CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

Raman Frequencies of Metal Cluster Compounds: $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$[1]

BY CARL O. QUICKSALL AND THOMAS G. SPIRO

Received April 3, 1968

Raman and infrared spectra are reported for the triangular, nonbridged cluster compounds $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$. Assignment of the CO stretching frequencies requires that stretch–stretch interaction across the triangles be comparable in magnitude to interaction across a single metal atom. The low-frequency Raman spectrum shows two sharp bands assignable to the stretching of metal–metal bonds. A normal-coordinate analysis reveals that the mixing of metal–carbon deformation with metal–metal stretching coordinates is slight for the A_1' and moderate for the E' cluster modes. The frequency ratio of the two bands is recognizably close to that predicted from a simple cluster approximation. The values of the metal–metal stretching force constant are 0.91 and 0.82 mdyn/Å for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$, respectively.

Introduction

The generally intense Raman effect associated with compounds containing metal–metal bonds offers a convenient method of studying the nature of the metal–metal linkage.[2,3] Of particular interest in this connection is the Raman scattering of metal cluster compounds. We have recently reported preliminary results[4] on $Ir_4(CO)_{12}$ which shows strong low-frequency Raman emissions that are adequately interpreted as primarily due to the metal cluster alone. Here we present a more complete analysis of the vibrational spectra of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$.

Corey and Dahl[5] have shown that $Os_3(CO)_{12}$ has approximately D_{3h} molecular symmetry in the crystalline state and that $Ru_3(CO)_{12}$ is isomorphous with $Os_3(CO)_{12}$. The idealized structure is shown in Figure 1. The triangular clusters are held together by metal–metal bonds alone, the carbonyls being all terminal. These molecules therefore provide an excellent starting point in the development of the systematics of metal cluster Raman bands. Questions of particular interest include the following. To what extent are cluster motions separated from other motions of the molecules in the normal modes? In the event that Raman bands are found which arise predominantly from cluster motions, to what extent do their intensities and shapes distinguish them from other bands? What are the values of the metal–metal stretching force constants?

Results

There are 34 Raman-active and 21 infrared-active fundamentals expected for an $M_3(CO)_{12}$ molecule with D_{3h} symmetry. Table I gives the predicted symmetries of these vibrations as well as the representations spanned by a complete set of internal coordinates. A consideration of site group and factor group splitting in the crystal (site group C_1, factor group C_{2h}) would lead to a vastly more complicated spectrum. Since the basic features of the spectrum with one exception (*vide infra*) could be explained without invoking crystal effects, these will not be considered further.

TABLE I

SYMMETRIES OF VIBRATIONAL MODES FOR $M_3(CO)_{12}$ (D_{3h})

$\Gamma(\text{vib}) = 9A_1' + 6A_2' + 15E' + 4A_1'' + 6A_2'' + 10E''$
$\Gamma(\text{M–M}) = A_1' + E'$
$\Gamma(\text{M–C def})^a = 3A_1' + 3A_2' + 6E' + 2A_1'' + 2A_2'' + 4E''$
$\Gamma(\text{C–O str}) = 2A_1' + A_2' + 3E' + A_2'' + E''$
$\Gamma(\text{M–C str}) = 2A_1' + A_2' + 3E' + A_2'' + E''$
$\Gamma(\text{C–O def}) = 2A_1' + 2A_2' + 4E' + 2A_1'' + 2A_2'' + 4E''$
$\Gamma(\text{Raman}) = A_1' + E' + E''$
$\Gamma(\text{ir}) = E' + A_2''$

[a] Contains $1A_1' + 2E'$ redundancies.

The observed Raman frequencies are presented in Table II along with infrared frequencies from the 1950–2150- and 350–650-cm^{-1} regions. The latter were obtained with the solid compounds (KBr pellets) for comparison with the Raman spectra. Solution infrared spectra have previously been reported.[6,7] The observed spectra for the two compounds are very similar and support the conclusion that they are isostructural. The vibrational frequencies are divided into three regions: 2150–1950, 650–350, and below 200 cm^{-1}. The higher energy regions were not of prime interest in this work, but a few observations and comments are required. The low-frequency region will then be discussed in detail.

