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Solid-State Studies. 18. Low-Frequency Raman Spectra of $Os_xRu_{3-x}(CO)_{12}$ (x = 0, 1, 2, 3) and of $[Os_3(CO)_{12}]_n[Ru_3(CO)_{12}]_{1-n}$ ($0 < n < 1$)

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Intermolecular vibrational coupling is shown to be absent in the low-frequency Raman spectra of the title compounds. The 400–600-cm^{-1} region is interpreted by using a molecular fragment approach while the mechanical coupling-only model of Quicksall and Spiro provides a good prediction of the frequencies of the ν(metal–metal) features of the Os_2Ru and $OsRu_2$ species.

It is now well recognized that intermolecular vibrational coupling makes a major contribution to the increased number of vibrational features seen in the vibrational spectra of a crystal compared with those of the same material in solution.[1] On the other hand, the observation of a 1:1 correspondence between spectral features (be they infrared or Raman) in dissolved and crystalline materials is itself no guarantee that intermolecular vibrational coupling is absent. An excellent example is provided by $Mn_2(CO)_{10}$, of which the ν(CO) infrared spectrum is so broad as to make any comparison with the Raman impossible. Here, despite the fact that the ν(CO) Raman spectrum can be interpreted on an isolated molecule basis, it has recently been shown that intermolecular vibrational coupling is present.[2] A second example concerns the species $M_3(CO)_{12}$ (M = Ru, Os) for which Quicksall and Spiro explained the entire Raman spectrum in terms of an isolated molecule model (with the exception of a postulated crystal-induced intensity in an isolated molecule silent mode).[3] Here, again, studies on mixed crystals $[Os_3(CO)_{12}]_n[Ru_3(CO)_{12}]_{1-n}$ ($0 \leq n \leq 1$) have shown that the frequencies of some ν(CO) features in the Raman spectrum vary smoothly with n, thus establishing the presence of intermolecular vibrational coupling.[4]

There would seem to be two main reasons for the concealment of factor group effects in vibrational spectra. First is a centrosymmetric unit cell with Z = 2. In such a case a comparison of infrared and Raman frequencies would be

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definitive but when, as for $Mn_2(CO)_{10}$, such a comparison is not possible, there is no overt evidence for the presence of coupling. Second, high molecular symmetry may be responsible. Thus, for $M(CO)_6$ (M = Cr, Mo, W), the Raman intensities of all but one factor group component derived from the totally symmetric modes are, within a Wolkenstein model,[5] predicted to be of zero intensity. The observation of single Raman A_{1g}-derived features in the crystal spectra is therefore not conclusive proof of the absence of intermolecular vibrational coupling (although it can be shown that such coupling is, in fact, negligible).[5] A similar argument may well be applicable to $M_3(CO)_{12}$ species. Not only is the molecular symmetry quite high (D_{3h}) but also it has been pointed out that the CO ligands are arranged in such a way that they define a cuboctahedron.[6] If this pseudocubic symmetry is manifest in the vibrational spectra, quite dramatic, and potentially misleading, simplifications may occur. Solid-state features might then well be interpreted as molecular in origin. Unfortunately, these species are too insoluble in all common solvents to permit solution Raman spectra to be obtained and, faced with the need to work with the Raman spectra of crystalline samples, it seemed to us to be necessary to positively establish the validity of a molecule-based analysis of the non-ν(CO) regions of their spectra, rather than to simply assume it. The present Raman study was undertaken with this objective in view. Essentially, then, we have studied the relative importance of inter- and intramolecular vibrational coupling in spectral regions for which the latter would be expected to dominate. Because of this expected dominance of intramolecular effects we have not only studied the effects of isomorphous substitution, the technique which has been developed to overcome the problems outlined earlier, but also studied the spectra of the species $OsRu_2(CO)_{12}$ and $Os_2Ru(CO)_{12}$ in order to compare them both with those of mixed crystals of approximate composition $[Ru_3(CO)_{12}]_2[Os_3(CO)_{12}]$ and $[Ru_3(CO)_{12}][Os_3(CO)_{12}]_2$ and with those of the pure Ru_3 and Os_3 compounds.

