituted phenyl groups such as found in triphenylphosphine also may yield Raman features in the metal–metal stretching region. Another possible complication is that the metal–metal stretch for a particular system may not have appreciable Raman intensity. For example, $Fe_2(CO)_9$ does not have an easily observed Fe–Fe stretch,[2] and in the present work we failed to detect a metal–metal stretch for pure samples of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. When due regard has been taken for these matters, Raman spectroscopy in the M–M stretching region can be a useful structure-sensitive tool. In the case of [DMTED][$Fe_2(CO)_8$] we would not have been able to elucidate the tautomeric equilibrium by infrared spectroscopy owing to absorption by the solvent, DMF, in the bridging CO stretching region. No such interference exists in the Raman spectral region characteristic of the Fe–Fe stretch.

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Registry No. $Co_2(CO)_8$ (bridged), 10210-68-1; $Co_2(CO)_8$ (nonbridged), 15226-74-1; [(π-Cp)Ru$(CO)_2]_2$ (bridged), 12132-87-5; [(π-Cp)Ru$(CO)_2]_2$ (nonbridged), 12132-88-6; $(Et_4N)[HFe_2(CO)_8]$, 26062-33-9; $(Et_4N)_2[Fe_2(CO)_8]$, 26024-88-4; $(Bu_4N)_2[Fe_2(CO)_8]$, 58341-98-3; (DMTED)[$Fe_2(CO)_8$] (bridged), 58281-29-1; (DMTED)[$Fe_2(CO)_8$] (nonbridged), 58341-97-2; $Co_4(CO)_{12}$, 17786-31-1.

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Mechanism and Steric Course of Octahedral Aquation. XVIII.[1] Spontaneous, Base Catalyzed and Mercuric Ion Catalyzed Aquation of *cis*-Chlorocyanobis(ethylenediamine)cobalt(III) Cations. The Trans Effect of Cyanide

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The kinetics of aquation of *cis*-[Co(en)$_2$(CN)Cl]Cl (en = 1,2-diaminoethane) have been studied over a range of temperature and pH. In acid solution, the rate is independent of pH and the product is exclusively *cis*-[Co(en)$_2$(CN)$H_2O]^{2+}$; $k = 6.2 \times 10^{-6}$ s^{-1} at 25 °C, $\Delta H^\ddagger = 24.6$ kcal mol^{-1}, and $\Delta S^\ddagger = -5$ cal deg^{-1} mol^{-1}. Base hydrolysis gives 90 ± 3% *cis*-[Co(en)$_2$(CN)OH]$^+$ product, the rest being the trans isomer; $k_{OH} = 8.9 \times 10^{-3}$ M^{-1} s^{-1} at 0.0 °C, $\Delta H^\ddagger = 23.2$ kcal mol^{-1}, $\Delta S^\ddagger = +18$ cal deg^{-1} mol^{-1}. The mercuric ion catalyzed aquation obeys the rate law $-d \ln [\text{complex}]/dt = kK[Hg^{2+}]/(1 + K[Hg^{2+}])$; $k = 1.30 \times 10^{-2}$ s^{-1}, and $K = 85$ M^{-1} at 50.8°, $\mu = 0.500$. Adduct formation is confirmed spectroscopically. A trans specific labilizing effect, opposed by a positionally nonspecific retarding effect, is proposed to account for the effect of the cyanide on the reactivity of the complex.

Introduction

A major interest in the study of substitution reactions of octahedral complexes has been in the way in which the rate and the stereochemistry of an act of substitution depend upon the nature and the position of the other ligands in the complex. The extensive range of examples to be found among the complexes of the type [Co(en)$_2$(A)X]$^{n+}$, where both cis and trans isomers are known and fully characterized, has enabled the effect of varying the nature and position of one ligand, A, upon the rates, activation parameters, and stereochemistry of displacement of ligand X to be studied in great detail, especially in the solvolytic aquation reaction.[2] In most cases it has been shown that, whereas the rate can be very sensitive to the nature of A, it is far less dependent upon its position with respect to the leaving group and so it is not realistic to talk about cis and trans effects in the way that can be applied most successfully to substitution of square-planar complexes[3] (and even of other octahedral centers, e.g., rhodium(III)[4]). Nevertheless, there is a group of ligands whose labilizing effect is greatest when they are cis to the leaving group, culminating in $-NH_2^-$ and $-NHR^-$, where it has been suggested that the exceptionally strong labilizing effect is cis specific.[5] This proposal, which rests on an interpretation of stereochemical data, has recently been challenged.[6] The ligands of this group are all characterized by the presence of a lone pair of electrons which can, in principle, be shared with the metal in the five-coordinate intermediate in the dissociative act of substitution. Such reactions are often accompanied by stereochemical change, especially when A is trans to X. The study of complexes containing ligands, A, that do not fall into this category is less systematically advanced, generally because one of the isomers either is missing or else reacts in an unwanted fashion. All substitution reactions take place with complete retention of configuration. Data are available for A = NH_3,[7] N_3,[8] and NO_2[9] for X = Cl and Br, and, in the first two cases, the labilities of the two isomers are similar. In the case of the chloro–nitro complexes, the trans isomer is more labile than the cis and, in order to see whether this is an indication of the development of a trans-labilizing effect which is strongly established when A = SO_3,[10] we have sought other complexes in this category. The *cis*-[Co(en)$_2$(CN)Cl]$^+$ cation was characterized some time ago[11] and this paper reports the kinetic and stereochemical data relating to the spontaneous aquation and the base and mercuric ion catalyzed hydrolysis in order to make comparison with the trans isomer[12] and also to compare the labilizing power of the cyanide and nitro groups.

Experimental Section

Preparations. *cis*-[Co(en)$_2$(CN)Cl]Cl·H_2O was made by the method of Shimura[11] except that the reaction between Na$_3$[Co(C-