2150–1950-Cm^{-1} Region.—Bands in this region arise from terminal carbonyl stretching. Six Raman-active and four ir-active fundamentals are predicted; seven Raman and six or seven infrared bands are observed. The extra Raman band may be explained as the inactive A_2' band rendered active by crystal effects. A slight lowering of symmetry to C_{3h} would give Raman activity to this fundamental. In the infrared spectra four bands are prominent and are assigned as the predicted fundamentals. The remaining minor features no doubt arise from crystal effects, since they are absent in solution spectra.[6,7]

The CO stretching frequencies may best be understood in terms of a simple splitting diagram as shown

---

[1] This investigation was supported by Public Health Service Grant GM-13498, from the National Institute of General Medical Services.

[2] L. A. Woodward, *Phil. Mag.*, **18**, 823 (1934).

[3] H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Commun.*, 616 (1966).

[4] C. O. Quicksall and T. G. Spiro, *ibid.*, 839 (1967).

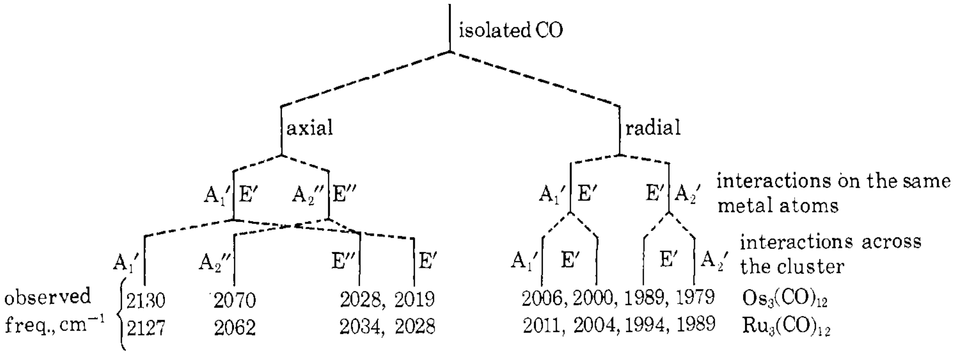
[5] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

[6] D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *ibid.*, **4**, 166 (1965).

[7] W. Beck and K. Lottes, *Chem. Ber.*, **94**, 2578 (1961).

SCHEME I

DIAGRAM FOR CO STRETCHING FREQUENCIES



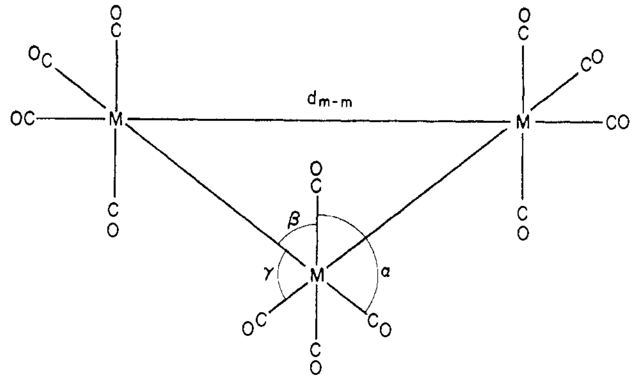


Figure 1.—Idealized structure for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ showing internal coordinates for metal–metal stretching and metal–carbon deformations.

TABLE II

OBSERVED FREQUENCIES[a] (CM^{-1})

$Os_3(CO)_{12}$		$Ru_3(CO)_{12}$	
Raman	Infrared	Raman	Infrared
2130 s	2070 s	2127 s	2062 s
2028 s, d	2062 sh	2034 s, d	2053 sh
2019 w	2040 sh	2028 w	2042 sh
2006 m	2028 sh	2011 m	2026 s
2000 m	2019 s	2004 s	2002 s
1989 m	1998 m	1994 m	1989 m
1979 m	1986 m	1989 w	606 sh
614 w	606 s	607 m	594 s
605 sh	583 s	596 w	574 s
561 w	562 m	546 w	546 m
533 w	533 w	513 w	512 w
512 w	496 s	489 w	466 m
490 s	474 w	458 s	448 s
470 m	462 s	446 m	400 m
454 w	428 m	392 m	389 m
402 s	410 s	185 s	
158 s		149 m	
Ca. 125 w		124 m	
117 s		100 w	
100 w		85 m	
85 m		48 s	
47 s			

[a] Symbols: s, strong; m, medium; w, weak; sh, shoulder; d, band shows evidence of splitting into a closely spaced doublet.

in Scheme I. The initial classification of the carbonyls into axial and radial components gives rise to two groups of bands. Inclusion of a force constant for stretch–stretch interaction between carbonyls on the same metal atoms splits these groups into four doublets. These are further split by stretch–stretch interactions across the cluster.