Results and Discussion

It is convenient to distinguish between the low-frequency region (below 200 cm^{-1}), a region already discussed in detail by Quicksall and Spiro,[3] and the 350–650-cm^{-1} region in which M–C–O stretching and deformation features occur. The infrared and Raman spectra in these regions of the four pure compounds and one mixed crystal (of approximate composition $[Ru_3(CO)_{12}]_{1.0}[Os_3(CO)_{12}]_{1.0}$) are shown in Figures 1–4 and frequency data collected in Tables I and II. Comparison with the data of Quicksall and Spiro shows that our Raman frequencies are between 1 and 4 cm^{-1} higher than those which they report.[3] In the 350–650-cm^{-1} frequency region we observe significantly more Raman peaks than other workers. For osmium and ruthenium compounds 14 and 13, respectively, peaks are observed compared with 9 and 8. This higher number does not itself indicate a need to invoke intermolecular vibrational coupling—16 molecular Raman features (originating in the M–C stretches and M–C–O deformations) are allowed in D_{3h} symmetry; site symmetry effects increase this number to 28. Experimentally, it seems quite clear that there is no need to proceed beyond the molecular level. The mixed crystal spectra, of which Figure 3 is representative, are clearly derived with a composition weighting from those of the pure components. Intermolecular vibrational coupling is thereby excluded; all of the available evidence indicates that all features are two mode[5] in nature.

The spectra of the Os_2Ru and $OsRu_2$ species strongly suggest that, in addition, intramolecular vibrational coupling may also be neglected as a first approximation. Consider the D_{3h} pattern of six stretching modes shown in Figure 5a. Elementary group theory shows that three Raman features are to be expected (A_1', 2 E'). Suppose that only two peaks are found. This number of peaks could equally well be accounted for by the entirely uncoupled fragment C_{2v} model