The assignments given in the diagram are consistent with the data but must be considered only tentative owing to the uncertainty in assigning the particular E′ and E″ bands. There is no doubt however about the assignment of the A_1' band, which is absent in the infrared, nor of the A_2'' band, which is missing from the Raman spectra. This latter assignment calls into question the interpretation of Huggins, *et al.*[6], who assigned the highest frequency infrared band for $Os_3(CO)_{12}$ in solution to E′. The present assignment implies that stretch–stretch interaction is as significant across a metal–metal bond as it is across a single metal atom. Cotton and Wing[8] reached a similar conclusion in the case of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$.

650–350-Cm^{-1} Region.—Bands in this region arise from metal–carbon stretching and carbonyl bending vibrations. A total of 16 Raman-active and 10 ir-active fundamentals is predicted, not all of which are observed or resolved. A detailed assignment of the observed frequencies would be difficult owing to considerable mixing among modes of like symmetry and various potential interactions similar to those described for the carbonyl stretches. From previous assignments,[9] however, the bands in the 350–500-cm^{-1} region may be attributed primarily to metal–carbon stretching, while the bands in the 500–650-cm^{-1} region are primarily due to carbonyl deformations.

Low-Frequency Region.—Below 200 cm^{-1} bands are expected from vibrations involving metal–metal stretching and metal–carbon deformation. A total of 12 Raman-active and 6 ir-active fundamentals is predicted. Six prominent bands are observed in the Raman spectra between 30 and 200 cm^{-1}, shown in Figure 2. The breadth and shape of some of the bands, however, leave little doubt that they are superpositions of more than one fundamental.

The spectra of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ are nearly identical except that two sharp, relatively intense bands shift from 158 and 117 cm^{-1} to 185 and 149 cm^{-1} for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$, respectively. These are assigned to the A_1 and E′ cluster vibrations, respectively.

---

[8] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 1328 (1965).

[9] L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963).

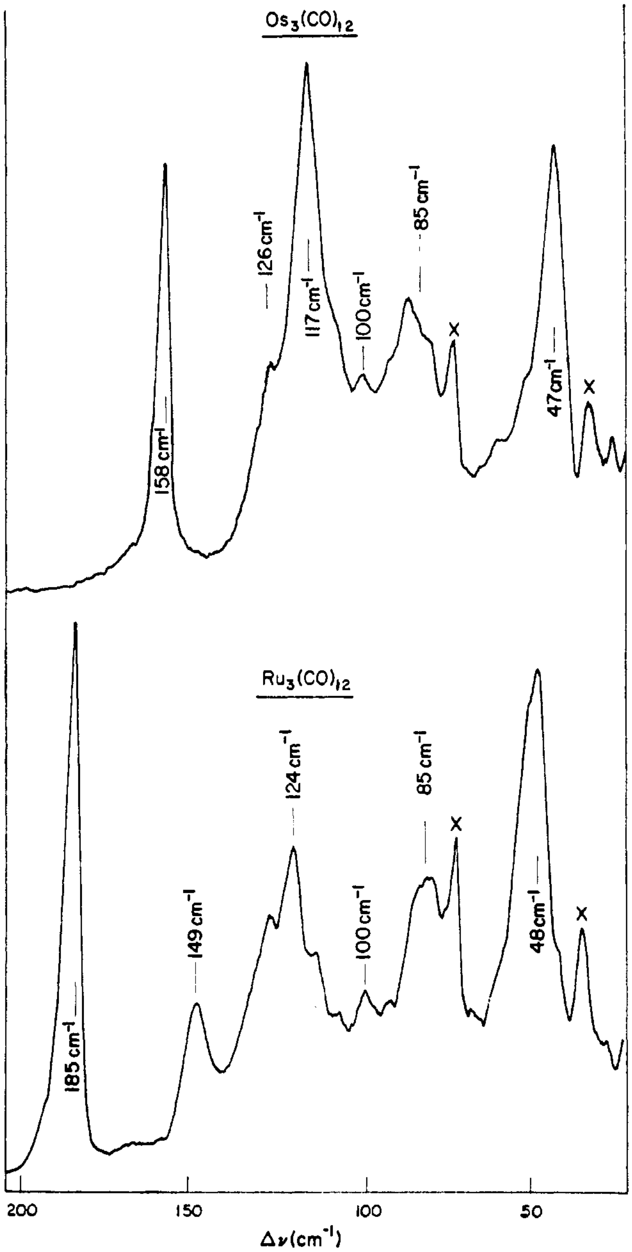


Figure 2.—Low-frequency Raman spectra for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$. × denotes grating ghosts. Obtained on polycrystalline samples, using He–Ne 6328-Å laser excitation. The scattered light was collected at 90°. Conditions: slit width 2 cm^{-1}; time constant 10 sec; scan rate 12 cm^{-1}/min.

TABLE III

MOLECULAR PARAMETERS FOR $M_3(CO)_{12}$

d_{M-M}	2.88 Å	∠MCO	180°
d_{M-C}	1.95 Å	$\angle\alpha = <\beta$	90°
d_{C-O}	1.14 Å	$\angle\gamma$	98°

In order to verify this assignment and to study the degree of mixing of the cluster motions with the bending motions, an approximate normal-coordinate analysis was performed. The G matrix was calculated by the method of Wilson, *et al.*,[10] employing Schachtschneider's program GMAT.[11] Molecular parameters, shown in Table III, for $Os_3(CO)_{12}$ were average values taken from the structure determination of Corey and Dahl,[5] except that the small deviations from mutual orthogonality of the axial and radial carbonyls were ignored. The same parameters were used for $Ru_3(CO)_{12}$, since the atomic radii for Os and Ru are nearly identical.[12] A diagonal valence force field was used to construct the F matrix. Both G and F matrices were factored using symmetry coordinates generated from the internal coordinates, using standard group theoretical techniques.[10]

The matrices were set up for calculation of all of the fundamental frequencies. However, our interest here is primarily in the M–M stretching and M–C bending vibrations. Consequently, only the low-frequency Raman spectrum was used to obtain a least-squares fit, using Schachtschneider's program FPERT.[11] Force constants for C–O and M–C stretching and for M–C–O bending were held fixed in a given calculation. Their values, estimated from the literature,[9] are given in Table V. In separate calculations, their magnitudes were varied over a reasonable range; there was no significant influence on the low-frequency fit.

A symmetrically complete set of internal coordinates for the cluster motions and the metal–carbon deformations is illustrated in Figure 1 and consists of a metal–metal distance and three angles: α, β, and γ. There are three redundancies, involving α and β, and these were removed by FPERT in the first step of the calculation. The valence force constants corresponding to the internal coordinates are K_{M-M}, K_α, K_β, and K_γ. K_{M-M} was initially estimated from the values of the A_1' cluster frequencies. The bending constants are expected to fall in the range 0.1–0.8 mdyn-Å. The expected relative magnitudes are $K_\alpha > K_\beta \sim K_\gamma$ from consideration of changes in M–C dπ–pπ^* overlap.[13]

During the course of initial calculations it was observed that the bending modes fell into four groups in the following order of decreasing frequency: $\alpha > \alpha + \beta > \gamma > \beta$, where the symbols refer to the angles contributing predominantly to the potential energy in each group. The Raman spectra show three prominent bands, at *ca.* 125, 85, and 47 cm^{-1}, assignable as M–C bending modes. Attempts to fit all four predicted groups to these three frequencies were unsuccessful, with reasonable values of the force constants. However if the band arising primarily from the β angle was assumed to lie at frequencies lower than 47 cm^{-1}, then all of the prominent bands, including the cluster frequencies, could be adequately fit. Additional bands were predicted within the range of our measurements, at *ca.* 100, 77, and 34 cm^{-1}. A weak band is in fact observed at 100 cm^{-1} in both spectra. The bands at 77 and 34 cm^{-1} would both be covered by grating ghosts which are found at 77 and 36 cm^{-1}. Thus the observed low-frequency Raman spectrum for each compound is satisfactorily accounted for with

---

[10] E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[11] J. H. Schachtschneider, Technical Reports No. 231-64 and No. 57-65, Shell Development Co., Emeryville, Calif.