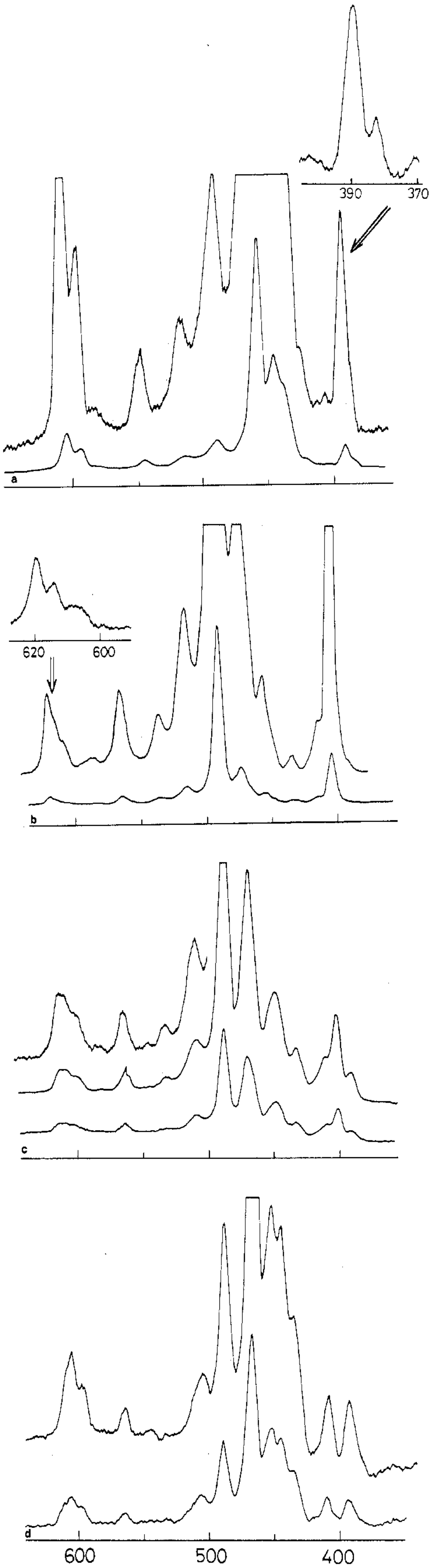

Figure 1. Raman spectra of polycrystalline $Ru_3(CO)_{12}$ (a), $Os_3(CO)_{12}$ (b), $Os_2Ru(CO)_{12}$ (c), and $OsRu_2(CO)_{12}$ (d) in the ν(M–C) and δ(M–C–O) region.

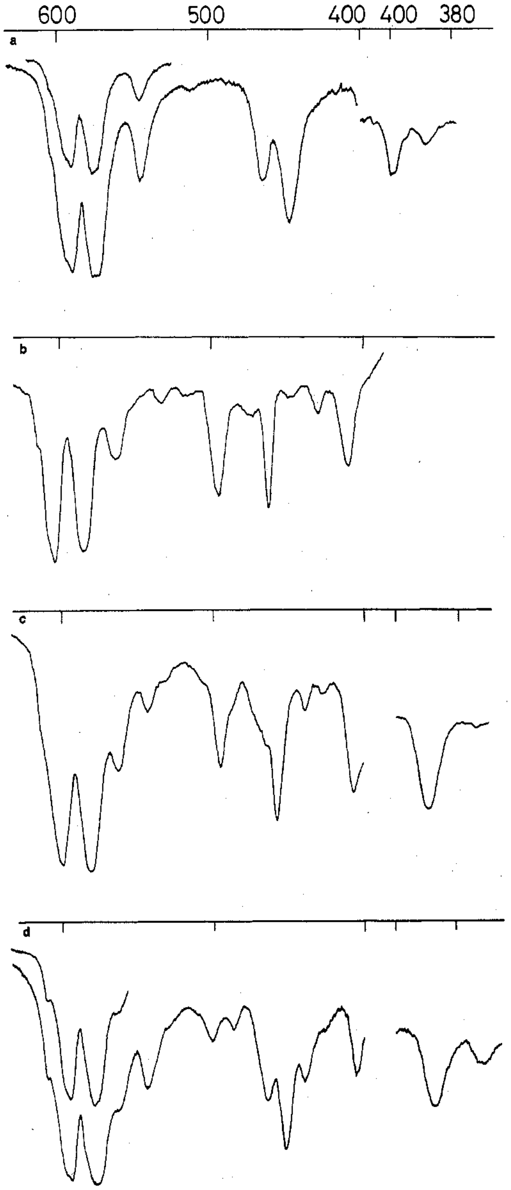

Figure 2. Infrared spectra of polycrystalline $Ru_3(CO)_{12}$ (a), $Os_3(CO)_{12}$ (b), $Os_2Ru(CO)_{12}$ (c), and $OsRu_2(CO)_{12}$ (d) in the ν(M–C) and δ(M–C–O) region.

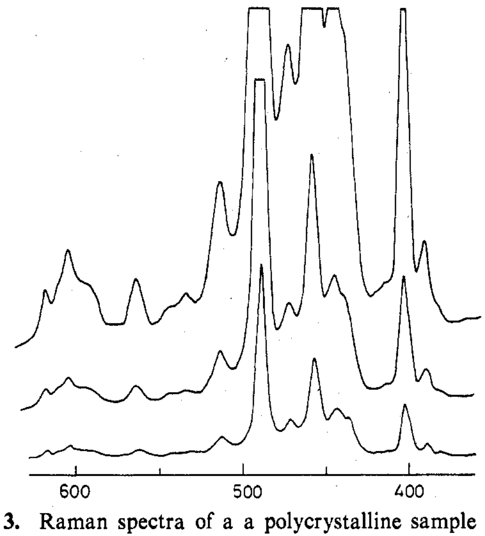

Figure 3. Raman spectra of a a polycrystalline sample of a cocrystallized ca. 1:1 mixture of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ in the ν(M–C) and δ(M–C–O) region.