[12] The recently published structure of $Ru_3(CO)_{12}$ (R. Mason and A. I. M. Rae, *J. Chem. Soc.*, *A*, 778 (1968)) justifies this assumption.

[13] I. J. Hyams, D. Jones, and E. R. Lippincott, *ibid.*, 1987 (1967).

four primary valence force constants. At the level of accuracy of interest here, no interaction constants are required. The calculated frequencies and potential energy distributions are listed in Table IV. The final force constants are given in Table V.

Table IV

Raman freq, cm^{-1}		Potential energy distribution[a]			
Obsd	Calcd	V_{M-M}	V_α	V_β	V_γ
		$Os_3(CO)_{12}$			
158	156.4 (A_1')	80	7	8	1
126	126.1 (E'')	0	78	4	0
	124.3 (E'')	0	81	1	0
117	122.7 (E')	52	24	14	4
100	99.8 (E')	0	58	32	6
	85.1 (E'')	0	2	94	0
85	84.8 (A_1')	16	37	40	1
	77.2 (E')	37	35	17	6
	48.1 (E')	3	0	0	94
47	46.4 (A_1')	2	0	0	96
	46.2 (E')	7	0	0	90
	34.0 (E'')	0	5	94	0
		$Ru_3(CO)_{12}$			
185	188.6 (A_1')	81	5	5	1
149	144.0 (E')	63	17	8	5
124	128.1 (E'')	0	80	3	0
	124.3 (E'')	0	81	2	0
100	102.6 (E')	0	61	28	2
	86.6 (E'')	0	1	94	0
85	81.7 (A_1')	12	42	38	1
	77.1 (E')	25	45	20	5
	48.8 (E')	4	1	1	92
47	46.7 (A_1')	2	0	0	95
	46.4 (E')	6	0	0	92
	31.7 (E'')	0	4	95	0

[a] V_i represents the percentage contribution to the potential energy from the force constant K_i. Deviations of the total from 100% are due to small contributions from M–C stretching and C–O deformations.

Table V

Valence Force Constants

Values Obtained by Least Squares Fit

	$Os_3(CO)_{12}$	$Ru_3(CO)_{12}$
K_{M-M}, mdyn/Å	0.91	0.82
K_α, mdyn-Å	0.66	0.65
K_β, mdyn-Å	0.36	0.30
K_γ, mdyn-Å	0.26	0.26

Values Estimated from the Literature[9] and Held Constant

	$Os_3(CO)_{12}$	$Ru_3(CO)_1$
K_{C-O}^{rad}, mdyn/Å	15.35	15.35
K_{C-O}^{ax}, mdyn/Å	16.50	16.50
K_{M-C}^{rad}, mdyn/Å	3.60	2.86
K_{M-C}^{ax}, mdyn/Å	2.67	2.20
K_{M-C-O}, mdyn-Å	0.90	0.90

Discussion

The primary aim of this work was to determine to what extent bands attributable to the stretching of metal–metal bonds can be identified in the Raman spectra of two symmetrical trigonal carbonyl clusters. The answer is that the A_1' "breathing" mode of the triangle is responsible for the most prominent feature, a strong spike, in the low-frequency region of both compounds. There is very little mixing in (less than 20% in the potential energy) of A_1' metal–carbon deformation modes, despite their proximity in the spectra. The E' cage mode is closer in frequency to the deformation modes, which mix in to a greater extent, although metal–metal stretching is still predominant (52% for $Os_3(CO)_{12}$, 63% for $Ru_3(CO)_{12}$). Its appearance in the Raman spectrum is still sharp, though less intense than the A_1' mode.