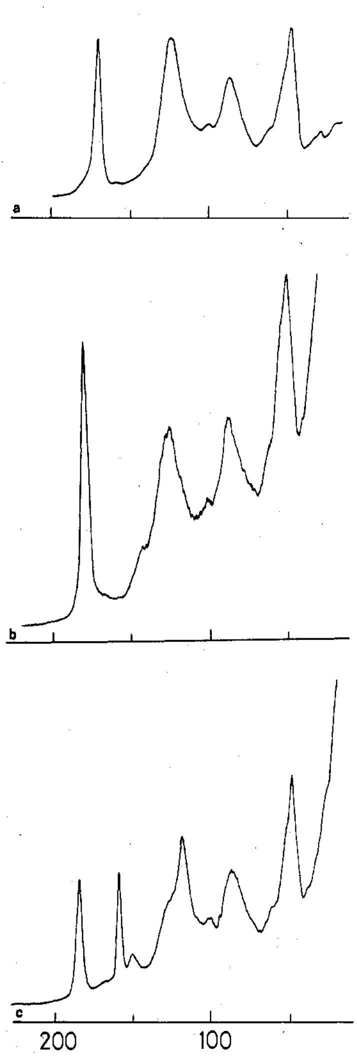

Figure 4. Raman spectra of polycrystalline $Os_2Ru(CO)_{12}$ (a) in the ν(M–M) region, polycrystalline $OsRu_2(CO)_{12}$ (b) in the ν(M–M) region, and a polycrystalline sample of a cocrystallized ca.1:1 mixture of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ (c) in the ν(M–M) region.

shown in Figure 5b, and the two models could not be distinguished by a peak count. For $M_3(CO)_{12}$ species 12 Raman-active features are predicted in the 350–650-cm^{-1} spectral region by an isolated C_{2v} $M(CO)_4$ unit model (four originating in M–C stretches and eight in M–C–O deformations). It could be argued that the observed number of peaks—together with the presence of some accidental coincidences or fortuitous weak features—is in good agreement with a D_{3h} model. On the other hand it might be that some of the weaker peaks are anharmonic in origin and not correctly assigned as fundamentals so that the C_{2v} model must be considered. Peak counting cannot distinguish between these alternatives, and we adopt the attitude that while it is unrealistic to expect complete decoupling, possible applicability of the isolated $M(CO)_4$ group model indicates that the assumption of ubiquitous intramolecular coupling should be experimentally tested.

A test is provided by the species $Os_2Ru(CO)_{12}$ and $OsRu_2(CO)_{12}$. In the absence of intramolecular coupling their spectra would be, essentially, the composition weighted sum of those of their $Ru(CO)_4$ and $Os(CO)_4$ components. Although peak counts of 15 and 13 for Os_2Ru and $OsRu_2$, respectively, lend but little support for this model (24 peaks being predicted), closer investigation reveals that there are, indeed, correlations which are consistent with the simple model. Thus in the Raman spectra, the medium-intensity peak at 391 cm^{-1} in Ru_3 persists with diminishing intensity through $OsRu_2$ and Os_2Ru (there is also an extremely weak peak in Os_3, of

Table I. Raman and IR Spectra of Trimetal Dodecacarbonyls in the ν(M–C) and δ(M–C–O) Regions