It has been suggested[4,14] that a consideration of the relative vibrational frequencies expected for an isolated homoatomic cluster, with neglect of all interaction force constants, might be useful in identifying metal–metal stretching bands for metal cluster compounds of the same symmetry. For tetrahedral and octahedral clusters, this "simple cluster" approximation predicts that the metal–metal Raman frequencies lie in the ratio $2:\sqrt{2}:1$, and the observed ratios were found to be not far from this for $Ir_4(CO)_{12}$,[4] $Pb_4(OH)_4^{4+}$,[14] $Tl_4(OC_2H_5)_4$,[15a] and $Bi_6(OH)_{12}^{6+}$.[15b] For an equilateral triangle the simple cluster approximation predicts the frequency ratio for the A_1' and E' modes to be $\sqrt{2}:1$. The observed ratios are 1.35 for $Os_3(CO)_{12}$ and 1.25 for $Ru_3(CO)_{12}$. The deviations from the prediction result from the mixing of metal–carbon deformations into the E' metal–metal mode. Nevertheless they are small enough that the predicted ratio could have been used to assign the E' metal–metal mode for either $Os_3(CO)_{12}$ or $Ru_3(CO)_{12}$ without benefit of intercomparisons between their spectra, considering that the assignment of the A_1' mode is obvious. Had the mixing of metal–carbon modes been more severe, however, this would not have been the case. Recently, Hartley and Ware[16] have shown that, for $Mo_6Cl_8X_6^{2-}$ clusters, metal–metal and metal–terminal halide stretching modes are completely mixed. Here the metal to ligand mass ratio is not large so that kinetic as well as potential coupling is substantial.

The calculated metal–metal stretching force constants are in the range found for other polynuclear carbonyls,[3,4] although the present values are the first to be based on a normal-coordinate analysis rather than simple approximations. K_{M-M} is 10% higher for $Os_3(CO)_{12}$ than for $Ru_3(CO)_{12}$ in conformity with the general expectation that homonuclear metal–metal bonds increase in strength with increasing atomic number.

Experimental Section

$Ru_3(CO)_{12}$ was obtained from Alfa Inorganics, Inc., and was used as received. $Os_3(CO)_{12}$ was prepared by the method of Bradford and Nyholm[17] and purified by recrystallization from chloroform. We are grateful to Mr. William McCarthy and the FMC Corp. for aid in the synthesis.

Infrared spectra were recorded on a Beckman IR-12 spectrometer using a KBr-pellet technique. The instrument was calibrated in the carbonyl region using CO gas. Raman spectra were ob-

---

(14) V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, **7**, 188 (1968).

(15) (a) (b) V. A. Maroni and T. G. Spiro, *ibid.*, **7**, 193 (1968); (b) V. A. Maroni and T. G. Spiro, *ibid.*, **7**, 183 (1968).

(16) D. Hartley and M. J. Ware, *Chem. Commun.*, 912 (1967).

(17) B. W. Bradford and R. S. Nyholm, *ibid.*, 384 (1967).

tained with a spectrometer[18] equipped with an He–Ne laser source. The instrument was calibrated using helium and argon discharge lines. Small polycrystalline samples were investigated by collecting the light scattered at 90° from the sample held between two thin glass plates. The low solubility of the compounds in available solvents precluded our obtaining Raman spectra in solution.

Acknowledgment.—We are grateful to Professor H. D. Kaesz for helpful discussion of the results of our work.[19]

---

[18] R. E. Miller, D. L. Rousseau, and G. E. Leroi, Technical Report No. 22, ONR contract 1858(27), NR 014-203, May 1967 (available from Defense Documentation Center, Cameron Station, Alexandria, Va. 22314).