$Ru_3(CO)_{12}$				$OsRu_2(CO)_{12}$[a]		mixed crystals (1:1)	$Os_2Ru(CO)_{12}$[a]		$Os_3(CO)_{12}$			
IR		R							IR		R	
a	*b*	*a*	*b*	IR	R	R	IR	R	*a*	*b*	*a*	*b*
		383 w										
388 w	389 m	391 m	392 s	391 w	393 m	390 w (Ru)		391 w				
399 w	400 m	~403 vw		407 m	408 m	402 m (Os)	396 w	402 m	~400 w, sh(?)		404 s	402 s
						414 vw (Os)	409 w	411 w	410 s	410 s	413 w	
		420 w										
~430 w, sh(?)		436 m		430 w, sh	436 w	~439 m, sh (Ru)	427 w	433 w	429 m	428 m	433 w	
448 s	448 s	445 s	446 m	440 m	445 m	445 m (Ru)	440 m	449 m	448 w		450 w, sh	
		459 vs	458 s	453 s	453 m	458 s (Ru)	458 s				454 w	454 w
464 m	466 m			465 m	468 s		464 m, sh		462 s	462 s		
						472 m (Os)	~470 w, sh	470 s	474 w	474 w	474 m	470 m
		489 m	489 w	487 w	489 m	489 vs (Os + Ru)	~488 w, sh	489 vs	495 s	496 s	491 vs	490 s
							495 m					
				502 w	~505 vw, br		~506 w, sh					
512 w	512 w	514 w	513 w			513 w (Os + Ru)		510 w	516 w		515 m	512 w
						534 w (Os)	532 w	532 vw	534 w	533 w	536 w	533 w
546 m	546 m	544 w	546 w		548 vw, br	544 w (Ru)	544 m	546 vw				
				565 m, sh	564 w	564 w (Os)	563 m	565 w	563 m	562 m	565 w	561 w
573 s, sh	574 s											
577 s		~580 vw		579 s			582 s	~585 vw	585 s	583 s	~587 vw	
590 s	594 s											
594 s, sh		593 w	596 w	595 s	597 w	~597 w, sh (Ru)	599 s					
				~598 s, sh(?)				602 w	604 s			
~604 m, sh	606 sh	604 m	607 m		606 m	605 m (Os + Ru)			~607 s, sh	606 s	607 vw	605 sh
				610 m, sh	~609 w, sh			~610 w, sh				
						~612 w, sh (Os)	~614 m, sh	614 w	614 w, sh		614 w	614 w
						619 w (Os)					619 w	

[a] This work. [b] Reference 3.

Table II. Raman Spectra: ν(M–M) and Low-Frequency Region

	$Ru_3(CO)_{12}$					$Os_3(CO)_{12}$	
	a	*b*	$OsRu_2(CO)_{12}$	mixed crystals (1:1)	$Os_2Ru(CO)_{12}$	*a*	*b*
	38 w		~36 w		~29 w	30 w	
	52 s	48 s	~50 s	48 s (Os)	~48 s	48 s	47 s
	55 m, sh			~52 m, sh (Ru)	~52 m, sh	54 w, sh	
	64 w, sh		~62 w, sh	~62 w, sh (Os + Ru)	~62 w, sh	62 w	
			~83 w, sh				
	86 m	85 m	87 m, br	87 m, br (Os + Ru)	87 m	89 m	85 m
	102 w	100 w	101 w	~102 w (Os + Ru)	100 w	103 w	100 w
	~120 w, sh						
	124 m	124 m					
ν(M–M)	151 m (E_1')	149 m	125 s ($A_1(2)$)	118 s (Os)	125 s ($A_1(2) + B_1$)	119 s (E_1')	117 s
			129 m, sh (B_1)	~127 m, sh (Os + Ru)			
	168 vw		143 w	151 w (Ru)	159 vw	128 w	125 w
				159 s (Os)			
ν(M–M)	187 vs (A_1')	185 s	179 s ($A_1(1)$)	168 vw (Ru)	171 s ($A_1(1)$)	160 s (A_1')	158 s
				186 s (Ru)			

[a] This work. [b] Reference 3.

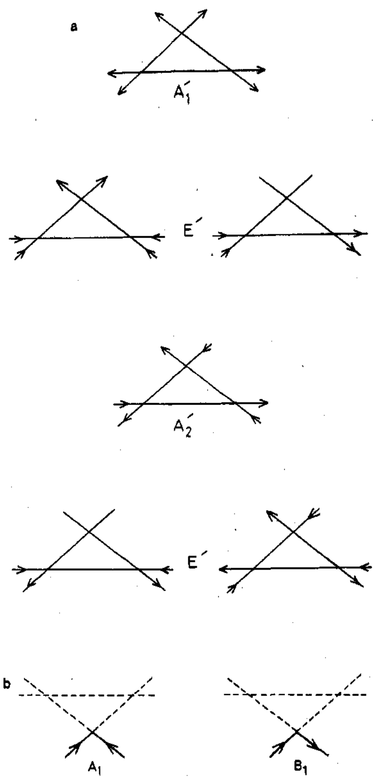

Figure 5. (a) Symmetry-adapted combinations of six coplanar vectors in a D_{3h} arrangement. (b) Symmetry-adapted combinations of two vectors at a C_{2v} site.

entirely different contour, which is probably of different origin). Conversely, an "osmium" peak appears at 405 ± 3 cm^{-1} in Os_3, Os_2Ru, and $OsRu_2$ with appropriately decreasing intensity. Table I has been constructed so as to show the correlations which seem plausible. A broad peak at 505 cm^{-1} in the $OsRu_2$ species, which has no apparent correlating feature in Ru_3 and Os_2Ru spectra and which is not due to an impurity, indicates that some intramolecular coupling does indeed occur, although it seems to us that the model in which it is neglected is a reasonable first approximation.

The infrared spectra closely resemble those of the previous workers,[3] although a slightly improved resolution has revealed a few additional bands. The number of infrared peaks is almost the same as the Raman, with coincidences, to within experimental error, being general. Such observations are entirely consistent with the model presented above.

For the region below 200 cm^{-1} (Table II), in which metal–metal stretching and several angle deformation modes are Raman active, a detailed discussion has been given by Quicksall and Spiro.[3] Their data indicated that intermolecular coupling can be ignored, a hypothesis which is confirmed by our mixed-crystal data. They further postulated that there is no electronic interaction between metal–metal stretches, even when a common metal atom is involved (as must always be the case in a triangular arrangement). The assumption of merely a mechanical coupling between the vibrators leads to a predicted frequency ratio of A_1' to E' feature of $2^{1/2}:1$,[3] which value may be compared with the experimental frequency ratios of 1.24 (Ru_3) and 1.34 (Os_3). It should be noted that if the difference between these values and 1.41 is to be explained by an interaction constant, then its sign must be such that it is easier to simultaneously stretch two metal–metal bonds sharing a common metal atom than to stretch one while the other contracts.

In the Raman spectra of the M_2M' species there are only two regions in which metal–metal stretching features appear. This could be a consequence of strong interaction between the M–M and M–M′ stretches (so that they tend to lose their individuality) and it was therefore of interest to extend the Quicksall and Spiro model to these systems. Because of the lower symmetry, additional assumptions are needed. We have assumed that the Os–Os and Ru–Ru stretching force constants retain the relative (but not necessarily the absolute) values reported for the Os_3 and Ru_3 systems. Further, we assume that the Os–Ru stretching force constant is the arithmetic mean of the Os–Os and Ru–Ru values. Finally, in the spirit of the model, we assume that only the masses of the metal atoms are involved in the reduced masses. This model predicts that the "E" mode is split by ca. 16 cm^{-1} in $OsRu_2$ and by ca. 4 cm^{-1} in the Os_2Ru species. Careful studies revealed a splitting of ca. 4 cm^{-1} in the former case but none in the latter, although there the lower frequency peak is broader than in either M_3 species. Repulsion between the two A_1 vibrations means that the ratio $\nu(A_1)_1/(^1/_2[\nu(B_1) + \nu(A_1)_2])$, where $(A_1)_2$ is derived from an E mode in the M_3 species, is predicted to increase to 1.47 in Os_2Ru and 1.46 in $OsRu_2$. The experimental values are 1.37 and 1.41, respectively. The model further predicts ratios of frequencies for the Os_2Ru species compared to $OsRu_2$ of $(A_1)_1$ 0.92 and "E" 0.91. For the former the experimental value is 0.96 and for the latter 0.98. Evidently, the simple model in which interaction constants are neglected provides a fairly good basis for interpolation from the M_3 species to the M_2M'; its approximate nature is most manifest in its incorrect prediction of the magnitude of the E-mode splitting.