[19] Since submission of this article, D. Hartley, P. A. Kilty, and M. J. Ware, *Chem. Commun.*, 493 (1968), have reported metal–metal stretching frequencies for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ in good agreement with ours. Their estimates of K_{M-M}, using $-M(CO)_4$ as the vibrating units, are nearly twice as large as the values reported here, with $K_{Ru-Ru} > K_{Os-Os}$. It appears that a better approximation for simple calculations of metal–metal force constants in polynuclear carbonyls is to use the metal atom masses alone, neglecting the carbonyl ligands: M. J. Ware, private communication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305

Electron-Transfer Reactions of Ruthenium Ammines

BY THOMAS J. MEYER AND HENRY TAUBE

Received May 8, 1968

The rate of self-exchange for the couple $Ru(NH_3)_6^{2+,3+}$ has been measured, taking advantage of the change in absorbance when the deuterated form of one of the oxidation states reacts with the protonated form of the other. At 25° and $\mu = 0.013$ in D_2O as solvent $k = 8.2 \pm 1 \times 10^2\ M^{-1}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 10.3 \pm 1.0$ kcal/mol, and $\Delta S^{\ddagger} = -11 \pm 3$ eu. The rate of self-exchange in the $Ru(en)_3^{2+,3+}$ system has been determined less accurately, but it appears certain that at 25° it is slower than that for $Ru(NH_3)_6^{2+,3+}$. The rates of oxidation of $Ru(NH_3)_6^{2+}$ and $Ru(en)_3^{2+}$ by Fe^{3+} and $FeOH^{2+}$ have been measured, and, in keeping with results for other outer-sphere electron-transfer processes, Fe^{3+} reacts more rapidly than does $FeOH^{2+}$. However, when $Ru(NH_3)_5OH_2^{2+}$ is the reductant, $FeOH^{2+}$ reacts more rapidly than does Fe^{3+}, and the possibility exists that the reaction with $FeOH^{2+}$ proceeds by proton transfer accompanying electron transfer.

Introduction

Endicott and Taube[1,2] have investigated the chemistry of the $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5OH_2^{2+}$–$Ru(NH_3)_5OH_2^{3+}$ complexes in aqueous solution, including the rates of oxidation of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5OH_2^{2+}$ by a series of cobalt(III)–ammine complexes and the reduction of $Ru(NH_3)_6^{3+}$ by various reductants.[3] They have shown that, under ordinary conditions, $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ are sufficiently inert to substitution in aqueous solution so that their electron-transfer reactions are of the outer-sphere type. Similar behavior is demonstrated in the present study for $Ru(en)_3^{2+}$ and $Ru(en)_3^{3+}$ (en = ethylenediamine).

The simplification arising from the absence of bond rupture in the activated complex for outer-sphere electron-transfer reactions facilitates theoretical calculations[4] of rate constants. Interest in the rates and mechanisms of outer-sphere reactions has been heightened by the possibility of direct comparisons between experimentally determined and theoretically calculated rate constants.

Many of the electron-transfer systems which have been investigated experimentally are between aquo ions, one or both of which are substitution labile compared with the rate of electron transfer.[5] For such systems it is difficult to distinguish between outer- or inner-sphere mechanisms or mechanisms involving net hydrogen atom transfer.

Complexes of back-bonding ligands such as 1,10-phenanthroline and cyanide are generally substitution inert, and their electron-transfer reactions are outer-sphere. However, in a reaction with such complexes involving electron transfer to or from metal t_{2g} orbitals, the exchanging electrons may be spread toward the surface of the complex onto the ligands, and the delocalization of electrons may facilitate electron transfer. Extensive delocalization is known to occur for ferrocyanides. The Mössbauer chemical shifts of ferricyanides and ferrocyanides are almost identical, and a detailed analysis by Shulman and Sugano[6] indicates that the electron added to $Fe(CN)_6^{3-}$, in going to $Fe(CN)_6^{4-}$, resides predominantly on the cyanide ligands and not on the iron. The mechanism of outer-sphere electron transfer for such systems may differ in important respects from that for complexes having only saturated ligands.

The mechanistic ambiguities which apply to aquo ion systems do not apply to the hexaammine and tris(ethylenediamine)ruthenium complexes. Here the mechanisms of electron transfer, at least where the rates of electron transfer are high, must be outer-sphere. The reactions of these ions are also free of the possible special effect associated with back-bonding ligands. Because of their importance in the study of outer-sphere re-

---

[1] J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **84**, 4984 (1962).

[2] J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

[3] J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

[4] For a recent review of chemical electron-transfer theory see R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964), and the references therein.

[5] N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

[6] R. G. Shulman and S. Sugano, *J. Chem. Phys.*, **42**, 39 (1965).