Other Raman frequencies in the region below 200 cm^{-1} remain almost invariant to changes in the triangle of metal atoms. This region has been interpreted before and we have no evidence which would lead us to question this interpretation.[3]

Conclusions

Three main features emerge from the present study. First, a simple, additive, first approximation to the 400–600 cm^{-1} features of some trinuclear metal carbonyls has been presented which it will be of interest to apply to other species. Second, Spiro's remarkable model of the vibrations of a metal cluster in which the cluster is, effectively, a very plastic unit, in which a change in one metal–metal bond length has but a small effect on the energy required to change another, has provided a good first approximation to the metal–metal bond stretching region spectra. Finally, we have been able to provide general support for the assumption that intermolecular vibrational coupling is negligible in all of the spectral regions in which these molecules are active with the exception of the $\nu(CO)$ region. That intramolecular coupling between CO groups on different metal atoms occurs through bonds which either are largely vibrationally uncoupled or are plastic strongly suggests that this CO coupling is through-space rather than through-bond.

Experimental Section

$Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ purchased from Strem Chemicals were purified by crystallization from acetone at −20 °C under nitrogen. $OsRu_2(CO)_{12}$ and $Os_2Ru(CO)_{12}$ were prepared and purified by methods cited in the literature.[4,7]

Mixed crystals of $Ru_3(CO)_{12}/Os_3(CO)_{12}$ were prepared by cocrystallization from acetone solutions. Their composition was determined by comparison with suitable mechanical mixtures of the two compounds. The relative intensities of the higher frequency bands in the CO stretching region and of the ν(M–M) A_1' bands were used for this purpose. Raman spectra were recorded on a Spex 1401 double beam monochromator with proton counting and Spectra Physics 165 Ar/Kr laser. The exciting line was 6471 Å and the power incident on the sample was $\simeq$20 mW. The resolution was 2–4 cm^{-1}. IR spectra were obtained by using KBr disks on a Perkin-Elmer 325 spectrometer at ca. 1 cm^{-1} resolution.

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Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $OsRu_2(CO)_{12}$, 12389-47-8; $Os_2Ru(CO)_{12}$, 12389-50-3; $Os_3(CO)_{12}$, 15696-40-9.

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Oxygen-17 FT NMR Study of the Effect of Pressure on the Exchange of Water on Nickel(II)[1]

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The solvent exchange of $[Ni(H_2O)_6](ClO_4)_2$ in water has been studied as a function of temperature and pressure (up to 225 MPa) by measuring oxygen-17 FT NMR chemical shifts and line widths of the free water resonance at 8.133 MHz. A volume of activation ΔV^* of $+7.1 \pm 0.2$ cm^3 mol^{-1} is obtained by using the full Swift and Connick equation and is found to be independent of pressure. The activation parameters ΔH^* and ΔS^* are very sensitive to the method of analysis used. The three activation parameters are in accord with a dissociative-interchange (I_d) mechanism. The temperature and pressure dependences of pure acidified water T_2's have also been studied by oxygen-17 FT NMR. The relaxation rate decreases with compression, suggesting that the effect of pressure is to destroy some of the water structure.

Introduction

Traditionally, the entropy of activation has been considered the parameter most useful for deciding whether a solvent-exchange reaction is associative or dissociative, a positive entropy indicating a dissociative process. The predictive power of ΔS^* is good only when the entropy is sufficiently positive or negative, but for values of ΔS^* near zero, the nonrandom errors associated with its determination often make the diagnosis highly dubious, and, additionally, the factors that affect ΔS^* are but poorly understood.

Advances in experimental techniques in the past decade have led to the increasing use of volumes of activation for the diagnosis of reaction mechanisms. The volume of activation ΔV^* is simply the difference between the partial molar volumes of the reactants and the transition state. It is considered the resultant of two contributions.[3] The first arises from volume changes due to molecules not directly involved in the formal reaction scheme and is mainly due to changes in electrostriction of the surrounding solvent in going from reactants to transition state. For solvent exchange this term may ordinarily be neglected. The second contribution is due to bond making and breaking occurring during the activation process, and thus a positive volume of activation indicates an expansion of the reactants in forming the transition state (a bond has stretched or broken) and implies a dissociative activation mode (D or I_d).

The effect of compression on the rate constant of aqueous reactions has been almost exclusively confined to slow reactions, but a few fast ligand complexation rates have been measured by T jump.[4] Early on, Connick and co-workers[5] showed that NMR could be a useful tool to study solvent exchange in transition-metal solutions and especially that ^{17}O NMR is the method of choice in studying water-exchange processes. The exchange of water molecules between the primary solvation shell of a cation and the bulk solvent is an important first step in the understanding of aqueous reaction mechanisms, especially complex formation and some redox reactions.

There are several reported studies on water exchange between the first coordination sphere of Ni(II) and the bulk solvent,[6,7] with a wide variety of values of the activation parameters, the most recent one being a careful ^{17}O CW NMR variable-temperature study reported by Bechtold et al.[8] In order to clarify the mechanism of this exchange reaction, we have chosen to study it by ^{17}O FT NMR as a function of pressure. Before attempting this variable-pressure study, we undertook a variable-temperature FT NMR study at 8.133 MHz to obtain the NMR parameters required for the accurate analysis of the variable-pressure data at this frequency as well as checking by Fourier transform techniques earlier results[7] obtained by continuous wave NMR.

Experimental Section

Preparation of Materials and Samples. Oxygen-17 enriched water (11.3 atom %, normalized in ^1H) was obtained from Yeda R+D Co. Ltd., Rehovoth, Israel. It was distilled three times in vacuo for purification before each use. Nickel perchlorate hexahydrate ($Ni(ClO_4)_2 \cdot 6H_2O$, Fluka, purum) was used without further purification. Sample solutions of aqueous nickel ion were prepared by direct dissolution of the weighed nickel salt in suitable amounts of weighed enriched water. The solutions and the blanks were acidified with 60% perchloric acid ($HClO_4$, Merck, pro analysi). Two solutions of $Ni(H_2O)_6^{2+}$ were prepared. Solution I was 0.0195 m in nickel and 0.0520 m in $HClO_4$. Solution II was 0.0601 m in nickel and 0.0850 m in $HClO_4$ (m = mol of solute/kg of solvent).

NMR Measurements. Line-broadening measurements were performed on a Fourier transform Bruker WP-60 spectrometer, interfaced to a Nicolet BNC-12 computer with 8K of data memory, operating at 8.133 MHz and using an external fluorine lock.

Ambient pressure measurements were made without spinning, with a Bruker 8–14 MHz multinuclear probe, the temperature being controlled by a Bruker ST 100 unit. The $\pi/2$ pulse length was 14 μs; sweep widths were either 10 or 25 kHz. The spectrometer frequency was adjusted to give the observed peak in the center of the sweep range. The pulse-repetition rate was between 0.2 and 2 s and the number of scans between 100 and 10000, depending upon the relaxation times for the particular sample and the temperature. The delay between the pulse and the start of data acquisition was 1–4 dwell times, adjusted to give a flat base line. The low-temperature line width

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